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EVALUATING THE IMPACT OF AMMONIUM BYPRODUCTS FROM MICROBIAL-INDUCED CALCITE PRECIPITATION ON ATTERBERG LIMITS OF STABILIZED CLAYEY SOIL

Rujira Pholtrai[1], *Nutthachai Prongmanee[2], Amorndech Noulmanee[3] and Thawatchai Suppaso[4]

[1,2,3,4]Faculty of Science and Engineering, Kasetsart University Chalermphrakiat Sakon Nakhon Province Campus, 59/5, Moo1, Chiangkrua, Muang Sakon Nakhon, 47000, Sakon Nakhon, Thailand

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ABSTRACT: This study investigated the release of ammonium (NH_4^+) byproducts during microbially induced calcite precipitation (MICP) and their impact on the Atterberg limits of treated clayey soil. MICP enhances soil strength and reduces permeability; however, its byproducts can influence soil properties, especially in clayey soils. This research examined the effects of NH_4^+ ions from MICP on clayey soil's plastic limit (PL) and liquid limit (LL) under varying curing times. PL, LL, and soil microstructure changes were analyzed using Atterberg limits tests, pH measurements, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). Four treatment cases were evaluated: untreated clayey soil (control), clayey soil combined with calcite powder, clayey soil mixed with $(NH_4)_2CO_3$ and $CaCl_2$ solutions, and clayey soil mixed with an NH_4Cl solution. The results demonstrated that NH_4^+ contamination significantly increased the PL and LL values by approximately 39.5% and 27.1%, respectively, due to enhanced water absorption capacity. In contrast, adding calcite powder decreased the PL and LL values by approximately 6.05% and 18.69%, respectively, compared to untreated clayey soil. NH_4^+ ions reduced pH levels from an initial value of 5.0 to 4.2, whereas calcite addition raised pH to 8.1. With increased curing time, PL, LL, and pH values stabilized for all cases. SEM analysis indicated the presence of calcite particles in treated soils at 1 and 28 days, suggesting rapid calcite precipitation. FTIR results confirmed that NH_4^+ remained stable over time, supporting the constancy of PL, LL, and pH across all treatments. These findings have significant geotechnical engineering implications, particularly for soil stabilization using MICP in construction applications, where NH_4^+-induced plasticity may affect soil compaction and strength. Proper management of NH_4^+ byproduct is essential to ensure the long-term performance of MICP-treated clayey soils.

Keywords: Ammonium, Soil stabilization, Microbially induced calcite precipitation (MICP), Clayey soil

1. INTRODUCTION

Geotechnical engineering has long focused on overcoming the challenges of problematic soils, particularly clayey soils [1]. These soils are a cornerstone of many construction projects but are often associated with complex geotechnical issues due to their inherent properties. Known for high natural water content, low shear strength, and high compressibility, clayey soils are prone to structural instability, leading to settlement, cracking, and even foundation failures in buildings and infrastructure [2–4]. In addition to their engineering limitations, clayey soils are susceptible to changes in environmental conditions, such as wet-dry cycles, freezing and thawing, and long-term water retention, further complicating their behavior under load. These challenges make clayey soil stabilization a critical area of research, especially in regions with expanding urban development or infrastructure projects located on suboptimal soil profiles. These risks require effective stabilization techniques to improve clayey soils' strength, stability, and durability.

Soil stabilization techniques are widely employed to enhance its engineering properties, reducing compressibility and enhancing strength. Traditional approaches, such as cement stabilization, have been practical but contribute significantly to carbon emissions. Cement production alone accounts for about 8% of global CO_2 emissions, making it a considerable environmental concern [6]. This has driven research toward sustainable alternatives that offer similar stabilization benefits without the high environmental cost.

A promising development in this area is microbially induced calcite precipitation (MICP), which has gained attention as an eco-friendly, cost-effective technique for soil stabilization [7–15]. MICP uses specific bacteria, such as Sporosarcina *pasteurii*, to precipitate calcite ($CaCO_3$) within the soil matrix, which enhances soil cohesion, shear strength, and stability. This process involves two principal stages; first, urea hydrolysis by bacteria produces ammonium ions (NH_4^+), carbonate ions (CO_3^{2-}), and hydroxide ions (OH^-), raising the pH and setting favorable conditions for calcite formation, as shown in Eq. (1):

$$NH_2CONH_2 + 2H_2O \rightarrow 2NH_4+ + CO_3^{2-} + OH^- \quad (1)$$

In the second stage, carbonate ions (CO_3^{2-}) react with calcium ions (Ca^{2+}) present in the soil, forming calcite and enhancing soil stability, as described in Eq. (2):

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (2)$$

While MICP has shown promise as a sustainable soil stabilization technique by enhancing soil cohesion and reducing permeability for sand, recent research has highlighted critical challenges when applied to clayey soils. One of the key concerns is the accumulation of ammonium ions (NH_4^+) as a byproduct of urea hydrolysis, which can alter soil properties and reduce stabilization efficiency. Prior studies, such as [7], have reported that the NH_4^+ ion produced during MICP can interfere with strength development, ultimately affecting the performance of MICP-treated clayey soils. However, the extent to which NH_4^+ influences these soils' plasticity and consistency limits remains unclear, creating a critical research gap. Although a few studies have investigated the role of NH_4^+ in stabilized clayey soils, existing findings are often inconsistent or incomplete, particularly regarding its influence on Atterberg limits. Since soil plasticity directly affects its shear strength, compaction, permeability, and long-term stability, a deeper understanding of NH_4^+-induced plasticity changes is essential for optimizing MICP-based stabilization. These concerns raise questions about the sustainability of MICP applications in clayey soils, emphasizing the need to evaluate NH_4^+ effects on soil plasticity systematically. This study addresses these gaps by systematically investigating how NH_4^+ byproducts influence the plasticity and consistency of MICP-treated clayey soils under varying conditions. By analyzing Atterberg limits, pH variations, and microstructural changes using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), this research provides a more comprehensive understanding of NH_4^+ behavior in stabilized soils. By advancing the understanding of MICP behavior in clayey soils, this study provides insights that can facilitate the scalability of MICP for field applications, particularly in soil stabilization. The findings contribute to developing eco-friendly and sustainable soil treatment methods that can be adapted to large-scale construction projects. This research lays the groundwork for MICP techniques, making them a viable alternative to traditional stabilization approaches.

2. RESEARCH SIGNIFICANCE

The significance of this study lies in advancing sustainable soil stabilization through microbially induced calcite precipitation (MICP). It addresses the impact of ammonium (NH_4^+) byproducts on soil plasticity and consistency, bridging a critical knowledge gap. Laboratory analyses, including Atterberg limits, pH measurements, FTIR, and SEM, provide insights into stabilization mechanisms. The plasticity of soil increases in the presence of NH_4^+ due to enhanced water retention, as NH_4^+ expands the diffuse double layer by increasing electrostatic repulsion between clay particles. In contrast, calcite reduces plasticity by promoting flocculation and aggregation, which enhances soil structure and stability. Effective NH_4^+ management could enhance large-scale MICP performance, improving soil stability and making MICP a viable alternative for sustainable geotechnical engineering.

3. MATERIALS AND METHODS

3.1 Materials

The study focused on clayey soil obtained from a specific location within the Kasetsart University Chalerm Phrakiat Sakon Nakhon Province campus in Thailand. It was air-dried thoroughly to prepare the soil for analysis, after which various index properties were assessed and classified to determine its characteristics. In the experimental setup, reagent-grade ammonium chloride (NH_4Cl) was selected as the source of ammonium cations, providing a controlled means to study interactions with the soil. Additionally, calcite powder was utilized alongside a 4M solution of ammonium carbonate ($(NH_4)_2CO_3$), prepared according to the method detailed in reference [7]. Before use, the ammonium concentration was determined via spectrophotometric analysis using a modified Nessler's reagent method [7]. The study employed various analytical techniques to evaluate these materials' effects comprehensively. These included Atterberg limits tests to assess the soil's plasticity and consistency, pH measurements to determine its acidity or alkalinity, Fourier transform infrared spectroscopy (FTIR) for molecular analysis, and scanning electron microscopy (SEM) to visualize the soil's microstructure. Through these methods, the research aimed to elucidate the impact of the ammonium cations and carbonate on the physicochemical properties of the clayey soil.

3.2 Methods

3.2.1 Soil sample preparation

The soil that passed through a No. 40 sieve was collected and oven-dried at 105°C for 24 hours to remove moisture. For Case 1 (Control), 300 g of the dried soil was mixed with approximately 130 ml of water to reach its LL value, as shown in Table 1. Then, the mixture was cured in an airtight plastic container for the designated curing time. For Case 2, 300 g of the soil was mixed with 12 g of calcite powder (4% by dry weight); then, deionized water was added to achieve a similar LL value in Case 1. The mixture was cured in an airtight plastic container. For Case 3, 300 g of soil was mixed with a 4M solution (30 ml) of $(NH_4)_2CO_3$ and a 4M solution (30 ml) of $CaCl_2$ and 70 ml of deionized water was added to match the LL value from Case 1, before the mixture was cured in an airtight plastic container. For Case 4, the soil was mixed with 30 ml of a 4M solution of NH_4Cl and an additional 100 ml of deionized water to match the total liquid volume of 130 ml, as in Case 3. Next, it was cured under the same conditions as the other cases. Each sample was collected for testing after the specified curing period had elapsed. In this study, Case 1 functioned as the control test, establishing a baseline for comparison. Case 2 was designed to explore the sole impact of integrating calcite into the mixture. Meanwhile, Case 4 examined the effects of pure ammonium ions (NH_4^+). In contrast, Case 3 combined the influences of both calcite and NH_4^+. This approach allowed for a comprehensive analysis of how each component contributed to the overall outcomes of the tests.

Table 1. Physical properties of clayey soil

Properties	Value
Gravel content (%)	5
Sand content (%)	33
Fine content (%)	62
Liquid limit, LL (%)	43
Plastic limit, PL (%)	20
Plasticity index, PI (%)	23
Specific gravity	2.91
Soil classification	CL

3.2.2 Atterberg limits testing

The Atterberg limits tests, which include the liquid limit (LL) and plastic limit (PL), were meticulously conducted on soil that had undergone treatment through the Microbially Induced Calcite Precipitation (MICP) process. The soil samples were cured for varying durations, specifically from 1 to 28 days, adhering to ASTM standards D4318. Initially, these tests provided valuable insights into each soil sample's plasticity and consistency characteristics prior to treatment. Following the curing periods of 1 and 28 days, the treated soil was subjected to an oven-drying process at a controlled temperature of 105°C. This step was crucial for effectively eliminating ammonium from the samples. After drying, the Atterberg limits tests were repeated to analyze any significant changes. The second round of testing focused on assessing the impact of NH_4^+ cations introduced during the MICP process on the overall properties of the soil. To ensure the reliability of the results, each test was performed a minimum of three times, providing a robust dataset for comparison and analysis.

3.2.3 Soil pH testing procedure

The pH of the soil was evaluated using a 1:1 ratio of soil to water. To begin the process, 10 grams of air-dried, sieved soil was carefully measured and placed into a clean container. Then, 10 milliliters of deionized water were added to create the mixture. This combination was stirred vigorously for about 5 minutes to ensure the soil was fully hydrated and well-distributed in the water. After stirring, the mixture was allowed to sit undisturbed for 30 minutes, giving time for the soil particles to settle and the water to clarify. Following this settlement period, the pH of the clear supernatant solution was precisely measured using a calibrated pH meter. To ensure the reliability of the results, each test was conducted at least three times, allowing for a robust comparison of the findings.

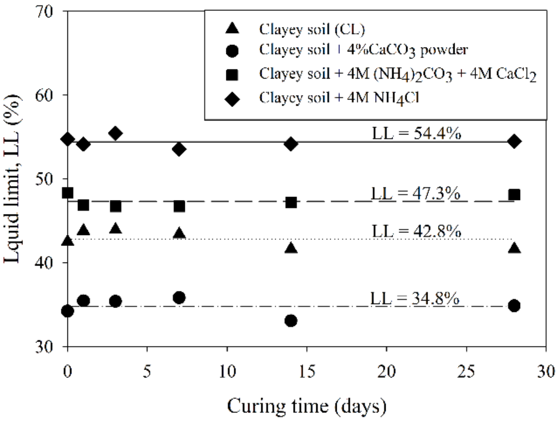


Fig.1 Effects on liquid limit values at different curing times.

3.2.4 Microstructure analysis

FTIR analysis was carried out using a PerkinElmer Scientific instrument, which operates over a 600 to 4,000 cm^{-1} wavelength range. This technique was crucial for identifying specific chemical bonds and functional groups within the soil, allowing for a detailed examination of changes in ammonium ion (NH_4^+) levels during the curing period. In parallel, scanning electron microscopy (SEM) was conducted with a JEOL JSM-IT510 instrument to capture high-resolution microscale images. These images provided valuable insights into the morphological changes occurring in the soil and the distribution of precipitated calcite, enhancing our understanding of the soil structure at a microscopic level. While FTIR concentrated on analyzing the fluctuations in NH_4^+ levels throughout the curing process, the SEM focused on the temporal development of calcite precipitation. Both analytical techniques were employed at critical intervals of 1 and 28 days to thoroughly evaluate how the duration of curing influences the chemical composition and structure of the soil matrix, explicitly examining the transformations of calcium carbonate ($CaCO_3$) and ammonium ions (NH_4^+).

4. RESULTS AND DISCUSSIONS

4.1 Atterberg Limits Results

The LL results are shown in Fig. 1. The LL values remained constant with increasing curing time, possibly due to the curing method used in this research. The closed system minimized air intake and prevented water evaporation, hindering bacteria in the soil from efficiently decomposing ammonium (NH_4^+) to produce nitrogen. Consequently, the concentration of NH_4^+ in the soil remained constant, resulting in no significant change in the NH_4^+ state. In Case 2, where soil was mixed with calcite powder, the LL remained steady. This could have been due to the rapid precipitation process between the $(NH_4)_2CO_3$ and $CaCl_2$ solutions, resulting in a stable calcite precipitate. Calcite's relative stability and minimal reactivity with clayey soil only initially reduced the LL value. This finding was consistent with Prongmanee et al. [8], who reported that the compressive strength of soil mixed with calcite powder significantly increased in the early stages as the compacted soil became denser, followed by a tendency to remain constant.

For the same curing time, in Case 1, the LL for soil mixed with calcite powder had the lowest average at 34.8%, which was lower than for the untreated clayey soil, which had an LL of 42.8%. This result reflected the non-plastic properties of $CaCO_3$, resulting in an average decrease in the LL by 18.7% compared to the untreated clayey soil. In Case 3, the clayey soil mixed with $(NH_4)_2CO_3$ and $CaCl_2$ solution, the LL value increased by 10.5% compared to the untreated clayey soil, resulting in an average LL of 47.3%. In Case 4, where clayey soil was mixed with a 4M NH_4Cl solution, the LL value reached 54.4%, an increase of 27.1% from the untreated clayey soil. The increase in LL values in Cases 3 and 4 could be explained by the osmotic (swelling) phenomenon, where ammonium significantly absorbs water [18]. The test results confirmed that treated clayey soil containing ammonium had a higher LL value than the untreated clayey soil. This differed from sand, which has a high permeability coefficient and can easily remove ammonium byproducts [19]. These findings indicated that in improving the quality of the clayey soil using the MICP method, it is necessary to consider the effects of NH_4^+ from the soil improvement process, as it can affect the soil's shear strength and water permeability values after treatment.

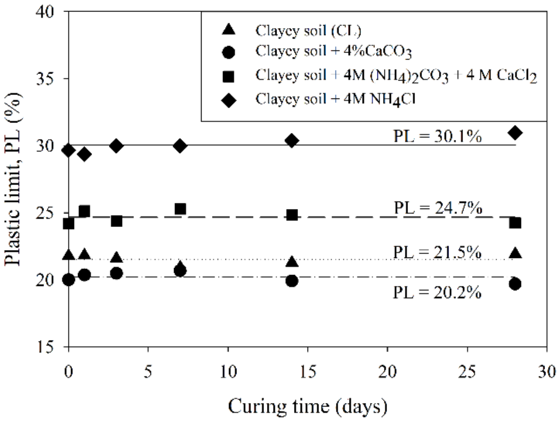


Fig. 2 Effects on plastic limit values of different curing times.

The tests on the PL of the clayey soil under different experimental conditions, as shown in Fig. 2, indicated that the trend in the PL values closely resembled that of the LL values in all cases. The results showed that the PL remained constant with increased curing time. The average PL value was 21.5% for the untreated clayey soil. In comparison, the average PL values for the clayey soil mixed with calcite powder (Case 2), clayey soil mixed with $(NH_4)_2CO_3$ and $CaCl_2$ solution (Case 3), and clayey soil mixed with NH_4Cl solution (Case 4) changed to 20.2%, 24.7%, and 30.1%, respectively. These results suggested that the presence of $CaCO_3$ and NH_4Cl substantially influenced the PL value of the treated clayey soil. Based on these test results, shown in Fig. 1 and 2, the quantity of the substances mixed with the soil did not change chemically or very little as the curing time increased. Additionally, observations suggested that the curing process did not necessarily need to prevent water evaporation since calcite does not require water for reaction in the short term [20]. Preventing water evaporation reduced the effectiveness of altering the ammonium level in the soil, which substantially affected both the PL and LL values.

Fig.3 was developed to facilitate a comparative plasticity index (PI) analysis across the different experimental scenarios. The PI serves as an indicator, where a higher PI value denotes soil with more remarkable plasticity. The findings illustrated in Fig. 3 indicated a discernible variation in the PI following the incorporation of $CaCO_3$ into the clayey soil, manifesting as a decrease in the PI. This decrease was indicative of a reduction in the soil's plasticity.

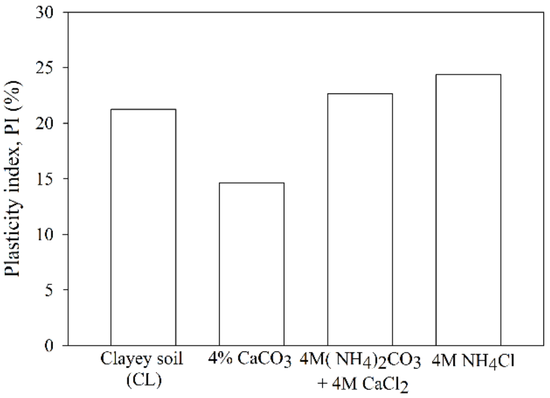


Fig. 3 Effects of different treatments on plasticity index values of clayey soil.

In contrast, the introduction of ammonium-containing mixtures to the clayey soil resulted in an enhanced PI. Specifically, adding a solution of $(NH_4)_2CO_3$ and $CaCl_2$ led to a 23% increase in PI, whereas including an NH_4Cl solution prompted a 25% rise in PI. These results confirmed that NH_4^+ could substantially increase the soil's plasticity. To confirm this hypothesis, additional tests were conducted by measuring the PL and LL values of soil treated with a 4M $(NH_4)_2CO_3$ and 4M $CaCl_2$ solution after removing ammonium from the clayey soil samples by heating at 105°C for 24 hours. The results were compared with those of the untreated samples and the clayey soil mixed with $CaCO_3$, as shown in Fig. 4. The test results indicated that soil samples subjected to removing ammonium ions had decreased PL and LL values compared to the treated samples (with ammonium). Furthermore, the LL and PL values of the ammonium-removed samples were similar to those of the soil mixed with calcite powder, albeit slightly higher. These results demonstrated that NH_4^+ removal by heating reduced the NH_4^+ content, thereby decreasing the soil's consistency.

Additionally, it was concluded that controlling the moisture content in the soil samples prepared for the various property tests (such as compressive strength) was unnecessary because the presence of ammonium does not enhance the soil's engineering properties. These findings confirmed the hypothesis that ammonium plays a substantial role in determining the plastic properties of soil, and its removal can lead to improvements in engineering properties suitable for various applications. These results align with [21], which examined EICP-based soil stabilization and found that calcite precipitation reaches equilibrium over time, leading to minimal further changes in plasticity. This suggests that NH_4^+-induced modifications to soil consistency stabilize after an initial reaction phase, likely due to soil buffering capacity and cation exchange processes. Additionally, carbonate precipitation reduces swelling and improves stiffness, supporting the hypothesis that MICP stabilization effects are NH_4^+ increases soil plasticity. Given these findings, NH_4^+ accumulation must be carefully managed in large-scale applications.

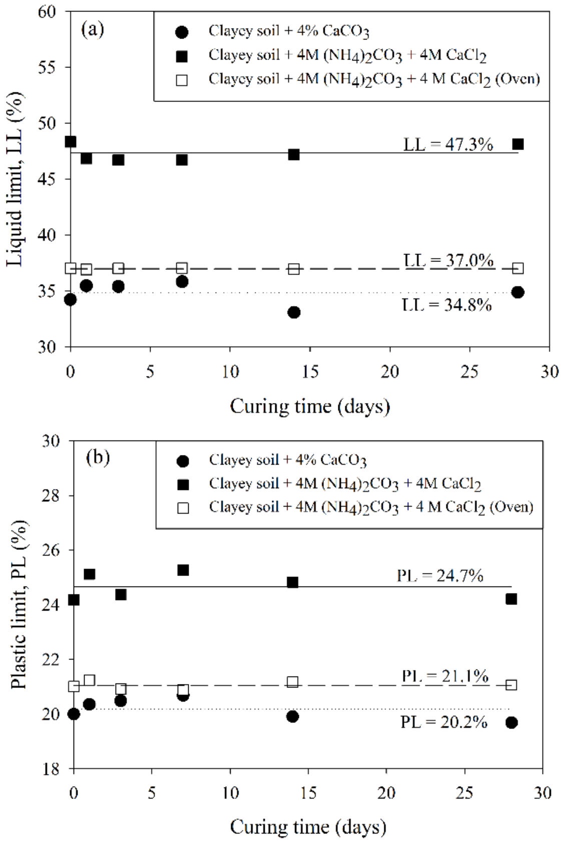


Fig.4 Effects on LL (a) and PL (b) values of clayey soil improved in Case 3 with and without NH_4^+ compared with soil improved in Case 2.

4.2 Soil pH Results

Fig. 5 presents a detailed illustration of the variation in average pH levels of the samples throughout the curing process. Initially, the untreated clayey soil had a pH of around 5.0, indicating a mildly acidic environment. Over 28 days, this pH gradually rose to 5.3. Clayey soils, influenced by their unique composition and natural weathering processes, typically exhibit a slightly acidic pH, usually within the range of 5.5 to 6.5 in various regions [22]. This gradual increase in pH suggests that chemical reactions, such as cation exchange, dissolution of soil minerals, and organic matter decomposition, may occur within the soil matrix during curing.

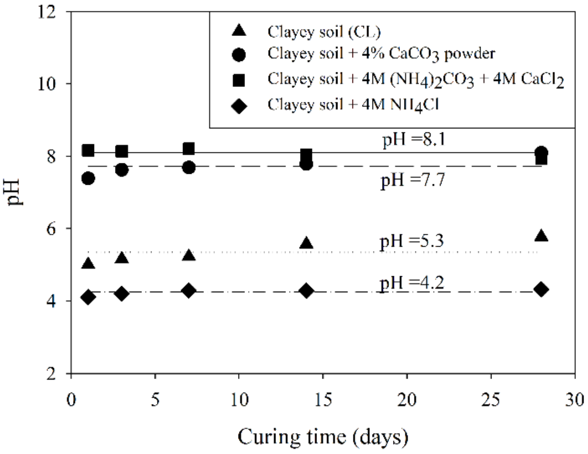


Fig. 5 pH changes in soil samples over different curing times.

The role of pH in soil stabilization is significant, as it directly affects the formation of cementitious compounds. In MICP-based stabilization, pH controls calcite precipitation efficiency, with an optimal range of 8.0 to 9.5, facilitating strong cementation between soil particles and improving overall soil strength. The test results show that when the clayey soil was mixed with 4M $(NH_4)_2CO_3$ and 4M $CaCl_2$, the pH increased to 8.1 after 28 days, creating favorable conditions for calcite precipitation. Conversely, in the soil mixed with 4M NH_4Cl, the pH remained low at around 4.2, reflecting the strong acidic influence of ammonium ions. The reduction in pH in this case was due to NH_4^+ hydrolysis, which produces H^+ ions, lowering alkalinity. Acidity directly influences the plastic limit (PL) and liquid limit (LL) by modifying the interaction between clay minerals and pore water. In highly acidic conditions, H^+ ions replace divalent cations on clay particle surfaces, leading to an expanded diffuse double layer [23]. This expansion increases water retention, explaining the increased LL and PL in NH_4^+-rich soils. In contrast, adding calcite ($CaCO_3$) increases soil pH and promotes cation exchange with Ca^{2+}, which induces clay flocculation and reduces LL and PL [23]. The reduced plasticity enhances soil strength and compaction properties. The pH levels observed in this study indicate that higher alkalinity improves calcite precipitation. On the other hand, lower pH conditions contribute to increased plasticity and weaker bonding between particles. The findings emphasize the importance of controlling pH conditions in field applications to achieve consistent and long-term improvements in soil strength. Stabilizing pH values over time suggests that further variations in LL and PL are minimal once equilibrium is reached, supporting the idea that early-stage reactions dominate in determining long-term soil behavior.

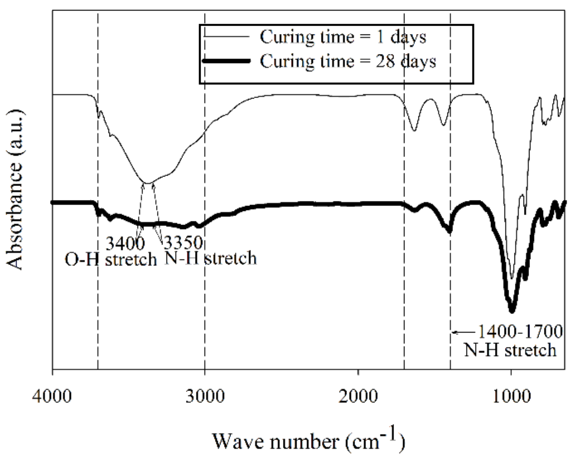


Fig. 6 FTIR results of treated soil (Case 3) at 1 and 28 days of curing time.

4.3 Microstructure analysis

4.3.1 FTIR results

FTIR analysis was performed on two specimens to examine NH_4^+ variations in treated soil after 1 and 28 days of curing, as shown in Fig. 6. The FTIR spectra, recorded over the 500 to 4000 cm^{-1} range, revealed critical observations in the 3000–3700 cm^{-1} region, corresponding to O-H and N-H stretching vibrations. The samples cured for 1 day had higher intensity peaks in the 3000–3500 cm^{-1} range, indicating more free water and less bonded ammonium ions. In contrast, the samples cured for 28 days had lower intensity peaks, suggesting reduced free water and more stable hydroxyl-containing compounds. The 1400–1700 cm^{-1} region, associated with N-H bending vibrations, showed no significant changes, indicating stable NH_4^+ levels between 1 and 28 days. Other spectral regions displayed stable peaks corresponding to the soil matrix and carbonate compounds. These results suggested that the NH_4^+ levels remained stable during curing due to conditions inhibiting its conversion to other nitrogen species, such as low moisture and limited oxygen, which inhibit microbial nitrification. The FTIR analysis indicated minimal changes in the NH_4^+ levels, consistent with reduced free water and more stable compound formation over time.

4.3.2 SEM and EDX results

The Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis, illustrated in Figs. 7a and 7b, along with the data in Table 2, confirmed rapid calcite precipitation. As shown in Fig. 8, EDX mapping identified calcium and oxygen as the primary elements, with carbon also present, aligning with the calcium carbonate composition reported in Table 2. This precipitation process resulted from ammonium carbonate supernatant produced through bacterial hydrolysis of urea. Remarkably, the formation of well-defined calcite crystals was observed after just one day of treatment, as seen in rhombohedral-shaped crystals. These crystals exhibited a composition of 35.48 wt% calcium (Ca) and 48.35 wt% oxygen (O), highlighting the method's effectiveness in promoting calcite formation. After 28 days, the calcite crystals demonstrated a slight increase in calcium concentration, measuring 45.15 wt%, alongside an oxygen concentration of 35.34 wt%. Notably, the crystals' overall shape and elemental composition remained consistent with what was observed on day 1. This indicates that most calcite formation happened during the initial day, with only minimal changes occurring in the subsequent weeks. Such findings highlight the rapid nature of the crystallization process, emphasizing how minor alterations transpired over the following days [17]. The swift formation of calcite plays a crucial role in soil stabilization, enabling quick and effective enhancements to soil quality. Comprehensive test results reveal that when clayey soil is blended with calcite powder, it retains its structural integrity even as curing time increases. This stability is attributed to the rapid precipitation of calcite, which solidifies the soil matrix and ensures long-lasting improvements.

Based on FTIR, SEM, and EDX results, this research found that the stability of NH_4^+ with curing time and the rapid precipitation of calcite observed in SEM and FTIR can be explained by differences in their chemical interactions within the soil matrix. NH_4^+ remains stable due to its strong adsorption of clay minerals via cation exchange with pre-existing cations, which limits its mobility over time. Unlike divalent cations, NH_4^+ does not readily form insoluble precipitates and remains trapped within the soil structure, maintaining its effect on soil plasticity. In contrast, calcite ($CaCO_3$) precipitates rapidly because of supersaturation-driven nucleation and crystallization. The reaction between Ca^{2+} and CO_3^{2-} forms calcite within hours to days, as seen in SEM images at both 1-day and 28-day curing times, indicating early and sustained mineral formation. Once $CaCO_3$ reaches equilibrium, further precipitation is minimal, explaining why Atterberg limits remain unchanged with longer curing times. Additionally, calcite flocculates clay particles, reducing the diffuse double layer and plasticity, whereas NH_4^+ increases water retention and maintains its plasticizing effect. This interplay between NH_4^+ stabilization and rapid calcite precipitation underpins the observed trends in soil consistency over time.

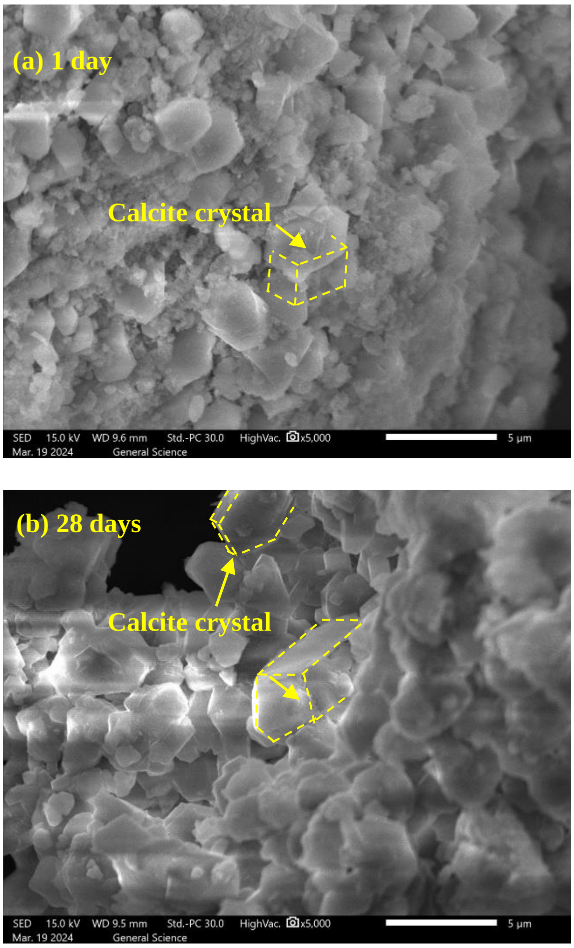
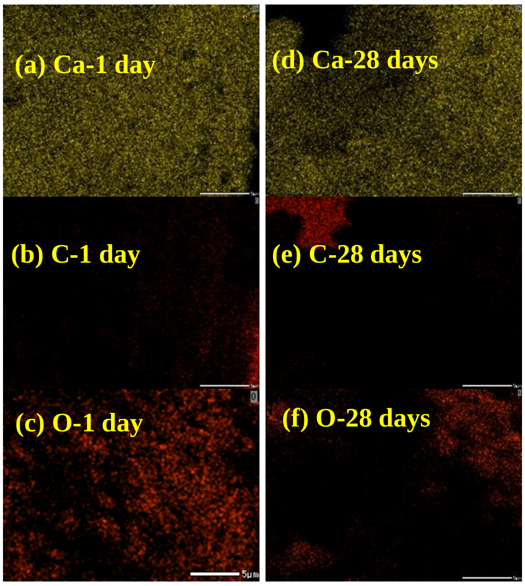


Fig. 7 SEM results: a) sample cured for 1 day and b) for 28 days.

The findings of this study highlight the negative impact of NH_4^+ byproducts on the plastic consistency of clayey soil treated with MICP. Since NH_4^+ is an unavoidable byproduct of urea hydrolysis, similar effects may also be observed in Enzyme-Induced Calcite Precipitation (EICP), as reported in [24]. While MICP relies on bacterial activity, EICP directly utilizes enzymes, yet both processes generate NH_4^+ during calcite precipitation. This inherent limitation underscores the need for effective mitigation strategies. This study suggests potential solutions to address this challenge, such as incorporating chemical stabilizers like gypsum and biochar to reduce NH_4^+ [25].

Additionally, utilizing bacterial strains that promote nitrification, such as ammonia-oxidizing bacterium (AOB), could help convert NH_4^+ into less harmful compounds, mitigating its long-term effects on soil stabilization [26]. These approaches enhance the feasibility of MICP/EICP for sustainable soil improvement. Further research should explore the effectiveness of these methods in reducing NH_4^+-induced alterations in soil consistency and long-term geotechnical performance.



Figs. 8 EDX mapping results: a to c) sample cured for 1 day and d to f) for 28 days.

Table 2. EDX results of specimens cured for 1 and 28 Days

Sample	1 day		28 days	
Elements	Mass (%)	Atom (%)	Mass (%)	Atom (%)
C	12.48	20.15	17.99	36.02
O	48.35	59.82	35.34	48.74
Mg	0.22	0.18	0.00	0.00
Al	0.80	0.59	0.64	0.49
Si	1.29	0.91	0.62	0.45
Cl	1.21	0.68	0.26	0.15
Ca	35.48	17.52	45.15	23.05
Fe	0.43	0.15	0.00	0.00
Total	100.00	100.00	100.00	100.00

The interaction of ammonium (NH_4^+) with clay minerals can significantly influence soil compaction and strength properties due to its impact on cation exchange, diffuse double-layer expansion, and soil microstructure. NH_4^+, being a monovalent cation, competes with other cations for adsorption sites on clay surfaces. Its absorption increases electrostatic repulsion between clay particles, expanding the diffuse double layer and enhancing water retention. This leads to a decrease in dry density during compaction, as excess water reduces particle rearrangement efficiency. Additionally, NH_4^+ weakens soil strength by reducing interparticle cohesion. Unlike divalent cations, which promote flocculation and aggregation, NH_4^+ tends to disperse clay particles, leading to lower unconfined compressive strength (UCS) and higher plasticity. Over time, NH_4^+ can also undergo cation fixation in certain clay minerals, further altering soil behavior by preventing beneficial cation exchange with stabilizers like lime or $CaCO_3$. The presence of NH_4^+ in MICP-treated soils may counteract the intended stabilization effects by increasing plasticity and reducing overall strength. Future research should explore strategies to mitigate these effects, such as cation exchange with divalent cations, chemical stabilizers, or microbial nitrification pathways to convert NH_4^+ into NO^{3-}, which is more mobile and less disruptive to soil structure.

5. CONCLUSIONS

This study focuses on the experimental investigation of the effects of ammonium (NH_4^+) ions and curing time on the plastic limit (PL) and liquid limit (LL) of clayey soil under various conditions. The conditions examined include untreated soil (control), soil mixed with calcite powder ($CaCO_3$), soil treated with a 4M solution of $(NH_4)_2CO_3$ and 4M $CaCl_2$, and soil treated with a 4M NH_4Cl solution. Based on the test results, conclusions can be drawn regarding these effects.

In examining the effects of ammonium (NH_4^+) on soil characteristics, it was observed that the addition of NH_4^+ significantly raised the plastic limit (PL) and liquid limit (LL) values. This increase can be attributed to osmotic swelling, which occurs when the soil absorbs water, leading to more remarkable plasticity. Notably, as the curing time extended, the PL and LL values stabilized and did not change further, a finding that was corroborated by Fourier-transform infrared spectroscopy (FTIR) results. Conversely, removing NH_4^+ from the soil decreased both PL and LL values, highlighting the critical role that ammonium plays in enhancing the plasticity of soil materials.

Further supporting these findings, scanning electron microscopy (SEM) analyses revealed that rapid calcite formation occurred within a day, leading to effective stabilization of the soil structure and a significant increase in pH levels. This calcite formation contrasts sharply with the effects of ammonium solutions, contributing to increased soil acidity and a corresponding drop in pH.

Overall, managing and controlling ammonium levels in the soil could have a transformative impact on its properties, potentially leading to significant improvements in soil quality for various engineering and construction applications. Future research should optimize these mitigation techniques to enhance the field-scale applicability of MICP-treated clayey soils.

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