Mitigating salt damage in lime-based mortars by built-in crystallization modifiers

Granneman, Sanne

DOI
10.4233/uuid:024d9d2e-cfbd-4753-b7cf-587799110824

Publication date
2019

Document Version
Final published version

Citation (APA)
Granneman, S. (2019). *Mitigating salt damage in lime-based mortars by built-in crystallization modifiers*. [Dissertation (TU Delft), Delft University of Technology]. https://doi.org/10.4233/uuid:024d9d2e-cfbd-4753-b7cf-587799110824

Mitigating salt damage in lime-based mortars by built-in crystallization modifiers

Sanne J.C. Granneman

Mitigating salt damage in lime-based mortars by built-in crystallization modifiers

Dissertation

for the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus, Prof. dr. ir. T.H.J.J. van der Hagen
chair of the Board for Doctorates
to be defended publicly on
Friday 15 March 2019 at 10.00 o'clock

by

Sanne Johanna Catharina GRANNEMAN

Master of Science in Chemistry,
Radboud University Nijmegen, The Netherlands
born in Wieringermeer, The Netherlands

This dissertation has been approved by the promotors.

Composition of the doctoral committee:

Rector Magnificus	chairperson
Prof. ir. R.P.J. van Hees	Delft University of Technology, promotor
Dr. B. Lubelli	Delft University of Technology, copromotor

Independent members:

Prof. dr. ir. K. van Breugel	Delft University of Technology
Prof. dr. M. Steiger	Universität Hamburg, Germany
Prof. dr. V. Cnudde	Universiteit Gent, Belgium
Dr. ir. H.P. Huinink	Eindhoven University of Technology
Prof. dr. ir. A.A.J.F. van den Dobbelsteen	Delft University of Technology, reserve member

This research was funded by the Dutch IOP program on Self-Healing Materials, under Grant number SHM012018.

Printed by: Ipskamp Printing, Enschede, The Netherlands
Cover by: Sanne Granneman

ISBN: 978-94-028-1394-4

Table of Contents

4. Characterization of lime mortar additivated with crystallization modifiers 57

5. Effect of mixed in crystallization modifiers on the resistance of lime mortar against NaCl and Na_2SO_4 crystallization 77

1

Introduction

1.1 Problem definition

An important part of our cultural heritage is formed by historical buildings and structures. Unfortunately, crystallization of soluble salts (e.g. chlorides, sulfates and nitrates) inside the pores of their materials poses a serious threat to their conservation [1]. Salts crystallizing inside porous materials (crypto-florescence[1]) can cause quite severe damage and lead for example to loss of cohesion or to different forms of layering of the material (see Figure 1.1 for examples); differently, salts crystallizing on the material surface (efflorescence) cause mainly esthetical damage in the form of an unattractive salt deposit. Salts can be present in building materials due to for example the use of road de-icing salts, sea salt spray or the building materials themselves (e.g. use of sea water for mixing mortars) [2]. The problems due to salt crystallization are expected to increase in future due to climate changes; for example higher temperatures and more precipitation may lead to an increased number dissolution/crystallization

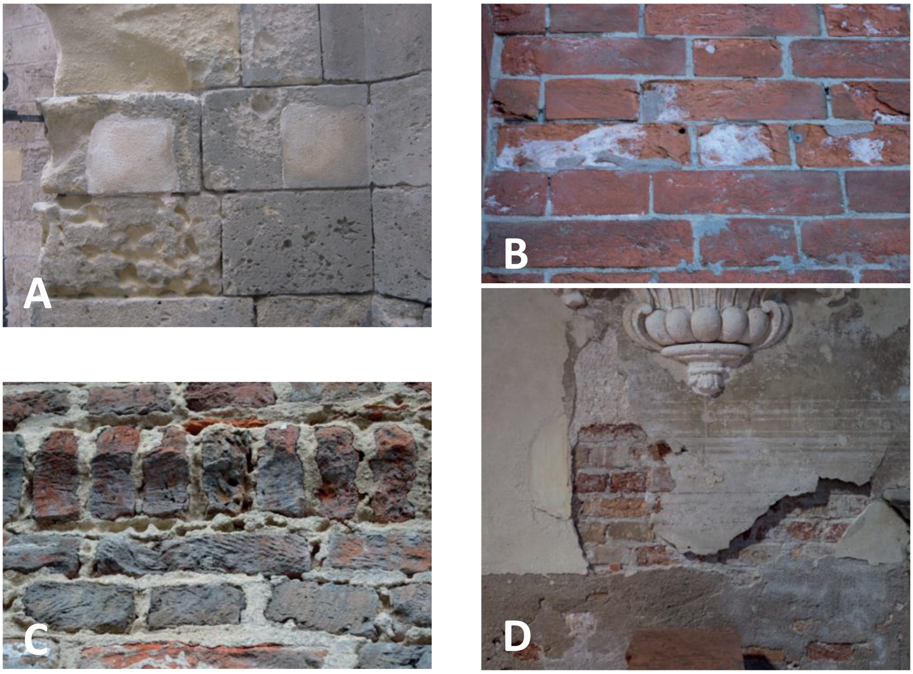

Figure 1.1: Examples of salt damage in porous building materials. Salt crystallization damage to natural stone (A), brick (B), pointing mortar (C) and plaster (D).

---

[1] This term is similar to ‘subflorescence’ as used in the ICOMOS-ISCS glossary. We use ‘crypto-florescence’, as defined in the MDCS damage atlas.

Figure 1.2: Example of damage to brick partly caused by replacement of the pointing with not compatible mortar.

cycles, fact which increases the risk of damage [3].

Although salt crystallization damage is a very common problem, no fully effective solution for its mitigation yet exists yet. The traditional approaches to prevent or mitigate salt crystallization damage are often based on modifying the material properties. In the case of mortars and plasters, this includes mixing water-repellent additives in the material to prevent water ingress or the use of a stronger binder, such as cement, to increase the mechanical strength. However, these methods usually have a low compatibility with the existing materials [4, 5] (see Figure 1.2 for an example).

Mortars, in particular lime-based mortars, often present as bedding and pointing mortar, render or plaster in the masonry of historic buildings, are especially prone to salt damage because they have both large and small pores. This fact is favourable to the development of damage by crystallizing salts, because the coarse pores provide for sufficient supply of solution, while the small pores allow for the development of high crystallization pressures [6-8]. Additionally, their mechanical strength is relatively low. In the presence of soluble salts, lime-based mortars have therefore a limited service life and need to be regularly replaced; the costs for replacing or repairing mortars constitute a considerable part of the total maintenance costs of cultural heritage buildings. Alternatives to the existing solutions discussed above are therefore urgently needed.

In the last years, research has shifted from the traditional approaches based on improving the material properties to the innovative idea of influencing the crystallization process itself by the use of crystallization modifiers [9]. Crystallization modifiers are ions or molecules that modify the nucleation and growth of salt crystals and thereby possibly mitigate the salt crystallization damage, e.g. by enhancing the transport of salts and crystallization at the surface as harmless efflorescence (see e.g. [9-12]).

Recently it has been proposed to mix crystallization modifiers directly into a mortar during its preparation [13]. This mortar with mixed-in crystallization modifiers would be a kind of responsive material; the modifiers are already present in the material and they are activated when the damaging salt solution enters the material. The results would be a more durable mortar and thus lower maintenance costs. Some promising results on the use of modifiers mixed-in (lime-cement-based) mortar have already been published [13], however, several questions still remain which need to be answered through systematic research.

1.2 Objectives of the research

This research systematically investigates the potentialities of mixing crystallization modifiers directly into a lime-based mortar, with as final aim to provide and validate the proof-of-principle under laboratory conditions for the use of mixed-in crystallization modifiers to prevent or mitigate salt crystallization damage. The research focuses on two commonly occurring and very damaging salts: sodium chloride and sodium sulfate. The research methodology includes both literature research and laboratory experiments.

Before modifiers can actually be mixed in a mortar, several issues still need to be clarified. First, suitable modifiers need to be identified which can withstand the high alkaline environment of mortars, and their working mechanisms should be elucidated. Additionally, hypotheses on how crystallization modifiers could limit damage when mixed in the mortar need to be defined. Next, suitable modifier concentrations need to be selected which sufficiently alter the salt crystallization in order to mitigate or prevent damage, but do not affect fresh or hardened mortar properties. Once these issues have been clarified, prototype recipes of mortars with mixed-in modifiers can be defined. Finally, the resistance against salt crystallization of the developed additivated mortars should be assessed with an accelerated salt weathering test in the laboratory.

1.3 Outline of the thesis

Chapters 2 to 5 of this thesis have been published as or are based on peer-reviewed articles, which together summarize the development and results of the research. The final chapter (Chapter 6) recapitulates and reflects on the main conclusions of the whole research, and gives an outlook for future research paths.

The first step in the research consisted of a literature review focused on the identification of suitable crystallization modifiers for sodium chloride and sodium sulfate, two of the most common and damaging salts, and on the existing knowledge about their working mechanism. The review concludes with the formulation of hypotheses, to be further validated in the experimental research, on the mechanisms underlying the envisaged damage reduction in building materials of the identified modifiers (Chapter 2).

Based on the literature review, suitable modifiers for sodium chloride (sodium ferrocyanide) and sodium sulfate (borax) were selected to be used in the experimental part of the research. Whereas sufficient experimental references can be found for the combination of sodium chloride and sodium ferrocyanide, literature on the solution properties and crystallization behaviour of sodium sulfate in combination with borax is lacking. Therefore, part of the research was focused on the assessment of the influence of borax on solution properties of water and sodium sulfate solutions, and the interaction between borax and sodium sulfate crystallization (Chapter 3).

The next step in the research was the study of the effect of the chosen modifiers on relevant mortar properties such as porosity and pore size, moisture transport behaviour and mechanical strength. Moreover, it was investigated whether the modifier would keep its effectiveness also after undergoing the carbonation process (and thus the pH change) of the mortar. Additionally, based on literature and new experimental results, the suitable concentration of modifier to be added to the mortar was chosen (Chapter 4).

Once prototype recipes of mortars additivated with modifiers were defined, the final step in the research consisted in the experimental assessment of their resistance against salt crystallization. An accelerated salt crystallization test was developed to effectively test the resistance of the developed mortars in the laboratory. Reference and additivated mortars were tested and their performance assessed by visual and photographical monitoring, by measuring the material and salt loss in time and the salt distribution in the specimen at the end of the test (Chapter 5).

In the conclusions chapter (Chapter 6) the main results of the research are summarized and discussed, and an outlook for future research is given.

2

Mitigating salt damage in building materials by the use of crystallization modifiers - a review and outlook

Before salt crystallization modifiers can be experimentally studied as a means to limit or stop crystallization damage, it is important to understand: (i) the mechanisms underlying crystal modification and (ii) how crystallization modifiers can limit damage once inside porous materials. In this chapter the available literature on working mechanisms of crystallization modifiers potentially usable in building materials is reviewed. Furthermore, the available experimental studies on crystallization modifiers applied to building materials are summarized and their results discussed and compared. Finally, hypotheses are formulated on how the use of crystallization modifiers in building materials can mitigate salt crystallization damage.

This review is the result of a literature study carried out during the course of the PhD research and finally updated with the results of this research. This chapter is a slightly modified version, incorporating minor suggestions of the PhD committee, of the paper submitted to the Journal of Cultural Heritage.

Abstract

Salt crystallization damage in porous building materials is a widespread phenomenon. Several solutions to prevent, or mitigate, salt damage in building materials, prolonging thereby their service-life have been proposed. One of the latest approaches is the use of crystallization modifiers, aiming at reducing the crystallization pressure and/or favouring the crystallization of salts at the surface (efflorescence) instead of in the pores of the materials (crypto-florescence). This paper summarizes the working mechanisms of crystallization modifiers and critically reviews the available literature on their use in building materials; finally, it provides an outlook on the potentials of modifiers for the mitigation of salt crystallization damage in building materials.

2.1 Introduction

Salt weathering is a ubiquitous phenomenon in porous building materials, known since ancient times (see e.g. [14]). Salts, if present in building materials in significant amounts, can cause damage when undergoing deliquescence/dissolution and crystallization cycles, as a consequence of their contact with water (either in liquid or vapour form). The water dissolves the salts, transports and accumulates them and, when it evaporates again, the salts recrystallize. These repeated dissolution and crystallization cycles of salts generate stress in the material and ultimately lead to damage. Salts can have different sources: they can originate from for example ground water, sea salt spray, de-icing or from building materials themselves; typical moisture sources are rising damp, relative humidity of the air and rain [2, 15, 16]. When the salts crystallize on the surface of the material as efflorescence they are aesthetically unpleasant but harmless. However, when the salts crystallize inside the pores as crypto-florescence, they can develop pressure and cause severe damage and ultimately deterioration of the material [1].

The exact mechanism underlying the salt crystallization damage has been object of scientific debate over the last decades (see e.g. [8, 17-19]). In the last years, a certain consensus has been achieved on the mechanism generating crystallization pressure in pores: the most accepted theory states that the development of crystallization pressure in pores is due to a repulsive disjoining pressure between the pore wall and the growing crystal, causing a thin liquid layer to be present between pore wall and crystal. The disjoining pressure exists because the energy of the salt/mineral interface, which would be created if the crystal grows against the pore wall, is higher than the sum of energies of the salt/solution and mineral/solution interfaces [8, 20-23]. Recently, this theory was summarized by Flatt et al. [6, 24]. The authors present a formula which links the crystallization pressure to the supersaturation in the liquid film. The upper limit of the crystallization pressure is given by the disjoining pressure: if the supersaturation is so high that the crystallization pressure is equal or higher than the disjoining pressure, the crystal will grow against the pore wall. This will stop the growth of the crystal and it will consequently no longer exert a pressure. Furthermore, the authors clarify that if and whether pressure will develop is related to an interplay between crystal curvature (small pores), salt load and distribution, and discontinuities of the disjoining liquid layer (large pores).

Over the years, many attempts have been made to mitigate salt damage in building materials. As salt damage can only occur in the presence of both salt and water, eliminating one of these two factors will stop the development of the damage. Interventions tackling the problem at the level of the construction in relation to its environment are for example systems to control the interior climate or to tackle rising damp. These measures aim at reducing salt accumulation and dissolution/crystallization cycles. Other measures have focused more on altering the damaging mechanism at the level of the material: techniques have been developed to reduce or inhibit water transport by for example the use of water repellent agents in restoration plasters, aiming to keep salts inside, or on purpose designed pore size distribution. Techniques for salt extraction from the material or for conversion of soluble salts into insoluble compounds have been proposed as well. However, these solutions are not always feasible and/or effective, and often lack compatibility with the historic materials [25, 26].

Another, more recent approach to mitigate salt crystallization damage has focused on changing the (repulsive) interaction of the salt and the pore wall by the use of surfactants. These compounds work by changing the interactions between the pore walls and growing crystals in such a way that the latter can no longer be damaging (see e.g. [27-30]). So far these compounds have not shown very encouraging results. In crystallization tests done in the laboratory, some compounds gave less damage initially, but more severe damage in a later stage, in comparison to the reference. Furthermore, some compounds have shown problems related to osmotic swelling, filling the pores and generating more stress than the salt crystals.

Also, if the pore surface is attractive to salt, this fact could potentially lead to thermal-expansive mismatch in case the pores get filled with a dense volume of salt [27-29].

In the last decade, research has addressed the possibility of altering the crystallization process by the use of crystallization modifiers, in order to make crystallization less harmful (see e.g. [9-11, 31, 32]). Crystallization modifiers are ions or molecules which can inhibit the nucleation and growth of salts, promote crystallization of a specific salt phase at or near the saturation concentration and/or change the shape of the grown crystals. Compounds added to a system to interfere with the crystallization process are called crystallization modifiers or, less specifically, additives and/or impurities. These terms will be used interchangeably in this text.

This paper reviews the literature on crystallization modifiers: firstly, the literature on crystallization modifiers and their working principles in bulk solution is summarized (section 2.2); secondly, the literature on modifiers applied to building materials for the reduction of salt damage is presented and critically discussed (section 2.3). Finally, an outlook on the potentialities and possible limitations of modifiers for the mitigation of salt crystallization damage in porous building materials is given (section 2.4).

2.2 Crystal modification

In this section, a very brief introduction on nucleation and crystal growth is given, in order to clarify the important steps of the crystallization process. These notions will then be referred to, to explain the effect of modifiers on crystallization and development of pressure. Finally, the specific factors important for damage development and crystal modification of two model systems (sodium chloride and sodium sulfate) will be discussed.

2.2.1 Crystal nucleation and growth

In this review, crystallization through evaporation of the solvent will be considered: this is the most common mechanism of salt damage in porous building materials in the field. Crystallization due to cooling (for salts with a temperature-dependent solubility cooling of the solution can cause crystallization) will not be discussed, because this is a much less common situation in the field.

The first step in the formation of crystals is nucleation. Crystal nucleation from solution is a first order phase transition where an ordered phase (crystal) is formed from a disordered state (solution) [33]. The process is usually described by the classical nucleation theory (CNT), which is based on the assumption that the nucleation clusters are spheres of a uniform density and with a sharp interface. Furthermore, the molecular arrangement of the initial nucleation cluster is assumed identical to that of the large crystal after growth. The driving force of nucleation is $\Delta\mu$, i.e. the difference between the chemical potentials of a molecule in solution, μ_s, and that of a similar molecule in the large crystal, μ_c. Nucleation and/or growth are only possible if $\Delta\mu > 0$ [34].

The nucleation process can thermodynamically be described by an equation developed by Gibbs [35]. The Gibbs free energy required for cluster formation (ΔG) is the sum of the free energy change for the phase transition (ΔG_v) and the free energy change for the formation of a surface (ΔG_s). ΔG_v is negative, because the solid state is more stable than the liquid, and the phase transition (i.e. nucleation), thus decreases the free energy of the system. ΔG_s on the other hand, is positive, because the introduction of a solid/liquid interface increases the free energy proportionally to the surface area of the cluster. Therefore, the formation of a cluster is the result of the competition between a decrease in ΔG_v, which favours growth, and an increase in ΔG_s, which favours dissolution [36]. For spherical nuclei:

$$\Delta G = \Delta G_v + \Delta G_s = -\frac{4\pi r^3}{3\Omega} \cdot \Delta\mu + 4\pi r^2 \gamma$$

With Ω being the volume of one molecule, r the radius of the cluster, and γ the solid-liquid interfacial energy.

The Gibbs free energy is thus a function of the radius of the clusters. For small radii the surface free energy, ΔG_s, dominates and the total free energy initially increases for increasing r. Thus the smallest clusters will typically dissolve. When the radius increases, the total free energy goes through a maximum (critical free energy, ΔG^*) at a critical radius:

$$\Delta G^* = \frac{16\pi\gamma^3\Omega^2}{3\Delta\mu^2}$$

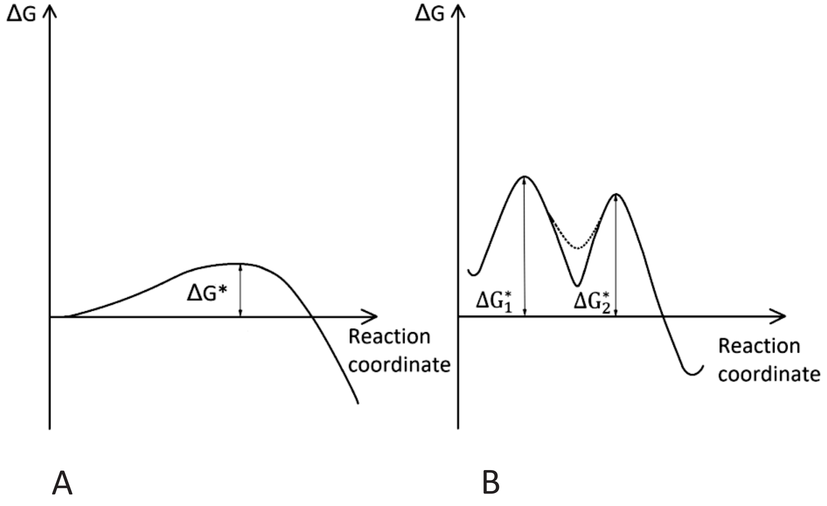

Figure 2.1: Examples of free energy barrier for (A) Classical nucleation and (B) two-step nucleation. The dotted line in B applies when the dense liquid phase is metastable with respect to the lower density solution.

Above the critical radius, the total free energy decreases continuously and growth becomes energetically favourable. This will eventually result in the formation of crystals. Each system has a different free energy barrier height (see Figure 2.1A) [36]. When the supersaturation level of the solution increases, the height of the nucleation barrier and the critical size of the nucleus will decrease. Therefore, either a very high supersaturation or a lowered surface free energy, due to for example the presence of modifiers, will result in fast nucleation of many small crystals [37].

So far the discussion dealt with homogeneous nucleation (HON), i.e. the nucleation of a spherical nucleus in the bulk of the solution. However, most of the time nucleation occurs on an available surface, such as a dust particle or substrate, as heterogeneous nucleation (HEN) [34]. Inside a porous building material, the pore wall is an example of a substrate for heterogeneous crystallization. In the case of HEN, the nucleation cluster is no longer approximated to be spherical, but cap-shaped (see Figure 2.2 for a schematic drawing) with a wetting angle θ, which is determined by the Young's equation:

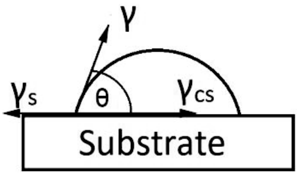

Figure 2.2: Example of cap-shaped nucleation cluster and corresponding wetting angle.

$$\cos\theta = \frac{\gamma_S - \gamma_{CS}}{\gamma}$$

Here γ_s, γ_{cs} and γ are the surface energy for the substrate/solution, cluster/substrate and cluster/solution interface, respectively. If θ = 180° there is complete non-wetting, which corresponds to HON [34]. To calculate the free energy barrier for HEN, the following equation can be used [38]:

$$\Delta G^*_{HET} = \Delta G^*_{HON}\,(\frac{1}{2} - \frac{3}{4}\cos\theta + \frac{1}{4}\cos^3\theta)$$

This implies that the crystal nucleation barrier for HEN will be (much) lower than for HON, i.e. lower supersaturation is sufficient for nucleation. This reduction of the nucleation barrier is the reason for the experimentally observed dominance of HEN over HON in insufficiently purified solutions (or with intentionally added impurities) or in solutions in contact with well-wetted substrates [34].

As discussed in the previous paragraphs, nucleation occurs both homogeneously and heterogeneously. This distinction is rarely made in literature about crystallization in porous materials, although it is known that some salts are more likely to crystallize homogeneously than others [39]. Inside the pores of materials, heterogeneous nucleation is expected; both due to the rough nature of the surface of a pore wall and to the fact that most likely foreign particles such as dust are present in the pore solution. Heterogeneous nucleation occurs at lower supersaturation than homogeneous nucleation, which in turn equals a lower crystallization pressure. However, it is not during nucleation that crystallization pressures in pores develop; this happens later on, during crystal growth, when solution gets trapped between the pore wall and the crystal [6]: this can occur also in the case the initial crystal started growing on the pore wall after heterogeneous nucleation. The actual mechanism of nucleation, homogenous or heterogeneous, is therefore not important for the development of crystallization pressure in pores and thus of damage.

Once a nucleus has formed, growth into a larger crystal will follow as long as the solution is still supersaturated. The morphology (shape) of the growing crystals can be modified by changing the growth conditions such as temperature or supersaturation, or by adding small amounts of impurities. These processes will be explained in detail in section 2.2.2. The morphology of crystals can be an important factor in the damage development, since a different crystal face can have a different surface energy [20, 40]. This also implies that different pressures might be exerted, depending on which specific crystal face is in the proximity of the pore wall [23]. As reported in literature (see e.g. [20, 41, 42]), these differences could play an important role to explain observed differences in the occurrence and extent of damage. Also, the contact angle between crystal and pore wall plays a role in pressure development (low angles equal small stresses) [21, 43]. Altering the morphology might therefore have potential to prevent or mitigate damage.

2.2.2 Mechanisms of crystal modification

Crystallization modifiers can act during both steps of the crystallization process: nucleation and growth. Nucleation modifiers can be grouped in two different categories: inhibitors and promoters. As it will be explained below, due to their working mechanisms, both nucleation inhibitors and promoters influence the growth of specific crystal faces altering therefore the shape of the grown crystals. Therefore, nucleation inhibitors and promoters can also be seen as habit modifiers of crystal growth. Additionally, some modifiers only act during the crystal growth, by adsorbing on preferential crystal faces, thereby altering the shape of the final crystal [44]. These modifiers are then called growth (habit) modifiers.

Crystallization inhibitors are modifiers that retard crystal nucleation and growth, i.e. increase the time between build-up of supersaturation and nucleation and thus favour the formation of a crystal phase at a higher supersaturation [32]. This could result in transport of solutes over longer distances in supersaturated salt solutions [45]. The working mechanism of inhibitors is not well understood. In general, two hypotheses exist, both involving the inhibitors being adsorbed on the crystal surface: the first hypothesis assumes that individual molecules adsorb and then block the growth of the crystal by step movement; the second hypothesis assumes that the whole crystal surface is covered with a layer that prevents the addition or detachment of salt growth units [46, 47] (see Figure 2.3 for schematic of both mechanisms). The second mechanism implies that a higher concentration of additive is necessary to obtain the desired effect.

Nucleation promoters act in exactly the opposite way of nucleation inhibitors. Instead of delaying the crystal nucleation, the rate of nucleation is increased, and the level of supersaturation at the onset of crystallization is decreased to at or near the saturation. The promoter lowers the nucleation barrier for crystallization by (temporary) attachment to the nucleus [48] or by offering a template that matches the structure of a specific crystal face and/or polymorph, for epitaxial crystal growth [44] (see Figure 2.4 for schematic).

Because both inhibitors and promoters usually adsorb preferentially (due to surface interactions or geometrical reasons), and thereby influence the growth of specific crystal faces, they often also change the morphology of

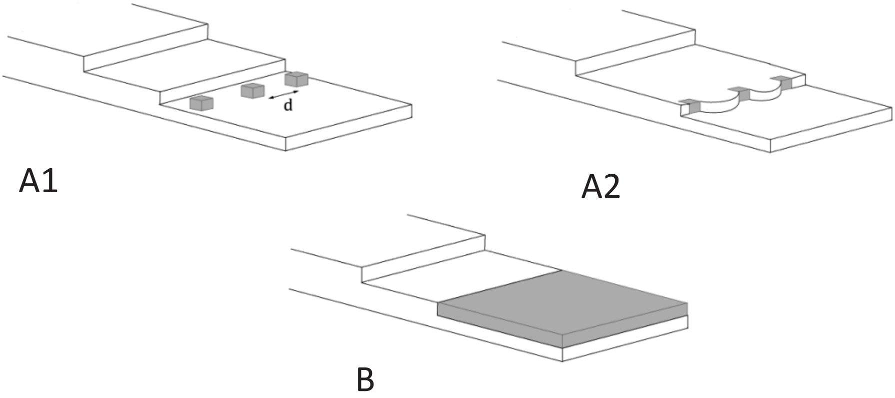

Figure 2.3: Schematic of possible working mechanisms for crystal growth inhibitors according to two hypotheses. The first hypothesis assumes that individual molecules adsorb (A1) and then block the growth of the crystal by step movement (A2); the second hypothesis assumes that the whole crystal surface is covered with a layer that prevents the addition or detachment of salt growth units (B). According to the hypothesis depicted in B, the modifier would cover the entire crystal surface. For clarity only one terrace is covered in this drawing.

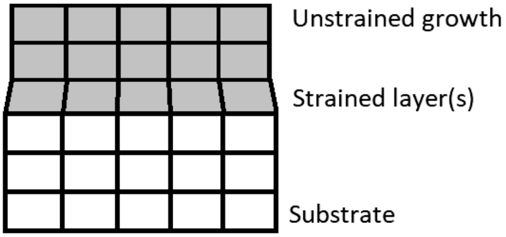

Figure 2.4: Schematic of epitaxial growth. A compound will grow (heterogeneously) on a substrate layer, if the lattice spacing differs maximally 15% [85]. The different lattice spacing will cause some strain (and possible defects) in the first layer(s).

the crystal and can therefore be seen as habit modifiers acting on the crystal growth [48-51]. In fact, the shape of a crystal is dependent on the relative growth rates of its faces, and the slowest growing faces determine the eventual shape of the crystal. Next to adsorption of the modifier on specific crystal faces, the habit of a crystal can also be influenced by the availability of solution during crystallization [52] and by the level of supersaturation at the moment of crystallization (kinetic roughening) [53].

The effect of the availability of solution on the (macroscopic) crystal habit has been researched extensively by Arnold and Zehnder [15, 54] for salt crystals growing on the surface of porous materials. They show that when plenty of solution is provided to the growing crystals (as it occurs in saturated materials at the start of evaporation), the (large) crystals will display shapes close to the equilibrium habit. However, when the liquid availability decreases, the shape changes. First, smaller crystals still displaying equilibrium shapes will grow; then, more columnar crystals will form and finally, when there is almost no liquid left, the salts will form whiskers.

The observation of nucleation behaviour which could not be described by CNT, as well as the finding of the effect of the supersaturation level on the nucleation pathway (i.e. the formation of (meta)stable phases) is underlined by recent publications [36, 48, 55], suggesting alternative theories to CNT. Although CNT is still the most widely used theory to describe nucleation, the many differences between theoretical predictions and experimental results suggest that nucleation does not always follow the classical pathway, but sometimes more complex routes. A good way to describe these complex routes seems to lie in the two-step model. This model describes the nucleation process in two steps; (i) the formation of unorganized clusters (not necessarily spherical) and (ii) the reorganization of these clusters into ordered structures. The free energy diagram corresponding to the two-step model will have two nucleation barriers, each corresponding to one of the steps [36] (see Figure 2.1B). If nucleation is indeed non-classical for some salts, this also implies that modifiers for these salts will interact differently. Recently, Olafson et al. [56] reported on the challenges associated with crystal modification and non-classical crystallization. Here, we assume that nucleation in building materials occurs via the classical pathway and we will explain the modifier behaviour in relation to this theory.

2.2.3 NaCl and Na_2SO_4

2.2.3.1 Crystallization

Two of the most abundant and damaging salts found in building materials are sodium chloride and sodium sulfate. These salts are chosen here as examples to illustrate the behaviour of appropriate modifiers because they have distinctly different crystallization behaviour. Sodium chloride only has one stable form at temperatures above freezing: the anhydrous crystal of halite [51]. This means that upon dissolution and recrystallization only one phase is involved in the damage process. Sodium sulfate, on the other hand, has two metastable phases (anhydrous phase III and heptahydrate (up to 22°C)) and two stable phases (anhydrous phase V (thenardite) and decahydrate (mirabilite, up to 32.4°C)) [28, 57-59] (see the phase diagram in Figure 2.5). While the solubility of sodium sulfate is strongly affected by temperature, that of NaCl is almost unvaried in the range of ambient temperatures (0 – 40 °C).

Supersaturation is the factor which determines the magnitude of the crystallization pressure, and thus the risk of salt crystallization damage to porous materials. However, there is no consensus on whether high supersaturation can actually develop for all salts inside porous building materials. In the case of sodium chloride, diverging results have been published. Some authors have observed (high) supersaturation in both model pore systems and building materials (see e.g. [12, 60, 61]), whereas others have not observed supersaturation in building materials (see e.g. [62, 63]). For sodium sulfate high supersaturation has been observed both in model systems and in materials (see e.g. [64-66]).

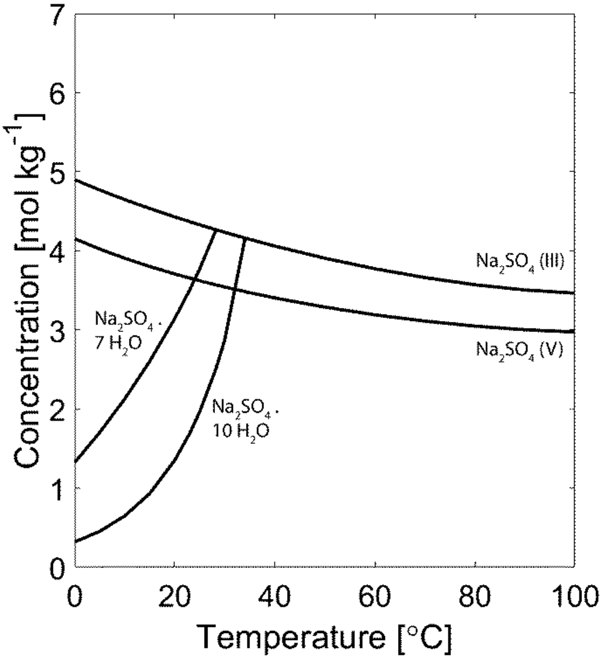

Figure 2.5: Phase diagram of sodium sulfate using the model from Steiger and Asmussen [57].

Another important variable affecting damage development is related to the existence of hydrated and anhydrous crystals and the pathway in which dissolution/crystallization takes place [19]. In the case of sodium chloride, a salt with only one phase, the crystals usually show a good interaction with the substrate: strong adhesion is reported in the case of growth on a stone substrate [19] and the salt is observed to form a layer on the pore walls of building materials [18, 39, 52]. Damage in building materials is generally observed after repeated dissolution/crystallization cycles (caused by relative humidity changes), leading to increasing supersaturation ratios (and thus higher pressures) [67-70]. Repeated recrystallization events will lead to more perfect (i.e. more resembling the equilibrium crystals shape due to absence of secondary nucleation and with less impurities) and less but larger crystals [68, 70, 71]. This could point at the fact that for this (anhydrous) salt, crystal habit and size are crucial factors for damage development.

Differently from sodium chloride, sodium sulfate can form several hydrates (each having different solubility) depending on the environmental conditions. For these types of salt system, the exact mechanism of damage development has been controversial for a long time, but now some consensus has been achieved. Although direct crystallization of anhydrous or lower hydrated crystals after evaporation can cause some damage [43, 57, 72], usually the very severe damage is observed after wetting (with liquid water) of materials contaminated with thenardite [65, 72, 73]. In this case, (partial) dissolution of the anhydrous crystals occurs, followed by precipitation of mirabilite [64, 65, 74, 75]. Not only do these crystals have a larger crystal volume [19, 76] than the primary formed anhydrous crystals, but they can also develop a larger crystallization pressure [65] because a saturated solution with respect to anhydrous crystals is heavily supersaturated with respect to mirabilite. The higher pore filling (due to larger volume) combined with high supersaturation is considered to be responsible for the high crystallization pressure developed and the consequent severe damage which can be observed when specimens containing anhydrous sodium sulfate crystals are re-wetted (below the transition temperature of 32.4 °C).

2.2.3.2 Modifiers for sodium chloride

The influence of (in)organic additives on the nucleation and growth of sodium chloride has been researched extensively; this is due to the fact that this is an ideal model system: NaCl has a cubic habit and a single phase above freezing temperature. The most effective modifier of sodium chloride crystallization is ferrocyanide. It is effective to alter the crystallization of sodium chloride even if present only in very small amounts. Ferrocyanide and its interaction with sodium chloride have been extensively researched [12, 50, 51, 77, 78]. Recently, its working mechanism as growth modifier has been experimentally validated by Bode et al. [79]. The authors report that, as a cluster of $[Fe(CN)_6]^{4-}$ has approximately the same size and shape as a $[NaCl_6]^{5-}$ cluster, the ferrocyanide cluster fits into the sodium chloride crystal lattice, blocking further step growth due to the charge difference. This leads to the formation of dendritic instead of cubic salt crystals. This morphological instability is caused by kinetic roughening due to low surface energy and a high supersaturation [80]. Ferrocyanide works therefore as growth inhibitor and habit modifier.

Additionally, ferrocyanide inhibits the nucleation of sodium chloride (i.e. it is a nucleation inhibitor), leading to a higher supersaturation ratio at the onset of nucleation. It has been suggested that this is due to the fact that the ferrocyanide clusters reduce the concentration of available solvent in the system because they have a strong tendency to solvate, thereby increasing the relative supersaturation (there is less ‘free’ water available for the salt to dissolve in). Additionally, the ferrocyanide clusters can adsorb Na ions, thereby interfering with ion transport and preventing sodium chloride nucleation clusters to develop beyond the critical radius [12].

Other (families of) modifiers of NaCl which have been recently proposed include iron(III)-*meso*-tartaric acid, ferrous tartrate, polymers and amides (see e.g. [51, 81, 82]). These modifiers are studied to be used as anti-caking agents, and they work by blocking crystal growth. Besides the prevention of caking, these compounds also induce creeping[2] of the salt. These modifiers are usually less effective than ferrocyanides (higher concentrations are needed) and/or effective only in a specific pH range. Their application to building materials is hindered by the fact that for example the pH inside the pores cannot be controlled. To our knowledge, these modifiers have not been applied in (laboratory) studies of porous materials, and will not be further discussed in this review.

2.2.3.3 Modifiers for sodium sulfate

Unlike for sodium chloride, the literature on modifiers for sodium sulfate is rather limited. A common group of crystallization modifiers for sodium sulfate are phosphonates (compounds containing $C{-}PO(OH)_2$ or $O{=}P(OH)_2(OR)$) (see e.g. [9, 10, 32, 83]). Phosphonates can work either as inhibitor (pH 8-8.5) or promoter (salt solution neutral pH 6.4) of sodium sulfate (mirabilite) crystallization. At pH levels higher than 8.5 the mirabilite crystal surface becomes increasingly negative and this leads to repulsive electrostatic forces between the ionized phosphonate molecules and the sodium sulfate which will limit the inhibitor effect [32]. Additionally, their effectiveness is strongly influenced by concentration. Next to phosphonates, other modifiers have been proposed for sodium sulfate, such as sodium dodecyl sulfate [28], with doubtful results. Based on modelling, recently phosphocitrate has been proposed as inhibitor of sodium sulfate crystallization with positive effects in reducing damage development [84].

---

[2] ‘Creeping’ is the gradual movement of crystals upon a surface through solution transport followed by solvent evaporation at the crystallite tips. Creeping should not be confused with ‘creep’, a term which relates to the slow movement or the time-dependent permanent deformation of a solid material under the influence of a long-term mechanical stress.

Another alternative to phosphonates recently proposed is borax ($Na_2B_4O_7 \cdot 10H_2O$). Borax is supposed to work as promoter of mirabilite [85], also at highly alkaline pH [86]. However, recent research [87], has shown that the effect of borax depends on the concentration and experimental conditions under which crystal growth takes place. Depending on the initial borax concentration, two phases of borax can crystallize. The decahydrate phase favours the precipitation of mirabilite at or near saturation whereas the pentahydrate phase (tincalconite) favours precipitation of thenardite with a crystal shape dominated by the {153} planes, resulting in needle-like crystals [87].

2.3 Crystal modification inside porous materials

In this section the way crystallization modifiers can alter crystallization in porous building materials, and the consequences for the damage development are presented. The general requirements posed to modifiers for their possible application in building materials are discussed. Finally, the available literature on application of crystallization modifiers in porous building materials is critically reviewed.

2.3.1 Working principles and expected positive effects of the use of modifiers in building materials

Several mechanisms of modifiers can be envisaged which could have a positive effect on salt crystallization damage. A first way consists in favouring efflorescence instead of crypto-florescence. This can be a consequence of both the modified crystal habit (caused both by inhibitors and promoters) leading to an increased evaporation rate. Furthermore, in the case of an inhibitor, the delayed nucleation can favour the transport of the solute to the surface and thus the occurrence of efflorescence.

The process leading to efflorescence or crypto-florescence is in a certain way analogous to the process of creeping of salts [12, 88]. Both creeping and crystallization in porous media are evaporation driven, and evaporation of the solvent, i.e. the mass transport of evaporated water molecules in air, is in both cases the rate-limiting step. Therefore, the processes used to describe creeping can also be used to describe the occurrence of efflorescence or crypto-florescence. Van Enckevort and Los [88] showed that the shape and size of the growing crystals play an important role in the creeping rate: thin needles and thin platelets grow faster than thick, block-shaped crystals [88]. By analogy to creeping, it is expected that crystallization modifiers, altering the habit of growing crystals towards thin needles and/or thin platelets, favour faster growth of the crystals, i.e. the crystals ‘creep’ towards the drying surface and efflorescence is stimulated. During creeping the crystals protruding from the liquid show enhanced evaporation and thus faster growth; because of capillarity effects, the growing crystals ‘draw’ solution from the bulk, and stay embedded in solution [12, 88]. This way, the salt aids the transport of the solution towards the drying front, at or near the surface of the porous material, by maintaining a continuous liquid film [11], increasing the amount of efflorescence by a self-amplifying process. Besides, nucleation inhibitors, by keeping the salt longer in solution, also favour the transport of the solute (the salt) to the surface, where this can then crystallize as efflorescence without causing damage.

A second way by which modifiers can reduce or prevent crystallization damage in porous materials consists in avoiding the build-up of high crystallization pressures. This could be achieved by: (i) using crystallization promoters to induce crystallization at or near supersaturation or (ii) using modifiers to change the crystal size and shape. Crystallization promoters favour crystallization at low supersaturation, and can thereby prevent the development of high pressure. Additionally, in the case of salts with multiple hydrates, promoters which favour the crystallization of anhydrous (or lower hydrated) crystals might be beneficial. However, if the anhydrous crystals undergo a dissolution/recrystallization cycle, rapid precipitation of (higher) hydrated crystals occurs: the high supersaturation of the solution with respect to the hydrated phase and the larger volume of the hydrated crystal would still result in severe damage to the material and the modifier would not have any positive effect. Only in the case the modifier favours the re-precipitation of the anhydrous or lower hydrated crystals following rewetting it can be expected that it will have a beneficial effect on the development of damage.

A modification of the size and shape of the crystals, is usually a side-effect of inhibitors and promoters. Salt observed in building materials in the presence of modifiers are generally precipitated as an agglomeration of very small crystals showing non-equilibrium crystal shapes (see e.g. [13, 49, 89]. See Figure 2.6 for examples of sodium chloride and sodium sulfate crystals grown in the presence of sodium ferrocyanide or borax, respectively.

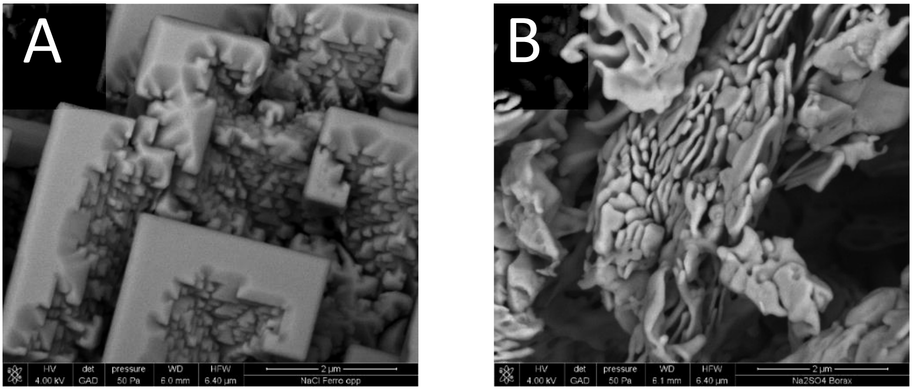

Figure 2.6: Examples of non-equilibrium crystal shapes under the influence of modifiers. A) NaCl with ferrocyanide, B) Na_2SO_4 with borax. Images kindly made available by the authors of [89].

A high nucleation density, smaller crystals and crystals with a non-equilibrium crystal shape may be beneficial to limit the development of (high) crystallization pressures. The inhibition of nucleation results also in a high nucleation density. A large number of nuclei and growing crystals implies that a high supersaturation can hardly be sustained for a long period of time, and therefore possibly no or limited pressure is exerted on the pore wall. If some pressure does occur, it will most likely be minor, since small crystals can exert a much smaller pressure than larger ones [23]. The crystals with non-equilibrium crystal habit could also have a different surface charge, when compared to the equilibrium crystal, and/or have a changed contact angle with the pore wall (see also section 2.2.1). The altered shape can also enhance solution flow towards the drying surface thanks to the increased evaporation surface of the salts and to the creeping effect. All these factors would promote the growth of harmless efflorescence instead of damaging crypto-florescence.

2.3.2 Possible limitations for the use of modifiers in building materials

The fact that crystallization modifiers alter crystallization in bulk solutions, does not mean that they will still have the same effect when present in porous materials. They might for example chemically react with or be physically bound to the components of the building materials losing their effectiveness. Especially modifiers which are effective as ions in solution might be prone to this risk. If they chemically react to form a different, ineffective compound or if they are physically bound to the substrate (and unable to dissolve again), they can no longer be effective as modifier. The effectiveness of modifiers in porous materials should therefore be verified with laboratory work, before an actual (practice) application. It has also been hypothesized that some modifiers, by forming a 2D network on top of the pore material, can act as a template for heterogeneous nucleation [49, 90], working thus as a nucleation promoter. In this last case, the physical bond of the modifier is likely not a limitation, but an advantage since it could potentially limit or prevent leaching of the modifier.

Another important parameter which might influence the effectiveness of modifiers is the pH of the pore fluid. For example phosphonates [32] and carboxylates [91] are known to work only in a specific pH range. As the pH level in some inorganic building materials varies between moderately alkaline (~8) in calcareous or siliceous materials [92] to highly alkaline in not carbonated cement and lime-based mortars (~13) [93], some modifiers might not be effective anymore when applied to building materials.

2.3.3 Review of studies on the use of modifiers in building materials

Only few studies on the application of crystallization modifiers inside porous building materials can be found in literature. In the following sections these are critically reviewed.

2.3.3.1 Ferrocyanide

The most studied crystallization modifier in porous building materials is ferrocyanide, a well-known nucleation and growth inhibitor and habit modifier of sodium chloride. Selwitz and Doehne [9] were the first to study the influence of ferrocyanide on the crystallization of sodium chloride and sodium sulfate in building materials. The modifier was added to the salt solution used to contaminate two different types of limestone. They observed that ferrocyanide enhanced salt solution transport favoured crystallization at the surface, instead of inside the stone, thanks to the inhibition effect of ferrocyanide. Furthermore, most of the salt crystallized as filament-like efflorescence, showing the effectiveness of ferrocyanide as habit modifier. Efflorescence was not adherent to the surface. After the test, all of the specimens containing ferrocyanide were totally intact and undamaged, whereas the reference specimens showed mild edge and corner erosion. Several concentrations of ferrocyanide were tested, and even the lowest amount used (10 ppm) showed an effect on the habit of efflorescence. The authors also tested the effect of ferrocyanide on desalination of the same limestones and they observed no enhancement of sodium chloride efflorescence. They attribute this result to the fact that ferrocyanide actually inhibits the dissolution of sodium chloride, and therefore it cannot enhance the dissolution of salt crystals; this implies that it can only be effective once the salt has dissolved in water. The absence of any positive influence of ferrocyanide on desalination effectiveness was also assessed by the authors, in experiments carried out in the framework for the EU project SALT CONTROL. As mentioned, Selwitz and Doehne [9] also applied the ferrocyanide mixed with sodium sulfate solution. In these experiments the effect of ferrocyanide is far less convincing. A delay in damage development was observed for a low concentration of sodium sulfate. However, at high sodium sulfate concentration degradation was severe despite the presence of the modifier.

Rodriguez-Navarro et al. [12] studied the effects of two different ferrocyanides (sodium and potassium) on sodium chloride crystallization in a limestone. The modifiers were added to saturated salt solutions prior to application. The authors observed much faster evaporation rates for the salt solutions containing ferrocyanides than for only sodium chloride solutions. They attribute this to the formation of a significant amount of porous efflorescence on the surface under the influence of ferrocyanide. This leads to an increase of evaporation surface and consequently to the observed increase in drying rate. In the presence of ferrocyanide crypto-florescence formation was negligible and thus no damage was observed, whereas in the control specimens granular disintegration occurred at the stone slab upper edges and corners. The habit of the efflorescence showed significant modifications towards skeletal and dendritic shapes. They report no differences between the effectiveness of the two different ferrocyanides used.

Lubelli [18] studied the dilation behaviour of lime-cement mortar specimens, contaminated with sodium chloride solution with and without the addition of sodium ferrocyanide, as response to relative humidity changes through the equilibrium relative humidity value of the salt. The author showed that the reference specimen suffered significant, irreversible dilation. Surprisingly, the specimen containing ferrocyanide showed only minor, reversible, dilation. The reference specimen showed severe damage in the form of sanding of the surface layer, while the specimen with ferrocyanide did not suffer any visible damage. The inhibitor was shown to have a significant effect on the shape of the salt crystallized within the pores of the material: in the case of the reference specimen, sodium chloride formed a layer on the wall of the pores; while in the presence of ferrocyanide, agglomerations of very small crystals with a non-equilibrium crystal shape and appearing as non-adherent to the pore surface, were observed.

Lubelli and van Hees [31] report that the effect of sodium ferrocyanide on the drying of specimens saturated with a solution of sodium chloride additivated with this inhibitor is strongly dependent on the substrate characteristics. They show that ferrocyanide enhances drying and therefore promotes salt accumulation near the surface in limestone and brick, but has no visible effect in case of coarse porous sandstone. This may be due to the different pore size distributions (and thus salt solution transport). Additionally, they report that ferrocyanide is very effective in changing the morphology of the sodium chloride from dense agglomerates to a branched shaped efflorescence, providing a much larger evaporation surface. This effect on morphology is also observed inside the pores: without inhibitor sodium chloride forms a layer on the pore wall but with it agglomerates of small crystals are formed (similarly to what was earlier observed in [18]). In this study, no conclusion could be drawn on the effectiveness of the inhibitor in preventing salt damage, considering that both the treated and untreated specimens did not show any damage.

Rivas et al. [94] also studied the effect of two different ferrocyanides (sodium and potassium) on the crystallization of sodium chloride solution (modifier added to the salt solution prior to contamination of the specimens) in granites and their effect on desalination of granite already contaminated with sodium chloride (modifier added to the desalination water). Similarly to Lubelli and van Hees [31], Rivas et al. attribute the differences in the effectiveness of modifiers observed in their experiments on granites to the pore structure of the porous material. For the medium to coarse-grained granite they report an acceleration of the evaporation of sodium chloride solution in the presence of the ferrocyanides, independently from the concentration used. In the medium to fine-grained granite, evaporation is also accelerated under the influence of the ferrocyanides; however, in this case the effect was concentration dependent, becoming less pronounced for lower concentrations of ferrocyanide. For both granites no difference in effectiveness between the two ferrocyanides was observed. In the presence of ferrocyanides, both granites developed a large amount of efflorescences in the form of small crystals with a dendritic habit, while in the absence of the inhibitor the efflorescence was massive and crust-like. The authors also describe a desalination experiment in which the addition of ferrocyanides is reported to increase the desalination effectiveness. This seems to contradict the results by Selwitz and Doehne [9] but support those by Gupta [95]. Gupta saturated brick specimens with a sodium chloride solution and freeze dried them to obtain a homogeneous distribution of the salt crystals. After freeze-drying, the specimens were placed at high vacuum to cause sublimation of the solid water to vapour, leaving behind only the salt crystals. Next, the contaminated specimens were sprayed with inhibitor solution and then covered for 4h to avoid the evaporation of water. This procedure was repeated for about 2 days, to allow the inhibitor to penetrate the material through diffusion. The author observed that not all salt could be dissolved in the presence of the inhibitor, but that efflorescence formation was enhanced. The contradictory results of [94] and [95] with [9] are most likely caused by the fact that in the test by Rivas et al., the salt was present in solution instead of in crystal form (as in the study by [9]) and in the test done by Gupta, sufficient time was given, after application of the inhibitor, for the inhibitor to diffuse into the specimens and thus for the salt to, at least partially, dissolve; only after this period, drying (and thus desalination) could start. Rivas et al. also report a change of colour of the ferrocyanide complexes turning to blue, most probably caused by a reaction between the ferrocyanides and Fe(III), under the influence of sunlight [94]. This might be an important practical issue for future applications.

Gupta et al. [62, 96] studied the crystallization of sodium chloride in brick and in limestone under the influence of ferrocyanide. The inhibitor was dissolved in the salt solution used for contamination of the specimens. For both materials tested, the ferrocyanide caused an increase in the drying rate of the specimens. This is attributed to the formation of dendritic efflorescences in the presence of ferrocyanide, which increases the evaporation surface, as also observed by other authors. An interesting result is that, when measuring the saturation level of the salt solution in the pores by Nuclear Magnetic Resonance (NMR), the authors do not observe high supersaturation levels inside the brick, although this could be expected by the inhibition effect of ferrocyanide. They also conclude that the application of ferrocyanide is probably most useful in an environment that promotes fast drying (room temperature, 1 L/min air flow, 0 %RH), as under slow drying conditions room temperature, 1 L/min air flow, 55 or 70 %RH) they did not observe any differences in the amount of efflorescence formed or in the time it took for the solution to saturate under the influence of the ferrocyanide.

All the experiments described until now, consist in adding the modifier either together with the salt in an aqueous solution or to material already loaded with salt. To the authors' best knowledge, the first attempt to mix the modifier in a material during its production, with the aim of developing a responsive, salt resistant material, has been done in the pilot study by Lubelli et al. [13]. In this research sodium ferrocyanide was mixed in different percentages in a lime-cement mortar, which was subsequently subjected to a crystallization test using sodium chloride solution. The results show a significant reduction of the salt crystallization damage in the presence of ferrocyanide in comparison to reference specimens. The observed reduction of the damage in the additivated mortar is explained by the effect of ferrocyanide in stimulating efflorescence instead of salt crystallization in pores. This research supports the viability of mixing-in ferrocyanide in mortar for the mitigation of sodium chloride damage; however, the possible effects of the modifier on the fresh and hardened mortar properties were not investigated.

The effectiveness of sodium ferrocyanide as modifier of sodium chloride crystallization was further investigated by Granneman et al. in lime-based mortar [89]. The modifier was added to the mortar during mixing, prior to the carbonation process. Once carbonated, the mortar specimens were subjected to an accelerated salt crystallization test using sodium chloride solution. The mortars additivated with the modifier showed a considerably improved resistance to salt crystallization damage in comparison to the reference mortar. The modifier stimulated the formation of harmless efflorescence and was also found to alter the habit of the precipitated crystals inside the pores of the mortar. The authors also studied the influence of sodium ferrocyanide on selected fresh and hardened properties of lime-based mortar: no significant effects were observed [97].

2.3.3.2 Citrate and organophosphorus compounds

The effectiveness of both citrate and the phosphorylated compound to inhibit crystallization of sodium sulfate in limestones was studied by Cassar et al. [83]. They applied the modifiers to the stones via absorption of an aqueous solution, before salt contamination. They report higher evaporation rates of the saline solutions and higher amounts of efflorescence in the presence of the inhibitors than in the reference specimens. The specimens treated with the inhibitor showed less damage than reference specimens. Sammut et al. [98] tested citrate and phosphocitrate as inhibitors not only for sodium sulfate, but also for sodium chloride, sodium nitrate and mixtures of these salts in limestone. The limestone specimens were treated with inhibitor before contamination with the salts. Similarly to Cassar et al., they observed an increase in the evaporation rate in the presence of the inhibitor. They report differences in effectiveness of the inhibitor depending on material type, salt type, environmental conditions during the test and depending on whether the modifier was applied before the salt contamination or vice versa. They observed that the inhibitor favoured non-equilibrium morphologies of the crystals, confirming that habit modification is usually a side-effect of inhibition. Franceschini et al. [99] also applied phosphocitrate, but mixed in a poultice, on a bedding mortar with a mosaic, contaminated with sodium and calcium sulfate, to favour salt extraction. Their results show that in the areas treated with the inhibitor the efflorescence is composed only of sodium sulfate. This means that the inhibitor suppresses the formation of calcium sulfate. They also observed a habit change of sodium sulfate crystals, from large elongated crystals, present in the untreated substrate, to rounded and significantly smaller crystals in the presence of inhibitor. The authors report that the presence of the inhibitor enhanced the extraction of sodium sulfate.

The effectiveness of DTPMP (diethylenetriaminepentakismethylphosphonic acid), a modifier of the phosphonates group, was studied by Lubelli and van Hees [31] as modifier for sodium sulfate crystallization in limestone, sandstone and brick. Lubelli and van Hees [31] added the modifier to the salt solution used to contaminate sandstone, limestone and brick specimens, and studied the effect of this modifier on the drying behaviour and the tendency of the salt to effloresce. They observed very different effects of the inhibitor, depending on the type of substrate and attribute these differences to the composition of the substrate. Considering that the effectiveness of this inhibitor is strongly dependent on pH and reaches its maximum at pH 8, the highly alkaline environment in some substrates might have limited the inhibitor’s effectiveness. Besides, phosphonates have a strong tendency to adsorb on a large variety of surfaces, a fact which could also limit their effectiveness. No effect of DTPMP on the habit of the grown crystals was observed. The salt crystallization resistance was only slightly increased for the limestone tested in this study; for the other materials no differences in damage in untreated and treated specimens could be observed. An important final remark from this study is that the application method of the inhibitor may be an important parameter to take into account; application by spraying of an aqueous solution on specimens contaminated with sodium sulfate enhanced damage development.

Ruiz-Agudo et al. [90] studied DTPMP as inhibitor of sodium and magnesium sulfate precipitation in limestone, by adding the modifier to the salt solution used to contaminate the limestone specimens. They observed a significant damage reduction for both magnesium and sodium sulfate in the presence of DTPMP. However, instead of the expected increase in efflorescence, they observed enhanced salt crystallization inside the material. Further research on sodium sulfate crystallization inside the limestone revealed that DTPMP caused a significant reduction in the supersaturation reached at the onset of crystallization, i.e. this modifier works as promoter of sodium sulfate crystallization. The authors propose the hypothesis that the phosphonate forms a template on the calcite, which favours crystallization of mirabilite by heterogeneous nucleation. Crystallization at lower supersaturation consequently means lower crystallization pressures and thus possibly less damage. A similar mechanism of damage reduction can be expected to occur for magnesium sulfate. However, as was suggested in section 2.1, it is most probably not during nucleation that crystallization pressures in pores develop; this happens later on, during crystal growth, when solution gets trapped between the pore wall and the crystal [6]. If the modifier favours nucleation inside the pores, at some point these pores will get filled and crystallization pressures can develop.

Ruiz-Agudo et al. [100] also applied DTPMP in a case study on limestone affected by magnesium sulfate crystallization. Their results indicate a reduction in the formation of efflorescence and a reduction of the on-going damage in comparison to untreated surfaces. This suggests that DTPMP can act as a promoter of magnesium sulfate in limestone, resulting in lower crystallization pressure and possibly less damage.

2.3.3.3 Borax

The effectiveness of borax as promoter of sodium sulfate (mirabilite) and magnesium sulfate (epsomite) crystallization in limestone was studied by Ruiz-Agudo and Rodriguez-Navarro [49]. The modifier was mixed in the salt solution used to contaminate the stones. The authors hypothesize that borax might form a 2D nucleation template on top of calcite, leading to epitaxial growth of the salt and thus favouring crystallization. They found that the evaporation rate of sodium sulfate solution decreased in the presence of borax, and attributed this to pore clogging due to sodium sulfate crystallization, which they observed in cracks, fractures and pores. The hypothesis that borax worked as promoter of sodium sulfate crystallization in pores at low supersaturation was also supported by the observed reduction of the amount of efflorescence and material loss, when compared to a reference specimen. In case of magnesium sulfate, no effect of borax on the evaporation rate was found, although massive pore blocking was observed. The authors attributed this to the measured reduction of the surface tension of the salt solution, enhancing the evaporation rate of the solution and counteracting the effect of pore blocking. The massive pore blocking indicates that borax promotes magnesium sulfate precipitation inside the material. This was confirmed by the absence of efflorescence. The crystals inside the pores show a large near-equilibrium habit in the presence of borax, indicative of nucleation occurring near saturation under the influence of the promoter; besides, no material loss or cracks were observed in specimens contaminated with magnesium sulfate and borax. These results show that borax could be considered as a promoter for both magnesium and sodium sulfate, resulting in a reduction both in efflorescence and damage development.

The effectiveness of borax as modifier of sodium sulfate crystallization was studied by Granneman et al. in lime-based mortar [89]. The modifier was added to the mortar during mixing, prior to the carbonation process. Once carbonated, the mortar specimens were subjected to an accelerated salt crystallization test using sodium sulfate solution. This test is an adaptation of the RILEM MS A.1 procedure [101], further modified in international research (e.g. [102]) and in previous work by Lubelli [18] (further details can be found in section 5.2.3). The damage to the specimens additivated with the modifier was significantly less than in reference specimens. The modifier stimulated the formation of harmless efflorescence and was also found to alter the habit of the precipitated crystals inside the pores of the mortar. No significant differences were observed between the rheological, mechanical and physical properties of the mortar additivated with borax and those of the reference mortar [97].

2.4 Discussion and conclusions

Based on the literature presented in the previous sections, the use of crystallization modifiers appears to offer a promising way to tackle salt decay in building materials. However, several issues need to be considered and some questions remain still open. These are summarized and discussed in the next paragraphs.

First of all, it can be concluded that, while for some modifiers, e.g. ferrocyanide, the working mechanism in bulk solution has been fully elucidated, for others, e.g. borax, this is still unclear and needs further research. When the application of modifiers in building materials is considered, a fundamental question is still open: the way and the extent up to which modifiers affect the crystallization pressure occurring in pores and influence the resulting damage. Moreover, several application-related issues need to be taken into account for a successful use of modifiers in building materials: one of these is whether the modifier will maintain its effectiveness, observed in bulk solution, when applied in building materials. In fact, aspects like pH of the pore solution and/or (chemical or physical) binding to the materials components might inhibit or reduce the effect of the modifier. Also modifiers that change their behaviour depending on their concentration may pose similar problems, as their concentration in the pore solution may vary in time depending on the moisture content in the material and/or due to leaching of the modifier. Aspects related to concentration of modifier in the pore solution and to leaching have as yet not been investigated up to now.

Besides, it has been shown that it might be problematic (it may lead to damage due to dissolution/crystallization of salts) or not always effective (modifiers do not increase salt solubility) to introduce the modifier (e.g. by capillary suction of solutions in water) in materials already contaminated with salts. A promising approach may consist in producing materials containing the modifier, in such a way that this can be activated by the ingress of water and salts. Mixing modifiers in mortar (including bedding, pointing, plaster and render mortars) might be a promising solution for the production of mortars with an improved resistance to salt decay. Apart from earlier studies by the authors [13, 89], no research on modifiers mixed in mortars has been found. When the above-mentioned approach is followed, it is important that the modifier, next to improving the resistance of the mortar, does not negatively affect its properties (including workability, mechanical strength and moisture transport behaviour).

As it is known that modifiers work generally in a selective way, i.e. they are effective only for a specific type of salt, studies on the application of the same modifier to different salts or to a mixture of more salts are still scarce.

Finally, health and environmental issues related to the use of modifiers should be taken into account. This issue is (almost) not considered in the screened literature on the application of modifiers to building materials; however, it should be considered as it may pose problems to the applicability.

The elucidation of the issues mentioned in this section will facilitate the application of modifiers in porous building materials for their protection against salt crystallization damage.

Acknowledgements

This research has been financed by the Dutch IOP program on Self-Healing Materials, under Grant number SHM012018.

3

Effect of borax on the wetting properties and crystallization behaviour of sodium sulfate

The previous chapter resulted in the identification of potentially suitable modifiers for sodium chloride and sodium sulfate: ferrocyanide and borax, respectively. However, before crystallization modifiers can be used in porous materials, it is important to understand their effects on solution properties such as contact angle and surface tension, factors which might influence the transport behaviour of salt solutions inside materials. Ferrocyanide is an extensively investigated crystallization modifier, and it has already been shown to have no effect on the mentioned solution properties. Furthermore, its effect on sodium chloride crystallization has already been clarified in previous research. Contrarily, not much is known about the influence of borax on water and sodium sulfate solution properties, and experimental studies on the influence of different concentrations of borax on the crystallization of sodium sulfate are lacking. To fill this gap, the research summarized in this chapter has been set up. First, the influence of different concentrations of borax on the contact angle and surface tension of water and sodium sulfate solutions has been studied. Next, the crystallization of borax from solutions at different concentrations followed by that of sodium sulfate has been investigated in experiments on droplets. Finally, the crystallization of mixed solutions of borax and sodium sulfate in glass microcapillaries has been studied.

This chapter is a slightly modified version, incorporating minor suggestions of the PhD committee, of the paper published in CrystEngComm, 2017, 19, 1106–1114.

Abstract

Borax has been identified as a possible crystallization modifier for sodium sulfate. Understanding the effect of borax on factors influencing transport and crystallization kinetics of sodium sulfate helps to clarify how this modifier might limit crystallization damage. It has been observed that the addition of borax to sodium sulfate solutions has no influence on the wetting properties (contact angle on glass, surface tension, or evaporation rate) and therefore will not influence solution transport. Additionally, the influence of borax on the crystallization kinetics of sodium sulfate was studied under controlled environmental conditions. This was carried out in mixtures in glass microcapillaries, and sequentially in droplets on glass plates. Under the here studied precipitation conditions, the addition of borax has no influence on the supersaturation ratio at the onset of crystallization, but it significantly affects the crystallization pattern of anhydrous sodium sulfate crystals (thenardite). Using RAMAN spectroscopy, two different hydrates of borax were identified after precipitation, depending on the initial concentration of the solution. Each hydrate has a different effect on the subsequent crystallization of sodium sulfate. The decahydrate polymorph of borax leads to the precipitation of hydrated sodium sulfate crystals (mirabilite) and the pentahydrate form favours the precipitation of the anhydrous sodium sulfate crystals (thenardite) with an altered crystal habit. Using X-ray diffraction, overdevelopment of the (111), (131), (222) and (153) faces of thenardite was identified. Additionally, the ratios between several peaks are reversed. These results confirm the deviation of the grown crystals of the equilibrium crystal shape of thenardite as observed with optical microscopy.

3.1 Introduction

The crystallization of salts in porous building materials is an undesired event that can lead to severe damage and eventually degradation of the material [1]. The problem is expected to worsen in the future due to climatic changes [3]. Salts can originate from e.g. sea salt spray, air pollutants or ground water penetrating via capillary absorption [4]. When salts crystallize on the outside of the material, they cause aesthetically unpleasant but harmless efflorescence. However, when they crystallize in the pores of the material as crypto-florescence, they are very harmful. Salt is damaging only if in combination with water: water dissolves the salt and transports it through the porous network of the material [16]. The wettability of the solution and material and the evaporation rate influence the solution transport. The constant interplay between advection of ions to the surface and diffusive redistribution determines the salt distribution in the material [63, 103].

Despite extensive research [2, 8, 15, 17, 72, 104], there is yet no definitive understanding of the mechanism of salt damage. The most discussed theory to describe the damage process is the theory of crystallization pressure [22, 105]. A confined crystal will exert pressure on the pore wall which depends on the supersaturation level of the solution in contact with the crystal and the confining wall. One of the most damaging salts found in buildings is sodium sulfate; its harmfulness is mainly due to its multiple hydrates with different solubilities. Under ambient conditions, the growth of two stable sodium sulfate crystal phases can be observed: the anhydrous thenardite and the decahydrated mirabilite [57, 75]. During both cooling and drying experiments, a metastable heptahydrate phase has also been observed [58, 59]. The destructive effect of sodium sulfate is usually attributed to rapid crystallization of mirabilite crystals following dissolution of anhydrous sodium sulfate. When the anhydrous crystals start to dissolve, the solution will become supersaturated with respect to the less soluble mirabilite [64, 73]. These rapidly expanding clusters of mirabilite create stresses which are in excess of the tensile strength of most building materials [19]. Besides, the damage development is related to the degree of pore filling by the salt crystals [24].

Additionally, recent publications highlight the importance of non-classical nucleation behaviour and that the level of supersaturation reached in solution has a clear effect on the pathway of nucleation [55]. Usually, the crystal polymorph with the lowest solubility is expected to crystallize first, however, several experimental results prove otherwise. This implies that thermodynamic equilibrium considerations cannot explain the dynamic process, and kinetics instead of thermodynamics dominates the process. The high interfacial free-energy barriers for the formation of hydrated sodium sulfate crystals inhibit their formation, resulting in highly supersaturated solutions, with respect to the hydrated phase, upon further evaporation [106].

Among building materials, lime-based mortars are particularly susceptible to salt damage, due to their limited mechanical strength and their bi-modal pore size distribution, with both fine and coarse pores, facts which are favourable to the development of damage. The traditional approach to mitigate damage is to alter the material properties to make them more resistant to salt decay. Examples are the use of water-repellent additives to prevent the ingress of (salt containing) water or the substitution of the lime binder with cement, in order to increase the mechanical strength. However, these solutions usually are not satisfactory due to their poor compatibility with the existing materials [4, 5].

Alternatively, it has been suggested to influence the damaging process itself, by using crystallization modifiers [9, 10, 31]. Previous research suggests the possibility of mixing these crystallization modifiers in a mortar already during its preparation [13]. This would make it possible for the modifier to be immediately activated when the salts and water enter the material. Modifiers which are to be mixed in mortar need to meet two prerequisites: first, they have to remain effective after undergoing the pH change during carbonation of a lime mortar (a fresh lime mortar has a pH of 13, and a carbonated one pH 9); second, they have to be effective at the whole pH range, because damaging salts may already enter or be present in the material before the end of the carbonation process. Possible mechanisms of modifiers which may help to reduce the damage are: (i) keeping salts dissolved in solution (inhibitors) allowing for transport to the surface during evaporation; (ii) promoting the crystallization of a specific crystal phase (promoters) at or near saturation; and (iii) changing the shape of the growing crystals (habit modifiers) [48]. Beneficial effects of habit modification can for instance be seen in the case of ferrocyanide modification of sodium chloride. Due to the presence of ferrocyanide, the shape of the crystals changes from cubic to dendritic. During drying, the salt solution will creep along the branches of the dendrites. The larger evaporation surface of the branched crystals enhances transport of the solution to the drying surface, leading to harmless efflorescence instead of harmful crypto-florescences (see for instance Gupta et al. [62]). Depending on the concentration, a modifier may exhibit a different behaviour [107].

A well-known group of modifiers for sodium sulfate are phosphonates [9, 10, 32]. Although they are effective as modifiers, they are most unsuitable to be mixed in mortar due to their pH sensitivity. Phosphonates can work either as an inhibitor or promoter depending on the pH range, and are typically active up to a pH of ~8.5. At pH levels higher than 8.5, as it occurs in mortar, the salt crystal surface becomes increasingly negative and this will lead to repulsive electrostatic forces between the ionized phosphonate molecules and the sodium sulfate which will limit the modifier effect [32]. A possible alternative to the phosphonates is borax ($Na_2B_4O_7 \cdot 10H_2O$, disodium tetraborate decahydrate), which is known to promote the precipitation of mirabilite at or near saturation [85]. Preliminary research suggests that borax can be used in a mortar, as it does not affect, for example, the carbonation process [86]. The influence of borax on sodium sulfate crystallization from solution has been studied in previous research [49, 66]. However, the influence of different concentrations of borax on the crystallization kinetics of sodium sulfate has not been investigated in detail yet.

In this paper, the interaction of borax and sodium sulfate was studied systematically. We show through thorough study of the physicochemical properties of water and sodium sulfate solutions, that the addition of borax has no influence on the wetting properties, i.e. contact angle and surface tension. However, when the impact of borax on the supersaturation level and the kinetics of growth of sodium sulfate solutions additivated with borax was assessed in glass microcapillaries during evaporation, different mechanisms of growth were observed. The consecutive crystallization of droplets of borax and sodium sulfate was studied with optical microscopy and RAMAN spectroscopy. This revealed that depending on the starting concentration of borax solution, two different crystalline phases can precipitate, each having a different effect on the subsequent sodium sulfate crystallization.

3.2 Materials and methods

3.2.1 Salt solutions and substrates

Salt solutions were prepared by adding Milli-Q grade water to borax (sodium tetraborate decahydrate, puriss., Sigma Aldrich) and/or sodium sulfate (sodium sulfate anhydrous, Ph Eur, Sigma Aldrich) and stirring until a homogeneous solution was obtained. For sodium sulfate a 1 mol kg^{-1} concentration was chosen, such that at the start of the experiments the solution was unsaturated with respect to all crystal phases, at the experimental temperature range of 20-25°C. This ensured that crystallization would not begin during the measurement of the solution properties or during preparation of the crystallization experiments. Borax concentrations ranged between 0.001-0.102 mol kg^{-1} in water (borax solubility is 0.13 mol kg^{-1} at 20°C [108]) and between 0.01-0.102 mol kg^{-1} in mixtures with 1 mol kg^{-1} sodium sulfate.

Evaporative crystallization of sodium sulfate with and without borax was studied in two series of experiments. First, in mixtures in glass microcapillaries, to simulate a single pore in a porous medium [109]. This experiment allowed for the determination of the supersaturation level at the onset of crystallization. Second, on glass slides, where sequential crystallization of borax and sodium sulfate allowed for the identification of the different crystallized phases. This simulates the situation where the modifier is already present (in the crystalline state) before interaction with the salt. In both experiments, the effect of borax addition on the kinetics of crystallization of sodium sulfate was studied.

In order to have a clean surface, the cylindrical glass capillaries with a 100 micrometre diameter were cleaned with ethanol. The Corning glass slides were cleaned in an ultrasonic bath for 10 minutes three times with acetone, ethanol and water, consecutively, and then left to dry under ambient conditions. All experiments were carried out under controlled environmental conditions, either using the set-up described by Shahidzadeh et al. [70], or in a walk-in climatic chamber (CTS). A rather high relative humidity was chosen in order to simulate values found in practice [15]. The details per experiment are summarized in Table 3.1.

3.2.2 Experimental procedures

The wetting properties of water and sodium sulfate additivated with different concentrations of borax were determined using a KRUSS apparatus (EasyDrop FM40Mk2). The surface tension was measured using the pendant drop method. This standard method is based on the balance, at the moment a droplet breaks off from a capillary of known size, between gravity and the restoring surface tension [109]. The obtained values for the surface tension are an average of 10 repetitions. The equilibrium static contact angle of 2 µL droplets deposited on glass slides was determined using imaging analysis. The contact angle is dependent on the wettability of the substrate and the surface tension of the solution [110]. The obtained contact angle is an average of 6 or more repetitions. The evaporation and crystallization in capillaries was monitored using optical microscopy (Leica DM IRB) and direct imaging by means of a digital microscope camera [109]. Following the menisci and the related volume variation in time allowed for the determination of the supersaturation level at the onset of crystallization. This method was already used in previous experiments to determine the supersaturation of sodium sulfate [70]. Here, the experiment

Table 3.1: Details of the different experiments.

	T/RH%	Substrate	Solutions [aq]
Surface tension	25.0°C ± 0.5 67 RH% ± 3[a]	-	Water 0.001, 0.005, 0.010, 0.051 and 0.102 mol kg^{-1} borax 1 mol kg^{-1} Na_2SO_4 1 mol kg^{-1} Na_2SO_4 + 0.010 mol kg^{-1} borax 1 mol kg^{-1} Na_2SO_4 + 0.051 mol kg^{-1} borax 1 mol kg^{-1} Na_2SO_4 + 0.102 mol kg^{-1} borax
Contact angle	25.0°C ± 0.5 67 RH% ± 3[a]	Corning glass slide	1 mol kg^{-1} Na_2SO_4 1 mol kg^{-1} Na_2SO_4 + 0.010 mol kg^{-1} borax 1 mol kg^{-1} Na_2SO_4 + 0.051 mol kg^{-1} borax
Capillary	23.1°C ± 0.5 65.7 RH% ± 1.8[a]	100 µm glass capillary	1 mol kg^{-1} Na_2SO_4 1 mol kg^{-1} Na_2SO_4 + 0.051 mol kg^{-1} borax
Droplet	20°C ± 0.2 65 RH% ± 1.4[b]	Corning glass slide	0.010, 0.051, 0.102 mol kg^{-1} borax 1 mol kg^{-1} Na_2SO_4 1 mol kg^{-1} Na_2SO_4 + 0.051 mol kg^{-1} borax

[a] The temperature and relative humidity were controlled, as described in Shahidzadeh et al. [70].
[b] Experiments were done in a CTS walk-in climatic chamber.

on pure sodium sulfate was replicated in order to have a reference. Then, the same experimental setup was used to determine the supersaturation for mixtures additivated with borax. Additionally, the possible effect of borax on the growth kinetics of sodium sulfate was studied. The experiment was replicated 4 times for both solutions.

Sequential crystallization of borax and sodium sulfate was studied by evaporating droplets of 25 µL. First, droplets of borax were evaporated on glass slides. Then, sodium sulfate droplets were evaporated on the glass or on the previously crystallized borax layer. During evaporation, the slides were placed in a box with a partially closed cover to reduce the draught (average air speed in the box was 0.13 m s^{-1}, measured with a Testo 435 sensor), which can influence the evaporation rate. The crystallized phases of borax and sodium sulfate were examined and identified using RAMAN spectroscopy. The crystallization pattern of sodium sulfate with and without borax was studied using optical microscopy (Zeiss Axioplan). The effect of borax on the habit of sodium sulfate crystals was additionally studied using X-ray diffraction (Bruker D8 Advance X-ray diffractometer in Debye-Scherrer geometry, with an XYZ sample stage. Cu-Kα X-rays were generated at 40 kV and 40 mA). The XRD pattern was recorded directly on the glass without any further sample preparation. Phase identification was performed using Bruker Eva 4.1 software and appropriate databases (ICDD PDF2 2011). Rietveld refinement on the sample was performed with Topas 5.0.

3.3 Results and discussion

3.3.1 Wetting properties

The characterization of the physicochemical properties of solutions is important to account for the crystallization by evaporation in droplets and capillaries. Generally, the addition of (high concentrations of) salt (ions) increases the surface tension of water. According to the Young-Laplace equation, the latter has a direct consequence on the spreading properties of the solution. As the evaporation rate of droplets is proportional to the perimeter of the droplet, this directly affects the evaporation rate which can lead to the precipitation of different polymorphs and therefore change the crystallization pattern [110-112].

The measurements of the contact angle and surface tension of water and sodium sulfate additivated with different concentrations of borax are depicted in Figures 3.1 and 3.2, respectively. The addition of borax has no distinct influence on the contact angle of sodium sulfate solution at any of the studied borax concentrations. In Figure 3.2, the horizontal lines represent the measured surface tension of pure water (71.5 mN m^{-1}) used to prepare the salt solutions and the measured surface tension of pure sodium sulfate solution at 1 mol kg^{-1} (73.9 mN m^{-1}). These values are in good agreement with those reported in the literature [71]. Upon addition of borax to water or sodium sulfate, there is only a slight increase of surface tension. These results show that the addition of small amounts of borax does not affect the physicochemical properties of the solution, and therefore the results reported here on the crystallization of sodium sulfate in the presence of borax are not due to a confinement effect at the contact line of the droplet experiments, i.e. a change in evaporation rate and contact angle [110]. Additionally, since no spreading of the droplets is observed, no effect on the dynamics of solution transport is expected.

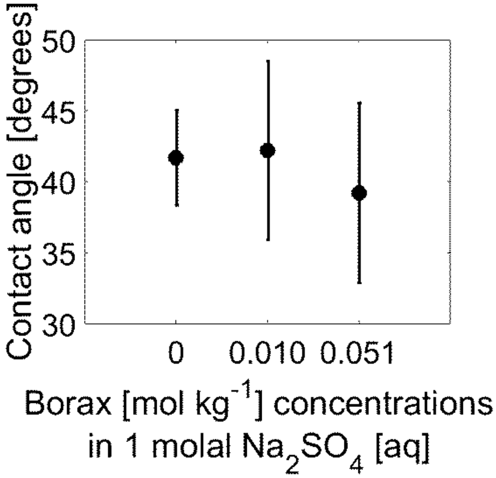

Figure 3.1: Contact angle on Corning glass slides of 2 µL droplets of 1 mol kg^{-1} sodium sulfate solution additivated with different concentrations of borax. Each point is an average of 6 or more repetitions.

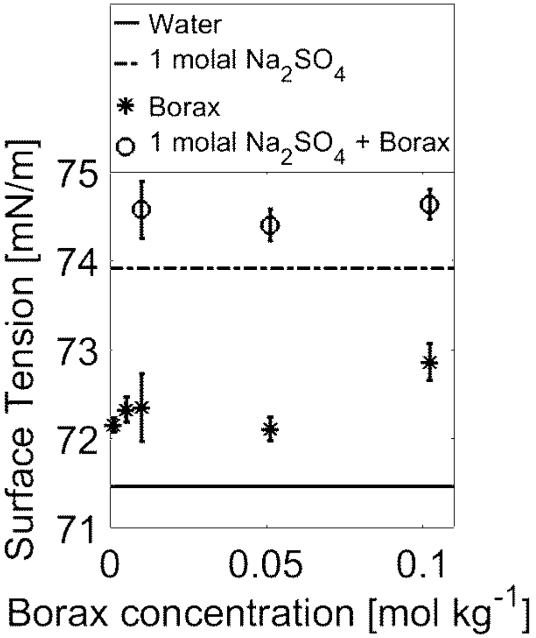

Figure 3.2: Surface tension values of borax in water or mixed with 1 mol kg^{-1} sodium sulfate in comparison with pure water and a 1 mol kg^{-1} sodium sulfate solution. Each point is an average of 10 measurements.

3.3.2 Crystallization in capillaries

Figures 3.3 and 3.4 show the precipitation and growth of the crystals within the first 300 seconds of the crystallization sequence in the capillaries. In Figure 3.3a it can be seen that, initially, phase(III) anhydrous sodium sulfate needles grow, which immediately dissolve again to form the more stable phase V prisms (Figure 3.3c). This sequence was also clearly observed in previous research [70]. In the case of the mixture with borax (Figure 3.4), crystallization of mirabilite was expected due to the promoter effect of borax reported in the literature [49]. Instead, growth of anhydrous crystals occurred (for a borax concentration of 0.051 mol kg^{-1}). The absence of a hydrate was confirmed by placing the capillary in an oven at 70°C for 3 hours, and photographing the capillary before and after. No dehydration of the crystals was observed. Interestingly, in the presence of borax, the anhydrous sodium sulfate needles and prisms do not grow sequentially, but seem to grow simultaneously from the start. Then, the needle crystals dissolve and at the end of the shown crystallization sequence, only the prisms remain (Figure 3.4c), similar to the crystallization sequence without borax (Figure 3.3c). However, when Figures 3.3c and 3.4c are compared, it is clear that at the concentration used, the addition of borax leads to an alteration of the habit of anhydrous sodium sulfate crystals.

All the evaporation experiments are done in a climatic chamber at RH 65% which is a relative humidity representative of situations found in the field (in indoor situations). Moreover, the initial evaporation rate at this fixed RH decreases even more with time during the experiments in microcapillaries. This can be clearly seen from the nonlinear behaviour of the volume change in the microcapillaries over time (Figure 3.5). In the microcapillaries, the evaporation rate is limited by diffusive vapour transport through the gas phase [60], following:

$$e = \rho_g D \frac{(c_i - c_\infty)}{\delta}$$

where ρ_g is the vapour density, D is the diffusion coefficient of water vapour through the gas, c_i and c_∞ are, respectively, the equilibrium relative humidity above the menisci and the relative humidity fixed in the climatic chamber (65%), and δ is the distance between the meniscus and the exit of the capillary. As it is clear from this equation, the evaporation rate slows down in our experiments firstly because the saturated vapour more concentrated, and secondly because δ increases in time.

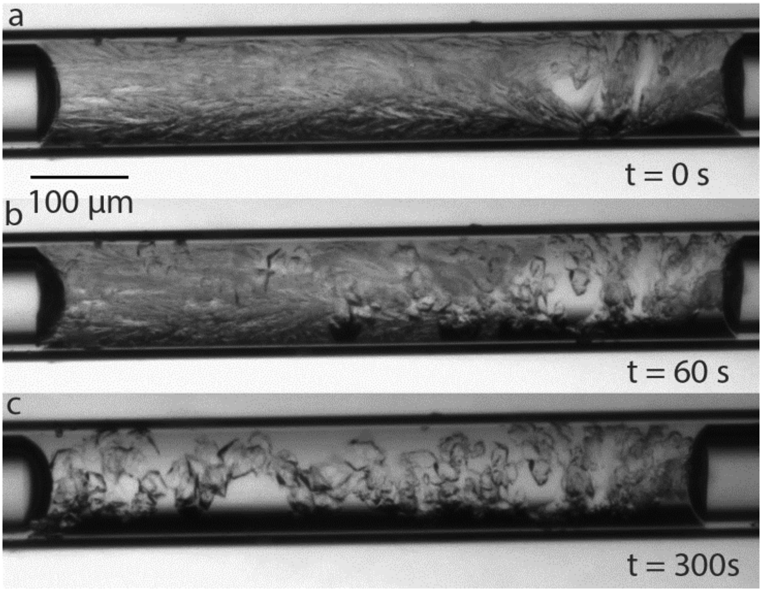

Figure 3.3: Crystallization of 1 mol kg^{-1} sodium sulfate solution in a glass capillary at the start (a) and after 60 s (b) and 300 s (c). Initially (a) anhydrous phase III needles form, which immediately dissolve to form the stable phase V prisms (c).

Figure 3.4: Crystallization of 1 mol kg^{-1} sodium sulfate solution mixed with 0.051 mol kg^{-1} borax in a glass capillary at the start (a) and after 65 (s) and 270 s (c). Both phase III and phase V anhydrous crystals form simultaneously (a). At the end of the shown sequence (c), all the needles (phase III) have dissolved. The crystal habit of phase V is altered with respect to that observed in the absence of borax (compared to Figure 3c).

The slow evaporation during the experiment leads to a very homogeneous solution. As was shown in Desarnaud et al. [60], the nucleation rate is only dependent on the supersaturation, and is negligible below the limit of supersolubility. If local concentration fluctuations would occur, reaching the supersolubility limit, crystallization would start there and consume the supersaturation. The absence of concentration fluctuations limits the possibility of local nucleation and explains why high supersaturation ratios in the whole solution can be reached.

The evaporation rate of the solution was determined by following the distance between the two menisci of the liquid in the capillary in time. As already expected on the basis of the measured solution properties, no effect on evaporation rate due to the addition of borax was observed. The distance between the menisci and the related volume was used for the determination of the supersaturation at the start of crystallization. m_0 is the initial concentration in solution (1 mol kg^{-1}) and m is the calculated concentration at the onset of crystallization. m_s is the saturation concentration of sodium sulfate phase III (4.4 mol kg^{-1} at the experimental

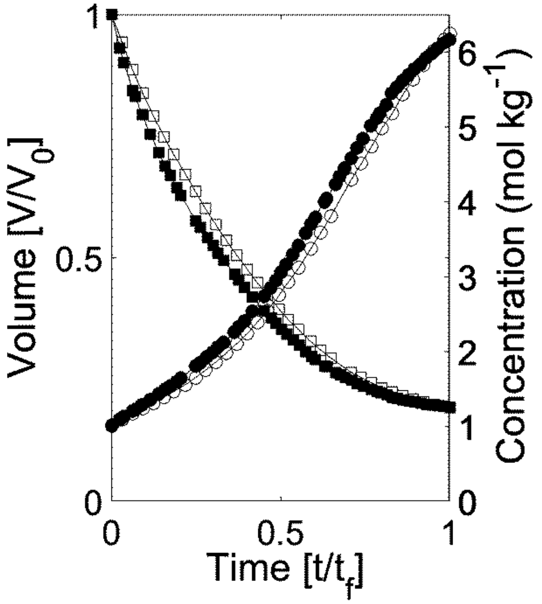

Figure 3.5: Normalized volume change and the corresponding increasing concentration during evaporation of solution in capillaries till precipitation. The squares correspond to volume and the circles to concentration. Open markers correspond to sodium sulfate while closed markers to sodium sulfate + borax.

condition of 23 °C). The supersaturation S of the solution can then be determined using:

$$S = \frac{m}{m_s}$$

The following S values were found: in the case of sodium sulfate $S = 1.25 \pm 0.13$, and for sodium sulfate with borax $S = 1.22 \pm 0.28$.

When expressed in molar values, these values correspond to S = 1.14 ± 0.2 and S = 1.13 ± 0.06, respectively, values which are in good agreement with those reported in Shahidzadeh and Desarnaud [70]. The change in volume of the solution in the capillaries and the corresponding increase in concentration are plotted in Figure 3.5 (open markers correspond to sodium sulfate, closed markers to sodium sulfate + borax). The starting concentration (diamond) and the concentrations at the onset of crystallization (circle is sodium sulfate, square is sodium sulfate + borax) are indicated in the phase diagram in Figure 3.6. The phase diagram clearly shows that in both cases the solution is heavily supersaturated with respect to mirabilite (S is 3.68 and 3.64, respectively); however, no crystallization of this phase occurred. This supports the statement that highly supersaturated solutions can be formed resulting in crystallization of the more soluble anhydrous phase instead of less soluble hydrated crystals.

3.3.3 Crystallization of droplets

The products of sequential evaporation of droplets of borax and then sodium sulfate on glass slides were studied using RAMAN spectroscopy (Renishaw InVia Raman spectrophotometer, 532nm laser). The position of the most abundant peak is given in Table 3.2 and the different salt phases were identified using literature spectra.

Crystallization of the different borax solutions resulted in two different phases of sodium tetraborate, depending on the starting concentration of solution. In the case of the highest concentration (0.102 mol kg-1), sodium tetraborate decahydrate (borax) was formed. This concentration is close to the solubility of borax (0.13 mol kg-1 at 20°C [108]). This could mean that small crystallites of borax were still present in the solution, which then acted as seed crystals for further growth of borax upon evaporation of the solution. Differently, for lower concentrations (0.010 and 0.051 mol kg-1) sodium tetraborate pentahydrate (tincalconite) crystals were formed.

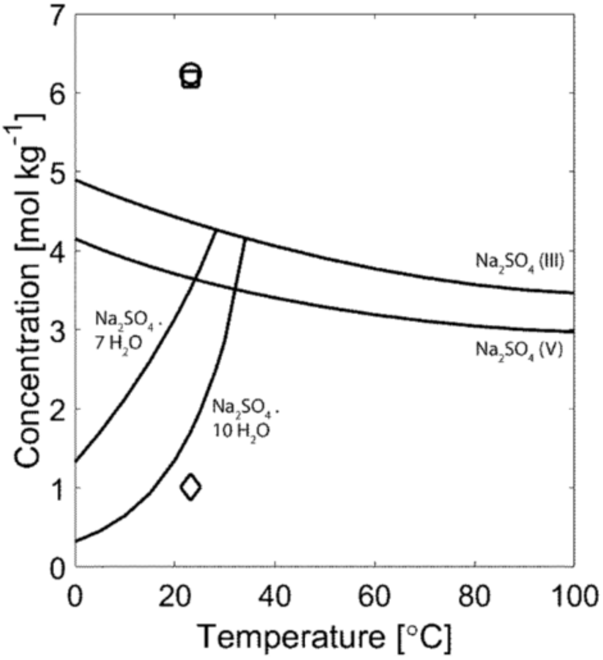

Figure 3.6. Phase diagram using the model from Steiger and Asmussen [57]. The diamond corresponds to the starting concentration in the capillary experiments. The circle (sodium sulfate) and the square (sodium sulfate + borax) correspond to an average concentration at the onset of crystallization of 4 replicas.

Table 3.2: Identification of crystal phases measured from evaporative crystallization from droplets, using RAMAN spectroscopy.

	Peak position (cm^{-1})	
Compound	**Measured (± 0.9)**	**Literature (phase)**
Borax 0.010 mol kg^{-1}	577.7	577.20 (tincalconite)[a]
Borax 0.051 mol kg^{-1}	577.7	577.20 (tincalconite)[a]
Borax 0.102 mol kg^{-1}	574.0	573.96 (borax)[a]
Na_2SO_4 (pure)	991.7	993.20 (thenardite)[b]
Na_2SO_4 (on 0.051 mol kg^{-1} borate)	991.7	993.20 (thenardite)[b]
Na_2SO_4 (mix with 0.051 mol kg^{-1} borate)	992.6	993.20 (thenardite)[b]

[a] Phase identification according to Lafuente et al. [113].

[b] Phase identification according to Linnow et al. [114].

Although it is known that, under the environmental conditions used, tincalconite and borax could convert to one another [115], it is not known how and if this behaviour can be related to the starting concentration of the borax solution.

Figure 3.7 shows different crystallized droplets of sodium sulfate. Figure 3.7A shows sodium sulfate crystals grown from a pure solution. These crystals were identified as the anhydrous phase V (thenardite). Sodium sulfate crystals grown on top of the tetraborate layers resulted in different sodium sulfate phases depending on the type of tetraborate phase. In the case of borax, hydrated crystals of sodium sulfate were formed (Figure 3.7B), which immediately dehydrated, leaving the characteristic opaque/white crystals, previously identified as the dehydration product [75]. This hydrate is most likely mirabilite, due to its lattice similarity to borax [49]. The hydrated crystals could not be identified using RAMAN, because it was not possible to control temperature and relative humidity in the set-up used during measurements. Therefore, as soon as the hydrated crystals were placed in the RAMAN spectrometer, they started to dehydrate, resulting in the identification of thenardite. Figure 3.7C shows crystals of sodium sulfate grown on top of a previous layer of tincalconite. These crystals gave the same indication as the ones without borax, and were thus also identified as the anhydrous sodium sulfate phase V (thenardite). However, the crystals show a clearly altered crystallization habit compared to the anhydrous sodium sulfate crystals grown without borax, which display the equilibrium crystal shape. Figure 3.7D shows sodium sulfate crystals grown from a mixture of sodium sulfate and 0.051 mol kg^{-1} borax. These crystals were identified as anhydrous sodium sulfate phase V crystals (thenardite) as well.

When comparing sodium sulfate grown in the presence of 0.051 mol kg^{-1} tetraborate, either mixed in solution (Figure 3.4 or Figure 3.7D) or in the crystalline phase (Figure 3.7C), a similarity in crystal habit can be observed. Apparently, for the tetraborate to be effective as a habit modifier, it is enough that it is present in solution, not necessarily in the crystalline state. During the evaporation experiment in the capillaries, the set-up was continuously monitored and no crystals other than needles or needles/prisms combined (thenardite) were observed. We cannot completely exclude that very small crystallites of a borax phase, not detectable with the technique used, might be present in solution prior to thenardite crystallization. It is important to note that both the capillary and

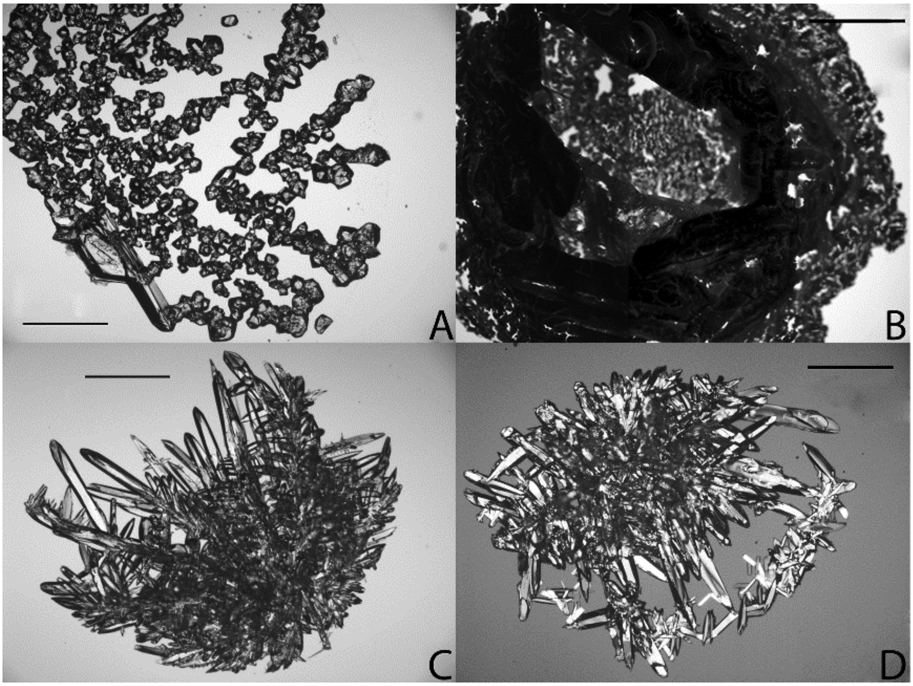

Figure 3.7: A: Sodium sulfate crystals without tetraborate, displaying the characteristic prisms of anhydrous thenardite. B: Dehydrated sodium sulfate crystals (mirabilite) grown on top of sodium tetraborate decahydrate (borax). C: Thenardite crystals precipitated by evaporation of sodium sulfate on top of sodium tetraborate pentahydrate (tincalconite). D: Thenardite crystals grown from a mixture of 0.051 mol kg^{-1} borax and 1 mol kg^{-1} sodium sulfate. Scale bars: 500 µm.

the droplet experiments deal with a first event of crystallization. The effect of tetraborate on repeated dissolution/crystallization cycles is unknown yet and will be the object of future research.

In addition to visual inspection of the crystals with optical microscopy, the thenardite crystals from Figure 3.7C were examined using X-ray diffraction. This method was applied as an indirect way to observe preferential orientation of the crystals in order to further study the habit change and determine which faces are overdeveloped. In Figure 3.8, the measured pattern is compared to the literature pattern in order to assign indices to the peaks. The peaks at 25.9 and 39.9 2Theta values belong to the (3 -1 -2) and (4 -1 5) planes of the underlying tincalconite, respectively, and were therefore not indexed. Peak splitting in the measured pattern is due to the fact that Cu X-rays are generated at two different wavelengths: Cu-Kalpha1:

1.54056 angstrom and Cu-Kalpha2: 1.54439 angstrom. This effect becomes more pronounced at higher 2Theta values. The literature pattern is predicted using only Cu-Kalpha1 = 1.54056 angstrom. To determine relative counts, the value of the 113 peak in the predicted pattern was set to 1. The measured pattern shows that there is an overdevelopment of the (111), (131), (222) and (153) faces of thenardite. Additionally, the ratios between several peaks, e.g. 111/113, 111/222 and 222/220, are reversed. These results confirm the deviation of the grown crystals of the equilibrium crystal shape of thenardite, as was already observed with optical microscopy. In summary, it can be stated that, at the concentration used in this study, borax acts as a habit modifier of thenardite.

In Figure 3.9, the equilibrium morphology of thenardite and an altered morphology in the presence of sodium tetraborate are visualized. To model the altered morphology of thenardite, the distance to the centre of the crystal of the (153) face was decreased, considering that this peak showed the largest alteration in the measured XRD pattern. As can be seen in Figure 3.9E and F, the shape of the altered crystal displays more of a needle shape than prismatic, as seen in the equilibrium crystal. Although tincalconite and thenardite are found together in nature (see e.g. Pabst and Sawyer [116]), to our knowledge, in the literature there is no mention about a possible interaction mechanism between them. It is clear that the presence of tetraborate has a kinetic effect on the crystallization process, altering the

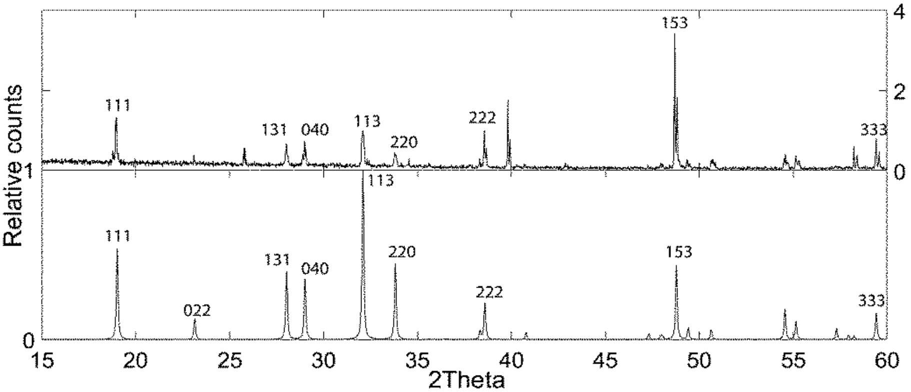

Figure 3.8: Top: Measured XRD pattern of the crystals shown in Figure 3.7C. The crystals were identified as thenardite, according to PDF 01-07402936. Bottom: Pattern from PDF 01-07402936 used for peak assignation. The measured pattern shows an overdevelopment of the {153} face.

growth of the crystal faces [117]. Considering that the altered crystal shape of thenardite is dominated by the {153} planes in the presence of tetraborate, this could indicate that the tetraborate ions incorporate on active sites on this crystal face. Tetraborate ions would hinder the growth of this crystal face, making it become more important for the final morphology of the grown crystals. A similar mechanism was already observed for the interaction between borax and epsomite [49]. If and how tetraborate adsorbs on thenardite might be determined using computer simulations (see e.g. Jiang et al. [107]). However, this is beyond the scope of the current research.

3.4 Conclusions

The contact angle, surface tension and evaporation rate of sodium sulfate solutions additivated with different borax concentrations were measured. The results showed that borax addition in low concentrations, as those tested in this research has no impact on these factors, which influence wetting and solution transport. Additionally, two types of experiments were carried out to study the crystallization kinetics and crystallization pattern of

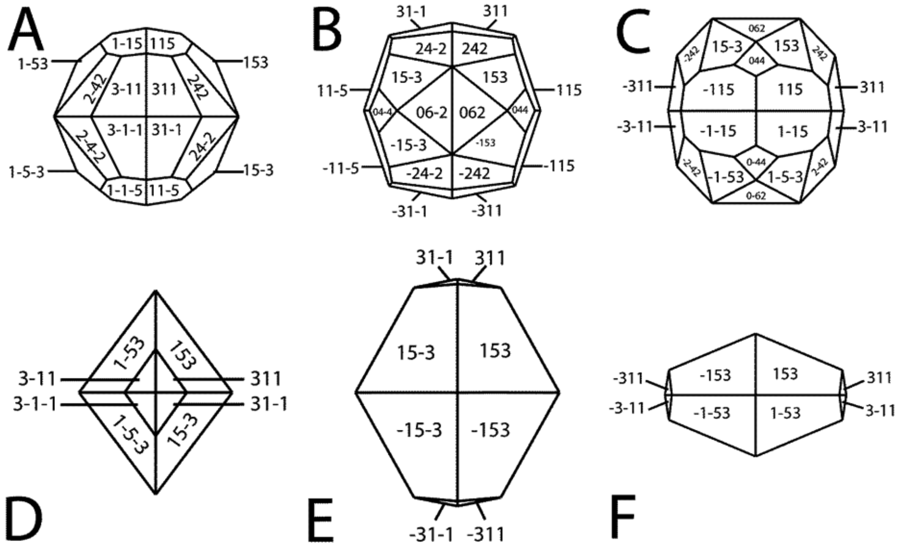

Figure 3.9: Crystal structures drawn using the software VESTA [118]. Top A-C: Equilibrium shape of thenardite using the lattice parameters of PDF 01-07402936, visualized along the a, b or c axis, respectively. Bottom D-F: Schematic of the overdeveloped {153} crystal shape of thenardite, as observed in the presence of sodium tetraborate, visualized along the a, b or c axis, respectively.

sodium sulfate. First, the evaporation of sodium sulfate solutions without and of solutions additivated with borax was studied in capillaries. The volume change and the associated concentration increase were determined, which allowed for the calculation of the supersaturation ratio at the onset of crystallization. Solutions without and solutions additivated with borax both resulted in anhydrous sodium sulfate crystals, at similar levels of supersaturation. This indicates that in our system there is no inhibitor or promoter effect of borax at the concentrations used. However, a clear alteration in the crystal habit of the sodium sulfate crystals was observed in the presence of borax. Second, in order to identify the different crystallizing phases, crystallization of borax and sodium sulfate was studied in sequence in droplets. Evaporation of borax solutions under controlled environmental conditions resulted in the crystallization of two different sodium tetraborate hydrates depending on the starting concentration of borax: a starting concentration of 0.102 mol kg^{-1} results in the decahydrate (borax), whereas a starting concentration of 0.010/0.051 mol kg^{-1} results in the pentahydrate (tincalconite).

Sodium sulfate crystallization on top of borax resulted in crystallization of hydrated sodium sulfate crystals (mirabilite), whereas crystallization of sodium sulfate on top of tincalconite resulted in anhydrous sodium sulfate crystals (thenardite). Apparently, mirabilite is only grown in the presence of borax crystals, and not with tincalconite, as a consequence of the similarity in crystal lattice structure. The thenardite crystals grown in the presence of tincalconite showed an altered crystallization pattern compared to thenardite crystals displaying the equilibrium crystal shape grown from a pure solution. The altered crystal habit in the droplets resembled the altered habit seen in the capillaries. Using X-ray diffraction, it was identified that the altered crystal habit is due to an overdevelopment of the (111), (131), (222) and (153) faces and a reversal of the intensity ratios between several of these peaks. These results confirm the deviation of the grown crystals of the equilibrium crystal shape of thenardite as observed with optical microscopy.

Acknowledgements

The authors would like to thank Johan Bijleveld for his help on the RAMAN spectroscopy measurement. The authors also wish to thank Willem Duvalois, Timo Nijland and Rene de Gelder for their help with the measurement and analysis of the X-ray diffraction pattern. Finally, we would like to acknowledge the Dutch IOP program on Self-Healing Materials for funding (Grant number SHM012018).

4

Characterization of lime mortar additivated with crystallization modifiers

The previous chapter showed that the selected modifiers (borax and ferrocyanide) do not alter water and salt solution transport but do affect salt crystallization in bulk solution. However, before assessing the salt crystallization resistance of mortar additivated with modifiers, it is imperative to study whether: (i) modifiers are still active in mortar after going through the carbonation process of the lime, and (ii) if adding modifiers to mortar leads to any unwanted changes in fresh and hardened mortar properties, possibly limiting their application in restoration or renovation works. In this research, the first aspect is only studied for borax, since it is known from literature that ferrocyanide is still effective after carbonation of the mortar. Additionally, a suitable concentration of the modifiers in the mortar was determined in this step. To clarify the effect of modifiers on the mortar properties, additivated and reference mortars were prepared and relevant fresh and hardened mortar properties were assessed and compared.

This chapter is a slightly modified version, incorporating minor suggestions of the PhD committee, of the paper published in the International Journal of Architectural Heritage, 2018, 12 (5), 849-858.

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.

4.1 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 [7] 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 [119].

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 [25, 26]. 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) [48]. This approach has already shown promising results; see e.g. [9, 10, 31]. 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 [12, 31, 62**,** 120]. A new application, and the focus of this study, consists in mixing the crystallization modifiers directly into the mortar during production [13, 121]. 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 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 [32], 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. [12, 50, 78]). Its mechanism of modification has been recently fully clarified by Bode et al. [79]. 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 [122]. 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 [13].

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 [9, 10, 32]. 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 ($Na_2B_4O_7 \cdot 10H_2O$) [49, 86]. Borax is supposed to work as promoter of mirabilite in (bulk) solution [49, 66, 85], also at highly alkaline pH values, as those present in fresh mortar [86]. 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 the crystal shape dominated by the {153} planes [87].

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 [86], 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 [49]. 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 4.3.1.2).

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. [123, 124]). 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 4.3.2).

4.2 Materials and methods

4.2.1 Materials

4.2.1.1 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 [125]) 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.

4.2.1.2 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 [78], the second is a modifier of sodium sulfate crystallization [49, 87]. 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 [13]. 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. [13], 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 resistance 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 [87]. Based on these results, two concentrations of borax were used to be mixed in the lime paste specimens (see section 4.3.1.2): 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.

4.2.1.3 Specimen types and preparation

For this research the following types of specimens were prepared (see Table 4.1):

(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.

Table 4.1: 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)

Besides, tap water may introduce small quantities of other ions, which may complicate the interpretation of the results. For the square specimens water content was 48.4 ± 0.5 wt%, for the round specimens 46.1 ± 1 wt%. 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 a Styrofoam mould, and compacted using a vibrating table according to EN196-1 [125].
- 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 [126]. 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/65% RH/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 4.2.2.3). 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 $mol \cdot L^{-1}$ 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 4.2.2.2).

4.2.2 Methods

4.2.2.1 Mortar flow test

The flow of the mortar was measured with a standard flow table test (EN1015-3 [127]). 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 4.2.

4.2.2.2 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. 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.

4.2.2.3 PXRD study

The carbonation rate of square lime paste specimens was assessed by PXRD. At defined time intervals, specimens were removed from their container, 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 ($\lambda = 1.5405$ 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 [128]. 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

Table 4.2: Properties of the 1:3 lime:sand fresh mortar mixtures.

Specimen type	Modifier content With respect to lime	With respect to total dry mortar weight	Flow table value	Water to lime ratio (w/w)
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

error of ± 1.68%. Subsequently, the grinded lime pastes were measured and their ratio of calcium hydroxide and calcite were determined using the same model.

4.2.2.4 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 [129].

4.2.2.5 Absorption and drying test

The capillary water absorption of the mortar with and without modifiers was determined according to EN1015-18 [130]. 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.

4.2.2.6 Measurements of the flexural and compressive strength

The flexural and compressive strength of the mortar was determined according to EN1015-11 [131] (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.

4.3 Results and discussion

4.3.1 Lime paste specimens characterization

4.3.1.1 Carbonation rate

The carbonation rate of the lime paste specimens (reference, with mixed-in ferrocyanide and with mixed-in borax) is shown in Figure 4.1. 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 4.1. 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.

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 [132]. 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).

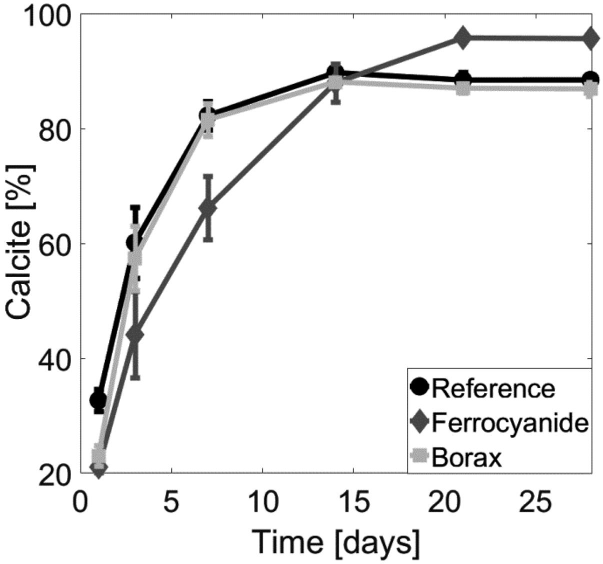

Figure 4.1: Carbonation rate determined by PXRD.

4.3.1.2 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 4.2. 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 4.2A) or with (Figures 4.2B/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 4.2B) and the sample in which borax has been added after carbonation of the lime (Figure 4.2C) 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 [121].

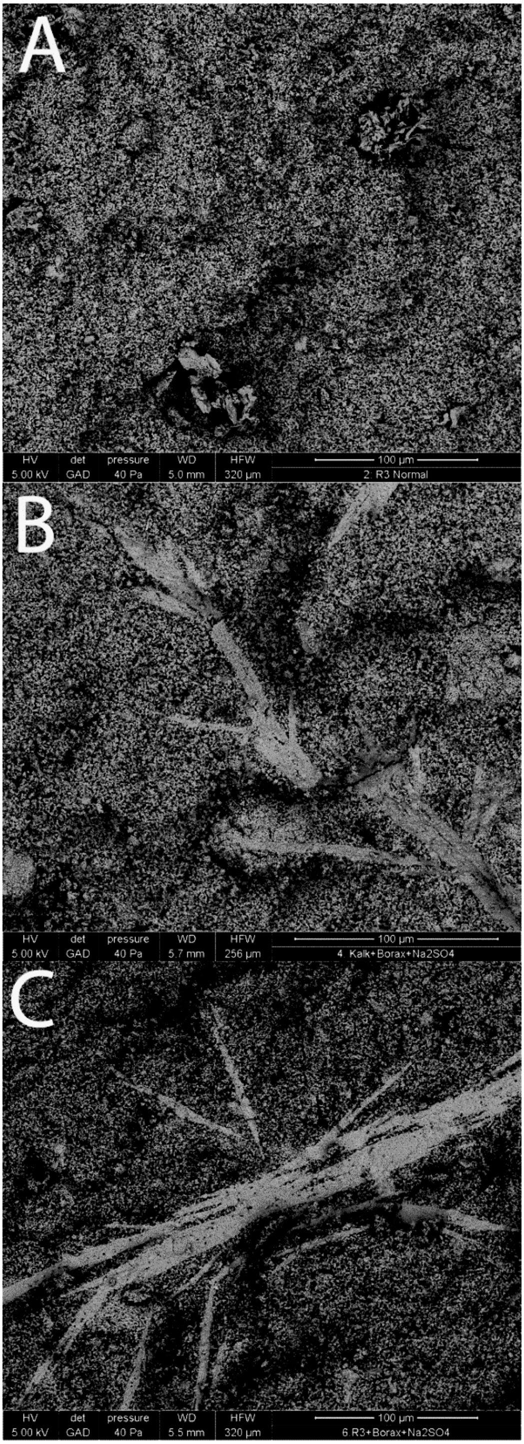

Figure 4.2: Figures reproduced with permission, see reference [121], Figures 2A, B & C, page 77.

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.

4.3.2 Mortar characterization

4.3.2.1 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 4.3 (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 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 reference 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.

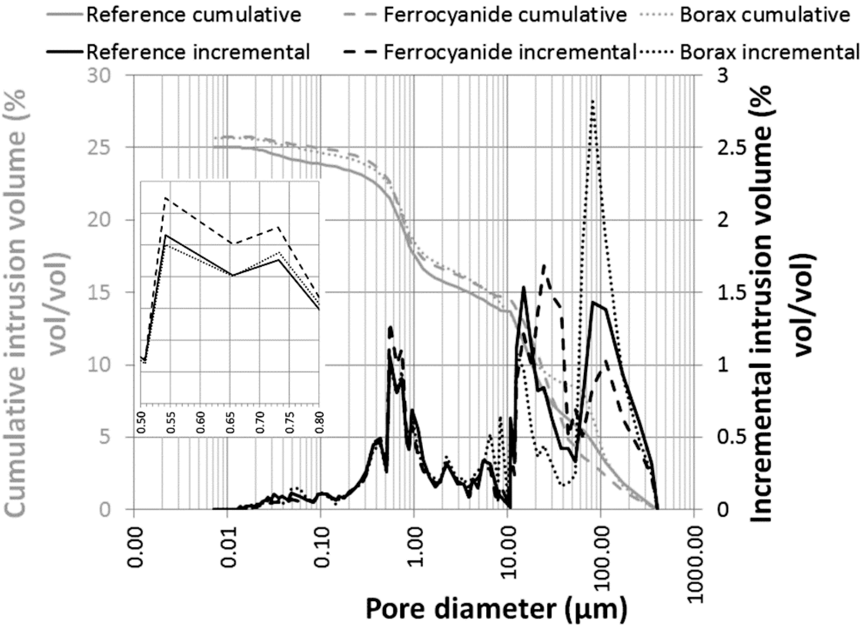

Figure 4.3: Cumulative and incremental pore size distributions measured with Mercury Intrusion Porosimetry (MIP). The insert shows a zoom of the incremental volume between 0.5 and 0.8 µm.

The open porosity and the density of the specimens as determined by immersion in water are reported in Table 4.3. 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).

4.3.2.2 Absorption and drying behaviour

The capillary water absorption curves of mortar specimens with and without modifiers are given in Figure 4.4. The calculated WAC values are given in Table 4.3.

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.

Table 4.3: Hardened mortar properties of the different 1:3 lime:sand mortar mixtures.

Property	**Method**	**Reference**	**Ferro-cyanide**	**Borax**
WAC [kg/m^{2}h$^{1/2}$]	Capillary rise	8.05	7.62	7.84
Density [kg/m^3]	Saturation at atm pressure	1943	1964	1933
Open porosity (%V/V)		26.7 ± 0.19	25.9 ± 0.24	27.1 ± 0.06
Bulk density [g/ml]	Mercury Intrusion Porosimetry	1.977	1.971	1.961
Open porosity (%V/V)		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

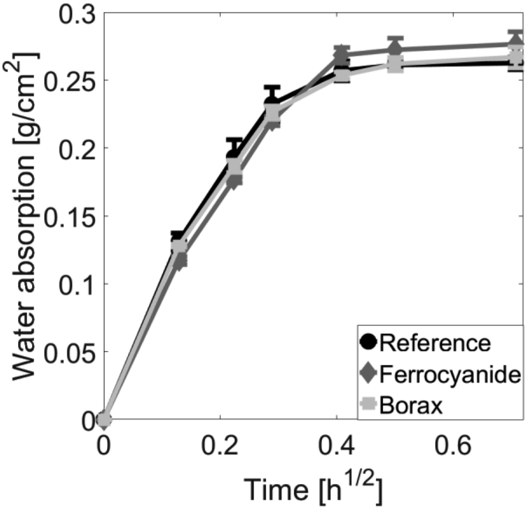

Figure 4.4: Capillary water absorption in time.

The drying curves are given in Figure 4.5. 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.

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.

4.3.2.3 Flexural and compressive strength

The flexural and compressive strength of the mortars with and without modifiers are given in Table 4.3. 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.

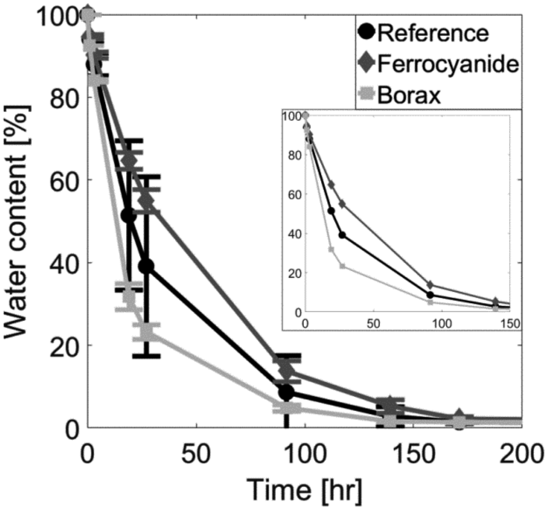

Figure 4.5: Water content in the specimens during drying at 50RH%, 20°C. The inset shows drying during the first 150 hr without error bars for clarification.

4.4 Conclusions

In this work, 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? and (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 resistance towards salt damage of mortars additivated with these modifiers.

Acknowledgments

The authors would like to thank Bert Kerk for the measurements of the flexural and compressive strength, Arjan Thijssen for the measurement of the MIP, and Hans Dalderop for his help with the PXRD.

Funding

This work was supported by the Dutch IOP program on Self-Healing Materials [Grant number SHM012018].

5

Effect of mixed in crystallization modifiers on the resistance of lime mortar against NaCl and Na_2SO_4 crystallization

The previous chapters resulted in the identification of suitable crystallization modifiers to be mixed in lime-based mortars and hypotheses were formulated on how these modifiers can limit crystallization damage in porous materials. Next, experiments in bulk solutions resulted in suitable concentrations to be used in the mortars. Finally, it was shown that the crystallization modifiers still work when mixed in a mortar and going through the carbonation process of the lime, and do not alter any fresh or hardened mortar properties that might limit their application. This chapter explores the main question in this research, i.e. it assesses the ability of modifiers to improve the resistance of lime-based mortar to salt crystallization damage. The salt crystallization resistance of additivated mortars is assessed and its improvement was confirmed at laboratory scale, by subjecting additivated mortar and reference mortar specimens to an accelerated salt crystallization test.

This chapter is a slightly modified version, incorporating minor suggestions of the PhD committee, of the paper published in Construction and Building Materials, 2019, 194, 62-70.

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 photographical 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 resistance with respect to salt crystallization damage. Both modifiers altered the growth morphology of the salt crystals inside the pores of the mortars.

5.1 Introduction

Crystallization of soluble salts is a common cause of severe deterioration of building materials (see e.g. [1, 52]). 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 [22, 105]. 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 [7].

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 [25]. 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. [9, 12, 31, 133]]. 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 [86, 97]. 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 [87]. 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 cryptoflorescence [134].

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.

5.2 Materials and methods

5.2.1 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 [125]), 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 [126]. 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 [97]) 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 had sufficient strength. 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, as determined by weight. Subsequently, the mortar specimens were artificially carbonated at 20 °C/65 RH%/1% CO$_2$ 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.

5.2.2 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 [97]; selected results are given in Table 5.1. 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 5.1).

Table 5.1: Selected mortar properties of the different 1:3 lime:sand mortar mixtures. Previously reported in Ref. [97].

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 [127]	170 mm	161 mm	161 mm
WAC $[kg/m^2h^{1/2}]$	3	Capillary rise	EN1015-18 [130]	8.05 ± 0.358	7.62 ± 0.097	7.84 ± 0.148
Density $[kg/m^3]$	3	Saturation at atm pressure	[129]	1943 ± 4.6	1964 ± 6.0	1933 ± 1.3
Open porosity (%V/V)				26.7 ± 0.19	25.9 ± 0.24	27.1 ± 0.06
Bulk density [g/ml]	2	Mercury Intrusion Porosimetry	-	1.977 ± 0.005	1.971 ± 0.006	1.961 ± 0.004
Open porosity (%V/V)				25.1 ± 0.11	25.4 ± 0.36	25.1 ± 0.55
Tensile strength (N/mm^2)	5	-	EN1015-11 [131]	0.79 ± 0.11	0.85 ± 0.03	0.92 ± 0.11
Compressive strength (N/mm^2)	10	-	EN1015-11 [131]	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.

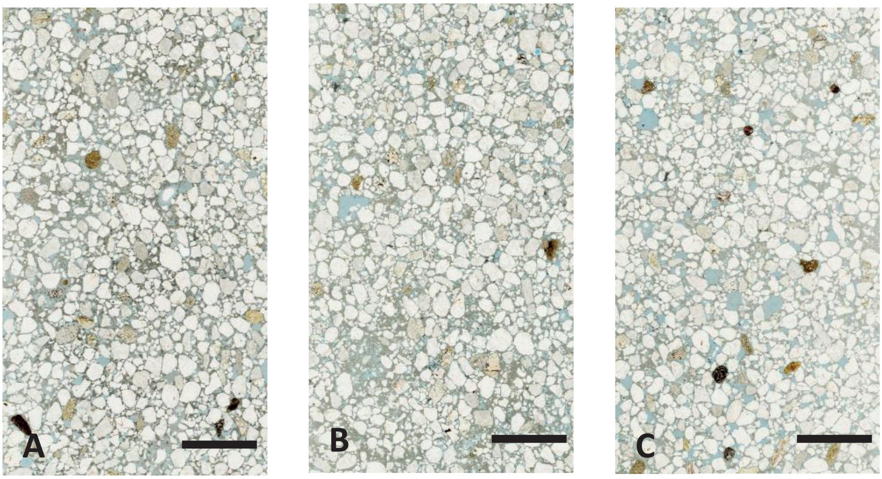

Figure 5.1: Thin sections showing the mortar structure. A: reference, B: with ferrocyanide, C: with borax. The black scale bar equals 1 cm.

5.2.3 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 5.2. This procedure is the result of the work of the authors towards an effective and reliable salt crystallization test [135]. It is an adaptation of the RILEM MS A.1 procedure [101], further modified in international research (e.g. [102]) and in previous work by the authors [18]. 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 of sodium chloride. Recrystallization of sodium sulfate only occurred after the wetting step (day 21). 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 1 wt% of sodium sulfate (anhydrous) or 2 wt% 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 5.2), 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

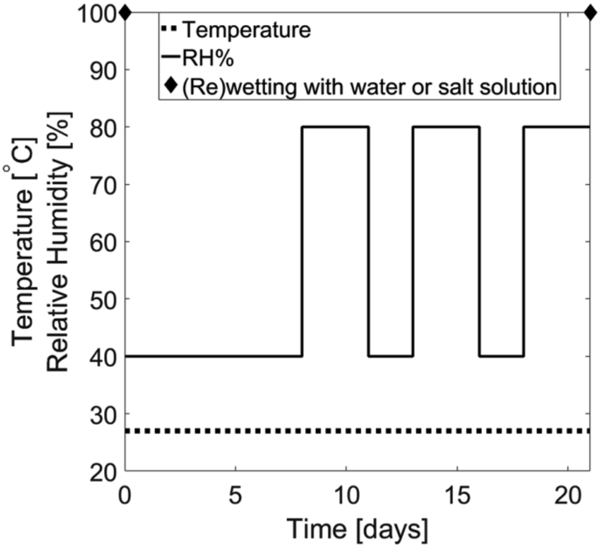

Figure 5.2: Temperature and RH cycles used in the accelerated salt weathering test. This entire cycle was repeated 5 times (in total 105 days). The diamonds correspond to wetting by capillarity at the start (day 0) or after each 3-week cycle outside the climatic chamber at 22.9°C ± 0.3, 29.1 RH% ± 2.4. 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.

photographed again before starting a new cycle.

The brushed off debris was separated from the salt by dissolution and filtration; this way, the salt and actual material loss could be distinguished and quantified. After finishing the complete test, one specimen of each series was desalinated by immersion in demineralized water, in order to assess potential caking effects of the salts (i.e. salts which crystallize between loose grains and hold them together). The water used during desalination of the ferrocyanide and borax additivated specimens was analysed with ICP-OES or ICP-MS (Inductive Coupled Plasma with Optical Emission or Mass Spectrometry) to determine the amount of modifier still present in the specimen after five crystallization cycles.

A thin section and polished chip were prepared with kerosene (to avoid dissolution of the salts) from one specimen of each series, with the aim of studying the salt distribution after the test and the habit of the crystallized salts inside the pores. However, no salt could be identified in the prepared specimens, probably due to the fact that the salt content after the crystallization test was really low (see section Results and discussion). Therefore, additional mortar specimens (also prepared in the lab 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 (1 wt% Na_2SO_4 or 2 wt% 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).

5.3 Results and discussion

5.3.1 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 5.3 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 5.4 and 5.5 for specimens with sodium chloride and sodium sulfate, respectively.

Figure 5.3A 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 [18]. As it can be observed in Figure 5.4, the severity of the damage, quantified as amount of material loss, was similar in each cycle, and seems not to depend on the total salt content present in the specimen.

Figure 5.3B shows the surface of a mortar additivated with ferrocyanide at the end of the crystallization test. Differently from 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 5.3B: 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.

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 5.2) during re-wetting [64, 73]. 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

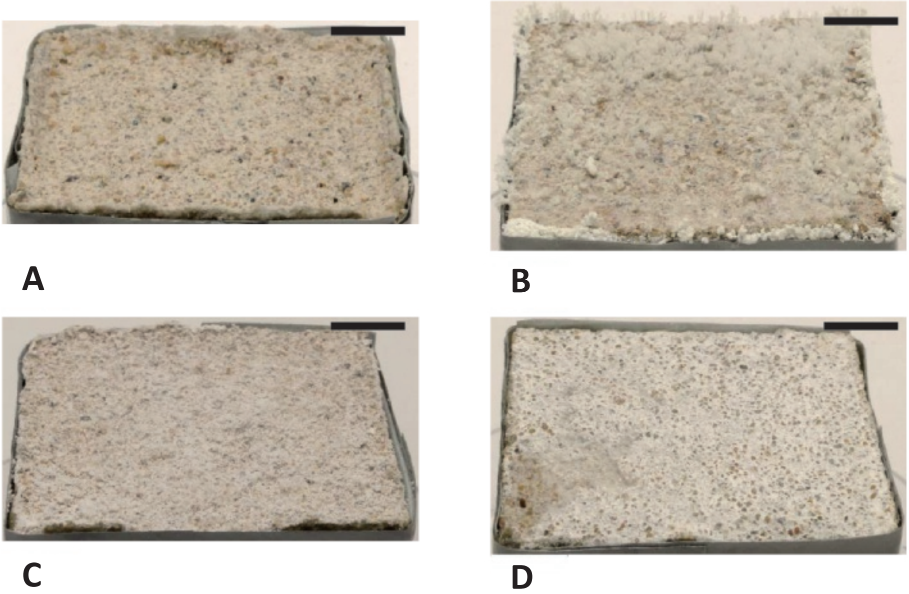

Figure 5.3: Reference (A, C) and additivated (B, D) specimens at the end of the 5th cycle (105 days, ~ 15 minutes after rewetting and brushing). A and B show the surfaces of the reference and ferrocyanide additivated mortars contaminated with sodium chloride, respectively. The reference shows sanding 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. The black scale bar equals 1 cm.

layer. As can be seen in Figure 5.5, 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 5.3C 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.

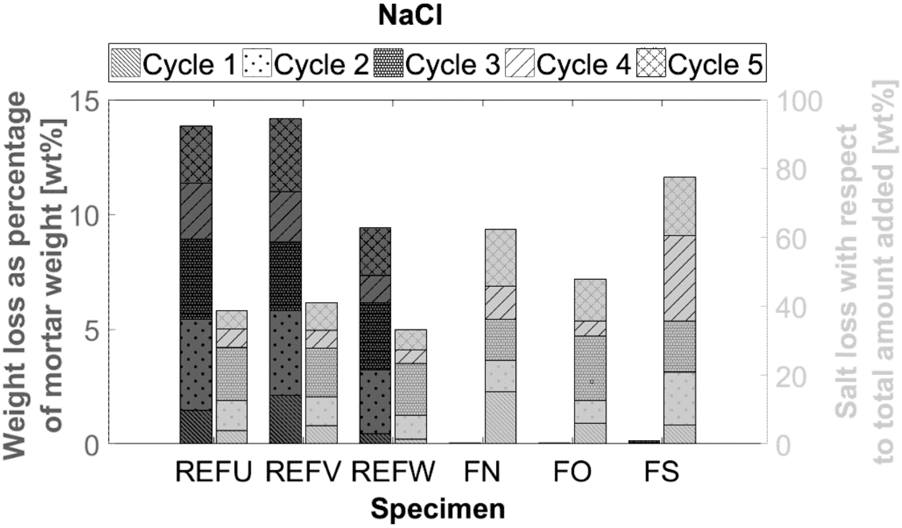

Figure 5.4: Material (dark grey) and salt (light grey) loss for the mortars contaminated with sodium chloride per cycle of the crystallization test. The material loss is given as a percentage of the total mortar weight. The salt loss is given as a percentage of the total amount of salt added after the two contaminations with salt solution. REFU, REFV and REFW correspond to reference specimens. FN, FO and FS correspond to ferrocyanide-additivated specimens.

One specimen for each mortar/salt combination (REFV, FN, REFR and BO) was desalinated after the 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 1 wt% and 10 wt% 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.

5.3.2 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

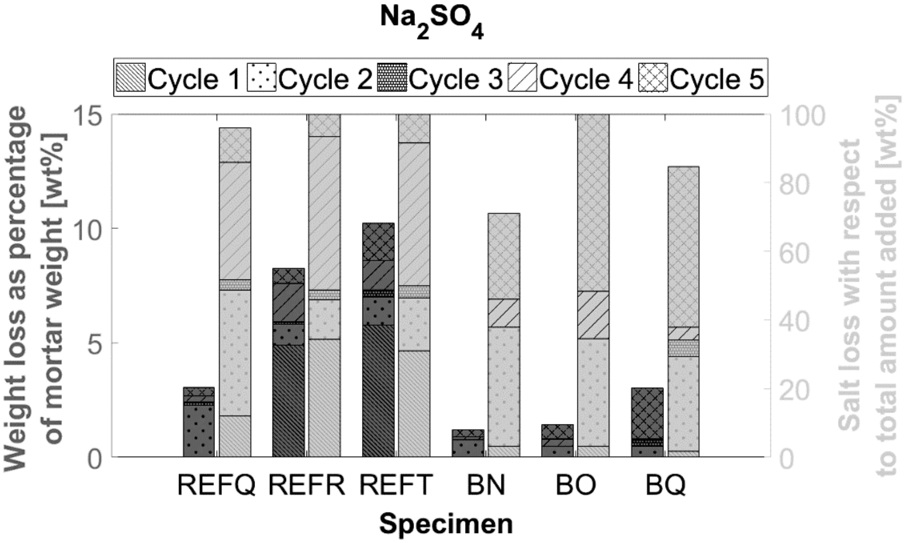

Figure 5.5: Material (dark grey) and salt (light grey) loss for the mortars contaminated with sodium sulfate per cycle of the crystallization test. The material loss is given as a percentage of the total mortar weight. The salt loss is given as a percentage of the total amount of salt added after the two contaminations with salt solution. REFQ, REFR and REFT correspond to reference specimens. BN, BO and BQ correspond to borax-additivated specimens.

described in the salt crystallization procedure section, were studied using Scanning Electron Microscopy (SEM).

Figure 5.6 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 5.6A 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 5.6C and D). These results confirm those reported earlier by the authors and other researchers (see e.g. [12, 13, 94]).

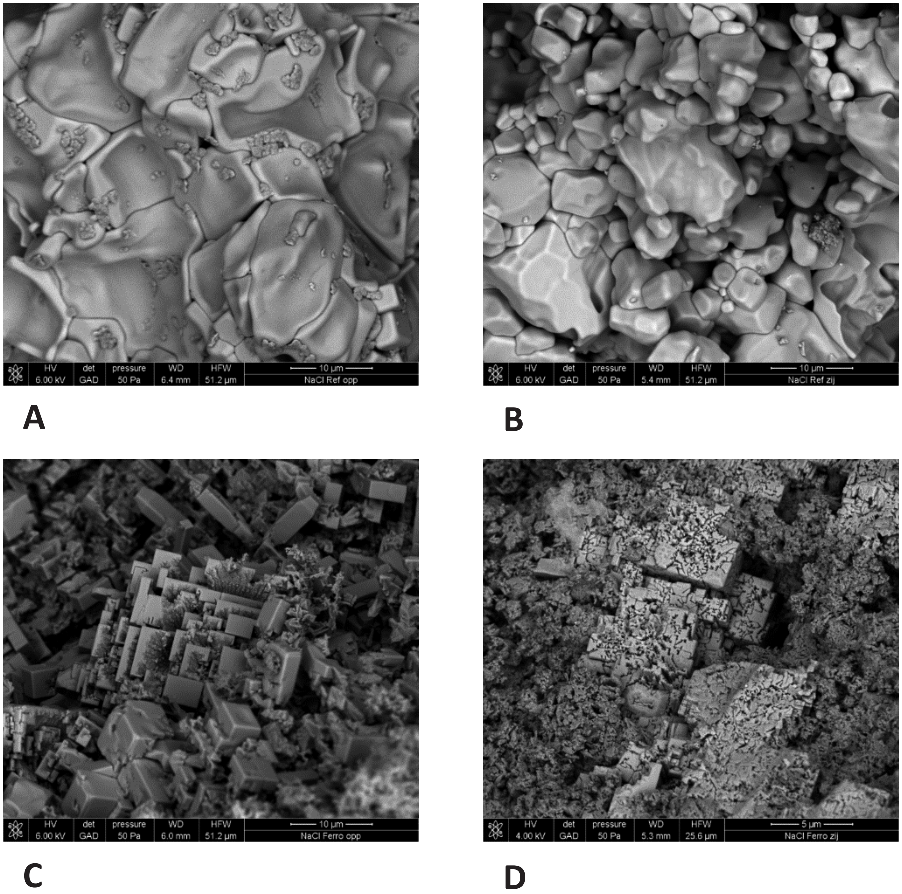

Figure 5.6: SEM images of mortar specimens contaminated with NaCl. A and B show the surface and cross section of the reference specimen, respectively. C and D show the surface and cross section of the ferrocyanide specimen, respectively. In both A and B the equilibrium cubic habit of NaCl can be observed. For C and D the habit is clearly different due to the influence of the ferrocyanide.

Figure 5.7 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 [97]. 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 5.8): the crystals

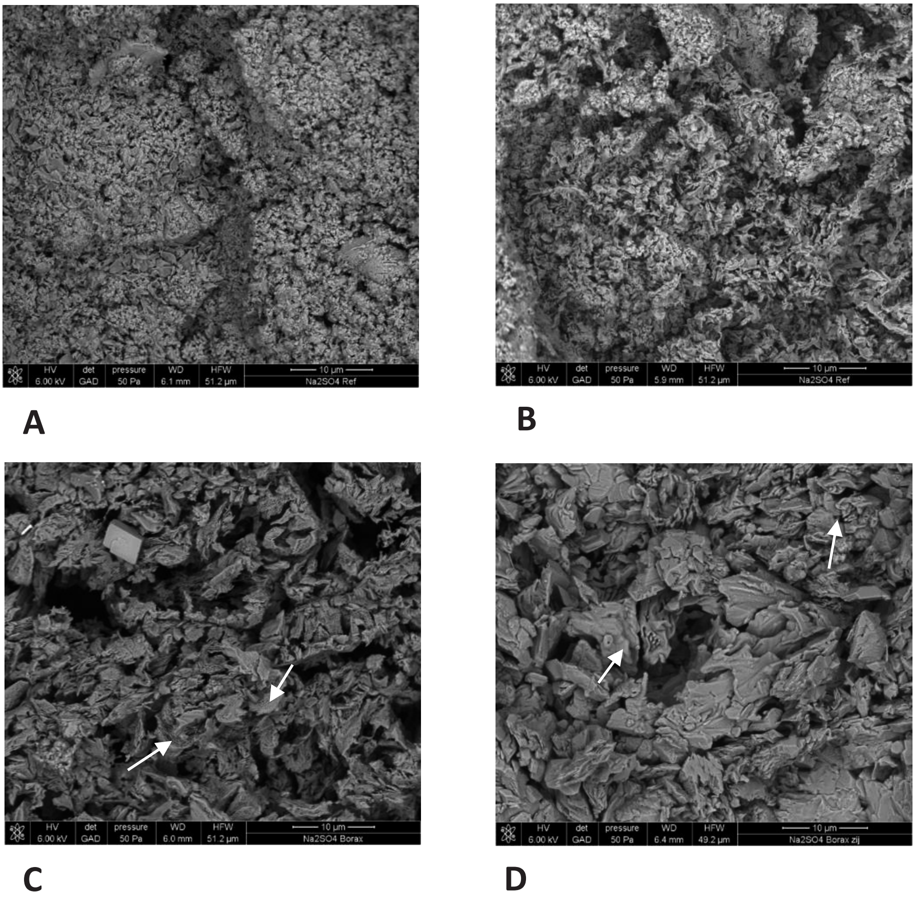

Figure 5.7: SEM images of mortar specimens contaminated with Na_2SO_4. A and B show the surface and cross section of the reference specimen, respectively. C and D show the surface and cross section of the borax specimen, respectively. Without borax the sodium sulfate crystals display a bulky habit and 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).

growing in the reference specimen (Figure 5.8A) are individual, irregular crystals with a dense structure, whereas those present in the additivated specimen (Figure 5.8B) 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

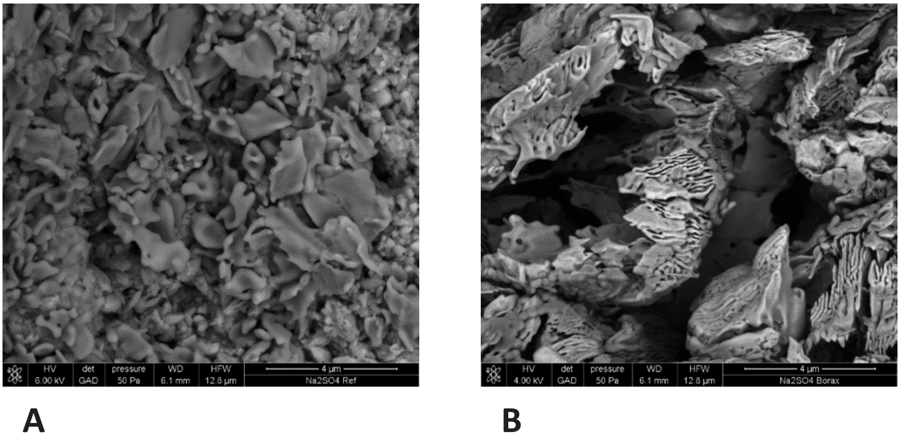

Figure 5.8: SEM images of mortar specimens contaminated with Na_2SO_4, A is reference and B is with borax. It can clearly be observed that borax considerably modifies the habit of sodium sulfate (B).

mirabilite crystals usually show a much more porous and irregular structure than the ‘bulky’ structures observed here [28, 32]. 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 [70, 87].

5.3.3 Discussion

It has been shown that both modifiers do not influence the wetting properties (contact angle, surface tension, evaporation rate) of the salt solutions [12, 87]. 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 5.4, 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 [24] and/or, due to the large number of small crystals (due to the high nucleation density), high pressures can hardly develop [23, 70].

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 [87]. If borax precipitates as its decahydrate phase, heterogeneous mirabilite nucleation is observed to occur at or near saturation [49]. 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 [87]. 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 [49] 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 [87]. Also in this case, different hypotheses can explain the observed beneficial effect of the additive on the reduction of the decay. 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 [88]. 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 [79]; 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 [87]; 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 [49]; 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 lifespan of their effectiveness and thus service-life of the additivated mortar. The results showed that only 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 [136]. However, although borax is currently classified as being possibly toxic to reproduction in the European CLP regulation [136], recent studies did not observe any connection between high levels of daily boron exposure and reprotoxicity [137, 138]. 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 [137, 139].

5.4 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 resistance 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 an improved resistance 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 salt resistance 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.

Acknowledgements

This research has been financed by the Dutch IOP program on Self-Healing Materials, under Grant number SHM012018. The authors wish to thank Willem Duvalois and Timo Nijland for their help with the Scanning Electron Microscope observations.

6

Conclusions

6.1 Results of the research

This thesis has researched the feasibility of mixing crystallization modifiers in lime-based (restoration) mortars with the aim to improve their resistance with respect to salt crystallization. In particular, the research focused on modifiers for two very damaging salts commonly found in buildings: sodium chloride and sodium sulfate.

This research therefore started with a literature review on the working mechanisms of crystallization modifiers and their application in building materials (Chapter 2). The literature review confirmed the good potentialities of the use of modifiers for mitigating salt damage and pointed out questions which need to be solved. A first issue to be solved was related to the identification of a modifier of sodium sulfate crystallization of proven effectiveness in a wide range of pH values and concentrations. Moreover, even though modifiers might work in bulk solutions, this would not guarantee their effectiveness once applied in building materials, as interactions between the modifier and the material itself may affect the behaviour. This issue becomes even more complex in the case the modifiers need to be mixed in a mortar, as they might negatively affect the mortar properties or become ineffective because of the pH change due to carbonation.

Based on the literature review, two potentially effective modifiers for sodium chloride and sodium sulfate were identified: sodium ferrocyanide and borax, respectively. The interaction of sodium chloride and ferrocyanide in bulk solution has already been elucidated and is well documented in the literature; besides, some pilot studies on its application on building materials and in mortar are already available. Literature on borax and its interaction with sodium sulfate was however limited. Therefore, a systematic study was conducted on the influence of borax on the wetting properties and crystallization behaviour of sodium sulfate (Chapter 3). It was found that the addition of borax to sodium sulfate solutions has no influence on the wetting properties (contact angle on glass, surface tension or evaporation rate) and therefore will most likely not influence solution transport in a porous material. Additionally, under the studied experimental conditions, it was shown that, depending on the starting concentration of the solution, two different hydrated phases of borax precipitate, each having a different effect on the crystallization behaviour of sodium sulfate. Both pathways have different implications for the damage development inside the pores of a material.

Although both selected modifiers were proven effective in bulk solutions, this does not guarantee their effectiveness inside a lime-based mortar. Their effectiveness depends on their concentration, as well as on their potential interactions with other components of the mortar. The effectiveness of ferrocyanide as modifier for sodium chloride when mixed in a (lime-cement-based) mortar was already verified, but nothing was known yet about borax’ effectiveness when mixed in a mortar. Moreover, for both ferrocyanide and borax, no data were available on their possible effect on fresh and hardened lime mortar properties. Therefore, firstly, the effectiveness of borax as modifier for sodium sulfate crystallization when mixed in a mortar was verified. Secondly, the effect of both ferrocyanide and borax on selected mortar properties was assessed. It was shown that none of the measured mortar properties was affected in such a way as to prevent the mixing-in of the modifiers in restoration mortars. Having found a suitable concentration of the modifiers and proven that the addition of these modifiers does not significantly alter any properties of fresh or hardened mortar, the final issue which needed to be addressed at this point was the effect of mixed-in crystallization modifiers on the development of salt crystallization damage.

The resistance of the additivated mortars against sodium chloride and sodium sulfate crystallization was assessed with an accelerated salt crystallization test in the laboratory (Chapter 5). Both types of additivated mortars showed a considerably improved resistance with respect to salt crystallization damage. Scanning electron microscopy (SEM) observations, which were conducted on the surface and cross-section of specimens taken from the mortar samples at the end of the crystallization test, showed that both modifiers altered the growth morphology of the salt crystals inside the pores of the mortars. The altered crystal habit, together with the observed increase in efflorescence, are considered to be responsible for the observed damage reduction.

The obtained results in this research show unambiguously that crystallization modifiers can be mixed in a mortar without losing effectiveness or changing any of the mortar properties, which might limit their application in repair materials, but they significantly increase the salt crystallization resistance of the studied mortars.

6.2 Outlook

This research has developed prototype recipes of lime-based mortars with mixed-in modifiers for an improved resistance with respect to salt crystallization and it has validated them at laboratory scale. To further develop these mortars towards a commercial product, suitable for renovation or restoration works, more research is needed. Based on the results obtained in this work, some important steps for future research and further development of the product can be defined.

In this thesis the effect of the modifiers has been studied for single salts. However, in practice, rarely only one salt is present. It is therefore necessary to assess the effect of the identified modifiers on other salts and also on salt mixtures. As modifiers tend to work mainly on a specific salt type, the possibility of combining different modifiers in the same material might be considered. Another issue, which was only briefly addressed in this thesis (Chapter 5), is the occurrence and speed of leaching of the modifiers. This needs to be studied systematically to see if and when leaching occurs; if necessary, possible solutions to guarantee durability need to be developed, e.g. encapsulation. Other research steps should include studying the effect of the modifiers in mortars with different composition (e.g. cement-based), assessing the effectiveness of the developed mortars (on test panels) in situ and addressing potential side-effects such as how to deal with the blue discoloration of ferrocyanide under the influence of sunlight, which was observed when applied on an iron containing substrate.

In the current research it is supposed that the mitigation of damage is a result of the altered crystal habit and the stimulation of efflorescence. However, it might be possible that an altered crystal size and/or nucleation density reduce the crystallization pressure and thus have a mitigating effect on the damage, even if the crystals precipitate inside the material. This would broaden the application field of modifiers.

The above identified issues, when properly solved, will open new perspectives for application of crystallization modifiers in building materials.

References

[1] A. Goudie and H. Viles. *Salt weathering hazards*. John Wiley & Sons, 1997.

[2] A. E. Charola. Salts in the deterioration of porous materials: an overview. *Journal of the American Institute for Conservation*, 39: 327–343, 2000.

[3] T. G. Nijland, O. C. G. Adan, R. P .J. van Hees, and B. D. van Etten. Evaluation of the effects of expected climate change on the durability of building materials with suggestions for adaptation. *Heron*, 54: 37–48, 2009.

[4] A. Arnold. *Origin, mechanisms and effects of salts on degradation of monuments in marine and continental environments. Protection and conservation of European cultural heritage.*, chapter Origin and behaviour of some salts in the context of weathering on monuments. Bari, 1994.

[5] R. P. J. van Hees, S. Naldini, and J. Delgado Rodrigues. Plasters and renders for salt laden substrates. *Construction and Building Materials*, 23: 1714–1718, 2009.

[6] R. J. Flatt, N. A. Mohamed, F. Caruso, H. Derluyn, J. Desarnaud, B. Lubelli, R. M. Espinosa-Marzal, L. Pel, C. Rodriguez-Navarro, G. W. Scherer, N. Shahidzadeh, and M. Steiger. Predicting salt damage in practice: a theoretical insight into laboratory tests. *RILEM Technical Letters*, 2: 108–118, 2017.

[7] R. Rossi-Manaresi and A. Tucci. Pore structure and the disruptive or cementing effect of salt crystallization in various types of stone. *Studies in Conservation*, 36: 53–58, 1991.

[8] G. W. Scherer. Stress from crystallization of salt. *Cement and Concrete Research*, 34: 1613–1624, 2004.

[9] C. Selwitz and E. Doehne. The evaluation of crystallization modifiers for controlling salt damage to limestone. *Journal of Cultural Heritage*, 3: 205–216, 2002.

[10] C. Rodriguez-Navarro and L. G. Benning. Control of crystal nucleation and growth by additives. *Elements*, 9: 203–209, 2013.

[11] R. M. Espinosa-Marzal and G. W. Scherer. *Limestone in the built environment: present-day challenges for the preservation of the past*, chapter Mechanisms of damage by salt, pages 61–77. Geological Society, London, Special Publications, 2010.

[12] C. Rodriguez-Navarro, L. Linares-Fernandez, E. Doehne, and E. Sebastian. Effects of ferrocyanide ions on NaCl crystallization in porous stone. *Journal of Crystal Growth*, 243: 503–516, 2002.

[13] B. Lubelli, T. G. Nijland, R. P. J. van Hees, and A. Hacquebord. Effect of mixed in crystallization inhibitor on resistance of lime-cement mortar against NaCl crystallization. *Construction and Building Materials*, 24: 2466–2472, 2010.

[14] Herodotus. *The History Book 2: Euterpe*, volume Chapter 12. 420 B.C.

[15] A. Arnold and K. Zehnder. Salt weathering on monuments. In *The conservation of monuments in the Mediterranean Basin: the influence of coastal environment and salt spray on limestone and marble. Proceedings of the 1st International Symposium, Bari, 7-10 June 1989*, 1989.

[16] A. E. Charola and E. Wendler. An overview of the water-porous building materials interactions. *Restoration of Buildings and Monuments*, 21: 55–65, 2015.

[17] R. M. Espinosa-Marzal and G. W. Scherer. Advances in understanding damage by salt crystallization. *Accounts of Chemical Research*, 43 (6): 897–905, 2010.

[18] B. Lubelli. *Sodium chloride damage to porous building materials*. PhD thesis, Delft University of Technology, 2006.

[19] N. Shahidzadeh-Bonn, J. Desarnaud, F. Bertrand, X. Chateau, and D. Bonn. Damage in porous media due to salt crystallization. *Physical Review E*, 81, 2010.

[20] C. W. Correns and W. Steinborn. Experimente zur Messung und Erklärung der sogenannten Kristallisationskraft. *Zeitschrift für Kristallographie-Crystalline Materials*, 101: 117–133, 1939.

[21] G. W. Scherer. Crystallization in pores. *Cement and Concrete Research*, 29: 1347–1358, 1999.

[22] M. Steiger. Crystal growth in porous materials-I: The crystallization pressure of large crystals. *Journal of Crystal Growth*, 282: 455–469, 2005.

[23] M. Steiger. Crystal growth in porous materials-II: Influence of crystal size on the crystallization pressure. *Journal of Crystal Growth*, 282: 470–481, 2005.

[24] R. J. Flatt, F. Caruso, A. M. Aguilar Sanchez, and G. W. Scherer. Chemomechanics of salt damage in stone. *Nature Communications*, 5: 4823, 2014.

[25] C. Groot, R. van Hees, and T. Wijffels. Selection of plasters and renders for salt laden masonry substrates. *Construction and Building Materials*, 23: 1743–1750, 2009.

[26] B. Lubelli, R. P. J. van Hees, and C. J. W. P. Groot. Sodium chloride crystallization in a "salt transporting" restoration plaster. *Cement and Concrete Research*, 36: 1467–1474, 2006.

[27] G. W. Scherer, R. Flatt, and G. Wheeler. Materials science research for the conservation of sculpture and monuments. *MRS Bulletin*, January, 2001.

[28] C. Rodriguez-Navarro, E. Doehne, and E. Sebastian. Influencing crystallization damage in porous materials through the use of surfactants: experimental results using sodium dodecyl sulfate and cetyldimethylbenzylammonium chloride. *Langmuir*, 16: 947–954, 2000.

[29] J. Houck and G. W. Scherer. Controlling stress from salt crystallization. In *Fracture and failure of natural building stones: application in the restoration of ancient monuments*, pages 299–312, 2006. Symposium on fracture and failure of natural building stones, Hellas, Greece.

[30] M. J. Qazi, R. W. Liefferink, S. J. Schlegel, E. H. G. Backus, D. Bonn, and N. Shahidzadeh. Influence of surfactants on sodium chloride crystallization in confinement. *Langmuir*, 33 (17): 4260–4268, 2017.

[31] B. Lubelli and R. P. J. van Hees. Effectiveness of crystallization inhibitors in preventing salt damage in building materials. *Journal of Cultural Heritage*, 8: 223–234, 2007.

[32] E. Ruiz-Agudo, C. Rodriguez-Navarro, and E. Sebastián-Pardo. Sodium sulfate crystallization in the presence of phosphonates: implications in ornamental stone conservation. *Crystal Growth & Design*, 6 (7): 1575–1583, 2006.

[33] T. Kawasaki and H. Tanaka. Formation of a crystal nucleus from liquid. *PNAS*, 107 (32): 14036–14041, 2010.

[34] D. Kashchiev and G. M. van Rosmalen. Review: Nucleation in solutions revisited. *Crystal Research and Technology*, 38: 555–574, 2003.

[35] J. Gibbs. *The Collected Works. Vol. 1. Thermodynamics*. Yale University Press, 1948.

[36] D. Erdemir, A. Y. Lee, and A. S. Myerson. Nucleation of crystals from solution: classical and two-step models. *Accounts of Chemical Research*, 42 (5): 621–629, 2009.

[37] P. G. Vekilov. Nucleation. *Crystal Growth & Design*, 10: 5007–5019, 2010.

[38] R. P. Sear. Nucleation: theory and applications to protein solutions and colloidal suspensions. *Journal of Physics: Condensed Matter*, 19 (3): 1–27, 2006.

[39] D. Benavente, M. A. García del Cura, J. García-Guinea, S. Sánchez-Moral, and S. Ordóñez. Role of pore structure in salt crystallization in unsaturated porous stone. *Journal of Crystal Growth*, 260: 532–544, 2004.

[40] S. Yu and C. T. Oguchi. *Limestone in the built environment: present-day challenges for the preservation of the past*, chapter Is sodium sulphate invariably effective in destroying any type of rock?, pages 43–58. Geological Society, London, Special Publications, 2010.

[41] R. J. Flatt, M. Steiger, and G. W Scherer. A commented translation of the paper by C.W. Correns and W. Steinborn on crystallization pressure. *Environmental Geology*, 52: 187–203, 2006.

[42] J. Desarnaud, D. Bonn, and N. Shahidzadeh. The pressure induced by salt crystallization in confinement. *Scientific Reports*, 6: 30856, 2016.

[43] S. Yu and C. T. Oguchi. Is sheer thenardite attack impotent compared with cyclic conversion of thenardite–mirabilite mechanism in laboratory simulation tests? *Engineering Geology*, 152: 148–154, 2013.

[44] I. Weissbuch, L. Addadi, M. Lahav, and L. Leiserowitz. Molecular recognition at crystal interfaces. *Science*, 253: 637–645, 1991.

[45] R. D. Cody. Organo-crystalline interactions in evaporite systems: the effects of crystallization inhibition. *Journal of Sedimentary Petrology*, 61 (5): 704–718, 1991.

[46] A. A. C. Bode, S. Jiang, J. A. M. Meijer, W. J. P. van Enckevort, and E. Vlieg. Growth inhibition of sodium chloride crystals by anticaking agents: in situ observation of step pinning. *Crystal Growth & Design*, 12: 5889–5896, 2012.

[47] K. Sangwal. *Additives and crystallization processes: from fundamentals to applications*. Wiley, 2007.

[48] F. Jones and M. I. Ogden. Controlling crystal growth with modifiers. *CrystEngComm*, 12: 1016–1023, 2010.

[49] E. Ruiz-Agudo and C. Rodriguez-Navarro. *Limestone in the built environment: present-day challenges for the preservation of the past*, chapter Suppression of salt weathering of porous limestone by borax-induced promotion of sodium and magnesium sulphate crystallization, pages 93–102. Geological Society, London, Special Publications, 2010.

[50] S. Al-Jibbouri and J. Ulrich. The growth and dissolution of sodium chloride in a fluidized bed crystallizer. *Journal of Crystal Growth*, 234: 237–246, 2002.

[51] A. A. C. Bode. *The mechanism of anticaking agents for sodium chloride*. PhD thesis, Radboud University Nijmegen, 2013.

[52] A. E. Charola and C. Bläuer. Salts in masonry: an overview of the problem. *Restoration of Buildings and Monuments*, 21: 119–135, 2015.

[53] D. Aquilano, L. Pastero, M. Bruno, and M. Rubbo. {100} and {111} forms of the NaCl crystals coexisting in growth from pure aqueous solution. *Journal of Crystal Growth*, 311: 399–403, 2009.

[54] K. Zehnder and A. Arnold. Crystal growth in salt efflorescence. *Journal of Crystal Growth*, 97: 513–521, 1989.

[55] S. Lee, H. S. Wi, W. Jo, Y. C. Cho, H. H. Lee, S.-Y. Jeong, Y.-I. Kim, and G. W. Lee. Multiple pathways of crystal nucleation in an extremely supersaturated aqueous potassium dihyrogen phophate (KDP) solution droplet. *PNAS*, 113: 13618–13623, 2016.

[56] K. N. Olafson, R. Li, B. G. Alamani, and J. D. Rimer. Engineering crystal modifiers: bridging classical and nonclassical crystallization. *Chemistry of Materials*, 28: 8453–8465, 2016.

[57] M. Steiger and S. Asmussen. Crystallization of sodium sulfate phases in porous materials: The phase diagram Na_2SO_4-H_2O and the generation of stress. *Geochimica et cosmochimica acta*, 72: 4291–4306, 2008.

[58] A. Hamilton and C. Hall. Sodium sulfate heptahydrate: a synchrotron energy-dispersive diffraction study of an elusive metastable hydrated salt. *Journal of Analytical Atomic Spectrometry*, 23: 840–844, 2008.

[59] T. A. Saidov, L. Pel, and G. H. A. van der Heijden. Crystallization of sodium sulfate in porous media by drying at a constant temperature. *International Journal of Heat and Mass Transfer*, 83: 621–628, 2015.

[60] J. Desarnaud, H. Derluyn, J. Carmeliet, D. Bonn, and N. Shahidzadeh. Metastability limit for the nucleation of NaCl crystals in confinement. *The Journal of Physical Chemistry Letters*, 5: 890–895, 2014.

[61] A. Naillon, P. Duru, M. Marcoux, and M. Prat. Evaporation with sodium chloride crystallization in a capillary tube. *Journal of Crystal Growth*, 422: 52–61, 2015.

[62] S. Gupta, K. Terheiden, L. Pel, and A. Sawdy. Influence of ferrocyanide inhibitors on the transport and crystallization processes of sodium chloride in porous building materials. *Crystal Growth & Design*, 12: 3888–3898, 2012.

[63] L. Pel, H. Huinink, and K. Kopinga. Ion transport and crystallization in inorganic building materials as studied by nuclear magnetic resonance. *Applied Physics Letters*, 81: 2893–2895, 2002.

[64] J. Desarnaud, F. Bertrand, and N. Shahidzadeh-Bonn. Impact of the kinetics of salt crystallization on stone damage during rewetting/drying and humidity cycling. *Journal of Applied Mechanics*, 80: 020911–1–020911–7, 2013.

[65] T. A. Saidov, L. Pel, and K. Kopinga. Sodium sulfate salt weathering of porous building materials studied by NMR. *Materials and Structures*, 50: 145, 2017.

[66] M. Schiro, E. Ruiz-Agudo, and C. Rodriguez-Navarro. Damage mechanism of porous materials due to in-pore salt crystallization. *Physical Review Letters*, 109, 2012.

[67] B. Lubelli, R. P. J. van Hees, H. P. Huinink, and C. J. W. P. Groot. Irreversible dilation of NaCl contaminated lime–cement mortar due to crystallization cycles. *Cement and Concrete Research*, 36: 678–687, 2006.

[68] J. Desarnaud, H. Derluyn, L. Molari, S. de Miranda, V. Cnudde, and N. Shahidzadeh. Drying of salt contaminated porous media: effect of primary and secondary nucleation. *Journal of Applied Physics*, 118: 114901, 2015.

[69] S. Gupta, L. Pel, and K. Kopinga. Crystallization behavior of NaCl droplet during repeated crystallization and dissolution cycles: An NMR study. *Journal of Crystal Growth*, 391: 64–71, 2014.

[70] N. Shahidzadeh and J. Desarnaud. Damage in porous media: role of the kinetics of salt (re)crystallization. *The European Physical Journal Applied Physics*, 60, 2012.

[71] J. Desarnaud and N. Shahidzadeh-Bonn. Salt crystal purification by deliquescence/crystallization cycling. *EPL*, 95, 2011.

[72] C. Rodriguez-Navarro and E. Doehne. Salt weathering: influence of evaporation rate, supersaturation and crystallization pattern. *Earth Surface Processes and Landforms*, 24: 191–209, 1999.

[73] R. J. Flatt. Salt damage in porous materials: how high supersaturations are generated. *Journal of Crystal Growth*, 242: 435–454, 2002.

[74] R. M. Espinosa-Marzal, A. Hamilton, M. McNall, K. Whitaker, and G. W. Scherer. The chemomechanics of crystallization during rewetting of limestone impregnated with sodium sulfate. *Journal of Materials Research*, 26: 1472–1481, 2011.

[75] C. Rodriguez-Navarro, E. Doehne, and E. Sebastian. How does sodium sulfate crystallize? implications for the decay and testing of building materials. *Cement and Concrete Research*, 30: 1527–1534, 2000.

[76] M. Steiger, K. Linnow, H. Juling, G. Gülker, A. El Jarad, S. Brüggerhoff, and D. Kirchner. Hydration of $MgSO_4 \cdot H_2O$ and generation of stress in porous materials. *Crystal Growth & Design*, 8 (1): 336–343, 2008.

[77] N. Radenovic. *The role of impurities on the morphology of NaCl crystals*. PhD thesis, Radboud University Nijmegen, 2006.

[78] M. A. van Damme van Weele. *Influence of additives on the growth and dissolution of sodium chloride crystals*. PhD thesis, Technische Hogeschool Twente, 1965.

[79] A. A. C. Bode, V. Vonk, F. J. van den Bruele, D. J. Kok, A. M. Kerkenaar, M. F. Mantilla, S. Jiang, J .A. M. Meijer, W. J. P. van Enckevort, and E. Vlieg. Anticaking activity of ferrocyanide on sodium chloride explained by charge mismatch. *Crystal Growth & Design*, 12: 1919–1924, 2012.

[80] E. R. Townsend, W. J. P. van Enckevort, J. A. M. Meijer, and E. Vlieg. Additive enhanced creeping of sodium chloride crystals. *Crystal Growth & Design*, 17: 3107–3115, 2017.

[81] L. Tian, K. Qian, S. Wei, C. Yao, and Y. Wang. Ferrous tartrate recognition of sodium chloride {111} and its effect on crystal growth. *Crystal Research & Technology*, 51 (10): 610–616, 2016.

[82] E. R. Townsend. *Insights into the role of additives as anticaking agents for sodium chloride*. PhD thesis, Radboud University Nijmegen, 2018.

[83] J. Cassar, A. Marrocchi, M. L. Santarelli, and M. Muscat. Controlling crystallization damage by the use of salt inhibitors on Malta's limestone. *Materiales de Construcción*, 58: 281–293, 2008.

[84] M. P. Bracciale, G. Bretti, A. Broggi, M. Ceseri, A. Marrocchi, R. Natalini, and C. Russo. Mathematical modelling of experimental data for crystallization inhibitors. *Applied Mathematical Modelling*, 48: 21–38, 2017.

[85] M. Telkes. Nucleation of supersaturated inorganic salt solutions. *Industrial and Engineering Chemistry*, 44 (6): 1308–1310, 1952.

[86] S. J. C. Granneman, E. Ruiz-Agudo, B. Lubelli, R. P. J. van Hees, and C. Rodriguez-Navarro. Study on effective modifiers for damaging salts in mortar. In *Proceedings of the 1st International Conference on Ageing of Materials and Structures*, 2014.

[87] S. J. C. Granneman, N. Shahidzadeh, B. Lubelli, and R. P. J. van Hees. Effect of borax on the wetting properties and crystallization behavior of sodium sulfate. *CrystEngComm*, 19: 1106–1114, 2017.

[88] W. J. P. van Enckevort and J. H. Los. On the creeping of saturated salt solutions. *Crystal Growth & Design*, 13: 1838–1848, 2013.

[89] S. J .C. Granneman, B. Lubelli, and R. P. J. van Hees. Effect of mixed in crystallization modifiers on resistance of lime mortar against NaCl and Na_2SO_4 crystallization. *Construction and Building Materials*, 194: 62–70, 2019.

[90] E. Ruiz-Agudo, C. V. Putnis, L. Pel, and C. Rodriguez-Navarro. Template-assisted crystallization of sulfates onto calcite: implications for the prevention of salt damage. *Crystal Growth & Design*, 13: 40–51, 2013.

[91] T. Rabizadeh, C. L. Peacock, and L. G. Benning. Carboxylic acids: effective inhibitors for calcium sulfate precipitation? *Mineralogical Magazine*, 78: 1465–1472, 2014.

[92] L. M. Ottosen and I. V. Christensen. Electrokinetic desalination of sandstones for NaCl removal—test of different clay poultices at the electrodes. *Electrochimica Acta*, 86: 192–202, 2012.

[93] A. Vollpracht, B. Lothenbach, R. Snellings, and J. Haufe. The pore solution of blended cements: a review. *Materials and Structures*, 49: 3341–3367, 2016.

[94] T. Rivas, E. Alvarez, M. J. Mosquera, L. Alejano, and J. Taboada. Crystallization modifiers applied in granite desalination: the role of the stone pore structure. *Construction and Building Materials*, 24: 766–776, 2010.

[95] S. Gupta. *Sodium chloride crystallization in drying porous media: influence of inhibitor*. PhD thesis, Eindhoven University of Technology, 2013.

[96] S. Gupta, H. P. Huinink, M. Prat, L. Pel, and K. Kopinga. Paradoxical drying of a fired-clay brick due to salt crystallization. *Chemical Engineering Science*, 109: 204–211, 2014.

[97] S. J. C. Granneman, B. Lubelli, and R. P. J. van Hees. Characterization of lime mortar additivated with crystallization modifiers. *International Journal of Architectural Heritage*, 12: 849–858, 2018.

[98] S. Sammut, J. Cassar, A. Marrocchi, C. Russo, L. Sommei, and M. L. Santarelli. Investigating a method to limit damage in Globigerina Limestone, a soft porous stone widely used in historic buildings. In *Proceedings of SWBSS 2014, Third International Conference on Salt Weathering of Buildings and Stone Sculptures, Brussels, 14-16 October 2014*, 2014.

[99] M. Franceschini, A. Broggi, M. P. Bracciale, L. Sommei, M. L. Santarelli, and A. Marrocchi. Effectiveness of phosphocitrate as salt crystallization inhibitor in porous materials: case study of the Roman Mosaic of Orpheus and the Beasts (Perugia, Italy). *International Journal of Architectural Heritage*, 9: 195–200, 2015.

[100] E. Ruiz-Agudo, B. Lubelli, A. Sawdy, R. van Hees, C. Price, and C. Rodriguez-Navarro. An integrated methodology for salt damage assessment and remediation: the case of San Jerónimo Monastery (Granada, Spain). *Environmental Earth Sciences*, 63 (7): 1475–1486, 2011.

[101] RILEM Recommendation MS-A1. Determination of the resistance of wallettes against sulphates and chlorides. *Materials and Structures*, 31: 2–19, 1998.

[102] R.P.J van Hees and H.J.P Brocken. Damage development to treated brick masonry in a long-term salt crystallisation test. *Construction and Building Materials*, 18 (5): 331 – 338, 2004.

[103] J. Petkovic, H. P. Huinink, L. Pel, K. Kopinga, and R. P. J. van Hees. Moisture and salt transport in three-layer plaster/substrate systems. *Construction and Building Materials*, 24: 118–127, 2010.

[104] E. Doehne. *Natural stone, weathering phenomena, conservation strategies and case studies*, chapter Salt weathering: a selective review, pages 51–64. The Geological Society of London, 2002.

[105] C. W. Correns. Growth and dissolution of crystals under linear pressure. *Discussions of the Faraday Society*, 5: 267–271, 1949.

[106] D. Bonn and N. Shahidzadeh. Multistep crystallization processes: how not to make perfect single crystals. *PNAS*, 113: 13551–13553, 2016.

[107] W. Jiang, H. Pan, J. Tao, X. Xu, and R. Tang. Dual roles of borax in kinetics of calcium sulfate dihydrate formation. *Langmuir*, 23: 5070–5076, 2007.

[108] A. Apelblat and E. Manzurola. Solubilities and vapour pressures of saturated aqueous solutions of sodium tetraborate, sodium carbonate, and magnesium sulfate and freezing-temperature

lowerings of sodium tetraborate and sodium carbonate solutions. *Journal of Chemical Thermodynamics*, 35: 221–238, 2003.

[109] N. Shahidzadeh-Bonn, S. Rafaï, D. Bonn, and G. Wegdam. Salt crystallization during evaporation: impact of interfacial properties. *Langmuir*, 24: 8599–8605, 2008.

[110] N. Shahidzadeh, M. F. L. Schut, J. Desarnaud, M. Prat, and D. Bonn. Salt stains from evaporating droplets. *Scientific Reports*, 5: 10335, 2015.

[111] N. Shahidzadeh-Bonn, S. Rafaï, A. Azouni, and D. Bonn. Evaporating droplets. *Journal of Fluid Mechanics*, 549: 307–313, 2006.

[112] T. A. Saidov, N. Shahidzadeh, and L. Pel. Crystallization of sodium sulfate on hydrophilic/hydrophobic surfaces during drying: an NMR study. *EPL*, 102: 28003, 2013.

[113] B. Lafuente, R.T. Downs, H. Yang, and N. Stone. *Highlights in Mineralogical Crystallography*, chapter The power of databases: the RRUFF project, pages 1–30. W. De Gruyter, 2015.

[114] K. Linnow, M. Steiger, C. Lemster, H. de Clercq, and M. Jovanovic. Ín situ Raman observation of the crystallization in $NaNO_3$–Na_2SO_4-H_2O solution droplets. *Environmental Earth Sciences*, 69: 1609–1620, 2013.

[115] C. L. Christ and R. M. Garrels. Relations among sodium borate hydrates at the Kramer deposit, Boron, California. *American Journal of Science*, 257: 516–528, 1959.

[116] A. Pabst and D. L. Sawyer. Tincalconite crystals from Searles Lake, San Bernardino County, California. *American Mineralogist*, 33: 472–481, 1948.

[117] S. Al-Jibbouri, C. Strege, and J. Ulrich. Crystallization kinetics of epsomite influenced by pH-value and impurities. *Journal of Crystal Growth*, 236: 400–406, 2002.

[118] K. Momma and F. Izumi. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, 44: 1272–1276, 2011.

[119] R. van Hees, S. Naldini, and J. Roos. *Durable past - sustainable future*. TU Delft, 2014.

[120] S. Gupta, H. P. Huinink, L. Pel, and K. Kopinga. How ferrocyanide influences NaCl crystallization under different humidity conditions. *Crystal Growth & Design*, 14: 1591–1599, 2014.

[121] S. J. C. Granneman, B. Lubelli, and R. P. J. van Hees. Lime mortar with mixed-in crystallization modifiers to mitigate salt damage. In K. Van Balen and E. Verstrynge, editors, *Structural Analysis of*

Historical Constructions: Anamnesis, Diagnosis, Therapy, Controls: Proceedings of the 10th International Conference on Structural Analysis of Historical Constructions, pages 75–79, 2016.

[122] A. R. Zimmermann, D. -H. Kang, M. -Y. Ahn, S. Hyun, and M. K. Banks. Influence of a soil enzyme on iron-cyanide complex speciation and mineral adsorption. *Chemosphere*, 70: 1044–1051, 2008.

[123] A. Izaguirre, J. Lanas, and J. I. Álvarez. Ageing of lime mortars with admixtures: Durability and strength assessment. *Cement and Concrete Research*, 40: 1081–1095, 2010.

[124] A. Arizzi and G. Cultrone. Aerial lime-based mortars blended with a pozzolanic additive and different admixtures: A mineralogical, textural and physical-mechanical study. *Construction and Building Materials*, 31: 135–143, 2012.

[125] EN 196-1: Methods of testing cement - part 1: Determination of strength, 2016.

[126] EN 1015-2:1998/A1:2006: Methods of test for mortar for masonry - part 2: Bulk sampling of mortars and preparation of test mortars, 1998/2006.

[127] EN 1015-3:1999/A2:2006: Methods of test for mortar for masonry - part 3: Determination of consistence of fresh mortar (by flow table), 1999/2006.

[128] N. Döbelin and R. Kleeberg. Profex: a graphical user interface for the Rietveld refinement program BGMN. *Journal of Applied Crystallography*, 48: 1573–1580, 2015.

[129] L. J. A. R. van der Klugt. Technological factors influencing the frost susceptibility of clay building materials. *ZI annual*, pages 24–33, 1993.

[130] EN 1015-18: Methods of test for mortar for masonry - part 18: Determination of water absorption coefficient due to capillary action of hardened mortar, 2002.

[131] EN 1015-11:1999/A1:2006: Methods for test for mortar for masonry - part 11: Determinatin of flexural and compressie strength of hardened mortar, 1999/2006.

[132] K. Van Balen. Carbonation reaction of lime, kinetics at ambient temperature. *Cement and Concrete Research*, 35: 647–657, 2005.

[133] S. J. C. Granneman, B. Lubelli, and R. P. J. van Hees. Mitigating salt damage in lime-based mortars with mixed-in crystallization modifiers. In *Proceedings of the 4th WTA International PhD Symposium*, 2017.

[134] S. J .C. Granneman, B. Lubelli, and R. P. J. van Hees. Mitigating salt damage in building materials by the use of crystallization modifiers - a review and outlook. *Manuscript under review at Journal of Cultural Heritage*.

[135] B. Lubelli, V. Cnudde, T. Diaz-Goncalves, E. Franzoni, R. P. J. van Hees, I. Ioannou, B. Menendez, C. Nunes, H. Siedel, M. Stefanidou, V. Verges-Belmin, and H. Viles. Towards a more effective and reliable salt crystallization test for porous building materials: state of the art. *Materials and Structures*, 51 (2): 55. 1871-6873, 2018.

[136] European Chemicals Agency (ECHA). |https://echa.europa.eu/home|.

[137] H. M. Bolt, Y. Duydu, N.Basaran, and K. Golka. Boron and its compounds: current biological research activities. *Archives of Toxicology*, 91: 2719–2722, 2017.

[138] Y. Duydu, N. Basaran, A. Üstündag, S. Aydn, C. Ö. Yalçn, H. G. Anlar, M. Bacanl, K. Aydos, C. S. Atabekoglu, K. Golka, K. Ickstadt, T. Schwerdtle, M. Werner, S. Meyer, and H. M. Bolt. Birth weights of newborns and pregnancy outcomes of environmentally boron-exposed females in Turkey. *Ărchives of Toxicology*, 92: 2475–2485, 2018.

[139] F. Petrova Simeonova and L. Fishbein. Hydrogen cyanide and cyanides: human health aspects. Technical report, World Health Organization Geneva, 2004.

Summary

Damage due to the crystallization of salts is a common problem in porous building materials. Also mortars used in the restoration of historic buildings are often subjected to a high salt load, resulting in a rapid degradation and high maintenance costs. Especially lime-based mortars, used for example as render, plaster, bedding mortar or pointing mortar, are vulnerable to this type of damage. Despite the extensive research efforts, no definitive solution yet exists to tackle the problem of salt decay in building materials. Existing solutions to improve mortar resistance with respect to salt decay such as modifying the moisture transport properties of the mortar (e.g. plaster with water-repellent properties) or increasing its mechanical strength of the plaster mortar (e.g. by using a different binder such as cement), often show compatibility problems and might cause even more damage to the to be restored (historic) fabric. Recently a new approach, based on the use of crystallization modifiers to alter the salt crystallization process, has been proposed. The aim of modifiers is to prevent or mitigate salt crystallization damage in building materials. Modifiers are ions or molecules that can keep the salts longer in solution (inhibitors), facilitate the precipitation of a certain crystal phase (promoters) and/or change the shape and size of the grown crystals (habit modifiers). These effects are often present in combination, i.e. a promoter or inhibitor can at the same time act as habit modifier.

The present work investigates the potentialities of mixing crystallization modifiers directly into a lime-based mortar, in order to produce a restoration material more durable to salt decay and at the same time, compatible with the old fabric. The modifier, present in the mortar, will become active at the moment that the damaging salt solution enters the material: a form of ‘self-healing’.

The first step in this research consisted in a review of the current literature on crystallization modifiers typically applied to building materials for the reduction of salt damage. The review focused in particular on suitable modifiers for two of the most common and damaging salts: sodium chloride and sodium sulfate. Based on this literature research, sodium ferrocyanide and borax were identified as promising modifiers for sodium chloride and sodium sulfate respectively. Furthermore, hypotheses, to be further validated in the experimental research, were formulated on the possible working mechanisms of these specific modifiers in lime mortar.

As data on the effects of ferrocyanide on sodium chloride crystallization in bulk solution were already known from literature, the first experimental part of the research focused on the study of borax, sodium sulfate and mixtures of the two in bulk solution. Assessing the solution properties and crystallization behaviour of these compounds was a necessary step in the research, because literature on these topics was scarce. It was shown that the addition of borax to the solution does not change any solution properties that might influence the wetting behaviour and transport of the salt solution in the porous materials. It was found that borax can crystallize as two different phases, depending on the starting concentration of the solution: each of these phases has a different effect on the crystallization of sodium sulfate. Based on these results and on previous research, effective amounts of both modifiers (borax and sodium ferrocyanide) to be mixed in the mortar were defined.

The next step in the research consisted in the assessment of the effectiveness of the modifiers once mixed in the lime-based mortar. For example, the high pH difference (13-9) between fresh and hardened mortar could limit or inhibit the effectiveness of the modifiers. It was experimentally demonstrated that both modifiers were active in the mortar, and that their effectiveness was not affected by the carbonation process of the lime. Moreover, the effect of modifiers on the fresh or hardened mortar properties was investigated, as any negative change could prevent their application in a restoration or renovation product. On the basis of the obtained results, it was concluded that both sodium ferrocyanide and borax can be added to lime-based mortars without significantly affecting the fresh or hardened mortar properties.

The final step in this research consisted in the assessment of the resistance of the additivated mortars against sodium chloride and sodium sulfate crystallization. To this aim, an accelerated salt crystallization test was designed and carried out in the laboratory on mortars with and without modifiers. The decay was assessed by visual observations and measurement of the material and salt loss at specific intervals during the test; at the end of the test the salt distribution in the specimens was measured and Scanning Electron Microscopy (SEM) observations were carried out. The results showed that the additivated mortars suffered no (in the case of ferrocyanide) or significantly less (in the case of borax) material loss than the reference mortars, confirming the positive effect of these modifiers on salt crystallization damage.

The accelerated salt crystallization test confirmed some of the assumptions on the working mechanisms of the modifiers formulated on the basis of the literature review. It was shown that both modifiers indeed promote crystallization at the surface instead of in-depth, reducing thereby the damage. Furthermore, the SEM observations revealed a significant habit change for both salts in the presence of the modifiers.

The research definitively shows that the selected modifiers can be mixed in a lime-based mortar and result in an increased resistance of the additivated mortars to salt decay without negatively affecting any other properties of the material. This opens possibilities for the future application of lime-based mortars additivated with modifiers in restoration and renovation interventions. The assessment of the effectiveness of the modifiers in the presence of salt mixtures (as common in buildings) and of the durability of the effect of the modifier (leaching may occur) are among the issues for future investigations. Besides, a validation of the results in practice (e.g. in case studies) will be necessary before the application of these mortars in conservation and renovation interventions can be considered.

Samenvatting

Schade aan poreuze bouwmaterialen veroorzaakt door de kristallisatie van zouten is een veelvoorkomend probleem. Ook mortels, gebruikt bij de restauratie van historische gebouwen, worden vaak blootgesteld aan grote hoeveelheden zout. Dit leidt vervolgens snel tot schade en hoge onderhoudskosten. Vooral kalkgebonden mortels, die bijvoorbeeld gebruikt worden als pleister, stuc, legmortel of voegmortel, zijn vatbaar voor dit soort schade. Hoewel er al veel onderzoek gedaan is naar het probleem van zoutschade in bouwmaterialen, is er nog steeds geen afdoende oplossing om dit probleem aan te pakken. Bestaande oplossingen om de zoutbestendigheid van mortels te verbeteren, zoals het aanpassen van de vochttransporteigenschappen (b.v. pleisterlaag met waterafstotende eigenschappen) of het verhogen van de mechanische sterkte van de pleistermortel (b.v. door het gebruiken van een ander bindmiddel zoals cement), hebben vaak een lage compatibiliteit met de bestaande materialen en kunnen zelfs meer schade veroorzaken aan de te restaureren (historische) gebouwen. Recentelijk is er een nieuwe aanpak voorgesteld, die gebaseerd is op het gebruik van kristallisatie modificatoren die het zoutkristallisatieproces veranderen om zo zoutkristallisatieschade aan bouwmaterialen te voorkomen of te verminderen. Modificatoren zijn ionen of moleculen die de zouten langer in oplossing kunnen houden (inhibitoren), het kunnen neerslaan van een bepaalde kristalvorm kunnen vergemakkelijken (promotoren) en/of de vorm en grootte van de gegroeide kristallen kunnen veranderen (habitus modificator). Deze effecten zijn vaak tegelijkertijd aanwezig, d.w.z. een promotor of inhibitor kan tegelijkertijd fungeren als “habitus modificator”.

Het beschreven onderzoek heeft betrekking op de mogelijkheden van het inmengen van kristallisatie modificatoren direct in een kalkgebonden mortel, om een restauratie materiaal te produceren dat beter bestand is tegen zoutschade, en tegelijkertijd compatibel met de oude materialen. De modificator, aanwezig in de mortel, zal actief worden op het moment dat de schadelijke zoutoplossing in het materiaal dringt: een vorm van ‘zelf herstellend gedrag’.

De eerste stap in dit onderzoek bestond uit een evaluatie van de huidige literatuur over kristallisatie modificatoren die het meest worden toegepast op bouwmaterialen voor het verminderen van zoutschade. De literatuurstudie focuste vooral op geschikte modificatoren voor twee van de meest voorkomende en meest schadelijke zouten: natriumchloride en natriumsulfaat. Aan de hand van deze literatuurstudie werden natriumferrocyanide en borax geïdentificeerd als veelbelovende modificatoren voor respectievelijk natriumchloride en natriumsulfaat. Daarnaast werden er hypotheses geformuleerd over de mogelijke werkingsmechanismen van deze modificatoren in kalkmortel, die vervolgens gevalideerd moesten worden in het experimentele deel van het onderzoek.

Omdat er in de literatuur al data bekend waren over de effecten van ferroycanide op natriumchloride kristallisatie vanuit de bulkoplossing, focuste het eerste experimentele deel van het onderzoek op de studie van borax, natriumsulfaat en mengsels van deze twee in bulkoplossing. Het vaststellen van de vloeistofeigenschappen en het kristallisatiegedrag van deze stoffen was een noodzakelijke stap in het onderzoek, omdat de literatuur op dit gebied schaars was. De resultaten lieten zien dat door het toevoegen van borax aan de oplossing, er in geen van de gemeten vloeistofeigenschappen veranderingen optraden, die mogelijk het bevochtigingsgedrag en het transport van de zoutoplossing in de poreuze materialen zouden kunnen beïnvloeden. Er werd verder aangetoond dat borax kan kristalliseren als twee verschillende vormen, afhankelijk van de concentratie van de oplossing aan het begin: elk van deze vormen heeft een ander effect op de kristallisatie van natriumsulfaat. Aan de hand van deze resultaten en van eerder onderzoek werden er van beide modificatoren (borax en natrium ferrocyanide) effectieve hoeveelheden gedefinieerd om te worden ingemengd in de mortel.

De volgende stap in het onderzoek bestond uit het bepalen van de effectiviteit van de modificatoren zodra ze ingemengd waren in de kalkmortel. Het zou bijvoorbeeld kunnen dat het grote pH verschil (13-9) tussen verse en verharde mortel de effectiviteit van de modificatoren kan onderdrukken of verminderen. Aan de hand van experimenten is van beide modificatoren aangetoond dat ze actief waren in de mortel, en dat hun effectiviteit niet werd beïnvloed door het carbonatatieproces van de kalk. Daarnaast werden de effecten van de modificatoren op verse en verharde morteleigenschappen onderzocht, aangezien een negatieve verandering hun gebruik in een restauratie of renovatie product in de weg zou staan. Aan de hand van de verkregen resultaten kon worden geconcludeerd dat zowel natriumferrocyanide als borax toegevoegd kan worden aan kalkgebonden mortels, zonder de verse of verharde morteleigenschappen significant te beïnvloeden.

De laatste stap in dit onderzoek bestond uit het bepalen van de weerstand van de geadditiveerde mortels tegen natriumchloride en natriumsulfaat kristallisatie. Om dit te bereiken werd er een versnelde zoutkristallisatietest ontworpen en uitgevoerd in het laboratorium op mortel met en zonder modificatoren. De aantasting werd bepaald aan de hand van visuele observaties en door het meten van het materiaal- en zoutverlies op specifieke tijdsintervallen tijdens de test; aan het einde van de test werd de zoutverdeling in de proefstukken gemeten en werden het oppervlak en de doorsnede van de proefstukken bekeken met een rasterelektronenmicroscoop. De resultaten lieten zien dat de geadditiveerde mortels geen (in het geval van ferrocyanide) of significant minder (in het geval van borax) schade hadden in vergelijking met de referentie mortels. Dit bevestigde het positieve effect van deze modificatoren op zoutkristallisatieschade.

De versnelde zoutkristallisatietest bevestigde sommige aannames over de werkingsmechanismen van de modificatoren die geformuleerd waren op grond van de literatuurrecensie. Er is gebleken dat beide modificatoren inderdaad kristallisatie aan het oppervlakte stimuleren in plaats van in het materiaal, waardoor schade wordt beperkt. Daarnaast toonden de rasterelektronenmicroscoopwaarnemingen een significante habitus verandering voor beide zouten in de aanwezigheid van de modificatoren.

Dit onderzoek toont onomstotelijk aan dat de geselecteerde modificatoren gemengd kunnen worden in een kalkgebonden mortel en dat dit resulteert in een verhoogde weerstand van de geadditiveerde mortels tegen zoutdegradatie. Daarnaast is bewezen dat door de toevoegingen van de modificatoren geen andere eigenschappen van het materiaal negatief worden beïnvloed. Dit opent mogelijkheden voor toekomstige toepassingen van kalkgebonden mortels geadditiveerd met modificatoren in restauratie of renovatie interventies. Het beoordelen van de effectiviteit van modificatoren in de aanwezigheid van zoutmengsels (zoals gebruikelijk in gebouwen) en van de duurzaamheid van het effect van de modificator (het is te verwachten dat uitloging kan voorkomen) behoren tot de onderwerpen voor toekomstig onderzoek. Bovendien moeten de resultaten ook in de praktijk gevalideerd worden voordat de toepassing van deze mortels in conservering en renovatie interventies overwogen kan worden.

Acknowledgements

During the whole process of the PhD, many people helped me in various ways; whether it was with experiments, useful discussions, or just by providing me with some much-needed (social) distractions. I am bound to forget some people, but in any case, many many thanks! Without your help, this thesis would not have been here.

First of all, I would like to thank both of my supervisors, my promotor Rob van Hees, and my co-promotor Barbara Lubelli. After about a year after I started working in Delft, you told me that at first you were a bit hesitant to hire a chemist to work at Architecture. I am however very glad you did, and I hope that you are looking back with as much satisfaction as I do. Thank you very much for many useful discussions, and for helping me improving my writing, presenting and just to become a better researcher in general. Finally, I would like to thank the both of you for showing so much patience, especially during the last months, while I tried to finish all the writing, while already working somewhere else. It took six years, but I am very proud of what we have accomplished.

My PhD project was part of the IOP research programme on Self Healing Materials. I would like to thank Annette Steggerda (RVO) and Sybrand van der Zwaag (Delft University of Technology) for their yearly visits for an update on the project, as well as the nice ‘self healing’ lunches, summer school and yearly symposium. An important part of the IOP projects is the involvement of university and industrial partners. In my case I want to sincerely thank: Timo Nijland (TNO), Noushine Shahidzadeh (University of Amsterdam), Leo Pel (Eindhoven University of Technology), Nico Karper (Strikolith), Anton van Delden (Fa. Delstuc) and Hans Geerken (Het Neerlandsch Stucgilde). I really enjoyed our meetings twice a year, and valued your comments and advice. I truly appreciated all the help you gave me, whether it was access to your research facilities, help with experimental techniques or visits to the factory or an actual work site to see mortar application in practice. Additionally, I would like to acknowledge Bert Kerk (TNO), Willem Duvalois (TNO), Willem Suitela (TNO), Johan Bijleveld (Delft University of Technology), Arjan Thijssen (Delft University of Technology) and Hans Dalderop (Eindhoven University of Technology) for their technical support in carrying out the experiments.

During my first year I had the opportunity to spend three months at the University of Granada, as a visiting researcher. For that I would like to sincerely thank Encarni Ruiz-Agudo and Carlos Rodriguez-Navarro. I had a really nice time, and thank you for helping me on my way with the first experiments on modifiers and lime. I would also like to thank Chiara, Gan, Iñaki, Eduardo and Yasmina for the nice lunches, dinners and getting to know Granada together.

I would like to thank all of the colleagues of Heritage and Architecture: thank you for allowing me as a stranger in your midst; I hope I was able to teach you all a little bit about chemistry. At least I have learned a lot about buildings from you, and certainly learned to appreciate them. A special thanks also to Giovanni and Dora, with whom I could share the process of doing a PhD. I would especially like to thank Wido; we shared many lunches and coffees together, and you brought along many of your tools from home when I needed them for my experiments in the basement. Also many thanks for all the help with layout for posters and this thesis, as well as for co-organizing the WTA symposium together! I would also like to thank Silvia for the nice time we had as office mates, it was always very ‘gezellig’ and we got to share many laughs together! Furthermore, I want to thank Barbara and Herdis for the nice times, and for making me remember all the Dutch grammar rules or laugh at the (small) mistakes in Dutch (‘proefkonijntje’).

I want to thank the committee members for thoroughly reading my thesis and providing me with suggestions for the improvement of the manuscript.

I also would like to say thanks to Peter Christianen and Hans Engelkamp from the High Field Magnet Laboratory of the Radboud University Nijmegen for giving me the opportunity of already starting a postdoc while I was still finishing my thesis.

A big thanks also to my friends (Marleen, Thomas, Jeanette, Jos, Paula, Vincent, Moniek, Laura, Mireille, Charlotte) for all their support, whether it was by commuting together, the joined experience of doing a PhD or politely not asking how things were going with the research (or more likely the writing). Many of you I have known already for years, and thank you for the much needed distractions you have all provided on a regular basis. Hopefully finishing this thesis will finally give me a bit more time to meet up with all of you on a more regular basis!

I would also like to thank my paranymphs for supporting me today and for standing in front of everyone together with me. Moniek, you were the very first person I met, when we were both walking with our bike at the Markt in Nijmegen, looking for ‘Café de Fiets’ for the very first meeting of the Introduction. Thank you for being my friend ever since. And Marije, my sister, over the years you have helped me move several times, and together we have painted many many square meters. Thank you for everything.

A special thanks goes to my family, especially my parents. For supporting me in the first place to go to Nijmegen to study Chemistry, and then again in my choice for a PhD position in Delft. Thank you, for all the support over the years, and for making the effort to ask about by work and to understand what it actually is I do on a daily basis.

And finally, Willem, my biggest supporter. You kept me going, especially during the hardest moments at the end of the process while finishing on one hand the papers and thesis, and on the other hand starting a new job and finding, buying and moving into a new house. I can’t thank you enough for your support and I think it’s now time to plan that much deserved vacation!

Publications

Journal papers

S.J.C. Granneman, N. Shahidzadeh, B. Lubelli and R.P.J. van Hees. Effect of borax on the wetting properties and crystallization behavior of sodium sulfate. CrystEngComm, 2017, 19, 1106–1114

S.J.C. Granneman, B. Lubelli, and R.P.J. van Hees. Characterization of lime mortar additivated with crystallization modifiers. International Journal of Architectural Heritage, 2018, 12, 849–858.

S.J.C. Granneman, B. Lubelli and R.P.J. van Hees. Effect of mixed in crystallization modifiers on resistance of lime mortar against NaCl and Na_2SO_4 crystallization. Construction and Building Materials, 2019, 194, 62-70.

S.J.C. Granneman, B. Lubelli and R.P.J. van Hees. Mitigating salt damage in building materials by the use of crystallization modifiers - a review and outlook. Under review at Journal of Cultural Heritage.

Book chapter

S.J.C. Granneman, R.P.J. van Hees and B. Lubelli, *Enhancing self-healing of mortars by built-in crystallization inhibitors*, in: Sybrand van der Zwaag & Eddy Brinkman (eds.), Self healing materials – Pioneering research in the Netherlands. IOS Press, Amsterdam, 2015.

Conference proceedings

S.J.C. Granneman, E. Ruiz-Agudo, B. Lubelli, R.P.J. van Hees, C. Rodriguez-Navarro, *Study on effective modifiers for damaging salts in mortar*. Oral presentation given at Ageing of Materials & Structures, 26-28 May 2014, Delft, The Netherlands.

S.J.C. Granneman, B. Lubelli, E. Ruiz-Agudo, and R. P.J. van Hees, *The use of crystallization modifiers in a lime mortar*. Oral presentation given at CRYSPOM IV, 11-13 June 2014, Amsterdam, The Netherlands.

S.J.C. Granneman, N. Shahidzadeh, B. Lubelli, R.P.J. van Hees, *Limiting salt crystallization in lime mortar by using crystallization modifiers*. Poster presentation given at SWBSS 2014, 14-16 October, Brussels, Belgium.

S.J.C. Granneman, B. Lubelli, R.P.J. van Hees, N. Shahidzadeh, *Using modifiers to mitigate salt crystallization damage in porous building materials: an optical microscopy study of borax and sodium sulfate.* Poster presentation given at ECCG5, 09-11 September 2015, Bologna, Italy.

S.J.C. Granneman, B. Lubelli and R.P.J. van Hees, *Borax influence on sodium sulfate crystallization in droplets and in carbonated lime*. Oral presentation given at CRYSPOM V, 6-8 June 2016, Toulouse, France.

S.J.C. Granneman, B. Lubelli and R.P.J. van Hees, *Lime mortar with mixed-in crystallization modifiers to mitigate salt* damage. Oral presentation given at the 10th International Conference on Structural Analysis of Historical Constructions, 13-15 September 2016, Leuven, Belgium.

S.J.C. Granneman, B. Lubelli and R.P.J. van Hees, *Mitigating salt damage in lime-based mortars with mixed-in crystallization modifiers*. Oral presentation given at the 4th WTA International PhD symposium, 14-16 September 2017, Delft, the Netherlands and at the 4th International Conference on Salt Weathering of Buildings and Stone Sculptures (SWBSS), 20-22 September 2017, Potsdam, Germany.

Curriculum Vitae

Sanne Granneman was born on November 17, 1987 in the Wieringermeer, The Netherlands. After completing her VWO (pre-university education) at RSG Wiringherlant in Wieringerwerf, she went to Nijmegen to study Chemistry at the Radboud University in 2006. In 2012 she obtained her Master's degree in Chemistry with the distinction 'Bene Meritum'. Her graduation project focused on the structure determination and adsorption mechanism of new anti-caking agents on {100} and {111} surfaces of NaCl. In March 2013 she started her PhD at the Faculty of Architecture and the Built Environment at the Delft University of Technology, where she worked on the development of more salt-resistant lime-based mortars by the use of crystallization modifiers. At the moment she is employed as a postdoc researcher at the High Field Magnet Laboratory of the Radboud University in Nijmegen. She works within the Horizon2020 framework MagnaPharm and studies the influence of high magnetic fields on the nucleation and crystallization behaviour of pharmaceutical crystals.