Influence of the curing period of encapsulated polyurethane precursor on the capillary water absorption of cracked mortar with self-healing properties

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Abstract. Cracks serve as preferential pathways for aggressive substances (H_2O, O_2, Cl^-, CO_2, etc.) that reduce the durability and service life of steel reinforced cementitious materials. The implementation of an autonomous crack healing mechanism counts as a solution to this problem. A very promising way to achieve that goal consists of incorporating capsules filled with polyurethane (PU) precursor in the mortar/concrete. Upon crack occurrence the capsules break, the PU precursor flows into the crack, reacts with surrounding moisture and seals the crack again once hardened. Now, depending on the specific exposure conditions of the structure (very humid versus dry), the reaction kinetics of the PU can vary. In this research it has been investigated by means of neutron radiography whether the crack healing efficiency is the same regardless of the curing period, i.e., when having direct exposure to water upon release of the healing agent (after 15 min to 3 h) versus when the PU is first given enough time (at least 24 hours) to harden completely. Preferably, the healing agent works under all circumstances. However, it was found that the first scenario resulted in the highest resistance to capillary water absorption for singular cracks, 300 µm in width. Neutron radiography images and water profiles extracted from those images during a two-hour water uptake experiment clearly show that this was the case for both a high viscosity PU precursor that was developed in-house and a commercially available low viscosity PU-based healing agent.

Introduction

Concrete is vulnerable to crack formation due to its low tensile strength. Cracks in concrete may appear due to several causes such as drying shrinkage, thermal contraction, restraints, differential settlement and applied loads [1]. These cracks count as preferential pathways for corrosion-inducing substances [2], e.g. H_2O, O_2, Cl^- and CO_2. This can lead to accelerated corrosion initiation and propagation of embedded reinforcing steel, which compromises the structural safety and service life of the concrete structure.

To avoid these problems, cracks need to be repaired as soon as possible. However, repair works require high direct and indirect costs and some cracked regions in concrete elements are not even visible or accessible. Therefore, it would be beneficial to give the concrete the ability to heal the cracks by itself without any human intervention. Different methods have already been explored to obtain autonomous crack healing in concrete [3]. One of the promising approaches is the

embedment of brittle capsules filled with healing agents inside the concrete matrix [4-6]. Crack formation leads to capsule breakage and release of the healing agent which fills up the crack and forms a barrier which prevents water ingress through the cracks.

Capillary water absorption in sound and cracked mortar and concrete has been investigated in several studies by X-ray [7-10] or neutron radiography [11-18] experiments. In the research of Van Tittelboom et al. [12] the self-healing efficiency of mortar with encapsulated healing agents was visualized for the first time by neutron radiography. From the moisture distribution profiles on the neutron radiographs it was found that encapsulation of polyurethane-based healing agents proved to be very efficient for autonomous healing of singular cracks.

The main aim of the current study was to investigate whether the healing efficiency of two polyurethane-based healing agents with different viscosity is very different depending on the curing period before being brought in direct contact with water, i.e. shortly after release of the healing agent into the crack, and thus before PU hardening, or after complete PU hardening which usually takes around 24-48 hours, depending on the surrounding moisture availability. It is important to investigate this difference because both situations, yet especially the former one, are often encountered in practice.

Materials

Mortar. Mortar with a water-to-cement ratio of 0.5 and a sand-to-cement ratio of 3 was made. Sand with grain sizes ranging from 0 to 2 mm was used in combination with Ordinary Portland cement CEM I 52.5 N. The proportioning of the different constituents per m³ of mortar was as follows: 1535 kg/m³ sand, 512 kg/m³ cement and 256 kg/m^3 water.

Capsules. To encapsulate the selected healing agents, borosilicate glass capillaries with a 30 mm length, an internal diameter of 3.00 mm and an external diameter of 3.35 mm were chosen. First, one side of the capillaries was sealed with 2-component polymethylmethacrylate (PMMA) glue. Next, the healing agent was injected by means of a syringe with a needle. Finally, the other end of the capsules was also sealed with PMMA. As glass is a very brittle material, breakage of the capsules upon crack creation was assured.

Healing Agents. Two different types of polyurethane-based healing agents were selected for this study. As the viscosity of the healing agent is a very important parameter that determines whether the healing agent will flow out of the capsules and fill the crack, healing agents with different viscosities were chosen. The first agent was developed within the framework of the SHEcon project (Self-healing concrete for structural and architectural applications) where a polyurethane-based healing agent was developed in order to meet the needs for self-healing of thermally induced cracks in concrete sandwich panels [19]. It has a viscosity of 6700 mPas at 25 °C. It is a polyurethane (PU) precursor that essentially consists of methylene diphenyl diisocyanate (MDI) and a polyether polyol. This precursor reacts with water to create a foam that heals the cracks. The moisture content of the concrete itself counts as the main water source. The second healing agent is a commercially available healing agent named Flex SLV AF from the company De Neef Conchem with a much lower viscosity of about 200 mPas at 25 °C. It is a MDI and polyether polyol based prepolymer. As such, the backbone of the product is an incomplete PU polymer containing residual isocyanate (-NCO) groups that react with the water present in the mortar upon capsule breakage to form a waterproof PU polymer. The polyurethane-based healing agent with the highest viscosity is named PU_HV and the one with the lowest viscosity PU_LV. Both healing agents are one-component healing agents that react upon contact with moisture in the matrix. Especially in case of PU_HV, foaming occurs upon reaction which causes a slight expansion of the healing agent. This is desirable to fill the crack space completely and assure that the crack is sealed against the ingress of aggressive substances.

Mortar Prisms with Encapsulated Healing Agent. Prisms with dimensions of 40 × 40 × 160 mm^3 were prepared. To create standardized cracks, thin metal plates, 40 mm in width, were positioned in the molds up to a depth of 20 mm. These plates had a thickness of 300 µm and were fixed at their position by means of a metal framework that was connected to the mold. Self-healing properties were obtained by embedding encapsulated healing agent in the matrix at the position where the crack would appear. In order to trigger the healing mechanism at the moment of crack appearance, a method described by Van Belleghem et al. [7] was used. Since standardized cracks were created, the capsules were put through the metal plates used for crack creation. Therefore, two holes with a diameter of 3.50 mm were drilled in the metal plates that were used to create the cracks in the samples with self-healing properties. The capsule's position (and thus also the position of the holes) was chosen in such a way that there was a mortar cover on each capsule of 10 mm at the side and the bottom of the sample. Two 30 mm long capsules were positioned through the holes inside the metal plate. Once the capsules were placed through the holes in the plates, their position was fixed by gluing them onto thin nylon wires, which were connected to the walls of the mold.

Once preparation of the molds was finished, samples were made by filling the molds with mortar in two equal layers. Each layer was compacted through vibration on a vibrating table. After casting, the samples were stored in an air-conditioned room at a temperature of 20 °C and a relative humidity of more than 95%. Twenty-four hours later, samples were demolded and then stored again in the same air-conditioned room until the age of 28 days.

Methods

Crack Creation, Healing and Sample Preparation. The metal plates were either removed after a curing period of 28 days (specimens A, B), or just before starting the water absorption test (specimens C, D). Autonomous crack healing was obtained for the samples with embedded capsules as the capsules were broken at the position of the crack plane at the moment that the metal plates were removed. Breakage of the capsules was followed by release of the healing agent which flowed into the cracks. Due to contact of the healing agent with moisture inside the cementitious matrix or directly with the exposure solution itself, the healing agent started to polymerize, resulting in crack repair.

As the crack creation technique with metal plates required the troweled surface to be the exposed surface, the test surfaces of the samples would be a little bit rough. During casting careful attention was paid to ensure a relatively smooth troweled surface finishing. For specimens A, B of each test series, the troweled surfaces were also mechanically flattened after removal of the plates after 28 days and at least 24 h of PU hardening. As such, a layer of approximately 1–2 mm was cut off. This was not possible for specimens C and D of each test series, because the metal plates could not be removed until the start of the absorption test.

All specimens were dried in an oven at 40 °C until constant mass (mass change less than 0.1% in 24 h) was achieved. For specimens A and B, the drying step was initiated shortly after mechanical flattening of the test surface. In case of the non-mechanically flattened samples C and D, drying started at the same age. By drying, a uniform moisture distribution was obtained inside the sample in a short time period. After the drying period, the sides of the specimens were covered over a height of 15 mm with a self-adhesive aluminum tape so that the water could only enter the samples unidirectionally through the test surface. Regular aluminum tape was used since it hardly attenuates neutrons (it is almost transparent for neutrons). Since the main aim of the research was the investigation of the water uptake in the crack region, a large part of the bottom surface was also covered with the aluminum tape so that only a 10 mm wide zone around the cracks was exposed to water during the absorption test.

Neutron Radiography Measurements. The visualization of the water ingress in cracked mortar was performed by real time neutron radiography at the thermal neutron imaging facility NEUTRA.

This facility is part of the spallation neutron source SINQ of the Paul Scherrer Institute (PSI) in Switzerland. The neutron beam of the spallation source was guided to a fixed size aperture of 2 cm in diameter by means of a convergent inner collimator tube. From there, a divergent outer collimator led the parallelized neutron beam to the object space with a useful area of 400 mm diameter. The thermal energy spectrum of the neutron beam was characterized by a Maxwell–Boltzmann distribution with peak energy of 25 meV. The neutron beam then passed through the studied samples to a 100 µm thick LiF/ZnS scintillator screen. This scintillator converted the neutrons to visible light, which was deflected by mirrors in a dark room and recorded by a cooled slow-scan Andor SCMOS camera with a 50 mm AF-S NIKKOR lens. For each series of specimens, open beam, dark current and black body images were acquired. The open beam image represents the spatial distribution of the neutron beam intensity and aimed at removing the inhomogeneity of the beam. The dark current image was taken while all shutters of the beam line were closed. It was used as a correction for the background noise level of the camera. The black body image was obtained by placing neutron absorbing blocks of boronated polyethylene in front of the scanned samples. This was used as a background scattering correction.

For the water absorption experiments, the mortar prisms were placed on aluminum line supports in small aluminum containers in front of the neutron beam source cf. [20]. A reference image of the samples in the dry state was taken before the containers were filled with water. Water was manually added to the containers by means of a syringe so that the immersion of the samples amounted to 3 ± 1 mm. When all containers were filled, radiographs were taken with an exposure time of 3 s, which resulted in a time step of 4.6 s due to a process delay. This resulted in a pixel size of 0.273 mm for all images. Radiographic scanning during the water absorption process continued for 2 h.

Image Analysis. To be able to accurately analyze the moisture distribution profiles in the samples, corrections needed to be taken into account. Dark current image and black body image were subtracted from each of the neutron radiographs in order to take into account the background noise of the camera and the background scattering. The same was done for the open beam image. Next, a flat field correction was applied by dividing the corrected neutron radiographs by the corrected open beam image. All image operations were performed using the image processing software ImageJ (1.48v, National Institutes of Health, Bethesda, MD, USA).

Visualization of the water front was done by dividing the images in the wet state by the reference image in the dry state. The moisture profile in the mortar samples was visualized in this way after 2 h of exposure. Next to the visual evaluation, a quantitative evaluation of crack healing was performed by plotting the water profiles of the obtained images. Calculation of the water content was done in a similar way as described previously in [12]. Horizontal water profiles were determined in the central 80 mm of each specimen at a height of 11.3 mm above the bottom of the samples as in Van den Heede et al. [20]. The height of the rectangular area perpendicular to the crack was chosen so that the profile was always determined above the capsule layer of the self-healing specimens. In this way, the presence of the capsules did not interfere with the water profile in the mortar. Water profiles were also taken along the cracks. Therefore, additional rectangular areas were defined that coincided with the crack and extended from the bottom to the top of the sample cf. [20].

Results and Discussion

Neutron Radiography Imaging of Crack Healing. A comparison was made between the neutron radiography images of the specimens where the PU was first given at least 24 h time to harden completely inside the crack (Figure 1: CR_1_PU_HV_A & B, Figure 2: CR_1_PU_LV_A & B), and those of the specimens where the exposure to water began not long (15 min to 3 h) after the removal of the thin metal plates (Figure 1: CR_1_PU_HV_C & D, Figure 2: CR_1_PU_LV_C & D). The latter option resulted in a water front in the vicinity of the crack that was much less

pronounced. In other words, based on a mere visual evaluation, a higher self-healing efficiency seems to be possible in case of direct contact with water before PU hardening. This statement holds true for both types of healing agent, i.e. the one with the high and the one with the low viscosity. This behavior could be explained as follows. Both PU precursors that have been used in this research require water to react. When bringing the specimen in contact with water upon release of the PU precursor, it apparently creates the optimal conditions for a more profound reaction. Normally, the moisture content of the cementitious matrix around the crack and the air humidity is sufficient for this reaction. Still, with more water around, the reaction conditions could be more beneficial.

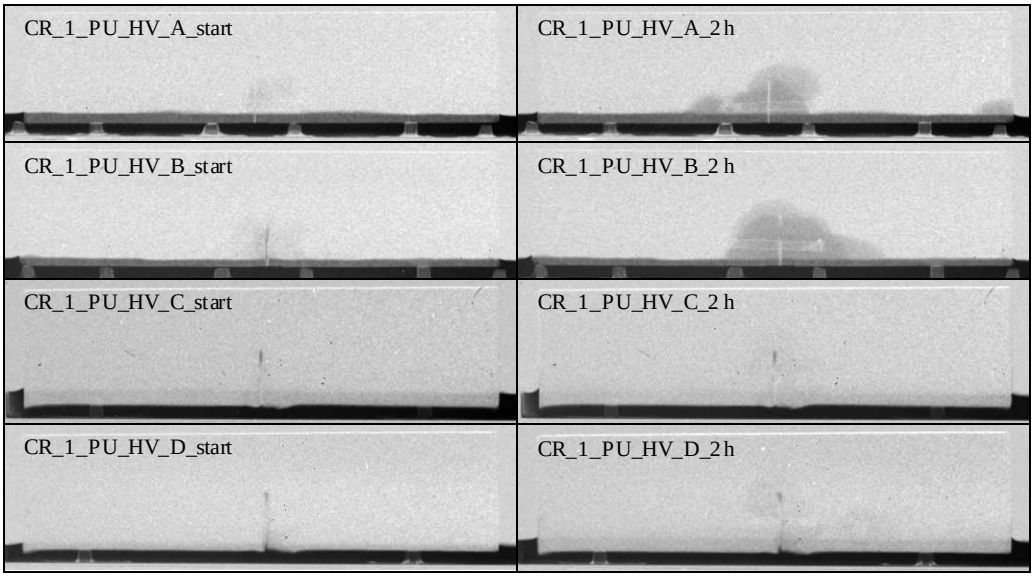

Fig. 1. Visualization of the water uptake in mortar prisms with encapsulated PU_HV using neutron radiography

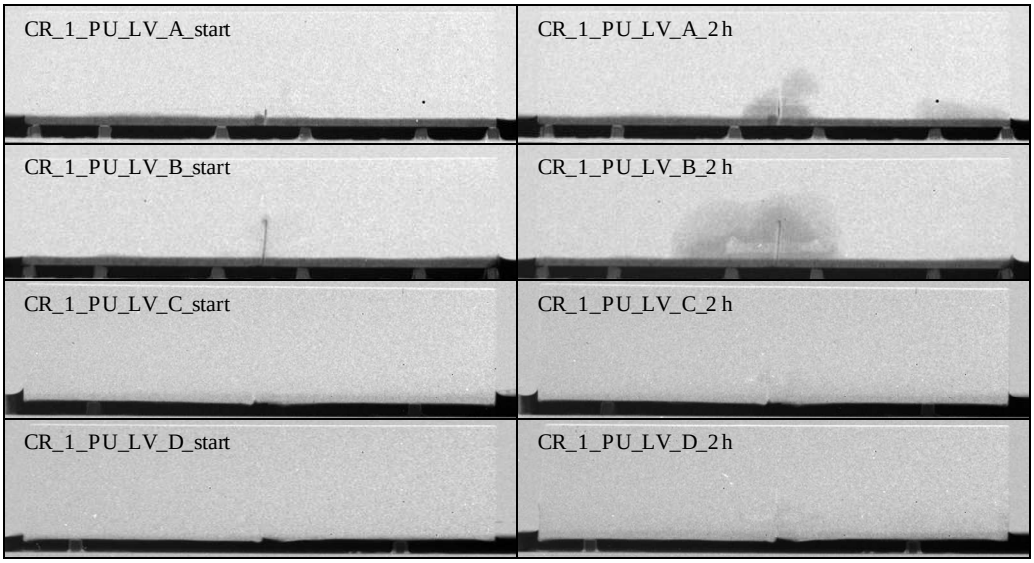

Fig. 2. Visualization of the water uptake in mortar prisms with encapsulated PU_LV using neutron radiography

Water Profiling of Crack Healing Perpendicular to the Crack. The conclusions drawn based on the visual interpretation (Figures 1 and 2) were further confirmed by quantitative water profiling perpendicular to the crack (Figures 3 and 4).

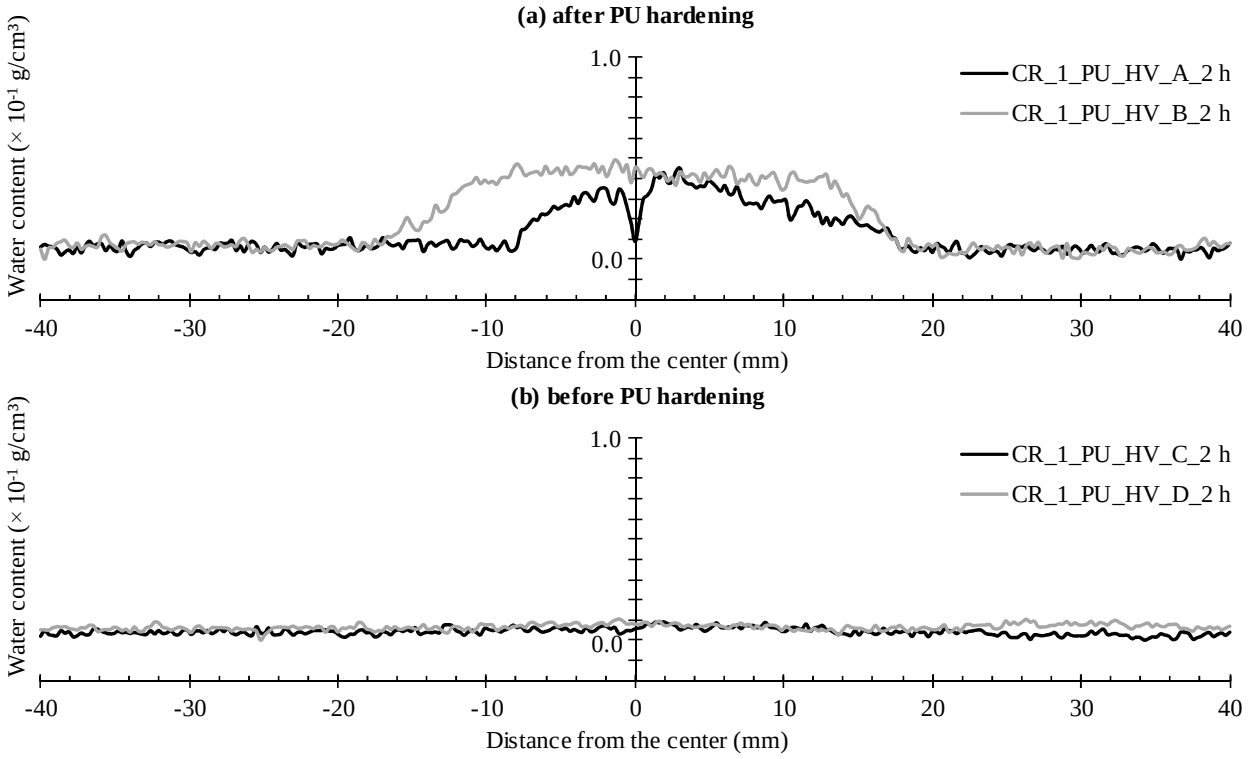

Fig. 3. Water profiles perpendicular to the crack in mortar prisms with encapsulated PU_HV after 2 h: (a) exposure initiated after PU hardening, (b) exposure initiated before PU hardening

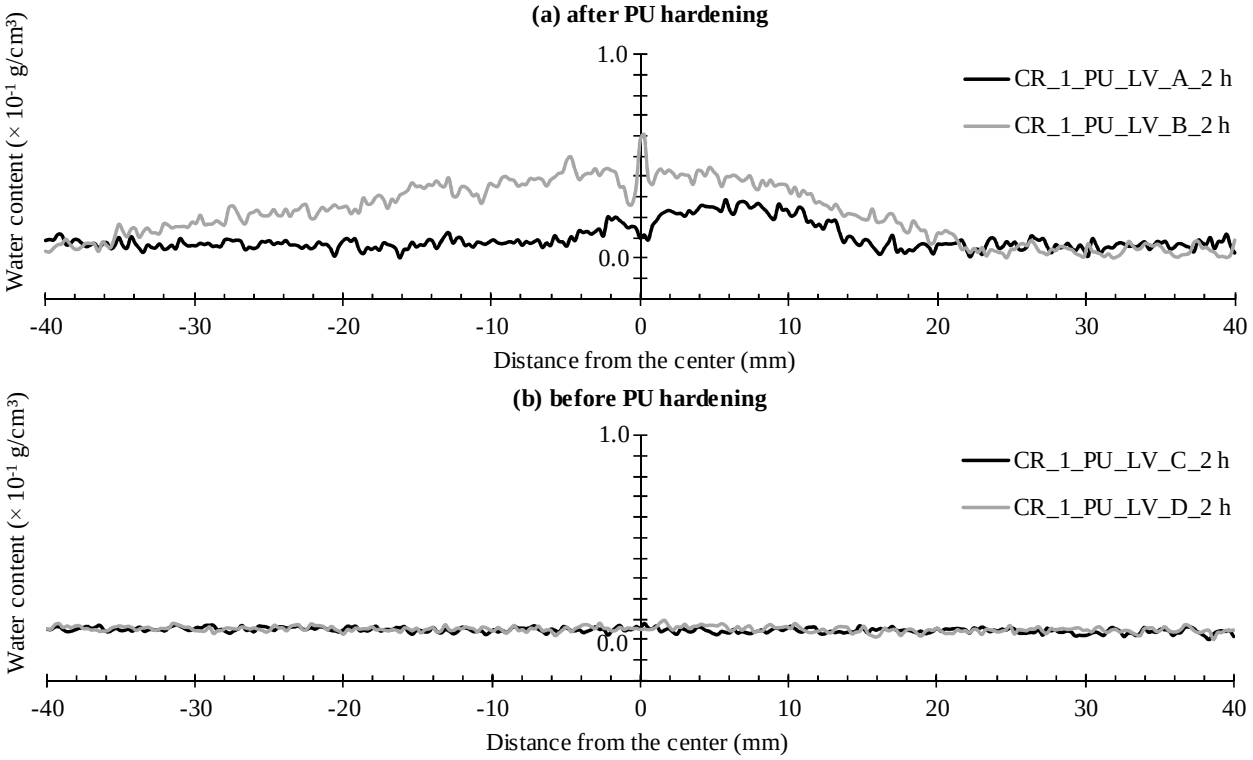

Fig. 4. Water profiles perpendicular to the crack in mortar prisms with encapsulated PU_LV after 2 h: (a) exposure initiated after PU hardening, (b) exposure initiated before PU hardening

Complete hardening of the high viscosity PU before the start of the water absorption test could not prevent an increased water content in the crack region. The central downward peak for specimen

A in Figure 3 indicates that the crack itself is healed quite properly, yet the mortar matrix around it still takes up some water. For specimen B the crack itself is not healed properly. On the other hand, the specimens that were brought in direct contact with water during PU hardening (samples C and D) were both characterized by a flat water profile over the entire 80 mm long region of study around the crack. Very similar observations were done for the specimens containing the encapsulated low viscosity healing agent (Figure 4).

Water Profiling of Crack Healing along the Crack. The difference in curing period for the PU-based healing agents before the start of the water absorption test is also clearly visible when extracting water profiles along the crack (Figures 5 and 6) from the neutron radiography images shown in Figures 1 and 2.

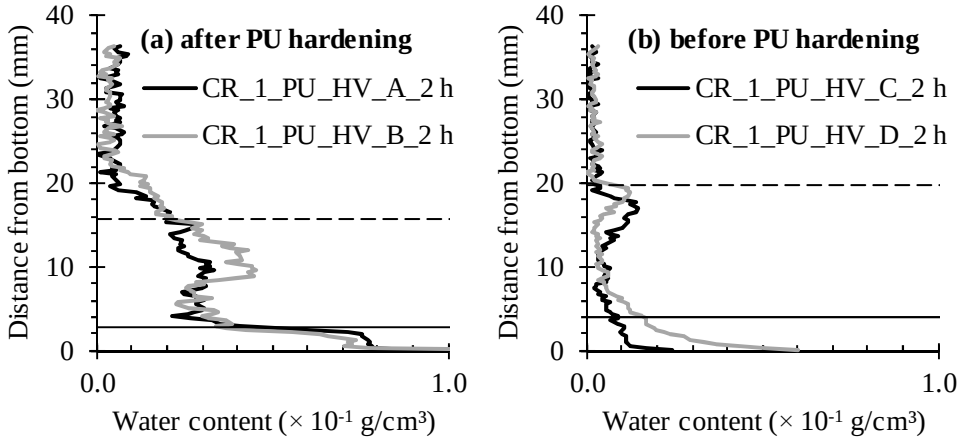

Fig. 5. Water profiles along the crack in mortar prisms with encapsulated PU_HV after 2 h: (a) exposure initiated after PU hardening, (b) exposure initiated before PU hardening

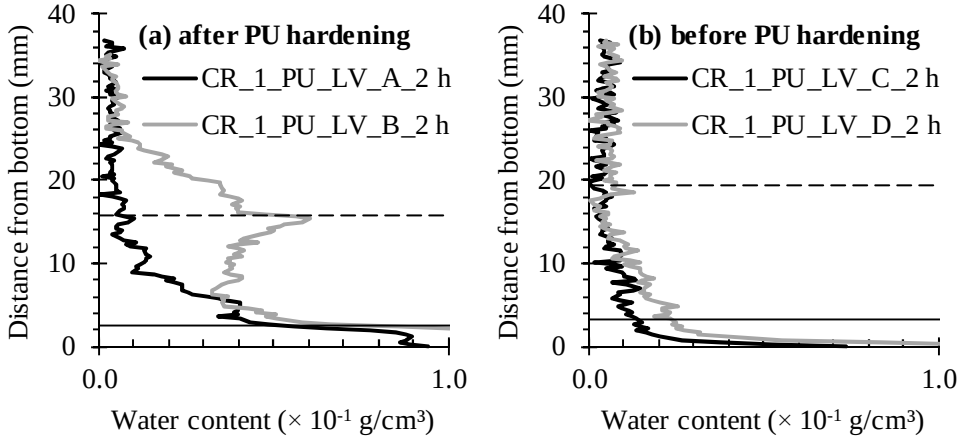

Fig. 6. Water profiles along the crack in mortar prisms with encapsulated PU_LV after 2 h: (a) exposure initiated after PU hardening, (b) exposure initiated before PU hardening

With completely hardened PU present in the crack before the start of the water absorption test (Figures 5a and 6a), increased water contents were recorded along the entire crack height (zone between the horizontal solid and dashed black lines in the graphs). This increased water content extended around 5-10 mm beyond the crack tip depending on the type of healing agent used (PU_HV versus PU_LV). Note that in case of PU_LV there seems to be quite a big difference in healing performance between the two tested samples. If water exposure takes place during PU hardening (Figures 5b and 6b) there seems to be barely water present in the crack. Only in case of the high viscosity healing agent a slightly increased water content seems to exist around the crack

tip. Nonetheless, the water profiles taken along the crack as well as those taken perpendicular to it, substantiate in a quantitative manner that direct contact with water does not compromise the healing efficiency at all. On the contrary, it would actually be preferred. It makes both healing agents quite suitable for very humid environments. For now, the benefits of direct contact with water before PU hardening are attributed to a more profound reaction of the PU. However, this still needs to be confirmed further on as the number of specimens that was tested until now was quite limited (two per curing period and type of healing agent). Additional specimens per test series will need to be subjected to water absorption tests to see whether the earlier mentioned more profound reaction is indeed causing all this or the fact that some of the non-hardened PU precursor seeping from the crack also tends to seal part of the 10 mm wide bottom area of the sample around the crack after reaction. The theory of the more profound reaction could be verified in the future by bringing controlled amounts of each PU precursor, not encapsulated nor embedded in mortar, in contact with fixed amounts of water and assessing the post-reaction volume. They could also be stored in environments with a predefined relative humidity, either corresponding with the one normally present inside 300 µm wide cracks in mortar or representing the typical moisture contents of the cementitious matrix around those cracks.

Conclusions

- Neutron radiography imaging and water profiling were found to be a very effective technique to assess the healing performance of two encapsulated PU-based healing agents – one with high and one with low viscosity – inside mortar upon cracking and a subsequent two hour capillary absorption test.
- Based on the neutron radiography results of a limited number of artificially cracked and healed mortar samples, direct contact with water shortly (15 min to 3 hours) after release of both types of healing agent, and thus before PU hardening, tends to establish much more effective crack healing. This conclusion followed from both the neutron radiography imagery and the quantitative water profiling perpendicular and along the cracks.
- Most probably, this behavior is caused by the fact that the PU-based healing agents react more profoundly in direct contact with a large amount of water than when merely exposed to the surrounding air humidity or the moisture content of the mortar matrix. Further testing of both precursors, encapsulated and embedded in mortar, as well as separately, is still needed to find further confirmation for this explanation.

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