SWBSS 2011

19 - 22 October
Limassol, Cyprus

Salt Weathering on Buildings and Stone Sculptures

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ISBN 978-9963-7355-1-8

Salt crystallization effect on the swelling behavior of clayey sandstones

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ABSTRACT

In order to assess the durability of potential restoration sandstones for the cathedral of Strasbourg (France), a comparative study was carried out on Triassic siliceous materials, so called Meules and Vosgien sandstones. During relative humidity variations, dilations were performed before and after salt contamination using two salts, sodium chloride and sodium sulfate, as well as two degrees of contamination on quarry and exposed sandstones. Sandstone behaviors were reversible whatever the salt type: swelling under high relative humidity conditions and shrinking during low relative humidity stages. Sodium sulfate promoted only slight variations of dilation whilst deformation behaviors were greatly influenced by sodium chloride that emphasized the contribution of deliquescence/recrystallization effect. As soon as the salt had been dissolved, a slope variation related to constant swelling during high relative humidity periods highlighted clay-salt interaction due to osmotic swelling. Thus, the dilation method allows determination of salt involvement on dilation behaviors during relative humidity cycles and the discrimination of sandstones.

Keywords: dilation, clay minerals, sandstone, sodium chloride, sodium sulfate

1 INTRODUCTION

Understanding salt damage is a fieldwork of major importance for cultural heritage preservation. According to the usual admitting theory nowadays, when salts are introduced in porous media, the dissolution-crystallization cycles impose a crystallization pressure on pore walls that leads to the continuous degradation of building materials (Flatt 2002, Scherer 2004, Steiger 2005). The volume changes of salt in pore structure has been investigated by dilation experiments (Lubelli 2006, Snethlage & Wendler 1997) which highlighted large variations in the macroscopic behavior of the salt-stone system, summarized as:

- dilation was controlled by salt dissolution associated to shrinkage during the wetting stages whereas swelling was caused by salt crystallization during drying;
- an irreversible residual strain occurred with increasing number of wetting/drying cycles.

Nonetheless, in order to modify macroscopic dilation with relative humidity (RH) cycles, the equilibrium relative humidity (RH_{eq}) of salt had to be exceeded ($RH>RH_{eq}$). This requirement attested that the deliquescence phenomenon of salts in pore structures was the controlling parameter involved in dilation modifications. As shown by Yu & Oguchi. (2010), one salt type can be damaging for one stone type and harmless to other ones. Hence, salt damage is a much more complex mechanism that depends on the stone properties (mineralogy, pore structure, transfer properties and strength resistance), the salt type and the climatic conditions in which each parameter interacts with the others.

The aim of our study was to investigate the first stages of salt weathering of clayey sandstones and the influence of clay minerals in the salt damage mechanism. Assessment of durability was carried out using the dilation method for an increasing salt contamination of sodium chloride (RH_{eq}=75% at 21°C) and sodium sulfate (RH_{eq}: The→Mir~75% and Mir→sol.~92% at 21°C) implemented for isothermal RH cycles. Dilation behavior of sound clayey sandstones was controlled by clay coating that interacts with water molecules. Clay coatings were defined as the amount of clay minerals and the extent of their specific surface that was linked to their nature and textural features (Colas et al. 2010). Moreover, the type of cation on clay mineral surfaces can also influence the amount of dilation (Wangler & Scherer 2008). Thus, there are still open questions on the role of salt-clay interaction in the damage mechanism. Is the dilatometric method able to discriminate the behavior of low salt-contaminated sandstones and to what extent the dilatometric response of clayey sandstone is controlled by either salt contamination or salt type?

2 MATERIALS AND METHOD

2.1 Sound and exposed sandstones

In order to select the most durable quarry stone for restoration and replacement works on the cathedral of Strasbourg (France), five quarry sandstones were studied. The R and L sandstone types were extracted from French local quarries and the G, B and Bj ones came from German quarries. Except the R Vosgien sandstone, all are Meules sandstones (Trias, Buntsandstein). In addition, two exposed Meules sandstones, SO and SA, were chosen for their differences in alteration state and damage speed rate. The earlier the sample was used on the building, the better is the state of its conservation. Hence, the oldest sandstone SO showed a good state of cohesion, whereas the newest one SA (~1900) had suffered from severe delamination.

All the stones were mainly composed of a quartz skeleton and a soft matrix of clay minerals associated with iron oxi/hydroxides located in pores or as a coating surrounding grains. Their open porosity, φ, values (EN 1936) were close ($15\% \leq \varphi \leq 22\%$), as well as their saturation coefficients (Hirschwald 1912), S=0.64±0.03. The structural properties of stones, which were investigated by mercury intrusion porosimetry, enabled to differentiate the macroporous structure of the Vosgien sandstone, represented by a medium pore access radius of 18±1 µm in size, from the finer networks of Meules sandstones which presented medium pore access radii ranging from 3.8 to 7.5 µm.

Clay coatings were extracted following Stokes law using a continuous collecting procedure confirming the clear difference between the small clay content in Vosgien sandstone (3%) and the large clay amount in Meules sandstones (6 to 9%). Clay mineral proportions (Table 1) determined by XRD decomposition procedure (Lanson 1997) were representative of diagenesis conditions in the sedimentation basin, thus discriminating between French and German sandstones, as evidenced by the illite/kaolinite ratio. The large amount of interstratified illite/smectite is characteristic of the Vosgien sandstone (Table 1). Furthermore, the fast decay rate of the SA altered sample was correlated to pure smectite even though this was present in small quantity. The specific surface area (SSA) was measured on the fraction f<2 µm using EGME method (Heilman et al. 1965), thus allowing the assessment of the total surface of clay minerals including interlayer spaces. The SSA varied from 204 to 284 m²/g for all sandstones and was related to the nature and the textural characteristics of clay minerals, especially to the needle clay shapes, illite and interstratified illite/smectite.

Table 1: Characteristics of the clay coatings (*f*<2 µm): weight content (w %), nature and proportion of each clay minerals and specific surface area (SSA) using EGME method.

Clay coating	Content	Nature proportion (%)					SSA
	(w %)	Illite	Kaolinite	I/S	Chlorite	Smectite	(m^2/g)
Quarry sandstones							
R	2,9	19	11	70	-	-	284
L	7	39	46	15	-	-	204
G	5,9	61	11	23	5	-	286
B	5,9	45	29	23	3	-	241
Bj	8,9	49	26	22	3	-	266
Exposed samples							
SO	7,9	23	57	20	-	-	216
SA	8,5	29	50	16	2	2	254

2.2 Salt contamination and dilation method

2.2.1 Contamination procedure

The salt contamination of the cylindrical cores (two sets: 80x40 mm and 60x20 mm) was carried out using the free porosity measurement procedure under atmospheric conditions. The concentrations of salt solutions were calculated in order to reach 0.2 and 0.8% increase in mass of the dried cores; that corresponded to sodium chloride and sodium sulfate concentration solutions of 45 and 180 g/l. After contamination, the cores were oven-dried (60°C) before the dilation measurements.

2.2.2 Dilation cyclic conditions

The dilatometric device was composed of 8 LVDT sensors, a Pt1000 temperature sensor associated with a RH capacitive probe connected to a HP acquisition station monitored with a BenchLink software (5-minutes scanspeed) (Figure 1). The sensors' accuracy (0.3 µm) was calibrated using a 100-µm standard gauge registered at the National Institute of Standard Technology (NIST). Previous stability control of the system versus time allowed estimating a maximal variation equal to 8%.

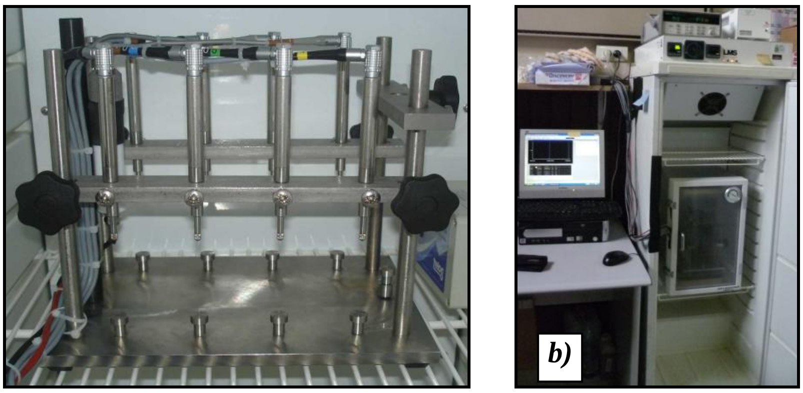

Figure 1: .The dilatometric device. *a)* the 8 LVDT sensors; *b)* the climatic chambers and the acquisition station linked to the computer.

Three successive relative humidity cycles were performed on cores (perpendicular to the bedding planes) before and after salt contaminations. The RH cycles in isothermal conditions were generated using silica gel grains and a K_2SO_4 supersaturated solution. The moisture gradient varied between 5-15% and 85-95% (Figure 2).

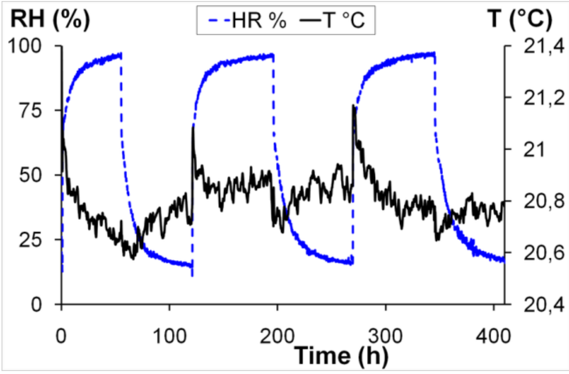

Figure 2: T-RH condition during the three isothermal relative humidity cycles.

3 RESULTS

3.1 Fresh sandstones dilation

RH cycles always promoted swelling under high RH conditions and shrinkage during low RH stages. Dilation carried out on four cylindrical cores for each material showed a rapid swelling or shrinking rate as soon as the RH condition had been modified. Dilation rate decreased progressively with time and water molecule introduction until reaching stabilization equilibrium with the applied T-RH conditions. The total dilation value (TDV) during the RH cycles varied from 0.03 to 0.20 mm/m, and discriminated the sandstone behaviors (Figure 3). The Vosgien sandstone (R) exhibited the lowest swelling behavior while Bj and SA sandstones presented the highest dilation. For different size of cores, although the experimental time to reach swelling stabilization increased with core volume, the TDV was similar and any variations were attributed to the natural heterogeneity of the sandstones.

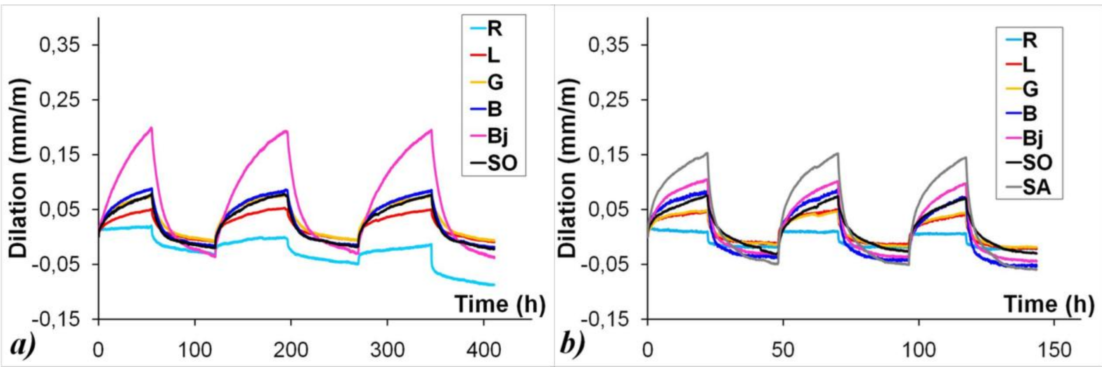

Figure 3: Dilation behavior of sandstones during relative humidity cycles on two cores (length: 8 cm, diam.:4 cm) (a) and two cores of length: 6 cm and diam.: 2 cm (b).

3.2 Dilation behavior of salt-contaminated sandstones

As sandstones showed differences (even slight) in open porosity and were contaminated using the same concentration of salt solution, the real salt content in them varied from one stone to the other (Table 2). Variations in salt contaminations were more prominent for the highest salt concentration, while differences were minimized for the lowest salt concentration. Nevertheless, the salt contamination increase ranged from a factor of 2.5 to 5 between sandstones.

Table 2: Achieved salt contamination for each sandstone type with two concentrated solutions (w %).

Salt contamination (w %)	45 g/l NaCl	Na_2SO_4	180 g/l NaCl	Na_2SO_4
Quarry sandstones				
R	0.20	0.22	1.02	0.89
L	0.22	0.25	0.88	0.87
G	0.15	0.16	0.58	0.59
B	0.17	0.19	0.67	1.07
Bj	0.14	0.15	0.56	0.53
Exposed samples				
SO	0.19	0.19	0.59	0.48
SA	-	-	0.70	0.61

3.2.1 Sodium sulfate

The swelling behavior of sodium sulfate salt contaminated sandstones did not show great modifications whatever the salt content. During RH cycles, the TDV showed no significant modifications with respect to the dilation behavior of fresh sandstone. Sandstones swelled during high RH periods and shrank during drying. For the highest contaminated cores, the influence of sodium sulfate deliquescence might be underlined through a slight change in slope on swelling curves. In addition, a significant change in the kinetics of shrinkage was recorded during drying. The slight delay in the shrinking process could be attributed to salt crystallization (Figure 4).

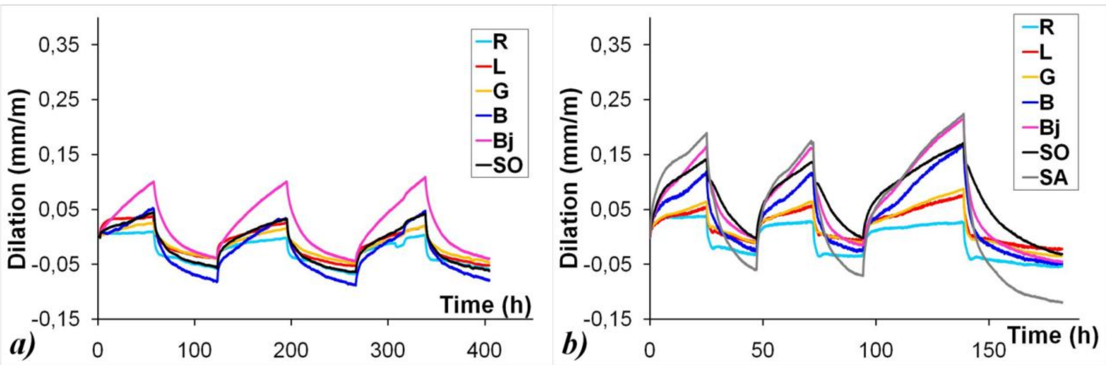

Figure4: Dilation behavior of sodium sulfate contaminated sandstones with increasing salt contamination; (a) 45 g/l solution and (b) 180 g/l solution.

3.2.2 Sodium chloride

The dilation behaviors of NaCl contaminated sandstones were modified both with respect to TDV and curve shapes. With increasing salt contamination, changes in dilation behavior were accentuated. However, the total deformation remained reversible with cycles and no residual strain appeared (Figure 5). The deliquescence/recrystallization cycles of salt were emphasized by dilation during both high and low RH stages. During high RH period, dilation could be divided in four successive stages:

- a rapid swelling for a few minutes as soon as K_2SO_4 supersaturated solution was introduced ;
- the effect of salt deliquescence resulting in a decrease of the dilation rate and a global shrinking of the total structure associated to stress relief;
- as soon as salt was dissolved, salt solution interacted with clay minerals. A slope coefficient could be calculated and this showed good correlation with clay coating characteristics

(SSA*clay content) (r = 0.73±0.01). Hence, the expansion of sandstones was promoted by osmotic swelling;

- in the last period, dilation stabilized progressively with stone-salt system equilibrium with T-RH conditions.

During drying stages, and after an initial rapid shrinking, some sandstone swelled. This swelling occurred due to NaCl crystallization in the porous network and the appearance of stress. Thus, sandstone could be discriminated with NaCl contamination using the dilation method. Only small modifications of the curves were observed for the L, B and in a lesser extent Bj sandstone (Figure 5). On the contrary, deliquescence/recrystallization impact was noticed even for low salt-contamination, on the Vosgien sandstone (R) and G Meules sandstone that were more prone to the NaCl effect. This particularity was more linked to clay mineralogy than salt content. Their higher sensitivity to NaCl deliquescence/recrystallization cycles was attributed to the significant amount of interstratified illite/smectite. Textural characteristics were also suspected to play a role in the salt-clay interaction that determined the growth of the salt crystals, especially the needle shape clays like illite

The two exposed sandstones developed particular dilation behavior. The altered sandstone (SA) was affected by salt deliquescence, whereas salt crystallization was not observed. For the non-altered sandstone (SO), dissolution of salt was also emphasized, while during drying dilation showed a slow continuous shrinkage with time. However, the two sandstones were naturally contaminated by gypsum during their exposure on the monument. Consequently, these two peculiar behaviors with NaCl contamination could arise from possible NaCl-gypsum interactions.

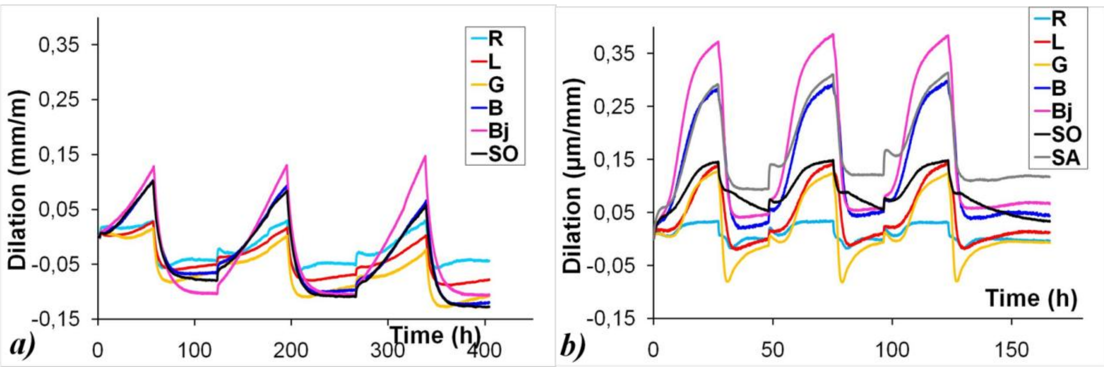

Figure 5: Dilation of sodium chloride contaminated sandstones with increasing salt contamination; (a) 45 g/l solution and (b) 180 g/l solution.

4 CONCLUSIONS

Dilation is a useful method to highlight behavior modifications of sandstones with salt contamination. Almost no modification of dilation was observed with sodium sulfate contamination. Crystallization of this salt could be weakly noticed during drying on highly-contaminated specimens, but did not promote an increase in TDV. Thus, the deliquescence of sodium sulfate did not generate significant dilation modifications with RH cycles. On the contrary, NaCl deliquescence phenomenon led to important changes in dilation behavior that remained reversible and did not develop residual strain with cycles. On both wetting and drying RH periods, deliquescence and recrystallization of NaCl could be highlighted whatever the salt amount. Variations of dilation allowed discrimination of sandstones. Furthermore, osmotic swelling was highlighted on both salt types by the increase of dilation as soon as the salt had dissolved. The increase in TDV on NaCl experiments confirmed the major role of osmotic swelling compared to the opposite effect of crystallization and stress relief with deliquescence of salt crystals.

Based on dilation experiments, both sandstones and salt effects were discriminated. Clay mineral characteristics, nature and proportion, affected salt-clay interactions and their impact on dilation. During RH cycles, sodium chloride greatly disturbed the dilation behavior of sandstones; therefore, we argue that sodium chloride damage may be more serious than sodium sulfate damage under RH cycles; this is in agreement with the findings of Desarnaud et al. (2011).

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