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Characterization of lime mortar additivated with crystallization modifiers

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ABSTRACT

Additivating mortars with crystallization modifiers is a novel approach to mitigate salt crystallization damage in historic masonry. Once verified the effectiveness of crystallization modifiers in bulk solution, the next step consists in verifying whether: (i) modifiers are still effective when mixed in mortar and going through the carbonation process and (ii) modifiers alter any mortar properties which might limit their application. This research addresses these issues for sodium ferrocyanide and borax, modifiers for sodium chloride, and sodium sulfate, respectively. Several experimental techniques have been applied to elucidate these questions. The results show that the selected modifiers are still able to alter the salt crystallization after going through the carbonation process of the mortar. Besides, no major effects of the modifiers on the fresh and hardened mortar properties were observed. It can therefore be concluded that there are no restraints for the future use of these crystallization modifiers in restoration mortars.

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Borax; ferrocyanide; lime mortar; mixed-in crystallization modifiers; mortar properties; salt decay

1. Introduction

Deterioration of porous building materials due to salt crystallization is a big threat to our built cultural heritage. The occurrence of salt damage is related to the location of the crystallization in the material: when salts crystallize on the surface of the material, they are aesthetically unpleasant but harmless; differently, salt crystallization in the pores of the material (crypto-florescence) can lead to severe damage in the form of e.g. sanding, crumbling, exfoliation and spalling. Lime-based mortars, regularly found in historic masonry as bedding mortar, pointing, or plaster/render, are especially susceptible to salt damage, due to their bimodal pore-size distribution (Rossi-Manaresi and Tucci 1991) and low mechanical strength. Considering that repointing and renovation of plasters and pointing often constitute a major part of the total costs of renovation or restoration interventions, improving the durability of these materials will result in a significant cost reduction (Van Hees, Naldini, and Roos 2014).

Typical solutions to deal with salt crystallization damage in mortar implies either (i) the modification of the moisture and salt transport properties of the material, or (ii) the removal of the salts and their source, or (iii) the increase of the tensile strength of the material or a combination of these options. However, these solutions can lead to compatibility problems with the existing materials and cause even more damage (Groot, Van Hees, and Wijffels 2009; Lubelli, Van Hees, and Groot 2006). Alternatively, recent studies have focused on the possibility of modifying the salt crystallization process by the use of crystallization modifiers, in order to make it less harmful. Crystallization modifiers are ions or molecules which alter the crystallization process by delaying nucleation (inhibitors), promote nucleation (promoters), and/or modify the shape of the crystals (habit modifiers) (Jones and Ogden 2010). This approach has already shown promising results; see, e.g., (Lubelli and Van Hees 2007; Rodriguez-Navarro and Benning 2013; Selwitz and Doehne 2002). Crystallization modifiers have been shown to reduce salt damage, e.g., by enhancing salt transport to the surface of the material, where crystallizing salts will not cause damage (Gupta et al. 2014, 2012; Lubelli and Van Hees 2007; Rodriguez-Navarro et al. 2002). A new application, and the focus of this study, consists of mixing the crystallization modifiers directly into the mortar during production (Granneman, Lubelli, and Van Hees 2016; Lubelli et al. 2010). This way, the crystallization modifiers are already present, and thus effective, at the moment the damaging salts enter the porous material.

Crystallization modifiers often act only on specific salts, due to the way they adsorb on, or are included in, the crystal. This consequently means that for each salt a specific crystallization modifier needs to be identified. Besides, some modifiers are effective only in a limited

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range of pH values. For example, a highly alkaline pH, like that of fresh mortar, might cause certain modifiers to be (temporarily) ineffective due to changes of their ionization state and consequently repulsive electrostatic forces between modifier and salt crystals (Ruiz-Agudo, Rodriguez-Navarro, and Sebastián-Pardo 2006), or the high pH may lead to the formation of different (insoluble) compounds decreasing the effect of the modifiers. Therefore, for a successful application of modifiers in mortar, next to the identification of effective modifiers for salts commonly present in buildings, the possible effect of pH of the mortar (changing from 13 to about 9 during the carbonation process) needs to be clarified.

In this study, we focus on modifiers for two of the most abundant and damaging salts found in building materials, sodium chloride and sodium sulfate. The influence of (in)organic modifiers on nucleation and growth of sodium chloride has been researched extensively. The most effective modifier for sodium chloride is sodium (or potassium) ferrocyanide, a well-known inhibitor of sodium chloride crystallization from bulk solution (e.g., Al-Jibbouri and Ulrich 2002; Rodriguez-Navarro et al. 2002; Van Damme Van Weele 1965)). Its mechanism of modification has been recently fully clarified by Bode et al. (2012). When considering the possible effect of pH on ferrocyanide effectiveness, this seems not to be an issue. In fact, although minor ferrocyanide adsorption on, for example, quartz is reported in literature, this usually decreases with increasing pH (Zimmermann et al. 2008). Under alkaline conditions like those present in the mortar (i.e., pH between 9 and 13), adsorption of ferrocyanide on mortar components with consequent loss of effectiveness is therefore not expected. Moreover, previous research by the authors on lime-cement mortar additivated with ferrocyanide has shown that this modifier can still be effective when mixed in a mortar and thus after it goes through the carbonation process (Lubelli et al. 2010).

In the case of sodium sulfate, the identification of a modifier which can be effective in mortar is more difficult. Phosphonates are a group of crystallization modifiers for sodium sulfate often mentioned in literature (Rodriguez-Navarro and Benning 2013; Ruiz-Agudo, Rodriguez-Navarro, and Sebastián-Pardo 2006; Selwitz and Doehne 2002). However, phosphonates are not very well suited to be added to building materials, as their effect is strongly dependent on pH. A suitable alternative for modification of sodium sulfate crystallization was found in borax ($Na_2B_4O_7 \cdot 10H_2O$) (Granneman et al. 2014; Ruiz-Agudo and Rodriguez-Navarro 2010). Borax is supposed to work as promoter of mirabilite in (bulk) solution (Ruiz-Agudo and Rodriguez-Navarro 2010; Schiro, Ruiz-Agudo, and Rodriguez-Navarro 2012; Telkes 1952), also at highly alkaline pH values, as those present in fresh mortar (Granneman et al. 2014). However, recent research by the authors on the crystallization of sodium sulfate from solution additivated with borax has pointed out that its modification mechanism is not so straightforward. It was shown that the effect of borax depends on the borax concentration and the experimental conditions. Depending on borax starting concentration, two phases of borax can crystallize, leading to a different effect on sodium sulfate crystallization. When borax crystallizes as the decahydrate, the precipitating sodium sulfate phase is the decahydrated mirabilite. However, when borax crystallizes as the pentahydrated tincalconite, the sodium sulfate crystallizes as anhydrous thenardite with {153} as the dominant crystal form (Granneman et al. 2017).

Moreover, differently than for sodium ferrocyanide, not much is known from literature on the possible interaction of borax with mortar components. Although it is not expected that borax will chemically react with mortar constituents (Granneman et al. 2014), it can be supposed that borax might form a periodic 2D network on a calcareous matrix, and that borax subsequently acts as template for mirabilite crystallization (Ruiz-Agudo and Rodriguez-Navarro 2010). Adsorption of borax on the calcareous matrix might prove beneficial to prevent future problems with for example leaching, but it might also make the modifier less effective. In this research the possible interaction of the modifier with the mortar was evaluated by adding borax to the mortar before and after the carbonation process, and studying its influence on salt crystallization in both cases (see Section 3.1.2).

While the crystallization modifiers are added to the mortar with the final aim to affect the salt crystallization, they might also have an effect on the properties of the fresh and hardened mortar. It is known that incorporation of (in)organic additives or admixtures in mortar, even in small quantities, can lead to alterations of the material properties (see, e.g., Arizzi and Cultrone 2012; Izaguirre, Lanas, and Álvarez 2010). Additives could for example delay the carbonation or decrease the strength of the hardened mortar; such alterations may limit the application of crystallization modifiers. To our knowledge, the influence of the addition of borax and ferrocyanide to lime mortar on its properties has never been assessed. It is therefore imperative to test the effect of these modifiers on the properties of fresh and hardened mortar, before assessing the salt resistance of additivated mortars. In this research, relevant properties of

fresh and hardened mortar additivated with borax or sodium ferrocyanide, modifiers for sodium sulfate, and sodium chloride, respectively, were assessed and compared to those of the reference mortar without modifiers (Section 3.2).

2. Materials and methods

2.1 Materials

2.1.1 Binder and sand

Two types of specimens were prepared: (i) lime binder only (lime paste) and (ii) lime + sand (mortar) specimens.

Lime paste specimens were prepared with highly pure lime powder (≥ 96% calcium hydroxide, Sigma-Aldrich, puriss.) to avoid any side reactions with impurities during experiments. For the mortar specimens, a commercial air lime in powder form (Supercalco90 by Carmeuse, minimal 90% calcium hydroxide) was selected. Standard sand (EN196-1) with a grain size between 0.25–1.0 mm was chosen in order to have a relatively weak mortar, which can develop salt damage in a short period of time in a future accelerated salt weathering test. A 1:3 volume ratio for lime:sand was selected, since this is a common ratio used in practice.

2.1.2 Modifiers

Two modifiers have been selected to be mixed in the mortar: sodium ferrocyanide (sodium hexacyanoferrate (II)-10-hydrate, Riedel-deHaën, puriss.) and borax (sodium tetraborate decahydrate, Sigma-Aldrich, puriss.). The first is a crystallization inhibitor and habit modifier of sodium chloride crystallization (Van Damme Van Weele 1965), the second is a modifier of sodium sulfate crystallization (Granneman et al. 2017; Ruiz-Agudo and Rodriguez-Navarro 2010). The effect of the carbonation process of the mortar on the effectiveness of the modifier was only studied for borax and sodium sulfate, as this was already studied for ferrocyanide and sodium chloride in previous research (Lubelli et al. 2010). In all other experiments both modifiers are considered.

In the case of additivated specimens, 0.94 wt% of ferrocyanide and 3.2 wt% of borax with respect to lime were used. The amount of ferrocyanide to be added to the mortar was defined, based on a previous research by Lubelli et al. (2010), that showed that 0.1 wt% ferrocyanide with respect to the total dry weight of the mortar (corresponding to 0.94% of the weight of the binder) was sufficient to considerably improve the resistance of the mortar towards salt damage; no further improvement of the durability was observed when increasing the amount of the modifier.

The amount of borax to be added to the mortar was defined based on a previous research by the authors on the interaction between the modifier and the salt in bulk solution (Granneman et al. 2017). Based on these results, two concentrations of borax were used to be mixed in the lime paste specimens (see section SEM study): 1.6 and 3.2 wt% with respect to lime (corresponding to 0.05 and 0.1 mol·L^{-1} borax concentration in the water used to make the pastes). As this experiment showed that a significant effect on sodium sulfate crystallization could be obtained only when using 3.2 wt% borax, this amount was used for preparing the mortar specimens. 3.2 wt% with respect to lime corresponds to 0.363 wt% of the total dry weight of the mortar.

2.1.3 Specimen types and preparation

For this research the following types of specimens were prepared (see Table 1):

i) Lime paste specimens:

- Specimens in plastic square containers (3x3 cm^2, 2–3 mm thick) without modifiers and additivated with 0.94 ferrocyanide or 3.2 wt% borax.
- Specimens in plastic cylindrical holders (3 cm diameter, 2 mm thick) additivated with 0, 1.6 or 3.2 wt% borax.

The specimens were prepared by mixing calcium hydroxide with distilled water with or without modifier. Distilled water was used in all experiments to ensure reproducibility and comparability of the results, considering that the quality and composition of tap water may differ between locations. Besides, tap water may introduce small quantities of other ions, which may complicate the interpretation of the results. For the square specimens the water content was 48.4 ± 0.5 wt%, for the round specimens 46.1 ± 1 wt

Table 1. Details of specimens prepared for each test.

Specimen type	Shape and size (lxwxh)	Test (number of replicas)
Lime, lime + 1.6 wt% borax, lime + 3.2 wt% borax	Round ø3 cm x 2 mm	SEM
Lime, lime + 0.94 wt% ferrocyanide, lime + 3.2 wt% borax	Square 3x3 cm^2 x 2-3 mm	PXRD (3)
Lime + sand, lime + sand + 0.94 wt% ferrocyanide, lime + sand + 3.2 wt% borax	Prisms 4x4x16cm^3	Flow (1) Flexural strength (5) Compressive strength (10)
	Slabs 5x5x2cm^3	Water absorption and drying (3) Porosity and pore size distribution (2)

%. The lime pastes were prepared by hand and water was added until a desirable consistency was reached for casting the pastes into moulds of different size and shape. As the two series of specimens were used for different experiments (which did not need to be compared to each other) the differences in water content of the pastes do not affect the validity of the results. In order to obtain a specimen where borax was added after carbonation, a carbonated cylindrical specimen was contaminated with borax solution via capillary absorption and then dried at 20°C/65%RH. The concentration of the borax solution was chosen such that the final concentration of modifier in the specimen was about the same as in the specimen in which borax was mixed-in before carbonation of the lime paste.

ii) Lime + sand (mortar) specimens, without modifiers or additivated with 0.94 wt% ferrocyanide or 3.2 wt% borax (with respect to lime):

- Mortar prisms (4x4x16 cm^3) made in Styrofoam mould, and compacted using a vibrating table according to EN196-1.
- Mortar slabs (5x5x2 cm^3) prepared in tailor-made polyurethane moulds and compacted by hand. As the mortar properties are strongly affected by the absorption of the substrate on which they are applied, it has been chosen to prepare the mortar slabs on a substrate instead of in a non-absorbing mould. A paper tissue was interposed between the substrate and the mortar in order to facilitate the detachment of the mortar, once this had hardened (after 2 days). Maastricht limestone, a high porous (50 vol%) and coarse (30–50 μm) natural stone was chosen as substrate. The substrate was pre-wetted prior to application of the mortar.

All mortar specimens were prepared according to EN1015-2. The reference specimens were made with distilled water. For the additivated mortars, a defined amount of water containing the desired amount of modifier was added, followed by additional water to obtain a good flow of the mortar.

After production, all specimens were covered with plastic, apart from the square containers, and stored under ambient conditions for one day. Then, the plastic was removed and the specimens were stored at 20°C/65%RH. The lime paste specimens remained under these conditions during the whole carbonation process (i.e., until the end of the test). The mortar specimens remained under these conditions until approximately 50% of the water had evaporated. Subsequently, the mortar specimens were artificially carbonated at 20°C/65RH%/1%CO_2 until full carbonation was obtained (2–3 weeks depending on specimen thickness).

Full carbonation of the round lime paste specimens was determined using infrared spectroscopy, the carbonation of the square specimens was determined at specific time intervals using PXRD (see Section 2.2.3). Full carbonation of the mortar specimens was assessed by breaking them and spraying the cross section with a phenolphthalein solution.

Carbonated round specimens with mixed-in borax and round specimens to which borax was added after carbonation were contaminated via capillary absorption with a 1.29 mol·L^{-1} sodium sulfate solution and left to dry at 20°C/65%RH. After drying, the specimens were broken and the cross sections were examined using SEM (see section SEM study).

2.2 Methods

2.2.1 Mortar flow test

The flow of the mortar was measured with a standard flow table test (EN1015-3). A flow between 160–170 mm was defined as requirement for all the mortars. The amount of water was defined consequently. The flow table value and final water content of each mortar mixture can be found in Table 2.

2.2.2 SEM study

Scanning Electron Microscopy (SEM) observations were carried out on lime paste specimens, in order to study the effect of borax on sodium sulfate crystallization. The SEM instrument used is a FEI NovaNanoSEM 650 with a gaseous analytical detector (GAD); this provides a very short beam gas path length able to minimize spurious signals from scattered electrons during X-ray analysis.

Table 2. Properties of the 1:3 lime:sand fresh mortar mixtures.

Specimen type	Modifier content		Flow table value	Water to lime ratio (w/w)
	With respect to lime	With respect to total dry mortar weight		
Reference mortar			170 mm	1.67
Mortar + ferrocyanide	0.94 wt%	0.106 wt%	161 mm	1.51
Mortar + borax	3.2 wt%	0.363 wt%	161 mm	1.57

The microscope was operated in low vacuum (39–40 Pa) mode; this allows for the reduction of charging phenomena and the investigation of electrically non-conductive specimen without applying a carbon coating. The applied accelerating voltage was 4-5 kV and magnifications between 470 and 2500 were used.

2.2.3 PXRD study

The carbonation rate of square lime paste specimens was assessed by PXRD. At defined time intervals, specimens were dried in an oven at 40°C and then removed from their container and ground to a fine powder before examination with powder X-ray diffraction (Panalytical X'Pert PRO. Analysis conditions: CuKα (λ = 1.5405 Å), 15–70°2Θ explored area, 40 kV voltage, 30 mA current intensity, and goniometer speed 0.016° 2Θ s^{-1} using a Si-detector X'Celerator).

Next, the measured patterns were examined with the program PROFEX (Döbelin and Kleeberg 2015). This program performs Rietveld refinement on the measured patterns, identifies crystalline phases using patterns from appropriate databases and calculates semi-quantitative weight percentages of the identified phases. Calcium hydroxide was identified as portlandite (PDF 04–010-3117) and calcium carbonate as calcite (PDF 04–008-0788). To test the PROFEX model, a calibration curve was defined for known ratios of calcium hydroxide and calcite. The measured values were accurate with a maximum error of ± 1.68%. Subsequently, the grinded lime pastes were measured and their ratios of calcium hydroxide and calcite were determined using the same model.

2.2.4 Porosity and pore size distribution

The open porosity and pore size distribution of the mortars, with and without modifiers, were determined on samples collected from slabs using Mercury Intrusion Porosimetry (MIP) (Micromeritics, AutoPore IV 9500). Additionally, the porosity and density of the mortar were determined by saturation in water at atmospheric pressure (Van Der Klugt 1993).

2.2.5 Absorption and drying test

The capillary water absorption of the mortar with and without modifiers was determined according to EN1015-18. The lateral sides of the 5x5x2 cm^3 mortar slabs were covered with epoxy, to prevent absorption and evaporation from the lateral sides during testing. After the measurement of the capillary absorption, the water absorption coefficient (WAC) was calculated. After capillary absorption, the bottom of the specimens was covered with removable tape and the specimens were placed under controlled environmental conditions (20°C/50%RH) while drying. The weight of the specimens was monitored at different time intervals during drying.

2.2.6 Measurements of the flexural and compressive strength

The flexural and compressive strength of the mortar was determined according to EN1015-11 (loading rate: 5 N/s for the bending test and 50 N/s for the compressive test). Measurements were performed on 28-day-old (fully carbonated) 4x4x16 cm^3 mortar prisms.

3. Results and discussion

3.1 Lime paste specimens characterization

3.1.1 Carbonation rate

The carbonation rate of the lime paste specimens (reference, with mixed-in ferrocyanide and with mixed-in borax) is shown in Figure 1. Both the calcium hydroxide and calcite content were determined and their refined phase quantities were normalized to 100%. However, for clarity, only the calcite content is shown in Figure 1. In the first week the carbonation rate of the ferrocyanide series is slightly lower than the other two. This indicates that ferrocyanide has an initial retarding effect on the carbonation. However, after two weeks all specimens have a comparable degree of carbonation. A lower initial carbonation rate could indicate that the strength of the ferrocyanide additivated mortars develops slower. However, this retarding effect is minor and is not expected to limit the application of the mortar additivated with ferrocyanide. The specimens additivated with borax carbonate at the same rate as the reference specimens.

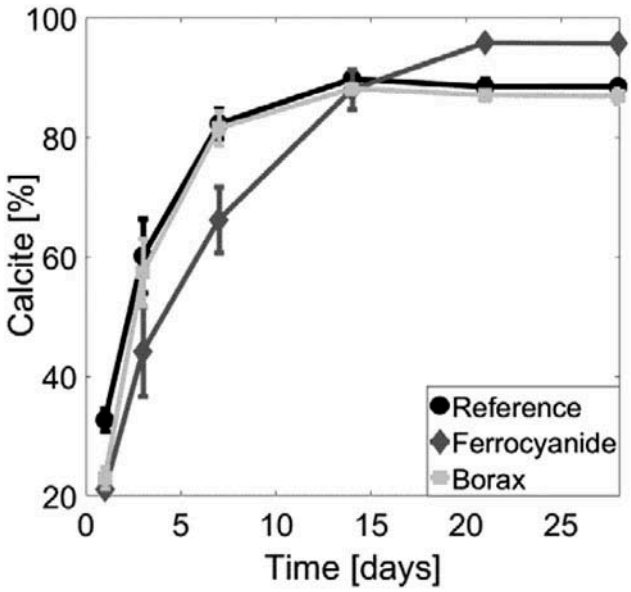

Figure 1. Carbonation rate determined by PXRD.

Additionally, it can be observed that the percentage of calcite, for all the specimen types, reaches a plateau at a lower calcite content than expected for full carbonation. This is most probably due to: (i) complete drying out of the specimens, leaving not enough water for the carbonation process; and/or (ii) formation of an (impenetrable) calcite shell around the remaining portlandite particles, preventing their further reaction with carbon dioxide (Van Balen 2005). At the end of the test, in order to check whether full carbonation could be obtained, the specimens were grinded to a fine powder (thus probably breaking the calcite shell) and rewetted with water by spraying; after this procedure, the specimens resulted to be fully carbonated (100% calcite was measured).

3.1.2 Sodium sulfate crystallization

The crystallization pattern of sodium sulfate in lime paste specimens with or without borax was studied using Scanning Electron Microscopy. The SEM images of the cross sections of the specimens are shown in Figure 2. For 1.6wt% of borax, no effect on sodium sulfate crystallization was observed and these results are therefore not further discussed.

For 3.2 wt% of borax, a clear difference in crystallization pattern of sodium sulfate is observed between specimen without (Figure 2a) or with (Figure 2b,c) borax. In the first case, sodium sulfate precipitated as irregularly shaped crystals in pores, in the second case large, finger-like crystals are observed which seem to have grown rapidly, thereby incorporating the binder particles. The observed crystal morphologies with or without borax are distinctly different. Therefore, it can be concluded that borax influences sodium sulfate crystallization inside the pores of the lime paste specimens. Additionally, the crystallization pattern of sodium sulfate in the sample with mixed-in modifier (Figure 2b) and the sample in which borax has been added after carbonation of the lime (Figure 2c) looks similar. It can therefore be concluded that the carbonation process does not influence the effectiveness of borax as a modifier for sodium sulfate, and the modifier is still expected to work when mixed in during the production of a mortar (Granneman, Lubelli, and Van Hees 2016).

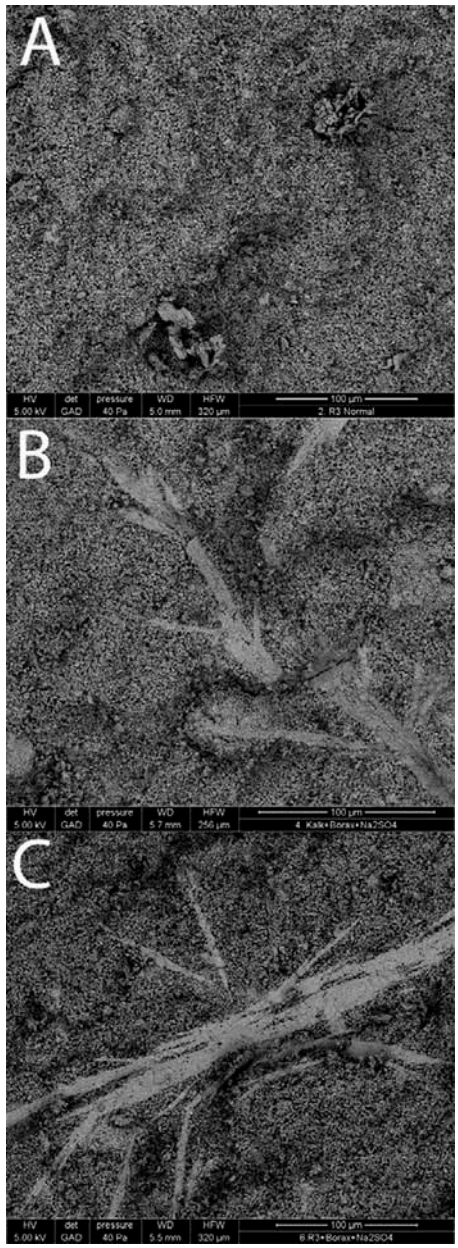

Figure 2. Figures reproduced with permission, see Granneman, Lubelli, and Van Hees (2016, Figure 2a,b & c, p. 77).

SEM images of lime paste specimens contaminated with sodium sulfate. A: reference specimen. B: specimen with 3.2wt% borax mixed in before carbonation. C: Specimen additivated with borax after carbonation. Specimens with borax (B/C) show a clear alteration for the sodium sulfate crystallization pattern compared to the reference (A). No differences can be observed for specimens with borax added before or after carbonation, indicating that the carbonation process does not influence the effectiveness of borax as a modifier for sodium sulfate. For all images the white scaling bar equals 100 µm.

3.2 Mortar characterization

3.2.1 Porosity and pore size distribution

The open porosity and the pore size distribution of the mortar with and without modifiers as measured by MIP are given in Figure 3 (for each mortar the curve of one of the two replicates is plotted, as the results of the replicates were almost identical). The open porosity determined by MIP is 25.1% ± 0.11 (reference), 25.1% ± 0.55 (borax) and 25.4% ± 0.36 (ferrocyanide). The cumulative curves show a slightly higher total porosity for the mortars additivated with ferrocyanide and borax. As the water content in the additivated mortars was slightly lower than in the reference

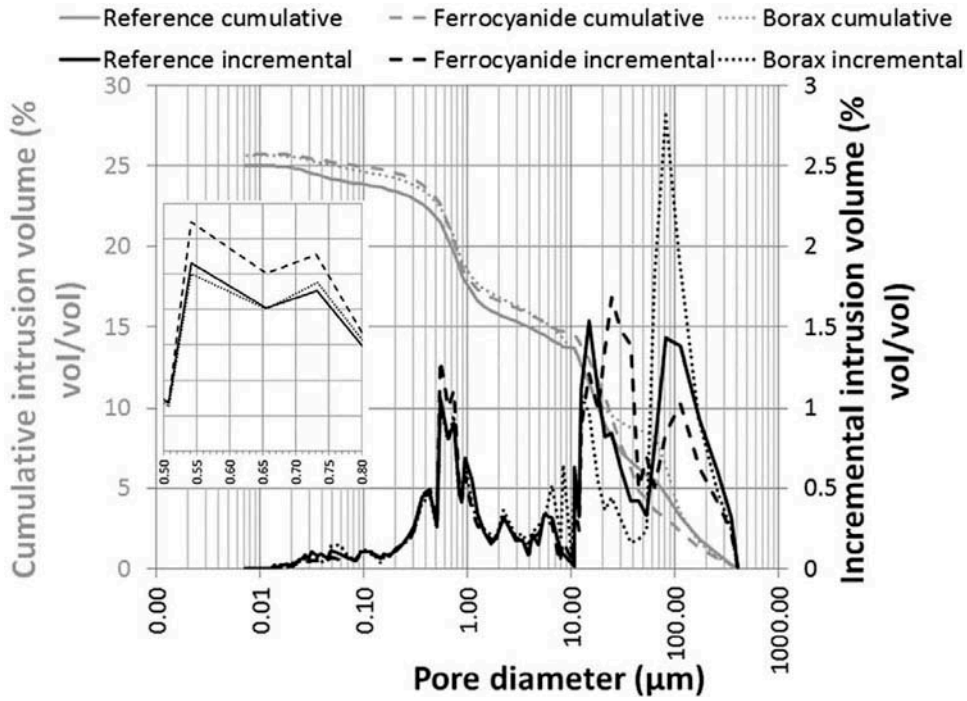

Figure 3. Cumulative and incremental pore size distributions measured with Mercury Intrusion Porosimetry (MIP). The insert shows a zoom of the incremental intrusion volume between 0.5 and 0.8 µm.

specimens, this can only be attributed to the presence of the modifiers. However, these differences are only minor and are therefore considered not relevant. Minor differences can be observed as well in their pore size distribution: the borax specimens have a higher amount of pores in the range of 6–9 µm and 80 µm diameter, compared to the references specimens; the ferrocyanide specimens have a slightly higher amount of pores in the range of 0.5–0.8 µm diameter than the reference specimens.

The open porosity and the density of the specimens as determined by immersion in water are reported in Table 3. The porosity values determined by immersion for the different mortars are very similar. In general, the porosity values measured by immersion are slightly higher than those measured with MIP. This can be explained either by the fact that the very coarse pores (> 400 µm) cannot be measured by MIP but are taken into account by the measurement by immersion or by minor differences in porosity within the specimens (the MIP measurement considers about 1 cm^3 of the material, whereas the measurements by immersion are carried out on 5x5x2 cm^3 specimens).

3.2.2 Absorption and drying behavior

The capillary water absorption curves of mortar specimens with and without modifiers are given in Figure 4. The calculated WAC values are given in Table 3.

The absorption curves and the calculated WAC values are very similar. Probably, small differences, as expected from the MIP measurements, between additivated and reference specimens are hardly distinguishable because of the fast absorption.

The drying curves are given in Figure 5. Small differences between the curves can be observed: the ferrocyanide specimens dry slightly slower and the borax specimens dry slightly faster than the reference specimens. This may be explained by the differences in pore size distribution of the mortars: in fact, specimens additivated with borax have a larger amount of coarse pores (in the range of 6–9 µm and 80 µm diameter) than specimens with ferrocyanide. However, the data of the reference specimens show a large variation, encompassing the drying curves of both types of additivated specimens.

Table 3. Hardened mortar properties of the different 1:3 lime:sand mortar mixtures.

Property	Method	Reference	Ferrocyanide	Borax
WAC [$kg/m^2h^{1/2}$]	Capillary rise	8.05	7.62	7.84
Density [kg/m^3]	Saturation at	1943	1964	1933
Open porosity (%V/V)	atm pressure	26.7 ± 0.19	25.9 ± 0.24	27.1 ± 0.06
Bulk density [g/ml]	Mercury Intrusion	1.977	1.971	1.961
Open porosity (%V/V)	Porosimetry	25.1 ± 0.11	25.4 ± 0.36	25.1 ± 0.55
Tensile strength (N/mm^2)		0.79 ± 0.11	0.85 ± 0.03	0.92 ± 0.11
Compressive strength (N/mm^2)		2.01 ± 0.33	2.08 ± 0.18	2.61 ± 0.22

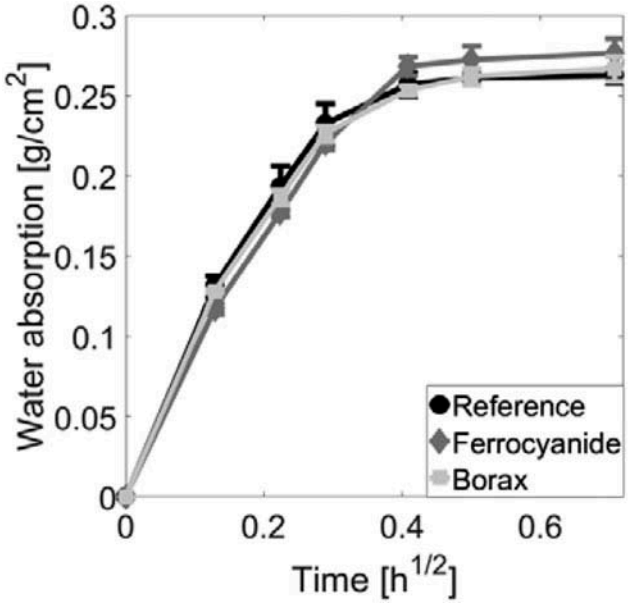

Figure 4. Capillary water absorption in time.

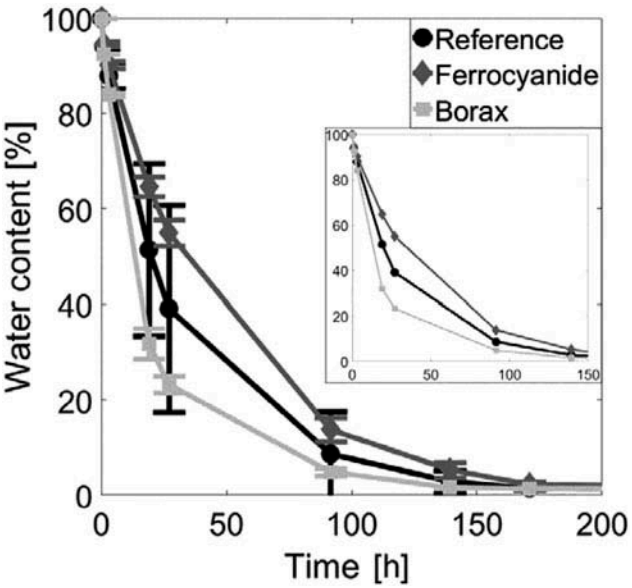

Figure 5. Water content in the specimens during drying at 50RH%, 20°C. The inset shows drying during the first 150 hr without error bars for clarification.

Summarizing, it can be concluded that no significant differences in water absorption and drying behaviour have been measured between the additivated mortars and the reference.

3.2.3 Flexural and compressive strength

The flexural and compressive strength of the mortars with and without modifiers are given in Table 3. The results show that the mortars additivated with ferrocyanide or borax have a slightly higher strength than the reference mortar. These differences might be caused by the small differences in water content, and not necessarily by the presence of the crystallization modifiers.

4. Conclusions

In this article, two different research questions were investigated: (i) Are crystallization modifiers still effective in altering crystallization when mixed in a mortar during production and going through the carbonation process? (ii) Does the addition of crystallization modifiers alter any mortar properties which might limit their application?

The effectiveness of sodium ferrocyanide to alter sodium chloride crystallization when mixed in mortar is known from previous research by the authors and was therefore not investigated in this study. The effectiveness of borax as modifier of sodium sulfate when mixed in lime paste specimens has been clearly demonstrated by SEM observations. It has been shown that the pH changes during the carbonation process of the mortar do not affect the ability of borax to alter sodium sulfate crystallization. The effect of ferrocyanide and borax on the carbonation rate was studied in specimens made of lime binder only. A minor delay in carbonation was observed for specimens additivated with ferrocyanide; borax had no effect on lime carbonation.

The modifiers have been shown to have no significant effect on the flow of the fresh mortar and on the mechanical strength of the hardened mortar, measured after accelerated carbonation at 1% CO_2 concentration. The open porosity of the mortar with and without modifiers is very similar. Small differences in the pore size distribution, as measured by MIP, have been observed: the mortar additivated with ferrocyanide has a slightly higher amount of fine pores, whereas that additivated with borax has a larger proportion of coarse pores than the reference mortar. This is in agreement with the results of the drying experiments, showing that mortars with mixed-in ferrocyanide dry slightly slower than those with borax.

Summarizing, is has been shown that, for this type of mortar, the modifiers have no major effect on the main properties of fresh and hardened mortar. This suggests that the modifiers tested in this research, when proven effective for reducing salt crystallization damage, can be mixed in the mortar without negatively affecting its properties. Research is on-going to assess the durability towards salt damage of mortars additivated with these modifiers.

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