Modification of Hydraulic Conductivity of Sandy Soil using Seawater and Alkaline Solutions

Osama Dawoud

1 Civil Engineering Department, Istanbul University, Topkapi Campus, Istanbul, Turkey
E-mail: osama.dawoud@istinye.edu.tr (Osama Dawoud)

Abstract. Altering soil characteristics by precipitation of the calcium carbonate between soil particles is attracting the interest of geotechnical engineers for a wide range of applications. However, current applied approaches still face challenges such as the high cost of materials, difficult handling of precursors, and hazardous by-products. The study described by the current paper investigated the modification of hydraulic conductivity of sandy soil by chemical precipitation of the calcium carbonate using seawater as the source of calcium. The designed experiment involved treatment of bench-scale soil columns by two readily mixed solutions. One of the solutions served as the source of calcium ions and the other contained carbonate ions. The current paper compares behavior of hydraulic reduction considering different resources. The results showed that the crystals formed in small sizes as a result of the instantaneous reaction of calcium precipitation; and thus, crystals transport with the solution as colloids. Accordingly, reductions in hydraulic conductivity were mainly governed by the filtration mechanisms; and the precipitated calcium carbonate was retained close to the injection point. Conducting treatment using seawater as the source for calcium ions induced 65% reduction in hydraulic conductivity at 5.5 g CaCO₃/g soil. This reduction is identical to the case when the artificial source was used. Further treatment by the artificial source of calcium reduced the hydraulic conductivity of sandy soil by 97.2%. These outcomes suggest that the chemically induced calcium carbonate precipitation from seawater can be employed by some geo-environmental applications which are conducted in the vicinity of the shore and require reduction of hydraulic conductivity.

Keywords: Calcium Carbonate Precipitation, Seawater, Alkaline Solution, Soil Conductivity

1. Introduction

Precipitation of calcium carbonate in between soil particles is one of the processes that recently acquired the interest of the scientific community and geotechnical engineers as a potential technique for soil improvement [1, 2]. However, the instantaneous occurrence of the chemical reaction hinders the in-situ precipitation, which drove researchers to focus on inducing precipitation by microbial activity (MICP). Thus, insufficient research can be found that consider chemical precipitation of calcium carbonate for geotechnical applications.

On the other hand, application of MICP on large scales still involves several pitfalls that could hinder its applicability. These pitfalls include the hazardous by-products, introduction of exogenous species to the environment, and the complications involved in materials delivery to the site.
The research described by the current paper employed an experimental approach in order to investigate the potential modification of hydraulic conductivity of the sandy soil using chemical precipitation of the calcium carbonate using seawater as the source of calcium ions. It was envisioned that such a process might be utilized for development of impermeable barriers in order to control seawater intrusion at the coastal aquifers.

1.1. Chemical Precipitation of Calcium Carbonate

The amendments that occur to the engineering characteristics of soil by precipitation of calcium carbonate are governed by a wide range of physico-chemical processes [3–7]. However, the following sections were restricted to the chemical factors that govern the precipitation process. Also, the previously reported studies on the soil behavior that contain calcium carbonate precipitation were briefly reviewed.

The chemical precipitation of calcium carbonate is an instantaneous irreversible reaction. It can be described by the equation:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow$$  \hspace{1cm} (1)

However, the precipitation process is governed by several factors that influence the characteristics of the resulting mineral.

Calcium carbonate occurs in several mineral forms that include the stable forms of calcite and aragonite, metastable vaterite, and other amorphous forms [8]. The precipitation reaction of calcium carbonates results initially in the mineral forms of calcium carbonates that are thermodynamically unstable. This comports with Ostwald’s Law of Stages, which states that ‘the least stable phases with the highest solubility, precipitates first and subsequently transforms to the more stable ones’ [9–11]. The calcite precipitation is a phased complex process, which is controlled by temperature, nucleation sites, ionic strength, pH, solution stoichiometry and degree of supersaturation [8, 12]. These factors control the essential processes necessary for the crystallization of calcite, which are the nucleation, the crystal growth, and the transformation process.

These processes govern the precipitation of calcium carbonate in the form of calcite, which is essential for the amendment of the engineering characteristics of soils. Other metastable and transformable forms do not contribute effectively to particles cementation. Moreover, they are vulnerable to dissolution in the pore water and being flushed out of the soil.

1.2. Hydraulic Conductivity

Previous studies reported differential behavior of the hydraulic conductivity of the soil that examines precipitation of calcium carbonate. Most of these studies describe the precipitation that is biologically induced.

A recent study revealed the actual sites of calcium carbonate precipitation within the soil pores by MICP [13]. The study showed that the precipitation occurs in the solution, and over the surface of soil particles. The solid particles that form in the solution transport by the fluid flow, and they could be intercepted by other soil particles.

As the concentration of calcite content increases by treatment, the flow paths get narrowed down to full clogging. The occurrence of this clogging depends on the treatment conditions. The rate of calcite precipitation and the growth rate of calcite crystals increases as the concentration of the treatment solution increases. The concentration also specifies the maximum sizes of calcite crystals that can form, which finally controls the behavior of the hydraulic conductivity of the bulk soil.

Such variable factors that control the bulk hydraulic conductivity may explain the differences in reduction of hydraulic conductivity that were reported by different researchers.
For example, a reduction of void ratio by 6\% and 17\% of the initial condition for ‘heavily’ and ‘moderately’ treated soils was reported [14]. The ‘moderately’ treated conditions were found to cause reductions not less than 31\% in a different study [15]. It is expected that hydraulic conductivity would change according to the calcite content for each zone, and the bulk hydraulic conductivity of treated soil is dependent on the homogeneity of the property along the flow paths.

In fact, most of the measured values found in literature for hydraulic conductivity comes as part of the parameters measured for different experiments of different designs, purposes, and conditions. One of the studies that were focused on the hydraulic reductions by MICP treatment showed that the concentration of treatment solutions alter the ultimate reductions that can be achieved [16]. The low-concentration treatment was found to maintain the hydraulic conductivity of the soil with no significant changes, while abrupt and severe clogging was noticed when high-concentration treatment was employed. This was explained on the basis of the size of calcite crystals and their relation to the concentration of the solution. Large crystals seem to clog the pores much faster than the small ones that instead get uniformly precipitated over the surface of soil grains, which was demonstrated few years later [13].

The mechanism described for clogging of the pores by calcite precipitation indicates that a full clogging of soil is possible if the treatment conditions are set properly. This has been validated by a different study [17] where a model of sand was treated with MICP by permeation, and circulating the effluent back again to the model. A thin crust of calcite with low permeability $1.6 \times 10^{-7}$ m/s at the surface of the model with thickness of 1.0 mm. However, the small depth of the crust gives an indication that clogging is more likely to happen close the injection point rather than to extend with a uniform distribution along the flow path.

Furthermore, the reduction in the hydraulic conductivity occurs according to two phases. The first phase was characterized by insignificant reductions in hydraulic conductivity that is accompanied by remarkable increase in calcium carbonate content in the soil. In the following phase, the hydraulic conductivity sharply decreases by any increase in the soil content [18].

1.3. Chemical precipitation of calcium from seawater
Calcium is of the most abundant ions in seawater, and its concentration is governed by the overall speciation of other ions. For example, oceans acidification causes dissolution of calcareous rocks and coral bleaching.

However, the precipitation of calcium carbonate might be affected by the presence of other ions in the seawater. Although the presence of unstable forms in natural systems is improbable, several studies have reported the presence of amorphous forms due to the presence of inhibitors of calcite crystallization [10], which acts in different mechanisms. Some of these inhibitors are inorganic such as Mg$^{2+}$. These ions were found to incorporate the inhibition of calcite formation process by blocking active growth sites, or straining the local crystal lattice increasing its solubility of the formed crystals [19]. The inorganic orthophosphate ions were found to retard the dissolution of vaterite and crystallization of calcite by blocking the active sites by the adsorbed phosphate [20]. Also, it was reported that the rate of calcite precipitation slowed down by a factor of 2 due to the presence of dissolved sulfate in the solution [21]. Furthermore, other forms of precipitates such as magnesium hydroxide might appear if precipitation is induced by elevating pH magnitude. This precipitate does not contribute the binding process.

1.4. Concluding comments on previous studies
The soil amendment by chemical precipitation of the calcium carbonate was downgraded due to the practical issues facing its application. However, it is still worthy to investigation of its feasibility for applications where the seawater fills the soil pores as the seawater would represent the source of calcium. The soil salinity in these environments would be already high and the chemical treatment would not pose extra contamination.
Many studies employed the soil columns for the sake of simplicity. These designs were found convenient for the current study. The concentrations of the calcium that were used for the current study comply with the magnitudes recommended by previous researchers for the

2. Design of the Experiment
The experiment design involved a controlled system for simultaneous injection of two chemical solutions in a column of a soil specimen, as shown in Figure 1.

Two separate tanks were used to store the chemical solutions. One tank contained the calcium-source solution, while the other was used to store the alkaline solution. Two tests were conducted using two different sources of calcium. For the first test, a solution of 0.1M CaCl$_2$ was used. For the second test, the seawater was used as the source of calcium. Seawater samples were collected directly from the sea in containers of 29L each. The Alkaline solution composed of 0.1M and 0.01M NaHCO$_3$ solution for Tests 1 and 2 respectively. The suction tubes from the two tanks are mixed at a tube junction that is fitted before the pump.

A peristaltic pump was used for injection of the solutions. The pump was sufficient to provide the flow and pressure required for the experiment. However, as a centrifugal pump, the flow rate and the exerted pressure varied during the experiment. Thus, the pump was characterized in order to identify the pump curve. The flow rate was measured, and the hydraulic head was identified using the pump curve.

A timer was used to run the pump intermittently. The timer was designed and programmed explicitly for the current experiment. A retention time of 1 hour was given after each injection. This retention time was suggested to allow for any short-term potential transformation of the crystal forms of calcium carbonate.

A soil specimen of silica sand-medium grade was used for the test. The initial hydraulic conductivity of the specimens was measured as 2.13 m/s and 2.49 m/s for Tests 1 and 2, respectively. The column was 15 cm in height, and 5 cm in diameter. A nylon filter of 0.2 mm-diameter of openings was used at the top and the bottom surfaces of the soil specimen. The effluent of the soil specimen was collected in a dedicated disposal tank.

Concentration of calcium ion in seawater was determined in the lab using EDTA method. The ion concentration reported as 0.0103 M with 0.12% relative deviation.

3. Results and Discussion
The measured flow rate during each injection was transformed into a hydraulic head using the equation fitted to the pump curve. This helps calculation of the hydraulic conductivity of the
specimen for every injection using Darcy’s equation:

\[ K = \frac{Q L}{A \Delta h} \]  

(2)

Where:

- \( Q \) is flow rate (cm\(^3\)/s);
- \( L \) is the length of the soil column;
- \( A \) is the cross-sectional area of the soil column (cm\(^2\));
- \( \Delta h \) is the head exerted by the pump (cm).

The calculated hydraulic conductivity from both tests is plotted together in Figure 2. For comparison reasons, the results of the two specimens were plotted against the cumulative number of moles of carbonate ion that were injected. This was applied since the available data is the number of injections. At the same time, the concentration of the chemicals used was different. The real indicator for the soil behavior is the amount of the precipitate. In the current case, it is presented by the amount of precipitate precursors that were injected since no approach is available for real-time measurement of the precipitate changes.

As shown in the figure, soil specimen in Test 1 (which employs CaCl\(_2\) as calcium source) exhibited a gradual reduction in hydraulic conductivity by treatment. The general behavior matches the behavior described in literature for the reduction of the hydraulic conductivity by microbial calcite induced precipitation [18].

However, the visual inspection of the effluent shows that the effluent contained a precipitate of small particles that behave as colloids. It was suspected that these colloids exhibit sedimentation by gravity, and they are stable such that they do not transform into larger crystals. It reported that the calcite crystals that form as a result of chemical reaction are considerably smaller than the ones that are triggered biologically [22]. This probably due to the lack of preferential surfaces of precipitation. Furthermore, the calcium carbonate accumulated close to the injection surface causing clogging. After injection of 10.9 mole/g of soil of Ca\(^{2+}\) and CO\(_3^{2-}\), the hydraulic conductivity of specimen from Test 1 dropped down to 2.7% of the original hydraulic conductivity. Figure 3 shows an optical microscopic scanning of the specimen from Test 1. The scanning was made to the specimen surface at the injection point. The precipitate appeared in white color filling the pores providing a visual evidence of the clogging that occurred.

35% reduction in the original hydraulic conductivity was attained after injection of 5.5 moles CO\(_3^{2-}\)/100 g of soil. This is comparable to the 28% reduction that was achieved using the artificial source of calcium ions.

However, the number of injections using the seawater was ten times the number of injections needed for Test 1 for the same amount of injected chemicals. This required huge amounts of water and a long time of the experiment; therefore, experiment was terminated at this stage. In fact, the effort and time required for treatment using seawater is an obstacle that has to be studied from a practical point of view.

4. Conclusion
The study described by the current paper investigated the reduction of soil hydraulic conductivity by chemical precipitation of the calcium carbonate. The experiment involved of injection of readily mixed solutions into a soil column. One of the solutions served as a source of calcium ions and the other contained carbonate ions. Two tests were conducted examining different sources of calcium. The first test employed two 0.1M solutions of CaCO\(_3\) and NaHCO\(_3\). The other test involved mixing a solution of 0.01M NaHCO\(_3\) with seawater (as the source of calcium). During the test, it was noticed that crystals formed in small size, and they were prone to mobility by fluid flow. These observations suggested that the precipitate followed the mechanisms of colloids transport and sedimentation; and thus reductions in hydraulic conductivity were governed by
Figure 2. Changes in hydraulic conductivity by treatment

Figure 3. Optical microscopic scanning of samples from Test No. 1 at injection surface after termination of the experiment
the filtration mechanisms. It was noticed that precipitate accumulated close to the soil surface at the injection point.

Employing seawater and artificial source of calcium ions induced reductions in hydraulic conductivity of 35%, and 28% of the original magnitude, respectively. These reductions were achieved after injection of 5.5 mole/100 g of soil. Both specimens exhibited the same general behavior of reduction of hydraulic conductivity by treatment.

Calcium content of seawater could be beneficial for geoenvironmental applications that focus on precipitation of the calcium carbonate. However, such application might be restricted to the vicinity of the shore. It could be utilized for applications such as impermeable barriers. The proposed technique offers several advantages against traditional methods. Using sweater would minimize the costs of treatment to a competitive level to other techniques and materials which are used for the same kind of soil treatment. The materials used by the current research are non-hazardous, and the applied treatment is easily reversible. However, the amount of injected water is considerably high. Therefore, this technique has to be assessed in terms of energy consumption and required time of treatment.

References
[1] Mitchell J K and Santamarina J C 2005 Journal of geotechnical and geoenvironmental engineering 131 1222–1233
[2] Jiang N J, Tang C S, Hata T, Courcelles B, Dawoud O and Singh D N Soil Use and Management
[3] Achal V and Pan X Applied Biochemistry and Biotechnology 1–11 URL 10.1007/s12010-014-0842-1
[4] Cheng L, Cord-Ruwisch R and Shahin M A 2013 Canadian Geotechnical Journal 50 81–90 URL 10.1139/cgj-2012-0023
[5] Gorospe C M, Han S H, Kim S G, Park J Y, Kang C H, Jeong J H and So J S 2013 Biotechnology and Bioprocess Engineering 18 903–908 URL 10.1007/s12257-013-0030-0
[6] Kawano J, Shimobayashi N, Kitamura M, Shinoda K and Aikawa N 2002 Journal of Crystal Growth 237-239, Part 1 419–423 URL 10.1016/S0022-0248(01)01866-8
[7] Nemati M and Voordouw G 2003 Enzyme and Microbial Technology 33 635–642 URL 10.1016/S0141-0229(03)00191-1
[8] van der Weijden C H and van der Weijden R D 2014 Journal of Crystal Growth 394 137–144 URL 10.1016/j.jcrysgro.2014.02.042
[9] Kralj D and Brečevic L 1995 Colloids and Surfaces A: Physicochemical and Engineering Aspects 96 287–293 URL 10.1016/0927-7757(94)03063-6
[10] Kralj D, Brecevic L and Nielsen A E 1990 Journal of Crystal Growth 104 793–800 URL 10.1016/0022-0248(90)90104-5
[11] Kralj D, Brecevic L and Nielsen A E 1994 Journal of Crystal Growth 143 269–276 URL 10.1016/0022-0248(94)90067-1
[12] Wolthers M, Nehrke G, Gustafsson J P and Cappellen P V 2012 Geochimica et Cosmochimica Acta 77 121–134 URL 10.1016/j.gca.2011.11.003
[13] Wang Y, Soga K, Dejong J T and Kabla A J 2019 Géotechnique 69 1086–1094
[14] DeJong J T, Mortensen B M, Martínez B C and Nelson D C 2010 Ecological Engineering 36 197–210 URL 10.1016/j.ecoleng.2008.12.029
[15] Whiffin V S, van Paassen L A and Harkes M P 2007 Geomicrobiology Journal 24 417–423 URL 10.1080/01490450701436505
[16] Qabany A A and Soga K 2013 Geotechnique 63 331–339 URL 10.1680/geot.SIP13.P.022
[17] Stabnikov V, Naeimi M, Ivanov V and Chu J 2011 Cement and Concrete Research 41 1143–1149 URL 10.1016/j.cemconres.2011.06.017

[18] Dawoud O, Chen C Y and Soga K 2014 Microbial Induced Calcite Precipitation for Geotechnical and Environmental Applications (American Society of Civil Engineers) pp 11–18 URL 10.1061/9780784413456.002

[19] Nielsen L C, Yoreo J J D and DePaolo D J 2013 Geochimica et Cosmochimica Acta 115 100–114 URL 10.1016/j.gca.2013.04.001

[20] Katsifaras A and Spanos N 1999 Journal of Crystal Growth 204 183–190 URL 10.1016/S0022-0248(99)00174-8

[21] Flaathen T K, Oelkers E H, ur R Gislason S and Aagaard P 2011 Energy Procedia 4 5037–5043 URL 10.1016/j.egypro.2011.02.476

[22] Mitchell A C and Ferris F G 2006 Geomicrobiology Journal 23 213–226 URL 10.1080/01490450600724233