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SIMULATION OF SELF-HEALING OF DOLOMITIC LIME MORTAR

Barbara Lubelli [a,b], Timo G. Nijland[b], Rob P.J. van Hees [a,b]
a. Faculty of Architecture, Delft University of Technology, b.lubelli@tudelft.nl, r.p.j.vanhees@tudelft.nl
b. TNO, Delft, barbara.lubelli@tno.nl; timo.nijland@tno.nl; rob.vanhees@tno.nl

Abstract

In the present research a test procedure was set up to reproduce self-healing on lime-based (both pure calcium and magnesium-calcium) mortar specimens in laboratory. After few months testing, during which the specimens were subjected to wet-dry cycles, thin sections of the specimens were prepared and observed by Polarization and Fluorescence Microscopy (PFM) and by Scanning Electron Microscope (SEM) equipped with Energy-dispersive X-ray spectroscopy (EDX). The specimens prepared with dolomitic lime showed the occurrence of self-healing: a magnesium compound is observed filling cracks and voids. These results suggest new possibilities for the development of dolomitic lime mortars with an increased self-healing capacity.

Keywords: self-healing, dolomitic mortar, PFM, SEM-EDX

Introduction

Autogeneous self-healing, i.e. the repair of (micro)cracks by the material itself without intentional human intervention, is known to occur spontaneously in historic lime and lime-pozzolana mortars. The self-healing process in lime mortar can be summarized as follows: water dissolves 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 compounds, in an autogeneous self-healing process. The occurrence of this phenomenon has for example been shown in a microscopic survey of over 1000 of samples of concrete and masonry mortars from structures of different periods in the Netherlands (Nijland et al., 2007, Lubelli et al., in press).

The property of engineered self-healing would greatly enhance durability of modern materials, including those for repair and restoration; a range of potential routes are open for this for different materials (e.g. Van der Zwaag, 2010). In case of mortars, mimicking the natural behaviour of historic mortars may be a potential way. This would imply stimulation of the re-crystallization of calcium hydroxide, $Ca(OH)_2$ or carbonate, $CaCO_3$ (either calcite, aragonite or vaterite) in response to cracking. This has also been advocated for concretes (e.g. Granger et al. 2006, ter Heide & Schlangen, 2007). However, in order to reach a durable self-healing effect, sealing of the crack by less soluble phases should be preferred.

In-situ (e.g. Polder & Larbi 1995) and laboratory (e.g. Leegwater et al. 2007) studies of concrete show that exposition of concrete in seawater may result in deposition of a surface layer of brucite, $Mg(OH)_2$, which, after deposition, protects the concrete from future degradation. Brucite is relatively insoluble; sealing of cracks in mortar by brucite would therefore be a more definitive self-healing than by Ca-phases. Engineered self-healing following the brucite path would, of course, require the presence of (soluble) magnesium in the mortar composition. A way to fulfill this bulk chemical requirement would be the use of mortars based on dolomitic lime. Such mortars have been used in different European regions from the Roman period up to the early 20th century (Mannoni et al., 2006, Diekamp et al., 2009) and are mentioned to have a better self-healing potential than pure calcium mortars (Anderegg, 1942). This paper reports the first results of a study to prospect the self-healing potential of dolomitic lime mortars.

A main difficulty in the study of self-healing is the difficulty of reproducing and following this process in laboratory on a realistic timescale. In the present research, an accelerated procedure has been developed which allowed to obtain self-healing in some of the studied mortar types in a few months time.

Materials and methods

Mortar specimens were prepared using different binder types and sand/aggregate ratios, in order to evaluate the effect of these variables on the self-healing capacity of the mortar. Both calcium and dolomitic lime binders were used. Calcium lime is a traditional binder, used nowadays mainly in restoration because of its high compatibility with ancient materials. Dolomitic lime mortar was common in some European region from the Roman period up to the early 20th century and appreciated for its long term strength, higher than that of high calcium lime (Diekamp et al., 2009). Nowadays dolomitic lime is scarcely used because of the delayed hydration of over burned MgO causing pitting of popping in the mortar and the risk of formation, in a wet environment, of harmful magnesium sulfate salts in the presence of sulfates from air pollution or gypsum containing building materials. Dolomitic lime was included in this study in order to stimulate the formation of brucite, which, being relatively insoluble, would lead to a more durable self-healing than calcium compounds. Besides, Anderegg (Anderegg, 1942) suggests dolomitic lime mortars might have a better self-healing capacity than pure calcium lime.

The following binder products were used to prepare the mortar:

- Pure calcium hydrated lime powder (Supercalco 90 by Carmeuse, NL)
- Dolomitic hydrated lime powder (by Piasco, I) having 60% CaO, 34% MgO and impurities of SiO_2, Al_2O_3, Fe_2O_3, CO_2 and sulfates.

Two binder/sand ratios were selected in order to investigate the influence of the amount of available lime components on the occurrence of self-healing: 1:3 and 1:1 by volume. A 1:3 ratio by volume is common nowadays, while higher binder/sand ratio were more usual in historic mortars (Van Balen et al., 2003). Siliceous sand (CEN Standard Sand certified in accordance with EN 196-1 - ISO Standard Sand conforming to ISO 679), sieved to select the grain fraction 0.08 - 1 mm.

Four different types of mortar were prepared. Two specimens were made for each mortar type: one was embedded in epoxy resin just after curing to seal the specimen; the other one was used in the ageing test. The mortar specimens were prepared in molds (4 x 4 x 16 cm) and unmolded as soon as they reached sufficient strength. The specimens were then cured at 20 °C / 65 % RH for 2 weeks and subsequently artificially carbonated at 20 °C, 70% RH and 1 % CO_2. The achievement of the complete carbonation was checked by spraying a freshly broken surface with phenolphthalein.

At this point, the test attempting to reproduce self-healing in laboratory could start. Specimens were immersed in boxes (one for each specimen) containing water at pH 5 obtained by the addition of CO_2. The boxes were stored at 5 °C. The low temperature and the slightly acid pH were chosen to favor dissolution of the lime components (Boynton, 1980). After a period of three months, the water in the containers was removed (but preserved), and specimens were dried at room temperature and a mold was built on the top of each specimen (figure 1). The previously removed water, enriched in Ca and Mg-compounds dissolved from the mortar in the first phase of the test, was poured at the top of the specimen, whilst the bottom surface was left free to dry. In this way, a percolation process was replicated. The water reservoir was refilled every two weeks in order to simulate wet-dry cycles. In total 10 cycles were performed in a period of about 5 months. This procedure was chosen because previous research on mortar samples collected from existing structures has shown that self-healing is most frequent in those situations (like bridges, defense walls, etc.) where an intermittent (abundant) supply of water is present (Lubelli et al., in press).

After a few months cycling, the specimens were dried at 40 °C and thin sections were prepared. The thin sections, vacuum impregnated with an epoxy resin containing a fluorescent dye, were observed by Polarization and Fluorescence Microscopy (PFM) to identify the eventual occurrence of self-healing and assess the extent of its eventual occurrence. Some of the thin sections were not covered with glass and studied by high resolution Scanning Electron Microscopy (SEM) (FEI NovaNanoSEM650) equipped with Electron Dispersive X-ray Spectroscopy for the identification of the compounds precipitated in cracks and voids. Thin sections have been prepared perpendicular to the length of the prisms.

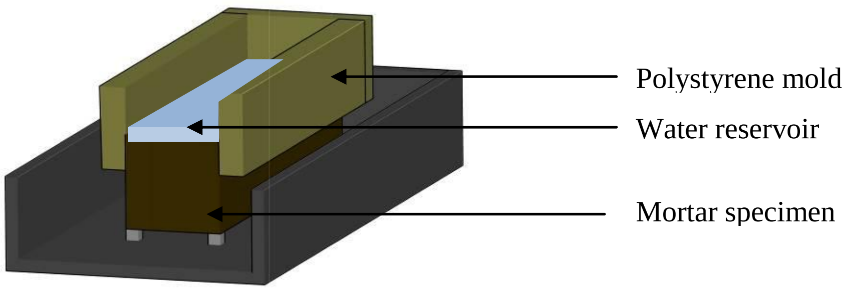


Figure 1: Test set up

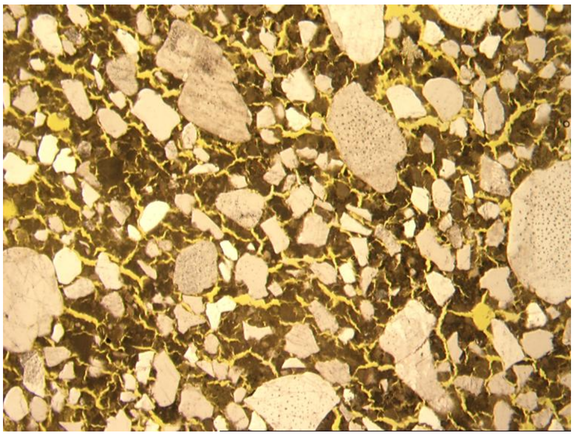
Results and discussion

Polarization and Fluorescence Microscopy (PFM) observations

PFM observations were carried out on thin sections obtained from the mortar specimens before and after the ageing test.

In the calcium lime mortar specimens, both 1:1: and 1:3 binder/sand ratio, no significant re-precipitation of calcium compounds in cracks and voids is observed after the test. The specimen with binder/sand ratio 1:1 shows severe cracking due to shrinkage (figure 2). The mortar with a lower binder/sand ratio is very lean, with a large amount of coarse pores (diameter up to 0.5 mm) (figure 3). The leaching of the binder in the first phase of the test might have contributed to increase the already high porosity.

The specimen prepared with dolomitic lime and a binder/sand ratio 1:1, also shows the presence of shrinkage cracks, but their amount is much less than observed in the calcium lime mortar. No self-healing is observed.



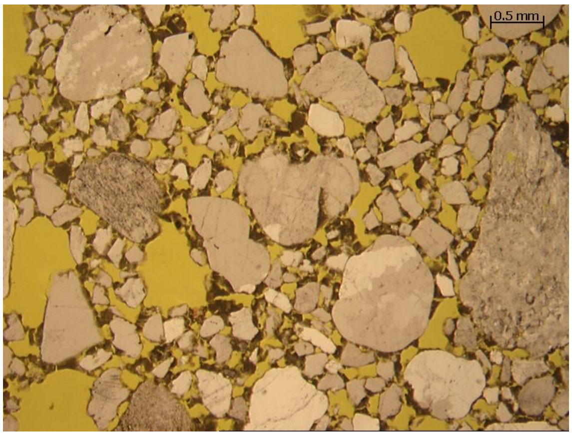
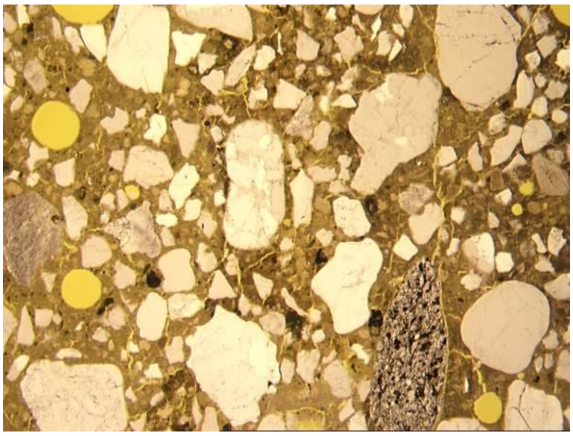


Figure 2: (left) Micrograph showing the presence of shrinkage cracks in a calcium lime specimen with 1:1 binder/sand ratio after testing (view 5.4 x 3.5 mm, plane polarized light)
Figure 3: (right) Micrograph showing the presence of high amount of coarse pores in a calcium lime specimen with 1:3 binder/sand ratio after testing (view 5.4 x 3.5 mm, plane polarized light)



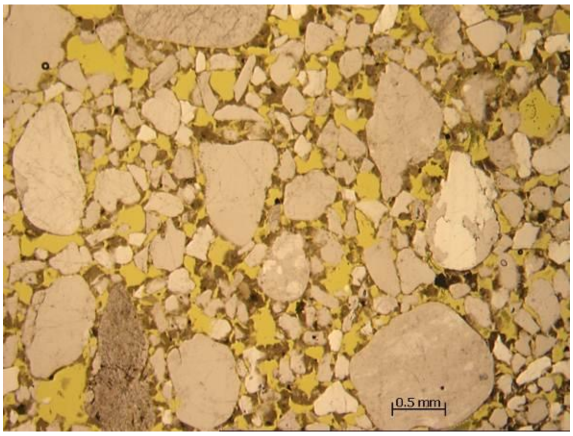
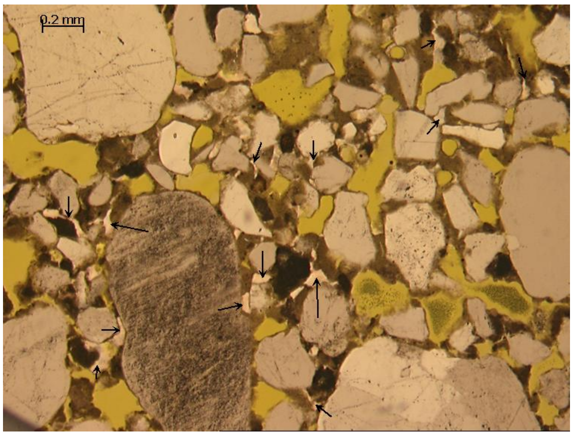


Figure 4: (left) Micrograph showing the presence of shrinkage cracks in the magnesium lime specimen with 1:1 binder/sand ratio after testing (view 5.4 x 3.5 mm, plane polarized light)
Figure 5: (right) Micrograph showing the presence of high amount of coarse pores in the dolomitic lime specimen with 1:3 binder/sand ratio after testing (view 5.4 x 3.5 mm, plane polarized light)

The mortar prepared with a dolomitic lime/sand ratio 1:3 shows the presence of large voids and cracks (figures 4-5), similarly to those observed in the calcium lime mortar. However, in this case both shrinkage cracks and irregular voids in part of the cross-section are filled with a newly precipitated compound (figures 6-7). The absence of self-healing in the reference thin section of the specimen made before the laboratory test demonstrates that this phenomenon is due to the dissolution of binder compounds during the immersion in water and subsequent re-precipitation during the wet/dry cycles. Morphology of the precipitated compound differs from that of brucite formed on concrete during natural or laboratory exposure to sea water, which tends to form thin, pallisade-like layers on the surface (Polder & Larbi 1995, Leegwater et al. 2007), or in cracks in historic mortars, in which it may occur as tiny radially arranged aggregates or rosettes (Blaeuer & Kueng, 2007). Individual crystals are significantly larger and the oriented arrangement of tiny individual crystals is lacking. Such textures, of course, strongly depend on reaction kinetics, degree of saturation and compositional gradients, etc. Optically, brucite, $Mg(OH)_2$, and hydromagnesite, $Mg_5[OH(CO_3)_2]\bullet 4H_2O$, another possible candidate, are difficult to distinguish. However, the relatively large birefringence (figure 9), seems to indicate hydromagnesite rather than brucite (birefringence of 0.022-0.029 and 0.015-0.021, respectively).

It appears that cracks and voids up to 100 µm can be completely healed. The amount of the cross section through the mortar in which self-healing occurs, is variable, 5.8 % and 0.6 % of the surface area in two different thin sections. In the domains in which self-healing occurs, by far the majority of cracks and voids are sealed (figures 8-9). Curiously, self-healing occurs in the mortar with a lower binder amount. The reason of this behaviour is not clear; it might be related to the different moisture transport properties of the two mortars.



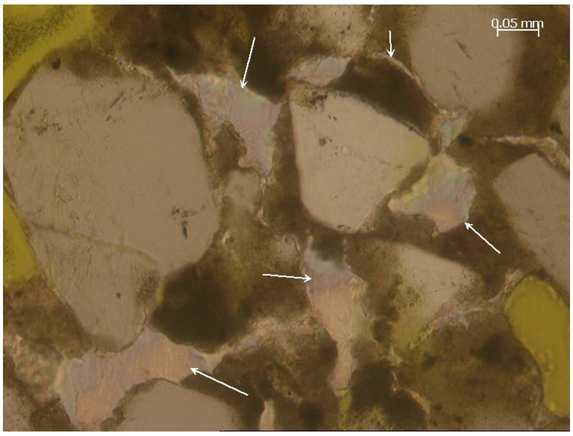
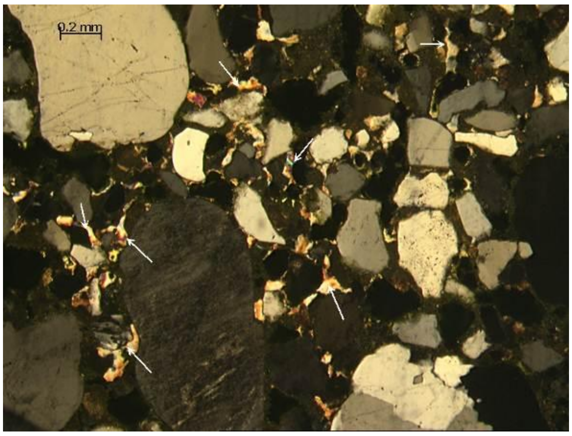


Figure 6: (left) Micrograph showing self-healing of cracks and irregular voids in the dolomitic lime specimen with 1:3 binder/sand ratio (view 1.4 x 0.9 mm, plane polarized light)
Figure 7: (left) Micrograph showing the self-healing of cracks and irregular voids in the dolomitic lime specimen with 1:3 binder/sand ratio (view 0.7 x 0.45 mm, plane polarized light)



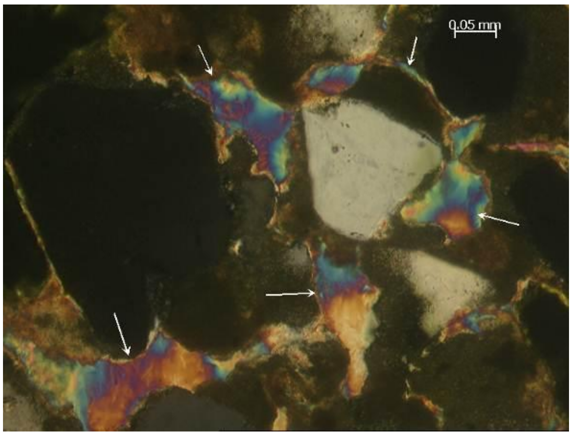
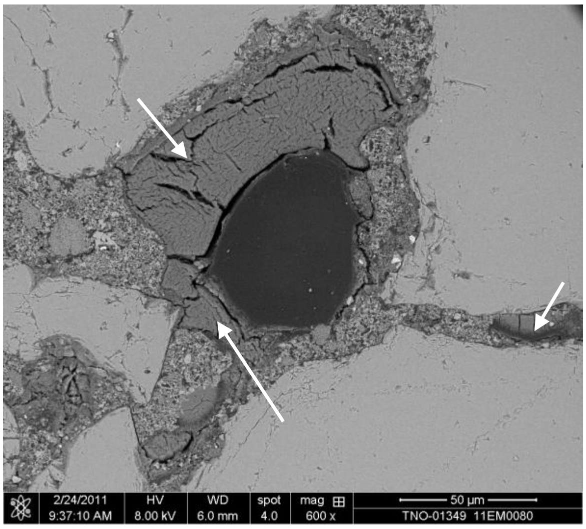


Figure 8: (left) Micrograph of the same area of figure 6 showing self-healing of cracks and irregular voids in the dolomitic lime specimen with 1:3 binder/sand ratio (view 1.4 x 0.9 mm, cross polarized light)
Figure 9: (right) Micrograph of the same area of figure 7 showing self-healing of cracks and irregular voids in the dolomitic lime specimen with 1:3 binder/sand ratio (view 0.7 x 0.45 mm, cross polarized light)

Scanning Electron Microscopy observations

Both mortar pieces an a thin section of the dolomitic lime mortar with 1:3 binder/sand ratio was studied by means of SEM-EDX using both BSE and SE modes. The newly precipitated compound is composed solely by Mg, except for O and C (no carbon coating was used); in the binder, Ca is present and the amount of magnesium is much lower. These results confirm that the cracks are healing by a magnesium compound, given the carbonate presence probably hydromagnesite. Figure 10 and 11 show examples of the newly precipitated compound (partially) filling cracks and voids. In BSE mode, even at high magnification, individual crystals can be distinguished with difficulty only, but the precipitates seem to show shrinkage cracks (figures 10-12). This seems may be due to the loss of crystal water, or, alternatively, development of the crystals from a gel (as with brucite, cf. Harrison 2005). In SE mode, precipitates seem to be made up by a stacked platy phase (figure 13).



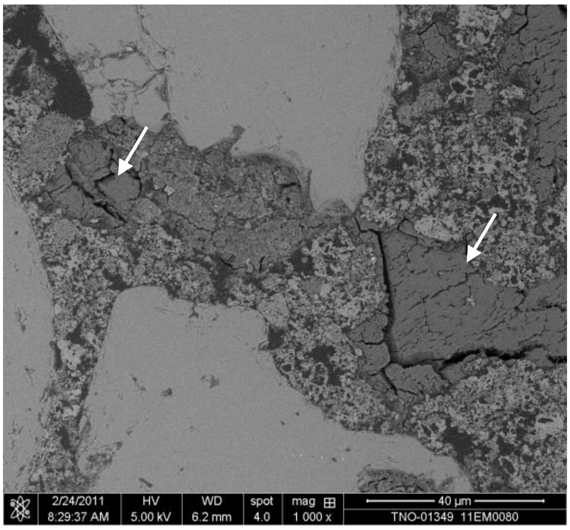
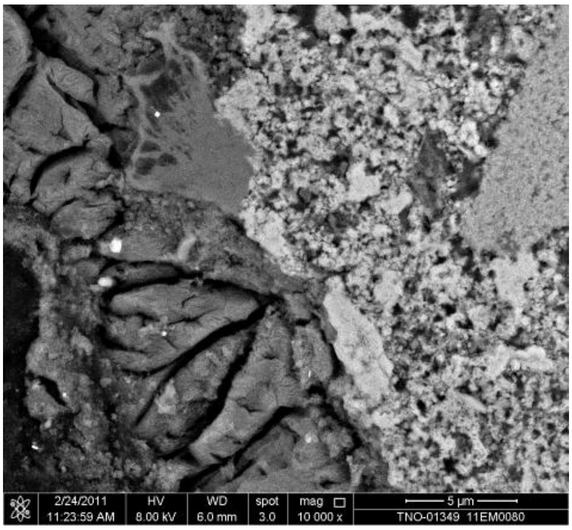


Figure 10: (left) Micrograph showing the partial filling of a void (indicated by the arrows) in the dolomitic lime specimen with 1:3 binder/sand ratio (BSE mode, 600x magnification).
Figure 11: (right) Micrograph showing the self-healing of a crack (indicated by the arrows) in the dolomitic lime specimen with 1:3 binder/sand ratio (BSE mode, 1000x magnification)



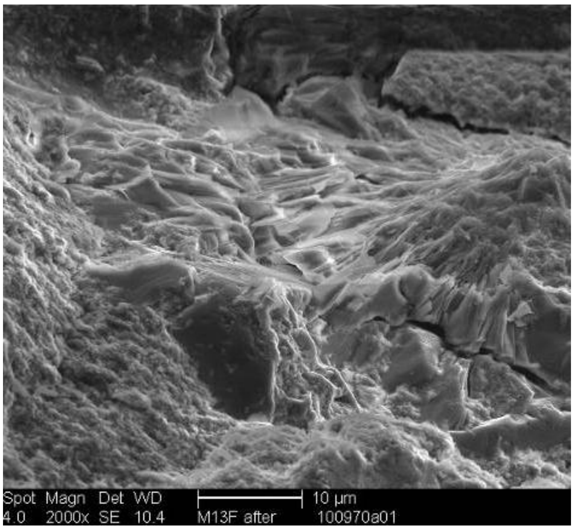


Figure 12: (left) Micrograph showing re-precipitated crystals; thin section of the dolomitic lime specimen with 1:3 binder/sand ratio (BSE mode, 10000x magnification)

Figure 13: (right) Micrograph showing lamellar crystals in a broken section of the dolomitic lime specimen with 1:3 binder/sand ratio (SE mode, 2000x magnification)

Conclusions

Mortars based upon dolomitic lime have a definitive potential to develop self-healing by precipitation of Mg-phases. This opens an interesting perspective for the development of future mortars with an enhanced self-healing capacity , both for new constructions and repair and restoration. However, several questions, including the definitive identification the re- precipitated Mg compound and the apparently opposite dependence of self-healing on binder content, require further explanation. Another question that may be raised is whether hydromagnesite represents the final stage of the self-healing process, or whether brucite may develop from hydromagnesite on long term. The possibility of Mg-based self-healing in dolomitic lime mortars also poses the interesting question whether magnesia-based cements (e.g. Vandeperre et al., 2008) would have a higher self-healing potential than traditional Portland-based cements, including those blended with supplementary cementing materials such as blast furnace slag or pulverized fly. In such cements, precipitation of brucite is believed to be one of the causes of enhanced strength development.

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