Microstructural Evaluation of Thermal Stabilization of Marl Soils Considering Permeability Variations

Mohammad Amiri (✉ amirii@hormozgan.ac.ir)

Hormozgan University <https://orcid.org/0000-0002-3751-0261>

Masoud Dehghani

Hormozgan University

Maedeh Papi

Hormozgan University

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Abstract

Heat alters the engineering behavior of soils. Marl soils are highly-erodible sedimentary deposits composed of clay minerals and calcium carbonate. Clay minerals and calcium carbonate in marl soils considerably influence the engineering behavior of such soils. Soils can be exposed to heat for a variety of reasons leading to changes in the physical, mechanical, and microstructural properties, in particular the engineering properties of marl soils. In the design of geo-environmental projects, the results of soil mechanics, especially the permeability coefficient, directly influence the design outcomes. Accordingly, this study aimed at evaluating the effect of heat treatment on the engineering behavior and permeability coefficient of marl soils from a microstructural perspective. To this end, the marl soil was heated to 25–900°C for 2 h. The changes in the engineering properties of marl soils at different temperatures were studied by macrostructural (gradation, Atterberg limits, loss-on-drying, Unconfined Compressive Strength (UCS) and permeability) and microstructural (XRD and SEM) investigations. The results were suggestive of the considerable effect of heat treatment on the engineering behavior of marl soils, as the compressive strength of marl soils increased by 100 folds, and the permeability coefficient reduced by about 6 times at 700°C.

Highlights

- The geotechnical properties of marl soils are strongly affected by the thermal history.
- The permeability coefficient of marl soils is strongly influenced by heat.
- The compressive strength of marl soil is improved with increasing temperature.

1 Introduction

Marl soil can be found in most regions across the world and are made up of 35–65% carbonate and clay (Elert et al., 2018; Vakili et al., 2019). Given their structural nature containing clastic rock particles and chemicals (including calcium carbonate, gypsum, anhydrite, and salts), marl deposits are more prone to erosion than others. Palygorskite and sepiolite are the clay mineral constituents of the marl soil leading to instability of such soils (Ouhadi, 1997; Lamas et al., 2002; Benyahia et al., 2020). Moreover, calcite and dolomite are the most common carbonate minerals in marl soils (Yong, 2000). Carbonate formation and decomposition can alter the soil structure, affecting the pore volume and permeability of the soil (Fukue et al., 2010).

Due to high plasticity, compressibility, erodibility, and a complex behavior, marl soils may cause such complications as foundation or embankment failure and tensile cracks on roads (Bensaifi et al., 2019). Furthermore, despite an acceptable dry strength, marl as a problematic soil suffers from the loss of strength, slaking, and swelling when exposed to moisture (Arifuzzaman et al., 2017; Elert et al., 2018; Bahadori et al., 2019).

Internal erosion and stability of marl soils depend on such factors as (1) the physical and chemical properties of the soil constituents, (2) soil sensitivity and plasticity, particularly its smectite content, (3) soil carbonate content, which can cause cohesion in the short-term and cementation and structural changes in the long-term, and (4) the different void ratios of soil samples (Ouhadi, 1997; Wijdenes and Ergenzinger, 1998; Lamas et al., 2002).

On the other hand, the remarkable effects of heat on the engineering properties of soils have long been utilized. Besides, clay soils are exposed to heat for a variety of reasons causing changes in the engineering behavior of the soil (Chen et al., 2018; Štubňa et al., 2018). Incorporating clay in construction materials and using it for protection in High-Level Waste (HLW) disposal are among the cases where clay is exposed to medium to high thermal regimes (Bag and Rabbani, 2017; Kale and Ravi, 2018). The thermal regime generated by HLW alters most characteristics of buffer

materials and adjacent soil including swelling, permeability, and cation exchange capacity (Sarıkaya et al., 2000; Abu-Zreig et al., 2001; Ouhadi et al., 2010).

Whether in a transient or steady-state, heat can alter the physical, mechanical, and microstructural properties of soils, particularly the engineering properties of clay soils, and the extent of these changes is a function of the type of mineral constituents, chemical composition, density, and moisture content (Joshi et al., 1994). By affecting the soil microstructure, heating reduces the size of calcite grains and silica and alumina contents, while increasing the silica-to-alumina ratio (D'Elia et al., 2018). Moreover, depending on the type of clay minerals, heating could affect the compressive strength of the soil (Çelik et al., 2019).

The removal of water and the formation of new minerals are two main reactions taking place by heating. Water is removed in two stages, namely dehydration (the ejection of pore water, adsorbed water, and interlayer water) and dehydroxylation (hydroxyl ions leaving the crystal structure of the clay mineral). In general, based on the type of the clay mineral, dehydration and dehydroxylation respectively take place at 100–200°C and 500–1000°C. Heating at 500–1000°C causes destruction of minerals and formation of new crystalline silicates. During dehydroxylation, silica and alumina in the soil undergo structural transformation. Moreover, by further heating, the soil melts, forming molten materials (Monsif et al., 2019; Cultrone and Rosua, 2020).

The plasticity decreases by heating the soil to high temperatures. Most soils lose their plasticity at 400–600°C. The exact temperature or range where this phenomenon occurs depends on the type of clay minerals (Morris and Wong, 2005).

Permeability and water transmission through the soil are among the most notable design parameters for landfills (Chai and Prongmanee, 2020; Lu et al., 2020). The soil permeability is dependent on several factors including fluid viscosity, pore size and distribution, gradation curve, void ratio, and saturation level. In clay soils, ion concentration and the electric double layer thickness have considerable effects on the permeability (Alamdar, 1999). A thinner double layer results in a higher permeability and lower plasticity (Spagnoli et al., 2012). Heating affects the permeability of clay soils and promotes porosity, causing an increase in the clay permeability at higher temperatures (Tian, 2019).

Carbonates are among the main factors changing the soil texture. Their presence drastically influences the marl soil structure, porosity, and permeability. The high carbonate content increases the soil permeability (Lamas et al., 2002). Affecting the soil carbonate content, the heat promotes a porous structure, changing the permeability coefficient. Heating the soil to around 350°C results in dolomite decomposition, whereas calcite decomposes in the range of 830–870°C, expelling gaseous carbon dioxide (Cultrone et al., 2001).

Heat treatment changes the engineering behavior of marl soils (Bag and Rabbani, 2017). On the other hand, the permeability coefficient has a direct impact on the results in the design of geoenvironmental projects (Dalla Santa et al., 2020). Accordingly, efforts were made to investigate the engineering properties of the South Iran Marl from a microstructural point of view considering the permeability coefficient variations.

2 Materials And Methods

The South Iran Marl, collected from the northern shore of the Persian Gulf was used for testing. The aim is to investigate the geotechnical properties of marl soils after heating and examine the permeability coefficient from a microstructural point of view and present solutions for using marl soils in geo-environmental problems in the area.

Geologically, the soil samples belong to the Mishan Formation and date back to the Lower to Middle Miocene (James and Wynd, 1995).

The marl was classified as low-plasticity clay (CL) based on the Unified Soil Classification System (USCS), and 95 wt% of the soil passed through the #200 sieve. An XRF chemical analysis of the soil is presented in Table 1. Some geotechnical and geoenvironmental properties of the soil are also presented in Table 2.

The majority of tests were carried out according to the ASTM standards (ASTM, 2014). The carbonate content of the soil was determined by titration (Hesse, 1971). Powder XRD samples were prepared from all soils by weighing 10 ± 0.001 g dry soil to be spread evenly across a slide. The XRD patterns were recorded on a PHILIPS-PW1730 X-ray Diffractometer using the Cu-K α radiation over a 2θ range of $2-60^\circ$ (Ouhadi and Yong, 2003). The SEM samples were prepared similarly to XRD samples but were gold-coated. The SEM images of the gold-coated soil samples were taken by TESCAN-Vega3 Scanning Electron Microscope (TESCAN, Czech Republic).

According to the XRD analysis of the natural marl (Fig. 1), palygorskite ($3.17 \text{ \AA}$ and $2.88 \text{ \AA}$), kaolinite ($7.04 \text{ \AA}$), and sepiolite ($1.87 \text{ \AA}$) are the main clay minerals, and quartz, calcite, and dolomite are the non-clay minerals of the marl soil. The marl soil pH was measured by a pH meter (Lovi Bond pH 110) according to ASTM D4972 at a soil-to-water ratio of 1:10.

Several tests, namely permeability (ASTM D2434-87), Atterberg limits (ASTM D4318), UCS (ASTM D2166), XRD, and SEM imaging, were carried out on the soil samples heated to 25, 100, 200, 300, 500, 700, and 900°C to study the effect of heating on the geotechnical parameters (ASTM, 2014). The kiln temperature was adjusted to increase automatically at $5^\circ\text{C} \cdot \text{min}^{-1}$ until reaching the intended temperature, which was maintained for 2 h before the kiln was switched off. Moreover, the effect of heating was investigated on the physical properties of Bandar Abbas Marl through testing for weight-loss-on-drying according to ASTM E1868-10.

The permeability coefficient was measured by the falling head method. The soil specimens with optimum moisture content and maximum dry density were compacted in 5×10 cm cylindrical molds. After being saturated for one week, all specimens were tested for determining the permeability coefficient.

The UCS tests were carried out according to ASTM D2166 by two methods: (1) preparing specimens from heat-treated soil and (2) heating the specimens. In the first method, the marl soil was first placed for 2 h in an electric kiln set at 25, 110, 200, 300, 500, 700, or 900°C . After determining the maximum specific weight and optimum moisture content, the heat-treated soil was compacted in three layers in 9.8×4.6 cm molds. To reach equilibrium, the specimens were kept in a plastic container at a constant humidity for seven days. It is noteworthy that the reference specimen was kept at 25°C . In the second method, the UCS specimens were prepared with an optimum moisture content of 16% and a dry density (γ_d) of 1.65 g/cm^3 and kept in a plastic container for 3 days at a constant humidity to reach equilibrium. The specimens were then placed in a 100°C oven for 24 h before being heated to 100, 200, 300, 400, 500, 700, and 900°C .

3 Results And Discussion

3.1 Effect of temperature on gradation of South Iran Marl

The gradation curve and changes in the percentage of clay-sized particles in the marl soil are illustrated in Fig. 2. According to the results, the gradation curve does not change significantly as the temperature increased to 110°C . As the temperature increased to 300°C , the diameter of particles finer than 0.01 mm decreased by about 8% and those finer than 0.002 mm by 6%. Raising the temperature to 500°C resulted in a significant increase in the particle size as

the percentage of clay-sized particles (0.002 mm) decreased from 34 to 9%. The start of dehydroxylation and structural destruction of the clay soil may lead to an increase in the particle size. The crystal structures in the clay minerals are broken down and connected through chemical bonds to form larger particles, reducing the percentage of clay-sized particles by 15%.

On the other hand, due to cementation caused by the formation of some salts and oxides, heating results in the combination and cohesion of particles, thus altering soil characteristics (Zhang et al., 2018). This process can affect soil gradation and its engineering properties. Elevating the temperature beyond 500°C did not significantly change the soil gradation so that no significant difference was found in the percentage of clay-sized particles at 900 and 700°C.

3.2 Effect of temperature on atterberg limits of South Iran Marl

The studied natural marl had a liquid limit of 28 and a plasticity limit of 18. According to the results in Fig. 3, elevating the temperature to 110, 200, and 300°C reduces the liquid limit by 0.5, 3, and 4 units, respectively.

On the other hand, the plasticity index decreased by only one unit as the temperature increased to 300°C. By further increasing the temperature to 500°C, the liquid limit decreased by another seven units, showing a transition in the soil behavior (classification) from plastic to granular behavior. It must be noted that the specimens immediately set when exposed to moisture at 700°C. This can be related to the formation of cement compounds in the soil.

The change in the Atterberg limits at different temperatures is a function of the type of clay mineral and the temperature. Dehydroxylation causes destruction of the structure of clay minerals in the marl soil, affecting the Atterberg limits of the soil. The plasticity limit also declined to 15 as the temperature increased to 300°C where dehydration took place. It should be noted that further heating the soil made it non-plastic, making it impossible to conduct the PL test. The decline of Atterberg limits can be related to the structural changes in the soil due to heating and the shift in the soil behavior (Abu-Zreig et al., 2001; Rondón-Quintana et al., 2020).

3.3 XRD analysis of heat-treated marl

Based on the results in Fig. 4, the intensity of the palygorskite characteristic peak (3.17 Å) was not significantly affected by raising the temperature to 110°C and was reduced by nearly 73 CpS due to the removal of physical water in the soil. Even further increasing the temperature to 500°C did not noticeably change the palygorskite characteristic peak. However, at 700°C, the intensity of the palygorskite peak declined by 37% from 1082 to 670 CpS. Raising the temperature helps to expel the interlayer water leading to a decrease in the intensity of clay mineral peaks (Dellisanti and Valdré, 2005; Vidonish et al., 2016). At 900°C, the palygorskite peak intensity was reduced to 301 CpS. Similar observations were made for other palygorskite peaks, such as the one at a 7.09 Å spacing, which decreased from 608 to 230 CpS. Palygorskite remains stable up to 550°C beyond which it becomes unstable (Wang et al., 2020).

Accordingly, it appears that dehydroxylation initiates at above 500°C, destructing the clay minerals in the marl soil. It must be noted that new peaks appear in the XRD patterns of the samples heated at 700 and 900°C.

The intensity of the main calcite peak at $d = 3.03$ Å did not change notably from 25 to 500°C, and the variations remained between 5 and 8%. By raising the temperature to 700°C, the calcite peak intensity was reduced by 820 CpS. This declining trend continued up to 900°C, where the peak completely disappeared, indicating the total breakdown of calcite. According to the literature, calcium carbonate is decomposed completely at 800–870°C (Cultrone et al., 2001).

(Cultrone et al., 2001) claim that calcium carbonate is decomposed by heating and transformed to quicklime, releasing carbon dioxide in the process according to reaction 1. The calcium oxide released at 700–900°C reacts with water according to reaction 2 and produces calcium hydroxide aka hydrated lime.

With silica, aluminosilicate, and sufficient moisture available, the calcium hydroxide produced in reaction 2 may form calcium silicate hydrate (C-S-H) and calcium alumina hydrate (C-A-H) nanostructures through pozzolanic reactions (Singh and Garg, 2006; Trindade et al., 2009).

Above 500°C, after the calcium carbonate is decomposed in the marl soil with a high carbonate content (38.5%), the carbonate oxide reacts with phases produced by destruction of phyllosilicates, forming carbonate silicates, such as gehlenite in accordance with reaction 3.

Moreover, dolomite is decomposed at a lower temperature than calcite at around 350°C, transforming into magnesium oxide and calcium oxide by releasing carbon dioxide according to reaction 4 (Cultrone and Rosua, 2020).

The gehlenite peaks at 2.85 Å and 1.75 Å appear in the XRD pattern of the marl soil at 900°C. Gehlenite is classified as a calcium aluminosilicate formed in a reaction between calcium oxide—produced by the decomposition of calcite—and amorphous phases such as silica and alumina (Cultrone and Rosua, 2020). When the temperature reaches 800°C, calcium carbonate is decomposed into calcium oxide, forming a semi-stable gehlenite (Trindade et al., 2009). Gehlenite continues to disappear as the temperature rises. The presence of gehlenite can be attributed to the higher calcite content than other minerals (Jordán et al., 1999).

At 700°C, weak peaks in the XRD pattern appear at $d = 3.25 \text{ Å}$, 3.2 Å , and 2.69 Å corresponding to alite (C_3S) and belite (C_2S) cement compounds. The formation of these compounds can be the primary reason for the studied samples to set at 700°C, making it virtually impossible to conduct the Atterberg limit test at this temperature.

Note that further increasing the temperature to 900°C weakens the quartz peaks but does not eliminate them. During heating, quartz is transformed into other silica polymorphs. According to (Weiss et al., 1970) alpha-quartz (low quartz or low-temperature quartz) is transformed into beta-quartz (high quartz or high-temperature quartz) at 573°C. Structurally, beta-quartz is similar to alpha-quartz, but with some distortion (Ringdalen, 2015). The process is reversible up to 800°C, and quartz grains are transformed into alpha-quartz by releasing heat under tensile stress, creating voids in the soil structure. In this process, quartz grains swell and microcracks appear, affecting the mechanical properties of the soil (Pabst and Gregorová, 2013; Štubňa et al., 2018).

3.4 Effects of temperature on weight loss

Dehydroxylation refers to the ejection of hydroxyl ions from the structure of clay minerals in the form of water, resulting in the sudden weight loss of the soil. Therefore, sudden weight loss is a proper criterion for determining the dehydroxylation temperature of clay minerals. Based on the XRD analysis results, dehydroxylation was expected to take place above 500°C in the marl soil.

According to Fig. 5, the weight loss is insignificant at 200–300°C. By raising the temperature to 500°C, the weight loss reached nearly 2.2%. At 700°C, the marl sample displayed a sudden weight loss of 14%. This considerable loss can be attributed to the start of dehydroxylation and destruction of clay minerals in the marl soil (D'Elia et al., 2018). Therefore, one can conclude that the dehydroxylation of clay minerals in the soil marl begins in the temperature range

of 500–700°C, which is confirmed by the XRD analysis. Dehydroxylation of palygorskite, as the main clay mineral in the marl soil decomposed above 500°C, is similar to what happens to kaolinite. Another reason for the weight loss can be the transformation of alpha-quartz to beta-quartz (Štubňa et al., 2018). The weight loss continues up to 900°C and reaches 20.5%.

In fact, the weight loss takes place in both clay and carbonate constituents of the marl soil. A weight loss of 14% at 700°C can be attributed to dehydroxylation of clay minerals in the marl soil, whereas the 6.5% loss at 700–900°C is due to the release of carbon dioxide (Trindade et al., 2009).

3.5 UCS Variations of the heat-treated marl soil

Figure 6 depicts the UCS curves of the heat-treated marl soil in two different cases. In the first case, the soil was first heated, the UCS specimens were prepared and then cured for seven days. In the second case, the UCS specimens were first prepared and then cured for three days before being heated to 25–900°C.

First, the effect of temperature on the compressive strength of specimens made of heat-treated soil is discussed. According to the results, the strength of the natural marl is 0.7 kg.cm^{-2} . Raising the temperature to 200°C increased the soil strength to 0.92 kg.cm^{-2} by a factor of 1.31. At 300 and 500°C, the compressive strength reached 1.05 and 1.84 kg.cm^{-2} , respectively. In this temperature range, the soil is dehydrated leading to an increase in the compressive strength. At 700°C, the soil compressive strength increased considerably, reaching 69.1 kg.cm^{-2} , 37.5 times higher than that at 500°C and nearly 100 times higher than the compressive strength of natural soil. This can be attributed to dehydroxylation taking place in this temperature range, as well as the structural changes in the soil and the formation of cement compounds, alite (C_3S) and belite (C_2S) (Joshi et al., 1994).

In fact, the applied heat causes the formation of cement compounds, and introducing moisture to the soil for preparing the uniaxial specimens causes the soil to set and harden at this temperature. Pozzolanic reactions and the formation of C-S-H and C-A-H nanostructures can be the main reasons for the improved compressive strength.

C-S-H and C-A-H compounds with complex and strong hydrogen bonds improve the compressive strength of the soil specimens treated at 700°C. By increasing the temperature to 900°C, the soil strength declines considerably (9 kg.cm^{-2}) compared to the specimen treated at 700°C. The studied marl contains 38.5% carbonate. Calcium carbonate is decomposed at 700–870°C, realizing gaseous carbon dioxide leading to a porous soil structure. On the other hand, glassy and highly-porous gehlenite compounds reduce the compressive strength of the soil (Cultrone et al., 2001). Structural transformations of quartz and formation of voids and microcracks also cause a decrease in the compressive strength.

In the second case, the UCS specimens were heat-treated after preparation. According to the results in Fig. 6, the marl soil has an UCS of 12.90 kg.cm^{-2} at 110°C, which is 18 times higher than natural marl. This enhanced strength can be attributed to the loss of moisture. The compressive strength gradually increases from 110 to 300°C and reaches about 13.9 kg.cm^{-2} at 300°C, and the interlayer water decreases with heating due to dehydration. The lower electrostatic repulsion between the clay particles also causes an increase in the compressive strength (Afrin, 2017).

The compressive strength reaches around 27.7 kg.cm^{-2} at 700°C, which is 39.5 times higher than that of natural marl. Given that dehydroxylation occurs above 550°C, the strength improvement can be attributed to dehydroxylation. In other words, the atomic configuration following dehydroxylation improves the compressive strength of the marl soil specimens (Joshi et al., 1994). Clay minerals in the marl soil are dehydroxylated, and the wrinkled clay particles and flakes are replaced by cohesive and homogeneous particles, improving the comprehensive strength.

The compressive strength reaches 14.73 kg.cm^{-2} at 900°C , suggesting a 46.8% decline. Decomposing at $830\text{--}870^{\circ}\text{C}$, calcium carbonate is transformed into calcium oxide (quicklime) and carbon dioxide is released (Cultrone et al., 2001). It is, therefore, safe to attribute the loss of strength to the structural transition of the soil above the dehydroxylation temperature and the increased soil porosity.

The XRD pattern of the soil sample at 900°C reveals the appearance of the new gehlenite peaks at $d = 2.85 \text{ \AA}$ and $1.75 \text{ \AA}$. The glassy and porous structure of gehlenite causes a decrease in the compressive strength of the specimens at this temperature. Accordingly, the strength of the marl soil can be said to be reduced by the poor strength of gehlenite compounds. Nonetheless, it must be noted that the strength of the specimen treated at 900°C is nearly 21 times that of natural soil.

Overall, the high-carbonate clays (marl soil), especially those containing calcite, have a positive effect on the compressive strength, as carbonates form pores and crystalline phases during curing, improving the compressive strength (Gualtieri et al., 2010). On the other hand, due to poor strength, gehlenite compounds reduced the strength of the soil treated at 900°C .

3.6 Permeability coefficient of the heat-treated marl soil

Figure 7 illustrates the permeability coefficient of the studied heat-treated marl soil. Natural marl has a permeability coefficient of about $1.1 \times 10^{-7} \text{ cm.s}^{-1}$, which is acceptable for geo-environmental projects (Daniel and Benson, 1990; Kalkan and Akbulut, 2004). According to the results, the permeability was slightly improved by 5% by raising the temperature to 110°C .

Further increasing the temperature to 200°C promoted the nucleation of new microcracks and the growth of existing ones, naturally, affecting the physical properties and improving the permeability coefficient (Sun et al., 2016). The permeability coefficient was improved 26-fold at 200°C , reaching nearly $2.87 \times 10^{-6} \text{ cm.s}^{-1}$. Heating up to 200°C ejects interlayer water, causing irreversible changes in the soil structure. The ejection of interlayer water increases the salt concentration around clays, reducing the thickness of the electric double layer and, consequently, the electrostatic repulsion. These conditions promoted microstructural changes, consequently, increasing the microscopic voids in the soil structure. Accordingly, more paths open up for the flow of water, increasing the permeability coefficient of the soil (Ouhadi et al., 2010).

Increasing the temperature to 300°C promoted the nucleation of microcracks, increasing the permeability coefficient to nearly $3.6 \times 10^{-6} \text{ cm.s}^{-1}$. In the temperature range of $300\text{--}500^{\circ}\text{C}$, the clay soils underwent a major structural transformation as a result of changes in their structural water.

The permeability was increased 246-fold compared to natural soil at 500°C , reaching $2.71 \times 10^{-5} \text{ cm.s}^{-1}$. According to (Chen et al., 2017), elevated temperatures cause a fundamental structural transition in the soil, develop larger interparticle voids, change the effective flow cross-section, and release absorbed water.

At 700°C , the soil behavior changed entirely and the permeability coefficient drastically reduced to $1.63 \times 10^{-8} \text{ cm.s}^{-1}$, indicating a 6-fold reduction compared to natural soil. According to the XRD analysis, the formation of cement compounds (C_2S and C_3S) at 700°C , and the resulting pozzolanic reaction and setting upon saturation and the formation of C-S-H and C-A-H nanostructures reduce the permeability coefficient. The permeability decreased as the cement compounds formed at 700°C begin to set. The formation of the highly-porous gehlenite at 900°C increased the permeability coefficient nearly 672-fold to $7.39 \times 10^{-5} \text{ cm.s}^{-1}$.

3.7 Morphology of heat-treated marl

The arrangement of soil particles and the microscopic texture of marl specimens were analyzed by SEM imaging to investigate textural changes in the soil samples treated at different temperatures.

Figure 8a illustrates the texture of natural marl and the fibrous morphology of palygorskite minerals. Moreover, the white masses are suggestive of the high concentration of calcium carbonate in the studied soil.

At 500°C (Fig. 8b), palygorskite rarely appears in the soil due to the start of dehydroxylation causing destruction of clay minerals and formation of larger particles, thus promoting pores and the growth of microcracks. The changes in the particle arrangement, destruction of clay minerals, and the formation of coarser compounds at this temperature can be the main reasons for the 246-fold increase of the permeability coefficient.

According to Figs. 8c and d, palygorskite is entirely disappeared in the temperature range of 700–900°C, as the fibrous and needle-like grains cannot be found in the SEM micrographs. With the initial melting of the soil at 700°C, calcium carbonate was reduced drastically by decomposition. The figure also confirms the limited formation of cement compounds, alite and belite.

A new gehlenite structure was formed following the heat treatment at 900°C (Fig. 8d). At this temperature, a porous structure (gehlenite) develops in the soil sample leading to the formation of multiple microscopic voids and pores. This can also be attributed to the decomposition of calcium carbonate and the release of carbon dioxide from the soil. Accordingly, the compressive strength of the soil treated at 900°C (Fig. 6) was reduced. Further, the glassy texture of the soil at this temperature is indicative of a phase transition and the formation of new compounds. This structure increased the permeability coefficient by a factor of 672 (Fig. 7) compared to the natural soil.

4 Conclusion

1. The geotechnical properties of the marl soil are strongly dependent on the temperature history, particularly the maximum temperature it was exposed to. Both microstructural and macrostructural properties of marl soils depend on the heat treatment, clay mineral type, and soil constituents, particularly the carbonate content.
2. Through dehydroxylation and by destructing the clay minerals and causing cementation in the soil particles, heating improved the interparticle cohesion and reduced the clay-sized particles by 15%.
3. At 500°C, the liquid limit decreased by nearly 7 units, resulting in a transition from plastic to granular behavior. At 700–900°C, the soil loses plasticity completely due to dehydroxylation and destruction of clay minerals.
4. Based on the results of XRD analysis and loss-on-drying tests, elevating the temperature above 500°C caused ejection of the interlayer water in palygorskite. In fact, dehydroxylation initiated at above 500°C destructed the clay minerals in the marl soil.
5. By further increasing the temperature to 700 and 900°C, the weights of marl samples reduced by 14 and 20.5%, respectively. The weight loss was found to take place in both clay and carbonate constituents of the marl soil. The 14% weight loss at 700°C can be related to dehydroxylation of clay minerals in the marl, whereas the 6.5% loss at 700–900°C is due to the release of carbon dioxide.
6. The weak peaks appeared at $d = 3.25, 3.2, \text{ and } 2.69 \text{ \AA}$ in the XRD patterns of the soil treated at 700°C were assigned to cement compounds, alite (C_3S), and belite (C_2S). The formation of these cement compounds can be the primary reason for the marl to set at 700°C, increasing the compressive strength of specimens prepared using the heat-treated soil and reducing the soil permeability.
7. Raising the temperature increased the compressive strength of the specimens prepared using heat-treated soil compared to the natural marl at all temperatures. The highest soil compressive strength of 69.1 kg.cm^{-2} was

achieved at 700°C due to dehydroxylation and the formation of cement compounds.

8. At 700°C, the compressive strength of the heat-treated specimens was 27.69 kg.cm⁻². Dehydroxylation at above 500°C and the resulting atomic configuration improved the compressive strength of specimens.
9. The development of the glassy and porous structure resulting from carbonate decomposition and the formation of gehlenite at 900°C caused a decrease in the compressive strength and a considerable increase in the permeability coefficient.
10. Natural marl has a permeability coefficient of around 1.1×10^{-7} cm.s⁻¹. On the other hand, the permeability coefficient of the marl soil is significantly influenced by temperature, as it was increased 26- and 246-fold at 200 and 500°C, respectively, due to the growth of microcracks and fundamental transformation of the marl.
11. Moreover, the formation of gehlenite and a porous structure at 900°C increased the permeability coefficient of the marl by a factor of 672.

Declarations

Data Availability Statement

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Conflict of interest

The authors declare that they have no conflict of interest.

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Tables

Table 1. Chemical properties of the South Marl

LOI	P ₂ O ₅	MnO	TiO ₂	K ₂ O	MgO	Na ₂ O	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Parameters Product type
19.51	0.124	0.085	0.475	1.605	6.597	1.688	19.863	5.222	8.341	35.555	<i>South Marl</i>

Table 2. Geotechnical properties of the South Marl

<i>References for method of measurement</i>	<i>Quantity measured</i>	<i>Physical properties of South Marl</i>
ASTM, D422-63	34.12	Clay (%)
ASTM D4972	8.74	pH (1:10; soil: water)
Hesse, 1971	38.5	Carbonate content (%)
ASTM D3080-90	0.57	C (kg/cm ²) Strength Parameters
ASTM D3080-90	29.5	ϕ^o
ASTM D2166-06	0.7	Unconfined Compression Strength (UCS) (kg/cm ²)
ASTM, D4318	28	Liquid limit (%)
ASTM, D4318	18	Plastic Limit (%)
ASTM, D4318	10	Plasticity Index (%)
ASTM D698	1.65	Maximum dry density (g/cm ³)
ASTM D698	16	Optimum water content (%)
		Maximum free – swelling (%)
	$1.1e^{-07}$	permeability coefficient (k) (cm/s)
ASTM, D85487	2.77	G_s
ASTM, D3282	CL	Classification
		Color
ASTM D2216	Palygorskite, Sepiolite, Kaolinite, Calcite, Dolomite, Quartz	Soil composition

Figures

Figure 1

X-ray diffraction pattern of natural marl soil

Pal: Palygorskite, Sep: Sepiolite, Kaol: Kaolinite, D: Dolomite, Ca: Carbonate, Q: Quartz

Figure 2

Effects of temperature on the gradation of the South Iran Marl Soil and the clay-sized particles

Figure 3
Liquid limit and plasticity limit variations of the marl soil treated at different temperatures

Figure 4
The XRD pattern of the marl soil stabilized at different temperatures

Pal: Palygorskite, *Sep*: Sepiolite, *Kaol*: Kaolinite, *D*: Dolomite, *Ca*: Carbonate, *Q*: Quartz, *Gh*: gehlenite.

Figure 5

The weight loss of the marl soil treated at different temperatures

Figure 6

The UCS variations of the South Iran Marl treated at different temperatures

Figure 7

The permeability coefficient of the marl soil heated to different temperatures

Figure 8

The SEM images (10000X) of marl samples; a) natural soil; b) treated at 500°C; c) treated at 700°C, and d) treated at 900 °C.

Pa: Palygorskite, C_2S : Belite (dicalcium silicate); C_3S : Alite (tricalcium silicate)