Arch. Min. Sci. **70** (2025), 3, 493-504

Electronic version (in color) of this paper is available: http://mining.archives.pl

DOI: https://doi.org/10.24425/ams.2025.156295

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SUSTAINABLE USE OF LEONARDITE BIOPOLYMERS AS A GREEN ALTERNATIVE IN SOIL IMPROVEMENT METHODS

Leonardite's ability to stabilise marl, a challenging construction material, was confirmed through mechanical tests, including unconfined compressive strength, unconsolidated undrained triaxial tests, and chemical and microstructural analyses in the study. Results confirmed that the strength improvement factor, cohesion improvement factor, and internal friction improvement factor significantly increased due to both the addition of Leonardite and the curing times. The addition of 15% Leonardite, along with curing periods of 7 to 14 days, resulted in considerable improvement factors ranging between 2 and 5, depending on the parameters investigated. Microstructural analysis confirmed that Leonardite could act as a filler, filling soil voids and reducing peak associated with calcite content, which is responsible for the unfavorable behavior of marls. The formation of various functional groups and strong bands, such as carboxyl, hydroxyl, and carbonyl, as evidenced by FTIR analysis, was found to be responsible for improving the mechanical strength of samples containing Leonardite.

Keywords: Soil stabilisation; Leonardite; Marl soil; Biopolymer; Microstructure; Sustainable materials

1. Introduction

Geotechnically speaking, expansive clays, collapsible, weak, and dispersible soils are troublesome for foundation soil and superstructure construction, as well as slope stability. Soil stabilisation methods have been widely used for the improvement of problematic soils in construc-

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tion projects [1,2]. Among various problematic soils, marl material, which contains clay and high amounts of calcareous material, is considered one of the most hazardous types [3]. Marl soils have a significant place among problematic soils due to their composition, typically consisting of 65-35% calcite and their swelling, erosion, and creep properties [4,5]. It is highly sensitive to both water and air and can experience significant loss of strength when exposed to them. To date, many studies have been conducted on the application of various materials to increase the mechanical properties of marl soils. The findings revealed that various additives specifically promoted the formation of secondary Calcium Silicate Hydrate gel, thus leading to increased strength and stability of treated marl soils. Again, previous research has shown that when cement-lime is mixed with nanomaterials, a pozzolanic environment is formed with the hydration process. As a result, it was stated that improvement had been achieved with these effects [3,6-8].

The effectiveness of traditional additives in soil improvement has been a topic of extensive discussion, and their role in enhancing problematic soils has been widely recognised [9]. Although cement and lime are the most common soil stabilisers, over time, with the leadership of various studies on the subject, various types of resins, fly ash, blast furnace slag, some nanoparticles, various types of agricultural and industrial wastes and biopolymers have also been widely used for this purpose [10-15]. Nevertheless, research and performance analysis of products suitable for alternative, sustainable, cost-effective, and environmentally friendly soil stabilisation remain pertinent topics of interest in geotechnical engineering [16,17].

Despite the long history of Leonardite (L) biopolymers being used to improve agricultural soil and mitigate soil contamination, their potential in enhancing mechanical strength and durability from a civil engineering perspective has not yet been addressed. L, recognised for its environmentally friendly and sustainable properties, plays a significant role in removing harmful materials from agricultural soil and is extensively utilised in the agricultural sector. L is a moistened organic material abundant in organic matter, positioned between peat and lignite in its composition. It originates from the burial of plant material millions of years ago and is primarily found in the upper layers of open-pit lignite (coal) mines [10]. L is an organic matter that has not yet reached the coal stage. It differs from lignite due to its higher oxidation content, higher humic acid grade, and greater abundance of carboxyl groups in the carbonisation process. Unlike other organic humic acid sources, L is highly bioactive due to its unique molecular structure. Acting as a soil conditioner, biocatalyst, and biostimulant for agricultural soils, L offers exceptional support for plant growth and soil fertility compared to other organic products.

The soil improvement potential of this environmentally friendly material, in terms of mechanical strength and durability, and its ability to mitigate the undesirable behaviour of problematic soils, such as marl, in geotechnical engineering, have not yet been examined. This study was conducted to address existing gaps and provide a comprehensive understanding of the durability and compatibility of L-stabilised marl. To assess the potential use of L in marl stabilisation, a series of mechanical, chemical, and microstructural tests including unconsolidated undrained (UU) triaxial tests and unconfined compressive strength (UCS) tests, as well as Fourier-transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF), X-ray diffraction (XRD), and Scanning electron microscopy with energy-dispersive X-ray spectroscopy SEM-EDX analyses, were performed to determine the optimal L content and suitable curing time.

2. Materials and methods

2.1. Materials characteristics

The marl samples utilised in this study were obtained from a marl slope situated in an urban area in Karabük, Turkey (Fig. 1a,b). The marl samples used in current study were taken approximately 30 cm below the surface of the sediment accumulated under the slope after superficial weathering. The sampled soil is dispersed in this area and occasionally causes slope stability problems on the slopes due to its low resistance to physical and chemical weathering. Temperature differences in the region and the resulting freezing and thawing events are the main causes of decomposition. The soil sample taken from the field was subjected to particle size distribution (PSD) test in accordance with ASTM D 422, and the PSD curve obtained accordingly is shown in Fig. 2. Following this, some physical and mechanical properties were evaluated

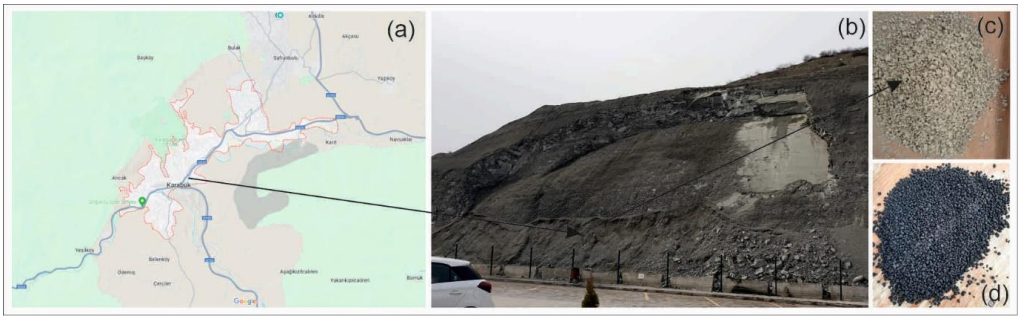


Fig. 1. Geographic location of the marl soils sampling area in Karabük (a) and (b), soil used in experiments (c) and leonardite (d)

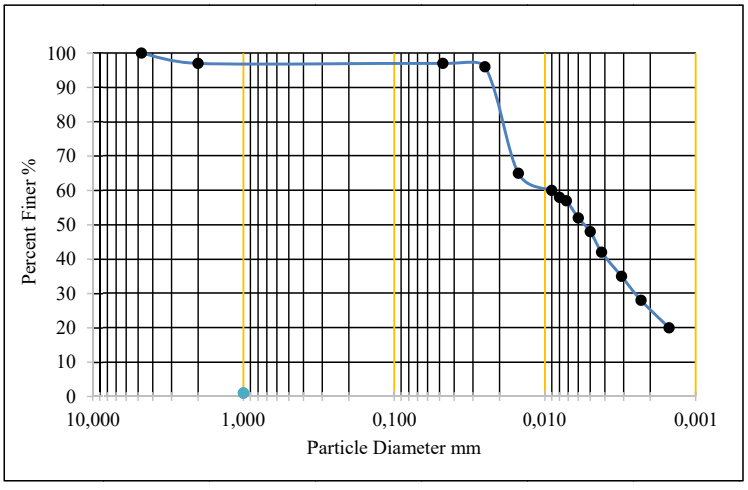


Fig. 2. Particle size distribution curve

with soil mechanics tests within ASTM standards. Considering the clumping state of the soils taken from the field, the No. 4 sieve was used in the experiments. The marl samples exhibited a grayish-green color (Fig. 1c), belonged to the high plasticity clay (CH) class, with a low UCS of 103.7 kPa, cohesion of 94 kPa, internal friction angle of 10 degrees, optimum moisture content of 15%, maximum dry density of 1.87 g/cm^3, plasticity index of 24, and pH of 7.76. In addition, the chemical contents of the marl samples were determined by XRF and the results are given in TABLE 1. A sample of soft, waxy, black-brown, shiny, vitreous mineraloid Leonardite (L), easily soluble in alkaline solutions, sourced from Humintech GmbH (Germany), was utilised as a marl stabiliser (Fig. 1d). Its properties include: organic matter content (50-60%), humic matter content (38-40%), dry matter content (68-72%), pH (5.0-6.0), bulk density ranging from (0.6-0.7 kg.L-1), and particle size (1-6 mm).

TABLE 1

Composition details of Marl soil obtained using XRF

Component	Result %
SiO_2	35.09
CaO	41.06
Al_2O_3	10.70
Fe_2O_3	6.26
MgO	3.07
K_20	1.74
$Ti0_2$	0.68
Na_2O	0.54
SO_3	0.42
Sr0	0.22

2.2. Sample preparations and test methods

Different mixtures were prepared by incorporating L at concentrations of 0%, 5%, 10%, 15%, and 20% into marl samples with an optimum water content of 15%. After being kept in plastic bags for 24 hours, these mixtures were compacted into three layers within molds used for UU and UCS tests to attain a maximum dry density of 1.87 g/cm^3. The curing of the specimens was carried out at room temperature (approximately 20±2°C) in sealed conditions to prevent moisture loss and ensure uniform curing. No additional wetting or freezing–thawing cycles were applied during the curing process. This method was adopted to evaluate the short-term mechanical performance of the stabilised soil under controlled laboratory conditions. While long-term durability under environmental stresses such as freeze-thaw or wetting-drying is crucial, it remains outside the scope of the current study. After being extracted from the mold, the compacted mixtures were individually covered with high-quality airtight plastic films and subjected to curing for various time intervals, including 1, 7, 14, 21, and 28 days. UCS and UU tests were conducted on each mixture after the predetermined curing time, following the corresponding ASTM standards. UCS was determined using a universal testing device in accordance with ASTM D2166 [18]. UCS tests were used to determine the optimum leonardite mixing ratio and the effect of the mixing amount on strength, and to evaluate its effect on soil behaviour. The axial strain rate was

controlled at 1%/min and continued up to 10% of the total strain; where the stress-strain behavior was automatically monitored and recorded by the machine. The experiments were repeated with three samples for each test, and the average was recorded as unconfined compressive strength. In this study, triaxial tests (undrained-unconsolidated, UU tests) were also performed on soil samples. In these tests, all samples were compressed under 100, 200 and 300 kPa hydrostatic pressure. Since there is no guarantee that the sample will return to its previous state after compression and loading, a sample was made for each hydrostatic pressure, and the application of both hydrostatic and loading pressures to the same sample was avoided to avoid possible errors. For the UCS tests, cylindrical specimens with a diameter of 37 mm and a height-to-diameter (H/D) ratio of 2.0 were prepared in accordance with ASTM D2166. For the UU triaxial tests, specimens were prepared with a diameter of 54 mm and an H/D ratio between 2.0 and 2.5, following the relevant ASTM standards to ensure consistent and reliable test conditions. In both UCS and UU tests, specimens were prepared at the optimum moisture content of 15% and compacted to a dry density of 1.87 g/cm^3 using standard Proctor compaction. The same compaction energy and moisture content were applied to all mixtures to ensure consistent and comparable test conditions. The shear strength parameters obtained from UU tests reflect relative changes in soil behaviour due to Leonardite content under uniform preparation conditions.

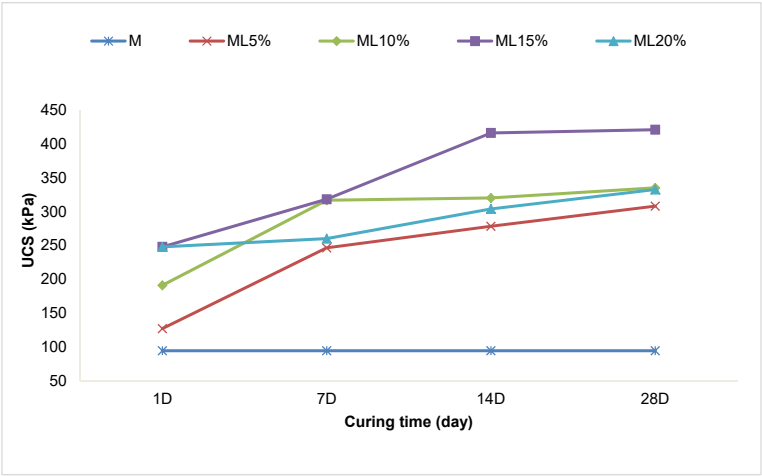
3. Results and discussions

The results of UU and UCS of all samples are presented in Fig. 3a and b. Fig. 3b compares the cohesion and angle of internal friction values, estimated based on the Mohr-Coulomb criterion, of all stabilised soils. The results were analysed to evaluate the effectiveness of L in improving the properties of the mixtures. In this case, three crucial parameters, namely strength improvement factor (SIF) (Eq. 1), cohesion improvement factor (CIF) (Eq. 2), and internal friction improvement factor (IFAIF) (Eq. 3) were calculated. SIF represents the improvement in compressive strength and is determined as the ratio of the UCS of L-stabilised marl to that of the unstabilized marl. Meanwhile, the UU test results are presented in terms of shear strength parameters, namely cohesion and internal friction angle. Therefore, CIF represents the enhancement in cohesion, and IFAIF represents the improvement in the friction angle of the samples, both calculated as the ratio of the corresponding shear parameters of the L-stabilised samples to those of the unstabilised samples. To comprehend the stabilisation mechanism facilitated by L, a series of XRD, XRF, SEM-EDX, and FTIR tests were conducted on two representative samples: untreated marl and L-treated marl.

$$SIF = \frac{UCS_{treated}}{UCS_{untreated}} \tag{1}$$

$$CIF = \frac{c_{treated}}{c_{untreated}} \tag{2}$$

$$IFAIF = \frac{tan_{(\varnothing treated)}}{tan_{(\varnothing untreated)}} \tag{3}$$



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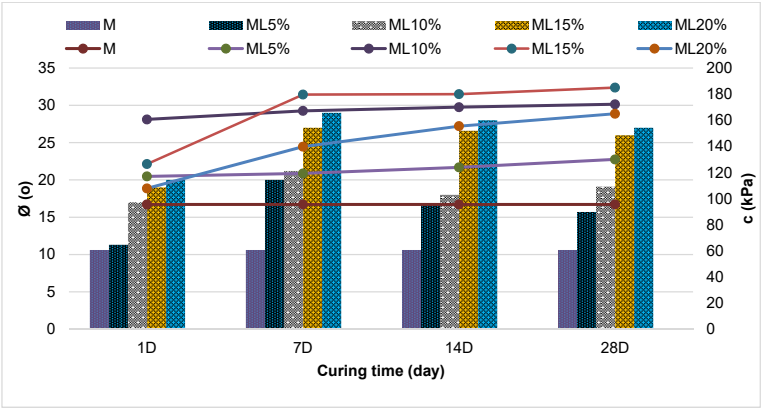


()b

Fig. 3. UCS of soil samples (a), Variation of internal friction angle (Φ, shown as bars) and cohesion (c), shown as lines) with curing time for different Leonardite contents (b)

The stress-strain behaviour of the untreated marl and leonardite-treated marl samples was evaluated based on the results of unconfined compressive strength (UCS) tests to investigate the effects of additive content and curing duration on strength gain and deformation response. As illustrated in Fig. 4, the untreated marl exhibited a ductile pattern, with a gradual increase in stress and a wide strain range before reaching peak strength. In contrast, the leonardite-stabilised samples showed a more rapid stress increase followed by relatively early peak points, indicating a transition toward more brittle behaviour. Among the treated samples, the ML15%-28Day specimen displayed the highest strength (~430 kPa) and a sharper stress-strain curve, reflecting increased stiffness with reduced deformability. The ML15%-14Day and ML10%-14Day samples also achieved notable strength gains but with slightly higher strain at failure, suggesting intermediate behaviour. These observations align closely with the UCS trends and highlight

the role of both additive ratio and curing time in shifting the material behaviour from ductile to semi-brittle. Furthermore, the strain values at failure offer valuable insights into the brittleness-ductility evolution, supporting the conclusion that leonardite incorporation not only enhances strength but also significantly modifies the mechanical response of marl.

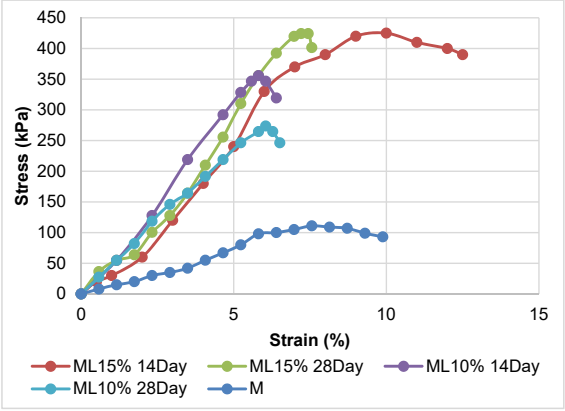


Fig. 4. Stress-strain curves obtained from UCS for untreated and leonardite-treated marl samples at different curing durations

Fig. 5 illustrates the effectiveness of L in stabilising marl by enhancing both compressive and shear strength. For UCS, the SIF values increased as the L content increased up to 15%. However, beyond this certain content, there was a decrease in SIF. Therefore, 15% L was considered optimum as it yielded the highest SIF. Although the highest SIF value, which was 4.48, corresponded to the sample stabilised with 15% L and cured for 28 days, the SIF of the same

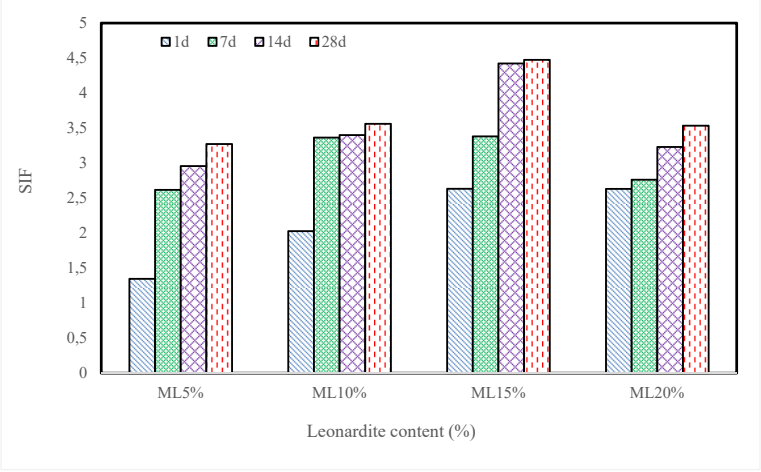
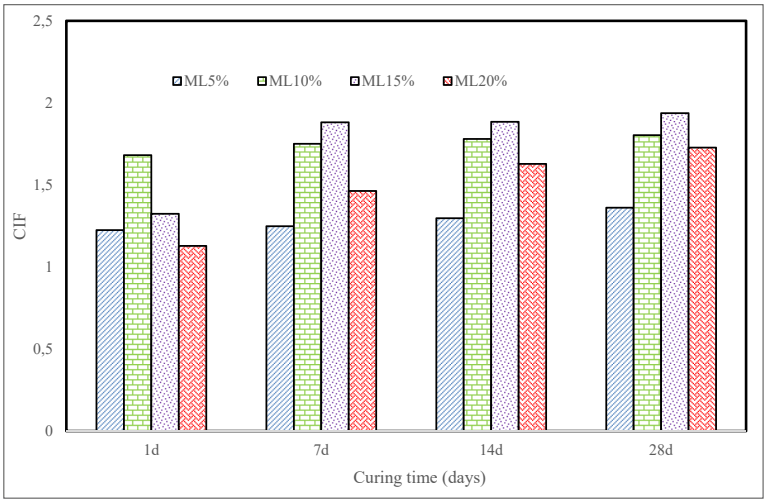
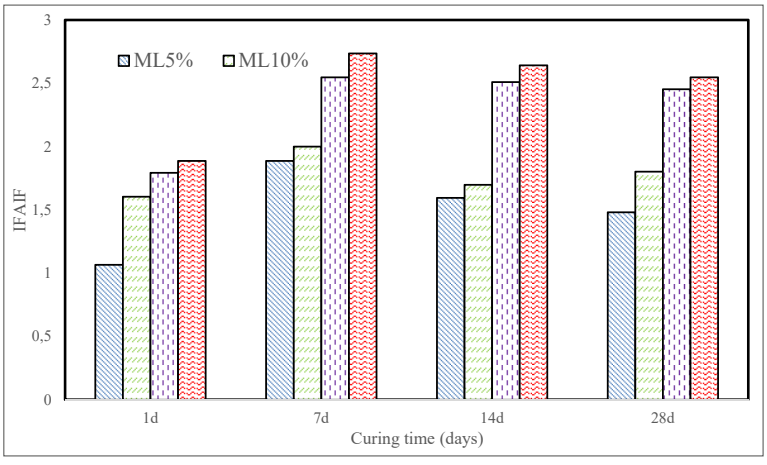


Fig. 5. Effectiveness of L in marl stabilisation represented by SIF

sample cured for 14 days was 4.42. This demonstrates that significant strength improvement occurred within 14 days of curing. In terms of cohesion improvement of the samples, except for those cured for 1 day, the best-performing sample was the one stabilised with 20% L. The CIF analysis revealed that for the optimum sample, the majority of improvement occurred within the first 7 days of curing, beyond which the improvement factor was not substantial. The IFAIF values exhibited an increasing trend with increasing L content and curing time up to 7 days. However, a slight decrease was observed for curing periods exceeding 7 days. These variations in CIF and IFAIF are illustrated in Fig. 6a and 6b, respectively. In terms of mechanical strength, L exhibited high potential in enhancing the problematic marl samples, achieving SIF of 4.48, CIF of 1.94, and IFAIF of 2.73. These values underscore the significant potential of L in soil stabilisation.



(a)



(b)

Fig. 6. Effectiveness of L in marl stabilisation represented by CIF (a), and IFAIF (b)

The SEM-EDX results presented in Fig. 7 indicate that L can serve as a filler to occupy the available voids between soil particles. In addition, as can be seen from Fig. 7, it can be said that L fills the pores in the soil mass and also coats the grains to bond adjacent particles together through various mechanisms. The voids percentage decreased from 11.54% in untreated marl to 7.32% with L addition, representing a reduction of about 40%. Thanks to the ion exchange and organic-metal complex formation properties of the rich humic acids within L, it disrupts and liberates the composition of minerals in the form of oxides, sulfates, carbonates, chlorites and silicate compounds in the soils [19]. In general, although it is unlikely that humic acids will react directly with calcite, there may be cases where humic acids can react with calcite. These reactions are often complex and depend on a variety of factors. Humic acids can adsorb to some mineral surfaces in water and acidic conditions. In this case, they may be in contact with calcite minerals and, in some cases, interact with calcite. Especially in acidic conditions, some groups of humic acids can bind to the surface of calcite minerals and increase their dissolution. Considering that the problem in marly soils may depend on the amount of calcite, it is possible to explain

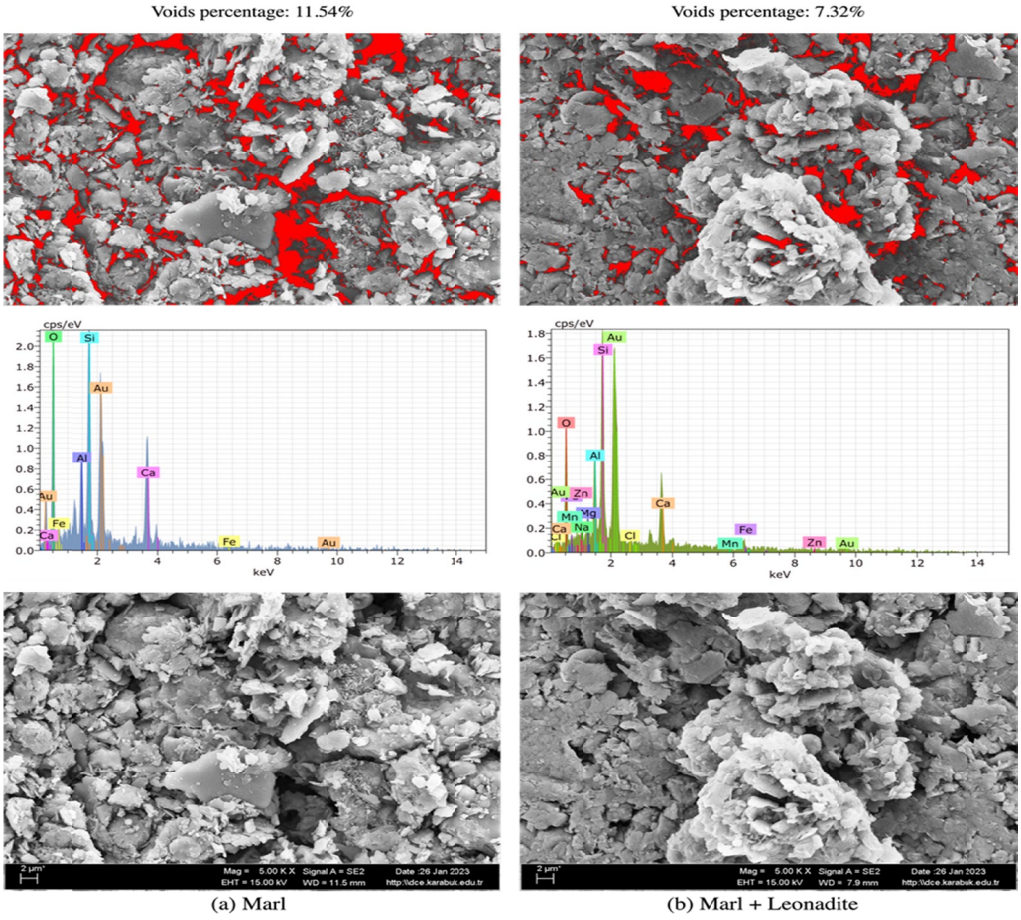


Fig. 7. SEM-EDX analysis and image processing of (a) marl and (b) L-stabilised marl sample cured for 28 days

this effect by the decrease in calcification. Moreover, the XRD analysis of samples (untreated marl and L-treated marl), as depicted in Fig. 8, revealed that no new peaks were detected upon comparing both samples. However, there was a reduction in the intensity of the peaks associated with calcite. Therefore, L not only improves the microstructure of marl samples but also decreases the calcite content of the samples, which is a favorable action because the main problem of marl is attributed to the high content of calcareous material.

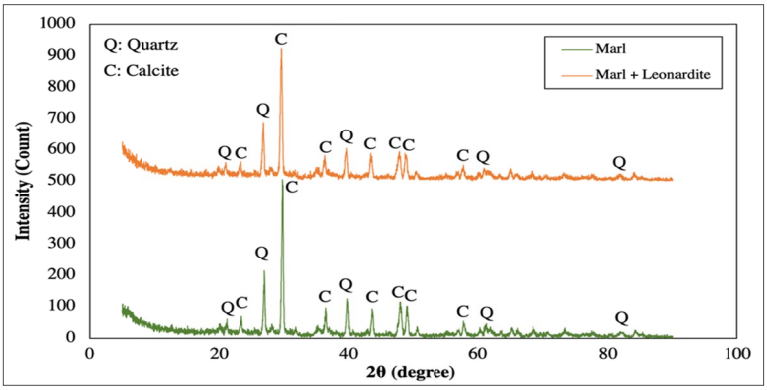


Fig. 8. XRD analysis of marl and L-stabilised marl sample cured for 28 days

To investigate the effect on the functional group of soil treated with L, the samples were observed and compared using FTIR. The comparison between the results of the samples containing L with untreated marl, as shown in Fig. 9, reveals that L produced new peaks corresponding to the wavenumbers of 3624, 3334, and 1631 cm^{-1}. Additionally, the peaks associated with wavenumbers of 1417, 868, and 789 cm^{-1} show an increasing trend compared to the marl sample. In general, L-stabilized marl samples exhibited various strong bands, such as H-bonded OH

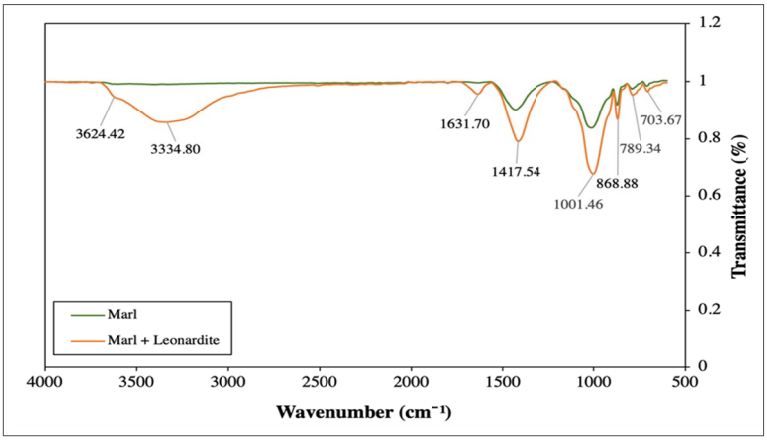


Fig. 9. FTIR analysis of marl and L-stabilised marl sample cured for 28 days

groups, H-bonded C=O group, carbonyl C=O group, aromatic C=C group, and aromatic C-H group, in the regions between 3334 cm^{-1} and 700 cm^{-1}. This is attributed to Leonardite's abundance with a wide variety of functional groups, such as carboxyl, hydroxyl, and carbonyl [10]. The formation of these new strong functional groups due to the addition of L to the marl samples might be a responsible factor for improving the mechanical response.

Finally, the chemical composition of marl and L-stabilized marl obtained by XRF analysis revealed that the chemical compositions of untreated marl, with CaO content of 43.3%, SiO_2 of 33.1%, Al_2O_3 of 10.5%, and Fe_2O_3 of 6.9%, were slightly altered to CaO of 41%, SiO_2 of 35%, Al_2O_3 of 10.7%, and Fe_2O_3 of 6.3% with the addition of L. Although there was an increase in other mechanical parameters, the increase in the internal friction angle was particularly high. The observed increase in the internal friction angle of Leonardite-treated samples may be attributed to the physicochemical interactions induced by the stabiliser. The SEM-EDX images revealed the formation of denser microstructures with improved particle bonding and reduced pore space, which can enhance interparticle friction resistance. Additionally, XRD and FTIR analyses confirmed the partial reduction in calcite peaks and the presence of humic-related functional groups. These changes may lead to surface roughening and improved interlocking between particles, both of which contribute to an increased angle of internal friction. Therefore, the mechanical improvements observed in the UU test results are considered to be consistent with the microstructural modifications caused by leonardite.

3. Conclusions

This study investigated the innovative role of L as an alternative to traditional additives in marl stabilisation. The results of various tests, including UU, UCS, XRD, SEM-EDX, and FTIR, supported the high potential of L in mitigating the problems associated with marl samples. Using 15% of L and curing for 7 to 14 days effectively increased the unconfined compressive strength (UCS) over four times, nearly doubled cohesion, and more than doubled the internal friction angle. The findings of this study can enhance researchers' insight, supporting that L can not only be used to reduce soil contaminants but also increase mechanical and erosional resistance.

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