

ENHANCING SELF-HEALING OF LIME MORTARS BY BUILT-IN CRYSTALLIZATION INHIBITORS

By Sanne Granneman,
Barbara Lubelli,
and Rob P.J. van Hees
Architectural Engineering and
Technology,
A&BE, TU Delft

The weathering of porous materials due to the presence of salts has been known since antiquity. However, serious studies and investigations were not conducted until the 19th century. One of the fields of interest includes historic masonry, where salt damage can affect natural stone, brick and mortar (see Figure 1). Mortars are building materials, which are for example used in masonry, as the bonding material in between bricks or stones or as a plaster or render. Because of its pore size distribution (with both coarse as fine pores) and its relatively low mechanical strength, mortar is one of the building materials most affected by salt crystallization damage. As a consequence, replacement of plasters, renders and pointing mortars often constitutes a large part of total restoration costs. Salts present in masonry can originate, amongst others, from sea salt spray, rising damp, road salt, salt storage and the building materials itself.

The damage caused by salt crystallization is closely related to the location of crystallization. Crystallization at the

surface of a material (efflorescence) is relatively harmless. However, crystallization inside the material (crypto- or sub-florescence) can lead to severe damage. The damage is attributed to crystallization pressure. When a crystal grows in a confined space such as a pore, it will eventually have no more room to grow. However, usually there is still salt in solution present. When water from this solution evaporates, a supersaturated solution will form. The combination of crystal and supersaturated solution results in a pressure against the pore wall. Eventually the pressure overcomes the tensile strength of the material and cracking and crumbling will occur [1].

Even though much research has been undertaken, no definitive solution to prevent salt crystallization damage has been found yet. Recently research has started to examine the use of crystallization modifiers. These molecules alter the crystallization behaviour. They can prevent or delay nucleation (inhibitors), promote nucleation (promoter) and/or adsorb onto specific crystal faces, thereby changing the crystal morphology (habit modifier). The positive effects of modifying the crystallization behaviour can be lowering the supersaturation, or promoting the formation of efflorescences instead of crypto-florescences [1,2]. One of the aims of the PhD research of the first author is to develop a better salt resistant repair mortar, which already contains an inhibitor. The molecules will have to

be added to a fresh mortar, which can subsequently be used for restoration or renovation. Then, when salts penetrate the materials, they will cause less or no damage at all.

Amongst the most damaging salts for building materials are sodium chloride and sodium sulfate. The initial phase of the research was directed towards finding suitable modifiers for these salts. Sodium chloride is a salt, which has been already extensively researched and one of the effective modifiers, that has been identified is sodium ferrocyanide. This molecule not only inhibits the growth of sodium chloride but also modifies the crystal habit from cubic to dendritic. Previous laboratory tests show that instead of forming a layer with cubic shaped crystals, the sodium chloride crystals form feather-like crystals, which only poorly adhere to the pore surface (see Figure 2) [2]. In the case of sodium sulfate, phosphonates are often used as modifiers. However, these molecules only work at a specific pH range. Due to the high pH difference between fresh (pH 13) and hardened lime mortar (pH 9) it would be better to have a modifier, which is not pH sensitive. A possible molecule could be borax (sodium tetraborate). This molecule does not have a pH dependency, but might encounter other limitations such as complex formation with other compounds in the mortar [3].

The research currently carried out >>

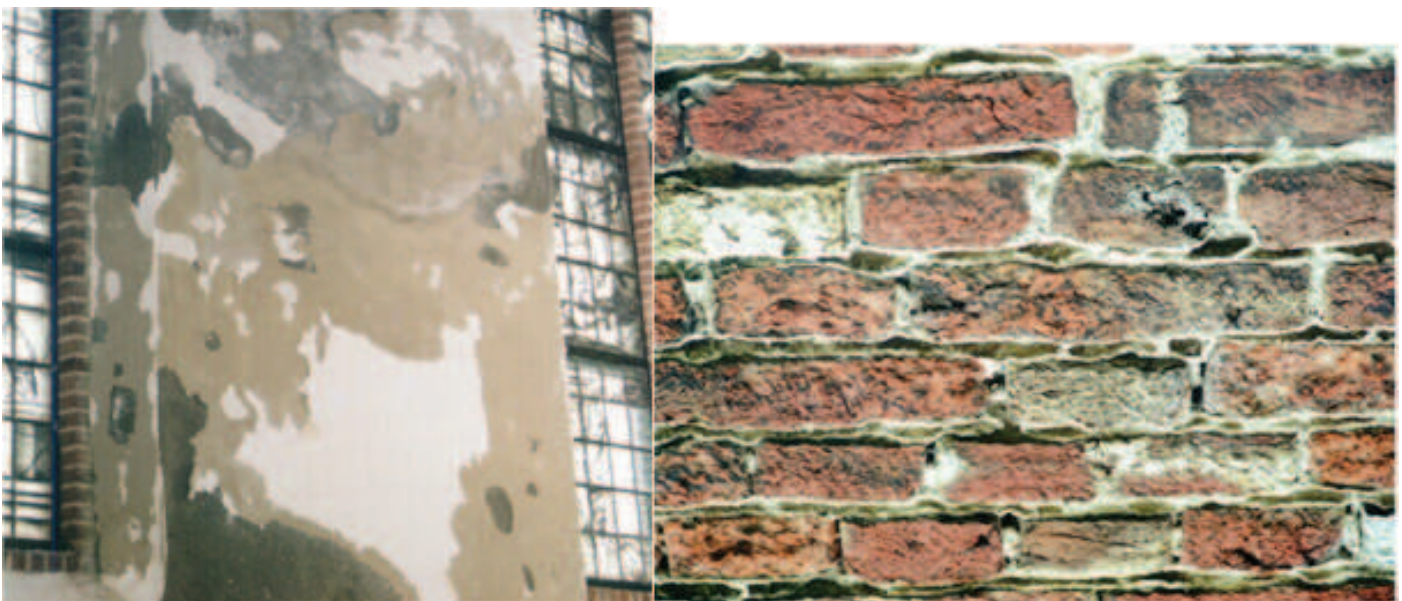


Figure 1. Salt damage in plaster (Church in de Rijp, the Netherlands) and pointing mortar (building in Oostkapelle, the Netherlands)

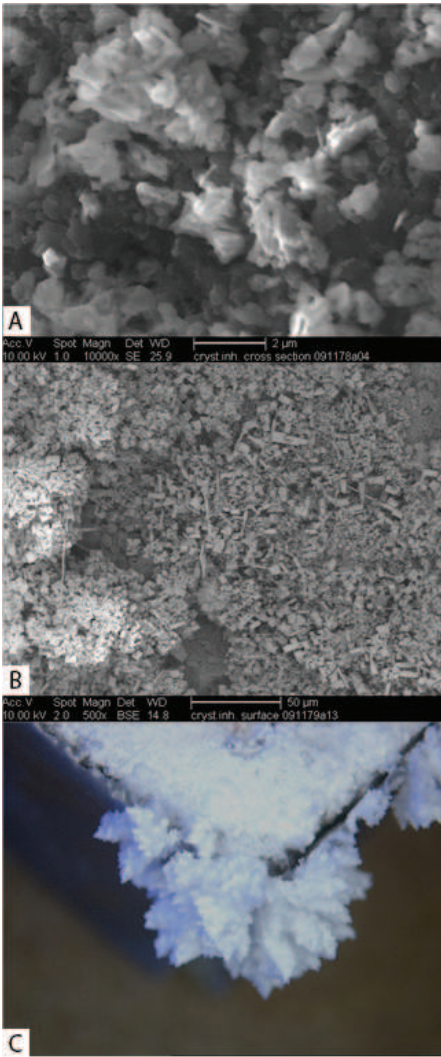


Figure 2. Images showing the effect of sodium ferrocyanide on NaCl growth. Inhibitor added to the salt solution. (A) SEM picture of a cross-section showing non-cubic crystallization in a pore, 10000x magnification. (B) SEM picture showing crystallization at the surface of a porous material, 500x magnification. (C) Macroscale picture of dendritic, feather-like crystallization at the surface of a brick

in this project focuses on the interaction of modifiers with the crystal surface, aiming at gaining in-depth knowledge on the influence of modifiers on the crystal growth and the crystallization damage. This process is studied by means of molecular modelling and laboratory experiments. Furthermore, bulk crystallization tests will be performed in order to study the influence of concentration and pH on the effectiveness of the modifiers and the possible interaction between lime mortar components and inhibitor

(e.g. complex formation, adsorption on calcite). In a later stage, the effect of the addition of modifiers on the workability of a fresh mortar, and on the hygric and mechanical properties of a hardened mortar will be studied.

References:

1. Template-Assisted Crystallization of Sulfates onto Calcite: Implications for the prevention of Salt Damage. E. Ruiz-Agudo, C.V. Putnis, L. Pel and C. Rodriguez-Navarro. *Crystal Growth & Design*, 2013, Vol. 13
2. Effect of mixed in crystallization inhibitor on resistance of lime-cement mortar against NaCl crystallization. B. Lubelli, T.G. Nijland, R.P.J. van Hees and A. Hacquebord. *Construction and building materials*, 2010, Vol. 24.
3. Damage mechanisms of porous materials due to in-pore salt crystallization. M. Schiro, E. Ruiz-Agudo and C. Rodriguez-Navarro. *Physical Review Letters*, 2012, Vol. 109.

A DEDICATED BBC 4 RADIO PROGRAM DCMAT RESEARCH ON SELF-HEALING MATERIALS !!

As we all know, the DCMat research often attracts international attention because of its quality and innovative features. Very recently BBC radio 4 did send a reporting team to Delft to make a 30 minutes documentary about the latest developments in Self Healing Materials and the leading position DCMat plays in this international field.

In the documentary our work on self-healing asphalt, concrete, polymers, coatings, ceramics, metals, catalysts and interfaces will be presented. The program will be broadcasted in November on BBC 4 and at a slightly later stage on BBC world. The link to the documentary will be placed on the DCMat website as soon as it is available.

FROM EARTH'S BUILDING BLOCKS TO METALLIC PLANETARY CORES: A HIGH PRESSURE, HIGH TEMPERATURES STUDY TO INVESTIGATE PLANETARY CORE FORMATION AND TERRESTRIAL PLANETARY INTERIORS

The largest differentiation event in Earth and other terrestrial planets was the process of early metal core segregation from a silicate mantle. As movement of molten metal generates a magnetic field that helps life on Earth to survive cosmic radiation, the study of core formation contributes to our understanding of the context of the origin of life on Earth and possibly elsewhere in the Solar System (fig.1). Studying core formation scenarios in terrestrial planetary bodies was topic of the PhD thesis of Josepha Kempf, who recently joined the Department of Environment and Materials, CEG as a post-doctoral researcher to study inorganic self-healing mechanisms in building materials.

Investigating planetary interiors is

nowadays experimentally performed at high pressure and high temperature (HPT) conditions. For the experimental set-up, HPT resistant materials are applied in machines such as e.g. multi-anvil presses. Sample materials, simulating rock compositions of the deep Earth are filled into noble metal capsules and exposed to temperatures of up to 2300°C and pressures of more than 25 GPa in a Tungsten-Carbide cubic assembly (fig.2). This equals Earth's depths of ca. 750 km and more.

The experimental set-up chosen in Josepha's thesis simulated the segregation of a silicon bearing molten iron metal alloy from a silicate melt between 9 and 15 GPa and 1800 - 2300°C (fig.3). Samples were

investigated by electron microprobe (EPMA) and multi collector (MC) inductively coupled plasma mass spectrometry (ICP-MS), to determine Si element partitioning and Si >>

