"Effect of mixed vs single brine composition on salt weathering in porous carbonate building stones for different environmental conditions"

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Abstract

The influence of different factors, brine composition, environmental conditions and pore structure, on salt weathering of porous carbonate building stones is investigated. The main goal of this study is to highlight the differences in weathering between single salts and a mixture of different salts. Two kinds of weathering mechanism are studied, the crystallization pressure and the deliquescence/recrystallization process. To achieve this purpose wetting and drying cycles and cycles varying relative humidity on samples containing salts were performed. The effect of total salt content with different salts and mixtures is simulated by weathering tests with solution of different compositions (NaCl, 6% in weight, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, 6% in weight, CaSO_4 at saturation, and a mixture of them at total concentration of 6.2%). Weathering tests were performed at room temperature and 50°C and under low and high relative humidity.

The results show that the final weathering depends on a complex combination of three parameters: (i) environmental conditions, (ii) salt composition and (iii) petrophysical properties of stones, and general conclusions on the impact of each parameter can be drawn. An important result is that salt mixtures have a lesser impact on weathering during crystallization cycles: single salt brines, especially sodium

sulphate, produce more weathering than complex brine compositions during wetting and drying cycles. Conversely during variations on RH, samples with salt mixtures suffer more damage than samples weathered with a brine of single salt composition.

1. Introduction

Salt crystallization is one of the most dangerous weathering agents in monumental stones. Salts are always present in any environment, natural or anthropogenic and under any climatic conditions. The composition of these salt is very variable (Goudie and Viles, 1997) and depends on many different factors such as proximity to sea; actual and historical air, soil and water pollution; mineralogical and chemical composition of affected materials, i.e. not only the studied material but also other materials such as mortars, cements, metals, etc. in contact with it. The behaviour of salts depends very much on the environmental conditions, mainly temperature and relative humidity (RH) that control the stability of phases present in the stone. For example, natural cycles of RH variations can cross the equilibrium curve between thenardite (anhydrous sodium sulphate) and mirabilite (sodium sulphate decahydrate) which is probably one of the most important causes of damage in natural rocks or in building materials (Steiger and Asmussen, 2008). Other salts such as gypsum can dehydrate to less hydrate or anhydrous salts but this reaction occurs on a geological time scale and therefore, phase changes of this species do not contribute to building stone weathering. Nevertheless, the importance of gypsum as a deterioration factor over time is recognised (Charola et al., 2007).

Material properties are also important, not all stones react in the same way under the action of one weathering agent. Benavente et al (2007) summarized the factors controlling salt weathering in porous materials as pore size and porosity, nature of the salt, transport properties of the solution in pores and strength and the material's resistance to crystallisation pressure.

Laboratory studies in salt crystallization impact on construction materials began more than a century ago. In 1824 the "Annales des Mines" published a note about the work done by M. Brard to determine if construction materials are vulnerable to frost action. To simulate the effect of water solidification,

stones, bricks and other materials were saturated with different salt solutions and it was found that the Glauber salt (sodium sulphate) produced the “best” results. Research concerning monumental stone durability began in the 1920s and 1930s to identify the role played by soluble salts on the degradation of building materials (West, 2000).

The most studied salt is sodium sulphate even if other salts have been tested as well. An extended bibliographic review of crystallization tests with sodium sulphate can be found in Steiger and Asmussen (2008). Other salts used in laboratory tests are sodium chloride (Rodriguez-Navarro and Doehne, 1999; Desarnaud, 2014), magnesium sulphate (Espinosa-Marzal and Scherer, 2013; Ruiz-Agudo, 2007), gypsum (Menéndez and David, 2013), etc. In nature and monuments a combination of different salts is usually present.

The weathering caused by salt crystallization in nature is a complex process also involving the action of different aqueous salt mixtures together with frost. McGreevy (1982) performed frost cycles in samples saturated by saline solutions of sodium chloride, sodium sulphate and magnesium sulphate and found that freezing of NaCl solutions is more destructive than freezing of sodium sulphate solutions.

Only recently has the behaviour of salt mixtures been investigated in laboratory. Sawdy and Heritage (2007) studied crystallization of binary salt mixtures in non-porous media. The authors combined nitromagnesite ($\text{Mg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$) and halite (NaCl) with nitratite (NaNO_3), niter (KNO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The obtained salt mixtures were exposed to different relative humidity, below and above their equilibrium RH at room temperature, and the mass variation was registered. After 2 hours under RH above the equilibrium, all samples had undergone some degree of deliquescence but none were completely dissolved. They concluded that in comparison to single salts deliquescence/dissolution rate increases, deliquescence began when the RH was above the lowest individual equilibrium RH of salts in the mixture and the evaporation rate decreases.

Lopez-Acevedo et al (1997) investigated the salt weathering of two calcareous stones with different salts and salt mixture compositions: sodium, potassium and magnesium sulphates. Their experiment

consisted in a continuous capillarity rise of salt brines without any control of environmental conditions. They observed differences in the weathering patterns as a function of the employed salt with efflorescences for sodium and magnesium sulphates and subflorescences and crusts for potassium sulphate.

Cardell et al (2008) carried out capillary rise crystallization tests with different sulphate solutions (Ca, Mg, Na, K) and with binary mixtures of them in a limestone. They observed differences in the weathering pattern depending on the salt composition. Calcium sulphate did not produce any apparent weathering, magnesium sulphate caused a hard crust on the lower part of the wet stone, potassium sulphate created a hard film on the surface of the sample and sodium sulphate caused granular disintegration and efflorescences. Mixed solutions only produced a thin crust on the surface. They found that single salt solutions cause more damage than do mixed brines.

De Clercq et al (2013) performed crystallization experiments in two limestones with two different brine compositions, a first one composed of sodium sulphate and nitrate and a second one composed of sodium and potassium sulphate. The RH conditions were sustained at 50% and 85%. They found different mineralogical compositions of efflorescences depending not only on the nature of the solution but also on the type of stone, mainly on their porosity and evaporation rate. They concluded that crystallization behaviour of mixed salt solutions in porous materials is more complicated than in bulk solutions.

Lindstrom et al (2015) studied the behaviour of salt mixtures of NaNO_3 and Na_2SO_4 in sandstones with comparison to simple salt behaviours. Samples previously saturated with salts were exposed to wetting and drying cycles with pure water. Among many other results they found that NaNO_3 is the least damaging salt and Na_2SO_4 the most damaging one. Tests with salt mixture were not in accord with previously obtained results in solution droplets. The authors suggested that more research should be done.

Investigation of the behaviour of salt mixtures equilibrium models provides an extremely useful tool for predicting crystallization behaviour as a function of brine composition and environmental

conditions. The results can contribute to define the safe ranges of climatic conditions for the optimal conservation of objects (Steiger and Heritage, 2012).

To summarize it has been recognized that salt crystallization weathering on stone with salt mixtures is different from weathering when only one salt is concerned. Cardell et al, 2008 reported that salt mixture produces less damage than single salts. To test the effect of salt mixture versus single salt on salt crystallization weathering a mixture of three salts: NaCl, Na₂SO₄ and CaSO₄ was used to perform accelerated ageing tests. The obtained results were compared to those obtained for the same kind of experiments but performed with a single salt. Other parameters considered in this paper are the temperature and relative humidity. Salt cycles were performed under two different RH conditions (high and low) and two different temperatures (20°C and 50°C). Low relative humidity values are different for the two temperatures due to experimental limits, 45% at room temperature corresponding to the room RH and 5% at 50°C, relative humidity in the oven.

The two principal mechanisms of salt weathering are crystallization pressure and phase transitions. Crystallization pressure plays an important role during brine evaporation and precipitation of salts. To test this mechanism wetting and drying cycles were performed under environmental conditions given above. To test the effect of salt phase transitions RH variation cycles were performed at 50°C and room temperature. The brine concentrations for all the tests were always around 6%, except for calcium sulphate (0.2%). The obtained results allow a better understanding of salt weathering phenomena under real conditions where salt mixtures are present.

2. Materials

Three different calcareous stones used in the construction of monuments in the NW of France, but also in other regions and countries were tested in this study. The selected stones are Lutetian limestone (“roche fine” variety), Vernon chalk and Caen limestone (“demi-ferme” variety). These stones were chosen due to their similar mineralogical composition (calcite) with different microstructure and pore size distribution.

Lutetian limestone (Fig. 1a) used in this study is a middle Lutetian limestone from the Saint Maximin quarry (Rocamat company) known as “Roche Fine”. The Lutetian formation has different stratigraphic levels with very different properties [Angeli et al, 2007; Fronteau et al, 2010; Vazquez et al, 2015). The selected variety is a homogenous yellowish limestone without macroscopic fossils and with brownish spots (ferruginous oxides). It is a detritic limestone formed by accumulation of calcite grains and foraminifers (Moreau, 2008). Macroscopically, numerous small pores can be observed (Noel, 1970).

Vernon stone (Fig. 1b) is a hard white Santonian chalk, probably equivalent to the Newhaven Formation in Great Britain. The selected samples correspond to the “Gros lien” level and come from the Vernon quarry (TERH company) in Vernon. It is a white stone with small black dots (manganese oxides) and flint nodules. The flint nodules can reach several tens of centimetres but in the studied samples their maximum size was only few centimetres. This stone underwent a complex diagenetic history through a dolomitization and dedolomitization process (Blanc, 1990).

Caen stone (Fig. 1c) samples come from the Cintheaux quarry (Societe des Carrieres de la Plaine de Caen) and correspond to the “demi-ferme” variety. It is a middle Bathonian light yellow limestone composed of lime sand (bioclasts and pellets) with calcite cement (Blows et al, 2003). Small pyrite crystals are locally present, producing an oxidation halo of rusty staining (Palmer, 2008).

Mineralogical analysis obtained by X-ray diffraction showed that the main mineral is calcite for the all three rocks with some quartz (~10%) in the Lutetian limestone.

Fig. 1. Studied stones: a) Lutetian Limestone, b) Caen Limestone and c) Vernon chalk. Left magnified lens image (width of the images is 3.5 mm). Centre and right optical polarized light microscope images, parallel and crossed nicols (width of the images is 0.9 mm).

Porosity of the studied rocks is given in Table 1, with mean, maximum and minimum values as well as standard deviation for 16 samples. It can be seen that Lutetian limestone has the highest porosity which is quite uniform for all the samples. Vernon Chalk has an average porosity of 25% but porosity varies very much from one sample to another. This variability can be explained by the presence of flint nodules. Caen limestone has the lower porosity with an intermediate variability compared to the other investigated rocks.

Table 1.
Open porosity of studied limestones

Stone	Mean (%)	Standard deviation	Maximum	Minimum
Lutetian	42.0	0.61	43.8	41.0
Caen	23.1	1.06	24.2	20.9
Vernon	25.0	2.89	30.9	20.5

The three stone have different pore size distributions. Lutetian limestone has the largest pores with a quite unimodal distribution around 12 μ m and a tail towards the smaller sizes (Table 2). In contrast, Caen limestone has the smaller pores with a maximum of 1.6 μ m. Moreover, it contains the largest amount of pores in the range from 0.1 to 1 μ m. Vernon stone has an asymmetric pore size distribution with a maximum at 7.3 μ m and a slightly higher content of bigger pores. One of the samples of Vernon stone presented a different distribution with a bimodal pore size distribution with maxima at 0.02 μ m and 1.6 μ m. This sample has a porosity of 17%- lower than the mean porosity of the Vernon chalk. Since specimens for mercury porosimetry are small, it can be assumed that this sample may contain a small flint nodule and has not been considered in Table 2.

Table 2.
Mercury porosimetry pore size distribution parameters

Stone	Mean	Median	Mode	Standard deviation	Skewness (Pearson coef)	Kurtosis (Fisher coef)
Caen	2.94	0.77	1.54	13.85	0.11	-0.78
Lutetian	11.04	9.34	12.66	18.50	-0.09	-1.33
Vernon	8.22	6.20	7.27	14.78	0.06	-1.58

Capillary properties of stones play an important role in salt weathering studies because salt brine usually gets into the building by capillary forces. Standard capillary tests were done on cubes of size 4x4x4cm. Furthermore, 4 vertical faces were monitored in order to obtain the evolution of water front in time. Capillary coefficients (C, in kg/(m²s^{1/2})) are very different for each stone: Lutetian limestone has an extremely high C of 1.15, Caen stone has a C equal to 0.097. These two stones are quite homogeneous and curves for different samples are very similar. In Vernon stone two different trends

can be observed, the majority of samples have mean C equal to 0.61 whereas one sample presents a capillary imbibition lower than the others, with a mean C equal to 0.022. Looking in detail, two different slopes were found in all the samples of Vernon chalk (V0, V1 and V2). The mean C can be decomposed into two different coefficients (C_1 and C_2) because during the first 30 min the imbibition is faster (C_1 is equal to 0.073 for V0 and V2 and to 0.031 for V1) whereas the rate of further imbibition decreases and C_2 is equal to 0.035 for V0 and V1 samples and to 0.017 for V2 sample.

In order to quantify the capillary rise anisotropy the height of the different faces was measured on recorded images. The water front was white flat and regular for Lutetian and Caen limestones. Based on the results it can be pointed out that Lutetian stone takes all the water in less than 2 minutes and that the capillary front in Vernon is quite irregular, capillary rise significantly varies between different faces of one sample.

3. Methods

3.1 Crystallization cycles

Nonstandard salt crystallization tests were performed to investigate the influence of brine composition and environmental conditions on salt weathering. Special interest was paid to the differences between single salt and salt mixtures behaviour during salt crystallization in porous media.

To simulate as closely as possible real conditions non classical cycles were used. Different samples were tested at different experimental temperature and relative humidity conditions. For some samples cycles were performed at room temperature and for others at 50°C and at both temperatures, for some samples RH was kept low and for others high. Cycles (Fig. 2) were the same for all the samples with two levels of cycles, cycles of one week and inside these, one-day cycles. At the beginning of the one week cycles, samples were wetted with brine by capillary imbibition for four hours. After this procedure samples were dried for three days. Everyday from day 4 to 7, after a cooling period of two hours for samples dried at 50°C, they were vaporized with brine. Tests at room temperature were performed inside vacuum bells, opened for low RH and closed with water on the bottom for high RH. Temperature and RH were continuously recorded as they were not precisely controlled. Both

parameters are quite constant during cycles without significant fluctuations. For tests performed at 50°C samples were placed into a climatic chamber for high RH and into a cooling oven for low RH. Table 3 shows the environmental conditions for all the samples. To avoid thermal shocks before and after imbibition at 50°C, temperature was decreased and increased slowly. The cooling oven unfortunately does not control temperature very precisely and 5°C fluctuations around fixed temperatures were observed.

Fig. 2. Schematic representation of salt weathering cycles

Table 3.
Environmental conditions for crystallization cycles and duration of the cycles.

	Room temperature		50°C	
	a) High RH	b) Low RH	c) High RH	d) Low RH
Temperature (°C)	20	20	50	50
Relative humidity (%)	90	45	90	5
Number of 1 week cycles	12	12	4	4

3.2 Brine composition

Different brines were used for capillarity imbibition and vaporization. For the experiments corresponding columns a to d of Table 3, each sample was wetted by a different brine composition (always the same for the same sample), NaCl, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, CaSO_4 or a mixture of the three salts. The concentration of the CaSO_4 brine was kept constant at saturation (CaSO_4 0.01 mol/kg), whereas NaCl and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ concentrations were increased during cycles, from 1.5% in weight during the first week, to 3% the second week and finally to 6% (NaCl 1.03 mol/kg; Na_2SO_4 0.19 mol/kg) for the rest of the cycles. For the brine with all three salts, the total concentration in weight is almost the same as the one of the single salt brines (6.2%). The low concentration of sodium sulphate in relation to NaCl was chosen due to their known differences in weathering capacities. Samples were tested at 50°C and room temperature and under low and high RH as explained before.

3.3 Relative humidity cycles

At the end of the series of one-week cycles with brine supply by capillarity imbibition and vaporisation all the samples followed new cycles where only RH conditions varied between low and high, first 15 two-days cycles (one day high RH, one day low RH) followed by 20 two-week cycles (one week low RH, one week high RH). Two-day cycles were not enough to allow real weight differences. For samples at 50°C during the initial two-week the high RH was set to 80%, after that it was raised to 90% as 80% was not enough to produce significant changes on the samples.

3.4 measurements

During the crystallization cycles samples were weighed at different times, before and after capillarity imbibition and before and after vaporization. The employed balance has a precision of 0.01g. During relative humidity cycles samples were weighed at every change of RH conditions. One to several pictures of every sample were taken before every wetting (capillarity or vaporization) for the crystallization cycles and every time RH conditions changed for the relative humidity cycles.

4. Result

Two kinds of results were obtained, mass evolution during cycles and visual observation of weathering. Investigation of salt distribution in tested stones was performed in scanning electron microscope equipped with X-ray detector enabling determination of different phases. For tests at room temperature (columns a and b of Table 3) one sample was always used for each humidity condition/brine composition due to the amount of different possibilities (3 stone types*2 RH*4 brine composition = 24 samples). At 50°C (columns c and d of Table 3) two samples per humidity condition/composition were tested. The samples were named according to the following code, the first capital letter corresponds to the stone (C, Caen; L, Lutetian, V, Vernon), after that the temperature is indicated (20 for room temperature and 50 for 50°C) and finally the RH conditions (D, dry, for low humidity and W, wet, for high humidity condition). Samples were weighed before and after imbibition or spray (vaporization).

4.1 Drying and wetting cycles at room temperature

The variation of weight with crystallization cycles can be observed in Fig. 3 during the twelve one-week cycles that were performed. The traditional measure of mass increment over original mass was substituted by mass increment over volume of the sample and it was multiplied by 100. The reason for this choice is that with weight/weight calculations for samples of low density, as in this case Lutetian limestone with 1530 kg/m³, values are magnified with respect to samples with higher densities such as Caen, 2060 kg/m³, and Vernon 2000 kg/m³. Several observations are summarized below:

For all stones and salts, samples dried under low humidity conditions (room RH) had lower weight variation than samples “dried” at high humidity. High RH prevents the samples from completely drying even if inside the one-week cycles fluctuations of mass increase are observed. These fluctuations are quite similar for both sulphates and are less important for NaCl and for salt mixture.

It can be seen that for the Lutetian limestone the amplitude of these fluctuations is higher at high RH than at low RH. For Caen Limestone and Vernon stone the variation is the opposite, higher for low RH than for high RH.

273 For samples “dried” under wet conditions, samples imbibed by CaSO_4 brine show fluctuations higher
274 than samples wetted just by water. Under dry conditions these fluctuations were very small, except for
275 Lutetian stone.

276 For tests done with NaCl the only sample that shows a decrease in weight is the Vernon sample under
277 dry conditions. All the others show a slight mass increment. Na_2SO_4 crystallization cycles at high
278 humidity do not produce any apparent change on samples after the initial mass increase produced
279 during the first imbibition by capillarity. Under dry conditions Lutetian limestone showed a slight loss
280 of mass at the end and Caen and Vernon stones suffer clear weight decrease. The most affected sample
281 was Caen limestone. Cycles with CaSO_4 just produced an accumulation of gypsum on samples dried at
282 low RH, especially on the Lutetian limestone.

283 During cycles done with a salt mixture the differences between samples dried at high and low RH
284 seemed less important than in cycles with simple solutions. All the samples dried at low RH showed a
285 beginning in loss of weight. The initial mass increase was more important than for any of the single
286 salt solutions, even if the concentration was almost the same (~6% weight) for all the solutions. For
287 example in Lutetian limestone, the maximum increment of mass was 23% for the complex brine, 15%
288 for gypsum, 16% for sodium sulphate and 20% for halite. On samples dried at high RH no apparent
289 changes were observed.

290

Fig. 3. Mass variation in percentage over sample volume evolution with cycles for samples dried at room temperature and with different brine composition (equal total concentration of 6% except for gypsum solution, 0.2%).

Cycles with NaCl only produced superficial efflorescences on Lutetian stones but a loss of material was observed in Caen and Vernon samples. This loss was more important for Vernon sample than for Caen sample (Fig. 4a). On the weight curves a loss of mass was only observed for Vernon, no apparent mass loss for Caen sample. No significant change was observed on any sample at high RH.

After cycles with sodium sulphate samples presented quite different behaviour as a function of lithology (Fig. 4b), Lutetian samples only showed a slight superficial granular disintegration, Caen limestone presented a more important granular disintegration on the upper face of the sample and Vernon limestone presented irregular behaviour with significant degradation in some areas. Mass loss was more important in Caen samples than in Vernon samples. At high RH Caen and Vernon samples presented efflorescences mainly in the upper side of samples.

306 Cycles with gypsum did not produce apparent degradation on the samples. Only precipitation in the
307 pores that could be observed as a sacaroid brightness and an intensification of colours. In samples of
308 Vernon, oxides stains, which were not present at the beginning of the cycles were observed

309 Samples that followed cycles with the mixed brine did not show any apparent damage, only
310 efflorescences and precipitation of salts on the surface could be seen (Fig. 4c). Caen limestone
311 presented less efflorescences than Lutetian and Vernon stones. Lutetian samples showed two different
312 kinds of efflorescences, one more attached to the surface and another one whiter, less compact and
313 easier to take off. Caen samples presented efflorecence located in the upper half of the sample. Vernon
314 limestone showed efflorescences not uniformly distributed on the sample, they were mainly located in
315 the upper part of the sample and also concentrated on the flint concretion surfaces.

316

Fig. 4. Samples weathered by a) sodium chloride b) sodium sulphate and c) salt mixture at room temperature and low relative humidity conditions.

4.2 Drying and wetting cycles at 50°

Four cycles of one week were done at 50°C, the results of mass evolution with cycles are shown in Fig. 5. Two samples of each stone were tested for each brine and environmental condition. It can be observed that the two samples of the same stone and in the same conditions showed relatively uniform behaviour in almost all the cases. Exceptions were some samples of Vernon limestone and Caen stone weathered by sodium sulphate at high humidity conditions for which one of the samples

showed a large mass decrease on the 21st day. This day the sample lost a piece of stone, producing this marked change in the weight.

It was also observed that samples wetted by NaCl did not show any mass decrease but mass continued to increase until the end of the test. This increase was more important on samples dried at high RH condition than on samples dried at low RH. Samples contaminated by sodium sulphate showed an initial mass increase smaller than samples tested with sodium chloride and after three one-week cycles started to lose mass. The most affected samples were Caen limestone but Lutetian samples revealed also an important beginning of mass loss. Samples tested with CaSO₄ did not show any significant change in weight.

For the samples with the brine mixture only an increase of mass is observed. For all samples dried at high RH this increment was similar to the one of NaCl samples. On samples dried in low humidity conditions Lutetian stone got less salt with the mixture than with NaCl and Caen and Vernon increased their weight more with the complex brine than with halite.

Fig. 5. Mass variation in percentage over sample volume evolution with cycles for samples dried at 50°C and with different brine composition.

344 Generally samples dried at 50°C were more damaged than samples weathered at room temperature
345 even if the number of cycles was much smaller at 50°C. In samples weathered with sodium chloride
346 only efflorescences were observed and these efflorescences were more visible on samples dried at
347 high RH than in samples dried at low RH. In samples wetted with sodium sulphate (Fig. 6) different
348 patterns were found for Caen and Lutetian stones. In Lutetian samples weathering under low RH was
349 more important than under high RH but on Caen stone high RH conditions induced more damage than
350 low RH. Vernon chalk did not show any visible degradation.

351 At low RH Lutetian samples showed uniform degradation all over the surface with the formation of
352 superficial detached layers and important efflorescences whereas Caen samples showed desegregation
353 on the upper surface. At high RH the weathering patterns were different with a blistering phenomenon
354 concentrated on the surface for Lutetian limestone and uniformly distributed desegregation all over the
355 surface for Caen samples.

356 Samples weathered by calcium sulphate showed an accumulation of gypsum on pores at the surface of
357 the samples. This accumulation was more evident on Lutetian limestone than in the others, especially
358 on samples dried at low RH conditions. Samples weathered with the salt mixture did not show any
359 visible degradation, even if the mass increase was similar to those of samples wetted by sodium
360 chloride.

L50D

L50W

C50D

C50W

Fig. 6. Details of samples weathered by sodium sulphate dried at 50°C at low (D) and high (W) relative humidity conditions.

Comparing samples altered at 20°C and 50°C it can be observed that only weathering produced by Na_2SO_4 seems enhanced by temperature increase. In samples weathered at 20 °C after the same number of cycles as samples weathered at 50°C (four one-week cycles) only efflorescences are observed on samples tested under dry conditions. Concerning samples weathered by sodium sulphate at room temperature after four one-week cycles, only Caen samples under dry conditions presented some degradation. On the samples weathered by gypsum or the salt mixture only a few efflorescences were observed at the end of cycles.

Lutetian samples looked more vulnerable to temperature than Caen and Vernon samples. At 50°C Vernon limestone did not suffer any apparent damage with any salt. Different behaviour between Lutetian samples tested at 20°C and 50°C can be explained by the low evaporation rate in this stone. At 20°C after the drying period most of the solution was still in the samples whereas at 50°C the

evaporation was accelerated. This was valid also for the Caen and Vernon samples. Nevertheless, higher evaporation conditions caused little differences among samples tested at both temperature conditions. .

4.3 Relative humidity cycles

In buildings and monuments deliquescence/dissolution cycles can occur on samples already contaminated with salts. To simulate similar conditions, RH cycles were performed on previous weathered samples. In this case phase transitions and deliquesce should be the principal ageing factor. Results of mass variations are depicted in Figs. 7 and 8 for the samples dried at room temperature and 50°C. For the samples at 50°C high RH had been set at 80% for 8 two-week cycles and after it was raised to 90%.

Fig. 7. Mass variation during relative humidity cycles for samples dried at room temperature.

Fig. 8. Mass variation during relative humidity cycles for samples dried at 50°C.

Samples dried at room temperature continue to lose mass during the cycles (Fig. 7), especially in samples weathered by sodium chloride. Visually the most common difference between before and after RH cycles is the appearance of salt efflorescences at the surface of the samples and the superficial degradation suffered by samples weathered with the salt mixture.

For samples dried at 50°C the most significant mass decrease was observed in Caen samples weathered by salt mixture (Fig. 8). Fig. 9 shows the visual variation before and after the RH cycles for samples dried at 50°C. RH cycles produced granular disaggregation in all samples weathered by pure NaCl solution and the appearance of surface efflorescence. In contrast, samples weathered with sodium sulphate, especially Lutetian limestone, lost superficial efflorescences after RH cycles. All samples weathered with salt mixture suffered real degradation during the RH cycles. Caen limestone seems to be the most affected one by RH cycles, especially with salt mixtures.

Fig. 9. Samples at 50°C tested with constant global concentration solutions before and after relative humidity cycles.

4.4 Salt mass variation

In order to interpret damage, the salt content added to the samples during each cycle should be determined. Mass increment, after capillary imbibition and after spray was measured for this purpose. The evolution of mass increase during capillary imbibition cycles in samples tested at 20°C is given in Table 4.

Table 4

Mas increase by capillarity absorption at each one week cycle for samples dried at room temperature.

Stone and conditions	Brine composition	Cycle										
		1	2	3	4	5	6	7	8	9	10	11
L20D	NaCl	18.88	14.38	10.96	6.88	4.52	2.81	7.71	5.98	2.39	2.75	4.86
	CaSO ₄	18.74	2.92	3.24	2.01	1.45	1.42	2.81	2.47	0.69	1.10	0.61
	All	17.64	17.05	12.80	11.24	12.93	7.69	13.20	12.71	7.10	8.19	6.20
	Na ₂ SO ₄	21.13	3.57	3.29	3.93	3.77	6.15	5.83	5.67	5.42	4.84	13.89
L20W	NaCl	19.81	19.06	11.92	9.59	5.74	5.29	4.15	4.10	2.48	1.57	4.52
	CaSO ₄	21.41	7.98	4.79	2.91	3.09	0.47	3.47	1.98	1.86	0.33	1.77
	All	19.27	15.85	12.34	7.69	6.22	4.21	10.97	6.80	5.43	7.40	7.38
	Na ₂ SO ₄	19.22	8.47	3.52	4.29		5.77	5.33	2.79	3.37	3.36	9.40
C20D	NaCl	11.58	5.04	4.79	2.83	2.06	1.18	1.27	1.15	0.57	0.48	0.39
	CaSO ₄	11.69	5.36	4.28	9.16	9.45	8.38	7.57	6.80	3.95	3.16	4.77
	All	11.76	8.34	7.21	4.90	2.87	0.99	1.88	1.22	1.04	0.44	1.21
	Na ₂ SO ₄	10.57	7.49	5.98	7.43	6.43	5.64	5.51	4.07	5.45	3.66	
C20W	NaCl	11.86	11.65	10.68	8.49	7.33	6.56	6.27	4.62	3.18	2.57	2.89
	CaSO ₄	11.17	11.62	11.34	11.61	11.57	10.66	11.50	11.38	11.22	11.18	11.13
	All	11.88	12.27	11.15	9.88	7.98	6.89	5.70	5.87	3.79	2.35	3.80
	Na ₂ SO ₄	9.63	12.16	11.65	11.64	11.8	9.61	12.42	11.10	10.06	10.70	10.85
V20D	NaCl	7.88	5.59	4.48	2.61	1.98	1.48	1.42	1.61	1.06	1.12	0.52
	CaSO ₄	6.69	6.06	6.69	7.44	7.50	7.81	7.56	7.51	7.66	7.27	8.05
	All	4.48	6.80	4.73	3.9	2.39	0.67	1.52	1.75	1.43	0.80	2.31
	Na ₂ SO ₄	7.60	8.23	7.39	8.12	7.86	8.39	8.24	6.90	8.16	5.80	9.20
V20W	NaCl	4.59	8.14	7.57	6.53	6.26	6.41	7.53	5.87	5.22	4.24	5.26
	CaSO ₄	6.21	7.65	7.14	7.14	7.05	6.87	7.24	7.16	7.50	7.50	7.29
	All	11.96	12.25	11.71	11.65	10.28	10.01	10.04	10.23	8.94	5.74	9.04
	Na ₂ SO ₄	4.76	7.98	7.08	7.23	6.85	6.78	8.20	7.37	7.38	7.43	7.77

Absorption of solution by capillarity in Lutetian stone tested at 20°C was the most significant at the beginning of experiment (cycle 1). Subsequent mass gain during following cycles gradually decreased up to cycle 4 (NaCl and mixture) or immediately dropped in cycle 2 (Na₂SO₄ and CaSO₄) and remained almost constant till the end of the experiment. The mass gain is quite similar among samples tested at low or high RH. At 50°C and low RH conditions mass gain was also similar for all the tested salt solutions and remained constant during the cycles. At high RH important differences were observed between solutions containing sodium chloride and other salts. In solutions containing NaCl mass gain considerably decreases after cycle 2 but for sodium and calcium sulphates it remains

426 constant. Sodium chloride probably inhibits capillary absorption more than sodium and calcium
427 sulphates.

428 Mass gain in Caen limestone at room temperature decreased also with increasing number of cycles.
429 The depletion was more significant in samples dried at low RH as well as in samples impregnated with
430 NaCl solution at high and low RH conditions. At 50°C the behaviour was similar to that in Lutetian
431 samples with a mass gain almost constant for all samples that decreased after cycle 2 for samples
432 wetted with solutions containing NaCl at high RH.

433 For Vernon samples tested at room temperature mass gain remained constant for samples wetted with
434 sulphates and gradually decreased with the number of cycles for samples wetted with NaCl and
435 mixture solution. This reduction of mass increment was more important in samples dried at low RH.
436 At 50°C all samples presented a similar behaviour, only slight diminution of mass was observed in the
437 samples containing NaCl solution dried at high RH.

438 The mass change in samples impregnated by spraying of salt solutions was also monitored. Mass
439 increments were quite constant during the experiment and the mean values for all cycles are listed in
440 Table 5. The final total mass of salt in each sample was calculated by equation (1)

441
$$\text{Salt Mass} = (\sum \Delta m(\text{capillarity})) + n \times 4 \times \overline{\Delta m(\text{vaporization})} \quad (1)$$

442 where *Salt Mass* indicates the final total mass of salt, $\Delta m(\text{capillarity})$ is the mass increment during
443 capillarity, n the number of one week cycles, and $\overline{\Delta m(\text{vaporization})}$ the mean mass increase during
444 spray.

445

Table 5.
Mass increase before and after spray process for samples dried at room temperature and at 50°C.

RH	Salt	Lutetian	Caen	Vernon	Lutetian	Caen	Vernon
		Room temperature			50°C		
D	NaCl	6.42	1.55	1.39	3.23	1.59	1.48
D	Na ₂ SO ₄	9.06	1.63	1.67	3.75	1.85	1.52
D	CaSO ₄	3.94	1.43	1.80	4.50	2.04	1.52
D	All	2.85	1.49	1.41	4.27	1.82	1.48
W	NaCl	1.55	0.65	0.69	2.83	1.18	1.44
W	Na ₂ SO ₄	2.48	1.06	1.33	3.76	1.44	1.63
W	CaSO ₄	3.17	1.21	1.14	3.73	1.82	1.79
W	All	1.96	0.69	0.55	5.78	1.82	1.52

Total mass gain after all cycles for samples wetted with solutions at equal concentration are listed in Table 6. The Total mass column for mirabilite (Na₂SO₄ 10H₂O) represents mass gain without water molecules.

Table 6.
Total salt mass gain during crystallization cycles for samples dried at room temperature and 50°C.

Solution	Sample	Total mass (g)	Sample	Total mass (g)	Sample	Total mass (g)
NaCl	L20D	21.87	C20D	5.97	V20D	5.46
Na ₂ SO ₄ 10H ₂ O	L20D	11.54	C20D	3.87	V20D	4.06
CaSO ₄	L20D	3.00	C20D	1.05	V20D	1.10
All	L20D	19.24	C20D	12.50	V20D	14.01
NaCl	L20W	9.37	C20W	6.29	V20W	5.87
Na ₂ SO ₄ 10H ₂ O	L20W	4.21	C20W	4.53	V20W	3.63
CaSO ₄	L20W	2.43	C20W	1.35	V20W	1.62
All	L20W	14.40	C20W	14.41	V20W	9.77
NaCl	L50D	7.60	C50D	4.35	V50D	3.65
Na ₂ SO ₄ 10H ₂ O	L50D	3.68	C50D	1.96	V50D	1.56
CaSO ₄	L50D	1.53	C50D	0.78	V50D	0.48
All	L50D	14.55	C50D	7.40	V50D	5.39
NaCl	L50W	5.55	C50W	3.03	V50W	3.38
Na ₂ SO ₄ 10H ₂ O	L50W	3.62	C50W	1.79	V50W	1.31
CaSO ₄	L50W	1.39	C50W	0.74	V50W	0.56
All	L50W	14.58	C50W	6.44	V50W	5.88

4.5 Salt volume model

In order to estimate the volume of crystallized salt in the samples the ECOS-RUNSALT (Bionda, 2005; Price, 2010) thermodynamic model was used. Calculations were performed using 100ml of standard solutions with the original brine compositions and the environmental variations

corresponding to experimental cycles. The obtained results with ECOS RUNSALT are depicted in Fig. 10 for each environmental condition. Drying corresponds to crystallization process after wetting phases. Just after saturation it can be considered that relative humidity in the pores is almost 100% and later it decreases to be in equilibrium with the environmental RH. Legends show the chemical composition of salts without considering their hydration degree. For example changes occurring around RH 77% in the Na_2SO_4 curve at room temperature correspond to mirabilite-thenardite transitions. In the simulation of tests performed at 50°C two different environmental changes were considered, drying and cooling. For tests done at room temperature no cooling period was necessary. To simulate what happens in a particular sample, the obtained amount of substances can be multiplied by the total amount of salt present in this sample. Taking into account these results it seems that the most important volume increases correspond to salt mixture under low RH conditions. The final composition of the precipitated salts given by the ECOS-RUNSALT model is Thenardite ($\sim 2.25\text{cm}^3$), halite ($\sim 2\text{ cm}^3$) and Glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) ($\sim 0.75\text{ cm}^3$). X-ray qualitative mineralogical analysis was performed at the end of the cycles on samples weathered at 50°C and dry conditions and only single salts, halite, thenardite and gypsum, were found.

Fig. 10. ECOS RUNSALT simulations with the employed brines and during the period of change in environmental conditions.

4.6 Microscopic studies on weathered samples

Investigation of salt distribution inside the stone was performed on samples of the series 50D in a scanning electron microscope (SEM, MIRA II LMU, Tescan corp., Czech Republic) equipped with energy dispersive X-ray detector (EDX, Bruker corp. Germany) enabling determination of chemical composition. Several differences can be observed among samples weathered by different salts (Fig. 11 and 12). Sodium chloride crystals are bigger than sodium sulphate ones and are uniformly distributed all over the surface (Fig. 11a et b). Calcium sulphate forms crystal aggregates with bigger crystals than

the other salts (Fig. 11c). On samples weathered by the complex brine a mixture of different salt crystals covers the surface of the sample (Fig. 11d).

Fig. 11. Scanning electron microscopy images of the surface of weathered samples at 50°C and under dry conditions: a) Vernon limestone V50D with NaCl, b) Caen limestone C50D with Na₂SO₄, c) Lutetian limestone L50D with CaSO₄, d) Caen limestone C50D with salt mixture of NaCl, Na₂SO₄ and CaSO₄. On the right the semi-quantitative element analysis of areas 1, 2 and 3 on d) image.

Fig. 12. Scanning electron microscopy images of weathered samples. a) Lutetian stone weathered by NaCl, b) Caen stone weathered by sodium sulphate c) Vernon stone weathered by a salt mixture of NaCl, Na₂SO₄ and CaSO₄. The element mappings obtained by X ray are given on the righthand side of these figures.

500 Element mapping enables determination of salt distribution in the samples. In all the stones sodium
501 chloride was concentrated mainly on the thin superficial part of the samples. Sodium sulphate
502 occurred almost 10 mm in depth in Lutetian and 13 mm in Caen stone, in Vernon stone only a few
503 crystals were detected close to the surface. Calcium sulphate crystals were detected in the inner part of
504 Lutetian sample affected by mixed brine solution (Fig. 12c) and on the surface of the sample exposed
505 to single CaSO_4 solution, where massive crystals of gypsum were observed (Fig. 11c). In samples
506 weathered by a complex brine, element mapping confirmed the presence of salt crystals mainly on the
507 surface of Lutetian and Vernon stones (Fig. 12c) although some salt was identified in the inner part. In
508 Caen stone no superficial deposition was detected by X ray analysis.

509 In general sodium chloride crystallizes along the surface of grains covering them, sodium sulphate
510 forms more extended areas with smaller crystals than sodium chloride. Calcium sulphate forms bigger
511 crystals than the other salts. Fig. 13 shows some details of salt crystals in polished sections. In picture
512 a) halite crystals covering the grain surface can be observed. Picture b) corresponds to sodium sulphate
513 crystal aggregates. Picture c) shows an aggregate of gypsum crystals in a pore. Pictures d) and e)
514 reflects a mixture of salts. No salt completely filling any pore was observed.

Fig. 13. Scanning electron microscopy images of polished cross sections of weathered samples at 50°C and under dry conditions: a) Lutetian limestone V50D with NaCl, b) Lutetian limestone L50D with Na₂SO₄, c) Lutetian limestone L50D with salt mixture of NaCl, Na₂SO₄ and CaSO₄, d) Caen limestone C50D with salt mixture of NaCl, Na₂SO₄ and CaSO₄ e) Vernon limestone V50D with salt mixture of NaCl, Na₂SO₄ and CaSO₄

5. Discussion

Degradation of porous stones is really a complex process depending not only on the nature of the salt and porous material but also on the environmental conditions and their variation. The main observations and outputs of present research are discussed below:

It was observed that during crystallization cycles under identical environmental conditions, samples tested with single brine compositions presented more damage than samples tested with a mixture of salts. These differences cannot be explained by the ECOS-RUNSALT equilibrium model. During RH cycles samples saturated by salt mixtures suffered more damage than those saturated by single solutions and more than during the crystallization cycles. Sawdy and Heritage (2007) stated that

deliquescence/ dissolution rates in salt mixtures increased with respect to single solution, which can contribute to the more significant weathering observed during the RH variation cycles. This fact can also explain the larger amount of salt cumulated in samples wetted with complex brines than in samples dried with single salt solution (Table 6). According to Sawdy and Heritage (2007) the rate of evaporation of salt mixture solutions is slower than in single salt solutions, contributing to the smaller weathering observed during the imbibition/drying cycles in salt mixtures.

Table 7 allows one to compare apparent weathering between samples tested in the same conditions, for crystallization and relative humidity cycles. Samples tested at 50°C are more affected by salts than samples tested at 20°C. In the group of samples tested at 20°C those wetted with sodium sulphate are the most weathered and samples wetted by the salt mixture the least. Samples tested at low relative humidity present more apparent damage than samples tested at high RH. Lutetian limestone is the least affected by crystallization cycles followed by Caen and Vernon samples.

544 Table 7
545 Comparison of the apparent degree of weathering for samples tested in the same environmental
546 conditions. Red indicates the most degraded sample, orange intermediate, yellow the least degraded
547 and white no apparent weathering.

T (°C)	Brine	RH	Crystallization	Relative
			Stone	Stone
20	NaCl	90	L20W	L20W
			C20W	C20W
			V20W	V20W
		45	L20D	L20D
			C20D	C20D
			V20D	V20D
	Na ₂ SO ₄ 10H ₂ O	90	L20W	L20W
			C20W	C20W
			V20W	V20W
		45	L20D	L20D
			C20D	C20D
			V20D	V20D
	Mixture	90	L20W	L20W
			C20W	C20W
			V20W	V20W
		45	L20D	L20D
			C20D	C20D
			V20D	V20D
50	NaCl	90	L50W	L50W
			C50W	C50W
			V50W	V50W
		5	L50D	L50D
			C50D	C50D
			V50D	V50D
	Na ₂ SO ₄ 10H ₂ O	90	L50W	L50W
			C50W	C50W
			V50W	V50W
		45	L50D	L50D
			C50D	C50D
			V50D	V50D
	Mixture	90	L50W	L50W
			C50W	C50W
			V50W	V50W
		5	L50D	L50D
			C50D	C50D
			V50D	V50D

548

549 The amount of solution absorbed by the samples during capillary imbibition or spraying depend on the
550 composition of brine. Brines with sodium chloride were more susceptible to be absorbed than other
551 brines. The volume of solution taken by capillarity decreased with increasing number of cycles, i.e.
552 with increasing salt content in the samples.

553 The weathering pattern also change with brine. Efflorescences of sodium sulphate were concentrated
554 in the zone of evaporation front. Sodium chloride mostly formed a surface crust more or less thick.
555 This fact can be explained by different solubility, sodium sulphate has a solubility almost one order of
556 magnitude lower than sodium chloride, and it precipitates before NaCl, on the evaporation front. It can
557 be seen on samples where Na₂SO₄ efflorescences under room temperature (slow evaporation) were
558 found on the upper surface of samples or following curved evaporation fronts.

559 The results show also that, whatever the salt solutions used in crystallization cycles, larger degradation
560 occurs in Caen and Vernon limestones than in Lutetian limestone. The only exception was Lutetian
561 stone affected by sodium sulphate solution at 50°C.

562 During wetting and drying cycles it can be assumed that the more active damage process is
563 precipitation with the associated crystallization pressure. The pressure can be estimated following the
564 equation proposed by La Iglesia et al (1997) based on the assumption that in an interconnected pore
565 structure with non-uniform distribution of pores, i.e. coarse pores are interconnected with finer pores,
566 salt crystals grow preferentially in coarse pores until they are filled. Subsequent crystallization into
567 finer pores and thus smaller pore entries can develop pressure on the pore wall expressed by equation
568 (2):

569
$$P = 2\sigma (1/r - 1/R) \quad (2)$$

570 where σ is the salt-solution interfacial tension, r radius of smaller pores and R radius of coarse pore. In
571 this work r was obtained by mercury porosimetry and R was estimated from thin sections as the radius
572 of the equivalent circle with the same area as the actual pore surface. The obtained values of r and R
573 are 9.37 μ m and 55 μ m for Lutetian limestone; 0.765 μ m and 40 μ m for Caen stone and 6.20 μ m and
574 40 μ m for Vernon chalk. For each brine composition salt-solution interfacial tension was constant so

the crystallization pressure could be compared for the different stones. Tensile strength for the different stones measured using Brazilian tests is 1.27 MPa for the Lutetian limestone, 2.35 MPa for Caen stone and 5.2 MPa for Vernon chalk. Estimated crystallization pressures, considering a mean σ of $40 \cdot 10^{-3}$ N/m, are $7 \cdot 10^{-3}$ MPa for Lutetian, $100 \cdot 10^{-3}$ MPa for Caen and $13.5 \cdot 10^{-3}$ MPa for Vernon stones. These values are smaller than the tensile strength and cannot explain the observed damage. To have a crystallization pressure higher than the tensile strength, pore radius should be smaller than $0.08 \mu\text{m}$, which is close to the resolution limit of the employed mercury porosimeter. For samples with similar open porosity - Caen (23%) and Vernon (25%) stone, the estimated values of crystallization pressure differ by about 10x factor, which can explain, at least partially, the higher sensitivity of Caen stone to salt weathering. The value of crystallization pressure estimated for Lutetian stone is the lowest one. However, Lutetian stone was at 50°C more prone to salt weathering than Vernon stone. Other factors linked to its higher porosity (42%) and its lower tensile strength can explain this observation. According to technical specifications uniaxial compression strength of Vernon stone varies between 35 MPa and 60MPa, Caen 25MPa and Lutetian 9MPa.

Caen and Lutetian limestones are quite homogeneous while Vernon chalk contains more compact zones, this fact was confirmed on the basis of both irregular capillary imbibition and mercury porosimetry data (pore radius of $0.12 \mu\text{m}$). This heterogeneity is probably caused by various flint content that produces non-uniform weathering as was observed in the sample V20D.

Generally it can be said that cycles performed at low RH conditions produced more damage than those at high RH. The only exceptions are samples weathered by sodium chloride at 50°C , in this case high RH during drying induced more damage than low RH, especially in Lutetian samples.

Concerning the contrasting behaviour between room temperature and 50°C it is possible to state that NaCl is more destructive at room temperature than at 50°C , and the opposite is true for Na_2SO_4 which is more damaging at high temperatures. This phenomenon can be explained by the phase equilibrium curve of sodium chloride, less dependent on temperature than sodium sulphate.

6. Conclusions

The presented data set reflects the complexity of salt crystallization in porous media and highlights the specific influence of various factors inducing degradation in different types of rock. The main conclusions obtained in this study are summarized below:

The obtained results confirm previous studies concluding that brines composed of a mixture of different salts, mainly NaCl and Na₂SO₄, produce less damage during crystallization cycles than single salt solutions. Particularly, it was shown that the presence of NaCl attenuate the damaging effect of sodium sulphate.

Crystallization cycles performed at high RH produced less damage than cycles done at low RH although in the case of samples dried at 50°C and wetted by sodium sulphate this fact was not always verified as Caen limestone showed more damage at high RH than at low RH.

Changes in RH can induce more damage in samples polluted with different salts mixtures than with single salts, contrary to what happen during crystallization cycles.

Different salts crystallize at different depths in sample, for example NaCl precipitates mainly on the surface and Na₂SO₄ on the inner part. This observation can explain the different weathering patterns produced by different salts.

To better understand the complexity of salt weathering in real cases, more research is needed including salts with magnesium, sodium and nitrates in the salt mixtures to be closest to salt composition in monumental stones.

The results of this work can be used to predict salt weathering (past, present and future) from climatic data. Most of the work done until now considers only individual salt behaviour, mainly NaCl and Na₂SO₄, which can induce large errors.

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