Mitigating salt damage in lime-based mortars with mixed-in crystallization modifiers

Sanne J. C. Granneman[1], Barbara Lubelli[1]* and Rob P. J. van Hees[1, 2]
[1] Delft University of Technology, Delft, The Netherlands
[2] TNO Technical Sciences, Delft, The Netherlands
****B.Lubelli@tudelft.nl***

Abstract

This paper presents the most important results of a research project which focused on the use of crystallization modifiers mixed in lime mortar to mitigate salt crystallization damage. The research focused on two of the most damaging salts, sodium chloride and sodium sulfate, and suitable crystallization modifiers (sodium ferrocyanide and borax). We report the major findings related to the effectiveness of the modifiers when mixed in the mortar, and the results of characterization of the additivated mortars in comparison with reference mortars. Moreover, the durability of the developed mortars to salt decay is discussed, based on the results of an accelerated salt weathering test carried out in laboratory. No major effects of the modifiers on the fresh and hardened mortar properties were observed which might restrain the application of crystallization modifiers in restoration mortars. Additionally, the mortars with mixed-in modifiers showed a considerable improvement of the salt resistance when compared to reference mortars. Considering these results an outlook for future research pathways is given.

Keywords: crystallization modifiers, self-healing, lime mortar

1. Introduction

Salt crystallization damage in porous building materials is a ubiquitous threat to our built cultural heritage. Low mechanical strength makes lime-based mortars especially susceptible to salt damage. In restoration or renovation works, replacement of renders and plasters often constitutes a large part of the total costs of the project. Current solutions, such as using a stronger binder or changing the moisture transport properties of the mortar, usually have a limited resistance to salt decay and low compatibility with the existing materials.[1, 2]

Alternatively, the use of crystallization modifiers has been proposed.[3] Crystallization modifiers do not aim to alter the material properties, but the damaging mechanism itself. Using crystallization modifiers in porous building materials has gained wide research interest in the last years (see e. g.[3-5]). However, the use of modifiers in a fresh mortar, thereby giving the mortar “self-healing properties”, is relatively new. By mixing modifiers in during mortar production, they can become active as soon as the damaging salts enter the porous material. Promising results have already been obtained in a pilot study.[6]

A research project was started to further study the feasibility of the use of crystallization modifiers to mitigate salt crystallization damage. This project had the following aims:

i) Identify suitable modifiers for two of the most abundant and damaging salts: sodium chloride and sodium sulfate,

ii) Study the modifier-salt interaction in bulk solution to elucidate the working mechanism and find a suitable concentration,

iii) Test the effect of modifier addition on mortar properties (which might limit their application), and iv) Test the durability of additivated mortars in an accelerated salt weathering test.

From literature research, sodium ferrocyanide and borax (sodium tetraborate decahydrate) were identified as potential modifiers for sodium chloride and sodium sulfate, respectively.[7] Ferrocyanide is a well-known modifier for sodium chloride. Therefore, this research focused on the study of its effect on fresh and hardened mortar properties and on its capability of mitigating salt decay in mortar. Ferrocyanide could reduce crystallization damage in two ways:

i) it keeps the salt longer in solution favouring transport to the drying surface, and

ii) it alters the crystallization habit of sodium chloride from cubic to dendritic, fact which also favours transport to the surface and enhanced drying.

Both factors lead to enhanced transport to the surface, where subsequently the salt can crystallize as harmless efflorescence.[8] Borax on the other hand is less well-known and was therefore first studied in bulk solution experiments. In this research, the effect of borax addition on solution properties and its effect on crystallization of sodium sulfate were studied. As has been reported in Ref.[9], depending on the starting concentration of the solution, two different phases of borax can precipitate, each having a different effect on sodium sulfate crystallization. One phase favours the crystallization of hydrated sodium sulfate (mirabilite) at or near saturation, meaning that no or lower crystallization pressures can develop. The other phase modifies the habit of anhydrous sodium sulfate (thenardite) to elongated needles. This habit modification can be supposed to lead, thanks to a larger evaporation surface, to enhanced salt transport to the drying surface. Similar to ferrocyanide, this would favour the formation of harmless efflorescence.[8]

In this paper the major findings relating to the effect of modifier addition on mortar properties and to the durability of additivated mortars are reported. First, an experiment to test whether borax' effectiveness is affected by the carbonation process is described. Then, the effect of modifiers on mortar properties such as workability, water absorption and drying and flexural and compressive strength are reported. Finally, the durability of the additivated mortars with respect to salt crystallization damage is discussed based on the results of an accelerated salt weathering test.

2. Materials and Methods

2.1. Mortar characterization

Two types of specimens were prepared: lime only specimens and mortar (lime + sand) specimens. The first, used to study the effect of borax on sodium sulfate crystallization, were prepared by mixing calcium hydroxide powder (Sigma-Aldrich, ≥ 96% purity) with distilled water only or with water additivated with the modifier. After carbonation, a blank specimen was treated with borax solution. Then, the blank and the two borax specimens contaminated with sodium sulfate solution. After drying, the specimens were broken and the cross section was studied using

SEM. By comparing specimens additivated with borax prior to carbonation and those to which borax was added later on, the effect of carbonation on the effectiveness of borax as modifier of sodium sulfate crystallization was assessed. Full details of this experiment can be found in Ref.[10]

The second type of specimens, used to test fresh and hardened mortar properties and assess the durability towards salt decay, was prepared according to EN1015-2. Commercial air lime (Supercalco90) and standard sand (EN 196-1, sieved to select the grain size between 0.25 and 1.0 mm, were used. The modifier was added to the water used to prepare the specimens: 0.94 wt% sodium ferrocyanide and 3.2 wt% borax were added with respect to the lime. Several fresh and hardened mortar properties were tested according to standard procedures or techniques: workability (EN1015-3), water absorption and drying (EN1015-18), porosity and pore size distribution (Mercury Intrusion Porosimetry) and flexural and compressive strength (EN1015-11). Full details on the preparation of the mortars and the testing methods can be found in Ref.[10]

2.2. Accelerated salt weathering test

The salt crystallization resistance of the reference and additivated mortar specimens was tested with a custom designed salt weathering test, shown in *Figure 1*, simulating circumstances found in practice. 80 RH% is above the equilibrium relative humidity of sodium chloride (RHeq = 75%), but below that of the sodium sulfate phases. Consequently, the sodium chloride crystals will deliquesce when the humidity goes up and recrystallize when the humidity goes down again. This ensures multiple crystallization cycles for sodium chloride, a requirement for this specific salt for damage development. Recrystallization of sodium sulfate was obtained only by rewetting with liquid water at the end of a cycle. To have a comparable test protocol, the specimens with sodium chloride were also rewetted with liquid water after each cycle.

Before the test, the specimens were contaminated with salt solution via capillary absorption from the bottom. A precise amount of solution was used to ensure contamination with 1 wt% sodium sulfate or 2 wt% sodium chloride with respect to the mortar. In total 3.46 (reference NaCl), 3.91 (ferrocyanide), 1.77 (reference Na_2SO_4) or 1.91 (borax) gram salt was added to the specimens during the complete test. These values include the brushed off efflorescences during the test. For each mortar type, 3 replicas were tested.

After each complete cycle, all specimens were rewetted with demineralized water equal to the initial amount used to contaminate the specimens. After 3 cycles (63 days), salt solution (exact amount to obtain again 1 wt% sodium sulfate or 2 wt% sodium chloride) was

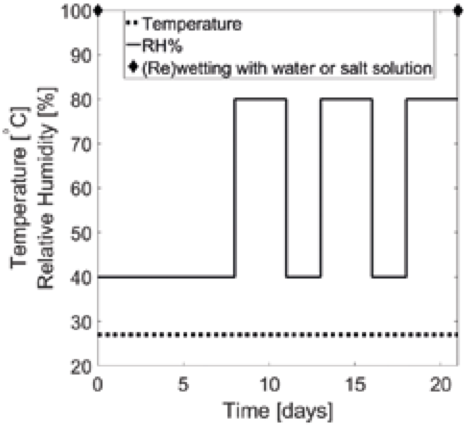

Figure 1: Temperature and RH cycles used in the accelerated salt weathering test. This entire cycle was repeated 5 times (in total 105 days). The diamonds correspond to wetting by capillarity at the start (day 0) or after each 3 week cycle (day 21) at 22.9°C ± 0.3/29.1RH% ± 2.4. At day 0 and day 63 salt solution was used, the other times demineralized water.

used for rewetting, in order to replenish the brushed off salt. After rewetting, any loose material was brushed off and the specimens started a new cycle. The brushed off material was washed and dried in order to separate the salt efflorescences from the debris. The debris was weighed and the amount of salt calculated by the difference. In total the specimens were tested for 5 cycles. Full details of the experiment can be found in Ref.[11]

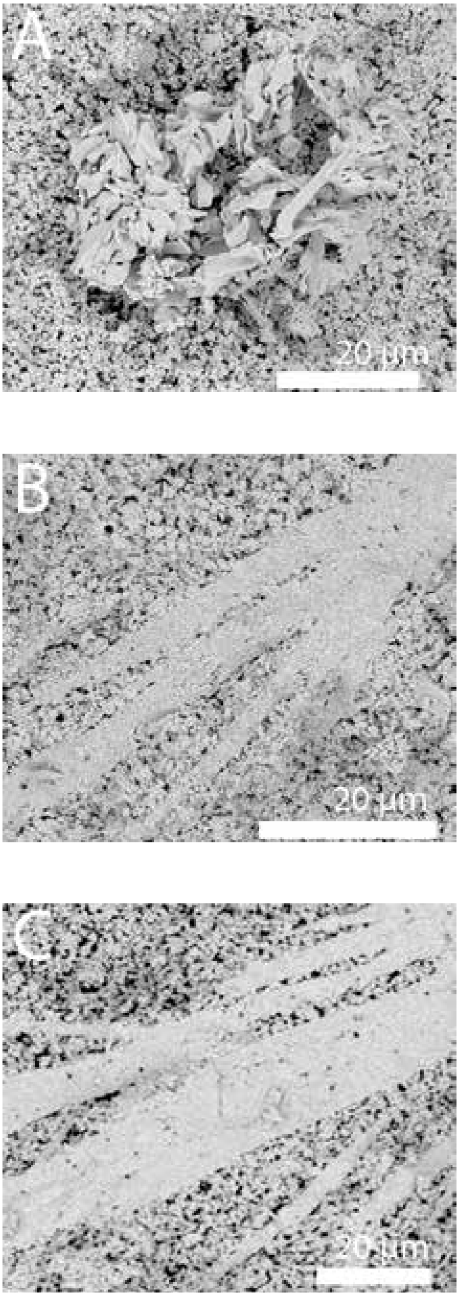

Figure 2: SEM images of lime-only specimens contaminated with sodium sulfate. A: reference specimen; B: specimen with 3.2wt% borax mixed in during preparation (thus before carbonation); C: Specimen additivated with borax after full carbonation of the specimen. A clear difference in crystal habit can be observed between the reference specimen and both specimens with borax. Contrarily, no distinction can be observed between B and C, meaning that the carbonation process has no effect on the borax effectiveness as modifier of sodium sulfate crystallization.

3. Results and discussion

3.1. Mortar properties

The effect of borax on sodium sulfate crystallization can be observed in the SEM pictures in *Figure 2*. When *Fig. 2a* is compared to *2b/c*, it is clear that the crystal habit of sodium sulfate without borax is different from the crystal habit in the presence of borax. If subsequently *Figures 2b and 2c* are compared, a similar crystal habit can be seen in both figures. This means that the carbonation process of the mortar has no effect on the effectiveness of borax as modifier for sodium sulfate. With this experimental technique it is not possible to investigate the nature of the precipitated phases, but this would be interesting for future work.

A selection of the measured fresh and hardened mortar properties is summarized in *Table 1* (additional characterization results can be found in Ref.[10]). When the values for additivated and reference specimens are compared, no notable differences can be observed. It can therefore be concluded that there are no negative consequences to mixing these quantities of modifiers in the mortar during production, as the addition of these modifiers does not negatively affect the mortar properties.

Property	Method	Reference	Ferrocyanide	Borax
Workability	Flow table test	170 mm	161 mm	161 mm
Water content	-	15.95 wt%	15.14 wt%	14.59 wt%
WAC [kg/m²h$^{1/2}$]	Capillary rise	8.05	7.62	7.84
Density [kg/m³] Open porosity (%V/V)	Saturation at atm pressure	1943 26.7 ± 0.19	1964 25.9 ± 0.24	1933 27.1 ± 0.06
Bulk density [g/ml] Open porosity (%V/V)	Mercury Intrusion Porosimetry	1.977 25.1 ± 0.11	1.971 25.4 ± 0.36	1.961 25.1 ± 0.55
Tensile strength (N/mm²)	-	0.79 ± 0.11	0.85 ± 0.03	0.92 ± 0.11
Compressive strength (N/mm²)	-	2.01 ± 0.33	2.08 ± 0.18	2.61 ± 0.22

Table 1: Fresh and hardened mortar properties of the different 1:3 lime:sand mortar mixtures. Results previously reported in [10]

3.2. Salt durability[11]

During the accelerated salt weathering test, the specimens were monitored both visually and gravimetrically. The weight loss of material (with respect to the mortar) is plotted in *Figure 3*, and the weight loss of salt is visualized in *Figure 4*. It is clear that for both salts, the reference specimens suffer considerable material loss after 5 cycles. Contrarily, the additivated mortars show no or only minor material loss. The ferrocyanide stimulates efflorescence of the salt, i. e. crystallization outside the material, as does borax but to a lesser extent. This is consistent with the hypotheses on damage reduction proposed in the introduction. *Figure 5* compares specimens contaminated with sodium chloride at the start and end of the test. The reference specimen shows considerable surface loss at the end of the test. Contrarily, the specimen with ferrocyanide shows no material loss, but extensive efflorescence, which developed very fast already just after rewetting via capillarity and brushing of the specimens. In *Figure 6* the specimens contaminated with sodium sulfate are compared. At the end of the test, both specimens show damage at the surface, but this is in the case of the specimen additivated with borax considerably less than in the reference specimen. Both the material loss and the visual observations show that both sodium chloride and sodium sulfate have the potential to cause considerable damage in the reference specimen. However, when the mortars are additivated with modifiers, damage does not occur or is considerably less.

Two additivated specimens were desalinated at the end of the test and the boron and iron content of the desalination water was analysed via ICP (Inductively Coupled Plasma) spectrometry. Approximately 10 wt% (borax) and 1 wt% (ferrocyanide) of the original modifier

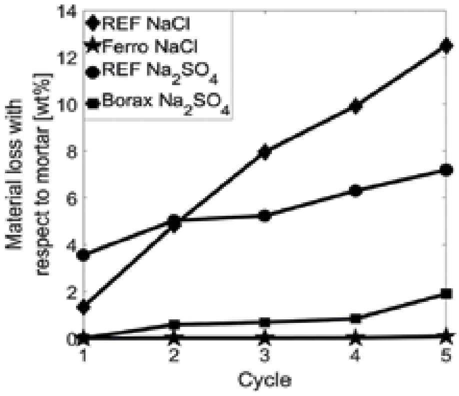

Figure 3: Cumulative material loss, comparison between reference and additivated specimens.

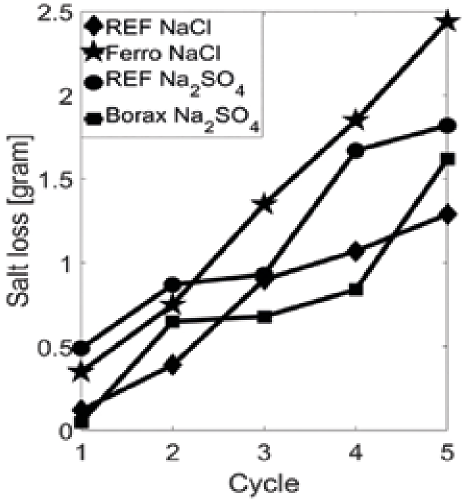

Figure 4: Cumulative salt loss, comparison between reference and additivated specimens.

amount was still present. These values indicate that either the modifiers have leached out (together with the salt efflorescence) or that they are (partially) tightly bound to the mortar structure. Modifier leaching is an important parameter to take into account in future applications, whereas the binding of the modifier could have implications for its effectiveness and working mechanism.

4. Conclusions

The additivation of mortars with crystallization modifiers during production has been proposed here to mitigate salt crystallization damage in porous building materials. Suitable crystallization modifiers for sodium chloride (sodium ferrocyanide) and sodium sulfate (borax) were identified to be mixed in a mortar during production. In this paper, at first the effectiveness of borax as a modifier for sodium sulfate crystallization when mixed in lime was assessed and confirmed. In a next step, additivated mortars were characterized and compared to reference mortars in order to identify potential (negative) effects on fresh and hardened mortar properties. None of the tested properties was affected by the addition of the modifiers, meaning that there are no contra-indications to mixing them in the mortar in the used concentrations during production.

Finally, the salt crystallization resistance of the additivated mortars was assessed using a custom designed accelerated salt weathering test. The mortars with mixed-in modifiers showed a considerable improvement of the salt resistance when compared to reference mortars. Combining all these results it can be concluded that additivating mortars with crystallization modifiers during their production is a feasible method in order to mitigate salt crystallization damage in porous building materials.

5. Outlook

The research presented in this paper shows the viability of using crystallization modifiers to mitigate salt weathering damage in porous building materials. Although the proof-of-principle has been shown on the laboratory scale, more research is needed to develop the material into a commercial product, suitable for

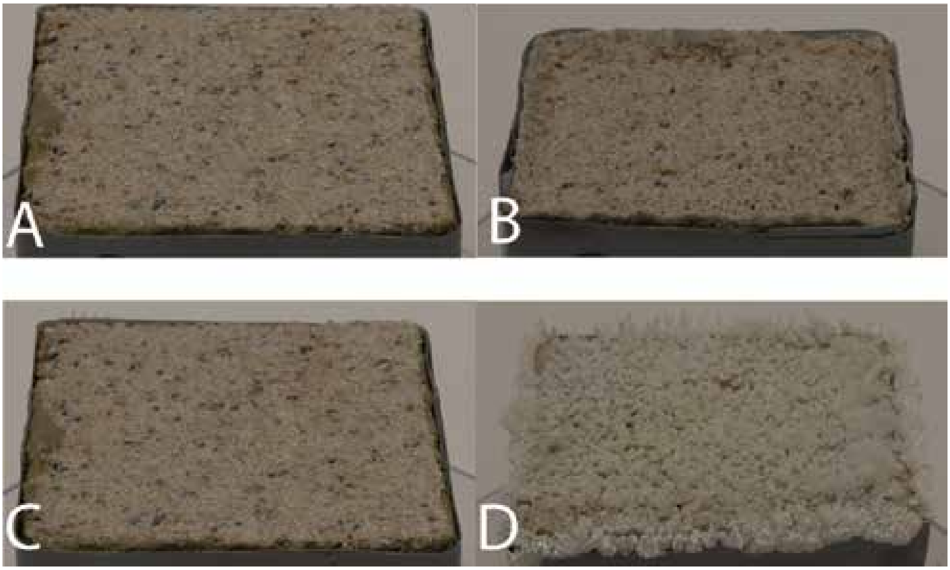

Figure 5: Comparison between reference (A/B) and specimens with mixed-in ferrocyanide (C/D), both contaminated with sodium chloride. A/C show the specimens at the start of the test, B/D show the specimens ~ 15 minutes after brushing after the 5th cycle. The reference specimen (B) shows sanding of the surface. The specimen with ferrocyanide shows no surface damage, only a large amount of efflorescence.

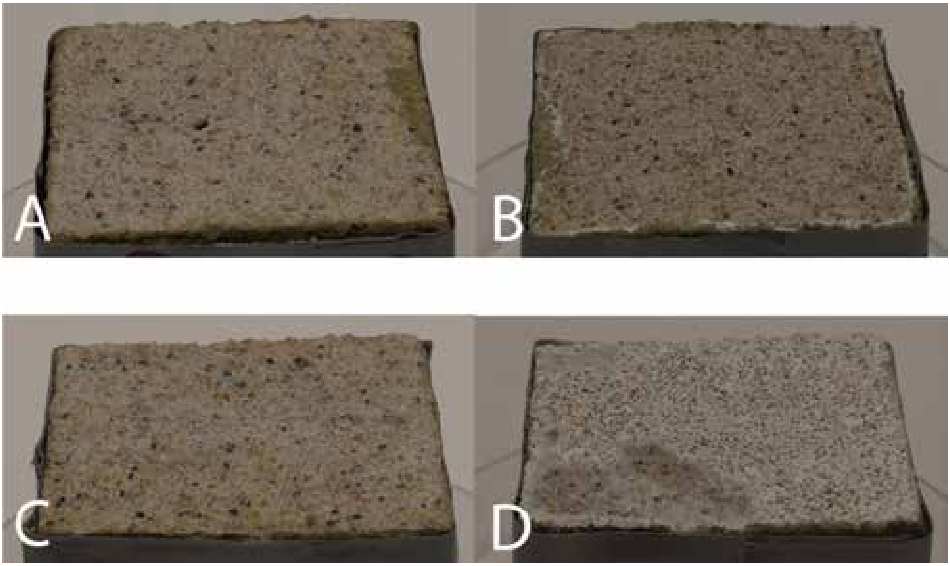

Figure 6: Comparison between reference (A/B) and specimens with mixed-in borax (C/D), both contaminated with sodium sulfate. A/C show the specimens at the start of the test, B/D show the specimens ~ 15 minutes after brushing after the 5th cycle. The reference specimen (B) shows clear damage at the surface. The specimen with borax shows only minor surface damage at the lower left corner (D).

renovation or restoration works. Interesting research paths to further develop the mortar designed in this project are:

- Studying the effect of modifier in mortars with different composition (e.g. cement-based).
- Studying the speed of modifier leaching and if necessary developing possible solutions, e.g. encapsulation.
- Assessing the effect of the identified modifiers on other salts and on salt mixtures and the possibility of combining different modifiers.
- Assessing the effectiveness of the developed mortar (on test panels) in situ.

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