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Superabsorbent polymers to mitigate plastic drying shrinkage in a cement paste as studied by NMR

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ABSTRACT

At early ages, a problem of plastic shrinkage can arise when a cement paste is subjected to harsh drying conditions during hardening. SuperAbsorbent Polymers (SAPs) are a promising admixture to mitigate shrinkage in cement pastes. By introducing internal curing by means of the stored mixing water in the SAPs, the plastic shrinkage can be partially mitigated, next to the mitigation of autogenous shrinkage during setting of the cement paste. The kinetics of water release by the SAPs towards the cementitious matrix have been studied in detail to understand the mechanism. Nuclear Magnetic Resonance (NMR) is an effective technique to non-destructively monitor the effects induced by the SAPs during this plastic period and hardening as a function of time. The SAPs are able to protect the cement paste internally from the harsh ambient drying conditions and are able to sustain the internal relative humidity. The plastic settlement was reduced and there was less plastic shrinkage measured. Below 5 mm of the surface in SAP specimens, the specimens were hardening as if put in sealed conditions.

1. Introduction

SuperAbsorbent Polymers (SAPs) are able to absorb several hundred to thousand times their own weight in fluids and to retain it within their structure. After application in the medical and hygiene industry [1], it was only a matter of time till this material was also applied in a cementitious material [2] to change the rheology [3], to increase the freeze-thaw resistance [4,5], to induce self-sealing [6–9] and self-healing [10–14]. Furthermore, a cement paste with a low water-to-binder ratio experiences high autogenous shrinkage deformation after it has set due to the occurring cement hydration. SAPs have therefore been proposed as an admixture to mitigate this self-desiccation and autogenous shrinkage [15–18].

However, shrinkage may also occur during the first hours after casting while the cement paste is still plastic and when it shows no significant strength development [19]. The cause of this plastic shrinkage is the (rapid) evaporation of water near the surface leading to high capillary pressures as water menisci begin to develop in between the solid particles [20]. This causes capillary tension among the solid particles and thus settlement and shrinkage. At some point, the water menisci disappear and air will flow in between the particles [21]. If the specimen deformation is restrained, it may crack [22].

Only a limited amount of studies have investigated the influence of SAPs in terms of plastic shrinkage mitigation. Dudziak and Mechtcherine investigated the influence of SAPs on the plastic behaviour of fresh cement pastes with a water-to-cement ratio of 0.265 [23]. They used a spherical SAP with an average size of approximately 150 µm in the dry state. The amount of entrained water by adding 0.6 m % of SAP by cement weight corresponded to an additional water-to-cement factor of 0.087. Dudziak and Mechtcherine found that the capillary pressure and the plastic deformations were reduced in the SAP mixtures, but the settlement deformation increased compared to reference samples with a water-to-cement ratio of 0.265 [23].

The SAPs retain their stored entrained water within water-filled macro-pore inclusions in the cementitious material. In that way, they are able to reduce self-desiccation shrinkage by internal curing and may possibly aid in mitigating plastic shrinkage as well. It is difficult to study the effect of SAPs without destructing the microstructure. Nuclear Magnetic Resonance (NMR), however, is a non-destructive technique to study the water amounts (¹H) in a material. It is a powerful technique to study the cement hydration and the fluid transport in porous materials [24–26]. The hydrogen atoms interacts with the pore wall and a result the NMR signal will decay. The resulting relaxation rate is proportional to the pore structure and can be quantified [27]. Friedemann et al.

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showed that water is available during post-internal curing of cement pastes, when most of the internal curing already took place [28]. Nestle et al. used NMR to study the water balance in a cement paste with SAPs [29]. NMR is thus a feasible technique to investigate the water states in cement pastes with SAPs.

The type and size of the polymers are important. If the SAP is releasing its water too fast due to a low resistance to capillary forces, i.e. before final setting, the total water-to-cement ratio would increase. This may cause the cementitious matrix to have inferior properties [30,31]. On the other hand, when it would be releasing its water too slow, the water is not available for curing. The SAPs thus need to release their water at the right moment in time. The SAPs also need to be homogeneously distributed. The most ideal swollen SAP size for mitigating autogenous shrinkage is 100–200 μm [15]. Too big SAPs would not be able to cure the complete cementitious matrix at the same amount. In this study, a small SAP with dry size of approximately 100 μm used to mitigate autogenous shrinkage [17] will be used. This SAP will be compared to a bigger SAP with a size of approximately 480 μm . This latter SAP is ideal to self-seal and self-heal a crack [9,14]. The bigger SAP was, as expected, inferior to the smaller SAP to mitigate autogenous shrinkage and to maintain the internal relative humidity [17,32]. A previous NMR study of the respective SAPs revealed that the smaller SAP gradually releases its stored water after time of final setting, ideally maintaining the internal relative humidity [32]. The larger SAP prematurely released its stored water after time of final setting, leading to an inferior internal curing compared to the smaller SAP [32]. However, this polymer may behave differently upon plastic shrinkage and was thus also included in the current study.

Plastic shrinkage may lead to different timing of water release by the SAPs and is therefore subject of this study. The water near the top surface may be released before setting or may act as a buffer zone. In this paper, the curing by the SAPs during plastic shrinkage and the change in water states as a function of time are monitored by means of NMR tests. NMR was used for the first time to study the SAPs' water release and kinetics as a function of time.

2. Materials and methods

In this section, the different studied mixtures and types of SAP are explained first (2.1), followed by the NMR apparatus and principle (2.2). In the end, thin-section analysis is explained (2.3).

2.1. Studied mixture compositions

Two reference cement pastes with a water-to-binder ratio (W/B) of 0.3 (R0.30) and 0.354 (R0.354), respectively, were made. The cement used was a CEM I 52.5 N Portland type. Superplasticizer was added in an amount of 0.5 m% and 0.3 m% (mass-% of cement weight) to ensure practical workability for the R0.30 and R0.354 mixture. The superplasticizer used was a polycarboxylate type (Glenium 51, conc. 35%, BASF).

Based on the model of Powers and Brownyard [33], the amount of needed entrained water in the SAPs for internal curing of the reference paste with a water-to-cement ratio of 0.30 can be theoretically calculated and amounts to an additional water-to-cement ratio of 0.054 [15]. In that way, the total water-to-cement ratio $(w/c)_{\text{tot}}$ equals 0.354, but taking into account that the amount of 0.054 is entrained in the SAPs $(w/c)_e$ it leads to an effective water-to-cement ratio $(w/c)_{\text{eff}}$ of 0.30. Two different mixtures containing different SAPs (BASF) were investigated. These were SAP A (for mixture A_e), a copolymer of acrylamide and sodium acrylate (particle size $100.0 \pm 21.5 \mu\text{m}$ ($n = 100$)), and SAP B (for mixture B_e), a cross-linked potassium salt polyacrylate (particle size $476.6 \pm 52.9 \mu\text{m}$ ($n = 100$)). Both SAPs are bulk-polymerized and consist of irregular crushed particles. They were stored in dry and sealed conditions prior to testing or mixing in the cement paste mixture. SAP A is able to absorb $305 \pm 4 \text{ g/g}$ SAP in demineralized

water and $61 \pm 1 \text{ g/g}$ SAP in cement filtrate solution and has a swelling time of 10 s [14,17]. SAP B absorbs $283 \pm 2 \text{ g/g}$ SAP in demineralized water and $58 \pm 2 \text{ g/g}$ SAP in cement filtrate solution with a swelling time of 60 s [14,17]. The absorption capacity was determined using the filtration method and the swelling time using the vortex method [34]. Both swelling times are fast enough to ensure complete swelling during mixing. In this way, the entrained water is completely absorbed by the SAPs and the $(w/c)_{\text{eff}}$ is 0.30.

The following mixing procedure was used. The SAP particles were added on top to the cement and were first dry mixed to ensure a homogenous distribution in the cement. After this dry mixing, the total water was added together with superplasticizer which was dissolved in the water prior to addition. The amount of superplasticizer in the SAP mixtures was the same as for the R0.30 mixture, to minimize possible influences of different amounts of superplasticizer on the setting properties of the respective mixtures [35]. The total amount of water for a water-to-cement ratio of 0.354 was added. The amount of SAP to be added to maintain the same workability as for R0.30 was 0.22 m% (mass-% of binder weight) SAP A (for mixture A_e) and 0.45 m% SAP B (for mixture B_e), respectively. These values were obtained by subsequent flow measurements [36] following the Standard EN 12350-5. X-ray computed micro-tomography [13] and microscopic analysis [30] were used to verify whether the formed macro pores had the expected size. No loss in workability because of SAP addition was observed.

A Vicat needle test following the Standard ASTM C191-08 (Method A: Reference Test Method using the manually operated Vicat apparatus) was used to determine the setting times of the mixtures. The time of final setting was defined as the time between initial contact of cement and mixing water and the time at which the needle did not leave a circular impression in the cement paste surface. This time is referred to as the optimal starting time of water release by the SAPs to mitigate autogenous shrinkage and to start internal curing [17].

2.2. Nuclear Magnetic Resonance (NMR) setup

Sample containers (cylinder $\varnothing 27 \text{ mm} \times 100 \text{ mm}$ high) were filled with fresh cement paste for approximately 45 mm and put in the NMR setup as shown in Fig. 1. Furthermore, dry air was blown over the top of the specimen in such a way that the evaporation rate exceeded 1 kg per square meter per hour, as in that way plastic shrinkage will likely develop (ASTM Standard C1579-06). This was verified using several dummy tests on the same mixtures and with water samples prior to testing with NMR. Different air inlet flows were used until the required evaporation rate was reached. The mass decrease was measured using a mass scale with precision of 0.001 g. In all tests, the intended evaporation rate was obtained ($1.04 \pm 0.02 \text{ kg/h/m}^2$).

An external magnetic field B_{main} of 0.8 T was applied corresponding to a frequency of 34 MHz. This field was provided by a water-cooled iron-cored electromagnet with poles 50 mm apart from each other. A coil was placed around the sample for creating and receiving the radiofrequency fields. A Faraday shield was added between the coil and the sample to suppress the effect of the changes of the dielectric permittivity by variations of the moisture content, hence making the NMR measurements quantitative. All NMR measurements were performed at room temperature ($23 \pm 1^\circ\text{C}$).

The magnetic field gradient was set at 0.3 T/m offering a one-dimensional resolution in the order of magnitude of 1.0 mm. The intensity of the signal was recorded along the height of the specimen by moving the specimen by means of a step motor (in steps of 1 mm). The spin-echo signal S was recorded after an echo time T_E equal to 180 μs . Carr-Purcell-Meiboom-Gill (CPMG) sequences were measured along the height and the overall total water signal intensity was recorded. Profiles were measured with 44 min intervals and a total measuring time of 48 h. Fast Laplace Inversion (FLI) was used to obtain the relaxation times T_2 as a spectrum [32,37]. All peaks were normalized to the first signal to obtain the percentage. The weighed percentage of each peak

Fig. 1. Sealed sample container (cylinder $\varnothing$ 27 mm $\times$ 100 mm high) filled with the cement paste (45 mm) mounted with an air in-/outlet. The sample can be moved through the NMR with help of a step motor. The NMR makes use of an electromagnet generating a main magnetic field of 0.8 T. Using Anderson gradients coils a constant gradient is applied of 0.3 T/m. A Faraday shield has been added to ensure quantitative NMR measurements.

was then multiplied with the normalized signal, resulting in the relative ratio of each studied peak as a function of time.

For the SAP-mixtures, a comparison was made between the signal of the SAP entrained water and the free water to investigate when and how the water is released by the SAPs for internal curing. The specimen was studied for 48 h after water contact with the cement. The first NMR measurement was performed after 10 min of contact time of water with cement paste.

2.3. Thin-section and microscopic analysis

Thin sections (approximately 45 mm $\times$ 27 mm $\times$ 25 μ m) were prepared from studied specimens after being studied with NMR upon plastic shrinkage. First, the specimens were cut to receive 45 mm $\times$ 27 mm faces along the axis of the cylindrical specimen, which were then glued on a glass slide with a thickness of 2.9 mm. The combined sample was cut and polished until a height of the specimen and glass of 10.1 mm was reached. Next, the specimens were impregnated under vacuum with a fluorescent epoxy. The excess epoxy was polished away and an object glass was glued on the smooth surface. Finally, the glass slides were cut off and the remaining part was polished until a thin section with 25 μ m thickness was achieved. The epoxy ensured stable handling of the whole specimen. A cover glass was glued on top to protect the thin section.

The thin sections were analysed with a Leica DMLP microscope with a DFC 295 camera. Normal light, polarized light and fluorescent light were used to study the change in microstructure at the exposed drying surface compared to the interior microstructure. Eventual cracking was also studied in detail.

3. Results and discussion

NMR was used to obtain the total water signal as a function of the height and time (section 3.1). CPMG measurements were conducted at the same time to study the relative amount of SAP entrained water and free water during hardening. These results are discussed in section 3.2. After NMR testing, the specimens were prepared for thin-section analysis. The effect of the plastic shrinkage on the microstructural change and the crack formation were studied and are discussed in section 3.3.

3.1. Total water signal distribution and plastic settlement

The overall total water signal distribution along the height of the specimens is shown in Fig. 2. The top of the specimen exposed to the

drying air current is found on the right-hand side. The bottom of the specimen is found on the left-hand side. In time, the curves of the total water signal shift downward as the free water is consumed due to hydration. The change in position of the inflection point in the curve at the surface of the sample exposed to air (right-hand side) served as a basis for the estimation for the plastic settlement. These points are shown as circles (°) on the figures. Plastic settlement is seen on the right as the profiles shift to the left due to the moving surface. All inflection points found are depicted on the figure as different drying front conditions may be present. These will be discussed in detail later on. All observed inflection points are shown in the figure, in order to provide a complete picture of drying.

Four distinct regions (zone 1–4) are found when studying the total water profiles. When a cement paste is hardening, the free water will be consumed and hydration products will be formed causing the material to become denser. There generally is a decrease in total water signal over time, i.e. the curves are shifted downwards. Two distinct regions with profiles narrower together are found (zone 2 and 4). The first upper narrow region (zone 2) corresponds with setting. Initial setting occurred at approximately 8 h of age and final setting was at approximately 11 h of age as determined with the Vicat needle test, for R0.30, Ae and Be. The setting of R0.354 occurred approximately 1 h earlier. The lower dense region corresponds with the total consumption of free water due to an increasing degree of hydration in time (zone 4). The specimen becomes hardened. Zone 1 starts at 10 min of contact with water, zone 2 starts after approximately 4 h of contact with water and zone 3 after approximately 10 h. Zone 4 starts after approximately 24 h of contact with water and the test ended after 4 days of measuring, showing the end of zone 4. In time, the curves would further decrease in value but plastic shrinkage has already occurred.

In the reference samples, the curves show a partial higher decrease in water content near the drying surface (blue region at the right-hand side, especially in the R0.354 mixture). This hints to the harsh drying conditions during hardening. Part of the water is moving towards the drying surface and moisture is lost. As the moisture content is decreasing, the capillary pressure will increase due to receding menisci leading to plastic shrinkage. For the R0.354 sample, the initial total water signal intensity is higher compared to the R0.30 sample due to the higher water-to-cement ratio. The ratio between both signal intensities corresponds to the ratio of both water-to-cement ratios. In the end (bottom curves for R0.354), the water profiles are somewhat tilted, showing that water has been used partially due to plastic shrinkage.

For the SAP samples, the found curves are more or less horizontal, showing the positive aspect of using SAPs for maintaining the internal

Fig. 3. Signal intensity [a.u.] as a function of the relaxation time T_2 [s] and in steps of 44 min from top to bottom showing different allocated peaks in the different studied specimens, close to the drying surface.

the harsh drying conditions. In the SAP systems, additional peaks are allocated to SAP-entrained water. This water is stored in the SAP particles and can be released for internal curing. In that way, as the T_2 is different, the water kinetics from the SAPs towards the cementitious matrix could be studied in detail as a function of time. It is clearly seen that also water from the SAP pores is consumed, especially for the SAP B systems as the SAP-peaks disappear in time.

The signal intensities for the entrained water and the free water could be compared (Fig. 4). In this figure both signal fractions are plotted relative to each other. The black curves are the ones closest to the drying surface and are prone to plastic shrinkage. The red curves are closer to the interior of the sample itself. For comparative reasons, all other curves (0–40 mm and 0–41 mm for the SAP A and SAP B specimen, respectively) are shown as red area comprising all curves found, showing the same behaviour. This thus is the boundary for the internal hydration of the samples.

The overall theoretical relation is depicted (30/5.4 inclination) as a straight line, as found by using the Powers and Brownard model [33]. In this model, an amount of 0.054 additional water-to-cement ratio is required to mitigate autogenous shrinkage of a reference system with a water-to-cement ratio of 0.30. During hardening, the signal is moving

from the top right to the origin in the bottom left, as water is consumed (red arrow). The theoretical water as found by the Powers and Brownard model is stored in the SAPs. As can be seen, as the signals travel in time from the theoretical point on the top-right to the origin, all expected internal curing water was stored in the SAPs and the amounts of SAP added are the correct ones. Other amounts of entrained water would lead to curves starting elsewhere. There thus was a good correlation between these theoretical expected values and the values obtained with NMR.

Due to plastic settlement, SAP A particles are packed closer together, leading to the higher signal value of total entrained water intensity near the surface (black arrow). The free water signal decreases rapidly and free water is consumed together with a release of the entrained water. The SAP seems to release little amount of entrained water in the beginning and store it within its structure. This water is then used to counteract the evaporation due to the imposed drying conditions once the material begins to set. This is seen as a more or less horizontal line in the curve, where the entrained-water signal is decreasing at approximately constant free water signal. The curves then move towards a normal hydration curve for a SAP A system. For A_{e_s} , just below 2.5 mm inwards (i.e. the red area), the cement paste is hardening

A_e B_e

Fig. 4. Comparison of the signal fraction of entrained water in the SAPs [–] to the signal fraction of free water [–] for the A_e and B_e mixtures showing a different kind of behaviour towards water kinetics near the drying surface. The arrows show the evolution in time of the curves in the top 5 mm of the sample and the red area the boundaries of the signals below 5 mm of the drying surface. The initial sample surface is positioned at 46 mm for A_e and 47 mm for B_e. The theoretical line following Powers' model is also shown as a solid line. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

as if no drying is occurring. The SAPs thus seem to act as protective layer and internal curing reservoir within the cement paste.

SAP B, however, seems to release its water prematurely due to the

larger particle size. They are less in total number and have a smaller surface area exposed to the drying matrix compared to the smaller SAP A. The plastic settlement, however, is still less compared to the

R0.30 **R0.354** **Ae** **Be**

Fig. 5. Thin sections with fluorescent light (left) and through-going normal light (right) showing the microstructural details for all studied mixtures. In the R0.354 microcracking is observed. The SAP macro pores are clearly seen for the SAP A and SAP B mixtures. The scale bar amounts to 1000 µm.

settlement of the reference samples. The water stored in the SAP B systems is quickly consumed and used in the overall cementitious system. When looking at the 47 mm line, one notices a quick

consumption of both free water and SAP stored water. This is due to the quick drying at the surface.

SAP A is also able to mitigate autogenous shrinkage, as we have

shown before [17]. This internal curing together with maintaining the internal relative humidity was also studied by means of NMR measurements in our earlier work [32]. The same overall trend in signal fractions of free water and of entrained water stored in the SAP was found. For SAP B, it seemed that the polymer was not as effective to mitigate autogenous shrinkage as compared to the ideal smaller SAP. The same conclusions can here be drawn in terms of the plastic shrinkage.

3.3. Thin-section analysis

The thin-sections for all studied mixtures are shown in Fig. 5. On the left-hand side the fluorescent images are shown and on the right-hand side the normal through-going light micrographs of the specimen at the same location and with the same magnification.

In reference samples, a densification of and change in the cementitious matrix is seen in the upper 700 μm from the surface. This is clear in the R0.30 specimen when studying the through-going light image. During testing, partial carbonation may also have taken place. Some minor cracking was observed and this cracking was more prominent for the R0.354 mixture. Clear drying cracks could be observed and these were due to plastic shrinking. Some partial densification was seen in the area of 10–15 mm below the surface due to the consumption of free water which diffused towards the surface as the surface was imposed to harsh drying conditions. This was the effect also seen in Fig. 2 for R0.354 (blue region).

When studying the SAP specimens, less densification can be noticed. The cementitious matrix resembles the inner matrix of the R0.30 mixture, if the macro pores are not taken into consideration. This is due to the same effective water-to-cement ratio [30,36]. As this ratio is the same, the same overall microstructure was expected. If the theoretical absorption of mixing water by the SAPs was not the same as would occur in the specimen, the cementitious matrix would have had either a higher or lower amount of mixing water when the absorption by the SAPs was lower or higher than expected. This would be seen as a difference in intensity in the micrographs, which was not observed.

SAP A was packed closer together at the surface due to the partial release of mixing water due to the harsh drying conditions. This functional layer upon plastic shrinkage was also expected from the results found in Fig. 4. SAP B, which was larger, did not accumulate at the surface to protect against plastic shrinkage. This also corresponds to the effects studied in Fig. 4. By means of image analysis, the pore sizes of SAP could be investigated. Theoretically, the size should be 257 μm and 981 μm for SAP A and SAP B, respectively, as calculated based on their swelling capacity of mixing water and the initial dry size. This average size ($n = 100$) was found in the bulk material of the specimens; $253 \pm 66 \mu\text{m}$ and $891 \pm 194 \mu\text{m}$ for SAP A and SAP B, respectively. The amount is thus the correct one as the cementitious matrix is formed at final setting, thus maintaining the size of the macro pores. This amount corresponds to the theoretical amount based on the needed water for internal curing as determined by the Powers and Brownayard model, as was previously discussed.

4. Conclusions

Based on the findings of the research on the mitigation of plastic shrinkage by SAPs as studied by means of NMR following conclusions can be drawn:

- In reference systems, there is clear plastic shrinkage and plastic shrinkage cracking due to the applied air current. Water from the interior is partially used to counteract the loss due to plastic shrinkage drying. This was seen as a local decrease in total water content 10–15 mm below the drying surface.
- The plastic shrinkage settlement is lower in SAP systems compared to reference systems. However, plastic shrinkage is still present due

to the harsh drying conditions but SAPs seem to be a promising admixture to partially mitigate plastic shrinkage.

- SAP A, which is smaller compared to SAP B, is able to mitigate plastic shrinkage better by providing its stored water towards the cementitious matrix during harsh drying conditions when a cement paste is hardening. In the interior of the samples, hydration occurs like in sealed conditions.
- Near the drying surface, the free water is consumed first, followed by a gradual release of the stored water in SAP A, thus effectively mitigating plastic shrinkage.
- SAP B releases its stored water quickly when exposed to harsh drying conditions. The bigger SAP B is less suitable to counteract plastic shrinkage as the larger particles are less present in the overall cementitious matrix.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.cemconcomp.2018.06.019>.

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