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Effect of mixed in crystallization modifiers on the resistance of lime mortar against NaCl and Na₂SO₄ crystallization

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Abstract

Weathering of porous building materials caused by the crystallization of soluble salts is a ubiquitous problem in the built cultural heritage. Especially lime-based mortars are susceptible to salt decay, due to both their bimodal pore size distribution and low mechanical strength. The addition of crystallization modifiers to mortars during mixing may confer them an improved resistance to salt decay. In this research, lime-based mortars additivated with ferrocyanide or borax (modifiers for sodium chloride and sodium sulfate, respectively) were prepared. An accelerated salt crystallization test was carried out to assess the effect of the modifiers on the salt resistance of the mortars. The development of damage was assessed by visual and photographic observations and by quantifying the salt and material loss. At the end of the test, SEM observations were performed on the surface and cross-section of the specimens, to study the effect of the modifiers on the crystallization habit of the salts. The ferrocyanide and borax additivated mortars showed a considerably improved durability with respect to salt crystallization damage. Both modifiers altered the growth morphology of the salt crystals inside the pores of the mortars.

Keywords: Salt crystallization, salt damage, crystallization modifiers, lime mortar, sodium chloride, sodium sulfate

1. Introduction

Crystallization of soluble salts is a common cause of severe deterioration of building materials (see e.g., [1, 2]). Damage occurs due to repeated dissolution and recrystallization cycles of the soluble salts inside the pores of the building materials. When a growing crystal gets confined, it will exert a pressure on the pore wall that is proportionate to the supersaturation level of the solution in contact with the crystal and the confining wall [3, 4]. Damage occurs if the crystallization pressure becomes higher than the strength of the material. Especially lime-based mortars are susceptible to salt damage, due to their bimodal pore size distribution and low mechanical strength [5].

An effective solution to deal with salt damage could be complete removal of the salts and/or the moisture source; however, this is not always feasible. In some cases, the replacement of the decayed material, e.g. pointing mortars, plasters and renders, is necessary. Mortars developed for application as a plaster on salt loaded substrates are often cement-based and/or possess hydrophobic properties, with the aims of conferring a high mechanical strength to the mortar and/or delay the transport of salts to the surface. However, these mortars are often not compatible with the existing historic fabric and may even cause more damage [6]. Recently, the modification of the salt crystallization process by the use of crystallization modifiers was suggested as a way to mitigate the damage. Some promising results have already been reported [see e.g., [7-10]]. The latest application, being also the focus of this study, consists in mixing the modifiers in a mortar during its production. In this way, the crystallization modifiers, which are already present in the mortar, will become effective, as soon as the damaging salt solution enters the material.

Crystallization modifiers are ions or molecules that can prevent nucleation (inhibitors), promote nucleation of a certain crystal phase (promoters) and/or modify the habit (shape) of the crystals (habit modifiers). In earlier research by the authors, sodium ferrocyanide and borax were chosen as modifiers to be mixed in the mortar [11, 12]. Ferrocyanide acts as an inhibitor of sodium chloride precipitation. In this way, the salt can be transported easier to the surface of the material, where it

crystallizes as harmless efflorescence. Additionally, ferrocyanide alters the habit of the normally cubic sodium chloride crystals to dendrites: the larger evaporation surface enhances the transport of salts to the surface. Borax acts on the crystallization of sodium sulfate, and its working mechanism is reported to depend on which phase of borax is actually present [13]. One phase (borax, sodium tetraborate decahydrate) favours the crystallization of hydrated sodium sulfate (mirabilite) at or near saturation, resulting in no or low crystallization pressure. The other phase (tincalconite, sodium tetraborate pentahydrate) modifies the habit of anhydrous sodium sulfate (thenardite) from prisms 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. Similarly to ferrocyanide, borax would thus favour the formation of harmless efflorescence instead of damaging crypto-florescence [14].

In this research, the resistance to sodium chloride and sodium sulfate crystallization of additivated mortar specimens in comparison with reference specimens has been assessed with an accelerated salt crystallization test. The effect of the modifiers on the damage and the salt distribution in the specimens has been evaluated. The effect of the modifiers on the morphology of the salts has been studied by scanning electron microscopy (SEM) on the surface and the cross section of the specimens.

2. Materials and methods

2.1 Specimen preparation

For the preparation of the mortar specimens, a very pure commercial air lime powder (Supercalco90 by Carmeuse, minimum 90% calcium hydroxide) was selected. Standard sand (EN196-1 [15]), sieved to a grain size between 0.25-1.0 mm, was used in order to obtain a coarse porous and relatively weak mortar. A 1:3 volume ratio for lime:sand was selected, since this is a common ratio used in practice. In order to better reproduce the properties of a plaster mortar when used on site, mortars were

applied on a substrate; Maastricht limestone, a highly porous (50 vol%) natural stone with coarse pores (30-50 μm) was chosen.

All mortars were prepared according to EN1015-2 [16]. The reference specimens were made with distilled water. For the additivated mortars, a defined amount of water containing the desired amount of modifier (determined in earlier research [12]) was added, followed by additional water to obtain good workability. The following concentrations (wt% relative to the binder) of modifier were used:

- No modifier
- 0.94% ferrocyanide (sodium hexacyanoferrate(II)-10-hydrate, Riedel-deHaën, puriss.)
- 3.2% borax (sodium tetraborate decahydrate, Sigma-Aldrich, puriss.)

The mortars (5x5x2 cm^3) were prepared in tailor-made extruded polystyrene moulds (in which first the Maastricht limestone substrate was placed) and compacted by hand. The mould and substrate were wetted with demineralized water prior to casting of the mortars. The moulds were removed after two days, when the mortar was firm enough. After casting, the specimens were covered with plastic sheets and stored under ambient conditions for one day. Then, the plastic sheets were removed and the specimens were stored at 20°C/65%RH until approximately 50% of the water had evaporated. Subsequently, the mortar specimens were artificially carbonated at 20°C/65RH%/1%CO₂ until full carbonation was obtained (2-3 weeks). Full carbonation of the mortar specimens was indicatively assessed by breaking them and spraying the cross section with a phenolphthalein solution.

2.2 Mortar characterization

The possible effect of the addition of modifiers on the fresh and hardened mortar properties (workability, carbonation rate, capillary water absorption and drying, pore size distribution and porosity and flexural and compressive strength) has been investigated in an earlier stage of this research. Full details of the characterization methods and results can be found in [12]; selected results are given in Table 1. The addition of the modifiers was shown to not significantly affect any of the above mentioned properties; also the structure of the additivated mortars was found to be similar to that of the reference mortar (see Figure 1).

Table 1: Selected mortar properties of the different 1:3 lime:sand mortar mixtures. Previously reported in Ref. [12].

Property	Replicates	Method	Standard/ reference	Reference mortar	Mortar with ferrocyanide	Mortar with borax
Water content	1	*	-	15.95 wt%	15.14 wt%	14.59 wt%
Workability	1	Flow table test	EN1015-3 [17]	170 mm	161 mm	161 mm
WAC [$\text{kg/m}^2\text{h}^{1/2}$]	3	Capillary rise	EN1015-18 [18]	8.05 ± 0.358	7.62 ± 0.097	7.84 ± 0.148
Density [kg/m^3]	3	Saturation at	[19]	1943 ± 4.6	1964 ± 6.0	1933 ± 1.3
Open porosity (%V/V)		atm pressure		26.7 ± 0.19	25.9 ± 0.24	27.1 ± 0.06
Bulk density [g/ml]	2	Mercury Intrusion	-	1.977 ± 0.005	1.971 ± 0.006	1.961 ± 0.004
Open porosity (%V/V)		Porosimetry		25.1 ± 0.11	25.4 ± 0.36	25.1 ± 0.55
Tensile strength (N/mm^2)	5	-	EN1015-11 [20]	0.79 ± 0.11	0.85 ± 0.03	0.92 ± 0.11
Compressive strength (N/mm^2)	10	-	EN1015-11 [20]	2.01 ± 0.33	2.08 ± 0.18	2.61 ± 0.22

*The water content of the fresh mortar was determined gravimetrically, by weighing a sample of the fresh mortar before and after drying it in an oven at 40°C until constant weight was reached; the water content was calculated as percentage of the initial weight of the fresh mortar.

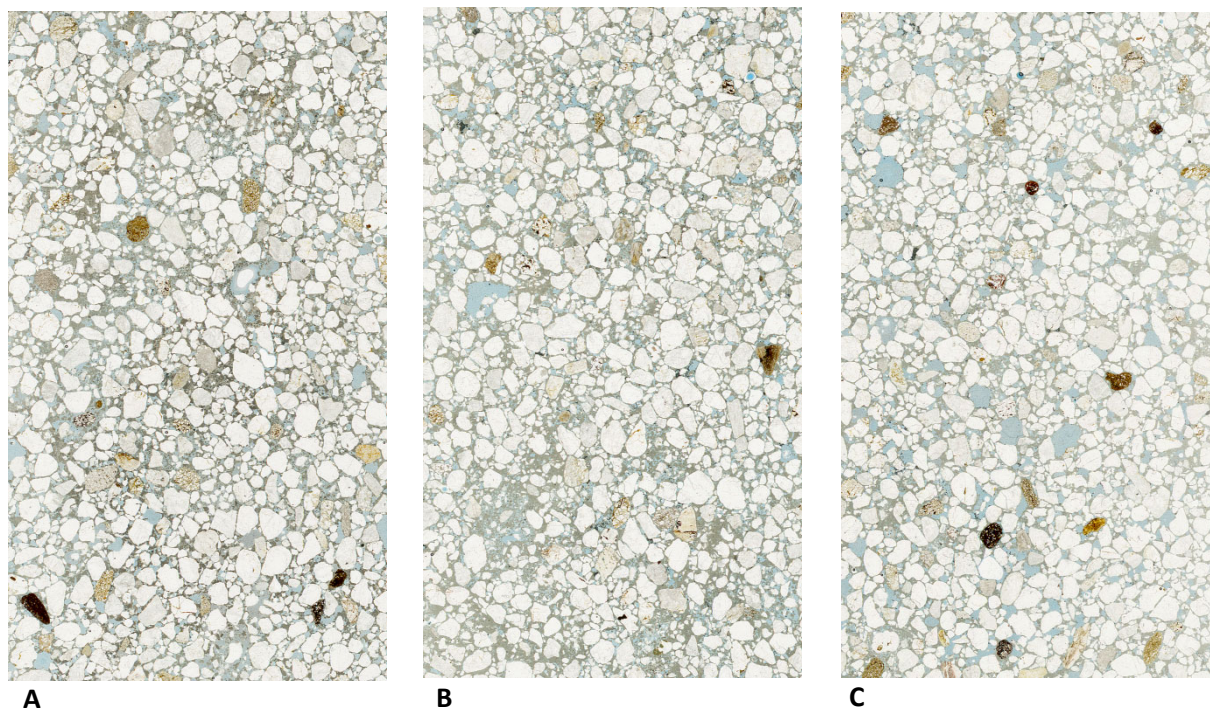


Figure 1: Thin sections showing the mortar structure. A: reference, B: with ferrocyanide, C: with borax.

2.3 Salt crystallization procedure

In this research a test procedure has been developed in order to assess the salt crystallization resistance of additivated and reference mortars in a short time period in a climatic chamber in the laboratory. The test cycle used in this accelerated salt crystallization test can be found in Figure 2. This procedure is the result of the work of the authors towards an effective and reliable salt crystallization test [21]. It is an adaptation of the RILEM MS A.1 procedure [22], further modified in international research (e.g. [23]) and in previous work by the authors [24]. In this specific research the range of RH changes has been further adapted to be effective for both sodium sulfate and sodium chloride salts. The relative humidity changes were programmed in order to cause salt dissolution and crystallization cycles. The entire cycle (21 days) was repeated five times (for total of 105 days). The test was carried out on 3 replicates for each mortar series. The lateral sides of the mortar specimens were sealed with epoxy resin (Wapex 201) and the bottom of the specimens was sealed with tape (which was removed during the re-wetting step). This way, evaporation could only take place via the top surface of the specimens, simulating what occurs in a plaster layer applied on a

masonry wall. The mortar specimens were contaminated with salt solution via capillary absorption from the bottom; enough solution to wet the upper surface of the specimen was used. The concentration of the salt solutions was chosen such as to result in 1wt% of sodium sulfate (anhydrous) or 2wt% of sodium chloride with respect to the total mortar weight. This resulted in relatively diluted solutions (0.27 mol kg^{-1} for Na_2SO_4 and 1.33 mol kg^{-1} for NaCl). The salt amount used in these experiments is known to be able to cause damage in the relatively weak lime mortar used in our research (as shown by the decay observed in the reference, non-additivated specimens at the end of the salt crystallization test).

After each 3-week test cycle (corresponding to the 'diamond' symbol at 21 days in Figure 2), the specimens were weighed and photographed. Then, the specimens were rewetted via capillary absorption with an equal amount of water as present in the salt solutions used in the first wetting step. In the fourth cycle, salt solution was used instead of water during wetting, in order to replenish the brushed-off salt. Next, the surface of the specimens was brushed with a soft toothbrush to remove any salt efflorescence and debris. After brushing, the specimens were weighed and photographed again before starting a new cycle.

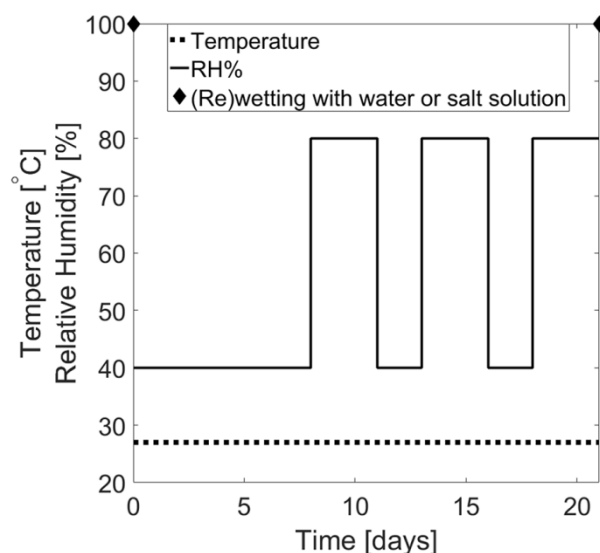


Figure 2: Temperature and RH cycles used in the accelerated salt weathering test. This entire cycle was repeated 5 times (in total 105 days). The diamonds correspond to wetting by capillarity at the start (day 0) or after each 3-week cycle outside the climatic chamber at $22.9^{\circ}\text{C} \pm 0.3$, $29.1 \text{ RH}\% \pm 2.4$. At day 0 and after 3 full cycles, the specimens were re-wetted with salt solution; the other times demineralized water was used. At the end of each 3 week cycle the specimens were photographed, re-wetted and brushed; the weight of the specimens was recorded at each step.

151

152 The brushed off debris was separated from the salt by dissolution and filtration; this way, the salt

153 and actual material loss could be distinguished and quantified. After finishing the complete test, one

154 specimen of each series was desalinated by immersion in demineralized water, in order to assess

155 potential caking effects of the salts (i.e. salts which crystallize between loose grains and hold them

156 together). The water used during desalination of the ferrocyanide and borax additivated specimens

157 was analysed with ICP-OES or ICP-MS (Inductive Coupled Plasma with Optical Emission or Mass

158 Spectrometry) to determine the amount of modifier still present in the specimen after five

159 crystallization cycles.

160

161 A thin section and polished chip were prepared with kerosene (to avoid dissolution of the salts) from

162 one specimen of each series, with the aim of studying the salt distribution after the test and the habit

163 of the crystallized salts inside the pores. However, no salt could be identified in the prepared

164 specimens, probably due to the fact that the salt content after the crystallization test was really low

165 (see section Results and discussion). Therefore, additional mortar specimens (also prepared in the lab

166 on a Maastricht limestone substrate and thus comparable to the ones used in the salt weathering

test) were contaminated with the same amount of salt as used in the salt weathering test (1wt% Na_2SO_4 or 2wt% NaCl). After drying in an oven for 3 days, at similar drying conditions as used in the salt weathering test, the specimens were rewetted with an equal amount of water as present in the original salt solutions. Next, the specimens were dried for 3 days in the oven. Following these two cycles, the specimens were broken and both the surface and the cross section were examined using Scanning Electron Microscopy (SEM, FEI NovaNanoSEM 650).

3. Results and discussion

3.1 Crystallization test

The salt crystallization resistance of the mortars was assessed with an accelerated crystallization test. During the test the specimens were monitored both visually and photographically and their weight was recorded at significant steps. Figure 3 shows the surface of reference and additivated specimens after the 5th cycle (105 days). The results of the loss of material and salt after each cycle are plotted in Figure 4 and 5 for specimens with sodium chloride and sodium sulfate, respectively.

Figure 3A shows the surface of a reference specimen contaminated with sodium chloride at the end of the salt crystallization test. During the test the reference specimens showed moderate efflorescence and severe material loss. Deterioration of the surface occurred in the form of sanding. This type of damage is typical for this salt, and is similar to the type of damage development as observed in practice [24]. As it can be observed in Figure 4, the damage developed linearly in time and seems not to depend on the total salt content present in the specimen.

Figure 3B shows the surface of a mortar additivated with ferrocyanide at the end of the crystallization test. Differently than in the case of the reference specimen, during the test the mortar specimens additivated with ferrocyanide showed a large amount of efflorescence and no or only

minor material loss. Ferrocyanide stimulates the appearance of efflorescence, as it can be clearly seen in Figure 3B: this picture, taken approximately 15 minutes after rewetting and brushing of the surface, shows the rapid formation of new sodium chloride efflorescence. As more efflorescence results in less crystallizing salts inside the pores of the material, this may also have contributed to limit the damage.



A



B



C



D

Figure 3: Reference (A, C) and additivated (B, D) specimens at the end of the 5th cycle (105 days, ~ 15 minutes after rewetting and brushing). A and B show the surfaces of the reference and ferrocyanide additivated mortars contaminated with sodium chloride, respectively. The reference shows sanding of the surface, whereas the specimen with ferrocyanide only shows a large amount of efflorescence, which appeared immediately after rewetting. C and D show the surfaces of the reference and borax additivated mortars contaminated with sodium sulfate, respectively. The reference specimen shows clear damage (scaling after the first test cycle, sanding after the following test cycles) to the whole surface, whereas the specimen with borax only shows minor damage (sanding) to the lower left corner.

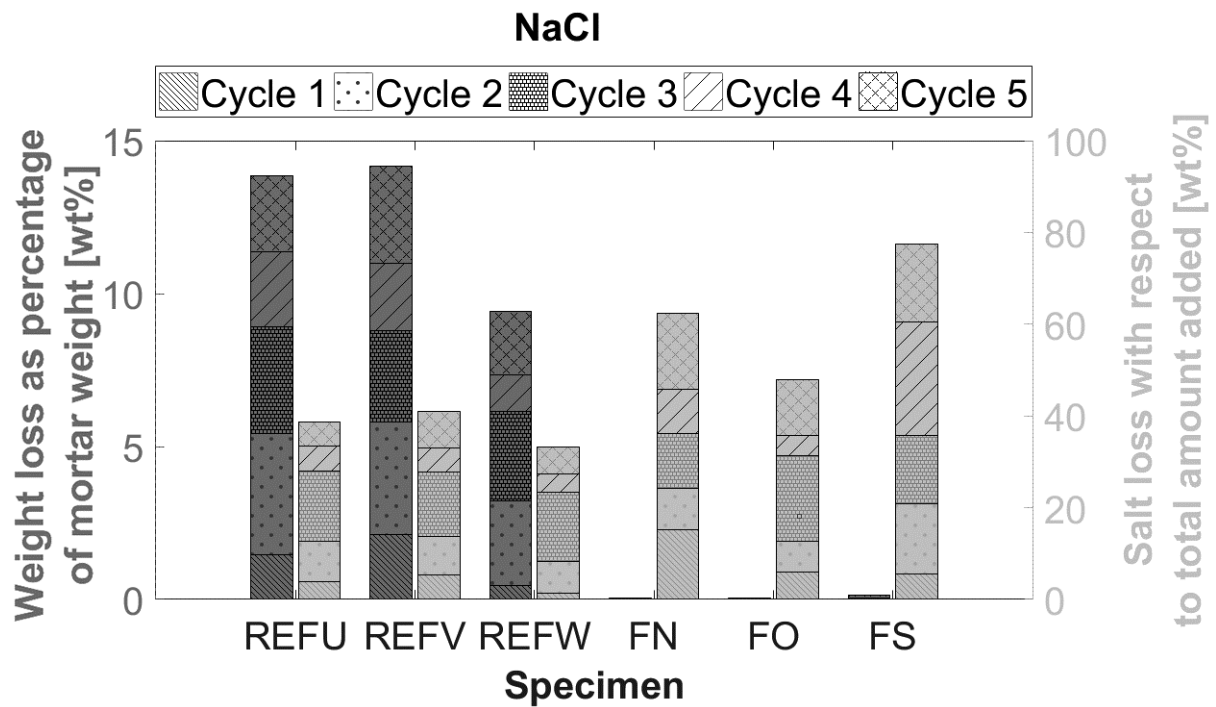


Figure 4: Material (dark grey) and salt (light grey) loss for the mortars contaminated with sodium chloride per cycle of the crystallization test. The material loss is given as a percentage of the total mortar weight. The salt loss is given as a percentage of the total amount of salt added after the two contaminations with salt solution. REFU, REFV and REFW correspond to reference specimens. FN, FO and FS correspond to ferrocyanide-additivated specimens.

At the end of the salt crystallization test, the reference specimens contaminated with sodium sulfate show considerable material loss. The material loss was most severe during the cycle in which damage occurred for the first time; in the following cycles damage developed more slowly. Two of the reference specimens contaminated with sodium sulfate (REFR and REFT) developed damage directly after the first rewetting with liquid water at the end of the first cycle and before the brushing. This damage can be attributed to the rapid crystallization of mirabilite crystals (at high supersaturation), following the dissolution of anhydrous sodium sulfate (expected at the drying conditions used in the test, see Figure 2) during re-wetting [25, 26]. The third of the reference specimens (REFQ) was left undamaged after the first cycle; this was also the only reference specimen showing efflorescence at the end of cycle 1, fact which might explain why no severe damage occurred in this case until cycle 2. In all reference specimens, damage occurred at first in the form of scaling of the entire surface. Later on, damage developed in the form of sanding of the outer layer. As can be seen in Figure 5, in the

case of specimens contaminated with sodium sulfate, the amount of material loss is related to the salt content present in the specimen.

Differently from the reference specimens, the specimens additivated with borax show only minor material loss, localized in a small area of the surface (compare Figures 3C and D), at the end of the crystallization test. Furthermore, in these specimens damage occurred in the form of sanding. The absence of damage can (at least in part) be attributed to the fact that more efflorescence developed on the additivated specimens than on the reference ones: more efflorescence results in less crystallization inside the pores of the material and consequently in less damage.

One specimen for each mortar/salt combination (REFV, FN, REFR and BO) was desalinated after the

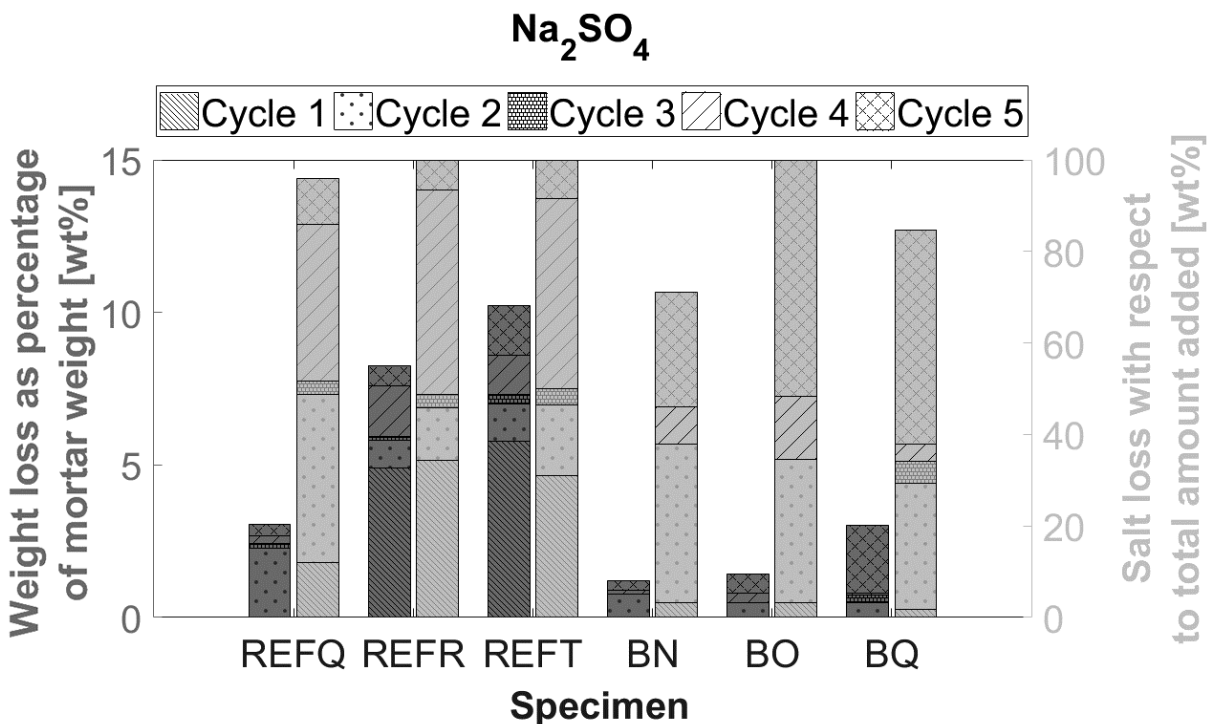


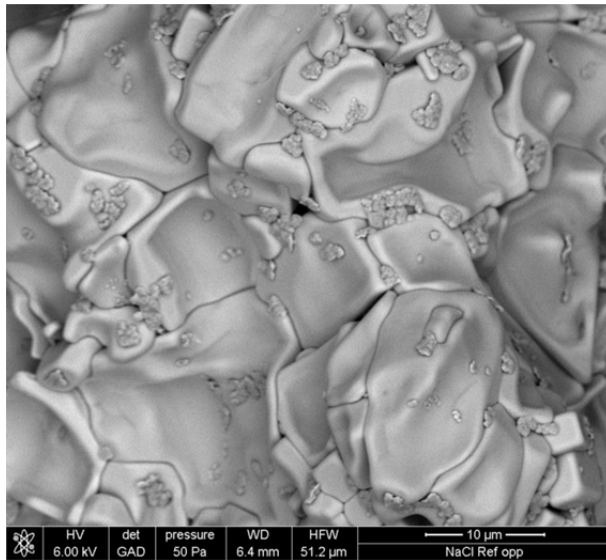
Figure 5: Material (dark grey) and salt (light grey) loss for the mortars contaminated with sodium sulfate per cycle of the crystallization test. The material loss is given as a percentage of the total mortar weight. The salt loss is given as a percentage of the total amount of salt added after the two contaminations with salt solution. REFQ, REFR and REFT correspond to reference specimens. BN, BO and BQ correspond to borax-additivated specimens.

test, in order to check whether there was any cementing effect due to the salt holding loose particles together and preventing brushing them off the surface. Wetting of the specimens did not result in any additional material loss. It can therefore be definitively concluded that both modifiers were able to considerably reduce the amount of damage. In order to quantify the amount of modifiers left in the specimens at the end of the test and thus the leaching of the modifiers, the iron and boron content present in the desalination water of the additivated specimens (FN and BO) were determined by ICP. It was found that only approximately 1wt% and 10wt% of the initial amount of ferrocyanide and borax respectively, was still present in the specimens at the end of the test. This indicates that either the modifiers have leached out with the salt efflorescence or that they are partially bound to the mortar components.

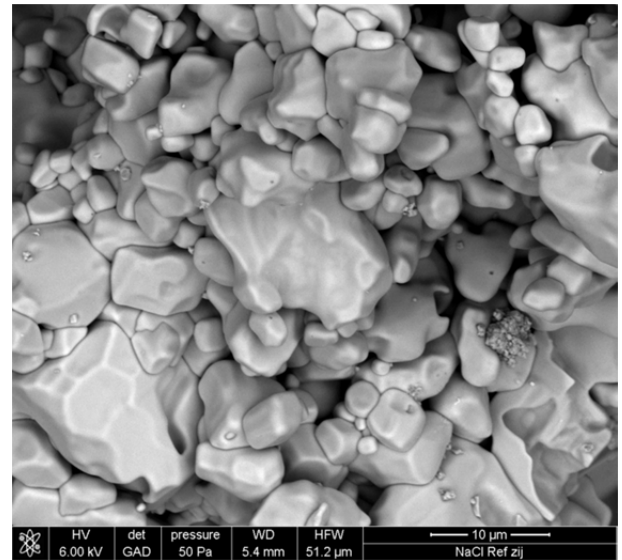
3.2 SEM study

In order to study the effect of the crystallization modifiers on the crystal habit and location of the salt in the mortars, the surface and the cross section (0-2 mm from the surface) of two additional specimens, prepared as described in the salt crystallization procedure section, were studied using Scanning Electron Microscopy (SEM).

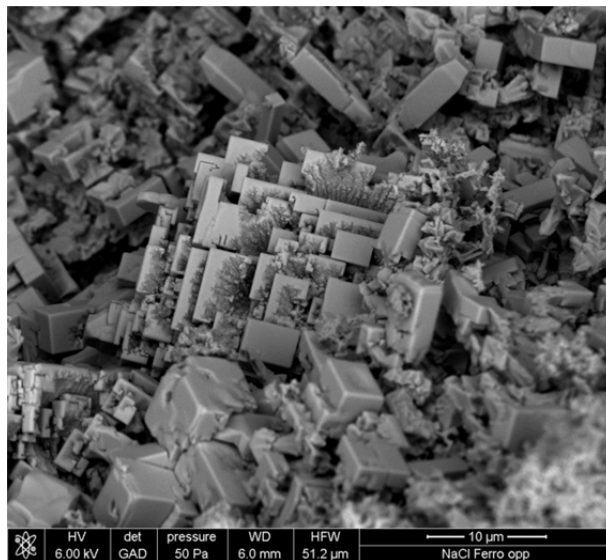
Figure 6 shows the surface and cross section of the reference (A/B) and ferrocyanide-additivated (C/D) mortars contaminated with sodium chloride. The crystals of sodium chloride formed on the surface and inside the reference mortar (Figure 6A and B) clearly show the equilibrium cubic crystallization habit of this salt. In contrast, in the presence of ferrocyanide the sodium chloride crystals show a more elongated and sometimes dendritic crystal habit (Figure 6C and D). These results confirm those reported earlier by the authors and other researchers (see e.g., [7, 27, 28]).



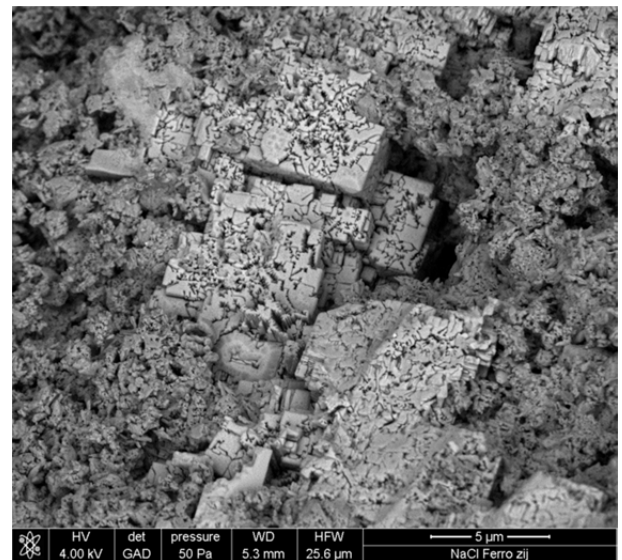
A



B



C

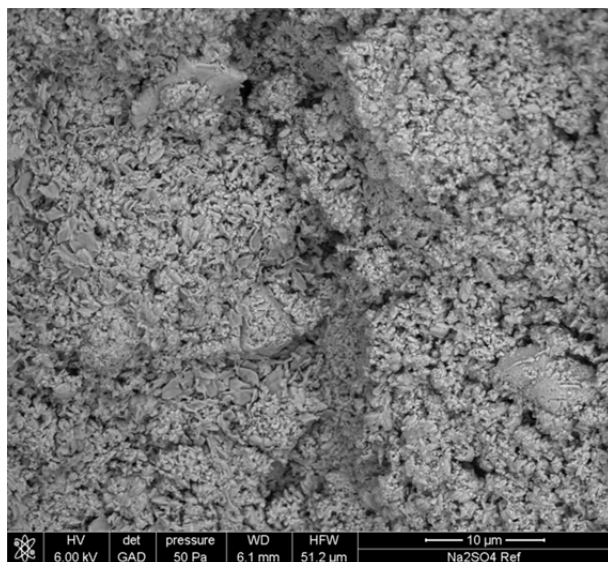


D

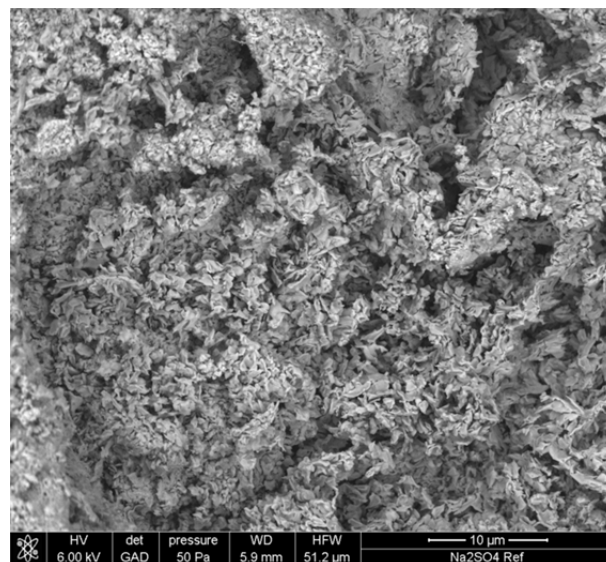
Figure 6: SEM images of mortar specimens contaminated with NaCl. A and B show the surface and cross section of the reference specimen, respectively. C and D show the surface and cross section of the ferrocyanide specimen, respectively. In both A and B the equilibrium cubic habit of NaCl can be observed. For C and D the habit is clearly different due to the influence of the ferrocyanide.

Figure 7 shows the surface and cross section of the reference (A/B) and borax-additivated (C/D) mortars contaminated with sodium sulfate. In the reference mortar, sodium sulfate crystals form bulky agglomerates, similar to those observed in earlier research [12]. Differently, in the presence of borax, sodium sulfate crystals seem to be less bulky and show an ‘open’ structure. This influence of borax on the habit of sodium sulfate crystals can be clearly observed at higher magnification (Figure

8): the crystals growing in the reference specimen (Figure 8A) are individual, irregular crystals with a dense structure, whereas those present in the additivated specimen (Figure 8B) seem to consist of stacked platelets. Unfortunately, the experimental technique used does not allow to differentiate between the different phases of sodium sulfate. However, in both specimens (with and without borax), it is expected that the observed crystals are anhydrous sodium sulfate (and not dehydrated mirabilite). In fact, dehydrated mirabilite crystals usually show a much more porous and irregular structure than the 'bulky' structures observed here [29, 30]. It is therefore more likely that in both cases anhydrous sodium sulfate crystals are grown, in spite of the fact that, at the drying conditions used, mirabilite would be expected; a similar behaviour has been reported also for crystallization experiments in bulk solution [13, 31].



A



B

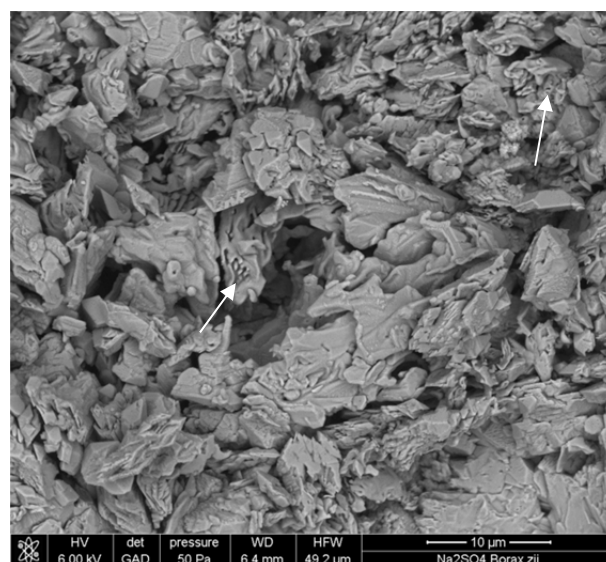
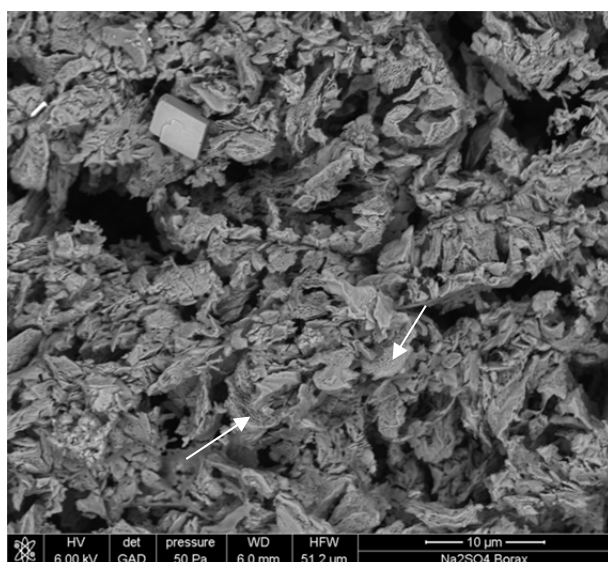
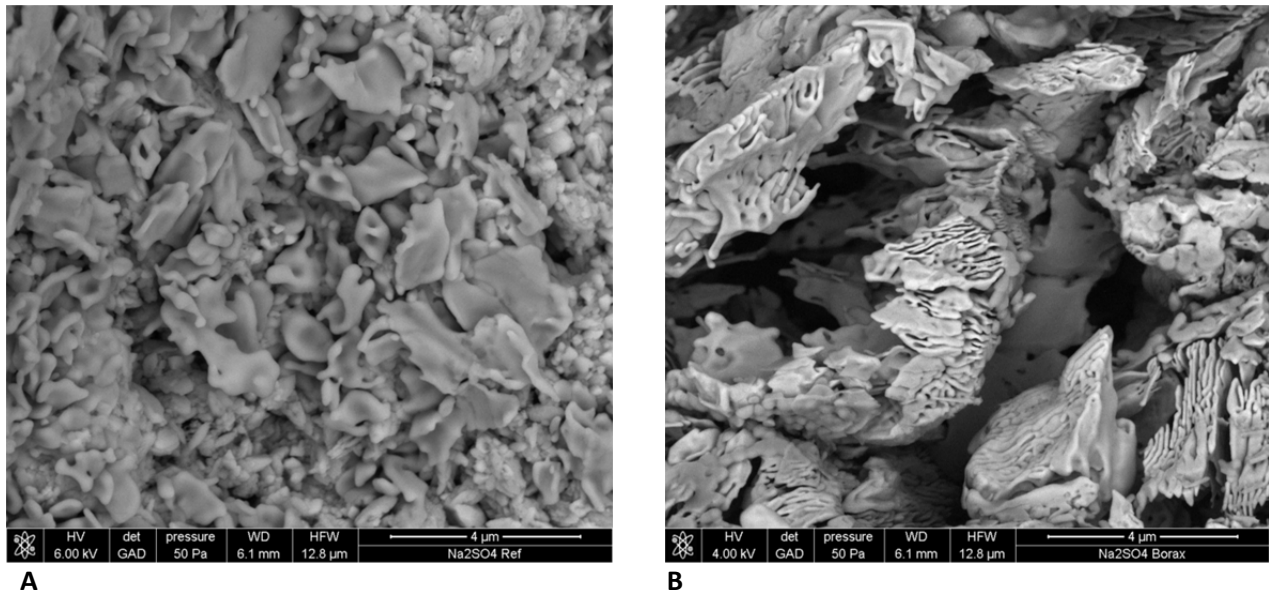


Figure 7: SEM images of mortar specimens contaminated with Na_2SO_4 . A and B show the surface and cross section of the reference specimen, respectively. C and D show the surface and cross section of the borax specimen, respectively. Without borax the sodium sulfate crystals display a bulky habit and stick together in agglomerates. In the presence of borax however, the habit of the sodium sulfate crystals is more plate-like and the crystals show small holes (see arrows for some examples).



A

B

Figure 8: SEM images of mortar specimens contaminated with Na_2SO_4 , A is reference and B is with borax. It can clearly be observed that borax considerably modifies the habit of sodium sulfate (B).

3.3 Discussion

It has been shown that both modifiers do not influence the wetting properties (contact angle, surface tension, evaporation rate) of the salt solutions [7, 13]. This means that any observed changes in salt resistance of the additivated mortars are due to the action of the modifiers on salt crystallization, and not to alterations in the mortar matrix or the wetting properties of the solution. From the SEM observations it is clear that both ferrocyanide and borax influence the crystal morphology of the salt crystallizing on the surface and inside the mortar specimens. Based on the experimental results, the following hypotheses can be formulated to explain the reduction of damage in the presence of crystallization modifiers.

In the case of sodium chloride, the ferrocyanide clearly influences crystallization in two ways:

- i) It is an inhibitor, thus it keeps the salt longer in solution, favouring transport of the salt to the drying surface, where it can crystallize in the form of harmless efflorescence.

ii) It alters the crystallization habit of sodium chloride from cubic to dendritic shape, fact which increases the evaporation surface and thereby enhances the drying and favours transport of the salt to the surface.

It can therefore be concluded that sodium ferrocyanide reduces the damage thanks to the fact that it enhances the formation of branched-like efflorescence. However, as it can be deduced from Figure 4, some salts are left in the additivated mortar specimens and, in spite of this, no decay is observed. This means that the crystallization pressure is not overcoming the strength of the (actually very weak) material. This may have different reasons: the pore filling by the salts is not sufficient [32] and/or, due to the large number of small crystals (due to the high nucleation density), high pressures can hardly develop [31, 33].

In the case of borax and sodium sulfate the mechanism of modification is less straightforward. As shown by the authors, two phases of borax can precipitate in bulk solution depending on borax starting concentration, each having a different effect on sodium sulfate crystallization [13]. If borax precipitates as its decahydrate phase, heterogeneous mirabilite nucleation is observed to occur at or near saturation [34]. If borax precipitates as its pentahydrate phase, anhydrous sodium sulfate crystals have been observed to grow with a different, more elongated, crystal shape than the equilibrium [13]. Supposing that the same processes would occur in the pores of the mortar, the decahydrate phase of borax would favour epitaxial mirabilite precipitation on a borax template formed on calcite. This is similar to what was reported by Ruiz-Agudo and Rodriguez-Navarro [34] for mirabilite precipitation on a borate template. In the presence of borax, Ruiz-Agudo and Rodriguez-Navarro observed a high nucleation density before crystal growth started, resulting in a large number of small crystals. Similarly to the sodium chloride/ferrocyanide combination, this might explain the reduced damage.

In the case borax precipitates in the mortar as its pentahydrate phase, elongated anhydrous sodium sulfate crystals are observed, in some way similar to those observed in bulk solution [13]. Also in this case, different hypotheses can explain the observed beneficial effect on the decay of the additive. The elongated crystal shape might be beneficial to reduce the salt weathering damage because the trapped layer of solution between the crystal tip and the pore wall will be small and, therefore, pressure will be exerted on a very limited area. Moreover, since crystal growth requires a constant supply of fresh solution, the salt solution will be transported over the crystal towards the growing tip, i.e. the drying surface. This effect is similar to the process of creeping, a phenomenon very common in crystal growth from solution [35]. Additionally, the habit modification of thenardite crystallizing at the surface can also lead, thanks to a larger evaporation surface, to enhanced salt transport to the drying surface. Similarly to ferrocyanide, this would favour the formation of harmless efflorescence.

Binding of the modifier to the mortar components as well as leaching of the modifier are important factors affecting both the effectiveness and the durability of the additivated mortars. The binding of the modifier could have implications for its effectiveness. In the case of ferrocyanide, the modifier works via ions in solution [36]; partial binding to the mortar components would mean that less modifier is available and a higher amount needs to be added to the mortar. In the case of borax, binding could not only reduce the amount of available modifier, and thus its effect, but also influence its working mechanism. As earlier stated, the effect of the modifier on sodium sulfate crystallization is dependent on the specific phase of borax present. For tincalconite (sodium tetraborate pentahydrate) it can be hypothesized that the modifier acts via ions in solution [13]; binding would therefore reduce this modifier mechanism. However, in the case borax (sodium tetraborate decahydrate) is present, the sodium sulfate crystals will grow epitaxial on top of the borax crystals [34]; therefore, bonding of the borax crystals to the mortar matrix would thus not change the working mechanism of the modifier, but mainly prevent its leaching out.

In this research ICP measurements have been carried out to get insight in the leaching of the modifiers during the crystallization test. Leaching of the modifiers would limit the durability of their effect and thus service-life of the additivated mortar. The results showed that only a little part of the modifiers is left in the specimens at the end of the test. However, it was not possible, with the experimental techniques used in this research, to definitively conclude whether this loss was due to only leaching or also to binding of the modifiers to the mortar components, preventing their dissolution in the water used to desalinate the samples. In future experiments, in order to differentiate between leaching or binding of the modifiers, the modifier content in the brushed off material should be determined as well (e.g. by means of ICP); the absence of the modifier in the brushed off material would be an indication of it being bound to the mortar matrix.

Another important fact to take into account is that borax is potentially damaging to the health [37]. However, although borax is currently classified as being possibly toxic to reproduction in the European CLP regulation [37], recent studies did not observe any connection between high levels of daily boron exposure and reprotoxicity [38, 39]. Ferrocyanide is a known food additive (E535), and no health effects are expected. Besides, both modifiers will only be used in the mortar in low doses. Care should be taken during handling of the modifiers in powder form, as the dust can cause (light) respiratory, eye or skin irritation [38, 40].

4. Conclusions

In this work the salt crystallization resistance of lime-based mortars, additivated with crystallization modifiers for sodium chloride and sodium sulfate crystallization, was investigated using an accelerated salt crystallization test. We have shown that both the ferrocyanide and the borax additivated mortars have a considerably improved durability to salt crystallization damage in comparison to not additivated mortar. No or minor material loss was observed in the presence of the modifiers. In the case of mortar specimens additivated with ferrocyanide, the modifier clearly

enhanced the tendency of sodium chloride to effloresce. This effect was present in a less pronounced way also in mortar specimens additivated with borax and contaminated with sodium sulfate.

SEM observations revealed that the crystal habit of both sodium chloride and sodium sulfate is significantly altered due to ferrocyanide and borax respectively. The increased efflorescence formation (in the case of ferrocyanide/sodium chloride combination) and the altered crystal habit (observed for both modifier/salt combinations) can explain the observed reduction of damage in additivated specimens.

The results presented here are promising for the development of mortars with mixed-in modifiers with and improved durability to salt crystallization damage. However, before an actual mortar product can be developed, some additional research questions need to be answered. First of all, the rate of leaching of the modifier needs to be monitored and, if necessary, possible solutions, such as encapsulation and controlled release, developed. Additionally, as in the field often salt mixtures are present, and most modifiers are salt-specific, the effectiveness of the modifiers in mortar contaminated with salt mixtures should be addressed. Moreover, the effect of modifiers on mortars with a different binder (e.g. cement-based) needs to be assessed. Finally, the increased durability of the developed mortars and their compatibility with the existing fabric should be assessed on test panels on site, before application of these mortars can take place in renovation interventions.

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