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Evaluation of cementation effect of sand mediated by enzyme-induced calcium carbonate precipitation

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ABSTRACT

A grouting technique that utilizes precipitated calcium carbonate as cementing material is presented. An enzyme of urease is used to enhance the rate and magnitude of the calcium carbonate precipitation. Evolution in the mechanical properties of sand samples treated, together with evaluation of porosity change resulting from the precipitation, is examined through unconfined compression tests. The grout is composed mainly of urease that bio-catalyzes hydrolysis of urea into carbon dioxide and ammonia, urea, and calcium chloride solution. This method employs chemical reactions catalyzed by the enzyme, and ultimately acquires calcium carbonate precipitated within sand samples. The experimental results show that even a small percentage of calcium carbonate precipitation against sand weight improves the strength drastically compared with that of untreated sand.

1. INTRODUCTION

Recently, a novel grouting method that utilizes precipitated calcium carbonate as a cementing material has been examined. The precipitation of calcium carbonate is induced by the microbial metabolism (e.g., Stocks-Fischer et al. 1999; Nemati et al. 2005; DeJong et al. 2006). The research on calcium carbonate precipitation by bacteria has been mainly conducted using ureolytic bacteria. These bacteria indirectly produce precipitated calcium carbonate by a urease enzyme. The bacterium selected for research on calcium carbonate precipitation, containing the urease enzyme, is typically *Sporosarcina pasteurii*.

In this work, the urease enzyme is adopted instead of using bacteria such as *Sporosarcina pasteurii*, often used as a promoter for the hydrolysis of urea, which, as described above, causes Ca^{2+} and CO_3^{2-} to precipitate as $CaCO_3$ and form into the void spaces and/or the surfaces of grains. Utilizing the enzyme itself is more straightforward than using bacteria, because the cultivation and fixation of bacteria (i.e., biological

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treatment) do not need to be considered in this work. After introducing the grouting reagents into the soil samples, the evolution in the mechanical properties is examined through unconfined compression tests. Moreover, the larger-sized sand samples are also treated using the same procedure in order to examine the feasibility of this technique.

2. SMALL CYLINDER TEST

In this suite of the tests, the purified urease extracted from jack bean meal having the urease activity of 2950 U is used as an enzyme. The function of urease is to dissociate the urea ($CO(NH_2)_2$) into the ammonium (NH_4^+) and the carbonate (CO_3^{2-}) ions. The dissociated carbonate ion will combine with the calcium ion supplied to form the precipitate of calcium carbonate, $CaCO_3$. The calcium carbonate may serve as bridges between the sand grains restricting their movement, hence improving strength and stiffness of the material, and subsequently reducing the liquefaction susceptibility. The deposited calcium carbonate also helps to reduce the porosity which is also considered as an important factor in reducing liquefaction susceptibility. The void surrounded by sand particle and calcite precipitated in unsaturated sand may work as an additional room for water during increased pore water pressure due to earthquake vibration.

Sand samples with the diameter of 5 cm and the height of 10 cm are treated with urea, urease and $CaCl_2$ in the different proportions. Strength and porosity of the treated samples are determined using unconfined compression tests and acid leaching process, respectively. The combinations of reagent and enzymes suggested by precipitation test are followed. Small PVC cylinders with a diameter of 5cm and height of 10cm are homogenously packed with silica sand (Keisa No.6) to obtain the relative density of 60% (i.e., porosity of 0.41). Urea-$CaCl_2$ solution is used as reagent. The urease crystals thoroughly rinsed in water and filtered is used as enzyme. The similar chemicals and enzymes used in precipitation test are used throughout this test. Enzyme and reagent solution are mixed together just before use and injected into the sand samples from the top at the rate of 10 mL/min. It is allowed to drain from a small hole at the bottom of PVC cylinders. Concentrations of the reagent solution range from 1.0-1.6 mol/L including 1.2, 1.3 and 1.4mol/L as suggested in precipitation tests. The amount of urease is fixed to be 12 g/L. Different experimental conditions are listed in Table 1.

Table 1 Test conditions of small cylinder test

S.N.	Urea and $CaCl_2$ [mol/L]	Urease [g/L]	Inj. Volume [mL]	Inj. no
R1	1.0	12	85	1
R2	1.2	12	85	1
R3	1.3	12	85	1
R4	1.4	12	85	1
R5	1.6	12	85	1

The samples treated are carefully removed from the cylinder 24hrs after the solution injection, and dried in oven at 100 °C for 24 hrs. The oven-dried samples are subjected to unconfined compression tests to obtain the stiffness and strength. Finally, the amount of $CaCO_3$ precipitated is evaluated by the acid leaching process. In this process, the dry weight of the sand is measured and washed by 0.2 mol/L hydrochloric acid, HCl, at least 3 times. It is again dried in oven and loss in weight during acid leaching is determined. The amount of $CaCO_3$ precipitated is examined and evolution in the porosity of the sand is evaluated. Each test condition is conducted two times to check the reproducibility.

The relations between the concentration of reagents and the amount of $CaCO_3$ normalized by the initial weight of the sand, and the unconfined compressive strength (UCS) of a sand sample are shown in Fig. 1. As apparent in the figure the maximum strength is achieved at the reagent concentrations of 1.2–1.4mol/L although the gain in strength varies. The high variation of strength at 1.2mol/L may be attributed to the handling mistakes. For the reagent concentration of 1.0mol/L, gain in strength is very low. It shows that adequate amount of precipitated $CaCO_3$ is needed to increase the stiffness of loose sand noticeably.

As apparent in Fig. 1b, the noticeable increase in strength can be achieved after 2.5 % precipitated $CaCO_3$ when urease is used as enzyme. The maximum strength of 1.5 MPa is achieved at around 4 % precipitated calcite. The relationship can be roughly assumed to be linear with several exceptions.

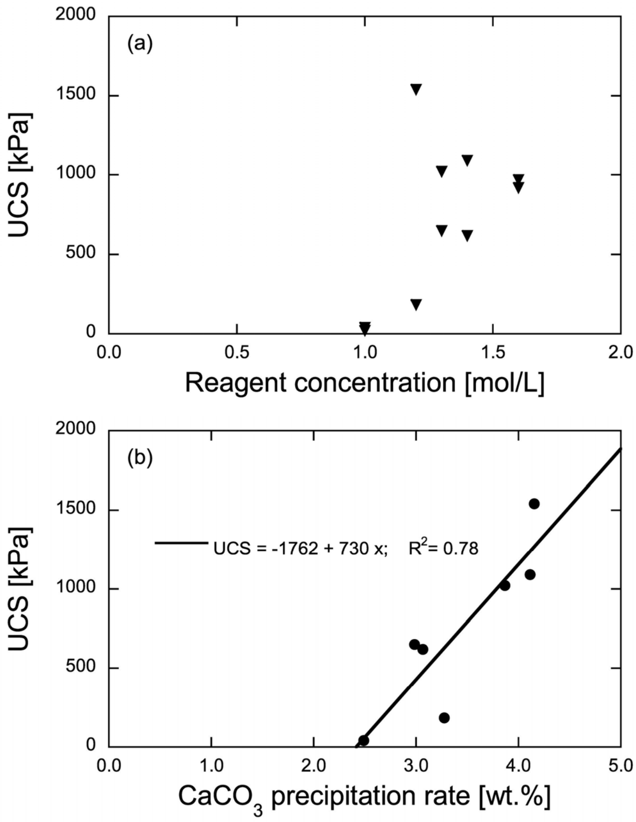

Fig. 1 Relation between UCS and reagent concentrations and $CaCO_3$ precipitation rate.

2. MID-CYLINDER TEST

Small cylinder tests are conducted to check the feasibility of $CaCO_3$ precipitation technique in sand to modify its mechanical properties. Considering gain in strength and change in sand porosity achieved, this technique is proved feasible in small scale samples. This section deals with the sand cylinder tests in larger sized samples.

Cylinders with a diameter of 10 cm and a height of 20 cm are taken. A small hole is made at their bottom for drainage but it is covered by porous stone to prevent the leakage of sand along with solution. These cylinders are homogenously packed with silica sand up to 8.5cm from the bottom. The injection tube is placed at the top of recently poured sand then sand is again poured till 17 cm from the bottom. A tube of internal diameter 3.5 mm is used as injection pipe. To prevent sand from entering inside the injection pipe and clogging of outlet of tube with precipitated calcite, a bulb of coarse sand (3.5 - 4.75mm) having diameter 2cm is devised by covering coarse sand with a fine cotton mesh and fixing it at the end of injection pipe with the help of rubber bands. Sand is poured in such a way to obtain relative density of 60 % (i.e., porosity of 0.41). A weight of 400g is placed at the top of the sand sample to prevent liquefaction during solution injection (hydraulic head applied for the injection is relatively high).

The same chemicals and enzymes used in precipitation test are used throughout this test. Enzyme and reagent solution are mixed together just before use. 0.5 mol/L solutions of urea and $CaCl_2$ is blended with 2 g/L urease and injected into the sand with the application of external pressure up to 30kPa. Solution volume was limited to 800 mL and injected two times, 400 mL each, at an interval of 2 hrs. The specimen treated is washed gently with water spray from the top 24hrs after the last injection. The improved sample was recovered carefully after washing the outer unimproved portion of sand. The porosity at different portions of improved sample is determined by acid leaching.

Colored solution is used to evaluate the distribution of solution inside the sample. Green color is added into urea-$CaCl_2$ solution and urease solution and injected inside the sand. Exactly similar procedures are followed until the cylinder is ready to remove from mold. This time the treated sample along with mold is cut into two halves and distribution of colored solution is observed. Samples from different locations are collected and porosity of collected samples is determined by acid leaching process.

The improved samples extracted from mid-cylinder test are shown in Fig.2. The porosity is calculated from the evaluated amount of $CaCO_3$ precipitated. The improved almost spherical sample of equivalent diameters 8.38 cm and 7.5 cm inside 10 cm cylinder are achieved from the two samples. This suggests improvement of sand is possible in small scales. However, the change in porosity attained by $CaCO_3$ precipitated varies highly in inner core and periphery of improved sample. The unsolidified portion may also have small percentage of precipitated $CaCO_3$.

The distribution of colour inside the specimen at different distance and in different directions from injection point is shown in Fig.3. As apparent in the figure, the portion of sand where there is no change in color. The portion with small change in color has small change in porosity. The portion near injection point and with dark color has appreciable change in porosity. It is also clear from the Fig.3 that no formation of flow path takes place. The flow is roughly uniform but is accumulated downward which is obvious. Appreciable distribution of color can be seen all round the injection point which suggests large area treatment is possible with some modification in injection device and flow regulation.

Fig.2 Improved portion of samples achieved from mid-cylinder

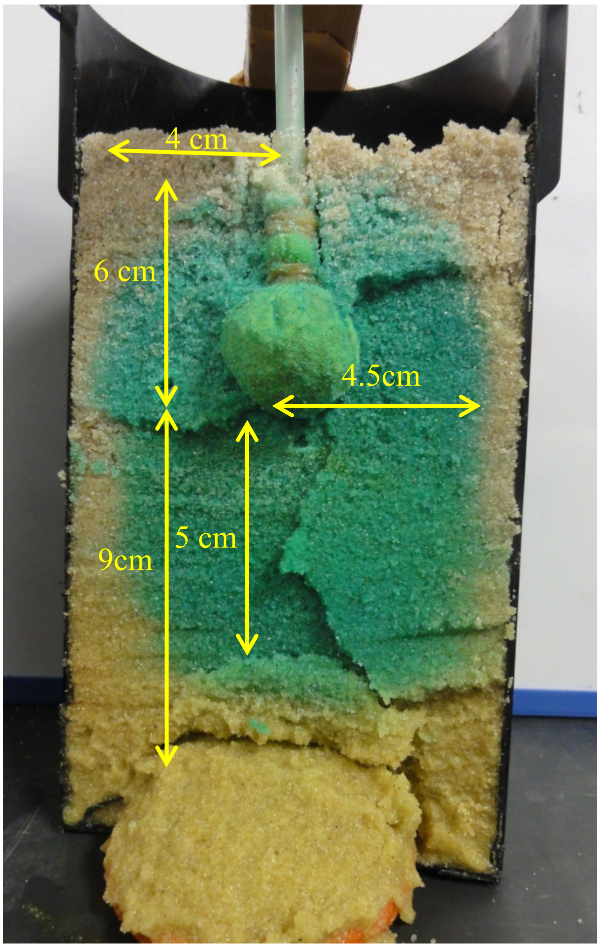

Fig.3 Solution distribution inside mid-cylinder

CONCLUSION

A series of small cylinder and mid-cylinder tests is conducted by introducing a novel grout comprising the reagent of urea-$CaCl_2$ and the biocatalyst of urease. Following conclusions are drawn from the test results.

- Noticeable increase in strength can be attained with appreciable reduction in porosity by the method of enzymatic calcite precipitation.
- Although the same procedure followed, the gain in strength and the reduction in porosity may vary.
- With several exceptions a rising trend can be seen in the relation between % of $CaCO_3$ precipitated and gain in *UCS.*
- Uniform distribution of solution can be achieved, although the change in porosity decreases with the distance from the injection point.

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