The Water Absorption-release of Superabsorbent Polymers in Fresh Cement Paste: An NMR Study

Jingbin Yang¹, Zhenping Sun²*, Yihe Zhao³, Yanliang Ji⁴ and Biyun Li⁵

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Abstract
Superabsorbent polymers (SAPs) can effectively reduce the risk of concrete cracks by acting as an internal curing material. In this study, ¹H low-field NMR was used to investigate the influence of the pre-absorbed water amount and the water-cement ratio of paste on the water absorption-release behavior of SAPs in fresh cement paste. Results show that when the water-cement ratio was 0.30, the SAPs without pre-absorption absorbed water from fresh cement paste and retained them with relative stability. The SAPs with pre-absorption would rapidly release the pre-absorbed water into a paste, and the water releasing speed increased with the amount of pre-absorbed water. Additionally, the water amount absorbed by the SAPs without pre-absorption increased with the water-cement ratio from 0.30 to 0.40. However, the water absorption of SAPs from the paste was also found to be severely inhibited when the water-cement ratio reached 0.50. SAP swelling in fresh cement paste is affected by the synergistic effects of multiple ions.

1. Introduction
High-performance concrete is produced and cured via modern technological means. The main characteristic of high-performance concrete is to use enough high-efficiency admixtures in the mix proportion design to ensure a lower water-cement ratio. However, autogenous shrinkage occurs when the water-cement ratio is too low, resulting in cracking (Mignon et al. 2017). For high-performance concrete with a compact structure, the environmental moisture provided via external curing hardly enters the concrete interior and compensates for the water consumed by hydration. This means that the traditional curing method can neither guarantee full hydration nor control autogenous shrinkage. Superabsorbent polymers (SAPs) are cross-linked hydrogel networks consisting of water-soluble polymers that absorb and retain hundreds of times their weight in water (Mignon et al. 2015). SAPs in cement and concrete have been the focus of many studies because they effectively reduce the autogenous shrinkage of high-performance concrete and even self-heal cracks (Snoeck et al. 2016, 2018).

Two SAPs and cement paste or mortar mixing methods exist in previous literature (Snoeck et al. 2015; Kim et al. 2019). First is for the SAPs to pre-absorb a certain amount of water before mixing, and control additional SAPs water content by changing the pre-absorbed water amount. However, it is not entirely clear whether and how factors such as the amount of pre-absorbed water affect SAPs behavior in the paste. Second is mixing the SAPs with cement and aggregate in dry conditions before adding water and controlling the fluidity of the sample containing SAPs so that it is the same as that of the reference sample. For the second mixing method, Yang et al. (2019) proved that SAPs have different swelling capabilities in pore fluids with different water-cement ratios, however, the result was derived from a filtrate of paste instead of the original cement paste. Further study needs to be conducted on the effectiveness of the two mixing methods when adjusting the additional water content of SAPs and SAPs evolution in the fresh cement paste.

In this study, ¹H low-field nuclear magnetic resonance (NMR), a more intuitive method, was used to monitor SAPs absorption-release behavior in fresh cement paste. A comparison was made between the effects caused by the amount of pre-absorbed water and water-cement ratio on the SAPs in the fresh cement paste, and the sodium (Na⁺), calcium (Ca²⁺), and aluminum (Al³⁺) ion concentrations in the filtrate of fresh cement.
paste with different water-cement ratios were determined via inductively coupled plasma optical emission spectrometry (ICP-OES). This study can better develop an understanding of SAPs behavior in cement and concrete and help choose an appropriate SAPs mixing method.

2. Materials and methods

2.1 Materials

In this study, a white Portland cement (P.W. 425, Anqing, China) was used, which has a ferric oxide content of 0.35 percent, and Table 1 shows its detailed chemical composition (determined via X-ray Fluorescence Spectrometer, PANalytical Axios, Netherlands). Sodium polyacrylate-based SAPs (Socochem, Qingdao, China) with irregular particle shapes were selected, they were vacuum dried in a desiccator with silica gel before testing or mixing in cement paste, and the average particle size was 302.6 μm. The SAPs were formed via solution polymerization, and the polymerization monomer was acrylic acid. Deionized water was used for mixing, pre-absorption, and the solution preparation.

2.2 Preparation of cement paste

In this study, SAPs were incorporated via two different methods. For the first method, mix the weighed SAPs and pre-absorbed water according to Table 2 and wait for the water to be absorbed, then mix the cement and deionized water at a water-cement ratio of 0.30 for 30 s, and, finally, add these pre-absorbed SAPs and stir for another 30 s. This procedure can obtain a relatively better dispersion of the pre-absorbed SAPs particles. For the second method, mix cement with the SAPs without pre-absorption, then add deionized water according to the water-cement ratios of 0.30, 0.40, and 0.50 and stir for 1 min. SAPs dosage (based on dry state) in every paste sample was 0.3% (by cement mass). Table 2 lists the cement paste mix proportions.

2.3 1H low-field NMR

The 1H low-field NMR instrument (MICRO-MR20, Niumag, Shanghai, China) used in this study has a magnetic field of 0.5 T and a 25 mm Radiofrequency (RF) coil. After mixing, 20 g of fresh paste was poured into a small glass bottle, which was sealed with a layer of polytetrafluoroethylene film. The transverse relaxation time (T2) was measured via the CPMG (Carr-Purcell-Meiboom-Gill) sequence and the parameters, including the echo time (τ1 = 0.302 ms) and the number of scans (NS = 4), were kept constant. The T2 relaxation curve was fitted to a multi-exponential curve via the application of the inverse Laplace transform algorithm.

2.4 Inductively coupled plasma optical emission spectrometry (ICP-OES)

After mixing, the fresh paste was immediately filtered and centrifuged, and the solutions were analyzed via ICP-OES (Agilent 7900, Japan) to determine the concentrations of Na+, Ca2+, and Al3+ as a function of the water-cement ratios (0.30, 0.40, and 0.50). Na+ and Ca2+ were measured during the experiment using the 100-times diluted solution, whereas Al3+ was measured using the 10-times diluted solution.

2.5 Swelling capacity test of SAPs

The swelling of SAPs in deionized water and other solutions was measured via the tea-bag method. A non-woven tea-bag was soaked in deionized water or other solutions for 3 h before testing. Then place 1 g of the SAPs without pre-absorbed water or 1 g the SAPs that absorbed 10 g of deionized water into a tea-bag for testing.

3. Results and discussions

3.1 Effect of the pre-absorbed water amount on the behavior of SAPs in the fresh paste

Figure 1 shows the transverse relaxation time (T2) distribution of samples 1, 2, and 3. Broad peaks in the T2 range of about 1 - 10 ms (P pores) and peaks in the T2 range of about 100 - 1000 ms (P SAPs) are attributed to water in the cement paste pores and water contained in the SAPs (Ji et al. 2015, 2019; Snoeck et al. 2017). The numbers below each P SAPs indicated the peak areas, which reflected the relative water content in the SAPs. For comparison, Fig. 1d is the T2 distribution of a paste sample without SAPs and with a water-cement ratio of 0.30.

Figure 1a shows that even if SAPs did not pre-absorb water, some mixing water was absorbed in the SAPs.

| Sample No. | Cement (g) | SAPs (g) | Mixing water (g) | Pre-absorbed water by SAPs (g) | Total water (g) | Total water-cement ratio |
|------------|------------|----------|------------------|-------------------------------|----------------|--------------------------|
| 1          | 100        | 0.3      | 30               | 0                             | 30+0           | 0.30+0                  |
| 2          | 100        | 0.3      | 30               | 3                             | 30+3           | 0.30+0.03               |
| 3          | 100        | 0.3      | 30               | 6                             | 30+6           | 0.30+0.06               |
| 4          | 100        | 0.3      | 40               | 0                             | 40+0           | 0.40+0                  |
| 5          | 100        | 0.3      | 50               | 0                             | 50+0           | 0.40+0                  |

Table 1 Chemical composition of the white Portland cement.

| Component | CaO | SiO2 | Fe2O3 | Al2O3 | MgO | SO3 | Na2O | K2O | P2O5 | Others |
|-----------|-----|------|-------|-------|-----|-----|------|-----|------|--------|
| Mass fraction/ % | 60.1 | 18.2 | 0.35  | 2.23  | 13.5 | 2.49 | 0.28 | 0.48 | 0.03  | 2.36   |

Table 2 Mix proportions of the cement paste.
from the paste 5 min after mixing. Between 5 min and 1 h after mixing, the $P_{\text{SAP}}$ area increased, indicating that the SAPs continued absorbing free water. And in the following 1 to 3 h, the $P_{\text{SAP}}$ area was relatively stable, indicating that SAPs did not undergo severe water exchange with fresh paste. Figures 1b and 1c show that SAPs pre-absorbed a certain amount of deionized water before; however, the $P_{\text{SAP}}$ area 5 min after mixing was no higher than that of SAPs at the same time in Fig. 1a. And, with hydration time increasing, the $P_{\text{SAP}}$ area in Figs. 1b and 1c gradually decreased. Figure 1b shows only a tiny $P_{\text{SAP}}$ can be observed 3 h after mixing, while the $P_{\text{SAP}}$ nearly disappeared 2 h after mixing in Fig. 1c. This demonstrates that SAPs with pre-absorption cannot absorb water in fresh cement paste after mixing. The pre-absorbed water would gradually release into the paste. Comparing results in Figs. 1b and 1c, the more water pre-absorbed by SAPs, the faster water is released into the paste.

To better understand SAPs behavior, a comparison was conducted between SAPs swelling with or without pre-absorption in deionized water and saturated Ca(OH)$_2$ solution ($\text{pH} = 12.11$, Ca$^{2+}$ concentration was 839.60 mg/L), and Fig. 2 shows the results. SAPs performance with or without pre-absorption in deionized water was similar, and they all achieved water absorption of about 250 times their weight. However, in saturated Ca(OH)$_2$ solution, SAPs without pre-absorption swelled slowly, water absorption was stable after 20 min, and it finally achieved about 75 times its weight of water absorption. While the final SAPs water absorption with pre-absorption was about 25 times its weight, only one-third of the SAPs did not have pre-absorption.

Figure 3 is a schematic of the water absorption process of sodium polyacrylate-based SAPs. When SAPs contacted water, the hydrophilic group within began to dissociate, and the anions increased, so the electrostatic repulsion force between ions made SAPs swell. Simultaneously, to maintain electrical neutrality inside the SAPs structure, the cations could not diffuse out of the structure. Therefore, the cation concentration inside the SAPs structure increased, which formed osmotic pressure between both sides of the SAPs, thereby water penetrated. With water absorption increasing, osmotic pressure tended to zero, which means water cannot enter the structure any further, and the SAPs finally reached water absorption equilibrium (Buchholz and Peppas 1994; Mechtcherine and Reinhardt 2012).

However, SAPs absorption capacity in cement paste depends not only on the SAPs but also on external pore fluid compositions (Snoeck et al. 2014). A considerable amount of ions (such as Ca$^{2+}$ and Na$^+$) came to be in the pore fluids because of the dissolution of cement.

Fig. 1 The transverse relaxation time ($T_2$) distribution of cement pastes (a: sample 1, b: sample 2, c: sample 3, d: the cement pastes without SAPs).

Fig. 2 SAPs absorption-release in deionized water and saturated Ca(OH)$_2$ solution.
particles (Wei and Li 2006), which increased the external ion concentration and reduced the concentration difference inside and outside the SAPs. Water would migrate from inside to the outside due to osmotic pressure when the external ion concentration was higher than the internal ion concentration, so the internal SAPs solution would be reversely released into the external solution (as shown in Fig. 4a). This explains why SAPs with pre-absorption released the pre-adsorbed water instead of absorbing water from the paste or the solution after adding SAPs to fresh paste or the saturated Ca(OH)₂ solution. Furthermore, the increase of pre-absorbed water in SAPs means that the internal SAPs solution was considered diluted, and the internal ion concentration decreased. Therefore, when the water-cement ratio was constant, the ion concentration difference both inside and outside the SAPs structure were further enlarged, and the pre-adsorbed water release was accelerated (as shown in Fig. 4b).

### 3.3 Effect of the water-cement ratio on SAPs behavior in fresh paste

To achieve better internal curing, SAPs water content occasionally has to be adjusted. However, the results above show that changing SAPs water content by pre-absorbing a certain amount of water might not be an effective method because the water pre-absorbed by SAPs before mixing would gradually release into the paste after mixing. Better results could be obtained by combining SAPs without pre-absorption with the cement paste, and controlling SAPs water content could be achieved by changing the water-cement ratio of the paste.

The transverse relaxation time (T₂) distribution of samples 4 and 5 are shown in Fig. 5. For comparison, Figs. 5c and 5d show the T₂ distribution of the paste samples without containing SAPs and with a water-cement ratio of 0.40 and 0.50.

When the water-cement ratio of the paste was 0.40, Pₜ was observed at 5 min after mixing could be observed, and this Pₜ area was higher than that of the Pₜ at the same time in Fig. 1a. Then, SAPs continued to absorb water until the Pₜ area slowly decreased after 1 h, and the Pₜ at each time in Fig. 5a was higher than at the same time in Fig. 1a, which indicates that increasing the water-cement ratio of the paste from 0.30 to 0.40 did increase the SAP water content.

However, Fig. 5b shows that when the water-cement ratio was further increased to 0.50, no Pₜ could be observed at other times except for a tiny Pₜ that occurred at 5 min after mixing, which indicated that SAPs water absorption from the paste was severely inhibited at this water-cement ratio.

Table 3 shows the results of the concentrations of Na⁺, Ca²⁺, and Al³⁺ in the fresh paste filtrate with different water-cement ratios. Cement paste with a low water-cement ratio generally contains a higher ion concentration, while a high water-cement ratio paste has lower ion concentration in the pore fluids (Wei and Li 2006). Therefore, the concentration of Na⁺ in the pore fluid
fluids decreased with the increase of the paste water-cement ratio, which was caused by the dilution produced by the increase of the water-cement ratio. However, a high water-cement ratio could also accelerate cement particle dissolution, such as accelerating Ca$^{2+}$ dissolution (Mounanga et al. 2004). Increasing the water-cement ratio from 0.30 to 0.50 caused the Ca$^{2+}$ concentration to increase significantly. The Ca$^{2+}$ concentration when the water-cement ratio was 0.50 was 2.46 times higher than when the water-cement ratio was 0.30. The Ca$^{2+}$ not only increased the ion concentration of the external solution (the pore fluids), but also combined the desirable groups in the SAPs structure to form stable complexes, therefore the absorption capacity was reduced (Mechtcherine and Reinhardt 2012). The difference in SAP swelling capacities without pre-absorption in deionized water and Ca(OH)$_2$ solution shown in Fig. 2 also proves it.

Therefore, SAPs absorbed more water from the paste when the water-cement ratio increased from 0.30 to 0.40, as the Na$^+$ concentration in the pore fluids decreased and the Ca$^{2+}$ concentration only increased slightly. However, SAPs swelling capacity was inhibited when the water-cement ratio further increased to 0.50, despite lower Na$^+$ concentration in the pore fluids, which was due to the large Ca$^{2+}$ concentration increase. These results are similar to those obtained by Yang et al. (2019) in the filtered slurry, where SAPs achieved the highest absorption with a water-cement ratio of 0.32. Furthermore, when the filtered slurry water-cement ratio continued to increase to 0.36 and 0.40, SAPs absorption decreased. The difference of water-cement ratio corresponding to the highest SAPs water absorption may be caused by the difference between the filtered slurry in the study of Yang et al. and the original cement paste in this study. The Al$^{3+}$ filtrate concentration was only about 1 mg/L. Although the Al$^{3+}$ concentration in the fresh cement slurry filtrate can also limit SAP swelling, it is relatively low compared with Na$^+$ and Ca$^{2+}$. Therefore, it may have a small effect on the SAPs water absorption-release behavior in the fresh paste. The results above indicate that SAPs swelling in fresh paste equals the result of multiple ions interacting in the pore fluids.

To verify the inhibitory effects of Ca$^{2+}$ and Na$^+$ on SAPs absorption in cement paste, referring to the Ca$^{2+}$ and Na$^+$ concentrations in the three pore fluids shown in Table 3, three solutions with the same Ca$^{2+}$ and Na$^+$ concentrations were prepared using CaCl$_2$ and NaCl analytical reagents, and SAPs absorption in the three solutions was determined via tea-bag method. Results are shown in Table 4. The Al$^{3+}$ was ignored in the solution preparation because the Al$^{3+}$ concentration in the
with 1H low-field NMR results, which could explain the lowest absorption. However, SAPs absorption in solution 3 was insignificant. Solutions No. 1, 2, and 3 in the three pore fluids was relatively low and the difference may be related to the similar Ca$^{2+}$ concentration in both solutions. However, SAPs absorption in solution 3 was the lowest, and the lowest absorption was consistent with 1H low-field NMR results, which could explain how SAPs were significantly inhibited when the water-cement ratio was 0.50.

4. Conclusions

In this study, the 1H low-field NMR test was used to determine the water absorption-release behavior of sodium polyacrylate-based SAPs in the fresh paste. The following conclusions were drawn:

1. The mixing method significantly affects SAPs water absorption-release behavior in the fresh paste. When the water-cement ratio of the paste was 0.30, SAPs without pre-absorption could absorb the mixing water from the paste and store it with relative stability, while the pre-absorbed water in the SAPs would quickly release into the paste within 3 hours of mixing, which cannot play an internal curing role. Furthermore, the more pre-absorbed water is obtained, the faster the water release after mixing.

2. The mixing method significantly affects SAPs water absorption-release behavior in the fresh paste. When the water-cement ratio of the paste increased from 0.30 to 0.40, SAPs without pre-absorption absorbed more water from the paste after mixing. However, when the water-cement ratio of the paste was further increased to 0.50, SAPs water absorption from the paste was severely inhibited, which relates to the high water-cement ratio promoting cement particle dissolution, increasing ion concentration (such as Ca$^{2+}$) in the liquid phase, and inhibiting SAP swelling.

3. Controlling SAPs water content by adjusting the amount of pre-absorbed water of the SAPs appears to be unfeasible. SAPs water absorption from the paste can be adjusted by changing the water-cement ratio of the paste. However, due to cement particle dissolution and the sensitivity of SAPs swelling to the ions in the fluid, focusing on selecting an appropriate water-cement ratio is necessary.

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