

Accelerated weathering tests on two highly porous limestones

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Abstract A major cause of weathering of building and historic monuments constructed using limestones is associated with the salt crystallization. This may typically occur at the surface (due to efflorescence) or in subsurface layers while limestones are drying. Due to this reason structural damage or material loss (granular disintegration, flaking, contour scaling) may occur. In this paper, imbibition-drying cycles are carried out with pure water and solutions of NaCl with different concentrations to simulate the weathering effect on two limestones with similar total porosity values. The imbibition kinetics of these limestones was significantly influenced by the number of applied imbibition-drying cycles. In addition, imbibition kinetics was also dependent on the concentration of salt solutions, the mineralogical composition as well as on the pore-size distribution of these two stones. The structural and textural modifications that arise in the limestones due to the influence of imbibition characteristics of drying cycles are qualitatively confirmed by scanning electronic microscope (SEM) and quantitatively with helium pycnometry measurements.

Keywords Limestones · Weathering tests · Soluble salts solution · Pore-size distribution · Salt distribution

Introduction

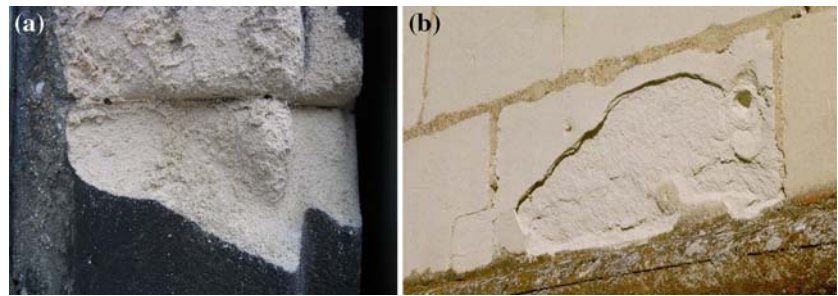
The presence of soluble salts in the building stones gradually induces textural and mineralogical modifications in the stones. This phenomenon in turn gradually degrades the stones. As Price (1996) summarizes, salts can originate from various sources: air pollution, soil, sea spray, inappropriate chemical treatment, or interaction between building materials such as mortars which may contain salts. Halite, (NaCl) is one of the most frequently found salts that damage the historical monuments. Behlen et al. (1997) and Steiger et al. (1997) present carefully their analysis of the different pathways for NaCl accumulation in marine environments. This salt is one of the key contributors towards degradation of monuments due to weathering action (Fig. 1). A method largely used for understanding the mechanics of natural deterioration is to observe stone behaviour in the laboratory by subjecting them to various agents of deterioration and carry out imbibition-drying tests (Benavente et al. 2001; Nicholson 2001; Chéné et al. 1999). In this paper, imbibition-drying cycles of weathering tests were carried out on two limestones with high total porosity in the order of 45%: white Tuffeau (extracted from the Lucet quarry in Saint-Cyr-en-Bourg in Maine-et-Loire, France) and Sébastopol stone (extracted from the Rocamat quarry in Saint-Maximin in Oise, France). The first stone is largely used in constructions of the castles of Val de Loire, and the second is used in Oise and the Paris

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Fig. 1 Main deterioration forms in monuments: **a** granular disintegration of Sébastopol stone, **b** contour scaling of white Tuffeau



area. Sébastopol stone is tested in order to compare its behaviour to that of white Tuffeau. The imbibition-drying cycles were applied on both the limestones with water and salt (NaCl) solutions of different concentrations.

Characterization of materials

The two limestones studied in this research program are characterized using different complementary techniques in order to evaluate various elements both qualitatively and quantitatively. These techniques include X-ray diffraction (XRD), thermogravimetric analyses (TGA), infra-red spectrometry, and scanning electronic microscopy (SEM). The characterization of pore space is carried out by mercury porosimetry. The physical characteristics of the studied stones are summarized in Table 1. The major minerals of these limestones are calcite (i.e., CaCO_3) and quartz (i.e., SiO_2). In white Tuffeau, predominantly clayey minerals and opal cristobalite–tridymite are found. The size and the shape of grains in white Tuffeau are significantly different and consist of smaller grains of clay, quartz, sparitic calcite, mica arranged with several types of minute grains such as micritic calcite and spherules of opal CT (Beck et al. 2003). In comparison, the grains of the Sébastopol stone are coarser with a more uniform size (Beck and Al-Mukhtar 2005a).

The white Tuffeau is a relatively light building material. It has an apparent density of 1.31 g cm^{-3} and a

total porosity of 48% under total dry conditions. Results of mercury porosimetry show that the white Tuffeau is a multi-scale material because it has a very wide pore-size distribution (from $20 \mu\text{m}$ to 6 nm) with mesoporosity ranging from 1 to $10 \mu\text{m}$ (representing nearly 50% of pore space). The pore-size distribution of Sébastopol stone is mainly unimodal and macroscopic in nature with a diameter of about $20 \mu\text{m}$. The major portion of pore space in Sébastopol is restricted to the range of 40 to $1 \mu\text{m}$. The texture of stones observed by SEM images illustrates the previous discussion about the size, shape, and arrangement of grains and pores. The complexity associated with the porous network of these grains can be observed in Figs. 2 and 3.

Experimental simulation of weathering in the laboratory

Experimental procedure

Prismatic samples of $70 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$ size of the two limestones were subjected to different cycles of imbibition drying. The following protocols were followed.

Table 1 Main characteristics of two tested limestones

	White Tuffeau	Sébastienopol stone
Mineralogical composition	Calcite $\cong 50\%$ Quartz $\cong 10\%$ Opale CT $\cong 30\%$ Clay and mica $\cong 10\%$	Calcite $\cong 80\%$ Quartz $\cong 20\%$
Skeletal density (g cm^{-3})	2.55	2.71
Bulk dry density (g cm^{-3})	1.31	1.58
Porosity (%)	48	42

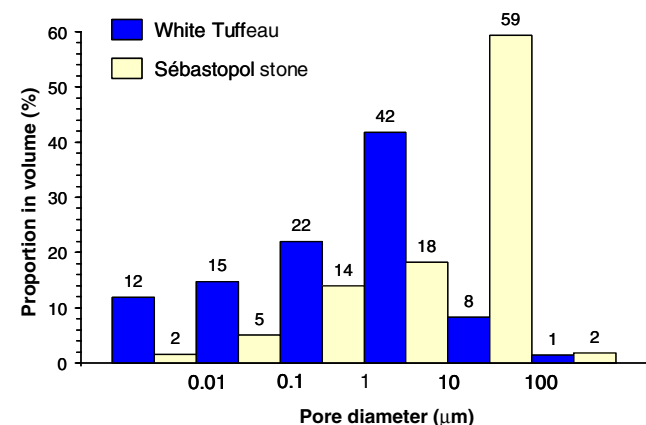
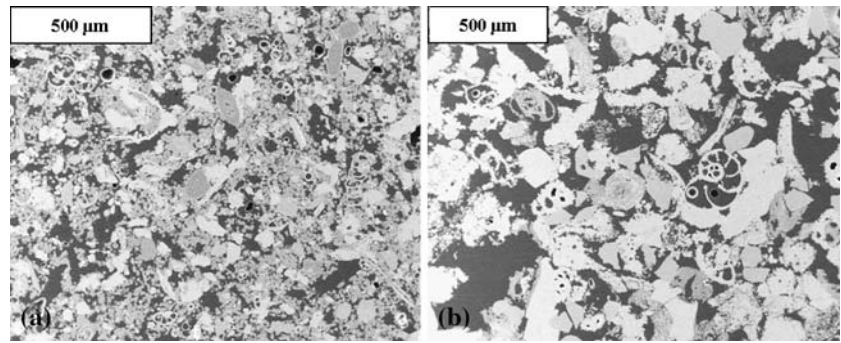


Fig. 2 Pore-size distribution determined by mercury porosimetry for the tested stones

Fig. 3 SEM photographs (scale 500 μm) showing the diversity of pores and grains in **a** white Tuffeau and **b** Sébastopol stone



First stage: imbibition

The porous material can imbibe water when it is in contact with water even without application of any external pressure. This imbibition phenomenon is due to capillarity and is dependent on the size and the shape of pores, as well as the connectivity of the porous media of the stone. For each type of stone, the samples previously dried are absorbed by capillarity at their base either with pure water or with soluble salt solutions with different concentrations of sodium chloride (i.e., NaCl). Two different salt concentrations of 30 and 300 g L⁻¹ were used in this study. The first concentration corresponds to the content of salt NaCl in the seawater, and the second one is practically the solubility of sodium chloride, NaCl. The capillary front height and the mass of samples are measured with increasing intervals of elapsed time. If the porous media are homogeneous, the imbibition curves plotted according to the square root of time are linear (Jeannette 1992).

A theoretical capillary model is based on absorption by capillarity for a vertical cylindrical tube of radius (*r*[m]) and of limited height (neglecting the influence of gravity). The pressure gradient Δ*P*[N m⁻²] allowing the drainage of the fluid results from capillary pressure and is mainly governed by Laplace’s equation:

$$\Delta P = \frac{2\sigma \cos \theta}{r} \cong \frac{2\sigma}{r} \tag{1}$$

where σ[N m⁻¹] is the water superficial tension.

For the air–water system, the contact angle θ[rad] is considered as equal to zero. The fluid flow in the steady laminar regime in a cylindrical tube is given by the Hagen–Poiseuille Law as given below:

$$Q = \frac{dV}{dt} = \frac{\pi r^2 dh}{dt} = \frac{\pi r^4 \Delta P}{8\eta h} \tag{2}$$

where *Q*[m³ s⁻¹] is the water flow rate, *h*[m] the capillary height, and η[N m⁻² s] the dynamic viscosity of water.

Using these two Eqs. 1 and 2, Eqs. 3 and 4 can be obtained (Washburn 1921). These equations are useful in calculating the capillary height (*h*[m]) and the mass uptake (Δ*m*[kg]) per surface unit (*S*[m²]) during the time (*t*[s]):

$$h = \sqrt{\frac{r\sigma}{2\eta}} \sqrt{t} = B\sqrt{t} \tag{3}$$

$$\frac{\Delta m}{S} = A\sqrt{t} \tag{4}$$

The mass coefficient *A*[kg m⁻² s^{-1/2}] and a visual coefficient *B*[m s^{-1/2}] for each of the imbibition cycle can then be determined (Standard NF EN1925 B10-613).

Second stage: drying

After completion of the imbibition stage, the sample is subjected to oven drying at 105°C. This temperature is applied to quickly eliminate water and thus, to strongly reduce the drying time. Oven drying time varies from 12 h to several days depending on the number of cycles used for imbibition. The period for oven drying increases when a sample takes more time to imbibe and is also dependent on the number of applied imbibition cycles. The mass of salt can be determined when the sample is completely dry. The dried out sample can then be subjected to a new imbibition test.

All samples are subjected to imbibition on the same surface of 40 mm × 40 mm for different cycles of imbibition drying. In addition, in the drying stage, all surfaces are packed by impermeable aluminous paper except the cycled surface.

At the end of the stage of drying, in the case of white Tuffeau, a fine salt crust settles on the cycled surface. However, a major part of the salt remains trapped inside the stone. On the contrary, for the Sébastopol stone, efflorescence is predominant. Due to this reason, a rather thick salt crust forms on the surface which can be removed from surface (Fig. 4).

The imbibition-drying tests were stopped when imbibition time and drying time became too important.

Densities and morphological measurements

Skeletal densities of stones polluted with salt are determined by helium pycnometry (using a pycnometer Accupic 1330). This method is based on the release of a volume of helium from a cell with pressure P_1 containing the porous sample towards a second cell first filled with helium but with a lower vacuum pressure (i.e., $P_2 < P_1$) applied before filling up the helium. The application of the Perfect Gases Law to the helium contained in the two cells, before and after the opening of the lockgate connecting them, facilitates the estimation of the skeletal volume. The skeletal density ρ_s is then determined with the mass measurements obtained at a dry state. Grain morphology and the localization of NaCl crystals are determined using images obtained by SEM coupled with EDX (X-ray diffraction) analysis. In addition, information on size, shape, and arrangement of the grains and pores is derived from SEM and EDX.

Experimental results

The results obtained show that imbibition coefficients, the mass coefficients A and the visual coefficients B change proportionally. In other words, both the coefficients change in the same manner (Figs. 5, 6, 8, 9). Due to this reason, in the remainder of this paper only the evolution of water mass taken by the samples will be presented and analysed. Thus, as noted (Fig. 7) in the two limestones, the solution contents absorbed by capillarity depending on the time (and thus the imbi-

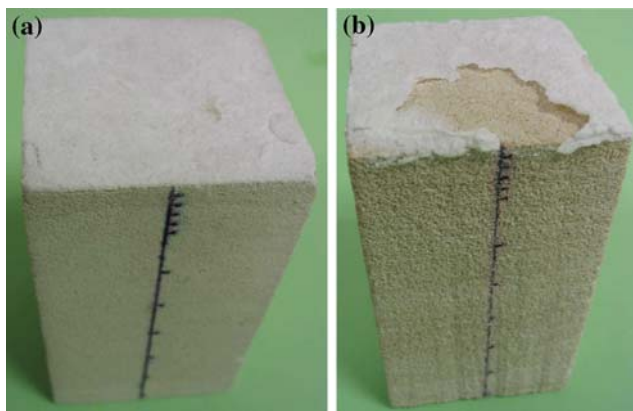


Fig. 4 Salt deposited on the cycled surface at the end of drying for two limestones at the 1st cycle: **a** white Tuffeau and **b** Sébastopol stone

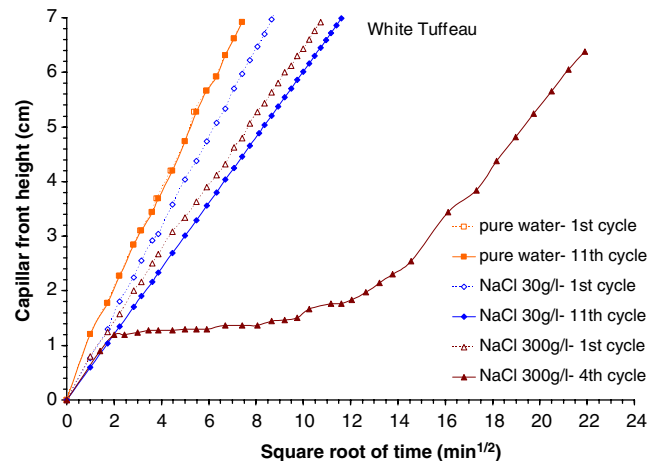


Fig. 5 Imbibition curves at 1st cycle and at the last cycle for white Tuffeau

tion rate) strongly changes according to the number of cycles and the concentration of the soluble salt solution used during imbibition.

The mass imbibition coefficients are constants when imbibition was carried out with pure water both in white Tuffeau and the Sébastopol stone. However, the number of cycles applied with pure water was not sufficient to induce structural modifications within the sample (Beck and Al-Mukhtar 2005b). The imbibition coefficients of the Sébastopol stone are almost twice those of the white Tuffeau (with the 1st cycle, the mass coefficients A are, respectively, $0.32 \text{ g cm}^{-2} \text{ min}^{-1/2}$ for white Tuffeau and $0.58 \text{ g cm}^{-2} \text{ min}^{-1/2}$ for the Sébastopol stone). Water penetration is quick in the Sébastopol stone due to capillarity. By the end of the imbibition, however, white Tuffeau absorbs a greater quantity of water.

The mass uptake is slightly lower in the Sébastopol stone than in white Tuffeau with an increase of the

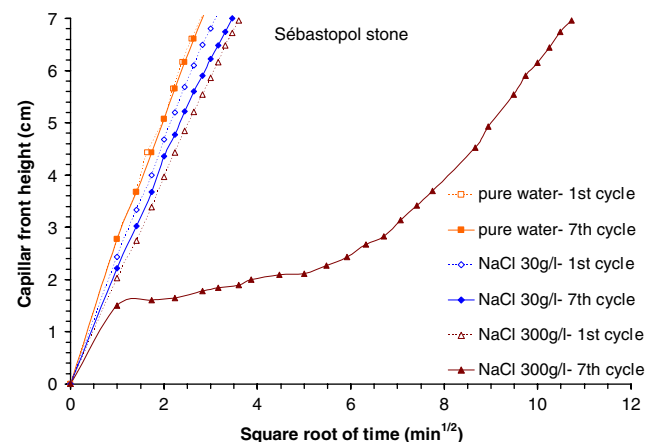
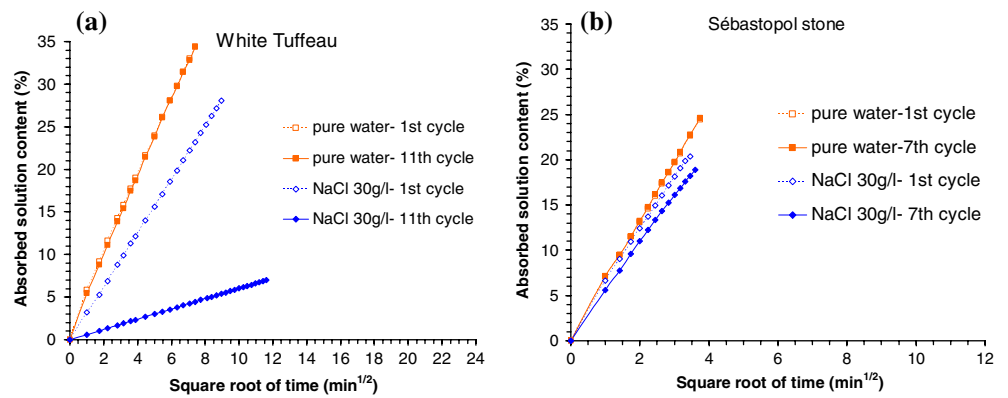


Fig. 6 Imbibition curves at 1st cycle and at the last cycle for Sébastopol stone

Fig. 7 Absorbed solution content for the solution of weak concentration in comparison with pure water for **a** white Tuffeau and **b** Sébastopol stone



NaCl concentration in the first cycles of imbibition. This behaviour can be attributed to the increase of viscosity and density of the absorbed solution. After 11 cycles, the absorbed solution content is strongly reduced in the Tuffeau when the imbibition is carried out with a concentration of 30 g L⁻¹ of NaCl. This could be explained by the relatively uniform distribution of salts in the stone. On the other hand, in the Sébastopol stone, the low NaCl concentration does not seem sufficiently strong to modify the pore size distribution and consequently the imbibition curve (Fig. 8).

For the high concentration of NaCl (i.e. 300 g L⁻¹), two distinct slopes on the imbibition curves for the two limestones can be observed: a first part corresponding to a depth of a few centimetres (remarkably low imbibition rate) and a second part corresponding to the rest of the stone (low imbibition rate) (Figs. 8, 9). The first slope reveals the strongly deteriorated zone of the face that was subjected to a number of imbibition cycles where salt accumulates and the second slope

represents the less deteriorated zone in the depth of the stone where the pore-size distribution is not significantly affected.

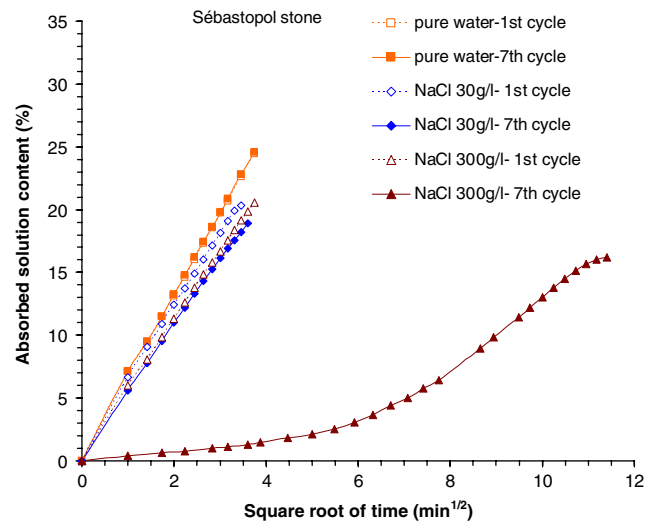


Fig. 9 Absorbed solution content for Sébastopol stone

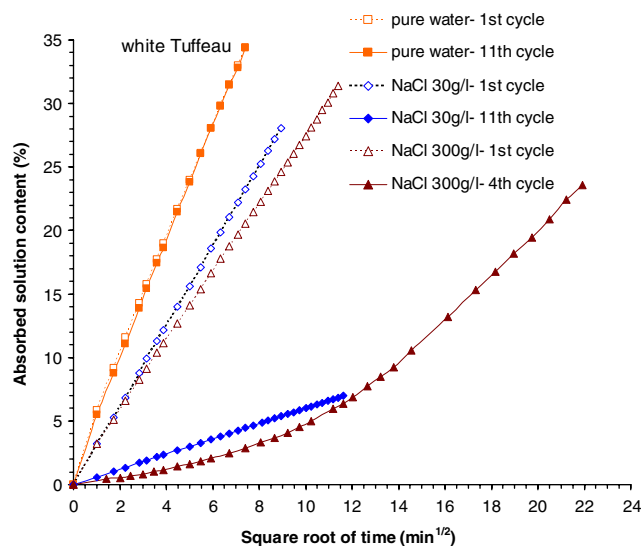


Fig. 8 Absorbed solution content for white Tuffeau

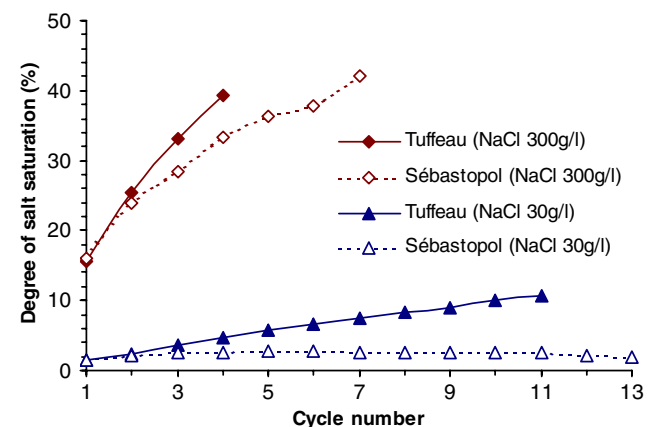


Fig. 10 Degree of salt saturation according to the cycle number in comparison between white Tuffeau and Sébastopol stone

In addition, it can be observed that the absorbed solution represented in terms of absorbed solution content is significantly different in each cycle.

Absorbed solution content

$$= \frac{\text{absorbed solution mass}}{\text{initial mass of the dry sample}}$$

It should be noted that only the initial cycles and end cycles are presented for the two limestones in this paper. The imbibition coefficients of pure water are higher than that of other solutions. Due to this reason, pure water has a high mobility to fill the pores relatively easily and more efficiently than salt solutions during the later stages of imbibition. This behaviour can be attributed to the intrinsic characteristics of pure water such as its low viscosity and higher superficial tension.

Figure 10 summarizes the evolution of the crystallized salt in terms of the degree of salt saturation in the samples with the number of cycles. The degrees of salt saturation are important and increase more quickly with the higher concentrated solutions of soluble salt. A slight increase in the degrees of saturation can be detected in the two limestones tested with low concentrations of NaCl (i.e., 30 g L⁻¹). The degree of salt saturation for the Sébastopol stone is rather stable and has a relatively low value of 3%. However, the degree of salt saturation of white Tuffeau increases significantly with each cycle and reaches 10% by the time it is subject to last applied imbibition cycle. On the other hand, the cycles which are carried out with the highest concentration of NaCl (i.e., 300 g L⁻¹) contribute to large increases in degree of salt concentration associated with significant deterioration of the tested samples. This behaviour is more predominant in white Tuffeau and less in the Sébastopol stone. Such a behaviour can be explained by different intrinsic characteristics: mineralogical composition, pore-size distribution, and specific surface. Microporous nature is predominant in white Tuffeau and hence it absorbs the solution by capillarity rather easily. On the other hand, Sébastopol stone is macroporous in nature and hence absorbs less solution in comparison to Tuffeau. Moreover, the specific surface of white Tuffeau is relatively large and is about 20 m² g⁻¹ while that of the Sébastopol stone is approximately 0.8 m² g⁻¹. More salt is absorbed around the particles having higher specific surfaces. Consequently, pores are partially filled by salt during imbibition cycles which reduces the adsorbed solution by capillarity.

The presence of salt within the stone induces crystallization pressure in the pores at the microscale level

(Scherer 1999; Rijniers et al. 2005) and tends to collapse (deteriorate) the stone at the macroscale level (Theoulakis and Moropoulou 1997; Moropoulou et al. 2003). For a porous material, such as the tested limestones, this pressure depends on the quantity of salt present inside the pores. Figure 10 shows that the degree of salt saturation changes with the number of imbibition cycles. Therefore, investigations of the relation between the degree of salt saturation and the filling of the pores are essential in order to calculate more pertinently the value of the crystallization pressure. This information is not only useful to predict the long-term behaviour of materials but also to diagnose deterioration behaviour of the building stones. These investigations are in progress and not presented in this paper.

The zones near the surface of the samples for white Tuffeau and Sébastopol stone are analysed using SEM at the end of imbibition-drying cycles with a soluble salt solution of NaCl equal to 300 g L⁻¹. The SEM photographs qualitatively show the modifications of the morphology and also the topology between a fresh sample and an altered one for the two stone types (Figs. 11, 12).

Important changes in the structure can be observed between the tested samples and the fresh samples (Figs. 11a, 12a) particularly for the white Tuffeau. Salt was found to be deposited within the pore spaces in white Tuffeau (Fig. 11b, c). This behaviour can be explained by a wetting stage during which the soluble salt solution fills the pores. However, during the drying stage, water evaporation takes place so that the NaCl crystallizes within the pore spaces. The presence of salt can also be observed on the particle surfaces (Fig. 11c, d).

In the sample of Sébastopol stone cycled with soluble salt solution of NaCl with 300 g L⁻¹, pores larger than approximately 0.5 mm were not more observed (Fig. 12b). This indicates that pore filling by salt is active. However, pores of diameter about 0.2 mm still exist (Fig. 12b). As discussed previously, the Sébastopol stone has a homogenous structure; consequently, salt crystals are uniformly distributed in the pore spaces and on the surface of calcite or quartz (Fig. 12d).

The skeletal densities are measured in the different fractions of tested samples at a different depth (Fig. 13) during the last cycle. This information is useful to determine the degree of salt saturation depending on the depth of the tested sample with soluble salt solution of different concentration (i.e., 30 and 300 g L⁻¹). These values are useful to understand quantitatively the distribution of salt inside when the

Fig. 11 SEM photographs for white Tuffeau **a** fresh samples and **b, c** tested samples with 300 g L^{-1} of NaCl solution, and **d** EDX analysis

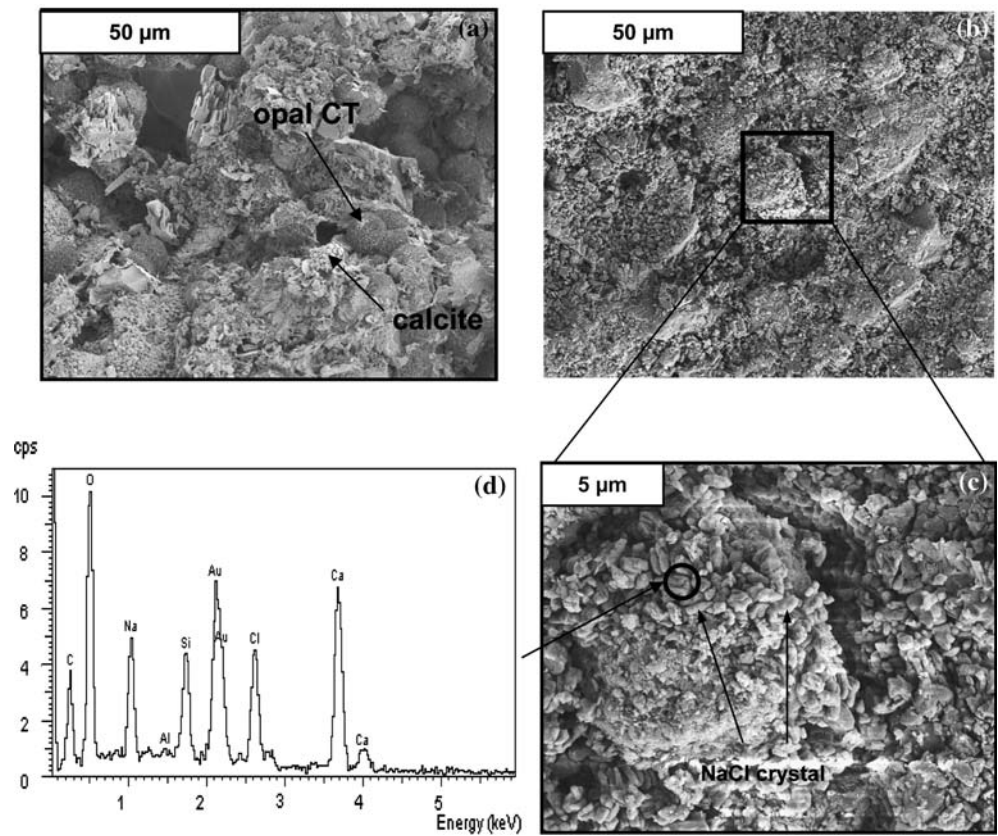
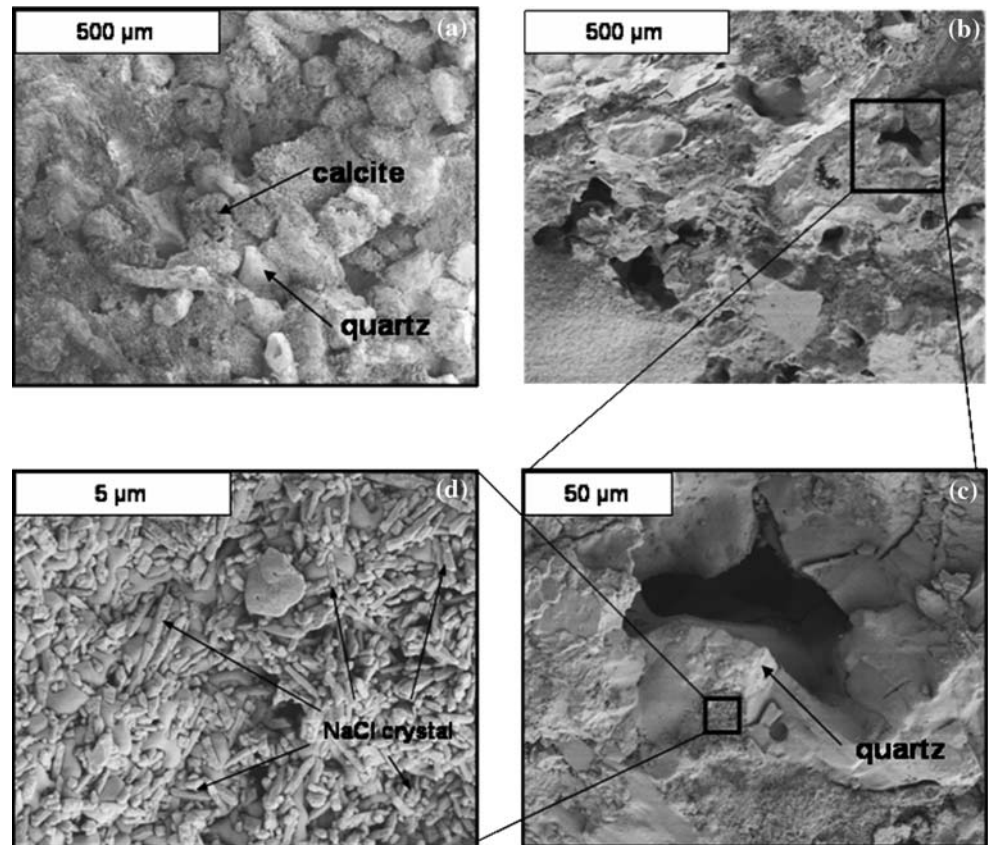


Fig. 12 SEM photograph for Sébastopol stone **a** fresh samples and **b–d** tested samples with 300 g L^{-1} of NaCl solution



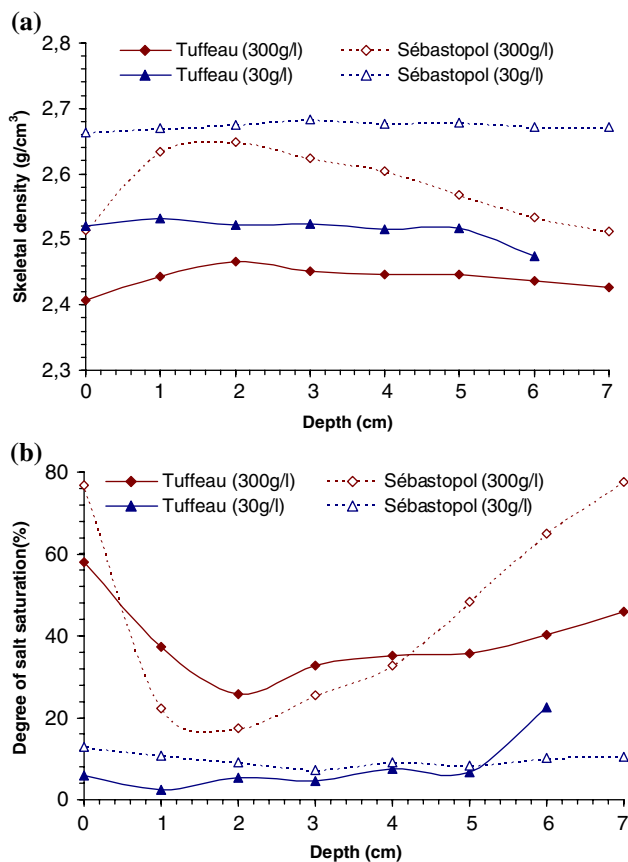


Fig. 13 **a** Skeletal density and **b** degree of salt saturation depending on height of the sample for white Tuffeau and Sébastopol stone

samples are subjected to different imbibition cycles. From Fig. 13 it can be clearly observed that salt concentration is higher in a 1 cm deep zone near the cycled surface (depth = 0 cm in Fig. 13). The difference between the curves of NaCl concentrations of 30 g L⁻¹ and that of 300 g L⁻¹ at each depth is important for both the Tuffeau and the Sébastopol stone. These data confirm results obtained from mass measurements during imbibition-drying cycles (Fig. 11). The salt distribution is more uniform along the depth of the sample for the Sébastopol than for the white Tuffeau when the lower salt concentration of 30 g L⁻¹ is used.

For the high salt solution 300 g L⁻¹, the NaCl seems to be inconsistently distributed along in the length of the sample. Just behind cycled surface, in the zone of 3–4 cm depth, the salt concentration first drops and then increases in the last few centimetres of the sample. This behaviour can be explained by the protocol used in these tests: complete imbibition and complete drying (105°C). During imbibition, a significantly large quantity of salt is imbibed in the pore spaces of the stone by convection. During drying, the majority of

water is eliminated by diffusion. The time necessary for the imbibition and mainly for the diffusion increases greatly with each cycle applied. The elapsed time for the imbibition in the last cycle is about five times that of the white Tuffeau in the first cycle. And, for the Sébastopol stone, imbibition takes ten times in the last cycle in comparison to the first cycle. For complete drying, the Tuffeau sample needs about 1 month and the Sébastopol stone needs about 1 week at the last applied cycle (the drying time is about 2 days for both the two stones in the first cycle). During this period, salt present in the last centimetres (close to depth = 7 cm in Fig. 13) of the sample has sufficient time to crystallize and so the concentration increases with imbibition-drying cycles.

This behaviour may not be fully representative of what happens in the monuments under environmental conditions where imbibition is generally partial and concerns mainly 2–4 cm from the exposed surface of the stone, and drying occurs under a temperature always less than 105°C. Moreover, salt concentration in field situation is generally lower than those applied in these tests. However, the studies presented here demonstrate how weathering tests may demonstrate the ways in which salts can have a significant influence on the deterioration of the monuments.

Conclusion

Various types of deterioration find their origins in an excessive NaCl concentration within the pore structure of limestones. In this paper, imbibition-drying cycles are carried out on two limestones having similar total porosities. For the two limestones, imbibition and drying rates depend directly on the pore size distribution. The kinetics of absorption changes strongly according to the number of applied cycles and the concentration of the soluble salt solution used during imbibition. Imbibition coefficients of the Sébastopol stone are close to twice the values of the white Tuffeau. This behaviour is mainly due to capillary pores larger in the Sébastopol stone than in Tuffeau. The total amount of adsorbed solution depends on the total porosity and the mineral composition of the stone. Due to this reason, at the end of imbibition, Tuffeau absorbs more salt solutions than Sébastopol stone.

The kinetics of capillary absorption and water desorption during drying seems to be a key parameter that should be considered in understanding the mechanics of deterioration. In Tuffeau stone, where pore sizes are multimodal and kinetics are lower than in Sébastopol stone, deterioration occurred even at low

concentration levels of NaCl. In the Sébastopol stone, the low NaCl concentration does not seem to have significant influence in modifying the pore size.

These results can be related to the in situ observations of the type of deterioration of these two stones: physical deterioration in Sébastopol (water transfers quickly through stone and so less salt crystallizes inside pores) and physicochemical deterioration in white Tuffeau (water transfers slowly through the stone and so salt crystallizes inside pores).

Skeletal density measurements based on the mass and height measurements of the samples allow the quantification of the distribution of salt inside the stones due to applied imbibition cycles. Finally, SEM observations provide information about salt deposition and how the structure of the samples is altered due to the influence of imbibition cycles.

The SEM photographs qualitatively show the important modifications of the morphology and the topology between fresh samples and the two stones that were subjected to different imbibition cycles with a high concentration of NaCl (i.e. 300 g L^{-1}). SEM images show that more salt is absorbed around the particles having higher specific surfaces ($20 \text{ m}^2 \text{ g}^{-1}$ for Tuffeau and $0.8 \text{ m}^2 \text{ g}^{-1}$ for Sébastopol stone). As discussed previously, the Sébastopol stone has a homogeneous structure; consequently salt crystals uniformly distribute in the pore spaces and on the surface of calcite or quartz. The presence of salt can also be observed on the opals CT which has a spherical form that is very favourable for salt deposition.

Filling pores with salt within a porous stone depends on the conditions of application: temperature, relative humidity, evaporation rate, and on the intrinsic characteristics of the stone (physicochemical properties, structure and texture) and finally on the concentration of the salt solution. A better understanding of the movement of water and salts during evaporation (drying stage) is required to explain salt weathering for different materials and ambient conditions. The degree of salt saturation changes depending on the number of imbibition cycles (i.e., no of cycles). Therefore, prior investigations are necessary to understand this relationship. This information will be useful to predict the long-term behaviour of the materials and also to identify how building stones deteriorate.

There were some interesting observations from the study undertaken on the two stones, white Tuffeau and Sébastopol: salt concentrates highly in the extreme end of the stones (opposite side of the cycled surface). This can be attributed to the protocol used in these tests: complete imbibition and complete drying at 105°C which ultimately is not a realistic or practical repre-

sentation of environmental conditions. Structures are subjected to variable environmental conditions during their life. Accelerated weathering laboratory tests provide only some indication to understand how different parameters influence in the deterioration of the monuments. To this end, it is advisable to control the dominating parameters such as humidity, temperature, and ambient air rate during the imbibition-drying cycles and to follow continual changes caused within material at the macroscopic level as well as at the structural and textural level based on the information derived from accelerated weathering tests.

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