

**SWBSS**  
**2011** 19 - 22 October  
Limassol, Cyprus

# Salt Weathering on Buildings and Stone Sculptures

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# Performance of limestone laden with sodium sulphate and sodium nitrate

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## ABSTRACT

*The behaviour of two types of limestones, having different porosity: Maastrichter and Euville, laden with an aqueous solution of an equimolar mixture of sodium sulphate and sodium nitrate was investigated. At 50% RH, the efflorescence on Maastrichter samples drying up to 30 hours consisted of similar amounts of thenardite and darapskite in case of an equimolar mixture of sodium sulphate/sodium nitrate while that on Euville samples under the same conditions contained mainly darapskite. At 20°C and 85% RH, thenardite was mostly detected in the efflorescence of both Maastrichter and Euville samples. Increasing the RH from 50 to 85% resulted in considerable damage on Maastrichter stone laden with an equimolar mixture of sodium sulphate/sodium nitrate, most likely as a consequence of high supersaturation of mirabilite.*

Keywords: limestone, sodium sulphate, sodium nitrate, mixture

## 1 INTRODUCTION

It is well-known that soluble salts present in building materials can cause damage, mainly by producing stress in the substrate, which leads to the formation of cracks and a lack of cohesion (Grossi et al. 1997). A lot has been done in the past concerning research of the behaviour of salts in historical monuments. However, those studies included single salts, while in situ one mostly finds complex salt mixtures, which makes the conservation strategy much more intricate.

Sodium sulphate is known for its destructive properties through a direct precipitation from a saturated solution on one hand (Rodriguez-Navarro et al. 2000) and related to different hydration states, among which thenardite ( $\text{Na}_2\text{SO}_4$ ) and mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ), on the other hand. While thenardite is stable at  $\text{RH} < 76.4\%$ , mirabilite prevails at  $\text{RH} > 76.4\%$  at  $20^\circ\text{C}$  (Steiger and Asmussen 2008).

In case of a solution containing both sodium sulphate and sodium nitrate, a third salt, darapskite, may precipitate (De Clercq 2008a; De Clercq 2008b). In Table 1, an overview of the salts involved and their deliquescence humidity value is given. Although darapskite is a rare mineral, it can be detected in efflorescent salts on building materials (Holtkamp and Heijnen 1991). Under equilibrium conditions, it can never occur together with both nitratine and thenardite/mirabilite, since the fields of the last two are separated by the darapskite field on the solubility diagram. According to the solubility diagram of  $\text{Na}_2\text{SO}_4\text{-NaNO}_3\text{-H}_2\text{O}$  system at  $20^\circ\text{C}$

and 55% RH (Linnow et al. 2010), the concentration of an equimolar mixture of the two salts increases as water evaporates first reaching saturation with mirabilite, which starts crystallising. The remaining solution becomes enriched in nitrate. If evaporation continues, the solution gets saturated with darapskite, so in conditions of equilibrium mirabilite will re-dissolve and darapskite will crystallise instead. In porous materials, the re-dissolution of mirabilite shouldn't occur as the evaporation front moves into the interior, and the precipitated mirabilite will be separated from the solution. The latter will first precipitate darapskite, and in the end nitratine.

Table 1: Deliquescence humidity of some sodium salts

Salt name	Chemical formulae	Deliquescence humidity (% RH) (Schwarz and Steiger 2009)
nitratine	$\text{NaNO}_3$	75.4 (20°C)
thenardite	$\text{Na}_2\text{SO}_4$	86.9 (25°C)
mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	95.6 (20°C)
darapskite	$\text{Na}_3(\text{SO}_4)(\text{NO}_3) \cdot \text{H}_2\text{O}$	79 (20°C) (*)

(\*) according to the ECOS-output for an equimolar mixture of sodium sulphate and sodium nitrate.

The objective of this research was to explore the theories of solubility diagrams by the determination of the behaviour of two types of limestones having different porosity, which were contaminated with a solution containing sodium sulphate and sodium nitrate in 1:1 molar ratio and submitted to extreme relative humidity values and to changes of relative humidity, at 20°C.

## 2 EXPERIMENTAL PART

Maastrichter and Euville limestones were selected for this research.

Maastrichter limestone is a pale yellow stone, consisting mainly of microfossils and sand-sized fragments of microcrystalline carbonate. The average porosity is 47.5%, the density is around 1400 kg/m<sup>3</sup> and the calcium carbonate content can go up to 98% (Roekens et al. 1998; Dubelaar et al. 2006).

Euville is a beige-coloured limestone. It contains grains made of fossils cemented by calcium carbonate. Like for the Maastrichter, the total calcite content can reach up to 98% (Dusar et al. 2009), while the average porosity is much lower, about 10% (De Witte 2002).

The stones were cut in 5x5x5 cm samples. Samples were placed in a solution containing 1.2 mol of anhydrous sodium sulphate and 1.2 mol of sodium nitrate per kilogram of water. This high concentration was chosen in an attempt to maximize precipitation of salts at the surface. 16 hours later the samples were taken out of the salt solution, and all except one side vapour tight sealed with aluminium foil in order to permit evaporation only from one side and left to dry.

Firstly, drying tests were carried out to evaluate the effect of the salt load on the evaporation properties of water present in both types of limestone.

Samples were drying at 20° and 50 or 85% RH. Efflorescence was collected regularly. It was examined by both X-ray diffraction (Bruker D8 Advance) and ion chromatography (IC, Metrohm 761 Compact IC). In order to set up ion profiles for samples drying for a specific period of time, each sample was cut into 0.5 cm thick slices, which were then grained. 1 g of this powder was mixed with 100 ml demineralised water and filtered. The ion content of the

filtered extract is analysed by IC. The results are presented graphically, as quantity of ions in mol per gram of slice, as a function of distance of that slice from the surface in millimetres.

Another group of samples was, after drying at 50% RH till at least 80% of the introduced amount of water had evaporated, submitted to 85% RH. The performance was compared to that of samples contaminated with a solution containing only 1.2 mol of sodium sulphate or 1.2 mol of sodium nitrate per kilogram of water.

### 3 RESULTS AND DISCUSSION

#### 3.1 Tests at 20°C and 50% RH

The drying behaviour of samples laden with a mixture of 1.2 mol of anhydrous sodium sulphate and 1.2 mol of sodium nitrate per kilogram of water was compared with that of the ones containing 1.2 mol of sodium sulphate or sodium nitrate as well as with the salt free ones. The results are presented in Figure 1 for the Maastrichter stone.

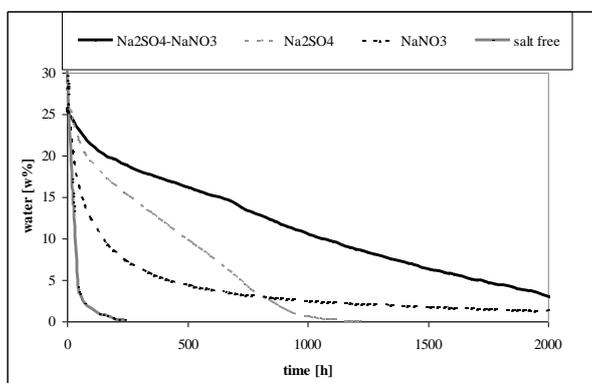


Figure 1. Drying curve of Maastrichter stone laden with 1.2 mol of anhydrous sodium sulphate and 1.2 mol of sodium nitrate per kilogram of water compared with that containing 1.2 mol of sodium sulphate or sodium nitrate as well as the salt free one (20°C, 50% RH).

The results presented in figure 1 show that salts significantly influence the drying behaviour of the Maastrichter stone. In case of single salts, a stronger reduction of the drying rate for sodium sulphate compared to sodium nitrate is noticed. The opposite effect applied for the Euville stone. For both limestones, the slowest drying was obtained in case of a mixture of an equimolar amount of both salts.

The efflorescence of samples drying up to 30 h was less than 9% of the introduced amount of salt mixture for Maastrichter stone while up to 43% for the Euville stone. The results obtained by XRD show a significant difference in efflorescence composition for the two types of limestone during the first 30 hours of drying (Fig. 2). A possible explanation might be differences in drying kinetics between both limestones. The efflorescence of Maastrichter samples contains similar amounts of thenardite and darapskite. For Euville samples, the efflorescence contains mostly darapskite, while the amount of thenardite is low and more or less constant during the whole period. According to the equilibrium pathway, thenardite was initially mirabilite, so it is strange why it hasn't been found in higher amount in the first phase of drying as expected from theoretical calculations. However, it is well-known that crystallisation of mirabilite is kinetically unfavourable. In effect, thenardite and darapskite can crystallise directly. The meta-stable sodium sulphate heptahydrate, as detected under cooling conditions (Hamilton and Hall 2008) or drying conditions (Saidov and Pel 2009), was not detected on both limestones using conventional powder X-ray diffraction.

Ion chromatography results confirmed results obtained by XRD. The sulphate and nitrate profile of the sample that was cut in slices after drying for 30 hours, revealed quite comparable quantities of sulphates and nitrates which are, apart from a minor enrichment at the surface, more or less equally distributed in depth.

A further group of samples containing 1.2 mol of  $\text{Na}_2\text{SO}_4$  and 1.2 mol of  $\text{NaNO}_3$  per kg of water was drying till at least 80% of the initial amount of water was evaporated. The corresponding drying time was almost 3 months. This time high prevalence of salts was noticed at the surface layer in case of both stones, while minor quantities were found further in depth (Fig. 3). Quite unexpectedly, one of the salts found in the efflorescence of both limestones was nitratine (Table 2). Due to its high solubility, it was supposed to be the last one to crystallise and this should have happened in depth of the sample because the evaporation front should be moved into the interior by then. A high deviation between the results of both samples contaminated and conditioned similarly is noticed. Euville efflorescence shows again prevalence of darapskite.

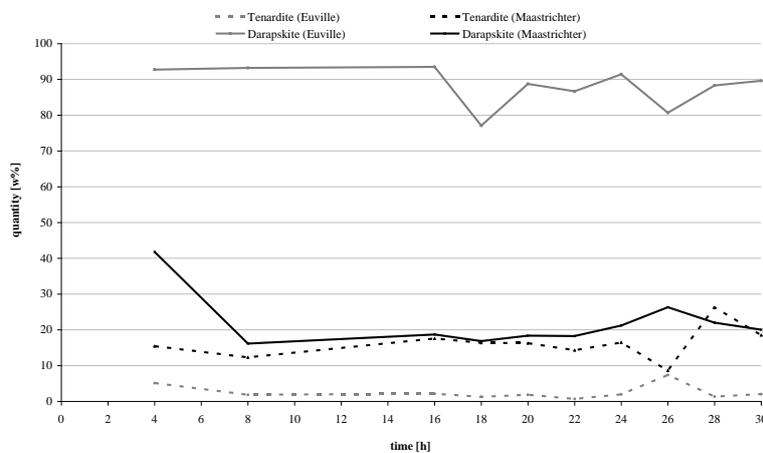


Figure 2. Composition of efflorescence (obtained by XRD) collected during 30 hours of drying at 20°C, 50% RH on Maastrichter and Euville stones contaminated with a solution containing 1.2 mol of  $\text{Na}_2\text{SO}_4$  and 1.2 mol of  $\text{NaNO}_3$  per kg of water; a constituent of the stones -  $\text{CaCO}_3$  was also detected, but not shown on the graph.

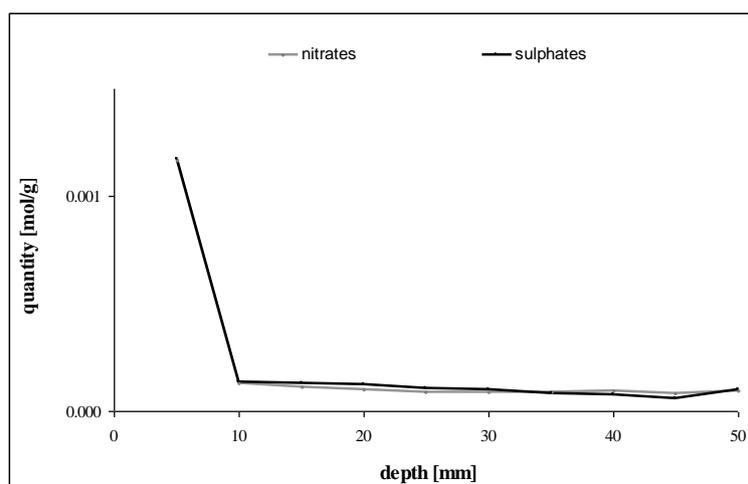


Figure 3. Sulphate and nitrate profile of Maastrichter stone after contamination with 1.2 mol of  $\text{Na}_2\text{SO}_4$  and 1.2 mol of  $\text{NaNO}_3$  per kg of water and drying at 20°C and 50% RH during almost 3 months (IC).

Table 2. Efflorescence composition (XRD) of Maastrichter and Euville stone contaminated with 1.2 mol of  $\text{Na}_2\text{SO}_4$  and 1.2 mol of  $\text{NaNO}_3$  per kg of water and drying at  $20^\circ\text{C}$  and 50% RH during almost 3 months. The residual water content before efflorescence removal is related to the introduced amount.

stone type	Sample code	water content (%)	Composition efflorescence (w%)		
			thenardite	darapskite	nitratine
Maastrichter	MT/SN/1	12.6	12.2	22.2	50.2
	MT/SN/4	18.8	23.9	3.1	42.1
Euville	EV/SN/1	3.3	13.5	40.2	36.4
	EV/SN/5	2.4	7.6	63.1	22.4

### 3.2 Tests at $20^\circ\text{C}$ and 85% RH

The drying behaviour of samples laden with 1.2 mol of anhydrous sodium sulphate and 1.2 mol of sodium nitrate per kilogram of water was compared with that of the salt free ones. The results are presented in figure 4 for the Euville stone from which an extremely slow drying process for the salt mixture laden sample is noticed which was interrupted after 3 weeks. Some efflorescence was observed of which XRD analysis revealed a composition of 84 w% of thenardite and, surprisingly, 16 w% of nitratine although it shouldn't be crystallising at 85% RH (Table 1). A possible explanation could be that the nitrate was in solution and got picked up along with efflorescence when it was removed from the sample, so when the water has evaporated it was possible for nitratine to crystallise. Finally, ion chromatography was performed on the slices of Euville and Maastrichter samples. As expected from the drying curves, quite an equal distribution of salts inside the whole sample was obtained.

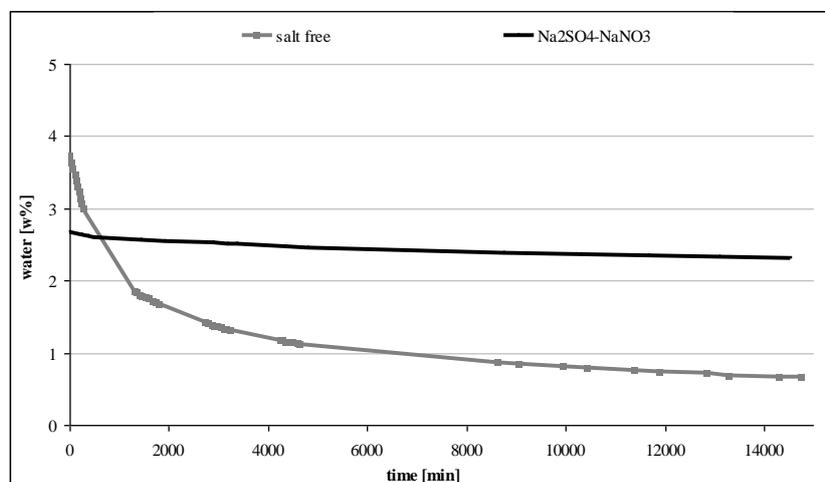


Figure 4. Drying behaviour of Euville stone laden with 1.2 mol of anhydrous sodium sulphate and 1.2 mol of sodium nitrate per kilogram of water compared with that of the salt free one ( $20^\circ\text{C}$ , 85% RH).

### 3.3 50 - 85% RH

After drying at 50% RH till at least 80% of the introduced amount of water had evaporated, samples laden with sodium sulphate and sodium nitrate, were submitted to 85% RH. The performance was compared to that of samples contaminated with a solution containing only 1.2 mol of sodium sulphate or 1.2 mol of sodium nitrate per kilogram of water. All samples were unwrapped before submission to 85% RH, so that the damage would be immediately visible.

During conditioning at 85 % RH, the weight was followed up as to determine the time at which equilibrium is obtained. The evolution of the uptake of moisture is presented in figure 5 for the Maastrichter stone.

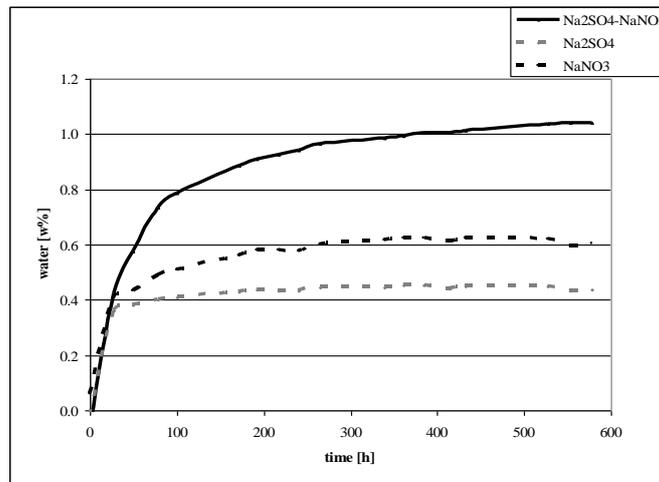


Figure 5. Moisture uptake of Maastrichter samples contaminated with 1.2 mol of Na<sub>2</sub>SO<sub>4</sub> and 1.2 mol of NaNO<sub>3</sub> per kg of water compared to that of samples laden with only 1.2 mol of sodium sulphate or 1.2 mol of sodium nitrate per kilogram of water and dried at 50 % RH, during conditioning at 85 % RH.

After 10 days at 85% RH, damage was noticed on the Maastrichter samples, laden with an equimolar mixture of sodium sulphate and sodium nitrate (Fig. 6). It was much more pronounced in case of Maastrichter samples than on Euville samples. Samples contaminated with only sodium sulphate showed severe efflorescence but hardly material loss while, as expected, those having only sodium nitrate looked wet since 85% RH is above the deliquescence humidity of sodium nitrate.

The main cause of degradation in case of the Na<sub>2</sub>SO<sub>4</sub>-NaNO<sub>3</sub> mixture could be the high supersaturation of mirabilite (Steiger and Asmussen 2008). Namely, at 85% RH nearly all ions are solubilised and since solubility of darapskite is higher than that of mirabilite, high supersaturation of the latter is achieved (Fig. 7). Therefore, adding nitrates to a material already contaminated with a sodium sulphate solution may increase, due to the formation of darapskite, the degree of supersaturation of mirabilite in the solution that might cause a lot of damage once it finally crystallises.



Figure 6. Maastrichter samples after 10 days at 20°C and 85% RH, previously contaminated with NaNO<sub>3</sub> (up), Na<sub>2</sub>SO<sub>4</sub> (middle) and an equimolar mixture of Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub> mixture (bottom).

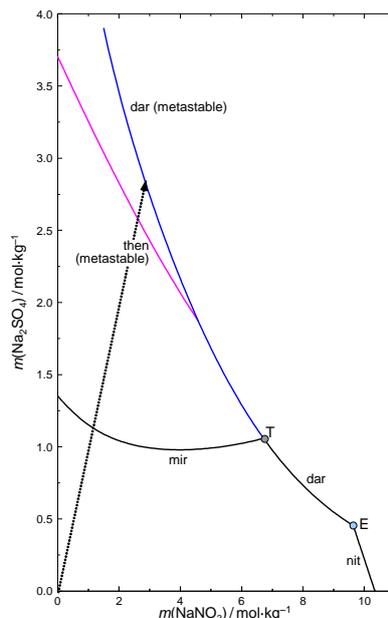


Figure 7. Solubility in  $\text{NaNO}_3\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  system at  $20^\circ\text{C}$  with metastable solubilities of thenardite (magenta) and darapskite (blue). (M. Steiger)

#### 4 CONCLUSIONS

The research consisted of a close examination of the behaviour of two types of limestones: Maastrichter and Euville, laden with an equimolar mixture of sodium sulphate and sodium nitrate. Stone samples were subdued to different amounts of relative humidity (50% and 85%) and to changes of relative humidity at constant temperature. The purpose was to find out more about the performance of salt mixtures in porous materials.

In the first round of tests with sodium sulphate and sodium nitrate ( $20^\circ\text{C}$ , 50% RH) a clear distinction could be noticed between the two substrates. Both thenardite and darapskite were detected in the efflorescence of the Maastrichter sample while that of the Euville sample consisted mainly of darapskite. The direct crystallisation of darapskite is indicative for a high supersaturation of mirabilite. The theoretical solubility diagram has already shown that the latter is a salt that doesn't crystallise easily (Steiger and Asmussen 2008). For the same reason, also thenardite can crystallise directly under conditions of high supersaturation with mirabilite. In fact, thenardite crystallisation requires a slightly lower supersaturation than darapskite. The meta-stable sodium sulphate heptahydrate was not detected on both limestones using conventional powder X-ray diffraction. When drying was almost completed analysis showed a clear concentration gradient within samples, as well as the presence of nitratine along with thenardite and darapskite in the efflorescences.

At  $20^\circ\text{C}$  and 85% RH, thenardite was mostly found in efflorescences of both Maastrichter and Euville samples. It was most probably initially mirabilite that got transformed during the analysis, which was performed at 50% RH. Thenardite domination was expected, since the theoretical calculations show that darapskite is not stable over 79% RH (at  $20^\circ\text{C}$ ) and mirabilite prevails.

Finally, changing conditions from 50% to 85% RH has left samples contaminated with sodium sulphate and sodium nitrate in a much worse state than the ones contaminated only with sodium sulphate. This is a consequence of high supersaturation of mirabilite which creates considerable damage upon subsequent crystallisation.

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