Sustainability of EICP treated sand: Permeated water and sequential loading

Jeehoon Ma[1], J.Y. Song[1], and T.S. Yun[1]

[1]School of Civil and Environmental Engineering, Yonsei University, 50, Yonsei-ro, Seodaemun-gu, Seoul, Korea.

ABSTRACT

The Enzyme Induced Carbonate Precipitation (EICP) is used to stabilize the soil in a less burden to the environment. Since the $CaCO_3$ by-product of the EICP reaction is susceptible to the acidic water and external forces, the permeability test with different pH values of the water and the sequential loading test are conducted for evaluating the sustainability. Before applying to the soil, the optimal EICP solution is measured with different urea-$CaCl_2$ molar ratio and urease concentration. The urease concentration of 0.5 g/L and 0.9 g/L with 1.5 urea-$CaCl_2$ molar ratio is the optimal condition for the 0.5M $CaCl_2$ and 1M $CaCl_2$, respectively. The $CaCO_3$ resists not only to the water with only 2.4% loss in stiffness by flushing, but also to the acidic water, showing similar permeability regardless of pH values. Also, the debonding induced stress is constant regardless of $CaCl_2$ molar concentration in dense soil while it increases as the increment of the $CaCl_2$ molar concentration in loose soil. The volume collapse in soil skeleton does not appear near the debonding induced stress.

Keywords: EICP; Loading sequence; Sustainability; Stiffness; SEM

1 INTRODUCTION

The Enzyme Induced Carbonate Precipitation recently brings an attention to improve soil stability in environmentally acceptable ways. The mechanism of EICP is as follows:

$$CO(NH_2)_2 + 2H_2O \xrightarrow{urease} 2NH_4^+ + CO_3^{2-} \tag{1}$$

$$CaCl_2 + CO_3^{2-} \longrightarrow CaCO_3 + 2Cl^- \tag{2}$$

The enzyme (urease) decomposes the urea ($CO(NH_2)_2$) and its by-product reacts with calcium ion originated from calcium chloride ($CaCl_2$) to produce calcium carbonate ($CaCO_3$). This reaction in soil then makes soil cementation to increase either strength or stiffness (Yasuhara et al., 2012). Along with this, the sustainability of the cemented soil is also serious problem to apply in-situ field. The quality of cementation highly depends on the external forces such as load applied to the surface and hydraulic effect by groundwater and rainfall. The pH of the rainfall is usually 5.6 by the reaction with the carbon dioxide (CO_2) in atmosphere, and pH of the acidic rain often decreases down to 4 because of the sulfur and nitrogen oxides. Since the $CaCO_3$ is reacted with acid solution, the understanding of resistance to the acid solution is essential for the sustainability. Also, because the inter-particle cementation can increase the stiffness of the soil which is susceptible to the external stresses, the stress leading to debonding should be investigated. Therefore, we focus on the effect by pH of permeate water and sequential loading stress. Before to proceed the experiments, the optimal condition for the EICP solution is determined with different urea-$CaCl_2$ molar ratio and urease concentration. The permeability test is to permeate the water into the specimen with different pH by measuring shear wave velocity and permeability. The sequential loading test is proceeded with different relative density and molar concentration of EICP solutions. The produced $CaCO_3$ is then visualized by SEM images to investigate the size and morphology.

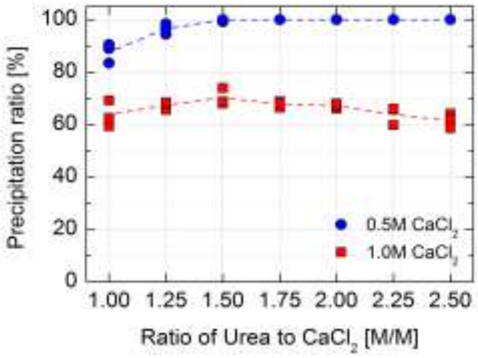
2 OPTIMAL CONDITION FOR SOLUTION

Since the production of $CaCO_3$ highly depends on the urea-$CaCl_2$ molar ratio and urease concentration, we perform the tests that 1) the urea-$CaCl_2$ molar ratio from 1 to 2.5 with 0.5 g/L urease and 2) urease concentration from 0.1 to 0.9 g/L with 1.5 urea-$CaCl_2$ molar ratio.

2.1 Experimental procedure

The urea (U5378, Sigma Aldrich), $CaCl_2 \cdot 2H_2O$ (C3881, Sigma aldrich), urease (U1500, Sigma aldrich, Jack Bean urease, 40,150 U/g activity) and NaOH (Duksan) are used for the test. The solution is divided into urease solution and urea-$CaCl_2$ solution because the urea is rapidly reacted with urease and the NaOH is added into the urea-$CaCl_2$ to make pH 8-9 which is favorable reaction environment. Each solution is poured by half into 15ml tube gently shaken with 3 times with lid closed. The reaction runs at a room temperature (20

(a)



(b)

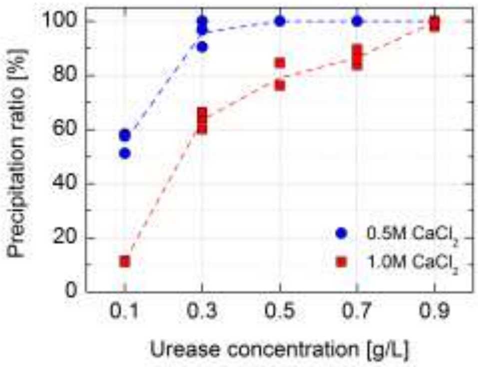


Fig. 1. Precipitation ratio with respect to (a) molar ratio of urea to $CaCl_2$ and (b) concentration of urease. Note that the precipitation ratio is produced $CaCO_3$ over the maximum $CaCO_3$.

± 1.5˚C) and after 7 days, the substance is dried at 80 °C for 24 hours with the supernatant being removed by pipet. The $CaCO_3$ is measured by produced CO_2 pressure resulting from the reaction with hydrochloric acid (ASTM 2014, D4373).

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O \qquad (3)$$

2.2 Results and Discussion

The precipitation ratio with respect to the urea-$CaCl_2$ molar ratio and urease concentration is presented in Figure 1. In Figure 1a, the precipitation ratio increases as the urea-$CaCl_2$ molar ratio increases in 0.5M $CaCl_2$. Here, the precipitation ratio remains 100% after the 1.5 molar ratio that calcium ion (Ca^{2+}) is limited to react the extra produced carbonate ion (CO_3^{2-}). In 1M $CaCl_2$, the production ratio proportionally increases with the molar ratio of urea-$CaCl_2$ up to 1.5 molar ratio, while the production ratio gently decreases with increment of the molar ratio. This phenomenon is caused by the urease that the solubility of it is affected by the total molar concentration in the solution resulting in showing salting in and out phenomenon (Hamdan 2015). Therefore, 1.5 molar ratio is optimal to yield the maximum $CaCO_3$ regardless of $CaCl_2$ molar concentration.

In Figure 1b, the precipitation ratio increases as the urease concentration increases in both cases. In 0.5M $CaCl_2$, it has constant value after 0.5 g/L while the precipitation ratio steadily increases up to 98% at urease concentration 0.9 g/L in 1M $CaCl_2$. From these results, the optimal conditions in 1M $CaCl_2$ is 0.9 g/L and 0.5M $CaCl_2$ is 0.5 g/L with fixed 1.5 urea-$CaCl_2$ molar ratio in both cases.

Table 1. Test conditions.

Test	$CaCl_2$ [M]	Permeated water pH	Condition
Water resistance	0.5	Deionized	Loose
	0.5	5	Loose
	0.5	4	Loose
Loading sequences	-	-	Dense
	-	-	Loose
	0.5	-	Dense
	0.5	-	Loose
	1	-	Dense
	1	-	Loose

3 CHARACTERISTICS OF CEMENTED SOIL

In this chapter, we describe the permeability with different pH of water for the sustainability, responses to the loading sequence, and SEM analysis for the inspection of size and morphology of $CaCO_3$.

3.1 Experimental procedure

The Jumunjin sand is used for the experiments that the mean grain size, maximum void ratio, and minimum void ratio are 0.542 mm, 0.897, and 0.6 respectively. The solution mixed with urease and urea-$CaCl_2$ solutions is filled into the cell and then the sand is poured by pluviation. The cell has bender elements that are socketed on the top and bottom. The cell is cylindrical shape with split top cap to simulate the k_0 condition. The reaction of $CaCO_3$ formation runs for 30 hours with 12 kPa applied on the top. In the measurement of shear wave velocity, the input shear wave is 50 Hz square (Agilent 33220A), and the reflected signal is filtered by filter amplifier (Krohn-hite 3944, low-pass filter at f=500 kHz, high-pass filter at f = 50Hz). The input and output signals are captured by the oscilloscope (Agilent DSO5014). The water resistance test is conducted by measuring not only the permeability with 50 cm constant head but also the shear wave velocity with the permeated water volume. The pH of permeated water is deionized, 5, and 4 for the response to the acid rain. All the sample used in this test is loose (D_r = 30%) sand with 0.5M $CaCl_2$. The loading sequences test is conducted to observe the changes of stiffness and void ratio during increment of the loading stresses ranging from 12 kPa to 1062 kPa. Each loading stage remains 15 minutes under the drain conditions. The specimens are used for loose (D_r = 30%) and dense (D_r = 70%) for 0.5M $CaCl_2$ and 1M $CaCl_2$.

3.2 Water resistance to the different water pH

The shear wave velocity seems to decrease rapidly as increase the number of pore volume, and has a constant value after 4 PV is flushed in all specimens. The loss of the shear wave velocity ranges from 2 to 2.4% which is

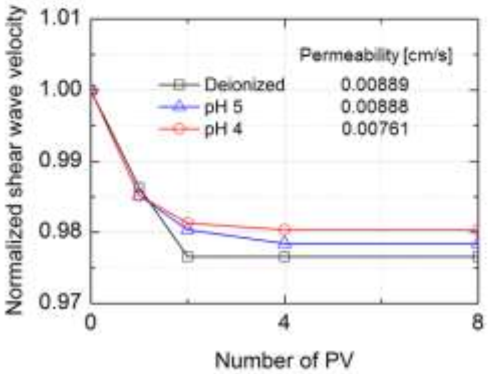


Fig. 2. The aspects of the shear wave velocity with respect to the number of pore volume. Note that normalized shear wave velocity is shear wave velocity over the initial shear wave velocity (0PV).

marginally affected by the hydraulic pressure. The effect of permeated water pH is not shown in this result. Also, the permeability with different pH of the water ranges from 0.00761 to 0.00889 cm/s which supports the previous result. From these results, the $CaCO_3$ cemented soil has the resistance not only to the repetitive flushed water but also to the acid rain condition which is pH 4.

3.3 Aspects of stiffness with loading sequences

The shear wave velocity of non-treated specimens (dense and loose) is shown in Figure 3a. The computed α, β values for loose (α = 61, β = 0.25) and dense (α = 96, β = 0.19) are well matched with proposed equation (Cha et al. 2014). The shear wave velocity increases with loading while unloading induces decrement of it which is above to those in loading. The initial shear wave velocity of 0.5M $CaCl_2$ treated specimens increases up to 589 and 686 m/s for loose and dense specimens, respectively in Figure 3b. The shear wave has constant value until 46 kPa and 180 kPa for loose and dense specimens followed by stiffness loss that is debonding of inter-particle contact $CaCO_3$. Also, in 1M $CaCl_2$ treated soil presented in Figure 3c, the initial shear wave velocity is 757 and 880 m/s for loose and dense specimens, respectively. It shows the same tendency to that of 0.5M $CaCl_2$ treated specimens that the 90 kPa and 180 kPa are the stresses being induced $CaCO_3$ debonding for loose and dense specimens. Figure 3d shows the changing aspects of the void ratio in 0.5M $CaCl_2$ and follows typical tendency to the changes of void ratio in non-treated specimen.

From these results, regardless of $CaCl_2$ molar concentration, the stiffness loss occurs at the same vertical stress in dense specimen while occurrence of it increases as increment of $CaCl_2$ molar concentration in loose specimen. Also, despite the stiffness loss, the void ratio is not significantly changed at the debonding induced stress which means skeletal collapse is not happened when compression is applied to the specimen.

3.4 Visual inspection by SEM images

The precipitated $CaCO_3$ is presented by scanning ele-

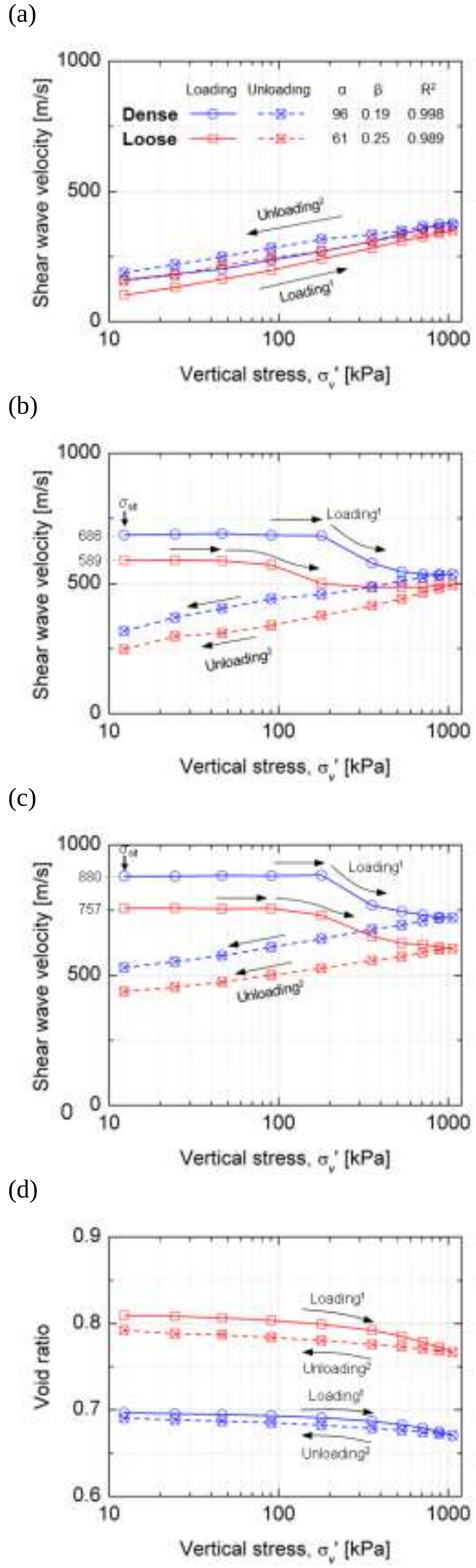


Fig. 3. Changes of stiffness to the applied load. (a) Non-trated soil, (b) 0.5M $CaCl_2$, and (c) 1M $CaCl_2$. The void ratio varied with

loading sequences of (d) 0.5M $CaCl_2$.

ctron microscope (SEM, JEOL JSM-7610F) in Figure 4.

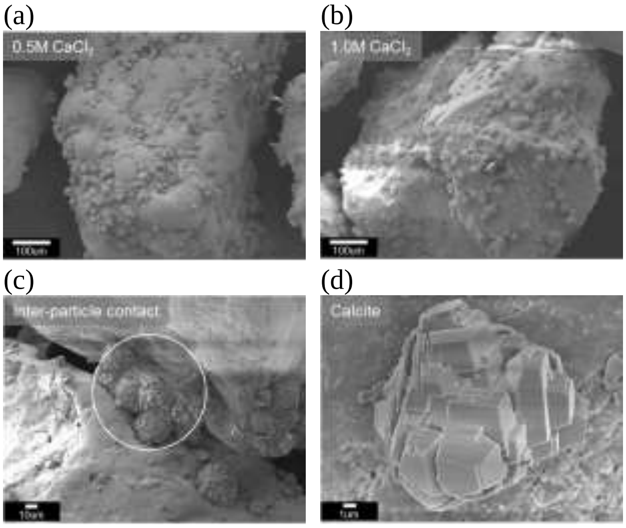


Fig. 4. SEM images of $CaCO_3$ with (a) 0.5M $CaCl_2$ and (b) 1M $CaCl_2$. (c) Inter-particle contact of $CaCO_3$ and (d) magnified of it which is rhombohedral shape.

The Figure 4a and Figure 4b show that small nodules are spreading over the soil surface. It seems that the size of precipitated $CaCO_3$ is about 15 μm and 25 μm for 0.5M $CaCl_2$ and 1M $CaCl_2$. The $CaCO_3$ is formed in the inter-particle contact resulting in the increment of stiffness (Figure 4c). Figure 4d shows the magnified $CaCO_3$ that we conclude the rhombohedral shape of $CaCO_3$ is calcite because of the shape characteristic (Al Omari et al., 2016).

4 CONCLUSION

This paper is composed of optimal conditions for precipitating $CaCO_3$ solution, exploration of water resistance, stiffness aspects with sequential loading, and inspection of precipitated $CaCO_3$. From these experimental results, the following conclusions can be drawn. The $CaCO_3$ is optimally generated at the 1.5 molar ratio of urea to $CaCl_2$ regardless of molar concentration of $CaCl_2$. Also, the optimal concentration of urease is 0.5g/L and 0.9g/L for 0.5M $CaCl_2$ and 1M $CaCl_2$ respectively. The bonding of $CaCO_3$ can resist to repetitive permeated water even in the acid rain condition (pH 4). The stiffness loss happens at the same vertical stress in dense specimen regardless of $CaCl_2$ molar concentration while the stress of it increases as increment of $CaCl_2$ molar concentration in loose specimen. The sequential compression can bring the stiffness loss while the volumetric collapse is not happened in the soil skeleton.

ACKNOWLEDGEMENTS

This work was supported by the Land and Housing Institute (LHI) grant funded by the Korea Land and Housing Corporation and the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (2016R1A2B4011292).

REFERENCES

Al Omari, M. M. H., Rashid, I. S., Qinna, N. A., Jaber, A. M., and Badwan, A. A. (2016). Calcium carbonate, In Profiles of Drug Substances, Excipients and Related Methodology, 41, 31-132.

ASTM (2014), Standard test method for rapid determination of carbonate content of soils, ASTM D4373-14, West Conshohocken, PA.

Cha, M., Santamarina, J. C., Kim, H. S., and Cho, G. C. (2014). Small-strain stiffness, shear-wave velocity, and soil compressibility, Journal of Geotechnical and Geoenvironmental Engineering, 140(10), 06014011.

Hamdan, N. M. (2015). Applications of enzyme induced carbonate precipitation (EICP) for soil improvement, PhD Thesis, Arizona State University.

Yasuhara, H., Neupane, D., Hayashi, K., and Okamura, M. (2012). Experiments and predictions of physical properties of sand cemented by enzymatically-induced carbonate precipitation. Soils and Foundations, 52(3), 539-549.