

Porosity changes after different temperature regimes for a salt weathering simulation test on Mokkattam limestone (Egypt)

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Abstract

This study deals with the characterization of the pore structure of fresh quarry limestone samples belonging to the Mid-Eocene Mokattam Group, and porosity changes in samples subjected to salt crystallization tests at different temperatures (20, 30 and 40 °C) in a purpose-made simulation chamber based on feeding samples by capillary imbibitions. NaCl with fixed concentration (10%) was used in the different experimental tests. One more experiment was performed using only distilled water to discriminate changes due to salt crystallisation from those resulting just from wetting. In order to characterize the changes of the pore structure, fresh and weathered samples subjected to different temperature regimes tests were investigated by means of Mercury Intrusion Porosimetry (MIP), and Scanning Electron Microscopy (SEM). These results show the critical role of temperature in controlling the porosity changes after salt crystallisation.

Key words: stone decay, limestone, salt weathering, pore structure.

1 Introduction

Many researchers have studied the relation between durability of building stones and their petrophysical properties, including pore structure and strength [1]. Salts are known to be one of the most effective agents in stone decay. Therefore it is very important to study the factors controlling their crystallisation to be able to establish measures to minimize their effects [2]. Also, porosity and pore-size distribution of the stone play an important role in determining the movement of water and its dynamic properties and therefore the extent of the decay process [3].

When a saline solution accesses the pore structure of a stone, different mechanisms can subsequently lead to crystal growth [4]. Most commonly, evaporation usually prompts salt crystallization [5]. The loss of cohesion between the stone grains/crystals, splitting and surface deterioration and the change of the pore size distribution can result from the repeated cycles of crystallization/dissolution of salt solution within the porous network of the stone, which may lead to the modification of the porous media and the petrophysical properties of the stone [5-6] and also crystallisation pressure is an important factor controlling the decay pattern during salt crystallisation test [7].

Recently, some models describing how the balance between capillary transport and evaporation processes determine the zone of salt accumulation and crystallisation are available [8-9]. In this study, a set of experimental tests based on the partial immersion of stone samples in a saline solution, which accesses into the specimens by capillary rise, have been carried out. This method is based on what Goudie [10] referred to as "the wick effect" in which the solution rises to a certain height characterised by the evaporation and salt crystallisation processes. In this area, efflorescences and/or subflorescences may appear, accompanied by material loss; this effect being mainly controlled by the mean pore size of the stone material [6, 11]. Temperature is also a factor controlling when and how salts crystallise on or within stone [3, 12]. The paper aims mainly to study the effect of temperature during this process and how it controls the occurrence of salt crystallisation, affecting the pore structure, and determining the decay forms.

2 Materials and methods

Limestone samples were extracted from Helwan quarries; an area South of Cairo, Egypt (Fig.1), which belongs to the Mid Eocene Mokattam Group, a biomicrite limestone, out of which cores of 2 cm diameter and 4 cm height were drilled.



Figure 1: General view of limestone quarry at Helwan, Egypt.

Limestone cores were subjected to different temperature regimes (20, 30 and 40°C) in a simulation chamber (Fig. 2a) based on continuous capillary imbibitions of samples designed by Hamed et al. [13]. Samples are placed in a set of drawers made of polyvinyl chloride (Fig. 2b). Each drawer can fit up to 32 samples, which are placed in connected containers, so all samples are fed continuously by a running solution. The chamber is equipped with temperature/humidity measuring sensors and connected to an air conditioning unit (Fig. 2c). A set of samples was tested for each temperature regime for 144 hours.

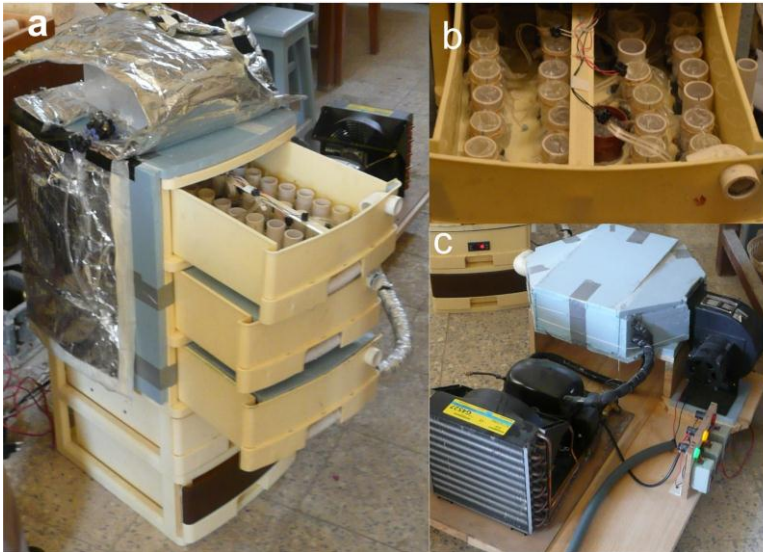


Figure 2: General view of the simulation chamber used for the experiments (a). Close up of one of the drawers showing sample holders. Air conditioning unit (c)

A 10 % sodium chloride solution in distilled water was used in this experiment as it is a common salt in building stones in Egypt and elsewhere [14-18]. In addition to this, another experiment was performed at 20 °C using distilled water to study the effects of a non-saline solution in the stone porosity.

The effect of the different simulation regimes on the porous media of the stone samples was evaluated by means of Mercury Intrusion Porosimetry (MIP). A Micromeritics Autopore IV 9500 with a maximum injection pressure of 230 MPa and a pore size range detection of 0.001- 400 micrometers was used. Pores below 5 micrometers were considered microporosity, as capillary height increases dramatically for pores below this threshold. Four cores were analysed after 144 h for each different simulation regime beside one fresh reference core.

Scanning Electron Microscopy in Secondary Electrons mode (SEM-SE) with a JEOL JSM 6400 microscope equipped with an Energy Dispersive X-ray (EDX) detector facility (Oxford INCA) was used for the examination of one fresh core and another one after 40 °C regime test to see how salts may have crystallised within the pores. Samples were around 5 mm oriented fragments and were either gold metallised or graphite sputtered depending if they were used just for taking pictures or for analyses.

3 Results

Figure 3 shows the visual appearance of the tested samples after the different experimental regimes. The samples show a variation after different temperature regimes: while samples submitted to a 20 °C regime appear undamaged, those tested at 30 °C displayed efflorescences at the top of the cores and the ones at 40 °C showed deep scaling, cracking and loose of material.

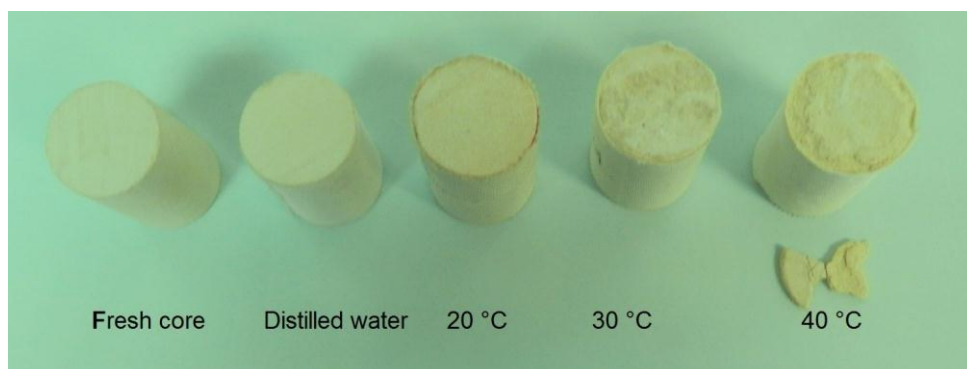


Figure 3: Visual appearance of limestone cores before and after the experiments.

3.1 Mercury Intrusion Porosimetry (MIP)

Table 1 and Figure 4 show the results of different porosity parameters and pore size distribution of fresh core and samples subjected to the different experimental regimes. Pore size distribution and porosity parameters changed after the tests for all different temperature regimes in comparison to the reference fresh core except for the porosity of cores tested with distilled water that did not change significantly.

Table 1: Mercury Intrusion Porosimetry parameters of fresh core, one contaminated with distilled water and salt laden cores submitted to different temperature conditions.

	Fresh core	Dist. water	20°C	30°C	40°C
Porosity (%)	33.4	33.6	22.5	29.9	20.6
Average pore diameter(4V/A) (µm)	0.14	0.17	0.16	0.13	0.16
Apparent Density (g/ml)	1.76	1.75	1.72	1.85	2.10
Total microporosity (%)	33.23	33.23	22.32	29.51	20.18

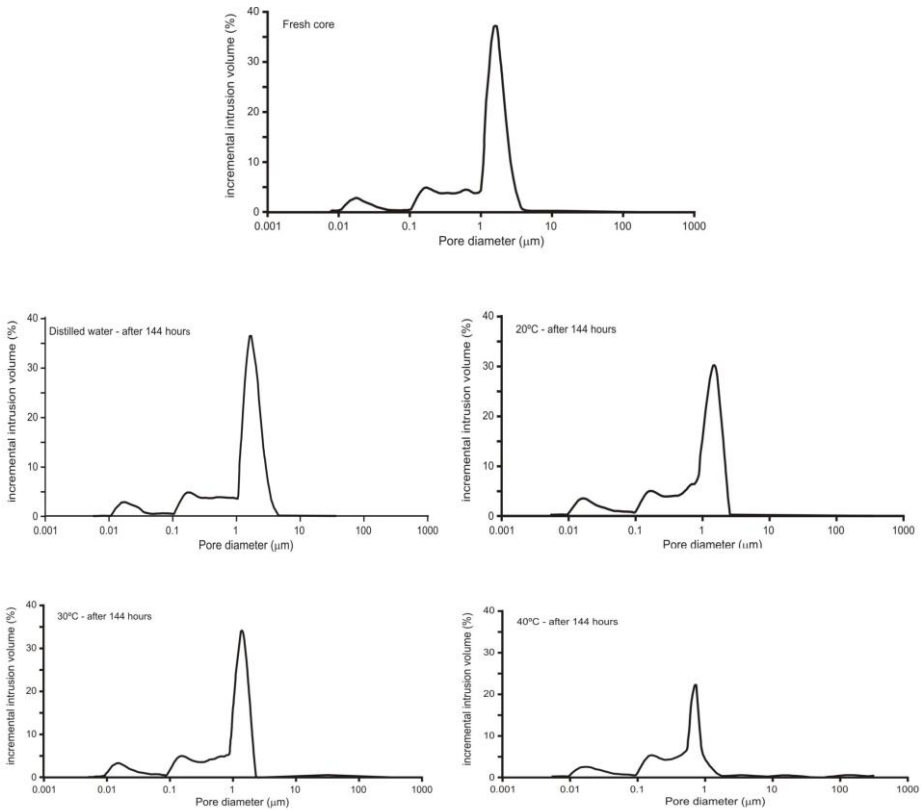


Figure 4: Pore size distribution of a fresh core (top), one contaminated with distilled water (middle left) and salt laden cores submitted to different temperature conditions (20°C, middle right; 30°C, bottom left; 40°C, bottom right)

After the 20 °C test the total Hg-porosity decreased to 22.5 %.The average pore diameter (4V/A) increased slightly from 0.14 μm to 0.16 μm and the relative intensity of a secondary peak at 0.65 μm increased.

After the 30 °C test the total Hg-porosity decreased slightly to 29.9%. The average pore diameter shows a very slight decrease to 0.13 μm.

After the 40 °C test the total Hg-porosity decreased significantly to 20.6%. The average pore diameter increases slightly to 0.16 μm and the main peak shifted from 1.50 μm to 0.75 μm and decreased its relative intensity.

3.2 Scanning Electron Microscopy (SEM)

SEM-EDX analysis show minor amounts of dolomite ($\text{CaMg}(\text{CO}_3)_2$) and quartz (SiO_2) and also P-rich skeletal remains (Fig. 5).

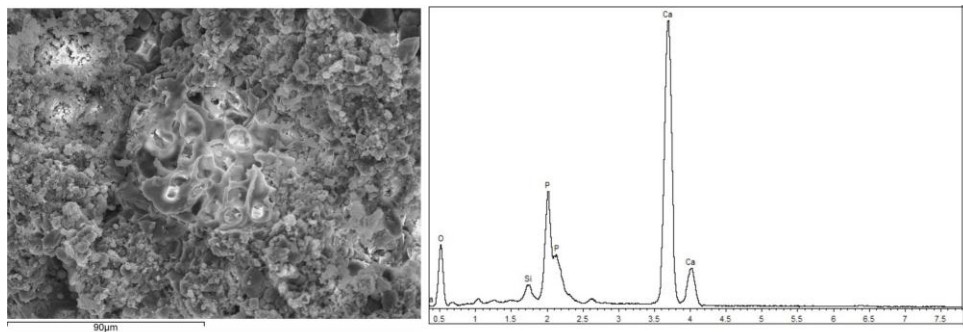


Figure 5: SEM – SE image (left) with EDX analysis (right) for the fresh limestone used in all the experimental tests.

Samples after 40 °C tests showed the largest decrease of porosity and this was verified through SEM observations in which halite crystals have been observed filling stone cracks (Fig. 6) and pores (Fig. 7).

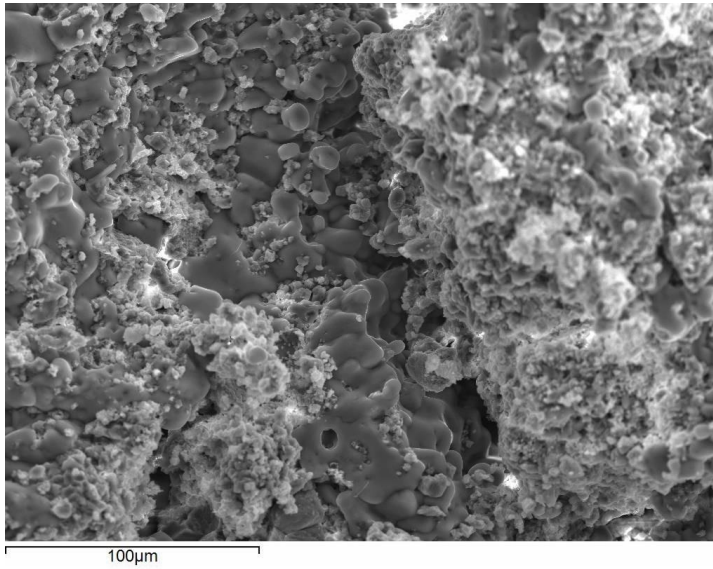


Figure 6: SEM – SE image after 40 °C test, halite crystals filling a crack.

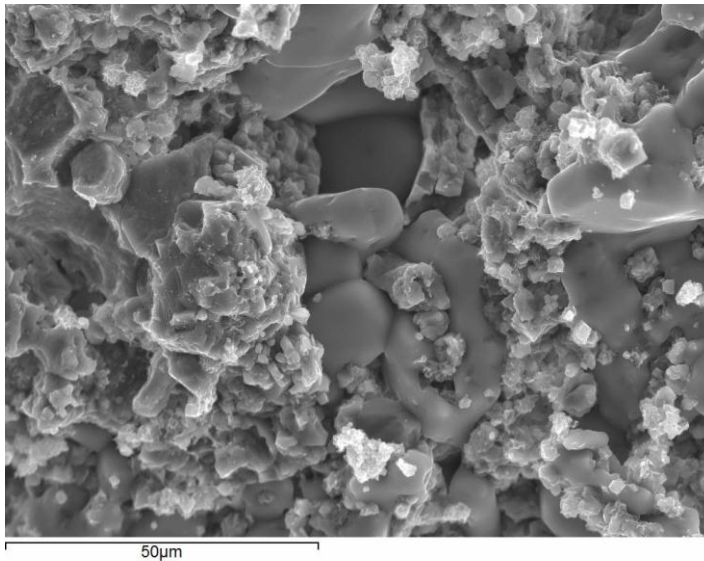


Figure 7: SEM – SE image after 40 °C test, halite crystals filling the stone pores.

4 Discussion and conclusions

Significant differences have been noticed, as a result of different temperature regimes, in the salt crystallisation occurrence under the same conditions of salt concentration and %RH during the partial immersion capillary method. MIP results confirm NaCl crystals tend to grow on the top surface (efflorescences) of most of the tested stone cores after the 30 °C regime cycles, as a result of increasing of the evaporation rate which promotes the growth of NaCl on the top surface. As a consequence, total Hg-porosity and average pore size show only a slight decrease. Pore size distribution and porosity parameters show a more intense change after 20 and 40 °C in experimental tests than at 30 °C, showing salt crystallisation tends to occur preferably within the pores. The extent of this process is limited during the 20 °C regimes and does not generate any real damage on the core surfaces nor lead to the development of cracks.

However, crystallisation of salts within pores during 40 °C regime is largely more predominant. Total Hg-porosity decreases significantly and obvious cracking was observed with SEM. NaCl crystals fill these cracks and the pore system as subflorescences. The crystallisation pressure leads to visible damage, with scaling and loss of material in most of the tested core surfaces.

These results show that when saline solutions enter into the rock by capillary imbibitions, environmental temperature regimes may be crucial to promote changes in the crystallisation occurrence for the same salt (i.e. efflorescence or subflorescence) and, therefore changes on the decay patterns exhibited, as a result of differences on the balance between water ingress and evaporation.

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