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Water vapor diffusion: A control factor in the selection of environmentally friendly waste sites in Mosul city, Iraq

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Abstract

Water vapour diffusion through porous media is an important part of water flux in the unsaturated zone, where fluid transfer is principally due to vapour diffusion. In this research, the suitability of Limestone, Gypsum stones and unsaturated plastic and non-plastic soils of Mosul city Iraq, for usage as barriers surrounding bunkers of chemicals and radioactive wastes were assessed in order to protect the environment. Laboratory experiments were conducted to investigate the water vapour transfer for the selected earth materials. Wetting/drying and freezing/thawing cycles were adopted to evaluate the water transfer properties of weathered stones. Saturated salt solutions in a special diffusion experiment were used to measure both the coefficient of permeability, and diffusivity of water vapour in the tested samples. The results were obtained using Darcy's and Fick's laws of water vapour transfer. X-ray Diffraction (XRD), optical Microscopic (OM) and Mercury Intrusion Porosimetry (MIP) tests were further performed to examine the mineralogical and microstructural characteristics of the materials. The results indicate a reduction of diffusion coefficient with an increase in relative humidity; water vapour diffusion decreases with the decrement in suction pressure, also there is a close relationship between total porosity and the diffusion coefficient of the tested samples. The results distinguished the variance in diffusion behaviour of plastic and non-plastic soils based on the difference in their microstructure fabrics. Further, the amount of hydraulic conductivity and diffusion coefficient was higher in limestone than in gypsum stone due to bigger pore size distribution of the limestone. It was equally confirmed that weathering factors have noticeable effects on the permeability and diffusion behaviour of the stones. In essence, the plasticity of soil, the type and degree of weathering of rocks are important factors to be considered in the choice of location for chemical and/or radioactive wastes sites.

Keywords: Diffusion, Porous media, Limestone, Gypsum, Plastic soil, Non-plastic soil

Nomenclature

$\frac{d}{dt}\ C_A$	The rate of change in concentration of compound	L	Thickness of the sample
V_D	Diffusion coefficient	ΔH	Suction gradient in terms of equivalent height
del^2	Laplacian operator of C_A	ρ_w	Density of water
x	Distance	$CaCO_3$	Calcite
S	Suction	$CaSO_4.2H_2O$	Gypsum
V_D	Water vapour diffusivity	$CaSO_4.0.5H_2O$	Bassanite
K_{wv}	Water vapour permeability	$Ca\ (OH)_2$	Calcium Hydroxide (Portlandite)
W	Water content	SiO_2	Silicon(iv)Oxide (Silica)
Q	Water vapour hydraulic discharge	$NaCl$	Sodium Chloride (Halite)
A	Surface area		

1. Introduction

Water vapour movement is an important part of the total water flux and energy balance in the vadose zone for many agricultural and engineering applications in arid and semiarid regions [1]. Chemical diffusion is the predominant transport medium for radioactive or hazardous waste in porous media. The major aim in utilizing engineered barriers in radioactive or hazardous waste applications is to stop or minimise vapour diffusion transport of hazardous chemical contaminants [2]. Understanding surface energy, water vapour, and heat movement in the porous media is critical for the performance evaluation of engineered surface covers for waste containment in landfills and other engineering applications. Water vapour diffusing through porous soils and stones can be absorbed for both long and short terms. Long-term absorption allows more water to enter than exit the soil, as reflected in the concentration gradient. Short-term absorption leads to an apparent reduction in the diffusion rate, as reflected in the diffusion coefficient [3, 4].

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Structures constructed on unsaturated porous media are damaged due to the movement of the media underneath. The movement is basically due to the flow of moisture through soil pores from the interior to outer layers; as a result of moisture changes, the strength of soil is decreased and this often causes failure of buildings and embankment slopes [5]. Hence, it is very important to study the diffusion properties of unsaturated materials. The study of diffusion properties requires the determination of the diffusion coefficient [4, 6-9]. Vapour diffusivity is the product of vapour permeability and suction water gradient. Hence, the knowledge of the water retention curve (WRC) is required in the modelling of both mechanical and hydraulic behaviours of unsaturated porous material [4, 7].

In unsaturated soils, there is coexistence of liquid water, water vapour and air, the flow of these fluids is due to thermo-hydro-mechanical loading in different nature [8]. The vapour flow is described by the Fick's diffusion law, contrary to the air and liquid water flow, which can be satisfactorily described by Darcy's advection law when the fluid pressure is within a specific value [3, 6, 7, 9]. The flow of these three fluids within an unsaturated soil are interconnected through suction or degree of saturation. To describe satisfactorily this coupling in laboratory, it is necessary to determine their diffusivity variations as a function of the suction pressure [10]. Prediction of the moisture flux boundary condition with respect to water flow across the soil surface boundary is essential for many problems in geotechnical engineering, including the design of soil cover systems for the long-term closure of hazardous-waste sites, saturated-unsaturated ground water flow modeling, fluid flow through stone media, and the prediction of heave for shallow foundation on expansive soils [11-13].

The fundamental mechanisms of air/water vapour diffusion in rock and construction materials have been previously studied [14-18]. Bartelt-Hunt and Smith [19] mentioned that the transportation of organic vapour in the unsaturated vadose zone is important in understanding the distribution of organic contaminants in the subsurface environments and their exchange between the subsurface environment and the atmosphere. Variables that influence air/water vapour diffusion such as diffusion coefficient, porosity, pore structure, hydraulic conductivity, dry density and sorption [14-16, 20] have been investigated. Previous studies have shown gaseous diffusion to be an important mechanism in the transport of vapours through the porous media [12, 13, 21-23].

Benavente and Pla [24] investigated the characteristics of CO_2 diffusion for a representative range of porous building stones to establish the effect of the water content in gaseous diffusion coefficient. The results showed that pore water condensation reduces both connected porosity and pore size. The pore size was identified as the conclusive parameter within the transport coefficients, which greatly affects both the tortuosity factor of the CO_2 gaseous diffusion and the slip parameter of the Klinkenberg's model for gas permeability coefficient. A new methodology to measure gas diffusion with a laboratory device that works under different hygrometric conditions was proposed. Beck et al. [7] investigated the water transfer properties through pores stone building material. A reduction in both suction pressure and diffusion coefficient with an increase in relative humidity was noticed.

Chelsea et al. [2] quantify the matrix diffusion of iodine through saturated volcanic rock with particular attention paid to the redox environment, whereas iodate diffusion was studied through welded tuff. Gens et al. [25] examined the interaction between host rock and a clay-based engineered barrier in the context of deep underground disposal of high-level radioactive waste. It was concluded that the interaction between clay barrier and host medium exhibits a high degree of complexity.

Furthermore, Kozaki et al. [26] studied the particle size of bentonite and its effect on the diffusion behavior of radionuclides in compacted bentonite. The bentonite was characterized by BET and EGME methods. The apparent and effective diffusion coefficients of tritiated water (HTO)/Cl^- ions/and CS^+ ions in compacted bentonite was also determined. Montes et al. [27] simulate the chemical transformations (geochemical and cation exchange reactions) coupled with diffusion of chemical elements into the engineered barrier under repository conditions. Also, a simplified method to estimate the swelling capacity evolution by a volume balance in the fluid-saturated engineered barrier was applied. Shackelford and Moore [28] published a review of literature with the goal of discerning the types of diffusion coefficients with respect to diffusion of radionuclides through engineered containment barriers.

Both unsaturated plastic and non-plastic soils are the predominant earth materials in Mosul city, Iraq. Their plastic properties are representative plasticity conditions of the soils in the city; as Limestone and Gypsum stones are the major stone units used in the construction of both historical and modern buildings. To determine the suitability of these locally available earth materials in Mosul city which was to be used as barriers around the containers of chemical and/or radioactive wastes, deportment bunkers etc., a series of tests on characterisation, vapour diffusion and permeability through these earth materials were executed. This paper presents the multi-scale tests, the results and their elucidations on the desirability for the specified use.

2. Materials and methods

2.1 Stone and soil materials

Two type of stones used in this study are Limestone and Gypsum stones extracted from Eski-Mosul quarry to the north of Mosul city, Iraq (i.e. location coordinates: Latitude 36º30̓49.88 N, Longitude 42º44̓6.35 E) at depth of about (2m), see Figure 1. These stones could be considered the predominant stones used in the historical and modern stone buildings in Mosul city, Iraq. In addition, two types of soil (plastic (P) from Al-Arabi which is location coordinates: Latitude 36o30'49.88 N, Longitude 42o44'6.35 E) and non-plastic (NP) soils from Al-Tyran which location coordinates: Latitude 36º19′31.34″ N, Longitude 43º8′24.85″ E)) (undisturbed conditions) extracted from Al-Araby and Al-Tayaran districts respectively at depth of about (3m) , were also used in this study, since their plastic properties could be consider the average plasticity conditions of the soils in Mosul city, Iraq.

2.2 Characterization methods

2.2.1 Mineralogical characterization and thermo gravimetric analysis (TGA)

X-ray diffraction (XRD) patterns were obtained on powders of stone and soil using Philips apparatus with the Kα line of copper ($\lambda Cu = 1.5406$ Å) with 2θ from 1.5° to 60°. To compare the obtained patterns, the main quartz reflection is used to scale the X-ray pattern intensities for all tested samples, three samples for each type were used. Thermo Gravimetric Analysis (TGA) test was adopted to obtain the amount of clay and non-clay minerals. In TGA test, the mass loss of a given sample was recorded under controlled temperature. The apparatus used is a Setaram TG-DTG 92-16 electro-balance operating within the 20-1000°C range, with a heating rate of 100°C per hour and under argon atmosphere. Finally, the results have been presented as a group of curves expressing the constitutes materials of the samples in percentages manner. Furthermore, images for the structure of the stone samples in both types

Limestone and Gypsum stones (fresh and weathered conditions) were snapped using an optical Microscope named Leica DMIRE2 microscope.

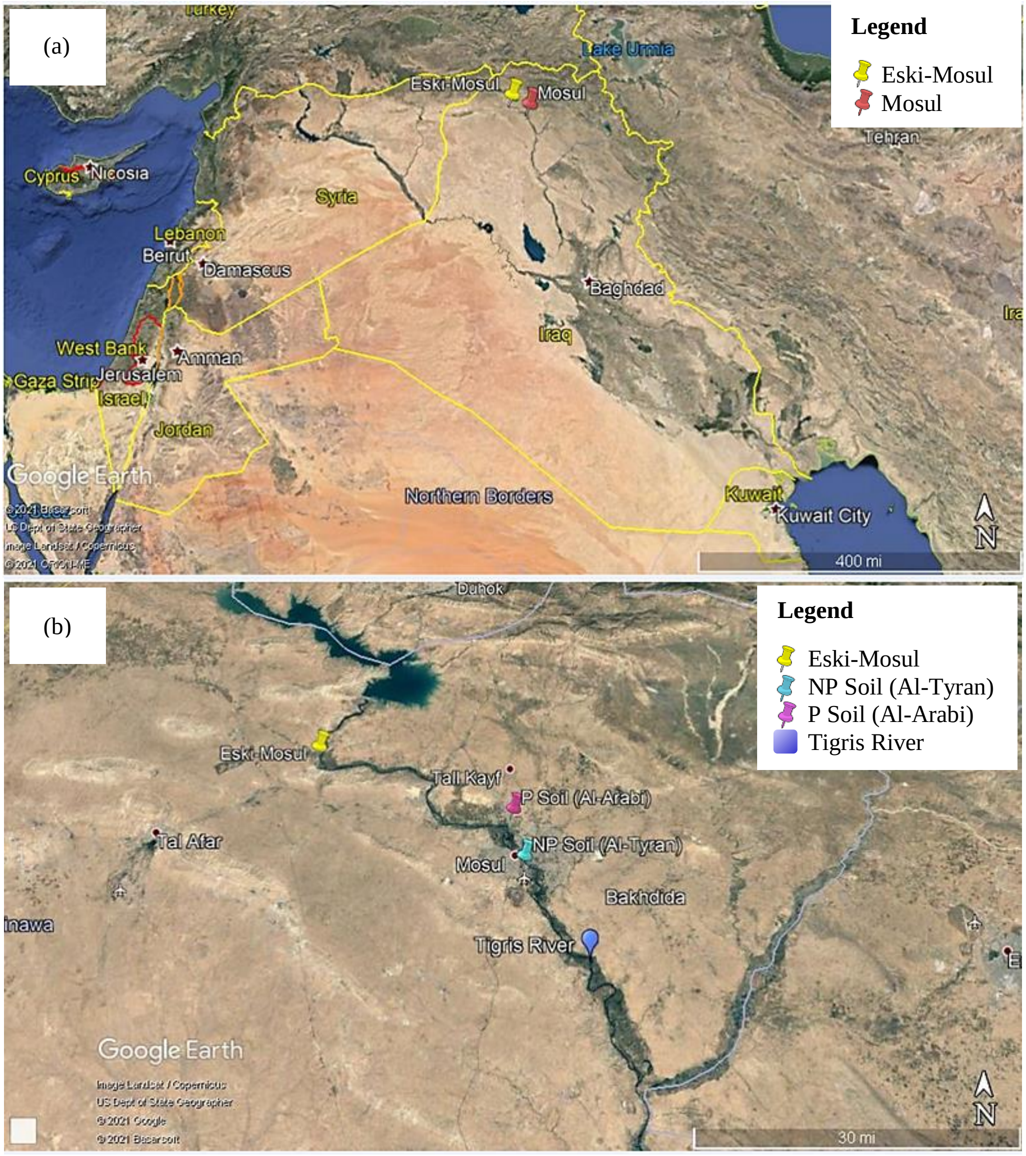


Figure 1 Map of (a) Iraq, and (b) Mosul, Iraq (focused sampling points of Eski-Mosul and (P)-(NP) soils)

2.2.2 Porosity tests

Mercury Intrusion Porosimetry (MIP) technique was used to measure porosimetric characteristics of the samples. The measurements were performed on both stones and soils samples by using Poresizer 9320 porosimeter apparatus, by applying pressure up to 210 MPa and continuously monitoring the volume of mercury in the pores of the tested samples, and the diameter of pores was estimated using Young-Laplace equation. Samples of about 1 cm^3 were dried at 105°C and 70°C for 24 hours for both Limestone and Gypsum stones and then tested. Also (P) and (NP) undisturbed soil samples were dried using the nitrogen gas in liquid phase at a temperature of (-198^{o}C), both the solid skeleton and the water inside the pores of the soil samples were subsequently frozen at this temperature. Then, the samples were transferred to a special machine (i.e. lyophilisateur α 1-2 plateaux M91276/bioblock scientific-France) to dry the samples by vacuum pressure by transforming the frozen pore water from solid phase to gaseous phase without going through the liquid phase. This operation retains the original pore size of soil samples. Three samples for each material type were employed in the test

2.2.3 Water retention curves (WRC)

The WRC shows the relation between the percentage of moisture content, degree of saturation, percentages of relative humidity of the soil and the matric suction under equilibrium conditions [29]. The WRC consists of three parts: (a) Salt Solutions: This technique is used to study the water retention curve in the range of suction 2.7 MPa . (b) Osmotic Solution Method: This technique is used to study the water retention curve in the range of suction values between 0.1 MPa and 1.5 MPa. (c) Tensometric Plates: This technique is used to study the water retention curve in the range of suction values between 0.001 to 0.01 MPa. Remolded soil samples, 63.5 mm in diameter and 19.05mm in height, prepared at maximum dry density and optimum moisture content conditions of modified proctor compaction test through static compaction at a rate of 1.27 mm/sec were used. The remoulded soil samples and 1 cm^3 limestone stone cubes were oven dried at 105°C for 24 hours before conducting the test, while the 1 cm^3 gypsum stone cubes were dried at 70°C for 24 hours before conducting the test. Two sample seats for each material type have been used in this test. In this study the wetting water retention curve have been obtained

Table 1 The saturated salt solutions used and their respective relative humidity (RH)

Saturated salt solution for RH2	Cell1, RH1%	Cell2, RH2%	Equivalent Suction ψ (MPa) @ 20°C
LiCl	32	11	298
$MgCl_2$	44	32	154
$K_2CO_3.2H_2O$	56	44	111
$Ca(NO_3)_2.4H_2O$	66	56	78
$NaNO_2$	76	66	56
NaCl	86	76	37
KCl	98* (i.e. $CaSO_4.5H_2O$)	86	20

*$CaSO_4.5H_2O$ gives a relative humidity= 98%, (ψ=-135.022In (RH) [29].

2.2.4 Vapour diffusion test

The size of the stone and soil samples used in diffusion test was the same used for the determination of water retention curve. The apparatus used for diffusion test was similar to those adopted by other earlier researchers [7, 30], designed and manufactured in soil laboratory of Mosul University, Iraq; and modified to be suitable for stone-soil samples (Figure 2). This modification allows for weighing the amount of water transfer as vapour through the soil and stone media without opening the cell. The apparatus consists of two cells with two containers of different saturated salt solutions separated by fiber ring in which the sample was fixed. Stone and soil samples were inserted in the diffusion device, the saturated salt solution containers were quickly weighed, and the cell was rapidly grouped. All tests were carried out in a controlled room temperature (20 ± 1°C). The containers were subsequently weighed every 48 hours for the first 2 weeks, then twice a week for another 8 weeks. The diffusion of water vapour continues till an equilibrium state was reached. This procedure was conducted by using seven apparatuses with different saturated solutions, thus allowing the construction of the complete water vapour diffusivity curve for the tested relative humidity (RH), while equivalent suction (ψ) was calculated using Kelvin equation (ψ=-135.022In(RH) [29] (Table 1). Three sets of samples for each material type were used in this test.

The principle of diffusion experiment was implemented by setting up a concentration gradient across stone and soil samples. Special attentions were taken to ensure the absence of hydraulic gradient in the set-up, the entire water transfer materialized solely by a diffusive mechanism (Figure 2). It is important to note that the initial humidity content of the tested samples restrains the free diffusivity of water vapour through the sample (i.e., initial humidity content of the tested samples is equal to the relative humidity of cell2) [1, 31]. Hence, it is only the linear segment of the curve, where the system is in a steady state, that was utilized to calculate the flow rate (Q). The flow rate (Q) was obtained by determining the gradient of each slope, i.e., the volume of water taken up during an elapsed time [7, 32]. Darcy's equation was used along with other known variables to calculate the permeability (Kwv) of stone and soil samples. The coefficients of water vapour permeability for the samples were employed to determine the vapour diffusivity.

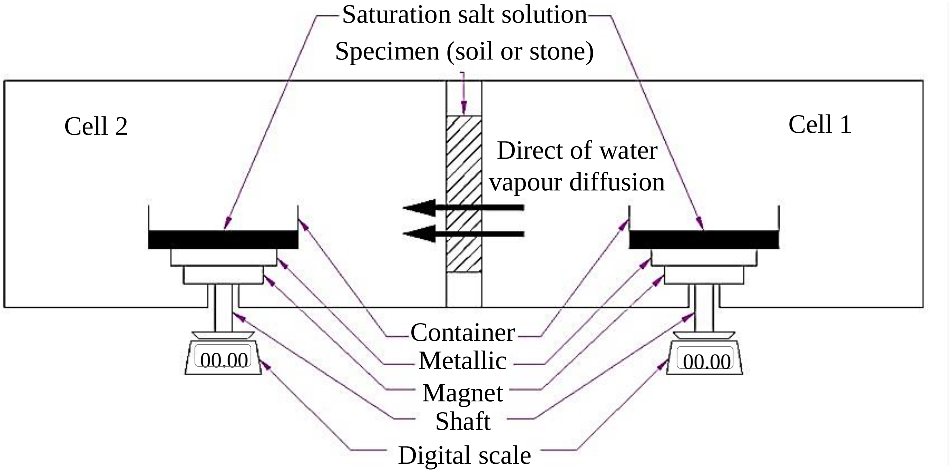


Figure 2 Water vapour diffusion apparatus

2.2.5 Diffusion theory

The diffusion is described by Fick s second law [18, 29]

$$\frac{d}{dt}C_A = V_D(del^2C_A) \tag{1}$$

where: $\frac{d}{dt}C_A$ is the rate of change in concentration of compound A,V_D the diffusion coefficient , and del^2 the laplacian operator of C_A (x, y and z directions)

Water vapour diffusion occurs because of suction gradient and diffusion coefficient depends upon the water content of the sample and the diffusion is carried out through the sample height due to suction difference applied in both sides of the sample. Hence, the above equation can be written as:

$$\frac{d}{dt}S = V_D \frac{d}{dx}\left(\frac{d}{dx}S\right) \tag{2}$$

Where x=distance moved by water front, t=time taken for water front movement , S=suction, and V_D=water vapour diffusivity.

For unsaturated materials, the equation becomes non-linear. The formula for the calculation of the water vapour diffusivity(V_D) is:

$$V_D = K_{WV}\left(\frac{d}{dw}S\right) \tag{3}$$

Where; K_{wv}=water vapour permeability (cm/sec.) as a function of the water content., S=suction (cm)(equivalent head of water), and W=water content (%). The flow rate was then introduced to Darcy s equation along with the other known variables to calculate the permeability:

$$K_{WV} = \frac{Q}{A\left(\frac{\Delta H}{L}\right)} \tag{4}$$

Where: Q=water vapour hydraulic discharge (flow rate), A=surface area of the tested sample, L=thickness of the sample, ΔH=suction gradient in terms of equivalent height of water (suction=H_{water}X γ_{water}), γ_{water}=$g\rho_w$ with ρ_w being the density of water ($Kg.cm^{-3}$) and g the gravitational acceleration [18, 29].

2.2.6 Effect of weathering factors on water vapour diffusion of stone samples

The temperature gradients created in stone by the heating effect of the sun ray may lead to surface decay if it is repeated often enough through a heating-cooling process. Wetting and drying is an inevitable part of the heating-cooling process, where the stone structure expands when wetted and contract on drying leading to what is known as fatigue failure [13, 21]. The Freezing-Thawing process damages only the wet parts of the stone building. When water freezes, a volumetric expansion of about 9% of the original volume will occur through the transformation of water into ice, and in turn exert a pressure on the adjacent materials. The degree of damage by freezing depends on the degree of saturation of the stone, where the partially saturated stone can resist breakage, while fully saturated stone, yields to freezing action regardless of its. strength [17, 33, 34].

2.2.6.1 Wetting-drying test

Limestone and gypsum stone samples of 63.5 mm diameter and 19.05 mm height were subjected to 30 cycles of wetting and drying in water. The samples were immersed in water for 12 hours in a closed container placed at room temperature, and they were subsequently dried for 12 hours at 70°C for one complete cycle, to obtain the variation of water vapour transformation [35]. Three samples per cycle of each stone type were used.

2.2.6.2 Freezing-thawing test

The stone samples were subjected to 20 cycles of freezing and thawing by immersion according to ASTM D5312 [36]. For one complete cycle, the samples were subjected to thawing at 40°C for a period of 8 hours and then the freezing state at a temperature of-15°C for a period of 16 hours.

2.3 Statistical analysis

Correlation coefficient analysis for soils and stones were used to explore the relationship between water vapour permeability (cm/sec) and Suction (MPa), in addition to correlation analysis between Diffusion Coefficient (cm/sec) and Suction (MPa) for soils and stones in Mosul city. Also One-way ANOVA was used for Diffusion Coefficients and water vapour permeability for soils and stones. The statistical analyses were performed utilizing SPSS data analysis software ver. 22.0 (IBM, Armonk, NY, USA).

3. Results and discussion

Figure 3 shows the XRD analysis of limestone, gypsum stones, plastic (P) and non-plastic (NP) soils. The analysis shows that the major mineralogical compositions of limestone are calcite ($CaCO_3$) and silica (SiO_2) in the form of quartz, with $CaCO_3$, the DTG figure shows that 94% of limestone are calcite ($CaCO_3$) and silica (SiO_2) in the form of quartz, with $CaCO_3$). For gypsum stone samples, the major mineralogical compositions are gypsum ($CaSO_4.2H_2O$), bassanite ($CaSO_4.0.5H_2O$), portlandit ($Ca(OH)_2$), and silica (SiO_2) in the form of quartz, with gypsum and calcite contents of about 89.34% and 1.119%, respectively according to the DTG figure. Both stones are pure stones (i.e. predominantly mineralogical compositions are: Calcite ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$) for limestone and gypsum stone respectively), with some clay and siliceous impurities. Table 2 shows the properties of the stones obtained from the MIP test, since the high porosity, open structure media is more prevalence in limestone than gypsum stone. Table 3 summarizes the properties of P and NP soils, both soils are approximately identical in their non-clay mineral compositions (i.e. Quartz (SiO_2), Calcite ($CaCO_3$), and Halite (NaCl)), but differ in their plasticity. The noticeable presence of monmorillonite mineral in the mineralogical composition of (P) soil, gained this soil more plastic consistency as compared with (NP) soil, which contain higher amount of illite and kaolinite minerals, with no presence of montmorillonite mineral (Figure 3) [37].

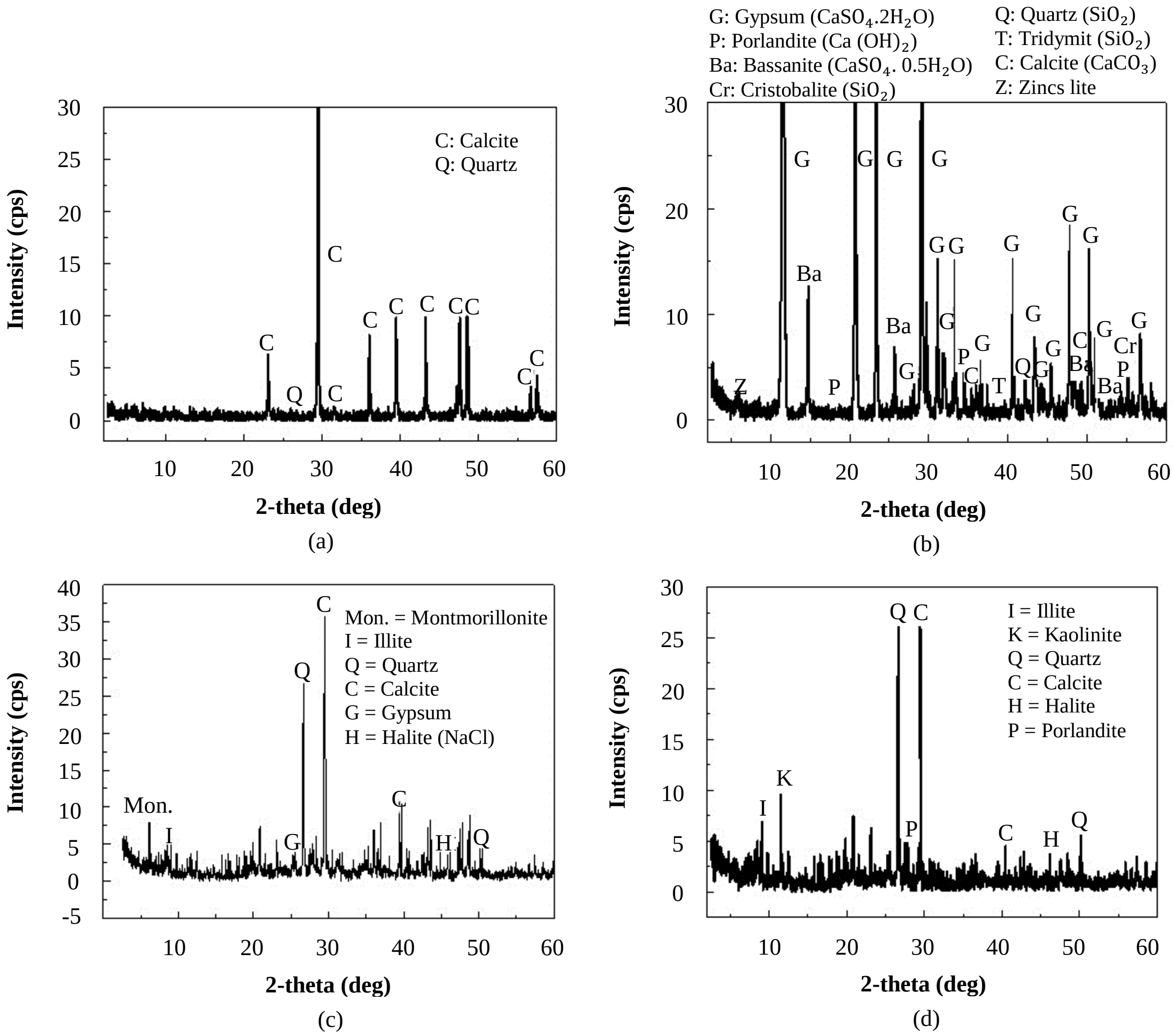


Figure 3 X-ray diffraction analysis of: (a) limestone (b) gypsum stone (c) plastic soil (d) non-plastic soil

Table 2 Properties of stone samples

Properties	unit	limestone	Gypsum stone
Bulk density	g/cm^3	2.04	2.25
Skeletal density (ρs)	g/cm^3	2.66	2.28
Porosity by mercury intrusion	%	21	1.2
*Gs=(ρs/ρw)	……	2.66	2.28

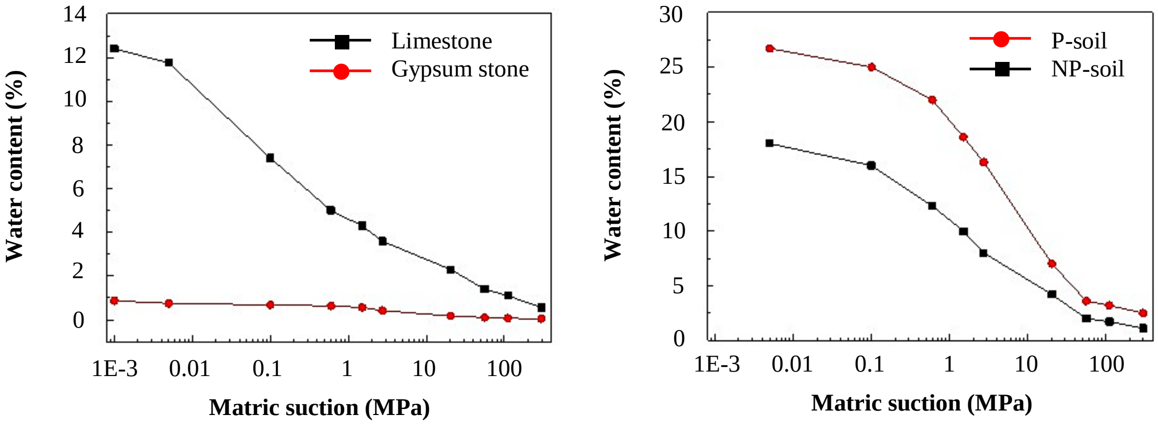
*ρw=Water density=1 g/cm^3

Table 3 Properties of soil samples.

Properties	Unit	Plastic soil	Non Plastic soil
G$_s$[38]	…..	2.72	2.65
LL [39]	%	52	24
PI [40]	%	28	NP
Sand [40]	%	12	45
Silt [40]	%	45	46
Clay [40]	%	43	9
Maximum Dry Density	g/cm^3	1.71	1.8
Optimum Moisture content	%	16.1	9.5
Bulk Density [41]	g/cm^3	1.68	1.58
Skeletal density [41]	g/cm^3	2.68	2.61
Porosity	%	28.2	38.4
USCS Classification	…..	CH	ML

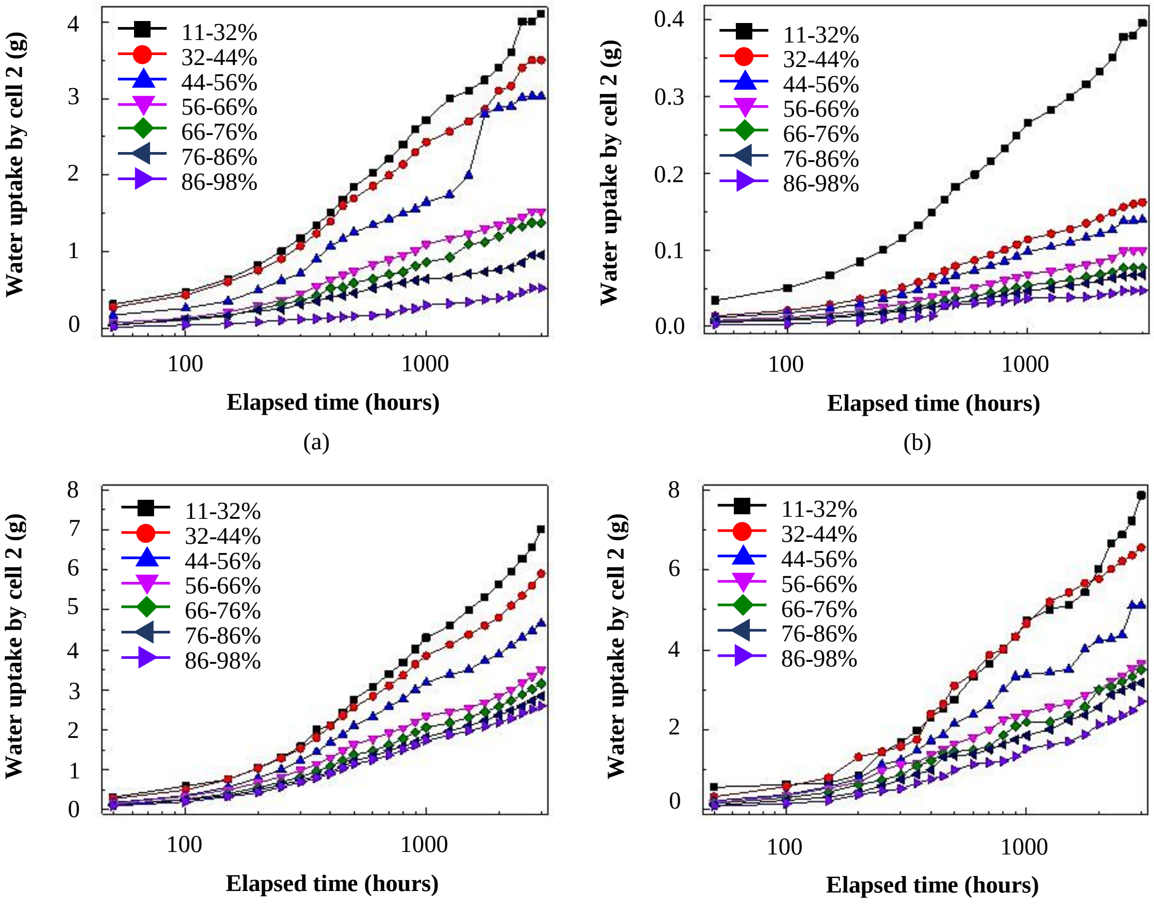
Figure 4 shows the ability of stone and soil materials to retain water molecules within their structure (i.e. wetting water retention curve), in terms of water content (%) and matric suction (MPa), due to the hysteretic effect of water filling in and/or draining out the pores, two types of the water retention curves can be distinguished: wetting curve (or desorption curve when the samples is in initial dry state) and drying curve (or adsorption curve when the samples is in saturated initial state) [32]. The water adsorption increases as suction decreases for all the samples, the limestone samples have higher water retention than the gypsum stone; this can be attributed to their structures having larger number of pores than the gypsum samples [6, 8]. Further, the values of suction at equal water content for the NP soil is lower than that of the P soil; this behaviour is due to the dominance of montmorillonite minerals in P soil compared to the kaolinite in NP soil, the montmorillonite mineral has a higher specific surface area than the kaolinite mineral [42].

The weight changes of cell (2) due to water uptake from the samples within elapsed time, in hour is represented by Figure 5. Figures 6 and 7 respectively, illustrate the vapour permeability and diffusion coefficients of stone and soil samples used in terms of matric suction (MPa). The results show that as the suction decreases, the permeability and diffusivity of water vapour decrease too, conversely, as the permeability and diffusivity of water vapour increase, the suction increases [43]. This behaviour is due to initial moisture content of the sample in the stone samples, i.e., the presence of water molecules within stone pores [15, 18]. However, for the soil samples, it is probably due to water transfer process and the amount of porosity accessible [6, 31, 43].



(a) (b)

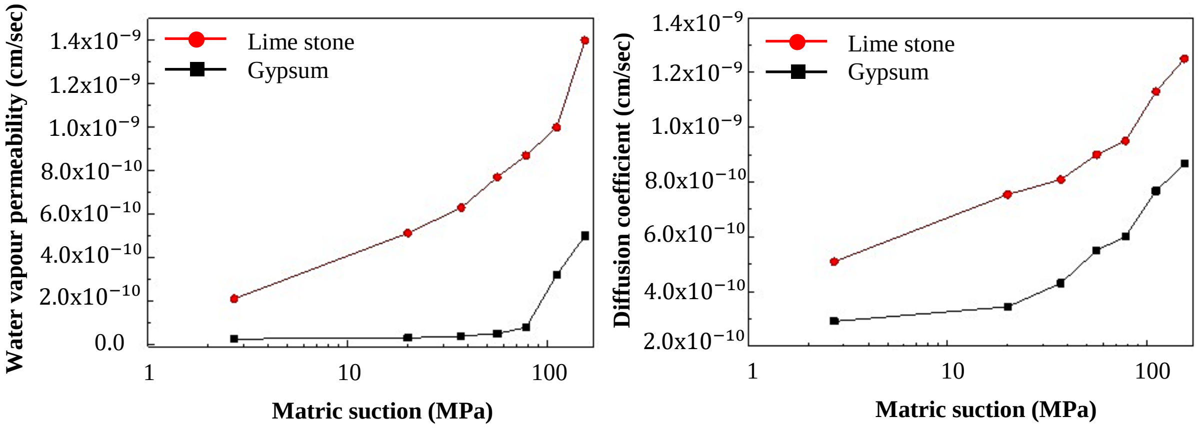
Figure 4 Water retention curve of (a) limestone and gypsum stone (b) plastic and non-plastic soils



(a) (b)

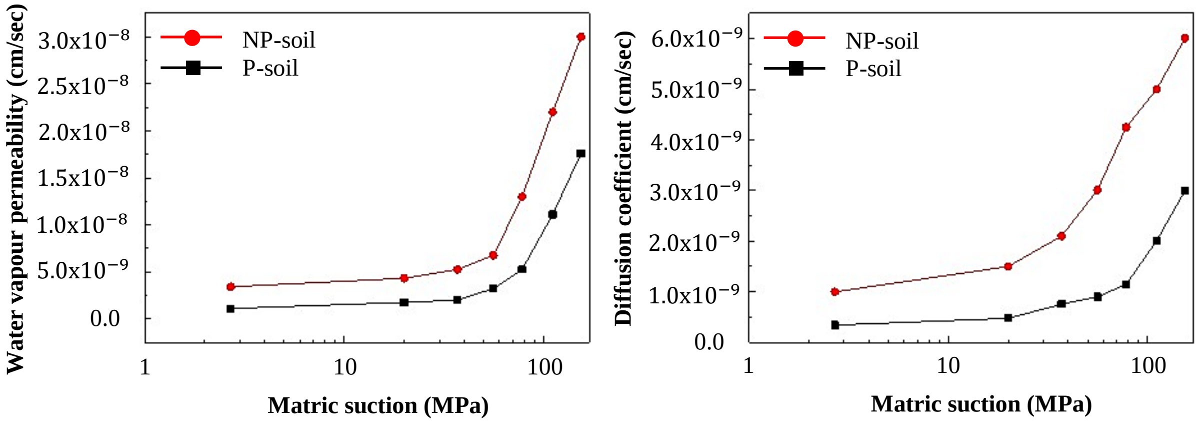
(c) (d)

Figure 5 Water uptake by cell (2) for: (a) limestone, (b) gypsum stone, (c) plastic soil, (d) non-plastic soil.



(a) (b)

Figure 6 (a) Water vapour permeability and (b) Diffusion coefficient of stones used



(a) (b)

Figure 7 (a) Water vapour permeability and (b)Diffusion coefficient of P and NP soils

There are statistically significant differences in the water vapour permeability due to the variable type of soil and rocks used. To examine this question, a one-way ANOVA test was conducted to discover whether there are statistically significant differences in the water vapour permeability in the samples under study according to the change of soils and rocks. Table 4 shows the test results and statistical significance.

Table 4 Results of the one-way ANOVA test according to the water vapour permeability of soils and stones used

Groups	Mean	Std. Deviation	F	Sig.	Statistical function
P-soil	1.21E-008	1.03E-008	6.055	0.003	Statistically significant
NP-soil	6.01E-009	6.15E-009			
Gypsum	1.49E-010	1.87E-010			
limestone	7.70E-010	3.78E-010			

Table 4 shows the results of the one-way ANOVA analysis, and from it, we conclude that there are statistically significant differences in the water vapour permeability of the rocks and soils used, where the (F) values reach to 6.055 with statistically significant 0.003 less than 0.05. Table 4 also shows the high value of the Means water vapour permeability of soils especially P-soil from the stones. Where Means value of water vapour permeability of P-soil were found to be 1.21E-008 from 21 samples test. To find out the reason for the differences, the Multiple Comparisons were tested (Tukey). And figure that explain the reason and what the statistical function differences

Table 5 Result tested multiple comparisons (Tukey) for water vapour permeability of soils and stones used

Groups	Mean Difference	Sig.	Statistical function
P-soil ----NP-soil	6.10E-009	0.251	Not statistically significant
P-soil ----Gypsum	1.20E-008	0.005	Statistically significant
P-soil ----limestone	1.13E-008	0.008	Statistically significant
NP-soil ---- Gypsum	5.86E-009	0.283	Not statistically significant
NP-soil ---- limestone	5.24E-009	0.377	Not statistically significant
limestone ----Gypsum	6.22E-010	0.997	Not statistically significant

*The mean difference is significant at the 0.05 level.

It is clear to us from Table 5 that the reason for the statistically significant differences in the for water vapour permeability in the soils and rocks used in the study is due to the difference between P-soil and Gypsum with Mean Difference is 1.20E-008 about P-soil and limestone with Mean Difference is 1.13E-008, where the significant values of P-soil and Gypsum, and P-soil and limestone are found to be 0.005, and 0.008 respectively which are less than 0.05.while Mean Difference for P-soil and NP-soil, NP-soil and Gypsum, NP-soil and limestone, and limestone and Gypsum, they were not statistically significant and the significant values are 0.251, 0.283,0.377, and 0.997 respectively which are more than 0.05.

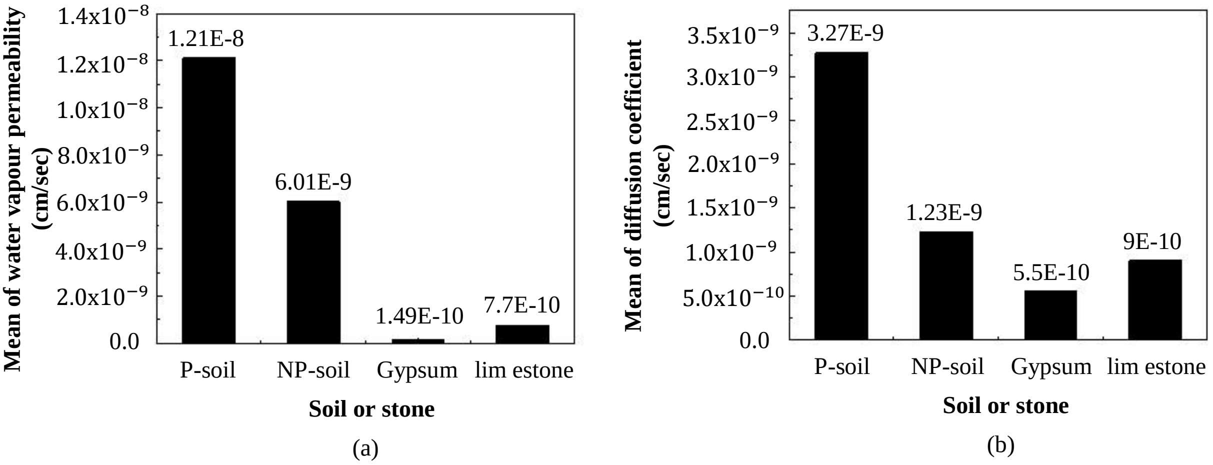


Figure 8 Shows the mean of (a) water vapour permeability, and (b) diffusion coefficient for soils and stones

According to the previous results from Tables 4 and 5 and Figure 8, the research hypothesis is accepted, which states that there are statistically significant differences in the water vapour permeability, which are attributed to the different composition of the soil and rocks used, in favor of NP-soil.

Table 6 shows the correlation analysis between water vapour permeability (cm/sec) and suction (MPa) for soils and stones. According to Table 6, the correlation coefficients analysis shows significant positive correlation between water vapour permeability with suction for all soils and stones. And the very strong correlation is for limestone (R=0.98) for suction, which confirms the results of experimental work also.

Table 6 Correlation analysis between water vapour permeability (cm/sec) and suction (MPa) for soils and stones

	Non-plastic	**Plastic**	**Gypsum**	**limestone**
Suction (MPa)	0.975	0.963	0.927	0.980

There are statistically significant differences in the diffusion coefficient due to the variable type of soil and rocks used. To examine this question, a one-way ANOVA test was conducted to discover whether there are statistically significant differences in the diffusion coefficient in the samples under study according to the change of soils and rocks. Table 7 shows the test results and statistical significance.

Table 7 Results of the one-way ANOVA test according to diffusion coefficient of soils and stones used

Groups	**Mean**	**Std. Deviation**	**F**	**Sig**	**Statistical function**
P-soil	3.27E-009	1.88E-009	9.15	0.0003	Statistically significant
NP-soil	1.23E-009	9.52E-010			
Gypsum	5.50E-010	2.13E-010			
limestone	9.00E-010	2.45E-010			

Table 7 shows the results of the one-way ANOVA analysis, and from it, we conclude that there are statistically significant differences in the diffusion coefficient of the rocks and soils used, where the (F) values reach to 9.15 with statistically significant 0.0003 less than 0.05.

Table 7 also shows the high value of the Means diffusion coefficient of soils especially NP-soil from the stones. Where Means value of diffusion coefficient of NP-soil were found to be 1.23E-009 from 21 samples test. To find out the reason for the differences, the Multiple Comparisons were tested (Tukey). And figure that explain the reason and what the statistical function differences**.**

Table 8 Result tested multiple comparisons (Tukey) for diffusion coefficient

Groups	**Mean difference**	**Sig.**	**Statistical function**
NP-soil ----P-soil	2.03E-009	0.008	Statistically significant
Gypsum ----P-soil	2.72E-009	0.0004	Statistically significant
limestone ----P-soil	2.37E-009	0.002	Statistically significant
Gypsum ---- NP-soil	6.83E-010	0.633	Not statistically significant
limestone ---- NP-soil	3.33E-010	0.936	Not statistically significant
Gypsum ---- limestone	3.50E-010	0.926	Not statistically significant

*The mean difference is significant at the 0.05 level.

It is clear from Table 8 that the reason for the statistically significant differences in the diffusion coefficient in the soils and rocks used in the study is the difference between P-soil and NP-soil with Mean Difference is 2.03E-009 about P-soil and Gypsum with Mean Difference is 2.72E-009 while P-soil and limestone with Mean Difference is 2.37E-009, where the significant values of P-soil and NP-soil, P-soil and Gypsum, and P-soil and limestone are found to be 0.008, 0.0004, and 0.002 respectively which is less than 0.05.while Mean Difference for NP-soil and Gypsum, NP-soil and limestone, and limestone and Gypsum, were not statistically significant and the significant values are 0.633, 0.936, and 0.926 respectively more than 0.05.

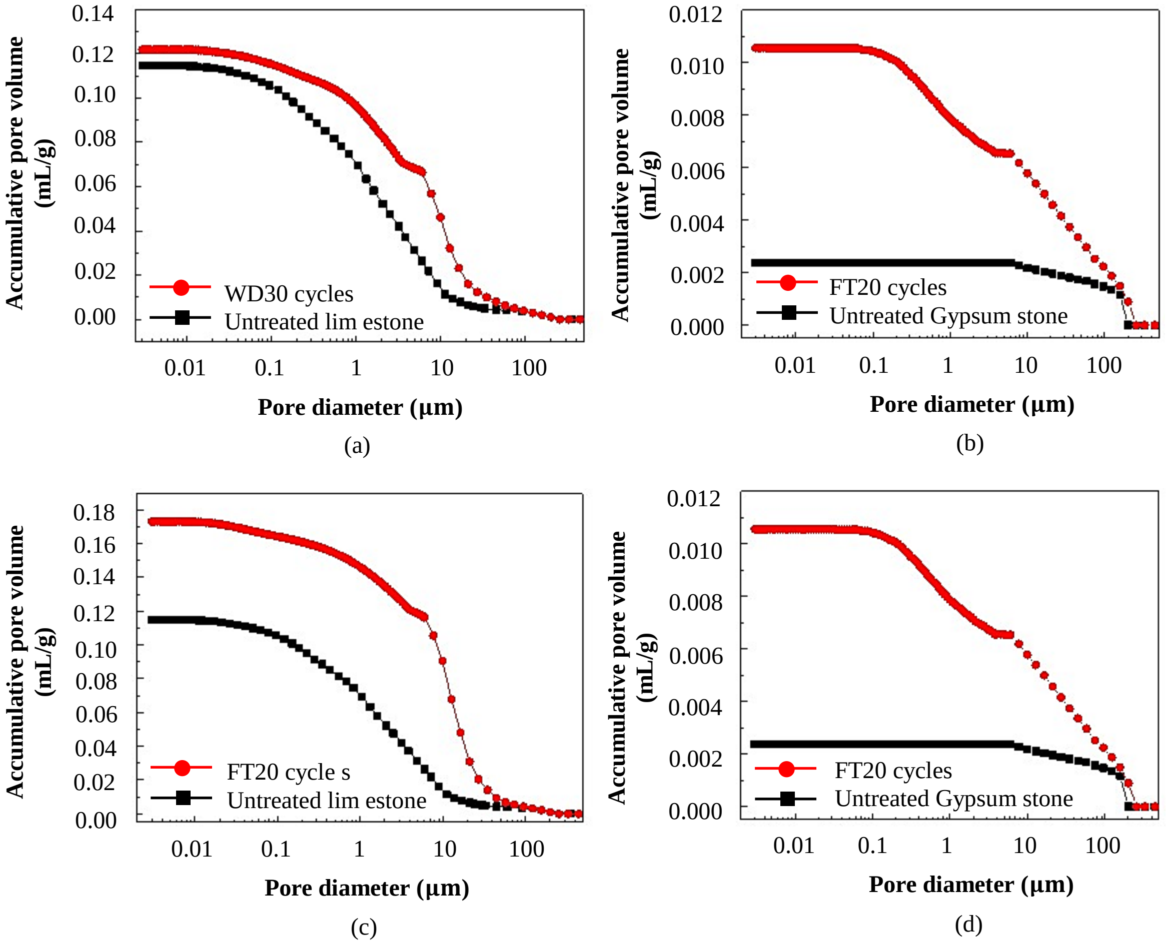
According to the previous results from Tables 7 and 8 and Figure 8, the research hypothesis is accepted, which states that there are statistically significant differences in the diffusion coefficient, which are attributed to the different composition of the soil and rocks used, in favor of NP-soil.

Also, Table 9 shows the correlation analysis between diffusion coefficient (cm/sec) and suction (MPa) for soils and stones. According to Table 9, correlation coefficients analysis shows significant positive correlation between diffusion coefficient with suction for soils and stones. And the stronger correlation is for limestone (R=0.99) for suction, which confirms the results of experimental work.

Table 9 Correlation analysis between diffusion coefficient (cm/sec) and suction (MPa) for soils and stones

	Non-plastic	**Plastic**	**Gypsum**	**limestone**
Suction (MPa)	0.988	0.980	0.970	0.991

Figure 9 and Table 10 show the MIP test and properties of both untreated and weathered stones due to wetting-drying and freezing-thawing cycles, respectively. The limestone and gypsum stone were subjected to shrinkage and contraction in their structures due to wetting/drying and freezing/thawing cycles, respectively. The shrinkage and contraction led to increase in their total porosity by 15.7% and 116.6% due to wetting/drying, and 60.7% and 225% under freezing/thawing effect, for limestone and gypsum stones, respectively [10, 30, 43].



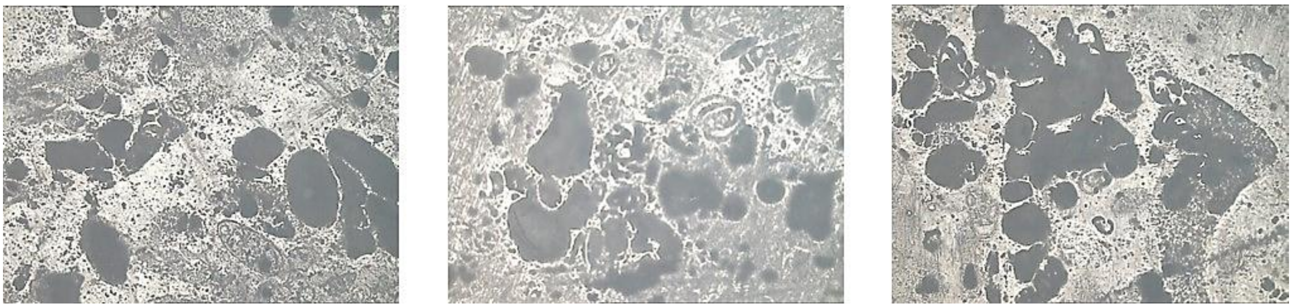
(a) (b)

(c) (d)

Figure 9 MIP of stone samples due to (a, b) wetting-drying cycles. (c, d) freezing-thawing cycles

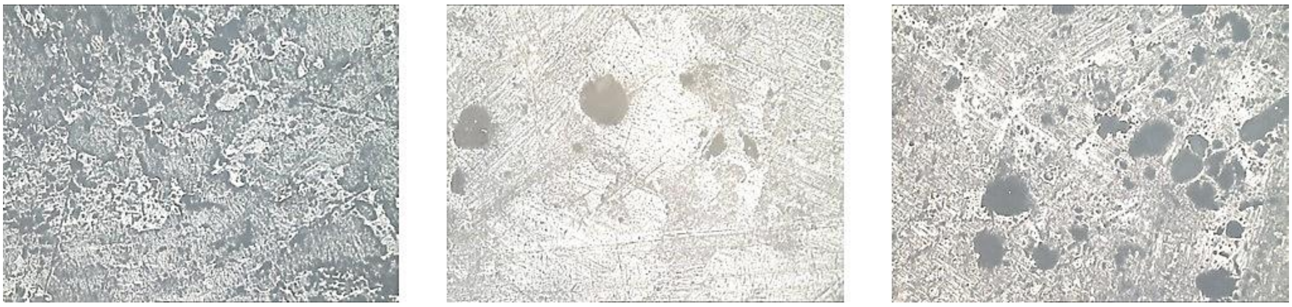
Table 10 Properties of stone samples treated with wetting-drying and freezing-thawing cycles

Properties	**Unit**	**Untreated stones**		**Wetting-Drying**		**Freezing-Thawing**	
		Limestone	**Gypsum**	**Limestone**	**Gypsum**	**Limestone**	**Gypsum**
Bulk dry Density ρb	g/cm^3	2.04	2.25	1.89	1.98	1.68	1.87
Skeleton Density ρs	g/cm^3	2.66	2.28	2.50	2.26	2.53	2.3
Porosity	%	21	1.2	24.3	2.6	33.75	3.9



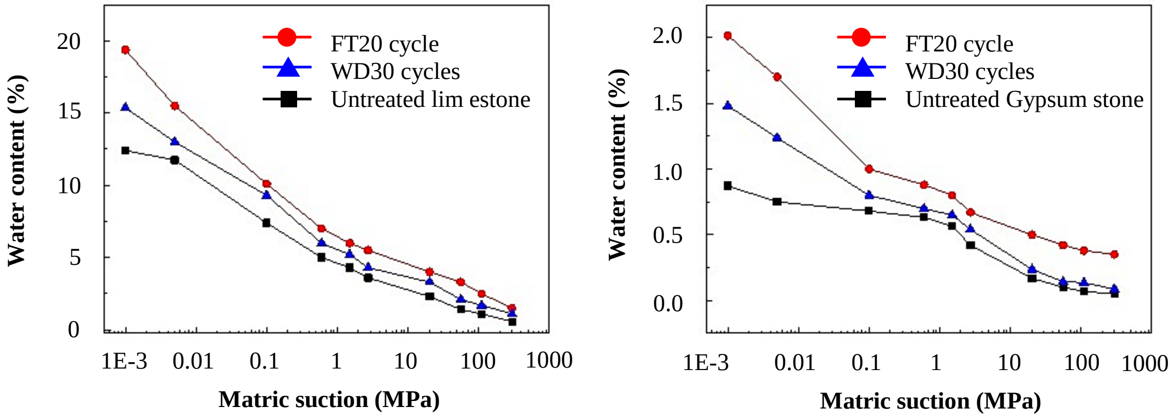
(a) (b) (c)

Figure 10 Optical microscope of (a) fresh limestone (b) wetting/drying effect (c) freezing /thawing effect



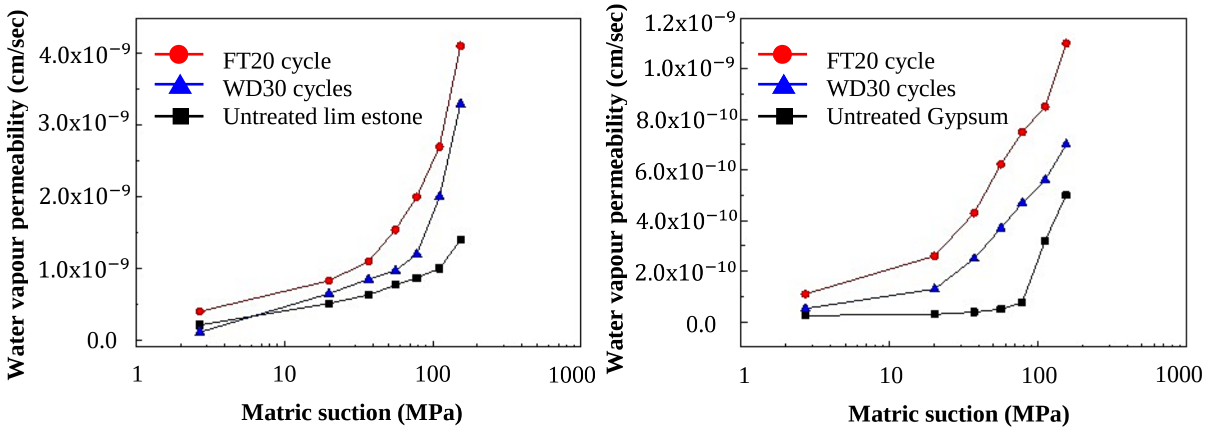
(a) (b) (c)

Figure 11 Optical microscope of (a) fresh gypsum stones (b) wetting/drying effect (c) freezing /thawing effect



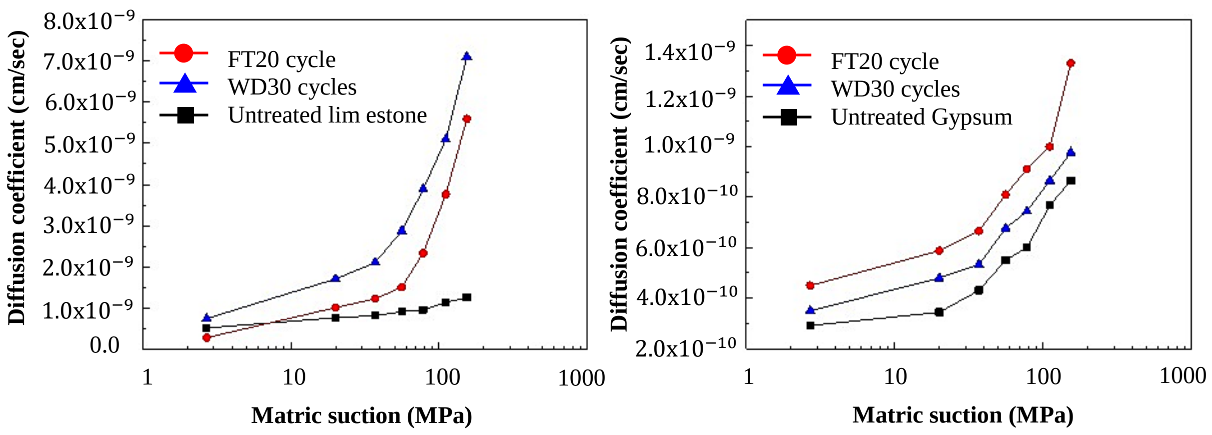
(a) (b)

Figure 12 Effect of wetting-drying and freezing-thawing on the water retention curve of stone samples



(a) (b)

Figure 13 Effect of wetting-drying and freezing-thawing on the permeability of the stone samples



(a) (b)

Figure 14 Effect of wetting-drying and freezing-thawing on diffusion coefficient of the stone samples

Figures 10 and 11 show the morphological microstructure characteristics of limestone and gypsum treated with wetting-drying and freezing-thawing cycles, respectively. Images with zoom of X100 for the fabric structure of the stone samples were snapped using an optical microscope. The disintegration in the stones fabric due to the weathering effect produced an increment in the pore channel size within the stones structure [10, 44]. Figure 12 represents the water retention curves of the stone samples treated with wetting-drying and freezing-thawing processes, as related with the increment of pore size distribution of treated stone (i.e. shows in Figure 10), an increasing in the ability of the treated stone samples to retain water molecules within their structures in humid condition have been noticed (suction $\leq$ 2.7 MPa) [34, 43]. In addition, Figures 13 and 14 illustrate the curves of both water vapour permeability and diffusion coefficients of the stones subjected to wetting-drying and freezing-thawing processes, the stone fabric disintegration enabled the water vapour to permeate and diffuse through weathered stone structure at a rate higher than those of fresh stones [7, 8, 15, 20].

4. Conclusion

The hazardous diffusion of fluids and contaminants in both phases liquid and vapour through the natural porous media are a concern for public health and security, therefore the prediction of the diffusion coefficients is essential. The present research studies the water vapour diffusion through limestone, gypsum stones, and P, NP soils. Water vapour diffusion through porous media is an important part in the water flux in the unsaturated zone of arid or semiarid regions, therefore the prediction of the diffusion coefficients is essential. This research investigated the water vapour diffusion through limestone, gypsum, plastic, and non-plastic soils available in Mosul city, Iraq. Both fresh and weathered earth materials were utilized, the index properties and mineralogical characterization of the earth materials were determined as applicable. The results exposed the variance in water diffusion behaviour of Plastic and Non-Plastic soils based on the differences in their microstructure fabrics. In Non-Plastic soil, important changes in the coefficient of diffusivity and hydraulic conductivity were observed with suction. However, in Plastic soil, only limited changes in the diffusivity parameters were observed. Further, the amount of hydraulic conductivity and diffusion coefficient is higher in limestone than in gypsum stone due to bigger pore size distribution of the limestone. It was confirmed that weathering factors such as wetting/drying, and freezing/thawing have noticeable effects on the permeability and diffusion behaviour of the stones. Hence, the plasticity of soil should be established, plastic soil should be the choice over non-plastic soil for utilization as barriers for chemical and radioactive wastes. In addition, the degree of weathering of rocks should be a factor; fresh rocks should be preferred over weathered rocks, and areas with gypsum as rock materials over areas with limestone, for earth materials in Mosul city, Iraq.

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6. References

[1] Reyzabal ML, Cfsar J. A method for measurement of water vapor diffusion in dry soils. Geoderma. 1992;53:105-10.
[2] Neil CW, Telfeyan K, Sauer KB, Ware SD, Reimus P, Boukhalfa H, et al. Iodine effective diffusion coefficients through volcanic rock: influence of iodine speciation and rock geochemistry. J Contam Hydrol. 2020;235:103714.
[3] Dashtpour O, Fallah H. Transport in porous media. Int J Oil Gas Coal Eng. 2013;1(1):1-6.
[4] Jabro JD. Water vapor diffusion through soil as affected by temperature and aggregate size. Transport Porous Media. 2009;77(3):417-28.
[5] Pachepsky Y, Timlin D. Water transport in soils as in fractal media. J Hydrol. 1998;204:98-107.
[6] Sood E. Determination of the diffusion coefficient for unsaturated soils [thesis]. Texas: Texas A&M University; 2005.
[7] Beck K, Al-mukhtar M, Rozenbaum O, Rautureau M. Characterization, water transfer properties and deterioration in tuffeau: building material in the Loire valley-France. Build Environ. 2003;38(9-10):1151-62.
[8] Pia G. Fluid flow in complex porous media : experimental data and IFU model predictions for water vapour permeability. J Nat Gas Sci Eng. 2016;35:283-90.
[9] Carmeliet J, Descamps F, Houvenaghel G. A multiscale network model for simulating moisture transfer properties of porous media. Transport Porous Media. 1999;35(1):67-88.
[10] Cui YJ, Tang AM, Loiseau C, Delage P. Determining the unsaturated hydraulic conductivity of a compacted sand-bentonite mixture under constant-volume and free-swell conditions. Phys Chem Earth. 2008;33(S1):S462-71.

[11] Ludwig N, Rosina E, Sansonetti A. Evaluation and monitoring of water diffusion into stone porous materials by means of innovative IR thermography techniques. Measurement. 2018;118:348-53.

[12] Wilson GW, Fredlund DD, Barbour SL. Coupled soil-atmosphere modelling for soil evaporation. Can Geotech J. 1994;31(2):151-61.

[13] Kozaki T, Liu J, Sato S. Diffusion mechanism of sodium ions in compacted montmorillonite under different NaCl concentration. Phys Chem Earth. 2008;33(14):957-61.

[14] Wels C, Lefebvre R, Robertson AM. An overview of prediction and control of air flow in acid-generating waste rock dumps. 6th International Conference on Acid Rock Drainage; 2003 Jul 12-18; Cairns, Australia. p. 639-50.

[15] Boving TB, Grathwohl P. Tracer diffusion coefficients in sedimentary rocks: correlation to porosity and hydraulic conductivity. J Contam Hydrol. 2001;53(1-2):85-100.

[16] Mosquera MJ, Silva B, Prieto B, Ruiz-Herrera E. Addition of cement to lime-based mortars: effect on pore structure and vapor transport. Cement Concr Res. 2006;36(9):1635-42.

[17] Suresh D. Heat and mass transfer modelling in a porous structure effect of body's heat and moisture loss on the microclimate of a hygiene product [thesis]. Gothenburg: Chalmers University of Technology; 2016.

[18] Belleudy C, Woloszyn M, Chhay M, Cosnier M. A 2D model for coupled heat, air, and moisture transfer through porous media in contact with air channels. Int J Heat Mass Tran. 2016;95:453-65.

[19] Bartelt-Hunt SL, Smith JA. Measurement of effective air diffusion coefficients for trichloroethene in undisturbed soil cores. J Contam Hydrol. 2002;56(3-4):193-208.

[20] Haupl P, Grunewald J, Fechner H, Stopp H. Coupled heat air and moisture transfer in building structures. Int J Heat Mass Tran. 1996;40(7):1633-42.

[21] Li C, Xu P, Qiu S, Zhou Y. The gas effective permeability of porous media with Klinkenberg effect. J Nat Gas Sci Eng. 2016;34:534-40.

[22] Moldrup P, Olesen T, Schjnning P, Yamaguchi T, Rolston D. Predicting the gas diffusion coefficient in undisturbed soil from soil water characteristics. Soil Sci Soc Am J. 2000;64(1):94-100.

[23] Yamanaka T, Inoue M, Kaihotsu I. Effects of gravel mulch on water vapor transfer above and below the soil surface. Agr Water Manag. 2004;67(2):145-55.

[24] Benavente D, Pla C. Effect of pore structure and moisture content on gas diffusion and permeability in porous building stones. Mater Struct. 2018;51(1):21.

[25] Gens A, Guimaraes L, Garcia-Molina AJ, Alonso E. Factors controlling rock-clay buffer interaction in a radioactive waste repository. Eng Geol. 2002;64(2-3):297-308.

[26] Kozaki T, Sato Y, Nakajima M, Kato H, Sato S, Ohashi H. Effect of particle size on the diffusion behavior of some radionuclides in compacted bentonite. J Nucl Mater. 1999;270(1-2):265-72.

[27] Montes G, Marty N, Fritz B, Clement A, Michau N. Modelling of long-term diffusion reaction in a bentonite barrier for radioactive waste confinement. Appl Clay Sci. 2005;30(3-4):181-98.

[28] Shackelford C, Moore S. Fickian diffusion of radionuclides for engineered containment barriers: diffusion coefficients, porosities, and complicating issues. Eng Geol. 2013;152(1):133-47.

[29] Fredlund DG, Rahardjo H. Soil mechanics for unsaturated soils. United States: John Wiley & Sons; 1993.

[30] Sahimi M. Flow and transport in porous media and fractured rock: from classical methods to modern approaches. 2nd ed. Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2011.

[31] Al-Omari A, Khattab SI. Al-Hadba Minaret, a contribution in Characterizing of its Brick. Key Eng Mater. 2020;857:48-55.

[32] Fredlund DG. Unsaturated soil mechanics in engineering practice. J Geotech Geoenviron Eng. 2006;132(3):286-321.

[33] Pia G, Casnedi L, Sanna U. Pore size distribution influence on suction properties of calcareous stones in cultural heritage: experimental data and model predictions. Adv Mater Sci Eng. 2016;2016:1-10.

[34] Al-omari A, Beck K, Brunetaud X, Torok A, Al-mukhtar M. Critical degree of saturation : a control factor of freeze-thaw damage of porous limestones at Castle of Chambord, France. Eng Geol. 2015;185:71-80.

[35] Ismail B. Environmental deterioration and conservation of monumental basalt, Egypt. Ass Univ Bull Environ Res. 2004;7(1):153-71.

[36] ASTM. ASTM D5312 / D5312M-12, Standard test method for evaluation of durability of rock for erosion control under freezing and thawing conditions. West Conshohocken: ASTM International; 2013.

[37] Grim RE. Clay mineralogy. 2nd Ed. New York: McGraw-Hill; 1968.

[38] ASTM. ASTM D 854, Standard test methods for specific gravity of soil solids by water pycnometer. West Conshohocken: ASTM International; 2002.

[39] ASTM. ASTM D4318, Standard test methods for liquid limit, plastic limit, and plasticity index of soils. West Conshohocken: ASTM International; 2000.

[40] ASTM. ASTM D422-63, Standard test method for particle size analysis of soils, Annual book of ASTM standards. West Conshohocken: ASTM International; 2003.

[41] AASHTO. T -180 Moisture density relations of soils using a 4.54 kg (10 lb) rammer and a 457 mm (18 in.) drop. Washington: AASHTO; 2011.

[42] Yuan C, Lei T, Mao L, Liu H, Wu Y. Soil surface evaporation processes under mulches of different sized gravel. Catena. 2009;78(2):117-21.

[43] Saheb M, Chabas A, Mertz J, Colas E, Rozenbaum O, Sizun J, et al. Weathering of limestone after several decades in an urban environment. Corrosion Sci. 2016;111:742-52.

[44] Pia G, Casnedi L, Sanna U. Porosity and pore size distribution influence on thermal conductivity of yttria-stabilized zirconia: experimental findings and model predictions. Ceram Int. 2016;42(5):5802-9.