X-Ray Micro Tomography of Water Absorption by Superabsorbent Polymers in Mortar

Claudia Romero Rodriguez[1(✉)], Maxim Deprez[2], Fernando F. de Mendonca Filho[1], Stefanie van Offenwert[2], Veerle Cnudde[2,3], Erik Schlangen[1], and Branko Šavija[1]

[1] Microlab, Department of 3MD, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands
{c.romerorodriguez, F.Filho, Erik.Schlangen, B.Savija}@tudelft.nl

[2] PProGRess/UGCT, Geology Department, Faculty of Sciences, Ghent University, Krijgslaan 281 S8, 9000 Ghent, Belgium
{Maxim.Deprez, Stefanie.VanOffenwert, Veerle.Cnudde}@UGent.be

[3] Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Princetonlaan 8A, 3584CD Utrecht, The Netherlands

Abstract. Superabsorbent Polymers (SAP) have been recently subject of investigation as smart admixtures for cement-based materials. The properties of these polymers enable their use for internal curing, increasing freeze/thaw resistance, boosting autogenous self-healing and providing a crack self-sealing effect in cementitious composites. Except for the earliest application, the functioning of these beneficial effects invloves the absorption by the polymers of ingress water in the hardened cementitious matrix and later release, as well as their capacity to complete multiple absorption/desorption cycles. In this work, the absorption of water in mortar with superabsorbent polymers is monitored during the first 60 min of absorption through micro-CT. The experimental series included the presence of cracks. The registration and differentiation of sub-minute (18 s) scans enabled the individuation of bulk water content distribution in the mortar with a resolution of 55 μm. The swollen volume of SAP could also be quantified and studied in time. The results point out that although embedded SAP absorb water from the matrix, this absorption is slow and reduced with respect to water absorption during mixing for the used SAP. Same effect is observed for SAP in the cracks.

Keywords: SAP · Mortar · X-ray micro computed tomography · Concrete durability

1 Introduction

Most of durability problems in cementitious composites involve the ingress of water into the matrix, as well as of harmful species in solution. Carbonation of cement, frost damage, chloride ingress, etc. are vivid examples of such problems. When cracks are

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present in the material, further acceleration of the degradation mechanisms listed above happens due to the additional surfaces from which deleterious substances can penetrate. In recent years, some studies have pointed out the use of superabsorbent polymers (SAP) to improve the durability of cement-based materials (Jensen and Hansens 2002). These admixtures are polyelectrolyte gels which absorb water many times their own weight. When SAP are added into fresh cementitious mixtures, they absorb water and swell, when the material sets and dries, the stored water is released and the SAP shrink leaving behind a macropore.

Internal curing of concrete with SAP has been proven to reduce shrinkage cracking significantly (Geiker et al. 2004) with respective positive implications for the durability of the studied materials. Same type of admixture was shown to be beneficial for increasing the frost resistance of concrete due to the creation of a uniformly distributed macropores system (Mechterine et al. 2017). Also crack self-sealing and self-healing effects have been associated to the presence of these polymeric particles (Lee et al. 2010; Snoeck et al. 2016). Moreover, there exist some studies that point out beneficial side effects of embedded SAP in the resistance of the material against carbonation and chloride ingress (Beushausen et al. 2014; Dang et al. 2017). Whereas some other researches show slightly worsened performances against carbonation (Reinhardt and Assman 2009).

In this work the authors studied the absorption behavior of embedded and in-crack SAP during capillary water absorption of cement-based materials through micro-CT (Cnudde and Bonne 2013). Such information could be used to understand and unveil the potential of these particles to improve the durability of cement-based materials.

2 Methods

2.1 Materials and Sample Preparation

Two mortars with water-to-cement ratio of 0.45 were made with and without super-absorbent polymers. Mix designs of the mortars are reported in Table 1. CEM I 52.5 R, from ENCI Netherlands, tap water, superplasticizer Master Glenium 51 from BASF Netherlands and dry quartz aggregates 0.125/2 mm from Dekker Grondstoffen were used for the preparation of the mortars. A commercially available SAP Floset 27 cc, in this paper denominated as SAP F, was used in the SAP mortar. This consisted of cross-linked copolymer of acrylamide and acrylate, supplied from SNF SAS (Andrezieux, France). Particle size distribution of the dry SAP is shown in Fig. 1 after measurement in ethanol via laser diffraction. For the design of the mixtures, attention was paid to compensate for the water absorbed by the SAP during mixing by adding extra water in the mortar with SAP. This quantity was determined by adding tentative water amounts until matching the same flow table test results of 185–190 mm. This way it was determined that SAP F absorption capacity during mixing, Abs_{mix}, was 20 g_{water}/g_{SAP}. Same amount of superplasticizer was added to both mixtures to prevent air bubble formation. The sand-to-cement ratio was kept the same for both reference and SAP mortar at 3.27. The mixtures differ on the total amount of mortar to compensate for the volume occupied by swollen SAP during mixing.

Table 1. Mix design of mortars (quantities in [kg/m^3].

Component	4REF	4F0.5
CEM I 52.5 R	527	499
Water	237	224
Additional water	–	50
SAP	–	2.5
Superplasticizer	1.2	1.2
Aggregates	1720	1628
1–2 mm	528	500
0.5–1 mm	444	420
0.25–0.5 mm	374	354
0.125–0.25 mm	374	354

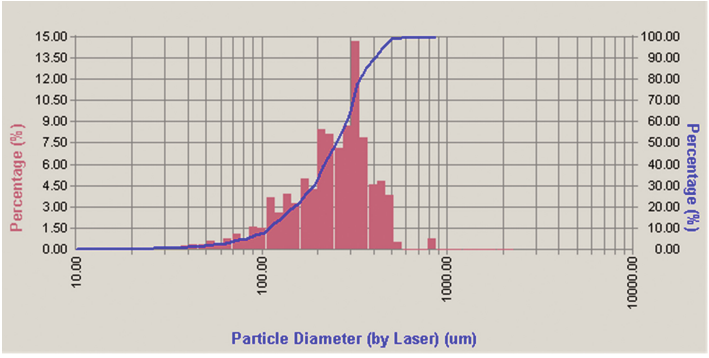

Fig. 1. Particle size distribution of SAP F by laser diffraction.

A Hobart planetary mixer with a capacity of 5 l was used to prepare the fresh mortar. All dry components, cement, sand and SAP (when applicable), were mixed for 1 min at speed 1. Previously mixed tap water and superplasticizer were added during the next 30 s while the dry components were still mixing and successively the whole mix was left for other extra 30 s at speed 1. The mixer was stopped for 1 min, time during which the walls and bottom of the bowl were scraped and mixed by hand in the fluid mortar. Next, the fresh mortar was mixed for 1 min and 30 s at speed 1 and 2, respectively. The mortar was left to rest for 10 min while covered by plastic foil to prevent water evaporation. This waiting time was necessary for the achievement of absorption equilibrium by SAP F.

The mortars were cast into the moulds in two layers and put 15 s in the vibrating table for each layer. Cylindrical moulds with diameter of 16 mm and height of 32 mm were employed. Two diametrically opposed groves with 2 mm side ran along the height of the mould. The samples were covered with plastic foil and left to set and harden for 24 h in laboratory conditions. After 24 h the samples were demoulded and stored in a fog room at 20 ± 1 °C and 95% Relative Humidity for 28 days. At 21 days they were sawn in smaller cylinders of 10 mm height and returned to the fog room.

At 28 days of age, the cylinders were put in an oven at 40 °C until constant weight attainment for approximately one week. All the surfaces were then sealed with duct tape until testing. To create the cracked samples, prior to the test, some wrapped cylinders were split in Brazilian Tensile Test configuration. The two parts were put back together by inserting a prismatic rod within the grooved space with width equal to 2 mm plus the desired crack width, 300 μm, and then by bridging the surfaces with bi-component glue Pleximon. The scheme is shown in Fig. 2(a). In this way the crack width was controlled to a certain extent.

2.2 Micro-CT Differential Dynamic Scanning

The Environmental micro-CT scanner (EMCT) from the Centre of X-ray tomography of Ghent University (UGCT) (Dierick et al. 2014) was employed to monitor the absorption of demineralized water in the mortar. The scanner consists of a standard directional microfocus 130 kV X-ray tube and a CMOS flat panel detector with 1316 by 1312 pixels with a 100 μm pitch. The aligned source and detector are mounted on a rigid horizontally rotating gantry, which allows to keep the sample stage static, therefore making more accurate the scanning of dynamic processes. A PMMA cell was specifically designed for subjecting the cylindrical samples to capillary absorption of water within the micro-CT scanner. The cell was connected from below to a pump via a hose in order to control the water head at the bottom of the sample during the capillary absorption experiment. Schematics of the cell can be observed in Fig. 2b.

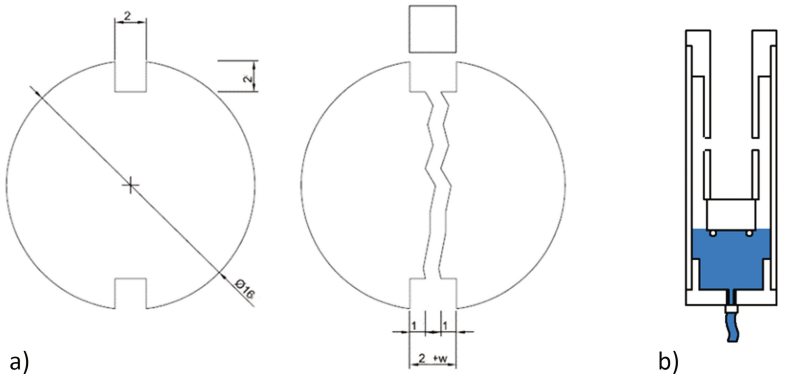

Fig. 2. Schematics of the sample and crack generation (Dimensions in mm).

Due to the poor attenuation contrast between water, air, SAP and cementitious materials and to the spatial resolution not being enough to resolve the pore space of cement-based composites, herein we employed a differential X-ray scanning procedure (Boone et al. 2014). The samples were scanned at the initial "dry" state and during saturation. The arithmetic difference between grey-value (GV) images at different states and normalization with respect to air and water GV resulted in the qualitative and quantitative monitoring of water absorption in the samples (Cui et al. 2018). The dry state

tomography was acquired with accelerating voltage of 120 kV and current of 80 μA, 2200 projections and exposure time of 80 ms for a final spatial resolution of 14 μm. The dynamic wet tomography was acquired with accelerating voltage of 120 kV and 133 μA current, 600 projections and exposure time of 30 ms for a final spatial resolution of 28 μm in binning mode 2x2. The latter were acquired continuously during the first 10 min of water absorption and every 10 min until 60 min of absorption.

The acquired projections were reconstructed in a 3D volume employing Tescan XRE reconstruction software Octopus Reconstruction® (Vlassenbroeck et al. 2006) and corrected for ring artifacts, spots and beam hardening. Different scans of the same sample were registered through DataViewer, available open source from Bruker. All image analysis was performed through the open source freeware ImageJ. Median filter was applied prior to subtraction of the stacks to avoid noise propagation.

Two segmentation procedures were used to separate (1) embedded SAP at the swollen state from mortar matrix and (2) SAP in the crack from water. Segmentation (1) was implemented on the wet stack through simple thresholding operation since there is enough contrast between air and water. Segmentation (2) required the use of Trainable Weka Segmentation plugin in ImageJ (Arganda-Carreras et al. 2017) where the characteristics of swollen SAP were trained from the swollen gel in the macropores. A post segmentation algorithm was implemented to filter segmented particles smaller than the minimum size of SAP at the dry state in order to exclude obvious segmentation errors.

3 Results

From the mix design and estimated amount of absorbed water from the rheological measurements, the expected volume fraction of SAP macropores was 5%. We could measure the real value via treatment of the dry state scan data in which SAP macropores and air voids were segmented through segmentation (1) described in the previous section. The air voids were filtered out by imposing that the sphericity of the segmented particles was to be smaller than 0.90. The counting of remaining objects in the stacks yielded an average SAP macropore total volume of 5.36% which was in agreement to the estimated volume. From the particle analysis performed in the segmented SAP macropores it emerged that the swollen particles had an average sieve diameter of 368 μm vs. an estimated sieve size, d_{mix}, of 480 μm. The latter was calculated through Eq. 1 by assuming a spherical particle shape and that the density of the swollen SAP, ρ_{mix}, is that of water:

$$d_{mix} = d_{dry}\sqrt{\frac{\rho_{dry}}{\rho_{mix}}Abs_{mix}} \tag{1}$$

Where Abs_mix is the absorption capacity of the SAP during mixing of mortar [g_wat/g_SAP] and d_dry is the diameter of SAP at the dry state. Figure 3a shows the 3D renders of absorbed water in mortar matrix and Fig. 3b in SAP after 60 min of capillary absorption of water. It can be observed that at the arrival of the waterfront at a certain height in the sample, SAP don't swell immediately as can be seen from the difference in

height of the wetting front and upper swollen SAP particles. Reasons for this occurrence could be the low level of saturation of the surrounding matrix at the wetting front position which results in a slower percolation towards the macropore.

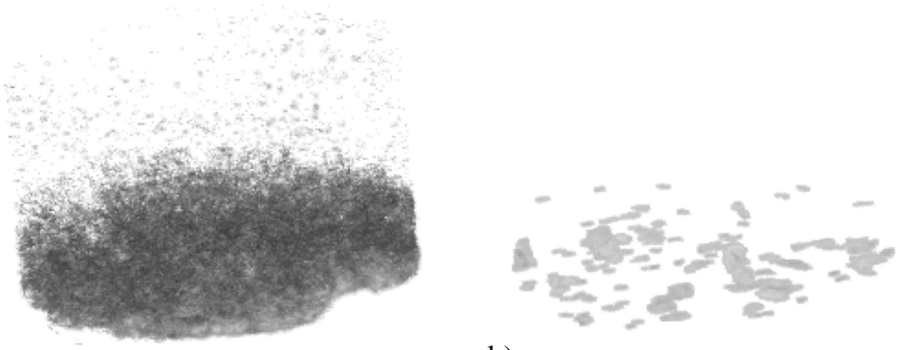

Fig. 3. 3D renderization of water absorption of (a) mortar matrix in sound sample and (b) swollen SAP in sound mortar sample.

Also a rough quantification of the capillary absorbed water was done via treatment of the differential micro-CT data. Noise in the stacks due to i.e. scattering was limited by imposing a cutoff to the calculated water content in the voxels minor or equal to the bulk porosity of the sample, measured a posteriori through gravimetry. In Fig. 4, a graph is shown of the water absorption for 4REF and 4F0.5 mor (quantified in the sole mortar phase from tomography of 4F0.5) and for 4F0.5 mor + SAP (quantified in both mortar and SAP phases from tomography of 4F0.5). From the graph it results evident that the mortar with SAP takes up more water than its reference, due to the absorption of water by the SAP, since the matrix absorption of 4F0.5 was very similar to the reference mortar absorption. This was previously proposed elsewhere (Rodriguez et al. 2018) from numerical simulations.

In Fig. 5 swollen SAP in a portion of a crack are shown. These were segmented using Segmentation (2) described before. Average sieve size measured from the segmentation resulted 644 μm. This means that during the capillary absorption experiment the SAP in the crack swelled to a sieve diameter 3.2 times the diameter of the SAP during mixing, much less than the estimated through free absorption capacity in demineralized water (7 times) (Pelto et al. 2017). This disagreement between the two values has been found in other studies regarding self-sealing before (Rodriguez et al. 2019). In a study from (Lee et al. 2018), the authors explain the changes in absorption capacity of SAP by the absorption of Ca2+ ions into the polymers during mixing of fresh cementitious mixtures.

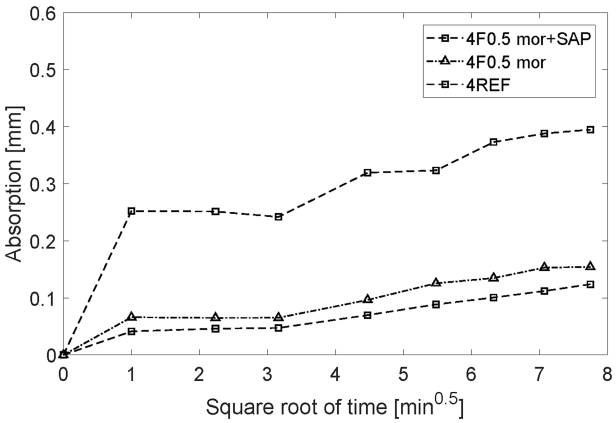

Fig. 4. Water absorption during sorptivity experiments in plain mortar 4REF and SAP-containing mortar 4F0.5 quantified through X-ray micro tomography.

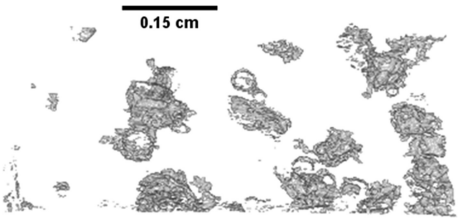

Fig. 5. Swollen SAP particles in the crack during capillary water absorption in mortar 4F0.5 segmented from X-ray micro tomography stack.

4 Conclusion

In this study, dynamic differential dynamic micro CT was used to monitor capillary water absorption in mortar with and without SAP. From the experimental results, the following conclusions are drawn:

- Differential dynamic micro CT is a powerful tool to monitor water absorption in cement-based materials.
- Some morphological data from the resulting composite can be studied: water absorption by the particles during mixing and during capillary water absorption.
- Water absorption due to SAP absorption can be separated from the total water absorption of the composite. We show direct evidence of the additional water absorbed by the embedded SAP. There is potential to study internal curing through this technique.
- Quantification of water retained by SAP in the crack can help in giving indications of potential of self-sealing and improved self-healing.

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