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Review

Review of Enzyme-Induced Calcite Precipitation as a Ground-Improvement Technique

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Abstract: Calcite-induced precipitation methods (CIPMs) have recently become potential techniques in geotechnical engineering for improving the shear strength of sandy soil. One of the most promising methods among them is enzyme-induced calcite precipitation (EICP). In this technique, a mixed solution composed of reagents and the urease enzyme, which produces calcite, is utilized as the grouting material. The precipitated calcite in granular soil provides ties among the grains of soil and limits their mobility, thus promoting an improvement in strength and stiffness and also a reduction in the hydraulic conductivity of sandy soil. This paper discusses the potential increase in the strength and stiffness of the soil, the additional materials for grouting, the effect of these materials on the treatment process, and the engineering properties of the soil. The possible sources of the urease enzyme and the applicability of the EICP method to other soil types are also discussed in this paper. The environmental and economic impacts of the application of EICP are also presented. The envisioned plans for application, potential advantages, and limitations of EICP for soil stabilization are discussed. Finally, the primary challenges and opportunities for development in future research are briefly addressed.

Keywords: calcite; engineering properties; environmental impact; microstructure; uniformity distribution

1. Introduction

Numerous feasible methods have recently been developed for various purposes related to ground improvement, such as soil densification, the utilization of synthetic materials [1–3], grouting or the deep-mixing method [4,5], and stone columns [4,6]. Most of the existing methods require a significant effort in terms of their preparation, production, and application [1,3]. For instance, a variety of materials can be applied for chemical grouting, including cement, lime, or other gel-like materials, depending upon the purpose of the stabilization [6–9]. In this technique, the compound solution is injected into the soil. Thus, it solidifies in the voids, binds the soil, enhances the soil's engineering properties, and reduces the soil's hydraulic conductivity.

The grouting method is prevalent because it can also be used to improve the strength of the soil underneath existing buildings. However, the use of a compound material may promote the pH in the soil to a profoundly basic level, and thus, pollute the soil [1,5,10,11]. The environmental aspect of the application of a chemical material should be given a great deal of thought. Moreover, the high thickness and quick pace of the solidifying process of the compound's materials can cause an unexpected decrease in the soil's hydraulic conductivity, subsequently restricting the area of improvement. The constraints of the current method for ground stabilization require the advancement of an elective method that is environmentally friendly, viable, and effective for increasing the properties of the soil.

Potential methods combined from the interdisciplinary fields of biology, chemistry, and geotechnics have been proposed. One of the advancing potential methods uses a type of bio-grout and is called the calcite-induced precipitation method (CIPM) [10,12–21]. It has been studied extensively as a possible ground-improvement method. It can enhance the strength and stiffness of the soil [12,19,21,22] and reduce the permeability [13–16,23].

2. Concept of Calcite Precipitation Method

In the calcite precipitation method, grouting material, which produces $CaCO_3$, is applied to the soil. The blended solution consists of urea and calcium chloride, and a catalytic agent is utilized in preparing the solution. Many studies on the calcite precipitation technique have used bacteria to hydrolyze the urea and to provide carbonate ions, thus forming $CaCO_3$ as the calcium [10,12,14]. The chemical processes of the formation of $CaCO_3$ are given by Equations (1)–(3):

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

$$CaCl_2 \rightarrow Ca^{2+} + 2Cl^- \tag{2}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\downarrow \ (\text{precipitated}) \tag{3}$$

The precipitated calcite in the soil can bind the soil particles, limiting movement and improving the soil's engineering properties [13,15]. The precipitated calcite blocks the voids, decreasing the porosity and permeability [13,15]. However, some difficulties are encountered in the use of microorganisms in this method; for example, it requires specific handling to control the bacterial cultivation [19,21]. Furthermore, the high amount of substances might hamper the ability of the bacteria to hydrolyze urea [24], and consequently, limit the bacterial activeness in the soil [23,25].

The elective method related to calcite precipitation, which utilizes an enzyme to produce carbonate ions instead of microorganisms, is called enzyme-induced calcite precipitation (EICP). It has been proposed in many studies [13,21,23]. Employing the urease enzyme is more straightforward than employing bacteria because biological treatments do not need to be considered [13], in contrast to the CIPM method, for which special treatment of the bacteria is required. In this method, urease powder was pre-mixed with sand in dry condition. Then, $CaCl_2$-urea solution was injected with a confining pressure of 50 kPa [13]. However, this grouting technique, in which the enzyme is pre-mixed with soil prior to applying the solutions, may be insufficient. A set of grouting solution should be applied to the soil in a group [13]. Neupane et al. [21] and Putra et al. [19] have evaluated the applicability of the grouting technique using EICP composed of purified urease and reagents. The strength of up to 0.6 MPa was obtained from the improved samples [19,21]. In this method, the solutions composed of purified urease, calcium chloride, and urea are introduced directly into the soil. The improvement in soil strength using the calcite precipitation method is shown schematically in Figure 1 [19,21].

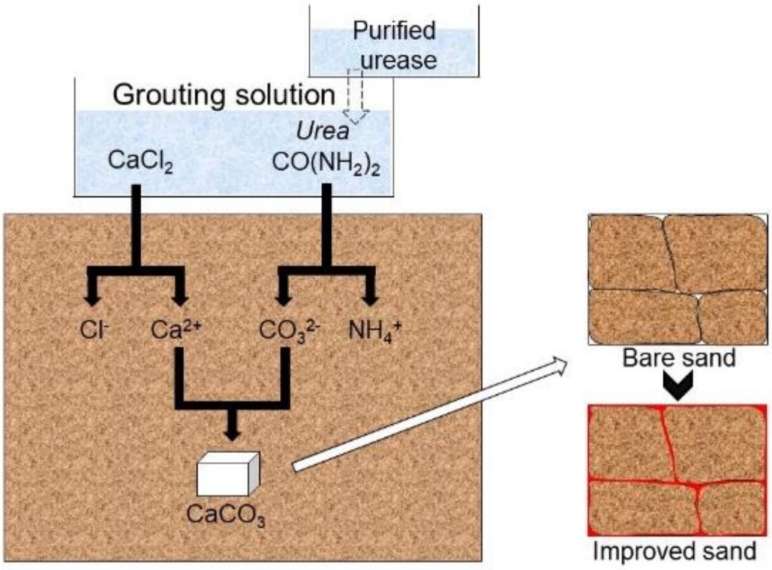

Figure 1. Schematic of precipitation process and grouting procedure in the enzyme-induced calcite precipitation (EICP) technique [19,21].

3. Amount of Precipitated Calcite

Enzyme-Induced Calcite Precipitation (EICP) is a grouting method that produces calcite minerals after the hydrolysis process using the bio-catalyst of the urease enzyme. The effectiveness of the urease enzyme as the bio-catalyst of the urea and in the promotion of the calcite crystals in the presence of calcium ions has already been examined in several studies [13,19,21,26]. Tube experiments were conducted in many of the studies to assess the mass of formed calcite [19,21,26–29]. Various concentrations of urease were blended with water, stirred for two minutes, and purified using filter paper to obtain the urease solution. Solutions of urea and $CaCl_2$ were also prepared, blended thoroughly in a tube, and then permitted to react in a various curing time. After the curing times, the amount of precipitated calcite was evaluated. The grouting solution was sieved through filter paper. Then the elements held on the filter paper, and the tube were dried at 60 °C for 24 h and calculated as the precipitated mass [20,21]. The procedure for the tube experiment is illustrated in Figure 2 [19,21].

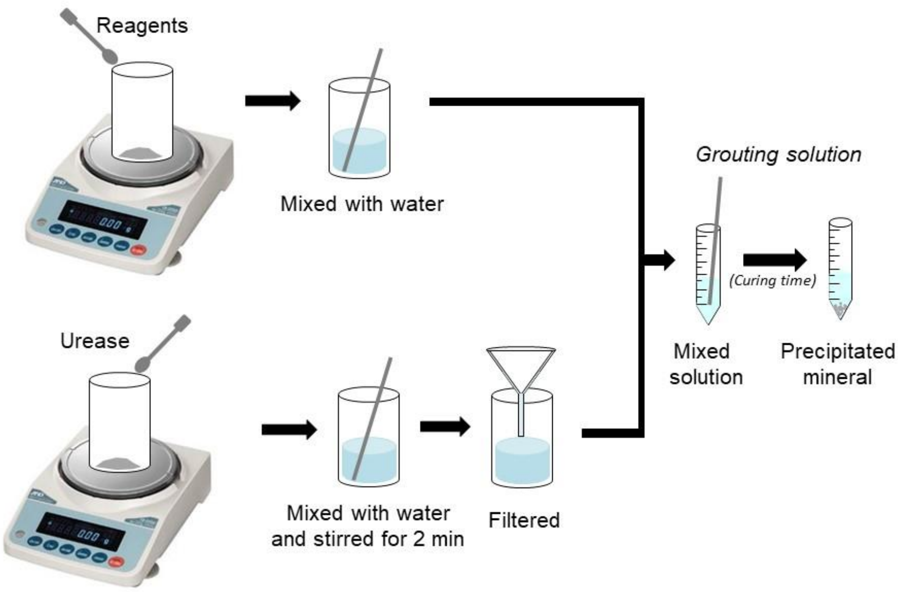

Figure 2. Procedure of the tube experiment [19,21].

Neupane et al. [21] investigated the mass of precipitated calcite from various combinations of reagents and urease [21]. The urea-$CaCl_2$ concentration of 0.5 mol/L was reported to have a higher calcite content than that of 1.0 mol/L [21]. It reached more than 80% with urease concentrations of 2.0 g/L and 3.0 g/L. Furthermore, the efficiency of the precipitated calcite was seen to decrease at a high level of reagent [27]. Putra et al. [19,20] evaluated the effect of magnesium compounds (i.e., $MgCl_2$ and $MgSO_4$) in improving the applicability of the EICP method as a soil-improvement technique [19,20]. Magnesium compounds are substituted for calcium chloride to make various combinations of $CaCl_2$-$MgCl_2$, and $CaCl_2$-$MgSO_4$, respectively. The existence of a magnesium compound brings about a critical impact on the improvement of the mass of the precipitated calcite. Increments in the calcite mass of 20% and 10% were obtained by the addition of $MgCl_2$ of 0.10 mol/L and $MgSO_4$ of 0.05 mol/L, respectively [27]. The precipitated mass of more than the maximum theoretical weight of the precipitation of $CaCO_3$ was found in previous studies [19,20,27]. The results revealed that precipitated materials, other than calcite, were also formed [20]. A summary of the results of the precipitated tests in several studies is shown in Figure 3 [19–21].

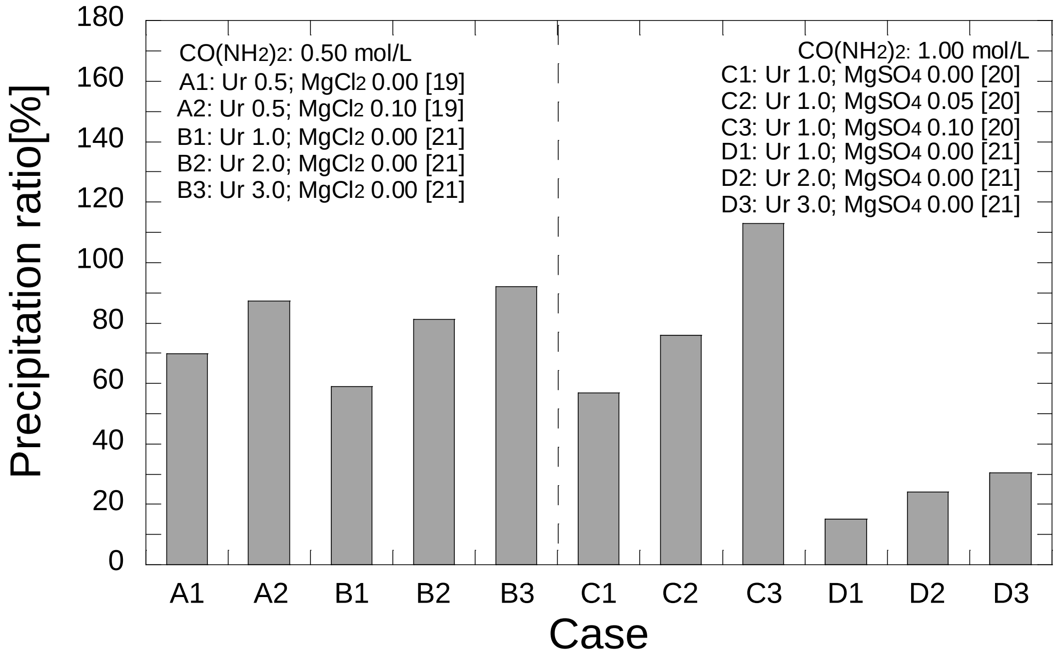

Figure 3. Summary of amounts of precipitated calcite [19–21].

4. Shear Strength

An improvement in the shear strength of cemented soil is essential for proving the applicability of EICP as a ground-improvement method. Compressive tests have been conducted in many studies to examine the improvement in soil cohesion after treatment by an EICP solution [13,19,20,23,27–31]. Neupane et al. [21] and Putra et al. [19,20] used cylindrical tubes to prepare the soil samples and poured in the solution from the top. The amount of solution was determined by the quantity of pore volume (PV). After the curing times of 3–5 days, depending on the tube experiment, the treated sample was pulled out and the unconfined compressive strength (UCS) test was conducted. The procedure for the sample preparation of the UCS tests is shown in Figure 4 [19,20].

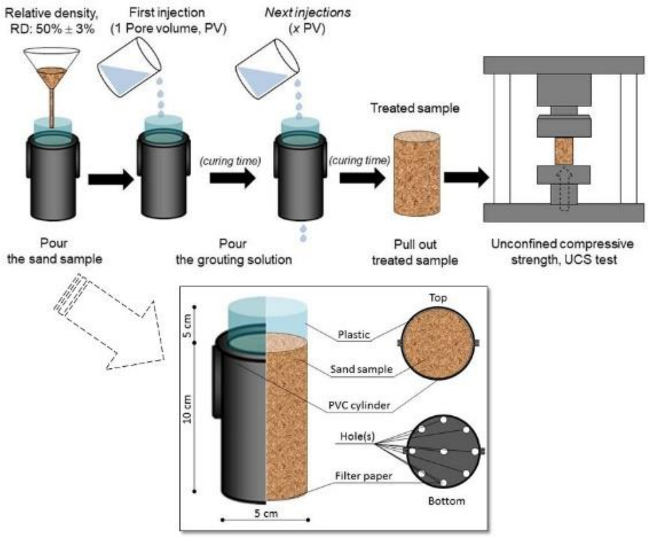

Figure 4. Procedure for sample preparation of UCS tests [19,20].

Strength levels varying from 0.2 to 1.6 MPa were obtained in previous studies. Yasuhara et al. [13] reported that cohesion of sand from 0.40 to 1.60 MPa might be obtained when precipitated calcite fills 5–10 pore volumes [13]. Putra et al. [19,20] evaluated the impact of magnesium compounds of magnesium chloride and magnesium sulfate as a substitution material for calcium chloride on the mechanical properties of cemented soil [19,20]. The substitution of 0.1 mol/L of $MgCl_2$ led to the acquisition of strength of 600 kPa from the treated specimens containing 8% calcite mass [19]. Putra et al. [20] explained that the mass of the calcite crystal, 4% to 10% of the soil mass, was achieved by 1–3 cycles of treatment with additional magnesium sulfate [20]. The highest cohesion of 0.6 MPa was obtained with the existence of 10% calcite when $MgSO_4$ of 0.2 and 0.4 mol/L were added. These improvements are 2.5-fold higher than that of the initial EICP. In addition, Putra et al. [29] also evaluated the improvement in cemented soil treated by a combination of EICP and zeolite [29]. Zeolite was applied to reduce the ammonia compound as waste in the hydrolysis process [29]. The precipitated amounts, ranging from 2%–9% of the soil mass and corresponding to cohesion of 20 to 300 kPa, were achieved by 1–3 cycles of treatment [29]. In order to examine the results of the EICP application, a graph correlating the amount of calcite and the strength was developed. It is given in Figure 5 [12,19,25,28,29,32].

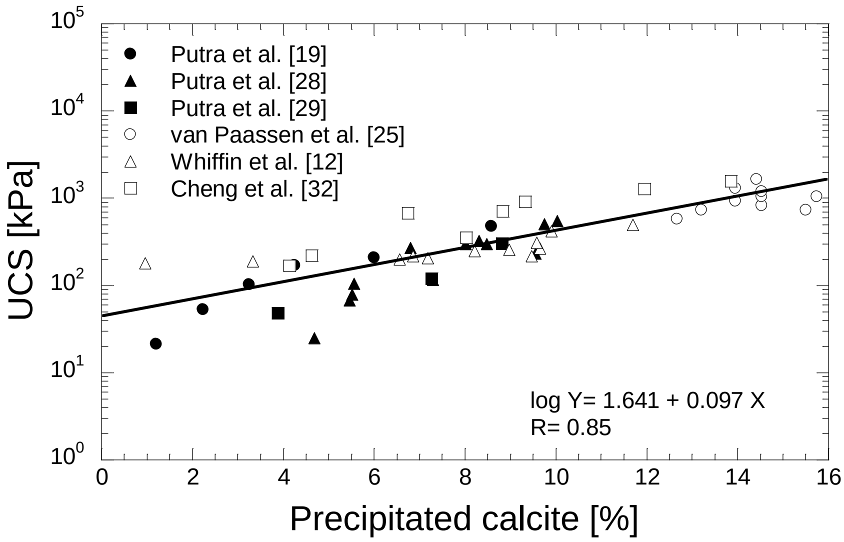

Figure 5. Strength of treated sand for several masses of precipitated calcite [12,19,25,28,29,32].

A variety of data on the strength ranging from 40 kPa to 1 MPa corresponding to the precipitated masses ranging from 1% to 16% of the soil, taken from relevant and adequate literature, is summarized and analyzed to provide a regression–exponential curve. This curve indicates that the improvement in strength provided by the calcite precipitation method may be estimated when the mass of the calcite crystal has been fit calculated with the coefficient of correlation R of 0.85.

5. Permeability

Among the essential tasks in soil-improvement techniques is controlling the soil permeability. The grouting solution should still be allowed to permeate within the improved soil to increase the amount of precipitated mineral and the strength of the soil [28]. Yasuhara et al. [13] and Putra et al. [28] conducted permeability tests on cemented sand after treating it with EICP grouting solutions. Permeability tests on improved sand after being treated by EICP grouting, reported in several studies, are depicted in Figure 6 [13,28].

As shown in Figure 6, the presence of a small amount of precipitated calcite can significantly reduce the hydraulic conductivity. The permeability of 1×10^{-2} cm/s was obtained when 8% of precipitated minerals existed within the sand sample. The permeability was roughly constant with the existence of a 6% calcite crystal. It is convincing that the hydraulic conductivity could be diminished even further with extra treatments. The mass of the precipitated calcite was able to be improved as long as further treatments were allowed to fill the voids of the soil.

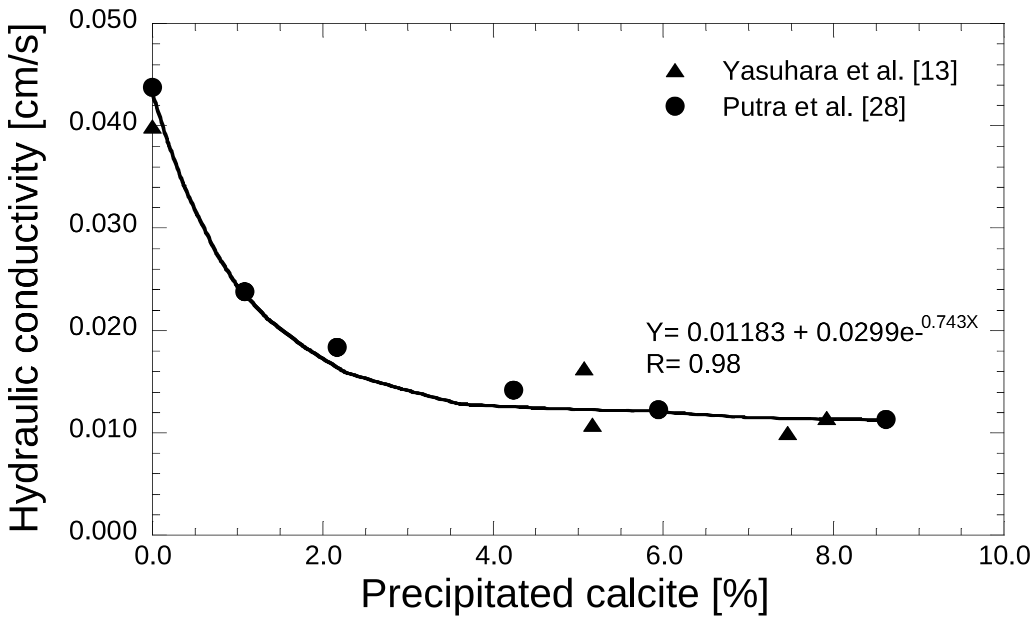

Figure 6. Permeability test results of cemented sand after treatment by EICP grouting solution [13,28].

6. Uniformity Distribution

It is considered essential to understand and control the distribution of precipitated minerals for the practical application of calcite precipitation techniques [14,28]. The upscale of the EICP technique on an extended sample has already been reported in previous studies [30]. A drum-can test was performed here to examine the uniformity of the calcite crystal within the soil sample. Spherical shapes were obtained for the improved sand, and the distribution of calcite was almost uniform [30]. A concentrated calcite crystal was obtained locally at the inlet; this might be attributed to the higher rate of precipitation [30,33]. The rate of the calcination process may have a notable impact on the growth of the treatment area. The improved sample in the drum-can, after treatment by the EICP grouting solution, is shown in Figure 7 [30].

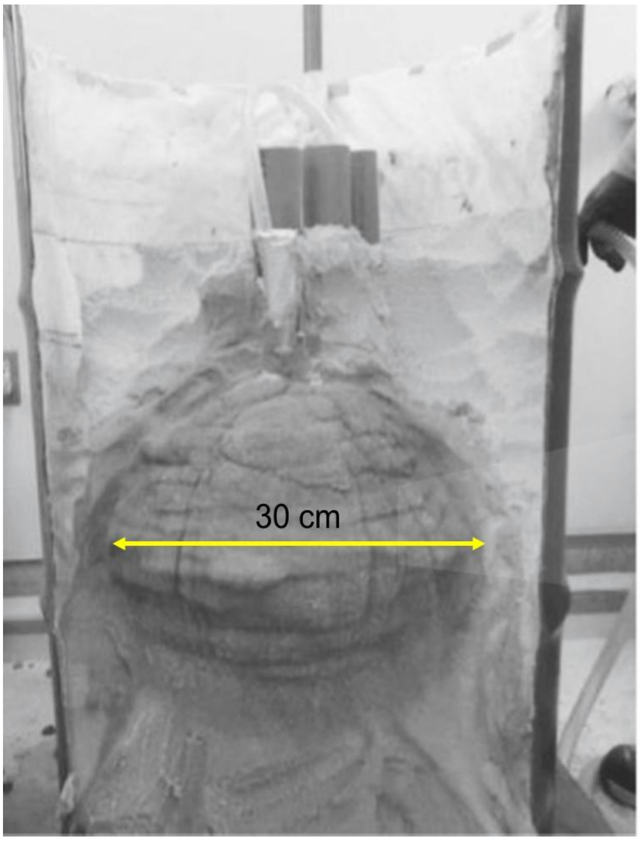

Figure 7. Improved sample after treatment by EICP grouting solution in a drum-can experiment [30].

Putra et al. [19,27,28] revealed that the substitution of a magnesium compound was able to control the hydrolysis rates in the calcite precipitation process. Mucci et al. [34] and Meldrum et al. [35] also reported that the precipitation rate of calcite decreases with an increase in the dissolved magnesium concentration [34–37]. The use of magnesium was seen as compelling in deferring the reaction by over 60 min [19,28]. Putra et al. [28] conducted 1 m sand column tests to assess the distribution of calcite in the soil. The homogeneous distribution of the calcite within the 1 m sand sample was achieved when 0.1 mol/L of magnesium chloride was added [28]. These results established that the presence of magnesium will delay the reaction process and improve the homogenous distribution of calcite in the soil [28]. Compared to the previous studies, in which calcite precipitation [33] was addressed, the distribution using magnesium was more homogenous. It is noticeable that, when using magnesium, it is possible to increase the uniformity of the calcite distribution within a soil specimen by 48% [28,30].

7. Microstructure Analysis

In order to evaluate the calcite formation and its mineralogical substances, scanning electron microscopy (SEM) and X-ray diffraction (XRD) were conducted. Putra et al. [19] reported that the rhombohedral calcite is promoted in calcite precipitation. Thus, this research also presents the impact of magnesium utilization on the shape of the precipitated calcite. It is reported that magnesium has a significant effect on the form of the precipitated mineral. The rhombohedral pattern of the calcite transforms the amorphous structure when the high amount of magnesium (50%) is substituted [19]. The evolution of the calcite structure as the outcome of the addition of magnesium is given in Figure 8 [19].

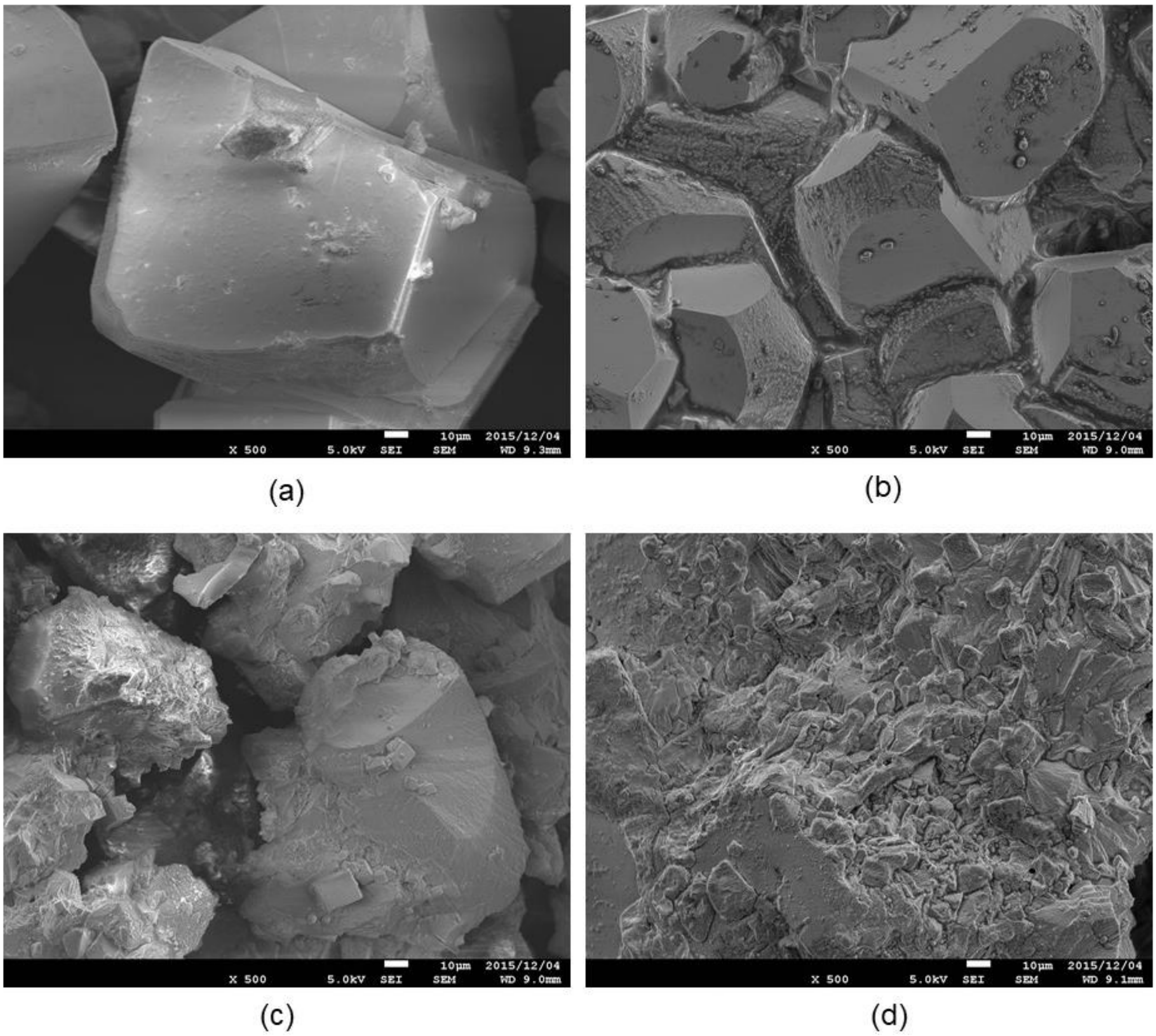

Figure 8. Evolution of calcite structure: (**a**) rhombohedral calcite (without magnesium), (**b**) addition of 10% magnesium, (**c**) addition of 20% magnesium, and (**d**) addition of 50% magnesium [19].

Putra et al. [28] also performed a SEM analysis of treated sand; the results are depicted in Figure 9a. The calcite is located on the surface and at the rounded parts of the soil particles. Simatupang et al. [26] also investigated the microstructure of treated sand using SEM. Figure 9b shows a SEM image of treated sand after treatment by an EICP solution [26]. It can be seen that the precipitated calcite is concentrated at the contact surface. The treated sand's SEM images confirm that the precipitated calcite coated the sand particles and formed bridges between them. Al Qabany et al. [38] reported that the amount of precipitated calcite in soil depends upon the reagent of the urea-$CaCl_2$ concentration. With a low concentration of reagent (0.25 mol/L), the precipitated calcite is found to be distributed uniformly. In contrast, with a high concentration of reagent, the distribution of calcite is accumulated over the surface of the sand grains [38].

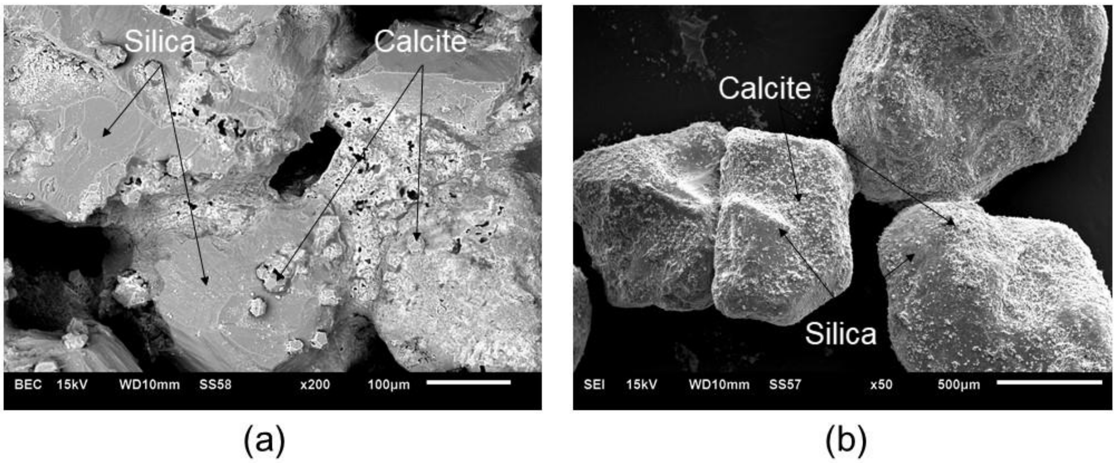

Figure 9. SEM images of precipitated material in treated sand: (**a**) at free surface and boundary of sand grains [28] and (**b**) on surface of sand grains [26].

The position of precipitated calcite on the sand grains has a significant impact on the strength of treated soil. A sufficient compressive strength can be achieved at a low calcite content if the location, pattern, and morphology of the precipitates are favorable [39]. Almajed et al. [39] also reported that the use of powdered milk can localize the carbonate precipitated at interparticle contacts, thus bringing about the significant impact on compressive strength. An UCS of 1.8 MPa can be achieved when 0.9% (w/w) of precipitated calcite was promoted in the joint contact of soil grains [39]. In comparison to the previous studies, which addressed that the precipitated calcite was formed along the surface of soil grains, a strength of 0.5 MPa may require the precipitated content in excess of 3% of soil mass.

8. Environmental Impact

The EICP method produces ammonia ions as a by-product of urea hydrolysis (see Equation (1)). Ammonia ions play an essential role in the precipitation process. The presence of ammonia ions raises the pH, and hence, encourages calcite formation [40,41]. However, ammonia ions are toxic, and the toxicity may contaminate the soil [11,42]. Hence, reducing the ammonia concentration without compromising the effectivity of EICP for ground-improvement is an important task in developing an environmentally friendly ground-improvement method.

Several promising methods of ammonia removal have been introduced, such as nitrification, striping, and ion exchange [43,44]. Ion exchange using natural zeolite of mordenite has been proved as a possible method for reducing the ammonia content [44–49]. The use of zeolite for eliminating ammonia is considered as a practical and effective method [50–53]. Putra et al. [29] reported that zeolite utilization significantly reduces the ammonia concentration during hydrolysis [29]. A certain concentration of zeolite and a certain mixing time are found to have a crucial impact on the reduction in the ammonia concentration [29]. It can lead to the removal of 75% of the maximum theoretical concentration and, namely, reduce the concentration of ammonia by 75%. These results elucidate that the use of zeolite in the EICP method may be a potential alternative for use as an environmental-friendly soil-improvement method [29].

9. Alternative Sources of Urease Enzyme

The EICP technique utilizes urease enzyme commercial products from jack beans to improve the properties of the soil [13,21,27]. The efficacy of the urease enzyme to hydrolyze urea to carbonate and ammonia ions was proved in previous works [19,27]. However, urease purification needs to be considered, especially in terms of the economic aspect. Jack bean meal, as the main source of the urease enzyme's commercial product, should be purified to promote a high purity enzyme. It may be very costly if the application of EICP is performed on a large scale [54,55]. Hence, finding an alternative source to the urease enzyme is an essential task for reducing costs, and thus, promoting the simple and low-cost application of EICP for ground improvement.

Several studies have recently investigated potential alternative sources to urease enzymes, such as crude extracts from watermelon seeds, soybeans, and outer leaves of cabbage [55–58]. Conductivity tests were performed to evaluate the hydrolysis rate of crude extracts. The reaction rates for crude extracts of cabbage and soybean are 93 and 104 U/g, respectively. Meanwhile, the commercial production of urease is 2950 U/g [28,55]. The utilization of the crude extract of watermelon seeds can effectively induce the precipitation of the calcium phosphate compound and promote the maximum strength of 125.6 kPa [57]. It has also been reported that the crude extracts of soybeans and cabbage are able to promote 60% of the theoretical mass of the precipitated calcium carbonate. The use of the crude extract of watermelon, soybean, and cabbage is also simple and cheaper, because the purification process does not need to be considered, thus the material cost may be reduced significantly [55,56,59]. The above studies showed that crude extracts of watermelon, soybean, and cabbage might be alternative sources to the urease enzyme.

10. Effect of Soil Type

The efficacy of the calcite precipitation method for improving the strength parameters of sandy soil has been proven in previous studies. It can promote strength ranging from 100 kPa to 1.6 MPa [13,27]. However, reports of the applicability of this method to other soils, i.e., clay, silt, and organic soil, are very limited. Sidik et al. [60] and Canakci et al. [61] reported that the application of the calcite precipitation method using the bacteria cell as a biocatalyst promotes an improvement in the soil strength of organic soil by 20% and reduces the permeability of the soil significantly [60,61].

These results showed that the application of the calcite precipitation method to organic soil is less effective compared to its application to sandy soil. The lower strength in this application may be promoted by the organic material and the complexity of porous organic soil [60]. In addition, the higher measured pH of 9.4 in organic soil may also hamper the reaction [60,61]. As reported by DeJong et al. [62], the ideal range of pH values for precipitate calcite was between 8.3 and 9.3. The calcite precipitation method has been reported for use with clay soil by Sun et al. [63]. Their results showed that the presence of clay inhibits urease activity, and hence, hampers the precipitation process [63]. Accordingly, it is essential that a calcite precipitation and treatment method be developed that is applicable for improving the shear parameters of organic and clay soils. As one of the key parameters of the carbonation process, pH plays an important role in the calcination process, hence, the handling of pH during the treatment process may be an essential factor to achieve a sufficient strength of treated organic soil.

11. Conclusions

This paper has presented a review of a recently proposed potential technique in geotechnical engineering for improving the engineering properties of sandy soil using enzyme-induced calcite precipitation (EICP). In this technique, a blended solution composed of reagents and an enzyme of urease, which produces calcite, is used as the grouting material. This paper also discussed the application of EICP for soil improvement, substitute materials, and their impact on the treatment process and engineering properties of the soil. The envisioned plans for application, potential advantages, and limitations of EICP for soil stabilization were also presented and discussed. Finally, the main challenges and opportunities for development in future research were briefly addressed.

All the references in this paper addressed the sustainability of the EICP method as a ground-improvement technique. Several potential materials (i.e., magnesium chloride, magnesium sulfate, and zeolite) were also added to the EICP grouting material composed of urea, urease, and calcium chloride to optimize its applicability. Attempts to improve the efficacy of EICP as a ground-improvement technique have been confirmed. Therefore, further studies that consider the optimum composition of all the potential materials will be the next challenge. In addition, a study on

EICP was conducted on a laboratory scale. In order to adopt the EICP technique for real applications, upscaling from the laboratory scale to the field scale should be considered. Hence, it is suggested that large-scale experiments be conducted in future studies.

The efficacy of natural zeolite for removing the ammonia concentration in the EICP technique has also been discussed in this paper. The addition of zeolite in the preparation of grouting material was seen to significantly reduce the produced ammonia ions. However, the adsorption and precipitation processes are reasonably complicated. Hence, understanding the entire process of ammonia removal is the next task for a further study. The examination of alternative sources to the urease enzyme, which are low-cost and effective for large-scale applications, is a crucial issue in the sustainability of calcite precipitation techniques. The further investigation of promising alternatives, such as watermelon seeds, soybeans, and cabbage leaves, is an essential task for future research. The efficacy of the calcite precipitation method for improving the strength parameters of sandy soil has been proved. However, this method's effect on organic and clay soils should be considered for developing suitable additional materials and a treatment method.

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