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Salt Weathering on Buildings and Stone Sculptures

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Experimental investigation of the influence of precipitated salts on the liquid transport properties of brick using an organic liquid

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ABSTRACT

The transport properties of porous materials change considerably when soluble salts precipitate in the pores. The porosity decreases, the connectivity between pores and pore size change, the surface properties are altered, etc. Hence, the precipitation of salts has an influence on all aspects of liquid moisture transport such as storage capacity, liquid retention and liquid permeability. One of the difficulties to study these phenomena, are the interactions between water and precipitated salt. In order to obtain information about the influence of the presence of these salts without ongoing precipitation or redissolution, a series of tests were performed using an organic liquid (decane) which is immiscible with water and in which the salts are not soluble. Besides capillary absorption tests, mercury intrusion porosimetry was performed. The substrate is a fired clay brick contaminated with different amounts of NaCl, NaNO₃ and Na₂SO₄. It was noticed that porosity decreases at the lower defined introduced salt content while it increases when the salt content increases because the brick dilates due to crystallisation pressure. Capillary absorption coefficient and capillary liquid content decrease, as is the case for the dominant pore size. The different behaviour of the three salts is demonstrated and hypotheses are formulated about the governing mechanisms.

Keywords: salt, brick, liquid transport, porosity, dilatation

1 INTRODUCTION

The presence of salt in porous stone materials causes different changes in transport properties of the liquid and gaseous phases:

1. changes in liquid properties (from water to a salt solution): viscosity and density increase;
2. changes in interface equilibrium: liquid-vapour equilibrium, liquid-gas surface tension and solid-liquid surface energy;
3. changes in the solid matrix: decrease of accessible porosity, clogging or blockage of certain pores and thereby reduction of pore connectivity, dilatation and crack formation due to precipitation of salt crystals.

Previous measurements with mercury intrusion porosimetry (MIP) and helium pycnometry on limestones contaminated with sodium sulphate revealed that the distribution of salt crystals can be assumed – as a first approximation – uniform over all the pores (Angeli, Benavente et al. 2008). Hence it can be expected that the pore size and the total porosity decrease and subsequently the liquid suction (capillary pressure) increases, whereas the permeability decreases for a comparable level of liquid saturation. Another investigation has revealed that the air permeability of Tuffeau, Sireuil or Richemont limestones drops up to two and a half orders of magnitude when salts are introduced, but the behaviour depends largely on the stone type (Birginie 2000).

When the crystallisation pressure is large enough and exceeds the tensile strength of the stone material the solid dilates and pore sizes and porosity increase. Measurements performed by Lubelli (2006) on lime-cement mortar laden with sodium chloride showed a dilatation of the material up to 0.4 mStrain during the crystallization process, part of which was irreversible and thus linked to the formation of micro-cracks. Further ESEM investigation illustrated that the crystals formed a regular thin layer adhering to the binder and partially filling the larger pores.

An investigation was carried out on the influence of three salts on the pore system and the absorption characteristics of a ceramic brick laden with different amounts of salt. Test specimens were submitted to MIP tests and to free capillary absorption tests using decane as absorbed liquid. This research aims at a better understanding of the local changes in transport properties of a ceramic brick caused by a contamination with salts. The results serve to further improve or develop models that simulate salt damage. Even though mixtures of salts are more representative for practical situations, knowledge on the effect of a contamination with single salts is important to better understand the behaviour of salt contaminated building materials.

2 MATERIAL: CERAMIC BRICK AND SALTS

The tested porous material is a ceramic brick, type ‘Spanish red’ produced by Wienerberger (Belgium), with nominal dimensions 188Lx88Wx63H mm³. The accessible porosity is 33.1±0.012% and the dry bulk density is 1786 kg/m³. The capillary saturated water content was found to be 206.7±0.26 kg/m³ with an absorption coefficient of 0.534±0.044 kg/m²s^{0.5}. The porosity of the brick is fairly unimodal with a median pore size of 1.7 micron. The liquid permeability at capillary saturation is estimated at 5.52·10⁻⁸ s (in units of mass flow). The brick has a relatively low strength (10.2 MPa) and Young’s modulus (1025 MPa).

Brick specimens were laden with salt solutions of NaCl, NaNO₃ and Na₂SO₄ at different concentrations [Table 1]. Salt contamination was performed by free capillary uptake of salt solutions in dry specimens, until capillary saturation. After this the specimens were wrapped in plastic foil and kept at 20°C during 24 h in order to obtain an equal distribution of the solution. The bricks were then dried at 105°C during 48h.

Table 1. Overview of the salt solutions used in the experiments on brick specimens.

	NaCl	NaNO ₃	Na ₂ SO ₄
Solubility 20°C [mol/kg]	6.14	10.26	1.4
Used concentrations [mol/kg]	1-3-5	2-4-6	0.5-0.75-1
Code of corresponding brick specimen	A-B-C	D-E-F	G-H-I

3 SALT CONTENT, POROSITY AND PORE SIZE DISTRIBUTION

3.1 Salt content in the brick specimens

As expected, a significant portion of the salts crystallised on the outer surface of the brick as efflorescence. Therefore, the outer 10 mm of the brick specimens which were enriched with salts, were cut off and not used for the experiments. The salt distribution within the specimens was controlled through conductivity measurements on the water extract of slices of the dry specimens. The results proved that some 30% of the original amount of salts remained within the bulk of the brick.

Table 2. Theoretical and measured salt content, expressed as weight percentage of the dry sample, for different salts and different concentrations of introduced salt solution.

Salt	Brick spec.	theoretical salt content	measured salt content in
		$100\% \cdot m_{\text{salt}}/m_{\text{brick}}$ (kg/kg)	bulk of specimens $100\% \cdot m_{\text{salt}}/m_{\text{brick}}$ (kg/kg)
NaCl	A	0.70%	0.18%
	B	1.85%	0.62%
	C	2.93%	0.94%
NaNO ₃	D	1.83%	0.55%
	E	3.44%	1.71%
	F	4.80%	1.93%
Na ₂ SO ₄	G	0.81%	0.16%
	H	1.19%	0.24%
	I	1.56%	0.44%

In order to check the uniform distribution of the salt crystals within the bulk of the brick, a salt concentration profile was measured across the width of one brick of specimen C, i.e. the brick which was laden with a 5 mol/kg NaCl solution. A slice of 1 cm thickness (height 63 mm; length 88 mm) was taken from the middle of the brick. 5 mm was removed from each of the edges and the remaining 78 mm was divided into 5 pieces each of ± 10 mm (with some loss due to the saw cut). Salt concentration was determined by conductivity measurements of water in which the 5 pieces were immersed during 48 hours (Figure 1). It appears that the salt content varies between 1 and 1.5%, except for slice 4. Because this is not a systematic trend and quite far from the efflorescence on the surface, we consider this point as an outlier and conclude that the order of magnitude proposed in Table 2 can be considered as a measure representative for the bulk of the brick.

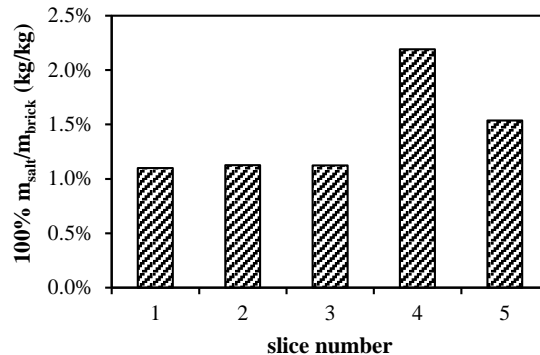


Figure 1. Salt profile over the width of a brick laden with NaCl (specimen C).

Moreover, a typical fraction of 1/3 of the initially present salt can also be expected because the critical moisture content of the brick is approximately 1/3 of the capillary saturated moisture content. This value was obtained from drying tests (at ambient temperature) and it corresponds to the water content above which liquid transport is the dominant mechanism, and below which vapour transport is important (see for example Hens 2007). When the brick, saturated with salt solution, is put in the oven, the solution starts to migrate to the surface, where water evaporates and the chloride precipitates as efflorescence, until the critical moisture level is reached. From then on, a drying front proceeds progressively towards the inside of the brick, so that evaporation takes place in the bulk and the remaining salt precipitates more or less evenly over

the volume. The amount of salt present at the moment the critical moisture content is reached determines the final amount left over in the brick.

3.2 Porosity of the brick with and without salt

Porosimetry measurements (MIP) using a Micromeritics Autopore IV were performed on all specimens. Each test consists of a low (up to 345 kPa) and a high pressure run (up to 228 MPa). Two samples per type of specimen were tested for the salt-loaded material, and four for the salt-free material. All tests were conducted with measurements at the same pressure levels so that average curves could be calculated easily. In Figure 2 the values of total volume fraction of intruded mercury, i.e. the accessible porosity, is plotted for all 9 cases. For each case, there is a measured value and a theoretical one. The latter is calculated as the porosity which would be expected in case there are no changes in the pore structure, apart from the filling of space through the deposition of salts. However, the results show that the measured values are much lower than the theoretical ones, at least at low concentrations. This means that phenomena like dilation of the system and clogging or blocking of pores have an important influence and are even more important than the filling of pores.

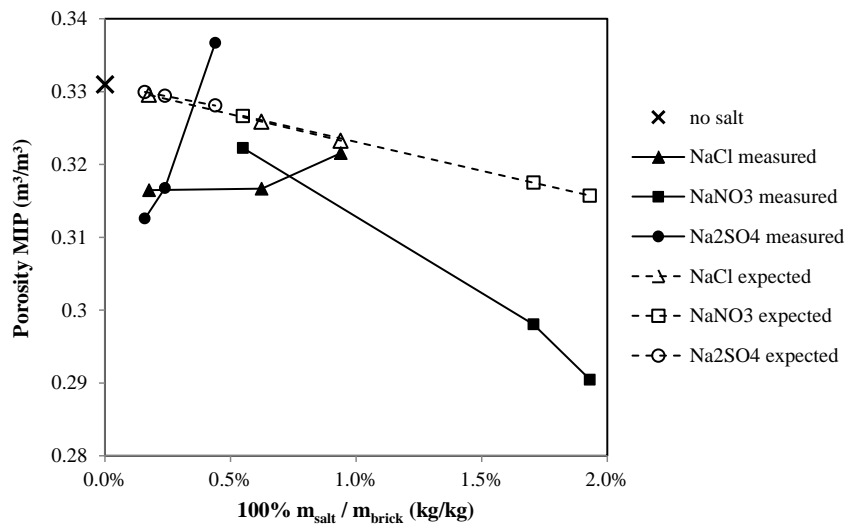


Figure 2. Porosity (MIP) of brick without salt and with different types and concentrations of salt: measured and theoretical values (noted as “expected”) calculated assuming the absence of dilation and cracking.

A further conclusion is that the effect of increasing salt content on the porosity is very different for the three salts. Specimens laden with an increasing amount of sodium nitrate follow quite a linear effect of salts filling the pores and hence little dilation. The opposite is found for the other salts, in which at first a decrease of the porosity at low salt content is noticed followed by an increase and an important dilation. This effect is most remarkable for sodium sulphate. While NaNO_3 is in general characterised by hygroscopic properties but not considered as a destructive salt, sodium chloride and sulphate are known to cause higher crystallisation pressures and hence severe damage.

3.3 Pore size distribution

The pore size distribution confirms the previous statement (Figures 3 to 5): a shift of the curve towards smaller pore radius is noticed, which is most clearly pronounced in the range of the small pores (1 to 10 micron). The shift is larger for contamination with sodium nitrate than for the other salts, and increases with the salt content. The similar shape of the curves suggests that salts are deposited in such a way that a more or less continuous layer is formed on the pore

walls regardless of the pore size. There is no clear indication of the formation of micro-cracks of a particular width.

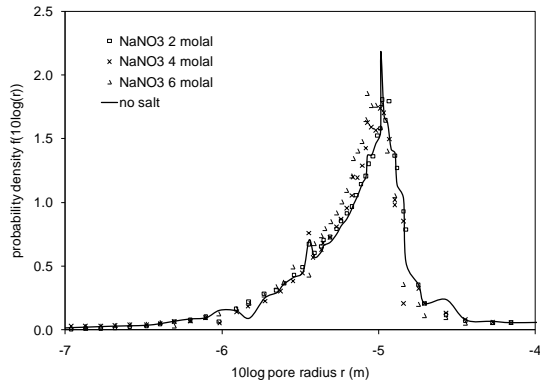


Figure 3. Pore size distributions for brick specimens without salts (solid line) versus those laden with various amounts of NaNO₃ (expressed as concentration of absorbed salt solution).

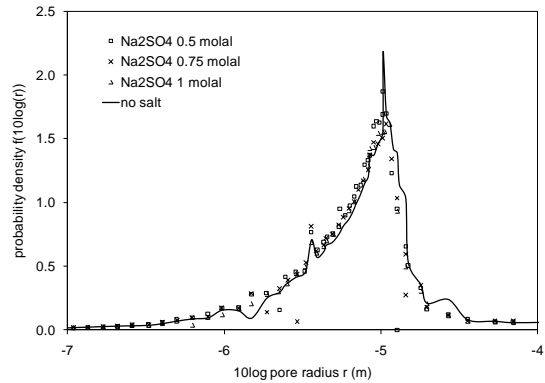


Figure 4. Pore size distributions for brick specimens without salts (solid line) versus those laden with various amounts of Na₂SO₄ (expressed as concentration of absorbed salt solution).

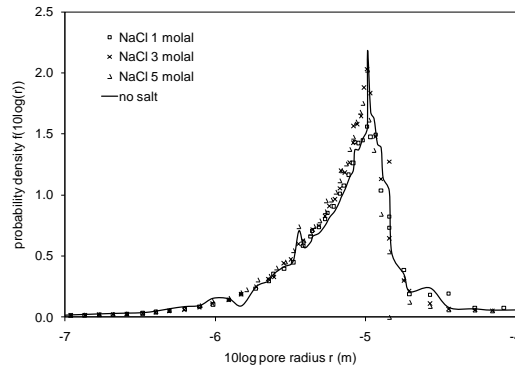


Figure 5. Pore size distributions for brick specimens without salts (solid line) versus those laden with various amounts of NaCl (expressed as concentration of absorbed salt solution).

4 CAPILLARY LIQUID ABSORPTION MEASURED WITH DECANE

When water is absorbed by a stone material containing salts, the latter will dissolve and the process becomes quite complicated, with spatial variations of ion concentration (and hence liquid properties) and the subsequent diffusion of ions, possibly re-precipitation, etc. We tried to reduce the complexity of the phenomena by using decane for the capillary absorption tests on salt-free and salt-contaminated bricks. Decane is a non-polar hydrocarbon with the chemical formula CH₃(CH₂)₈CH₃ which is immiscible with water and cannot act as solvent for salts. It has considerably lower surface tension, density and viscosity than water (Table 3). The assumption of a zero contact angle is usually made for contact between aqueous liquids and stone or brick, but it cannot be made for decane, which has a larger measured contact angle in reported experiments using glass and siliceous powders.

When compared to the capillary uptake of water in the salt-free brick, decane resulted in a slightly higher capillary saturated liquid content (8% higher in volume terms), but also in slower absorption (coefficient 24% lower in volume terms). It is known that the entrapment of air during absorption is the limiting factor for the capillary saturation level: probably the slower process (explained by the lower surface tension, which is the driving force), allows for better

filling of the pores, maybe also for filling of smaller pores, and hence less entrapment of air. Therefore, the results obtained for decane are not directly applicable to water, but should be used in the first place as comparative data between the bricks with different salts and salt content.

Table 3. Overview of liquid properties of decane versus water.

	Water	decane
Density [kg/m ³]	998	730
Surface tension [mN/m]	72.75	23.83
Contact angle [°]	~0	22-43*
Viscosity [mPas]	1	0.92

*(Siebold, Nardin et al. 2000), others based on (Lide 2000)

The capillary absorption in salt-contaminated bricks (Figure 6 and Figure 7) shows quite a different tendency compared to the total porosity measured by MIP. In general the decrease of the absorption coefficient - up to 30% - is more important than the decrease in saturation level, which is between 6 and 11%. While a progressive decrease of the total porosity and little or no dilation is observed in the case of contamination with sodium nitrate, the strongest decrease in capillary absorption, both in speed and in amount, is noticed. Deposition of sodium chloride and especially sodium sulphate resulted in an increase of the porosity for increasing salt content. However, this is not reflected in a stronger capillary behaviour; on the contrary, the absorption coefficient decreases continuously. This might be explained by the different structure of the new pores which may have a lower connectivity and/or a higher tortuosity than the original ones of the ceramic matrix of the brick.

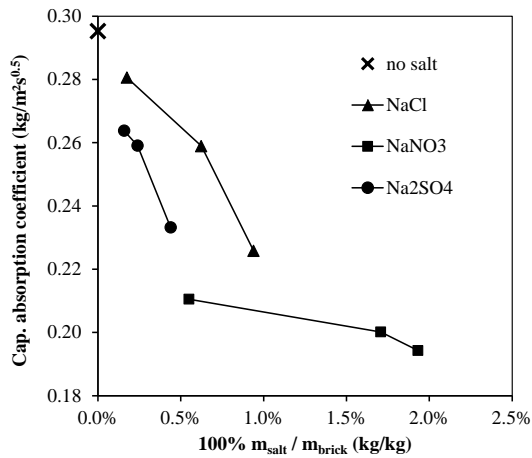


Figure 6. Capillary absorption coefficient for decane in bricks contaminated with NaCl, Na₂SO₄ and NaNO₃ at different concentrations and comparison to the salt free brick.

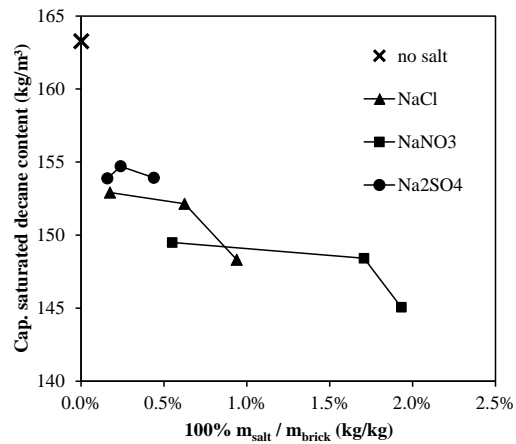


Figure 7. Capillary saturated decane content for bricks contaminated with NaCl, Na₂SO₄ and NaNO₃ at different concentrations and comparison to the salt free brick.

The capillary uptake of decane was monitored in an X-ray setup, allowing the determination of decane content profiles over the specimens during uptake. The configuration of the setup is shown in Figure 8. Details on the procedure and the calculation method of the liquid content are published in Roels (2006). Two specimens were cut from each brick and used in the measurements (dimensions 15Dx30Wx60H mm³).

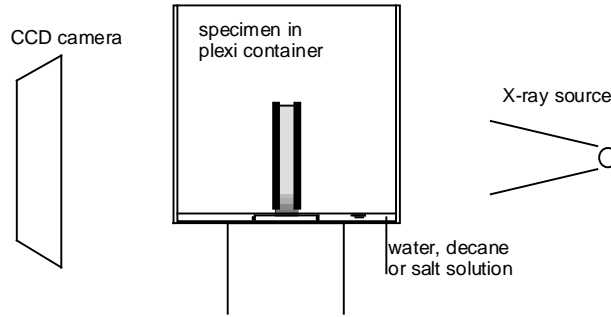


Figure 8. Schematic representation of the X-ray setup for the monitoring of the absorption of liquids.

In the case of contamination with sodium nitrate and sodium chloride, a typical evolution of the profiles of the uptake curves is noticed, illustrated in Figure 9 for sodium nitrate. This figure shows a decrease of the overall liquid content (vertical) and the progressive time lag of the absorbed liquid front when the salt content decreases (horizontal). In principle, the integral of the curve equals the absorption coefficient.

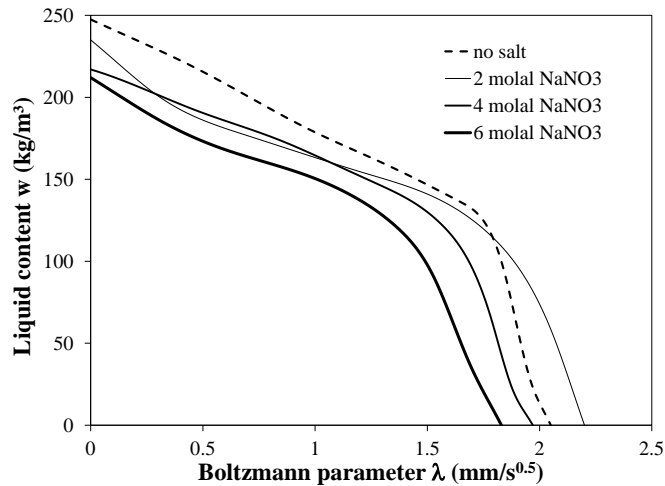


Figure 9. Decane uptake profiles in salt-free brick and bricks with three different amounts of sodium nitrate (expressed as concentration of absorbed salt solution). The Boltzmann parameter is the distance to the liquid surface divided by the square root of time.

5 CONCLUSIONS

The influence of the amount of deposited sodium chloride, sodium nitrate and sodium sulphate on the pore structure of a ceramic brick was investigated with MIP and capillary absorption tests. The contamination with the salts was performed by capillary absorption of a salt solution followed by oven drying. It appears that the fraction of the absorbed salt, which remains in the bulk of the brick, corresponds more or less to the critical water level of the material, indicating the limit between dominant liquid and vapour transport to the surroundings in the drying procedure.

The influence of these salts on the porosity depends on the nature of the salt: sodium nitrate leads to a progressive decrease of the porosity and the pore size, indicating a simple filling of the pores. In the case of the more destructive sodium sulphate, an increase of the pore volume and of the pore size is noticed at higher salt content, probably due to dilation caused by crystallisation pressure. The deposition of sodium chloride results in an intermediate behaviour.

These changes in the pore system are to a certain level also reflected in the capillary absorption behaviour, which was investigated using decane as a ‘workable’ replacement for water. The increased porosity does not systematically result in an increased capillary behaviour, probably due to differences in pore morphology. In the near future, examinations with scanning electron microscope (SEM) are planned to observe differences in pore shape.

From this investigation, one might conclude a safe limit of salt content for mechanical damage on this particular brick. The limit appears much higher for sodium nitrate (2% by mass) compared to that for sodium chloride (approximately 0.5%) and certainly sodium sulphate (0.1%). However: 2% by mass of nitrate is beyond the acceptable level if hygroscopic behaviour is a problem.

More research is needed to extend these findings to other materials, but also to try and use them for transport parameter estimation in simulations. Furthermore it seems interesting to investigate the importance of moisture transport characteristics, like the critical moisture content for liquid transport, on damage mechanisms and the severity of salt damage. Whereas thermodynamics and poromechanics are often addressed to explain experimental observations, heat and moisture transport modelling may still provide many useful concepts.

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