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SIMULATION OF THE SELF-HEALING OF DOLOMITIC LIME MORTAR

SIMULACIJA SAMOPOPRAVE DOLOMITNE APNENE MALTE

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A test procedure was set up to reproduce laboratory self-healing on lime-based (both pure calcium and magnesium-calcium) mortar specimens. After a few months of testing, during which time the specimens were submitted to wet-dry cycles, thin sections of the specimens were prepared and observed using a polarization and fluorescence microscope (PFM) and a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX). The specimens prepared with dolomitic lime showed the occurrence of self-healing: a magnesium compound was observed to be filling the 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

Pripravljen je bil postopek laboratorijskega reproduciranja samopoprave vzorcev (na osnovi čistega kalcija in magnezij-kalcija) apnene malte. Po nekaj mesecih preizkušanja, med katerim so bili vzorci ciklično močeni in sušeni, so bile pripravljene tanke rezine za opazovanje s polarizacijskim in fluorescenčnim mikroskopom (PFM) ter z vrstičnim elektronskim mikroskopom (SEM), opremljenim z energijsko disperzijsko spektroskopijo (EDX). Vzorci, pripravljeni iz dolomitnega apna, so pokazali pojave samopoprave: magnezijeva sestavina je napolnila razpoke in praznine. Ti rezultati nakazujejo nove možnosti za razvoj dolomitnih apnenih malt s povečano sposobnostjo samopoprave.

Ključne besede: samopoprava, dolomitna malta, PFM, SEM-EDX

1 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 the calcium bearing compounds and transports them from a zone rich in binder to voids and cracks present in the mortar. In this way small cracks can 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 samples of concrete and masonry mortars in structures from different periods in the Netherlands[1,2].

The property of engineered self-healing would greatly enhance the durability of modern materials, including those for repair and restoration; a range of potential routes are open for this for different materials (e.g.,[3]). In the 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.,[4,5]). 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.,[6]) and laboratory (e.g.,[7]) studies of concrete show that the exposition of concrete in seawater may result in the deposition of a surface layer of brucite, $Mg(OH)_2$, which, after deposition, protects the concrete from future degradation. Brucite is relatively insoluble; the 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 fulfil 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[8,9] and are mentioned to have a better self-healing potential than pure calcium mortars[10]. This paper reports the first results of a study to prospect the self-healing potential of dolomitic lime mortars.

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

2 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, nowadays used mainly in restoration because of its high compatibility with ancient materials. Dolomitic lime mortar was common in some European regions from the Roman period up to the early 20th century and appreciated for its long-term strength, higher than that of high calcium lime[9]. Nowadays, dolomitic lime is scarcely used because of the delayed hydration of over-burned MgO causing the pitting of popping in the mortar and the risk of formation, in a wet environment, of harmful magnesium sulphate salts in the presence of sulphates 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[10] 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 sulphates.

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 ratios were more usual in historic mortars[11]. 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 moulds (4 cm × 4 cm × 16 cm) and unmoulded as soon as they achieved 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. Complete carbonation was checked by spraying a freshly broken surface with phenolphthalein.

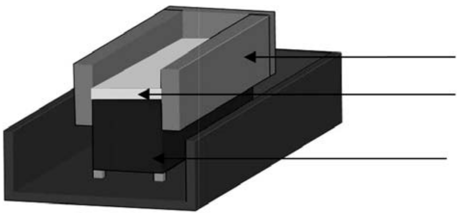

Figure 1: Test set up
Slika 1: Shematski prikaz preizkusa

At this point, the test attempting to reproduce self-healing in the 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 favour the dissolution of the lime components[12]. After a period of three months, the water in the containers was removed (but preserved), and the specimens were dried at room temperature. A mould 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 on the top of the specimen, while 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. A total of 10 cycles were performed over 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, defence walls, etc.) where an intermittent (abundant) supply of water is present[2].

After a few months of 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 using 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 using high-resolution scanning electron microscopy (SEM) (FEI NovaNanoSEM650) equipped with energy-dispersive X-ray spectroscopy for the identification of the compounds precipitated in the cracks and voids. Thin sections were prepared perpendicular to the length of the prisms.

3 RESULTS AND DISCUSSION

3.1 Polarization and Fluorescence Microscopy (PFM) observations

The 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 the 1 : 1 and 1 : 3 binder/sand ratios, no significant re-precipitation of calcium compounds in the cracks and voids was observed after the test. The specimen with the 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 an increase in the already high porosity.

The specimen prepared with the dolomitic lime and the binder/sand ratio 1 : 1 also showed the presence of

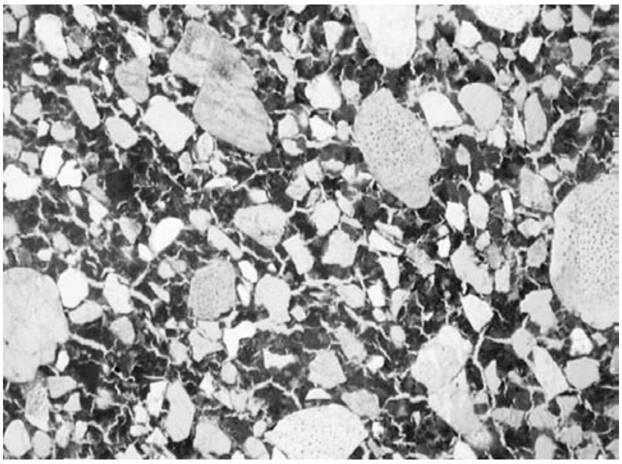

Figure 2: Micrograph showing the presence of shrinkage cracks in a calcium lime specimen with a 1 : 1 binder/sand ratio after testing (view 5.4 mm × 3.5 mm, plane polarized light)

Slika 2: Mikroposnetek, ki kaže prisotnost krčilnih razpok v kalcijevem apnenem vzorcu z razmerjem vezivo/pesek 1 : 1 po preizkusu (pogled na ploščino 5,4 mm × 3,5 mm, ravninsko polarizirana svetloba)

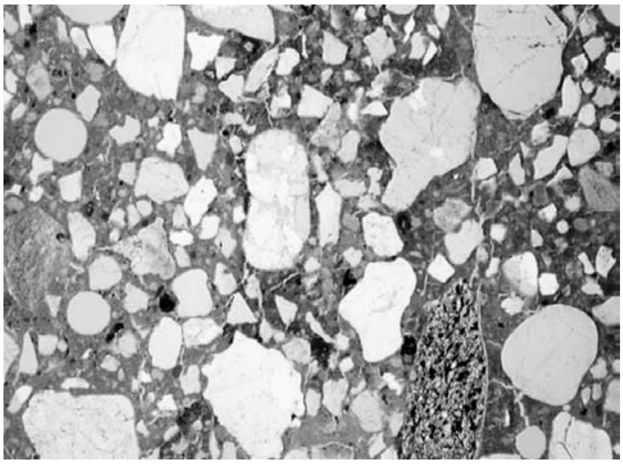

Figure 4: Micrograph showing the presence of shrinkage cracks in a magnesium lime specimen with a 1 : 1 binder/sand ratio after testing (view 5.4 mm × 3.5 mm, plane polarized light)

Slika 4: Mikroposnetek, ki kaže prisotnost krčilnih razpok v magnezijevem apnenem vzorcu z razmerjem vezivo/pesek 1 : 1 po preizkusu (pogled na ploščino 5,4 mm × 3,5 mm, ravninsko polarizirana svetloba)

shrinkage cracks, but their quantity is much less than observed in the calcium lime mortar. No self-healing is observed.

The mortar prepared with the dolomitic lime/sand ratio 1 : 3 shows the presence of large voids and cracks (**Figures 4** and **5**), similar 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** and **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 the binder compounds during the immersion in water and the subsequent re-precipitation during the wet/dry cycles. The morphology of the precipitated compound differs from that of the brucite formed on the concrete during natural or laboratory exposure to sea water, which tends to form thin, pallisade-like layers on the surface[6,7], or in cracks in historic mortars, in which it may occur as tiny, radially arranged aggregates or rosettes[13]. Individual crystals are significantly larger and the oriented arrangement of tiny individual crystals is lacking. Such textures, of course, strongly depend on the reaction kinetics, the degree of saturation and the compositional gradients, etc. Optically, brucite, $Mg(OH)_2$, and hydromagnesite, $Mg_5[OH(CO)_3)_2] \cdot 4H_2O$, another possible candidate, are

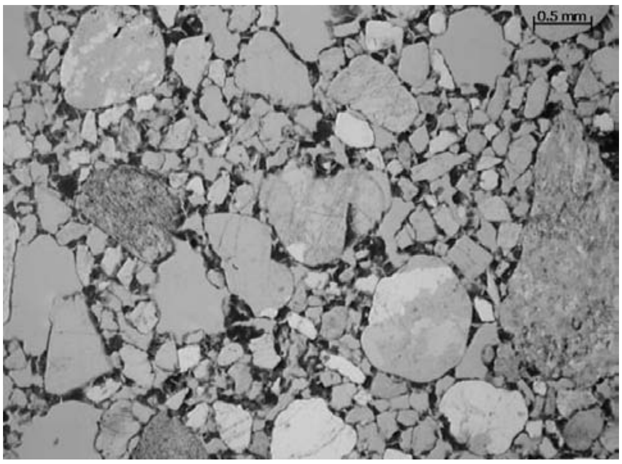

Figure 3: Micrograph showing the presence of a large quantity of coarse pores in a calcium lime specimen with a 1 : 3 binder/sand ratio after testing (view 5.4 mm × 3.5 mm, plane polarized light)

Slika 3: Mikroposnetek, ki kaže prisotnost velikega deleža grobih por v kalcijevem apnenem vzorcu z razmerjem vezivo/pesek 1 : 1 po preizkusu (pogled na ploščino 5,4 mm × 3,5 mm, ravninsko polarizirana svetloba)

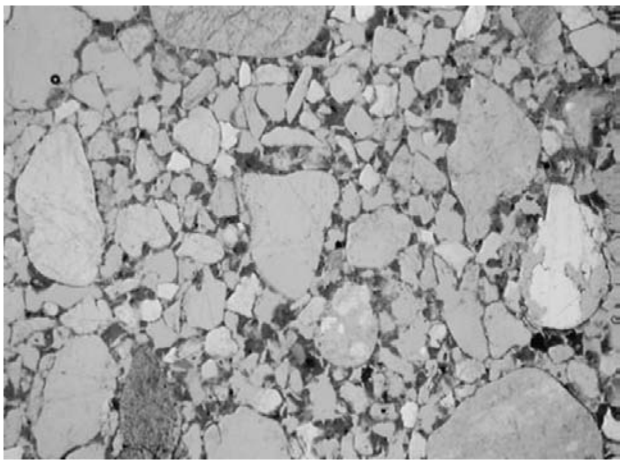

Figure 5: Micrograph showing the presence of a large quantity of coarse pores in a dolomitic lime specimen with a 1 : 3 binder/sand ratio after testing (view 5.4 mm × 3.5 mm, plane polarized light)

Slika 5: Mikroposnetek, ki kaže velik delež grobih por v dolomitnem apnenem vzorcu z razmerjem vezivo/pesek 1 : 3 po preizkusu (pogled na ploščino 5,4 mm × 3,5 mm, ravninsko polarizirana svetloba)

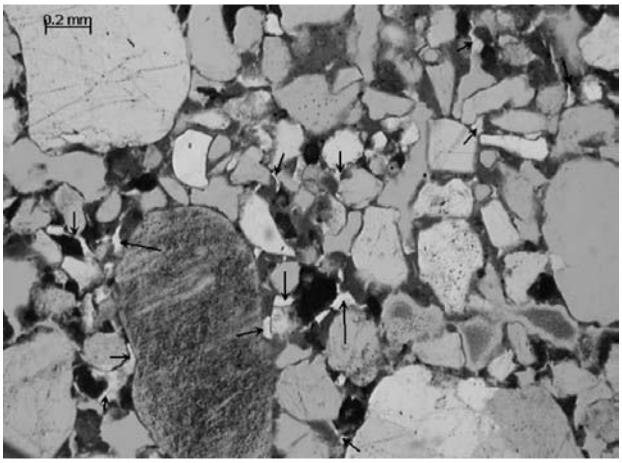

Figure 6: Micrograph showing self-healing of cracks and irregular voids in a dolomitic lime specimen with a 1 : 3 binder/sand ratio (view 1.4 mm × 0.9 mm, plane polarized light)

Slika 6: Mikroposnetek, ki kaže samopopravljene razpoke in nepravilne praznine v dolomitnem apnenem vzorcu z razmerjem vezivo/pesek 1 : 3 (pogled na ploščino 1,4 mm × 0,9 mm, ravninsko polarazirana svetloba)

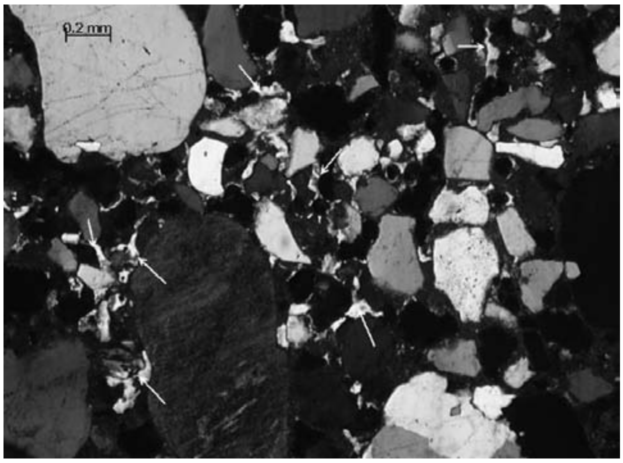

Figure 8: Micrograph of the same area of **Figure 6** showing the self-healing of cracks and irregular voids in a dolomitic lime specimen with a 1 : 3 binder/sand ratio (view 1.4 mm × 0.9 mm, cross polarized light)

Slika 8: Mikroposnetek istega področja s **slike 6**, ki kaže samopopravljene razpoke in nepravilne praznine v dolomitnem apnenem vzorcu z razmerjem vezivo/pesek 1 : 3 (pogled na ploščino 1,4 mm × 0,9 mm, navzkrižno polarizirana svetloba)

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 the 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 the cracks and voids are sealed (**Figures 8** and **9**). Curiously, self-healing occurs in the mortar with a lower amount of binder. The reason for this behaviour is not clear; it might be related to the different moisture-transport properties of the two mortars.

3.2 Scanning Electron Microscopy observations

For both mortar pieces 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 of 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 with a magnesium compound, given the carbo-

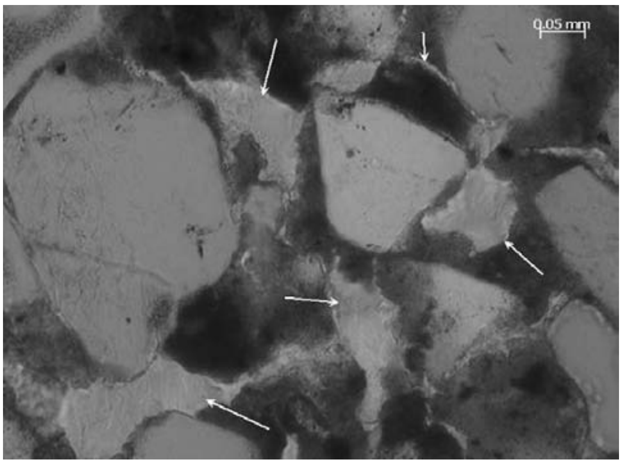

Figure 7: Micrograph showing the self-healing of cracks and irregular voids in a dolomitic lime specimen with a 1 : 3 binder/sand ratio (view 0.7 mm × 0.45 mm, plane polarized light)

Slika 7: Mikroposnetek, ki kaže samopopravljene razpoke in nepravilne praznine v dolomitnem apnenem vzorcu z razmerjem vezivo/pesek 1 : 3 (pogled na ploščino 0,7 mm × 0,45 mm, ravninsko polarizirana svetloba)

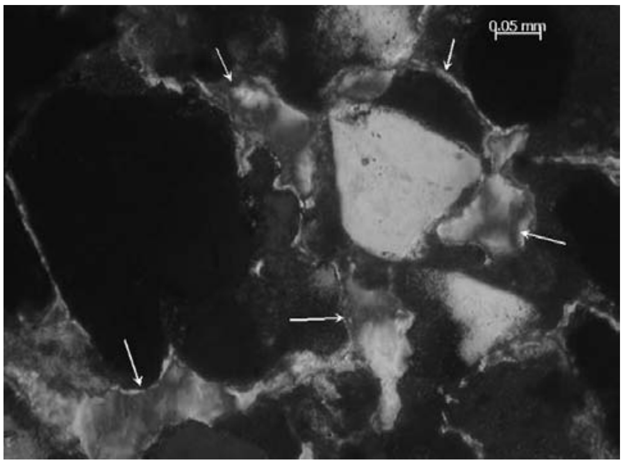

Figure 9: Micrograph of the same area of **Figure 7** showing the self-healing of cracks and irregular voids in a dolomitic lime specimen with a 1 : 3 binder/sand ratio (view 0.7 mm × 0.45 mm, cross polarized light)

Slika 9: Mikroposnetek istega področja s **slike 7**, ki kaže samopopravljene razpoke in nepravilne praznine v dolomitnem apnenem vzorcu z razmerjem vezivo/pesek 1 : 3 (pogled na ploščino 0,7 mm × 0,45 mm, navzkrižno polarizirana svetloba)

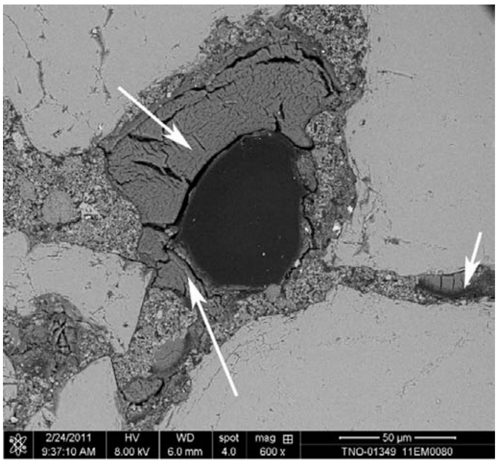

Figure 10: Micrograph showing the partial filling of a void (indicated by the arrows) in a dolomitic lime specimen with a 1:3 binder/sand ratio (BSE mode, 600-times magnification)

Slika 10: Mikroposnetek, ki kaže delno zapolnjeno praznino (označeno s puščico) v dolomitnem apnenem vzorcu z razmerjem vezivo/pesek 1 : 3 (način BSE, povečava 600-kratna)

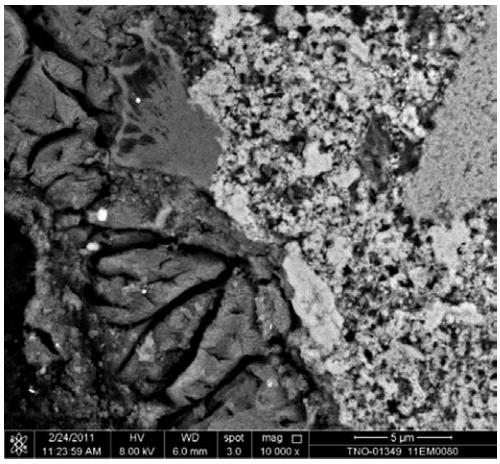

Figure 12: Micrograph showing re-precipitated crystals; thin section of the dolomitic lime specimen with a 1 : 3 binder/sand ratio (BSE mode, 10000-times magnification)

Slika 12: Mikroposnetek, ki kaže ponovno izločene kristale; tanek rez dolomitnega apnenega vzorca z razmerjem vezivo/pesek 1 : 3 (način BSE, povečava 10000-kratna)

nate presence probably hydromagnesite. **Figures 10** and **11** show examples of the newly precipitated compound (partially) filling the cracks and voids. In BSE mode, even at high magnification, individual crystals can only be distinguished with difficulty, but the precipitates seem to show shrinkage cracks (**Figures 10** to **12**). This may be due to the loss of crystal water, or, alternatively, the development of the crystals from a gel (as with brucite, cf.[14]). In SE mode the precipitates seem to be made up of a stacked platy phase (**Figure 13**).

4 CONCLUSIONS

Mortars based on dolomitic lime have a clear potential to develop self-healing by the precipitation of Mg phases. This opens up an interesting perspective for the development of future mortars with an enhanced self-healing capacity , both for new constructions as well as repair and restoration. However, several questions, including the definitive identification of 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 over the long term. The possibility of Mg-based self-healing in dolomitic lime mortars also poses the interesting question as to whether magnesia-based cements (e.g.,[15]) would have a higher self-healing potential than traditional Portland-based cements,

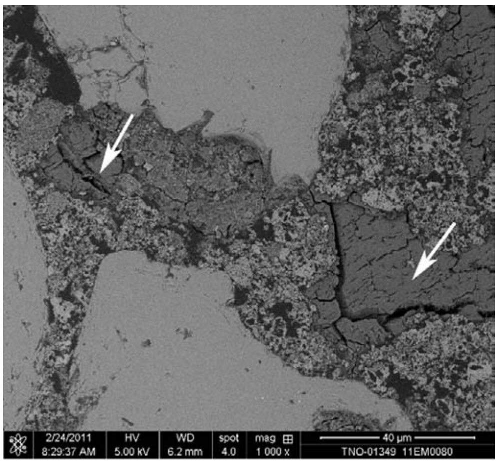

Figure 11: Micrograph showing the self-healing of a crack (indicated by the arrows) in a dolomitic lime specimen with a 1 :3 binder/sand ratio (BSE mode, 1000-times magnification)

Slika 11: Mikroposnetek, ki kaže samopopravo razpoke (označeno s puščico) v dolomitnem apnenem vzorcu z razmerjem vezivo/pesek 1 : 3 (način BSE, povečava 1000-kratna)

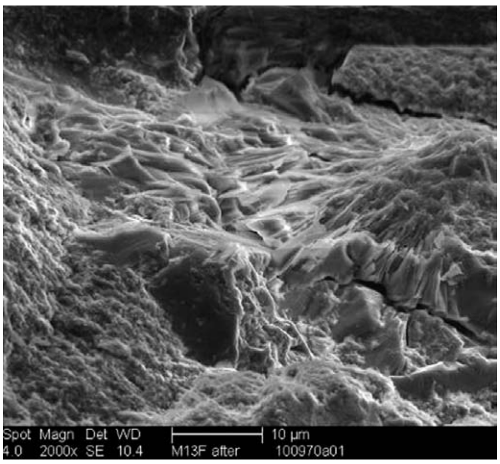

Figure 13: Micrograph showing lamellar crystals in a broken section of the dolomitic lime specimen with a 1 : 3 binder/sand ratio (SE mode, 2000-times magnification)

Slika 13: Mikroposnetek lamelastih kristalov na področju preloma dolomitnega apnenega vzorca z razmerjem vezivo/pesek 1 : 3 (način SE, povečava 2000-kratna) including those blended with supplementary cementing materials, such as blast-furnace slag or pulverized fly. In such cements, the precipitation of brucite is believed to be one of the causes of enhanced strength development.

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