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# Performance of Limestone Contaminated with Binary Mixtures of Sodium Sulphate and Treated with a Water Repellent

**H. De Clercq**
Royal Institute for Cultural Heritage (KIK-IRPA), Brussels, Belgium

## Abstract

One of the main causes of decay in porous materials is the growth of salt crystals within pores. Their presence in masonry is generally considered as a counter-indication for surface treatments. In the past, threshold values were determined for sodium- and magnesium sulphate, sodium chloride and sodium nitrate tested as single salt contaminants on samples treated with a water repellent product. Knowing that building materials seldom contain one particular type of salt, but a complex mixture of ions, further study researched mixtures of sodium sulphate, sodium chloride and potassium nitrate. The results showed that threshold values of salt contents from which damage is obtained are different than those from studies carried out with a single salt contamination. Moreover, the prediction of the behaviour of salts in a mixture is complex due to the formation of other (double) salts resulting from ion exchange. This research aims to clarify the type of salts formed in case of a contamination of sodium sulphate, being the most destructive, combined with different amounts of sodium nitrate, potassium nitrate or potassium sulphate.

**Keywords:** water repellent treatment, binary salt mixtures

## 1 Introduction

Deterioration of buildings and monuments, which are exposed to weathering and pollution, is becoming a serious life-cycle problem, causing economical and cultural damage [1]. One of the main causes of decay in porous materials is the growth of salt crystals within pores, generating stresses that are sufficient to cause disintegration. The presence of soluble salts in masonry is generally considered as a counter-indication for surface treatments. On the other hand, knowing that almost all building materials contain an analyzable salt content, there are many examples of treated monuments where no damage has been observed, even after 20 to 30 years [2].

Within the framework of the European Project "SCOST" [3], a systematic research was carried out with the aim of determining threshold values of salt contents in relation with material properties and types of ions present. Based on salt crystallization tests, executed with sodium sulphate, magnesium sulphate, sodium chloride and sodium nitrate according to a protocol developed in this study, it was concluded that the type of salt plays a major role on the salt limit content, while the type of treatment plays a minor role. For example, sodium- and magnesium sulphate show a higher destructive index than sodium chloride and sodium nitrate on both treated and untreated samples.

An inventory of the type of cations and anions in almost 1000 samples taken from Belgian historic buildings proved that building materials seldom contain one particular type of salt, but a complex mixture of ions. Hence, a further study was carried out to evaluate the performance of porous treated and untreated substrates contaminated with a mixture of salts [5,6]. The composition of the salt mix was based on the threshold values of sodium sulphate for the selected single materials, as obtained in the SCOST-project [3], to which a varying amount of sodium chloride and potassium nitrate was added. This combination of salts is in line with the average salt contamination found in Belgian monuments.

The results obtained after 4 salt crystallization cycles served to show that threshold values of single salt contents for which damage is obtained are generally no longer valid in case of combination with other types of salts. Moreover, the prediction of the behaviour of salts in a mixture is complex due to the formation of other (double) salts.

The present research continued the former studies for the case of contamination with sodium sulphate in combination with different amounts of sodium nitrate, potassium nitrate or potassium sulphate. The stone used for this study is the French Massangis limestone and the water repellent product is a solvent based oligomeric siloxane product which has been tested previously so that its efficiency is known.

# 2 Experimental

## 2.1 Substrate

The properties of the French Massangis limestone are listed in Table 1.

**Table 1:** Properties of the French Massangis limestone

| Substrate | Description | Properties determined by Hg-porosimetry | | Capillary water absorption | |
|---|---|---|---|---|---|
| | | Porosity *(v%)* | Bulk density *($kg.m^{-3}$)* | Capillarity (A) *($kg.m^{-2}. h^{-0.5}$)* | C.M.C. *(weight %)* (a) |
| French limestone Massangis | Oolitic and crinoidal limestone | 13 | 2330 | 2.2 | 4.2 |

(a) : amount of water that can enter a sample by capillary rise

The samples were cut in prisms of 10 x 5 x 10 $cm^3$ and dried at 40 °C.

## 2.2 Treatment

The selected water repellent is an oligomeric methylsiloxane with ethoxy as reactive group diluted in white spirit so that the corresponding dry weight is 6.5 %. The treatment was carried out on dried samples by capillary rise on the front face (10 x 5 $cm^2$) for 10 seconds. The consumption is determined from the weight difference before and after treatment. The treated samples were conditioned at 20 °C and 55 % relative humidity (R.H.) for 1 week.

## 2.3 Contamination of the samples - salt crystallization tests

After drying of the samples at 40°C to constant weight, the salt solution, consisting of the defined salt mix (see part 2.5) dissolved in 80 % of the C.M.C., is introduced on the back face by capillary rise. If necessary, the top side of the container used for the introduction of the salt solution is closed to prevent evaporation. After introduction, the samples are put in a container with a layer of gravel (2-3 mm), in such a way that drying can only occur through the front face. The samples are conditioned at 20°C and 55 % R.H.. The drying is registered by periodic weighing till 90 % of the introduced water is evaporated. The front surface is cleaned with a soft brush. The collected material, consisting of salt efflorescence and loose material from the substrate, is analyzed quantitatively by X-Ray Diffraction (XRD, Bruker D-8). For further salt crystallization cycles, an amount of water equal to 80 % of the C.M.C. of the sample is introduced followed by conditioning as described above. Four salt crystallization cycles have been performed, corresponding with a total duration of 20 months [5].

## 2.4 Threshold values of single salts

First, the threshold values for the individual salts $Na_2SO_4$, $KNO_3$ and $K_2SO_4$ were determined. By threshold values, the highest salt content up to which no damage is obtained and the lowest salt content at which damage is obtained, systematically for treated and untreated samples. For treated as well as untreated Massangis limestone, these values are presented in Table 2.

**Table 2:** Threshold values, expressed as weight percentage of the dry substrate, of $Na_2SO_4$, $KNO_3$ and $K_2SO_4$ for the Massangis limestone

| | Highest content up to which no damage is obtained (w%) | | | Lowest content at which damage is obtained (w%) | | |
|---|---|---|---|---|---|---|
| | $Na_2SO_4$[(a)] | $KNO_3$[(b)] | $K_2SO_4$[(b)] | $Na_2SO_4$[(a)] | $KNO_3$[(b)] | $K_2SO_4$[(b)] |
| Untreated | 0.12 | 2,0 | 1,2 | **0.25** | > 2,0 | > 1,2 |
| Treated | 0.12 | 2,0 | 1,3 | **0.25** | > 2,0 | > 1,3 |

(a) : determined within the SCOST project [3]

(b) : determined within present research

The threshold values for treated samples generally match well with those for untreated samples. In some cases, the lowest content at which damage occurs could not be defined because no damage is obtained at the highest tested salt content. This was the case for both $KNO_3$ and $K_2SO_4$. The threshold values of $Na_2SO_4$, presented in bold in Table 2, form the basis for the research program with binary salt mixtures.

## 2.5 Experiments with binary salt mixtures

The $Na_2SO_4$ limit at which damage is obtained, 0.25 % by weight, forms the basis for the research program of binary salt mixtures with $NaNO_3$, $KNO_3$ or $K_2SO_4$. The set up of the research program is presented in Table 3.

**Table 3:** Set up of the research program.

| Combinations | Weight ratio (% of the dry material) | | | | Molar ratio | | | |
|---|---|---|---|---|---|---|---|---|
| $Na_2SO_4$ - $NaNO_3$ | 0,25–0,15 | 0,37-0,15 | 0,50–0,15 | 0,50–0,30 | 1-1 | 1,5-1 | 2-1 | 2-2 |
| $Na_2SO_4$ - $KNO_3$ | 0,25–0,18 | 0,37–0,18 | 0,50–0,18 | 0,50–0,36 | 1-1 | 1,5-1 | 2-1 | 2-2 |
| $Na_2SO_4$ - $K_2SO_4$ | 0,25–0,31 | 0,37–0,31 | 0,50–0,31 | 0,50–0,62 | 1-1 | 1,5-1 | 2-1 | 2-2 |

## 3 Results and discussion

### 3.1 Consumption of the water repellent product

The consumption of the water repellent product is 130 (±20) $g.m^{-2}$.

### 3.2 Salt crystallization tests

The results obtained during salt crystallization tests are presented in Tables 4 to 6.

These results show that a combination of $Na_2SO_4$ with $NaNO_3$ generally results in efflorescence of darapskite ($Na_3(NO_3)(SO_4).H_2O$) and $Na_2SO_4$, but hardly any damage. The amount of $Na_2SO_4$ decreases in the efflorescence with increasing salt crystallization cycle number but increases at the 4th cycle. The more $Na_2SO_4$ in the initial salt mixture, the more it tends to be present in the efflorescence. From the 2nd salt crystallization cycle on, darapskite is in general the major deposited salt and most intensively in case of a contamination with a 1-1 molar ratio. $NaNO_3$ is only formed at the end of the salt crystallization procedure and this occurs with increasing concentration of this salt in the initial salt mixture.

A combination of $Na_2SO_4$ with $KNO_3$ results in the same efflorescing salts as in the case with $NaNO_3$, as well as $KNO_3$ and aphtitalite ($K_3Na(SO_4)_2$). Aphtitalite is formed especially for a molar ratio $Na_2SO_4$-$KNO_3$ of 1,5-1 for treated limestone while it is hardly detected on untreated limestone having the same contamination and after the same salt crystallization cycle numbers. For untreated limestone, this double salt is preferentially formed in case of a contamination with a $Na_2SO_4$-$KNO_3$ mixture of a molar ratio 2-2. It is surprising that the same molar ratio but higher concentrations of both salts (molar ratio 1-1 and 2-2) does not necessarily produce the same type of efflorescence, as is the case for untreated limestone after the 1st and 3rd salt crystallization cycle. From the 3rd crystallization cycle on, darapskite is the major deposited salt and more so in the case of a 1,5-1 molar ratio for untreated Massangis limestone while for the treated stone this occurs for a 2-1 molar ratio. $Na_2SO_4$ as such is generally deposited at the beginning of the salt crystallization procedure while $KNO_3$ is preferentially deposited at the end together with $NaNO_3$. The worst combination for untreated limestone, resulting in the highest amount of efflorescing $Na_2SO_4$, corresponds to a binary mixture with a high $Na_2SO_4$ content (a molar ratio of 1,5-1 and 2-1).

Combining $Na_2SO_4$ with $Ka_2SO_4$, the latter is hardly detected as such on untreated limestone. However, it appears in the efflorescence at the beginning of the crystallization cycling for the limestone treated with a water repellent. Potassium salts are generally detected in the form of aphtitalite. $Na_2SO_4$ as such is deposited during the whole salt crystallization cycling and causes damage in the form of scaling on untreated limestone having a contamination corresponding to a molar ratio of 2-1. Surprisingly, treated limestone showed some scaling in case of a 1-1 and 1,5-1 contamination while not in case of a 2-1 nor 2-2 contamination.

**Table 4:** Composition of the efflorescing salt (w%) for Massangis limestone contaminated with a mixture of $Na_2SO_4$ and $NaNO_3$

| $Na_2SO_4$ – $NaNO_3$ | | salt efflorescence | Salt crystallization cycle number | | | |
|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 |
| Molar ratio | Weight ratio | | | | | |
| *Untreated* | | | | | | |
| 1 - 1 | 0,25-0,15 | $Na_2SO_4$ | 66 | 6 | 8 | 7 |
| | | $NaNO_3$ | - | - | - | 43 |
| | | $Na_3NO_3SO_4.H_2O$ | 34 | 94 | 92 | 50 |
| 1,5 – 1 | 0,37-0,15 | $Na_2SO_4$ | 83 | 8 | 14 | 22 |
| | | $NaNO_3$ | - | - | - | 11 |
| | | $Na_3NO_3SO_4.H_2O$ | 17 | 93 | 86 | 66 |
| 2 - 1 | 0,50-0,15 | $Na_2SO_4$ | >90 | 14 | 21 | 43 |
| | | $NaNO_3$ | - | - | - | 3 |
| | | $Na_3NO_3SO_4.H_2O$ | < 10 | 86 | 79 | 54 |
| 2 - 2 | 0,50-0,30 | $Na_2SO_4$ | >90 | <10 | 3 | 35 |
| | | $NaNO_3$ | - | - | - | 3 |
| | | $Na_3NO_3SO_4.H_2O$ | < 10 | > | 97 | 52 |
| *Treated with water repellent* | | | | | | |
| 1 - 1 | 0,25-0,15 | $Na_2SO_4$ | No efflorescence | 5 | No efflorescence | |
| | | $NaNO_3$ | | - | | |
| | | $Na_3NO_3SO_4.H_2O$ | | 95 | | |
| 1,5 – 1 | 0,37-0,15 | $Na_2SO_4$ | No efflorescence | | 13 | 42 |
| | | $NaNO_3$ | | | 4 | 8 |
| | | $Na_3NO_3SO_4.H_2O$ | | | 83 | 50 |
| 2 - 1 | 0,50-0,15 | $Na_2SO_4$ | No efflorescence | 89 | 15 | 38 |
| | | $NaNO_3$ | | 11 | - | 3 |
| | | $Na_3NO_3SO_4.H_2O$ | | - | 85 | 59 |
| 2 - 2 | 0,50-0,30 | $Na_2SO_4$ | 56 | - | 4 | 6 |
| | | $NaNO_3$ | - | - | 4 | 44 |
| | | $Na_3NO_3SO_4.H_2O$ | 44 | >90 | 92 | 50 |

**Table 5:** Composition of the efflorescing salt (w%) for Massangis limestone contaminated with a mixture of $Na_2SO_4$ and $KNO_3$.. No efflorescence was formed during the 1st and 2nd cycles of the samples treated with a water repellent.

| $Na_2SO_4$ – $KNO_3$ | | Salt efflorescence | Salt crystallization cycle number | | | | |
|---|---|---|---|---|---|---|---|
| | | | *Untreated* [(a)] | | | *Treated with water repellent* [(b)] | |
| Molar ratio | Weight ratio | | 1 | 3 | 4 | 3 | 4 |
| 1 - 1 | 0,25-0,18 | $Na_2SO_4$ | 59 | - | - | - | - |
| | | $KNO_3$ | 13 | 19 | 31 | 21 | 30 |
| | | $NaNO_3$ | - | - | 18 | - | 8 |
| | | $Na_3NO_3SO_4.H_2O$ | - | 72 | 47 | 62 | 60 |
| | | $K_3Na(SO_4)_2$ | 28 | 9 | - | 17 | 2 |
| 1,5 – 1 | 0,37-0,18 | $Na_2SO_4$ | 67 | 11 | - | <1 | <1 |
| | | $KNO_3$ | 6 | - | 31 | 8 | 9 |
| | | $NaNO_3$ | - | - | 18 | - | 3 |
| | | $Na_3NO_3SO_4.H_2O$ | - | 89 | 47 | 53 | 48 |
| | | $K_3Na(SO_4)_2$ | 27 | - | - | 38 | 39 |
| 2 - 1 | 0,50-0,18 | $Na_2SO_4$ | 65 | 4 | 20 | <1 | <1 |
| | | $KNO_3$ | - | 13 | 20 | 12 | 28 |
| | | $NaNO_3$ | - | - | 4 | - | 15 |
| | | $Na_3NO_3SO_4.H_2O$ | 24 | 75 | 46 | 87 | 56 |
| | | $K_3Na(SO_4)_2$ | 11 | 9 | 2 | - | <1 |
| 2 - 2 | 0,50-0,36 | $Na_2SO_4$ | 23 | 21 | - | <1 | <1 |
| | | $KNO_3$ | - | 4 | 40 | 25 | 29 |
| | | $NaNO_3$ | - | - | 12 | - | 19 |
| | | $Na_3NO_3SO_4.H_2O$ | 23 | 51 | 46 | 70 | 48 |
| | | $K_3Na(SO_4)_2$ | 53 | 25 | 2 | 4 | 3 |

(a): the efflorescence after salt crystallization cycle 2 was not sufficient for XRD analysis

(b) :the efflorescence after salt crystallization cycles 1 and 2 was not sufficient for XRD analysis

**Table 6:** Composition of the efflorescing salt (w%) for Massangis limestone contaminated with a mixture of $Na_2SO_4$ and $K_2SO_4$

| Combination | | Salt efflorescence | Salt crystallization cycle number | | | |
|---|---|---|---|---|---|---|
| $Na_2SO_4$ – $K_2SO_4$ | | | | | | |
| Molar ratio | Weight ratio | | 1 | 2 | 3 | 4 |
| *untreated* | | | | | | |
| 1 - 1 | 0,25-0,31 | $Na_2SO_4$ | No efflorescence | | 32 | 40 |
| | | $K_3Na(SO_4)_2$ | | | 68 | 59 |
| 1,5 – 1 | 0,37-0,31 | $Na_2SO_4$ | No efflorescence | | 41 | 86 |
| | | $K_3Na(SO_4)_2$ | | | 59 | 14 |
| 2 - 1 | 0,50-0,31 | $Na_2SO_4$ | > 90 | Damage after cycle 1 | | |
| | | $K_3Na(SO_4)_2$ | < 10 | | | |
| 2 - 2 | 0,50-0,62 | $Na_2SO_4$ | No efflorescence | | | 73 |
| | | $K_3Na(SO_4)_2$ | | | | 27 |
| *Treated with water repellent* | | | | | | |
| 1 - 1 | 0,25-0,31 | $Na_2SO_4$ | 42 | 52 | Damage after cycle 2 | |
| | | $K_2SO_4$ | 58 | - | | |
| | | $K_3Na(SO_4)_2$ | - | 48 | | |
| 1,5 – 1 | 0,37-0,31 | $Na_2SO_4$ | 46 | 51 | | |
| | | $K_2SO_4$ | 54 | - | | |
| | | $K_3Na(SO_4)_2$ | - | 49 | | |
| 2 - 1 | 0,50-0,31 | $Na_2SO_4$ | > 66 | 51 | 40 | 86 |
| | | $K_2SO_4$ | X [(a)] | - | - | - |
| | | $K_3Na(SO_4)_2$ | X [(a)] | 49 | 60 | 14 |
| 2 - 2 | 0,50-0,62 | $Na_2SO_4$ | No efflorescence | | 58 | 96 |
| | | $K_3Na(SO_4)_2$ | | | 42 | 4 |

(a) : not quantified

## 4 Conclusion

Salt crystallization tests have been carried out on Massangis limestone by itself and treated with an oligomeric methylsiloxane. The samples were contaminated with mixtures of $Na_2SO_4$ with $NaNO_3$, $KNO_3$ or $K_2SO_4$. Among these, $Na_2SO_4$ shows the highest destructive index. The results from the salt crystallization cycles have confirmed that different salt mixtures behave differently when found in treated and untreated material.

Moreover, the study has shown that threshold values of salt contents up to which no damage is obtained, resulting from salt crystallization tests on samples contaminated with single salts, generally are no longer valid in case of combination with other types of salts. In fact, the prediction of the behaviour of salts in a mixture is complex due to the formation of double salts. Adding $NaNO_3$ or $KNO_3$ to $Na_2SO_4$ results in the formation of $Na_3(SO_4)(NO_3).H_2O$ (darapskite). Aphtitalite ($K_3Na(SO_4)_2$) is in general the major potassium salt formed in case of a combination with $K_2SO_4$. Hence, the deteriorating effect of $Na_2SO_4$ by itself is diminished with the result that higher amounts of this salt can be present before damage is obtained.

The sequence at which the salts are deposited at the drying surface is not uniform during the whole salt crystallization test. This difference in sequential salt deposition stresses the importance of a sufficient amount of crystallization cycles prior to a final evaluation of the salt compatibility of a material. Furthermore, it highlights the difficulty in predicting the behaviour of porous materials contaminated with a complex mixture of anions and cations as observed in practice.

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