Self-healing of lime based mortars: microscopy observations on case studies

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Lime mortars have, up to a certain extent, a self-healing capacity which may contribute to their durability. Self-healing in lime mortars consists of a process of dissolution, transport and re-precipitation of calcium compounds to heal cracks and fissures.

The spontaneous occurrence of self-healing in lime-based mortars is a well known phenomenon; to date, however, little research has been done on its occurrence in the practice. This study aims at gaining a better understanding of the self-healing mechanism in lime-based mortars through the investigation of case studies where self-healing has been observed. On the basis of the results obtained the relevance of the various controlling factors, the way in which they potentially interact, and how they affect the occurrence of self-healing is evaluated.

Lime-based mortar samples collected from several case studies were studied. Thin sections were prepared and studied by means of Polarization & Fluorescence Microscopy (PFM). The influence of selected parameters (moisture content, degree of carbonation, binder-sand ratio, binder type, etc.) on the nature (calcium carbonate or calcium hydroxide) and crystal habits of the precipitated products has been investigated.

The results obtained indicate that some recurrent patterns exist in the nature and the crystal habits of the re-precipitated products depending, among other factors, on the moisture content and on the degree of carbonation of the mortar.

Key words: Self-healing, lime mortars, calcite, portlandite, microscopy

1   Introduction

Historical masonry buildings testimony that lime based mortars can have a very good durability. The durability of lime mortars is partly due its good deformability, i.e. to its

capability of following the deformation of the constructions, better than current (stiff) cement-based mortars. Besides, lime mortars have, up to certain extent, a self-healing capacity, which contributes to their durability.

A self-healing process can be defined as a spontaneous (or with small external trigger) in-situ repair of micro-damage occurring to materials as consequence of weathering or overloading processes. The self-healing process in lime mortar can be summarized as follows: (rain) water allows the dissolution of calcium bearing compounds and transport them, from a zone rich in binder, to voids and cracks eventually present in the mortar. In this way small cracks may be filled with re-crystallized calcium compounds, in a natural self-healing process. Self-healing of historical lime mortar is therefore a natural and spontaneous process, and not the result of special design features.

For the sake of clarity, it is necessary to distinguish the process of dissolution and re-precipitation of calcium compounds from the process of dissolution and re-crystallization of soluble salts. The first process interests little soluble calcium compounds and occurs therefore in materials with high moisture content, where water percolates in fissures and cracks; its effect is either self-healing, if re-precipitation occurs in the voids and crack in the material, or formation of encrustations, if re-precipitation occurs at the surface. The second process interests soluble salts: these can be dissolved even in the presence of a relatively low moisture content in the material and transported in solution through the pore system of the material mainly by capillary forces. The effect is the formation of efflorescences, if crystallization occurs at the surface, or crypto-florescences, if crystallization occurs in the pores of the material. Where efflorescences cause only an aesthetical damage, crypto-florescences may lead to high crystallization pressures in pores and possibly damage the material.

It is tempting to compare self-healing of lime mortar with carbonate diagenesis in sedimentary basins. Here diagenesis progresses by dissolution and re-precipitation of calcite. Similarly, dissolution and precipitation processes determining (destroying) porosity and permeability in carbonate oil and gas reservoirs [e.g. Nickel 1976, Bjørlykke 1989, Morse & Arvidson, 2002] are processes at least to some extend comparable to self-healing mechanisms. However, major differences exist between diagenesis in sedimentary basins and self-healing in lime mortars:

- In nature mainly $CaCO_3$ occurs, whereas in not yet carbonated lime mortars, next to $CaCO_3$, also $Ca(OH)_2$ is present. Besides, lime mortars may also contain little amount of CaO.

- Pressure solution, which is likely to occur in sedimentary basins, is not a relevant factor in masonry.

- Temperature in sedimentary basins is in many cases higher than in masonry.

- pH in sedimentary rocks can be comparable to that lime mortar; however, when cement or pozzolanic material is added the pH of the mortar is likely to be higher [Moropoulou et al 2004].

While several literature sources on carbonate diagenesis are available, little specific research has been done on the self-healing process in lime mortars. Up to now, most of the research on self-healing in building materials has been carried out on cement based materials [Dhir et al., 1973; Jacobsen & Sellevold, 1996; Hearn & Morley 1997; Edvardsen, 1999; Neville 1999, Reinhardt & Jooss, 2003; Granger et al. 2007; ter Heide & Schlangen, 2007, Qian et al., 2009], whereas only few experiments on lime-based mortars are reported in literature [Anderegg, 1942]. Question regarding the factors affecting self-healing and the time-span at which it occurs are still subject of discussion.

Solving these questions will allow improving the self-healing capacity of (restoration) lime mortars by, for example, choosing the most favourable binder/sand ratio or type of lime binder.

In this paper, the parameters possibly influencing the self-healing process are suggested and discussed on the basis of the results of investigations performed on case studies.

2 Factors possibly influencing self-healing

Self-healing occurs by dissolution and re-precipitation of calcium compounds. This implies that the following parameters can be identified as possibly influencing the self-healing process in lime mortars:

- Amount and nature of available calcium compounds
- Degree of carbonation of the mortar
- Presence of other phases or elements influencing the solubility of Ca-bearing compounds
- Exposure and microclimate conditions (moisture content, temperature, pH)

Amount of available calcium compounds

The content of calcium compounds increases with the binder/aggregate ratio and with the use of a carbonaceous (limestone) aggregate. Ancient mortars have usually higher binder content than modern ones [van der Kloes, 1924], which might be an explanation of their good self-healing capacity.

Degree of carbonation of the mortar

In high calcium lime mortars, two Ca-bearing compounds are present: $Ca(OH)_2$ and $CaCO_3$, the latter usually as calcite, though minor amounts of (metastable) aragonite and vaterite might be present. The first prevails in relatively fresh mortars, the second in mortars with a high degree of carbonation. Since carbonation is a slow process, proceeding from the surface in contact with air towards the inner part of the mortar, it is not unusual to find not carbonated mortar even in century old walls.

The degree of carbonation is relevant since self-healing is likely to be influenced by the solubility of the calcium compounds; without dissolution, no transport and re-precipitation can occur. The solubility of $Ca(OH)_2$ being about 100 times higher than that of all three $CaCO_3$ polymorphs, the process of dissolution will be much easier in the first case. It can therefore be expected that self-healing will preferentially occur in not fully carbonated lime mortars, where the not yet carbonated part will provide $Ca(OH)_2$ to fill thin cracks.

Presence of other phases or compounds influencing this solubility

The presence of other components or impurities (organic and inorganic) may influence the solubility of Ca compounds. $Na(OH)$ and Na_2CO_3 can strongly decrease calcite solubility, while K_2SO_4 and $CaSO_4$ slightly decrease it. Among inorganic compounds which might be present in masonry, Na_2SO_4, and KCl are the ones increasing $CaCO_3$ solubility at most. NaCl and MgCl have a smaller effect [Boynton, 1980]. In all cases, however, calcite remains moderately soluble only. More relevant to self-healing are probably the effects on the solubility of $Ca(OH)_2$. Among inorganic phases NH_4Cl considerably increases $Ca(OH)_2$ solubility (it can triply it), while NaOH causes a strong decrease of this solubility, even at low NaOH concentrations. The presence of impurities (mainly salts) in masonry can therefore be expected to affect dissolution and re-precipitation of calcium compounds. MgO and impurities such as silica, and alumina, do not affect $Ca(OH)_2$ solubility, but may retard its rate of solution [Boynton, 1980]. Impurities can not only inhibit or enhance the processes of dissolution and precipitation but also favour crystallization of a specific

polymorph of $CaCO_3$ (calcite, vaterite or aragonite). For example the presence of Mg (as in dolomitic limes) may favour the precipitation of aragonite instead of calcite [Boynton, 1980]. Aragonitic grains are more susceptible to leaching than calcite [Longman, 1980]. This may be relevant for dolomitic mortars and trass- and pozzolanic-lime mortars and explain the better self-healing capacity observed for dolomitic lime [Anderegg, 1942].

Another difficulty in modelling the dissolution of relatively insoluble minerals as calcite is given by the fact that, taking into account diffusion controlled kinetics only is not enough. In fact, diffusion controlled dissolution prevails for diluted solution, but as soon as the solution reaches a higher concentration, surface controlled dissolution prevails. This means that dissolution rate of calcite (or other crystals) is not simply linearly related to the concentration of the surrounding solution, but is affected by several factors such as defects, dislocations, kinks and edges in the crystal [Morse & Arvidson, 2002].

Microclimate conditions (moisture content, temperature, pH)

Being calcite much less soluble than calciumhydroxide, we can suppose that the speed of carbonation will influence the occurrence of self-healing. Carbonation can only occur in the presence of some liquid water: a completely dry mortar does not carbonate [Korneev & Tsvang, 1986; Moorehead, 1986] even at very high RH [ter Heide & Schlangen, 2007], neither does a water-saturated mortar. Moreover, the presence of wet-dry cycles enhances carbonation.

The moisture content in the mortar is expected therefore to be one of the key-factors for the occurrence of self-healing. Without water no dissolution and transport can occur; on the other hand if the mortar is constantly immersed in water, no carbonation will occur and re-precipitation will be inhibited and leaching of the binder instead of self-healing will be favoured.

The temperature and pH are also relevant for the self-healing process, because they both influence the rate of dissolution. Since the solubility of calcite decrease with temperature, precipitation will be favoured at higher temperature. A slightly acid pH, as it occurs in rain water rich in CO_2, favours calcite dissolution: experimental studies have shown that the effect of pH on the rate of dissolution of calcite is only relevant for values lower than 6 [Morse & Arvidson, 2002].

3 Set up of the research

An archive of thin sections of mortars from (historic) masonry buildings located in the Netherlands has been screened. For each of the samples showing self-healing in lime mortar, information has been collected on the type of mortar (binder and aggregate type and ratio) and on the boundary conditions (moisture content in the wall, presence of damage processes). Microscopy observations have been then carried out on thin sections by the use of polarization and fluorescence microscopy (PFM).

Figure 1: Masonry wall of the drink water company in Rotterdam

Figure 2: Polarization-and-fluorescence microscopy (PFM) image showing re-precipitation of calcite in cracks; (200x magnification (0.7 x 0.45 mm), cross polarized light (Drink water company, Rotterdam)

Particular attention has been given to identify the type of re-precipitated compounds, their size and crystal habit and mutual arrangement, the place of precipitation of the new Ca-compounds (e.g. on the crack walls, in thin cracks in lime lumps, in voids, etc.) and the location of the healed crack (near the surface in contact with the atmosphere or at depth in the wall). These parameters have been related to the factors considered relevant for the occurrence of self-healing, i.e. amount of calcium compounds (i.e. binder-aggregate ratio and presence of calcitic aggregate) and moisture content.

The results of the PFM observations on the case studies showing self-healing are presented in the following sections.

4   Results of PFM study on thin sections

4.1   Drink water company, Rotterdam

This brick masonry structure dates back to 1873; the mortar binder is air lime with the addition of some trass providing hydraulic properties to the mortar. The masonry is partially immersed in water, and it has therefore a high moisture content. Calcite encrustations are visible on the masonry surface (Fig. 1), due to leaching of the mortar binder.

Thin sections of samples taken from the masonry show the occurrence of re-precipitation of $CaCO_3$ in cracks (Fig. 2). Calcite crystals are observed to grow on the crack walls, and to fill 50-70 μm wide cracks.

Figure 3: Hunting Lodge St. Hubertus – overview

4.2   Hunting lodge St. Hubertus

The hunting lodge St. Hubertus is a brick masonry building dating back to 1915-1920 (Fig. 3). The mortar binder is hydraulic lime. Calcite encrustations, due to leaching of the mortar, are visible at the surface of the masonry of the walls of the balcony (Fig. 4). Here a high moisture content (between 7 and 15 wt%) was measured.

In the thin sections of the cores sampled from the balcony wall, re-precipitation of $CaCO_3$ has been observed. Small $CaCO_3$ crystals have grown in voids, cracks (Fig. 5) and lime lumps (Fig. 6). The $CaCO_3$ crystals do not completely fill the cracks, but only reduce their width.

4.3   Defence wall, Den Bosch

The defence wall in Den Bosch is a brick masonry structure, partially immersed in water. The moisture content in the wall is very high (up to 20 wt %). The mortar binder is air lime, with the addition of some trass.

In the cores sampled at the masonry surface, re-precipitation of $CaCO_3$ in cracks has been observed. The $CaCO_3$ has crystallized as relatively well developed, rhombohedral crystals, nucleating on the crack walls and growing outwards to completely (Fig. 7 and 8) or partially (Fig. 9) fill the cracks. In the core sampled in depth in the masonry (65 cm from the surface) well developed, large $Ca(OH)_2$ crystals have been observed, filling voids and cracks (Fig. 10 and 11).

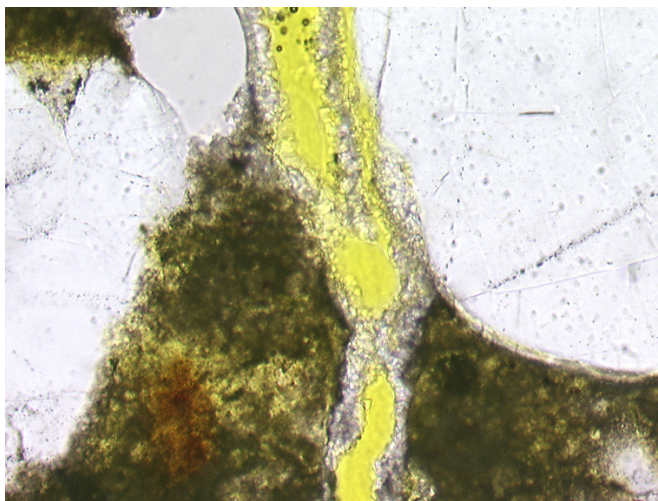*Figure 4: Hunting Lodge St. Hubertus – balcony wall*

Figure 5: Polarization-and-fluorescence microscopy (PFM) image showing re-precipitation of calcite on crack walls; 200x magnification (0.7 x 0.45 mm), cross polarized light (Hunting Lodge St. Hubertus)
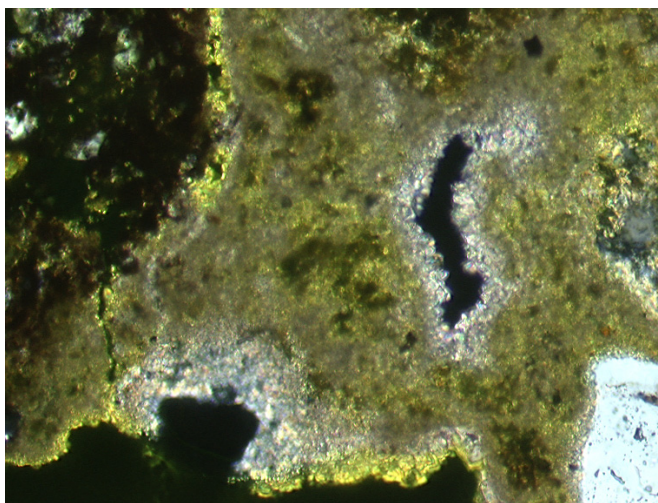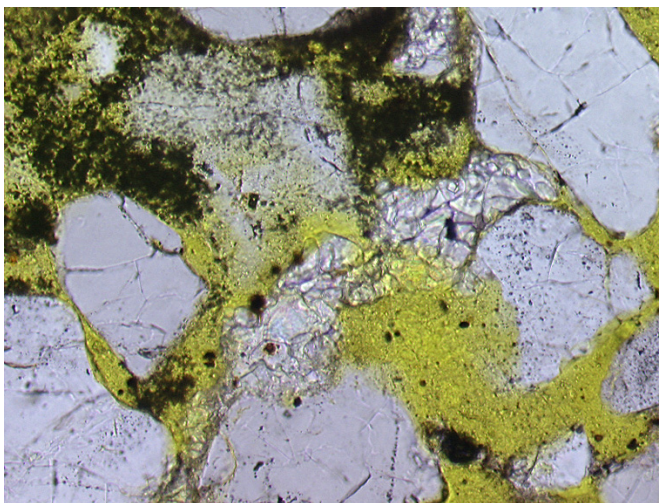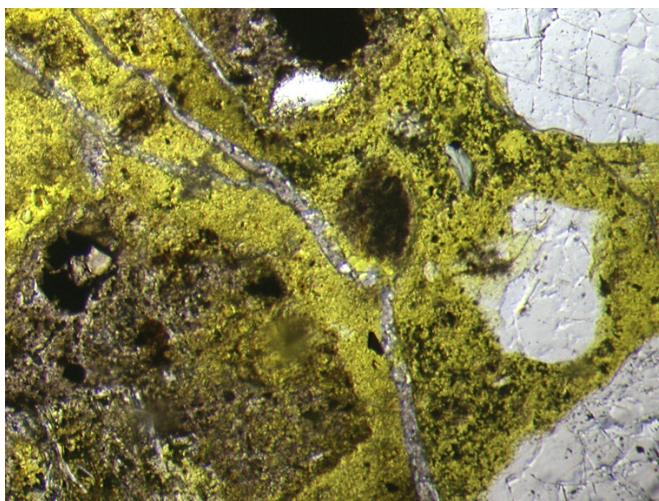

Figure 6: PFM image showing re-precipitation of calcite in voids; 200x magnification (0.7 x 0.45 mm), cross polarized light (Hunting lodge St Hubertus)

Figure 7: PFM image showing re-precipitated CaCO$_3$ entirely filling a crack;
200x magnification (0.7 x 0.45 mm), plane polarized light
(Defence wall, Den Bosch)

Figure 8: PFM image showing re-precipitated CaCO$_3$ effectively filling a crack;
100x magnification (1.4 x 0.9 mm), plane polarized light
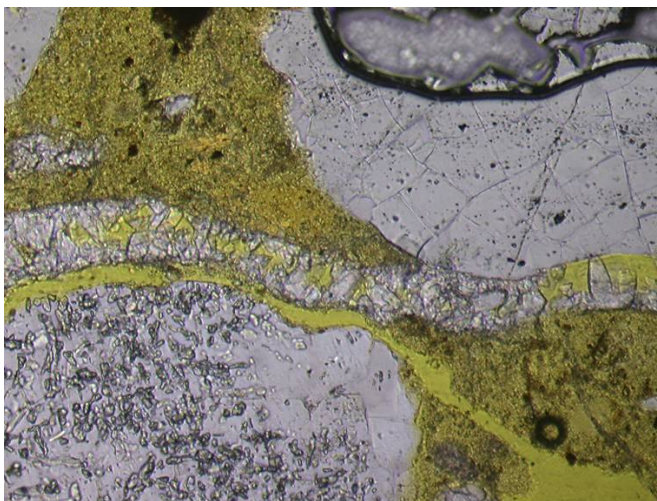*(Defence wall, Den Bosch)*

Figure 9: PFM image showing re-precipitated CaCO₃ effectively closing a crack without completely
filling it; 200x magnification (0.7 x 0.45 mm), plane polarized light
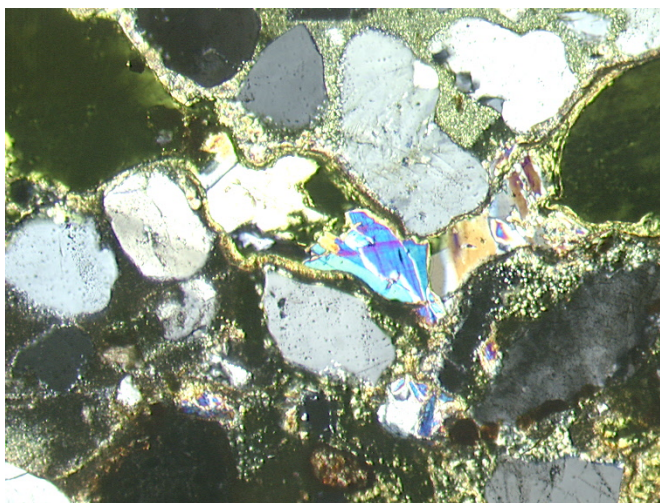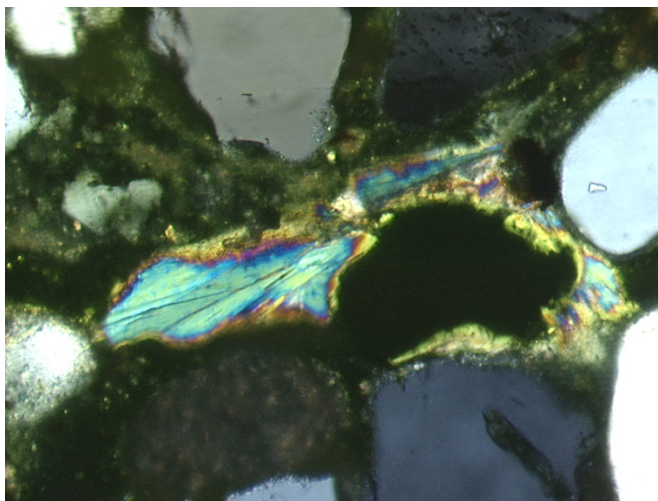*(Defence wall, Den Bosch); note the relatively well developed crystal faces.*

Figure 10: PFM image showing Ca(OH)₂ completely filling a void;
100x magnification (1.4 x 0.9 mm), cross polarized light
(Defence wall Den Bosch, about 65 cm from the surface of the wall). Note the remarkably large size
of the portlandite crystals, with single crystals bridging the void, their longest crystal axis oriented
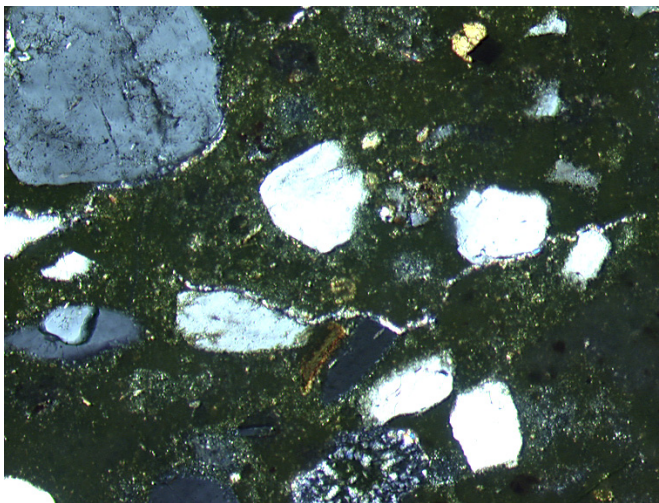*more or less perpendicular to the void walls*

Figure 11: PFM image showing re-precipitation of portlandite in a void;
200x magnification (0.7 x 0.45 mm), cross polarized light
(Defence wall Den Bosch, about 65 cm from the surface of the wall)
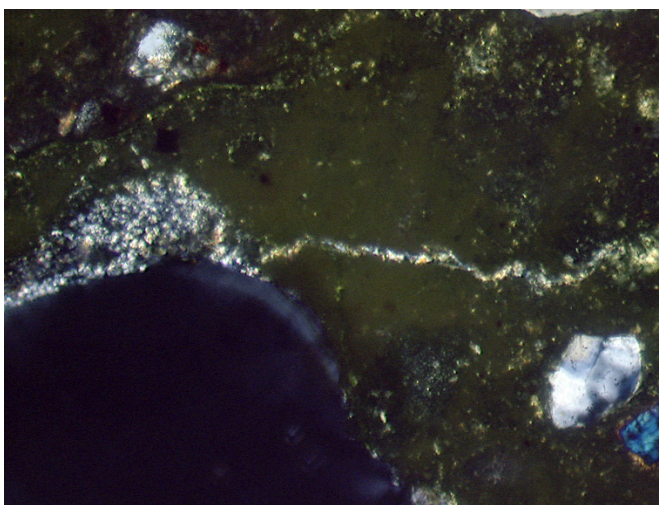
4.4   *Defence wall in Bergen op Zoom*

The brick masonry structure of the defence wall in Bergen op Zoom dates back to the beginning of the 18th century. The mortar is a trass-lime mortar. The moisture content in the wall is very high (up to 50 wt%), due to the fact that the structure is partially immersed in water. Encrustations, due to leaching of the mortar, are visible on the surface of the masonry.

In the thin sections, besides wider open cracks, narrow cracks are present filled by secondary phases. Both $CaCO_3$ (Fig. 12) and portlandite (Fig. 13) crystals fill some of the narrowest cracks; they do, however, never occur together in the same crack, nor in mutual contact. Both $CaCO_3$ and portlandite crystals are very small. Larger $CaCO_3$ crystals also occur in layered precipitates at the mortar – brick interface and in voids. Portlandite occurs at locations far from the masonry surface. Portlandite filled cracks are subordinate to carbonate filled ones. In addition to cracks filled by either calcium carbonate or portlandite, cracks filled by gypsum occur. Given the potential of gypsum for further sulfate attack, these cannot be considered a self-healing feature (cf. Nijland et al. 2007).

*Figure 12: Polarization-and-fluorescence microscopy (PFM) image
showing narrow crack filled by carbonate;
100x magnification (1.4 x 0.9 mm), cross polarized light
(Defence wall, Bergen op Zoom)*

*Figure 13: Microphotograph showing a crack in 19th century lime mortar,
filled completely by fine grained portlandite;
200x magnification (0.9 x 0.45 mm), cross polarized light
(Defence wall, Bergen op Zoom)*

4.5 Bridge, Amsterdam

The bridge (Fig. 14), located in Amsterdam, dates back to 1728. It is a masonry structure composed by fired clay bricks and trass-lime mortar. The moisture content in the masonry structure is very high (up to 42 wt%). On the surface of the masonry encrustations, due to leaching of the mortar, are visible.

In the thin section re-precipitation of $CaCO_3$ in cracks has been observed. The $CaCO_3$ crystals have grown to close the cracks and fill them almost completely (Fig. 15).
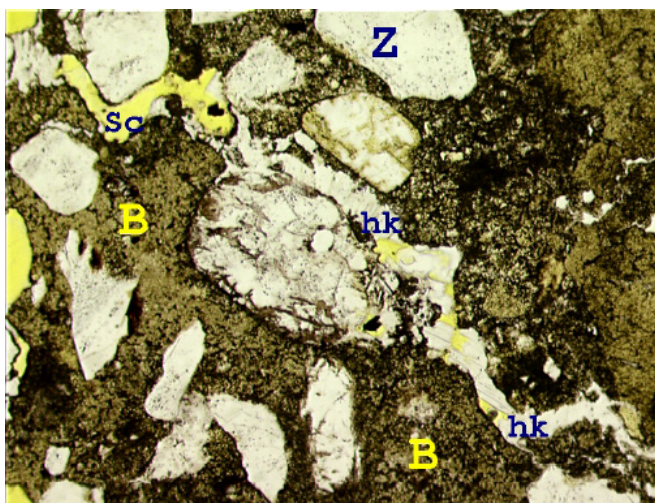

Figure 14. The bridge in Amsterdam

Figure 15. Microphotograph showing a crack filled by calcite;
50x magnification (2.7 x 1.4 mm), cross polarized light (Bridge, Amsterdam)

5   Discussion and conclusions

Self-healing has been observed in air lime-, hydraulic lime- and pozzolanic lime-based mortars. A necessary condition for the occurrence of self-healing seems to be the presence of a considerable amount of free lime: in mortars with only cement as binder no self-healing has been observed. Apparently, the amount of free $Ca(OH)_2$ produced by hydration of portland cement clinker is not enough to result in any effective self-healing. This suggests that adding free lime to cement-based mortars might provide their self-healing capacity. The optimal amount of free lime to be added in order to reach self-healing and, at the same time avoid excessive leaching in wet conditions, needs to be investigated.

A second necessary condition for the occurrence of self-healing is the presence of a high moisture content in the wall. In fact, due to the low solubility of calcium compounds, sufficient water should be available for their dissolution and transport towards the crack. At the same time drying periods are necessary since they enhance re-precipitation of the calcium compounds in cracks and voids and allow carbonation of portlandite. All cases in which self-healing has been observed in this study are buildings which have a high water supply but also the possibility to dry. The presence of wet-dry cycles has been shown to be a key-factor for the occurrence of self-healing.

Re-precipitation of both $CaCO_3$ and $Ca(OH)_2$ in cracks has been observed. $Ca(OH)_2$ is found as large, well formed crystals, in depth in the wall, in structures with extremely high moisture content, where carbonation is inhibited. $CaCO_3$ is more frequently observed as small crystals, growing on the cracks' sides, not far from the evaporation surface. Sometimes $Ca(OH)_2$ small crystals filling thin cracks are observed next to cracks healed by $CaCO_3$. These findings suggest that self-healing of cracks by calcite can take place by re-crystallization of portlandite and subsequent carbonation to $CaCO_3$. Alternatively, direct precipitation of $CaCO_3$ in cracks may also occur. It should also be mentioned that the different polymorphs of $CaCO_3$ (vaterite, aragonite, calcite) may influence dissolution and re-crystallization and therefore the occurrence of self-healing [Nijland et al., 2007].

The observations on thin sections from a building can not definitely clarify the exact sequence of dissolution/ re-precipitation / carbonation of calcium compounds leading to self-healing. Mortars are sampled from centuries-old masonry and most of the time we only observe the final result of a process which has occurred in several decades. Laboratory experiments, aiming at reproducing the dissolution/re-crystallization processes occurring in self-healing, are running at the moment and might elucidate this issue.

As closing remark, it should be mentioned that the nature of self-healing observed in these mortars (natural, without any additions or special design features), poses an important question, i.e. the source of the Ca. This is the mortar itself, implying that whereas at one location self-healing occurs, at other locations new porosity will be generated which may decrease the durability of the mortar. However, blocking the cracks is likely to have a more relevant effect, resulting in overall improvement of the mortars durability.

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