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PHYSICOCHEMICAL AND GEOTECHNICAL EVALUATION OF STABILITY OF NATURAL SMECTITE/KAOLINITE SOILS AS GEOLOGICAL DISCHARGE SITE OF ACIDIC SOLID WASTE IN TUNISIA

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Abstract:

This study aims to investigate the effects of acidic phosphate solution (PS) from phosphogypsum collected from the Tunisian Chemical Group in Gabes, with a pH of 2.6, on the physico-chemical and mechanical properties of Tunisian clay soils, Aleg (AG) and El Haria (EH). Here, the feasibility of employing these soils as natural impermeable barriers for phosphogypsum (PG) disposal sites has been explored. Mineralogical and chemical compositions of raw and modified clays were identified using XRD and XRF. The contact effect of phosphoric aqueous waste in comparison to tap water on raw clays, was revealed by a clear disappearance of the carbonate peak. The drained shear strength of Aleg soil decreased to 48 kPa. Conversely, the cohesion of El Haria soil increased with phosphate solution. Triaxial test results showed c' and φ' decreased to 44 kPa and 21° for AG and increased to 155 kPa and 27° for EH. AG and EH clays showed an important support capacity that reached 38 m and 57 m, respectively.

Key words: clay soil, mineralogical analysis, direct shear test, phosphogypsum, discharge site.

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INTRODUCTION

Over the recent decades, rapid urbanization, industrialization, and population growth have led to dramatic rise in pollution levels of water, soil and air. Indeed, several industries have generated huge amounts of sludge that differ according to the nature of their processes (such as chemical, physical, or biological treatments) and the characteristics (such as composition, moisture content and toxicity) of the sludge. Moreover, the discharge of contaminants containing heavy metals, fluorides, sulfuric acid and radioactive materials, poses several health and environmental risks, such as reduced soil fertility, acidification of soil and water, toxicity of flora and fauna as well as groundwater contamination. Among these contaminants, phosphogypsum (PG) is particularly problematic due to its volume and chemical hazards. It is a toxic calcium sulfate hydrate generated by the chemical reaction between the extracted raw phosphate and the sulfuric acid during the manufacturing process of phosphate fertilizers. This reaction is presented as follows (Abouloifa *et al.*, 2023):

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O = 6H_3PO_4 + 10(CaSO_4{\cdot}2H_2O) + 2HF \quad (1)$$

Phosphogypsum (PG) production is intrinsically tied to the manufacture of phosphate-based fertilizers, necessitating the processing of substantial volumes of this by-product. Due to escalating global fertilizer demand, PG generation has reached critical levels, exceeding 280 million tons annually worldwide (Cichy *et al.*, 2018). Alarmingly, approximately 58% of this quantity is stockpiled, posing considerable environmental risks (Al-Hwaiti *et al.*, 2019).

However, no clear regulatory guidelines were defined to store phosphogypsum waste, from the Tunisian Chemical Group (TCG) activities. The management of PG discharge, which presents a major problem for environment balance, remains a significant challenge. Currently, two main management strategies are employed in Tunisia to treat PG waste. The first strategy consists of surface disposal (case of TCG of Sfax and Skhira station). On the other hand, the second strategy requires the direct discharge of PG into the sea (the case of Gabes station). Nevertheless, both methods pose risks to human health and may damage soil and groundwater contamination.

Considering the adverse environmental impact of existing disposal practices, various studies have examined the impact of these strategies on environmental sustainability and public health, as well as evaluated pollution levels in regions close to the storage sites. For instance, Zairi and Rouis (1999), revealed high contamination near two storage sites (near the IAPE and NPK factories) in Sfax, with concentrations of fluoride, phosphates and heavy metal exceeding Tunisian discharge standards by over 100 fold. Another research work, focusing on the TCG plant in Gabes showed high concentrations of heavy metals in seawater where phosphogypsum discharge occurs (El Ayeb *et al.*, 2020). As a solution, several authors have proposed the development and the reuse of PG as a raw material in agriculture as amended for soils and as fertilizers (Gabsi *et al.*, 2023; Gao *et al.*, 2025). In the same context, some researchers suggested combining PG with other materials to create fire-resistant panels and ceramic tiles having improved thermal and mechanical properties (Rakhila *et al.*, 2018; Guedri *et al.*, 2023). Despite the development of phosphogypsum recycling methods, its large-scale integration remains difficult, and these solutions have not yet met the storage demand.

In response to this challenge, an alternative strategy consists in containing phosphogypsum in situ through a natural barrier system. Among these, the use of clay as sealing barrier for PG presents a promising and practical solution, due to its abundance, good biocompatibility, high cation exchange capacity (CEC), large internal surface area and excellent swelling capacity (Garcia-Guzman *et al.*, 2023). Additionally, clays have unique properties such as low permeability and a high ability for pollutant retention. These materials are commonly used as a natural sorbent for wastewater treatment and as a potential barrier in landfills to inhibit the leaching of radioactive materials into the soil and groundwater (Oladoye, 2022; Li *et al.*, 2023). However, another study has drawn attention to the risk of using clay in the storage sites and has focused on its susceptibility to cracking, which can compromise its impermeability (Yahia *et al.*, 2005). In fact, cracks in clay barriers may increase contaminant transport rates, affecting the overall effectiveness of the storage system. Furthermore, experiments on dry PG storage indicated that the lower layers become saturated, even in arid climates without rain infiltration, possibly due to the self-weight consolidation and settlement of gypsum (Fuleihan, 2012).

Most previous research has focused on the acid decomposition effects on the physicochemical properties of clay materials (Önal and Sarikaya, 2007; Wallis *et al.*, 2007). However, only a few studies have addressed their geotechnical behavior (Atterberg limit, shear strength, compressibility, permeably) in contact with acid solution.

This study focuses, first, on the evaluation of physicochemical and geotechnical properties of two local Tunisian natural clay materials in contact with phosphate solution purchased from the storage sites of phosphogypsum used by the Tunisian Chemical Group in Gabes. In second place, to study the behavior of phosphoric solution on the clay structure, and finally, to evaluate the potential use of these clays as natural barriers for phosphogypsum storage.

MATERIALS AND METHODS

Soil sampling

The natural clays used in this study were collected from two different deposits occupying the flanks of Jebel Haidoudi anticline (El Hamma region), located in Gabes, South Tunisia (Fig. 1). The Jebel Haidoudi structure is located in the El Hamma region of Gabes governorate. It forms part of the south-central Atlas, more specifically in the northeastern part of pre-Saharan Tunisia. It covers an area between latitude 34°2’9.7”N and longitude 9°42’51.5”E. This structure is bounded to the east by Zemlet El Beidha anticline and the Mediterranean Sea, to the south by Sebkha El Hamma and the northeast by the Menzel El Habib Region.

The simplified geological formations, allows describing the geology of the studied site. In fact, Aleg formation has been the subject of numerous studies, scientific applications and research exploitations. For example, Bouaziz (1995) demonstrated that the Coniacian Campanian soils of Aleg (AG) consist of a clay complex containing carbonate intercalations, fibrous gypsum filling voids and bedding joints. Moreover, Burollet (1956) proved that the soil of El Haria (EH) formation is represented by a predominantly clayey soil with marly series belonging to the upper Maastrichtian Paleocene.

A disturbed sampling technique was employed to collect clay samples from the Aleg and El Haria formations. A

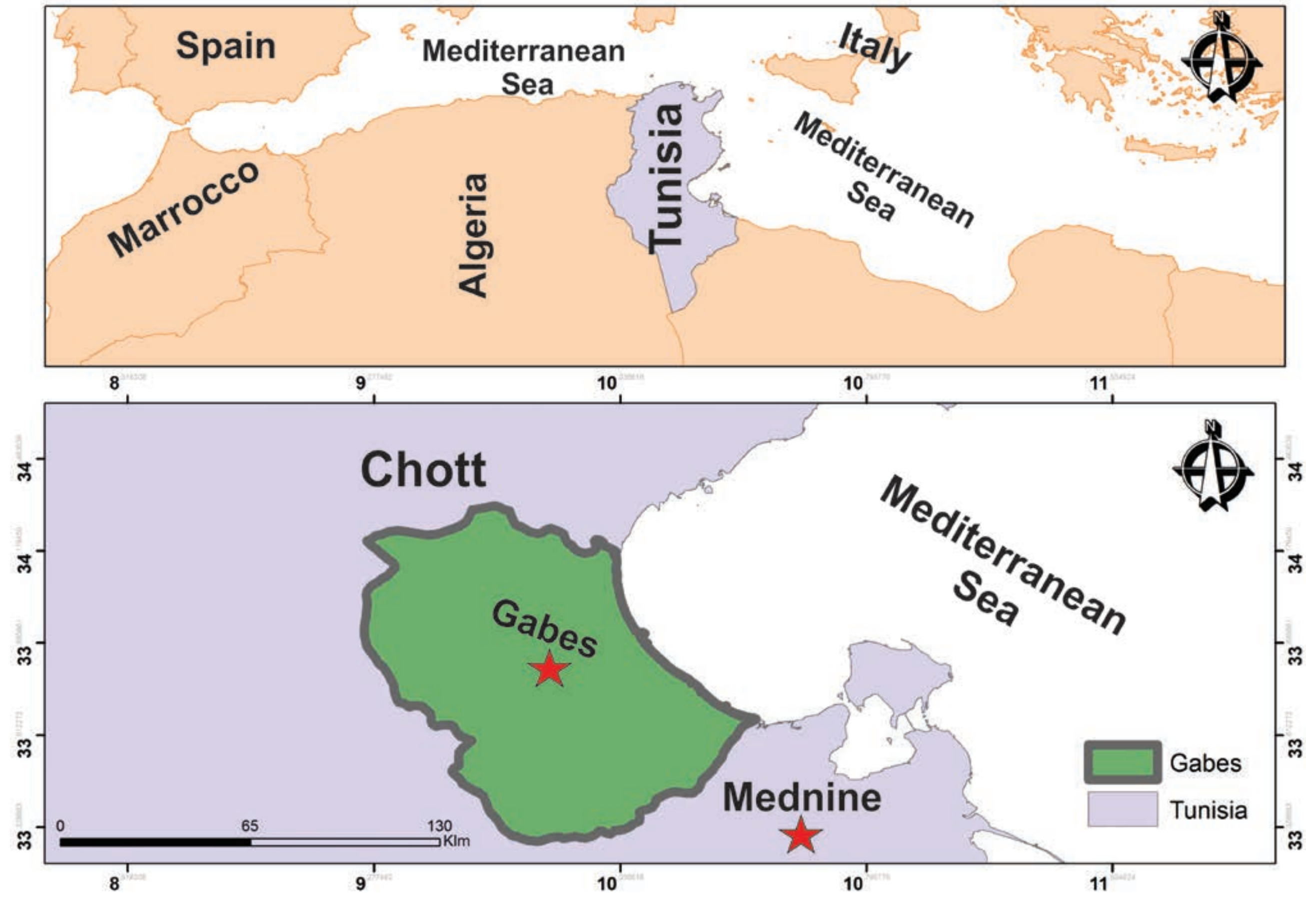

Fig. 1. Location of clay materials.

hand auger was used to extract material from surface layers at depths between 0.5 and 1 m below the ground surface. The sampling aimed to obtain representative bulk material for laboratory analysis. The distributed samples, intact rock fragments were placed in bags, were brought to the laboratory to perform index tests. On the other hand, the natural soil was first tested, in this study, for their physical properties. Natural water content (w_n) was measured at 60°C until reaching constant mass.

Then, bulk density (ρ) of soils was determined by the clod method using paraffin. Specific gravity of the clay particles was determined applying the pycnometer method. The organic matter content (%OM) of soils samples was estimated applying the Loss on ignition technique. Samples, in porcelain crucibles, were heated for 6 hours at 425°C in a muffle furnace. The organic matter content in samples as shown in Table 1 allowed the classification of soils according to the LCPC (Central Laboratory of Bridges and Roads method) (Magnan, 2006). EH and AG are non-organic soils (%OM < 3) and low-organic soils (3 < %OM < 10), respectively. It is noted that the densities of soils were higher than that of phosphogypsum. Grain size distribution analyses were carried out using a laser diffraction (Microtrac S3500) and by wet sieving (using distilled water). Fig. 2 represents the grain size distribution curves of the two types of studied soils. The soil composition of clay, silt and sand, as well as their texture was determined based on the texture classification diagram. The locations and the designations of the examined regions as well as their physical properties and texture are presented (Table 1).

The employed sludge material (phosphogypsum), characterized by a specific density ranging from 2.32 to 2.33 g/cm^3, bulk density of 1.4–1.6 g/cm^3, an initial water content of around 7% and an initial void ratio of approximately 1.022, was provided from the phosphate industry of the Tunisian Chemical Group (TCG).

Table 1. Physical properties and the texture of raw soils.

		Location	
		Aleg	El Haria
		Symbol	
		AG	EH
Soil properties	Gs	2.61	2.61
	ρ (g/cm^3)	1.90–1.95	2.00–2.05
	w_n (%)	30.0	12.0
	%OM	5.44	1.98
	Clay (%) < 2 µm	30.0	19.5
	Silt (%) 2–63 µm	70.0	80.5
	Sand (%) >63 µm	0	~0
	Texture	fine silty clay	fine silty

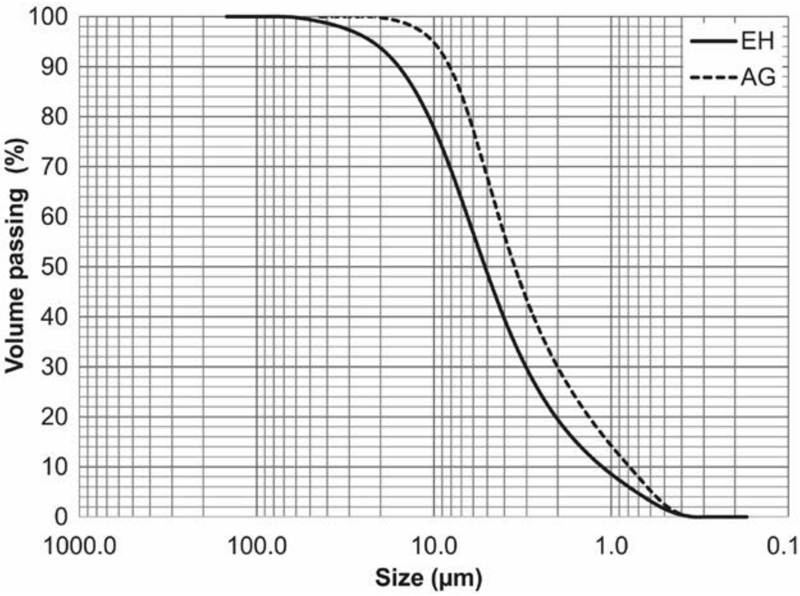

Fig. 2. Grain size distribution of raw soils.

Phosphoric solution preparation

The phosphoric solution (PS), with initial pH of 2.6, was prepared by mixing phosphogypsum obtained from the Tunisian Chemical Group (TCG) in Gabes with distilled water. Then, it was stirred at 400 rpm for two hours until homogeneous. It was subsequently centrifuged and filtered. The concentration of trace elements in the reconstituted solution was estimated using ion chromatography-mass spectroscopy (IC-MS) and inductively coupled plasma mass spectrometry (ICP-MS) instruments. The results presented in Table 2 indicate that the solution contains a significant amount of harmful substances, notably fluoride, phosphate, sulfate and chloride. For the other studied elements, the concentration of sodium was high while the amounts of calcium, magnesium and potassium were low.

Table 2. Composition of leaching solution reconstituted.

Ions	Concentrations (mg/L)
F^-	4484
Cl^-	840
PO_4^{3-}	1665
SO_4^{3-}	2312
Na^+	2200
Ca^{2+}	743
Mg^{2+}	31
K^+	92

X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was used to determine the mineralogical composition of clay soils. The X-ray diffractometer used is (PANalytical) with Cu-Kα radiation for (2θ) range between 2° and 70°, at the scanning speed of $3°min^{-1}$ and a wavelength $\lambda = 0.154056$ nm. The diffractograms were analyzed employing "HighScore plus" processing software.

X-ray Fluorescence spectroscopy

The chemical compositions of raw and contaminated clays were determined using a Bruker S8 Tiger wavelength-dispersive X-ray fluorescence (WDXRF) spectrometer equipped with a 3 kW Rh anode tube in vacuum atmosphere.

Geotechnical tests

Geotechnical experiments are generally conducted to examine the properties and the behavior of soil and rock materials, particularly in the context of environmental management and material testing. In the case of phosphogypsum, geotechnical assays allow determining the behavior of these materials under different conditions, such as plasticity, shear strength, compressibility, and permeability. These tests require the preparation of the specimens to determine these parameters.

This section describes the preparation of the disturbed specimens of soil from the samples extracted from the studied region. Specimens utilized in Atterberg limits tests were prepared according to BS 1377-2 (1990) standard. Pieces of natural soil were placed in a container under enough tap water to submerge it for 24 hours. After that, the mixture was stirred until forming a slurry, which was poured through a 400 µm sieve and placed in a receiver. The fine soil particles in the water were dried in a current of warm air until it formed a stiff paste. To prepare specimens using compacted soil in shear strength, compressibility and permeability tests, the dried pieces of soil were first put in ambient air for 7 days. Two kilograms of each dry soil were thoroughly mixed with the initial content of tap water (TW) or phosphoric solution (PS). Each mixed soil was, subsequently, sealed in an airtight container and stored for, at least, 24 h. After one day, the calculated amount of each sample was introduced into the box shear mold and underwent static compaction by the CBR loading machine through the CBR piston and the loading cap of the shear box. The application of load compaction continued at a rate of 0.5 mm/min to achieve a minimum of 95% of bulk density of raw soils. Afterwards, samples were demolded and trimmed at prefixed sizes.

Atterberg limits

The plasticity was measured by the Atterberg limits method, which determines the plasticity index by the arithmetic difference between the liquid limit (w_L) and plastic limit (w_P), according to Casagrande (1947) technique.

Drained direct shear test

To evaluate the variation of the strength properties of these soil samples, drained direct shear tests were performed at the laboratories of the Higher Institute of Technological Studies of Rades following the standard BS 1377-2 (1990). Samples were prepared and subsequently subjected to testing in consolidated drained (CD) conditions. To saturate soil, each shear box (with a sample) was immersed in a tank containing one of the two solutions (tap water / phosphoric solution). The assembled sample was installed on an oedometer apparatus, within this period, allowing the simultaneous consolidation phase of the studied samples under effective normal stress in the following range: 50, 100 and 200 kPa. At the end of the consolidation phase, the samples were drained and subjected to horizontal shear loading at effective normal stresses of 50, 100 and 200 kPa and at a low shear speed.

Triaxial tests

A consolidated drained triaxial test was used to determine the cohesion and initial friction angle of clay soils according to ASTM D7181-20. The test involves three specimens. A cylindrical reconstituted sample, with an initial diameter of 50 × 100 mm, is mounted in the testing apparatus. The sample is then saturated and consolidated. The specimen is then subjected to a radial stress (σ_3) applied by the fluid pressure and an axial stress (σ_1) that is gradually increased until the sample fails. A lateral effective confining stress about 1, 2 and 3 bars was applied. The Triaxial test was applied on both clay soils using tap water and phosphogypsum leachate solution. The failure is defined by the maximum value of the deviator stress ($\sigma_1 - \sigma_3$) expressed by the following equation:

$$(\sigma_1 - \sigma_3) = \frac{F}{A} \qquad (2)$$

where σ_1 is the axial stress, σ_3: radial or confining stress, F – the axial force applied of the specimen and A – the cross-section area of the specimen.

Oedometer tests

Compressibility tests were conducted, according to BS 1377-5 (1990) standard, utilizing the compression oedometer apparatus with an oedometer cell (Ø = 50 mm and H = 20 mm). Soil samples were prepared after they were subjected to a loading/unloading cycle of effective normal stresses (σ') ranging between 25 and 3260 kPa on saturated soil samples with tap water or phosphoric acid. Each load duration was 24 hours. The dial gauge was read before applying the next incremental load. The compression index (C_c) was approximated as the slope of the (e-log σ') curve in the normally consolidated range and was determined using the following equation:

$$C_c = \frac{\Delta e}{\Delta(\log \sigma')} \qquad (3)$$

where Δ (log σ') denotes the effective stress increment and Δe is the corresponding void ratio decrease.

Accordingly, the swelling index (C_s) was defined from the curve presenting the unloading phase.

Permeability

Permeability (by oedometer cell) was determined according to ISO 17892-11:2019 using oedometer cell fitted with a drainage duct and manometer. Soil specimens were prepared and placed on the oedometer apparatus. Then, they were saturated during 7–8 days. The liquid was allowed to pass through the soil while measuring the time of water flow between two different levels of the manometer. Coefficient of permeability, k, was calculated utilizing the equation written below:

$$k = \frac{a.L}{A.t} \operatorname{Ln}\left(\frac{h1}{h2}\right) \qquad (4)$$

where K is the coefficient of permeability (m s^{-1}), a designates the inside area of the manometer, L corresponds to the length of the sample, A represents the inside area of the specimen, t refers to the time that water spent to pass through the soil from h1 to h2, h1 denotes the level of water in the manometer at time t = 0 and h2 is the water level in the manometer at time equal to t.

RESULTS

X-ray diffraction (XRD)

The identification of the mineralogical fractions of the raw samples and the leached ones using the XRD in-

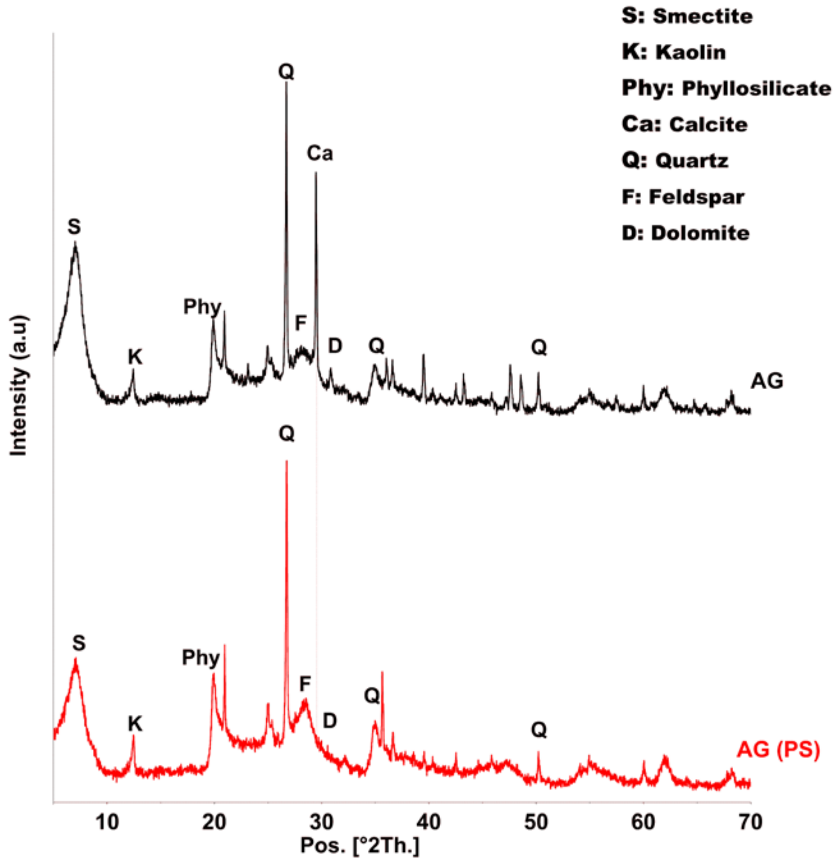

Fig. 3. Diffractogram of AG and AG (PS) samples.

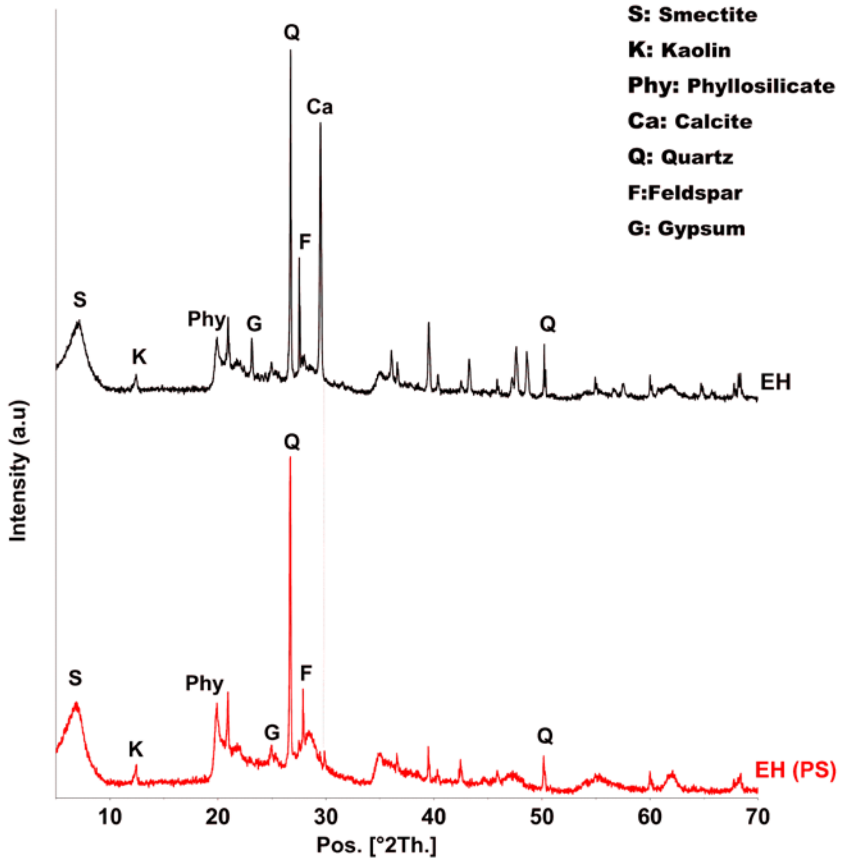

Fig. 4. Diffractogram of EH and EH (PS) samples.

strument is shown in Figs 3 and 4. The X-ray diffraction patterns of both starting soil specimens (diffractogram of AG and EH samples) revealed that the samples were predominately composed of kaolinite-smectite represented by the reflection peak at d-spacing = 12.51Å (Moneim and Ahmed, 2015) and kaolinite with d-spacing = 7.11Å (Kumar and Lingfa, 2019). The non-clay minerals, corresponding to quartz (d-spacing = 3.34 Å) (Baccour, 2008) and calcite (d-spacing = 3.03Å), were detected in the samples.

The degradation of mineral phases after exposure to phosphate solution in AG and EH clays was evaluated by comparing areas of the main basal reflections before and after exposure to the phosphogypsum leachate. This comparison revealed notable mineral transformations, which can be quantified through the reduction in peak counts under identical measurement conditions. In the AG clay, the surface area of smectite decreased from 528 to 450 counts, representing a 15% reduction, while calcite completely disappeared, indicating a 100% degradation and kaolinite slightly decreased from 33 to 30 counts, a 9% reduction. In contrast, the EH clay exhibited different behavior: smectite increased from 482 to 521 counts, possibly due to a reorganization or improved crystallinity, feldspar decreased moderately from 71 to 54 counts, about 24%, calcite was completely dissolved, as shown by its disappearance from the diffractogram and kaolinite dropped from 46 to 26 counts, a 43.5% loss. These variations confirm that the acidic leachate induces selective mineral degradation, with calcite being the most reactive phase, while feldspar and kaolinite are moderately affected.

X-ray Fluorescence (XRF)

X-ray Fluorescence (XRF) is usually investigated to deduce the elemental composition of the examined materials and determine the chemical composition of a sample, which helps scientists analyze the investigated materials accurately and efficiently. Table 3 shows the chemical composition of raw soil and that of acid-treated soil. The obtained results revealed that both soils AG and EH were primarily composed of silica (SiO_2) and alumina (Al_2O_3) without net change indicating the strong alumino-silicate structure. The experimental findings proved that EH contained more quartz and less clay minerals than AG, which made the SiO_2/Al_2O_3 ratio in EH (3.65) higher than that in AG (2.60). Iron oxide (Fe_2O_3) constituted a significant proportion of the composition content. Small amounts of other trace elements, such as CaO, MgO, Na_2O, and K_2O, were also detected. After interaction with the phosphoric solution, the chemical analysis showed a decrease of CaO content accompanied by a few decline of the percentage of Al_2O_3 and Fe_2O_3 in both samples due to the attack of the octahedral layer of the clay fraction.

Table 3. Results of chemical analysis.

Samples/ Elements	SiO_2	Al_2O_3	Na_2O	MgO	CaO	Fe_2O_3	K_2O
AG (%)	47.77	18.40	1.75	2.01	3.72	6.29	1.69
AG (PS) (%)	50.41	17.14	1.74	1.74	1.95	5.94	1.60
EH (%)	51.41	14.06	1.55	1.98	4.38	5.30	1.17
EH (PS) (%)	55.21	14.95	1.57	2.11	2.08	5.66	1.24

Atterberg limits

Atterberg limits are applied to determine the plasticity of fine-grained soils and, consequently to predict the behavior of soils under different moisture conditions. The impact of contaminants on the plasticity of the studied soil was measured on two types of soil: soil saturated with Tap water and that saturated with water containing the phosphogypsum discharge. The Atterberg limits tests were conducted to measure the liquid limit (w_L), the plastic limit (w_P) and the plasticity index (I_P). Table 4 illustrates the measured of liquid limit, the plastic limit and the plasticity index of AG that reached a value of 80%, 50% and 30% respectively. However, EH clay reached a value of 88%, 41% and 47% for liquid limit, plastic limit and plasticity index, respectively. These results proved that EH discerned a high soil plasticity and high susceptibility to shrinkage-swelling for EH soil, according to Prian *et al.* (2000). The changes in the Atterberg limits due to interaction with PS are presented in Table 4. The obtained results show that the reaction between PS and soil increase the liquid limit and the plasticity index of AG sample. In the case of EH sample, the liquid limit and plasticity index decrease because of partially degradation of octahedral sheet of clay.

Table 4. Results of Atterberg limits tests. MH: silt with high plasticity, MH/CL: silt or/and clay with high plasticity.

Properties	AG	EH	AG (PS)	EH (PS)
Liquid limit w_L (%)	80	88	92	75
Plastic limit w_P (%)	50	41	39	56
Plasticity index I_P (%)	30	47	53	19
Consistency index I_C	1.67	1.65	1.19	3.32
Natural water content w_n (%)	30.0	12.0	30.0	12.0
Activity	1	2.41	–	–
Plasticity chart of USCS	MH	MH	MH/CH	MH

Drained direct shear tests

The drained direct shear tests are commonly conducted to estimate the shear strength properties of soil under drained conditions. The shear strength is a critical parameter considered to assess the stability of the examined material. In the present work, the drained direct shear tests were performed to study the mechanical behavior of Aleg and El Haria soils saturated by two types of water: the tap water and the phosphogypsum solution. These types

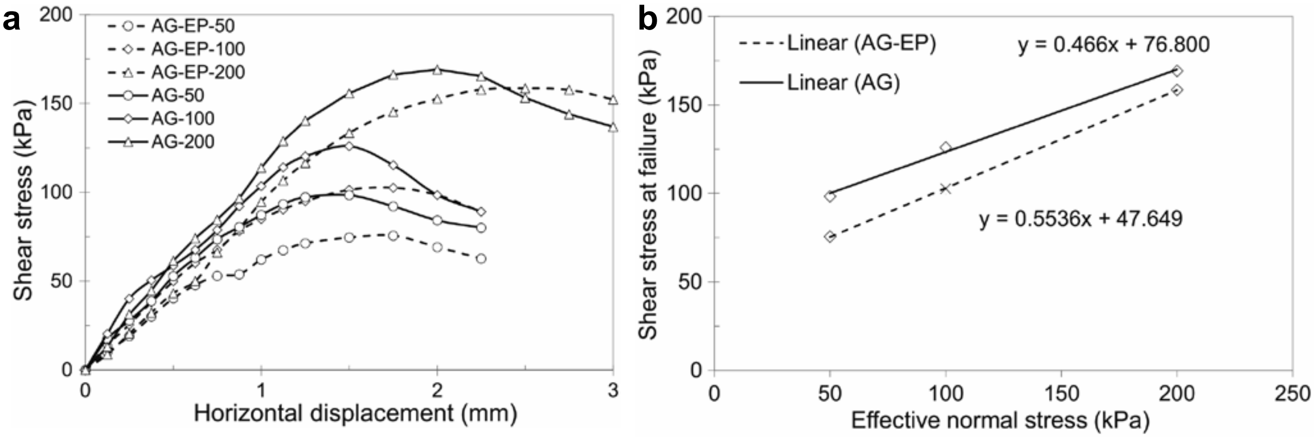

Fig. 5. (a) Shear stress-horizontal displacement curves of AG (continuous lines) and AG-PS (broken lines) samples; (b) Mohr-Coulomb failure envelope of AG (continuous lines) and AG-PS (broken lines) samples.

of water were used to mix and saturate the samples. The conducted consolidated drained (CD) direct shear tests produced stress-displacement curves reflecting the shear stress (τ) of the sample as a function of the horizontal displacement (ΔL) at an effective normal stress. The tests were repeated for three values of effective normal stress. They demonstrated that τ – ΔL curves exhibited a distinct peak, which refers to the peak shear stress. The plot of peak shear stress versus the effective normal stress using these three points allowed plotting the Mohr-Coulomb failure envelope in order to identify the shear strength parameters: drained cohesion (c') and drained internal friction angle (ϕ').

Fig. 5a (continuous lines) exposes the recorded maximum shear stress for the stress-displacement curves of the AG sample mixed and saturated with tap water. The Mohr-Coulomb failure envelope (continuous line in Fig. 5b) showed that the drained friction angle was about 25°, with drained cohesion of 77 kPa. The data points, obtained at the leaching condition of PG for the same material of soil, are shown in Fig.5a (broken lines). The results obtained from the Mohr-Coulomb failure envelope (broken line in Fig. 5b) proved that the drained internal friction angle was about 29° at drained cohesion of 48 kPa.

On the other hand, Fig. 6a–b demonstrates that the drained friction angle and the drained cohesion of EH are 35° and 80 kPa, respectively, using tap water. With the water accompanying the phosphogypsum, these values are 31° and 148 kPa at effective normal stresses of 50, 100 and 200 kPa. The results showed that EH exhibited the highest values of drained cohesion (c') and drained friction angle (ϕ') because of the presence of a larger quantity of smectite in AG compared to that in EH sample. The results obtained by the drained direct shear tests conducted on acid leachate-compacted samples revealed a decrease in drained cohesion and friction angle for AG. In contrast, significant increase of drained cohesion (c') was observed for EH.

Triaxial tests

The correlation between deviator stress and axial displacement for the soils, saturated, consolidated and drained in tap water and with phosphoric solution (PS) is illustrated (Table 5). The curves indicated that an increase in effective consolidation stress leads to a higher maximum deviator stress for both soils with the different drained solutions. The

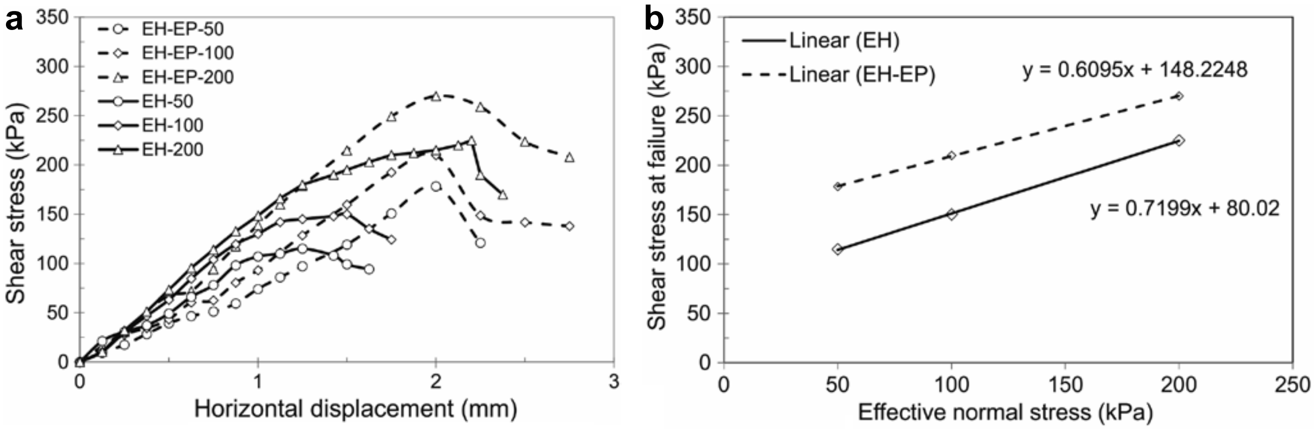

Fig. 6. (a) Shear stress-horizontal displacement curves of EH (continuous lines) and EH-PS (broken lines) samples; (b) Mohr-Coulomb failure envelope of HS (continuous lines) and EH-PS (broken lines) samples.

maximum deviator stresses of tested specimens were plotted in Mohr circles. The cohesion (c’) and internal friction angle (ϕ’) values can be determined from the test results as follows: c’= 77 kPa, ϕ’ = 29° (for AG), c’ = 83 kPa, ϕ’ = 32° (for EH), c’= 44 kPa, ϕ’ = 21° AG (PS) and c’= 155 kPa, ϕ’ = 27° for EH (PS).

These results align closely with those obtained from direct shear tests, affirming the consistency and reliability of both methodologies in characterizing the mechanical response of clay soils under chemically altered conditions.

Table 5. Results of triaxial tests.

	AG	AG (PS)	EH	EH (PS)
Cohesion (kPa)	77	44	83	155
Friction angle (°)	29	21	32	27

Odometer test: compressibility

The odometer test was used to evaluate the consolidation and the compressibility properties of soils. The compressibility tests were conducted on four disturbed specimens of soil (AG and EH) mixed and saturated with tap water or phosphoric solution. Fig. 7a–b shows the changes of void ratio as a function of effective stress of both samples of soil saturated with different solutions (TW and PS). Laboratory data indicated that the acidic leaching exerted the minimal influence on the compressibility of two soils. As demonstrated in Table 6, the compression index of AG exhibits a negligible variation from 0.354 to 0.359, indicating that its properties remained practically unchanged. In addition, Fig. 7b shows that the compression index (C_c) of the specimen EH in the tap water is higher compared to that of the same soil in phosphoric solution. The value of (C_c) decreases from 0.201 to 0.164, respectively (Table 6). It is also noted that the EH soil is more compact than AG soil according to the initial void ratio (Table 6) and the organic matter content (Table 1). The obtained results demonstrate that the void ratio of AG soil is practically unchanged with the use of water mixed with phosphogypsum while that of EH soil decreased faintly.

Table 6. Compressibility parameters of samples.

Sample	AG	EH	AG (PS)	EH (PS)
Bulk density of specimen (g/cm^3)	1.90	2.01	1.85	2.03
Initial void ratio	0.7937	0.4903	0.8433	0.4728
Compression index (C_c)	0.354	0.201	0.359	0.164
Swelling index (C_s)	0.133	0.045	0.090	0.042
Effective preconsolidation stress (σ'_c) (kPa)	885	1000	645	954

Permeability

Soil permeability presents a fundamental parameter considered to quantify the ability of soil to allow water to pass through it. However, low permeability barriers (often made of clay or synthetic materials) are employed to inhibit the migration of contaminants into the surrounding environment.

In the conducted permeability tests, both tap water (TW) and acid leachate solution (PS) were employed in the oedometer cell. The permeability values decrease for the both soils (EH and AG) using PS. However, the decline of EH permeability is more significant; it decreases from $2.14\ 10^{-10}$ to $1.51\ 10^{-10}$ m/s. In the case of AG soil the permeability is around 0.510^{-10}. This reduction can be explained the consolidation of soil and by the precipitation of F, P, Na and free Ca^{2+} ions due to the dissolution of the carbonate (Hamdi *et al.*, 2008). In addition, Özçoban *et al.* (2022) stated that the decrease in permeability is caused by physical and chemical interactions between the leachate and the soil. The infiltration of contaminants into the soil pores leads to clogging. Moreover, suspended particles and the precipitation of some compounds fill the void spaces

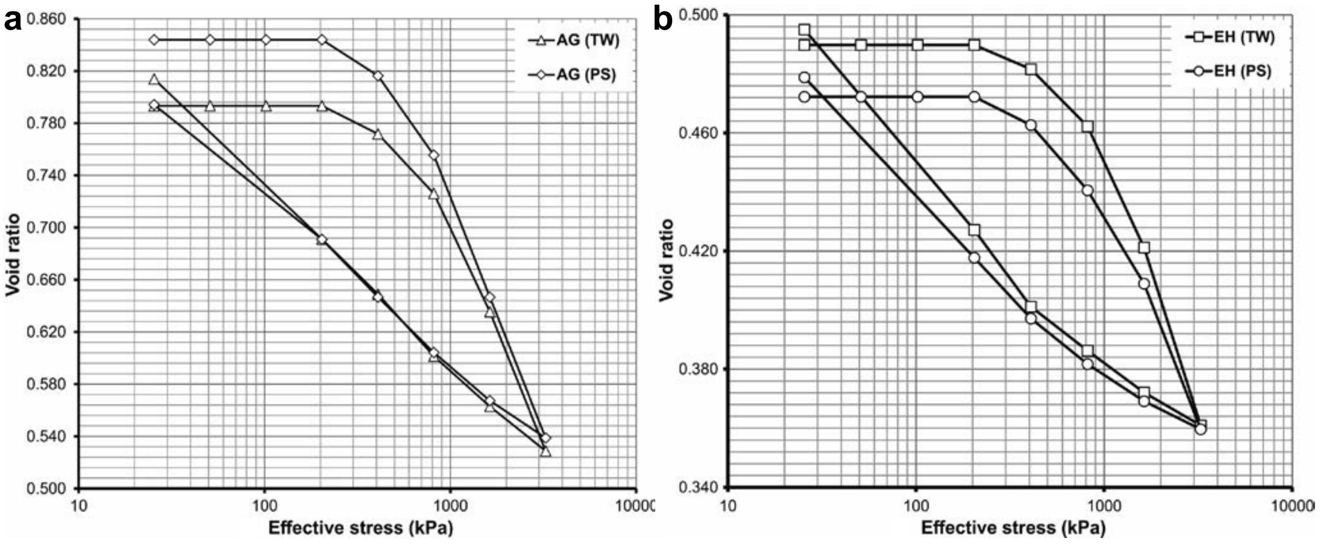

Fig. 7. Compressibility curve: (a) AG samples and (b) EH samples.

between soil particles, further reducing the permeability of the compacted clay. The estimated values of soil permeabilities in both solutions were on the order of 10^{-10} m/s, which corresponds to the category of impermeable soils.

Evaluation of the performance of clay materials as natural barrier for phosphogypsum disposal

To evaluate the suitability of selected materials as a natural barrier at the base of a phosphogypsum storage site, this section examines their mechanical performance by determining the maximum allowed height (H) of the phosphogypsum deposit that the materials can support without experiencing structural degradation. The storage site is designed with a trapezoidal cross-section. The storage cell covers 45 ha, with a 1500 m long by 300 m wide heap at its base. A 2-m thick layer of compacted clay is installed to function as a natural sealing barrier, reducing the migration of contaminants and guaranteeing long-term stability. In this case study, the soils are presumed to be significantly over consolidated soils taking into account the OCR value (OCR >>1). The main concept is to estimate the height (H) of phosphogypsum so that $\sigma'_{v0} + \Delta\sigma'_v \leq \sigma'_c$. The initial effective vertical stress σ'_{v0}, is given by equation 5:

$$\sigma'_{v0} = \gamma' \cdot \frac{h}{2} \qquad (5)$$

where σ'_{v0} is effective vertical stress (kPa), γ' – saturated bulk density (Kn/m^3) and h – thickness of the clay barriers (m)

The stress Increment is calculated:

$$\Delta\sigma'_v = \sigma'_c - \sigma'_{v0} \qquad (6)$$

where $\Delta\sigma'_v$ is increment of effective stress (kPa), σ'_{v0} – effective vertical stress (kPa) and σ'_c – effective preconsolidation stress (kPa)

The maximum height (H) of phosphogypsum deposit is estimated according to the geotechnical design of Eurocode7 (EN 1997-1), is assessed as a function of saturated bulk density (16.5 kN/m^3) of PG (in extreme case of PG weight) by the following equation:

$$H = \frac{\Delta\sigma'_v}{16.5} \qquad (7)$$

where H is the maximum height of phosphogypsum (m) and $\Delta\sigma'_v$ – Increment of effective stress (kPa).

According to the numerical results, the maximum heights of phosphogypsum calculated for AG and EH are respectively 38 m and 57 m.

DISCUSSION

The present study highlights the structural alteration of clay materials upon exposure to phosphoric solution, as evidenced by changes across multiple geotechnical and mineralogical parameters. X-ray diffraction (XRD) analysis of AG (PS) and EH (PS) samples revealed the disappearance of the calcite peak in both soils following acid treatment, indicating dissolution of carbonate phases. This observation aligns with Mitchell (1993), noting that acidic environments readily degrade cementing agents such as calcium carbonate. Similarly, Imai *et al.* (2006) reported that leaching Osaka Bay clays with HCl resulted in the dissolution of calcium carbonate, subsequently disrupting interparticle carbonate bonding.

Consistent with these findings, modifications in the Atterberg limits reflect the direct influence of acidic solutions on soil consistency and mineralogical stability. Several studies have significantly advanced our understanding of how acidic environments affect soil behavior. Bowders and Daniel (1987) showed that montmorillonite-rich soils exposed to high concentrations of H^+ ions exhibit reduced diffuse double layer (DDL) thickness, thereby lowering the liquid limit (w_L). In contrast, Gratchev and Towhata (2011) observed an increase in w_L and plasticity index (I_P) under low pH conditions due to carbonate dissolution in acidic fluids. According to the previously mentioned studies on, the two different responses observed may be attributed to the distinct mineralogical compositions of the tested soils.

Shear strength and compressibility tests underscored divergent mechanical responses between the two clay types. EH soil demonstrated enhanced strength, whereas AG soil exhibited a decline in performance. These trends were corroborated by triaxial shear testing. According to the literature, acidic contamination can substantially influence the compressibility and strength of clay soils. Gratchev and Towhata (2011) reported increased compression indices in clay soils from Osaka and Ariake Bays when leached with acidic solutions, with Kawasaki mud showing the opposite trend, attributed to differences in mineralogy and soil structure. Similarly, Gajo and Maines (2007) attributed compressibility reduction in smectite/montmorillonite soils to diffuse double layer (DDL) collapse under acidic exposure. In contrast, Wang *et al.* (2024) revealed that moderate acidity (pH 3–5) can induce nano-scale silica cementation that contributes to improved soil strength.

A condition assessment was carried out on the phosphogypsum (PG) stockpiles in Aqaba, Jordan. The phosphate industry in Aqaba, located along the Red Sea, approximately 15 km south of the port, generates around 3 × 10^5 tons of phosphogypsum annually. Currently, the PG is dry-stacked in unlined valleys, forming stockpiles that can reach up to 200 m in height (Husein Malkawi *et al.*, 2022).

In comparison, the evaluation of AG and EH deposits revealed that the maximum heights they could sustain were 38 m and 57 m, respectively. Chaari (2013) examined PG stockpile stability in Skhira and estimated a maximum deposit height of approximately 60 m under dry disposal conditions. Nonetheless, challenges related to slope stability and settlement behavior were identified. These embankments rest on heterogeneous foundations comprising gypsous silt, clay loam, and sand (Geotechnical Engineering Research Unit, 2007). According to Bouassida (2012), stability assessments of the Sfax stockpile suggest that wet deposition may allow for heights exceeding 70 m, which, when reinforced with geotextile layers, could reach up to 100 m. In contrast, dry deposition without HDPE reinforcement cannot exceed 100 m without incurring significant settlements, lateral displacements, and deformation of the embankment profile.

Based on the acid treatment results, EH soil consistently demonstrated superior geotechnical performance compared to AG. These findings were validated through numerical simulations adhering to Eurocode 7 standards, which confirmed that EH can support a greater volume of PG waste, reinforcing its suitability as a mechanically resilient barrier material under chemically aggressive conditions.

CONCLUSIONS

This study systematically evaluated the influence of phosphogypsum waste on two Tunisian clay soils, Aleg (AG) and El Haria (EH), through a comprehensive suite of mineralogical, physicochemical and geotechnical analyses. The findings further assessed the feasibility of utilizing these soils as natural barrier materials in phosphogypsum storage sites. XRD results aligned with XRF profiles, confirming the presence of quartz, kaolinite, smectite, and carbonate minerals in the untreated soils. The contact with PS solution led to the dissolution of calcite, evidenced by the disappearance of its characteristic diffraction peak, consistent with the breakdown of interparticle carbonate bonds under acidic conditions. However, the consistency limits indicated divergent soil responses: AG exhibited increased liquid limit and plasticity index due to carbonate dissolution, which generated larger pore spaces and enhanced soil plasticity. In contrast, EH clay showed reductions in these parameters, attributable to diffuse double layer (DDL) collapse under elevated H^+ ion concentrations. Mechanical testing revealed further differentiation. In addition, the direct shear tests demonstrated the decrease of cohesion and internal friction angle for AG following exposure to acidic leachate. Conversely, EH sample displayed a substantial increase in cohesion, suggesting improved structural resistance under similar chemical conditions. In addition, the permeability tests showed a reduction in permeability in both soils, which can be explained by the precipitation of certain compounds due to the dissolution of carbonates.

These trends were corroborated by numerical simulations, which estimated the maximum phosphogypsum heights supportable by AG and EH as 38 m and 57 m, respectively. Integrating geotechnical, mineralogical, and permeability data, the results conclusively demonstrate that EH possesses superior stability and mechanical resilience under chemically aggressive conditions. Accordingly, EH is identified as the more suitable candidate for use as a natural sealing barrier in PG disposal facilities.

This work highlighted the effectiveness use of Tunisian clay in PG discharge management and long-term monitoring of in situ barrier performance under real field conditions is recommended to validate laboratory predictions and ensure containment efficiency.

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