EFFECTS OF THE PRE-ABSORPTION OF SUPERABSORBENT POLYMERS AND THE WATER-CEMENT RATIO OF PASTE ON THE ADSORPTION-DESORPTION OF SUPERABSORBENT POLYMERS: AN NMR STUDY

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Abstract

As an internal curing material, superabsorbent polymers (SAPs) can effectively reduce the risk of volume shrinkage of cement-based materials. By preparing the cement paste mixed with SAPs, the amount of pre-absorbed water and the water-cement ratio of paste on the water absorption-release behavior in the fresh cement paste were studied by using ^{1}H low-field NMR. The results showed that when the water-cement ratio was 0.30, the SAPs without pre-absorption could absorb the mixing water from the fresh paste and stored the mixing water in the SAPs relatively stable, while the pre-absorbed SAPs released the absorbed water into the paste rapidly, and the more pre-absorbed water, the faster the water released after mixing. When the water-cement ratio was increased to 0.40, the mixing water absorbed by SAPs without pre-absorption was more than that absorbed by SAPs when the water-cement ratio was 0.30, but in the system with super high water-cement ratio of 0.50, the SAPs cannot absorb mixing water from the paste after mixing.

Keywords**:** superabsorbent polymers, ^{1}H low-field NMR, mixing method, water-cement ratio

1. INTRODUCTION

High-performance concrete is produced and cured by modern technology. The main characteristics of high-performance concrete in mix proportion design are to use enough high-efficiency admixtures to ensure a low water-cement ratio. However, when the water-cement ratio is too low, autogenous shrinkage will occur, resulting in cracking[1]. For the high-performance concrete with compact structure, the environmental moisture provided by external curing can hardly enter the interior of concrete and compensate for the water consumed by cement hydration reaction. This means that the traditional curing method cannot guarantee the full hydration and control the autogenous shrinkage. Superabsorbent polymers (SAPs) are cross-linked hydrogel networks consisting of water-soluble polymers, and they can absorb and retain water hundreds of times their own weight[2]. In recent years, many studies have focused on SAPs in cement and concrete, SAPs are effective in reducing the autogenous shrinkage of high-performance concrete or high-strength mortar, and even self-sealing and self-healing cracks.

There are two mixing methods of the SAPs and concrete in previous literature[3-5]. The first is to mix the SAPs pre-absorbed a certain amount of water before mixing, and control the amount of additional water of SAPs by changing the amount of these pre-absorbed water. However, in this mixing method, whether and how the factors such as the amount of pre-absorbed water affecting the behavior of SAPs in the paste is not fully known. The second is to dry mix the SAPs with cement or supplementary cementing materials before adding water, and control the fluidity of the sample containing SAPs is the same as that of the reference sample, so the difference between the water-cement ratio of the SAPs sample and that of the reference sample is the amount of additional water of SAPs. In the second mixing method, Yang et al.[6] proved that SAPs have different swelling capabilities in the pore fluids with different the water-cement ratios, but the result was evaluated in the filtrate of paste, not in the original paste. Whether these two mixing methods can effectively adjust the amount of additional water of SAPs, and the effects of factors such as the two mixing method and the water-cement ratio of paste on the evolution of SAPs in fresh cement paste are also insufficient.

In this study, a more intuitive method, ^{1}H low-field NMR, was used to monitor the absorption-release behavior of SAPs in the fresh cement paste. The effects of the different mixing methods, the amount of pre-absorbed water and the water-cement ratio on the SAPs in the fresh cement paste were compared. This study can help to better understand the behavior of SAPs in cement and concrete and choose the appropriate mixing method of SAPs.

2. MATERIALS AND METHODS

2.1 Materials

To reduce the interference of paramagnetic substances to the ^{1}H low field NMR signal, the cement used in this study is white Portland cement (P.W. 425, Anqing, China), and its chemical composition (determined by an X-ray Fluorescence Spectrometer, PANalytical Axios, Netherlands) is shown in Table 1. A sodium polyacrylate-based SAPs (Socochem, Qingdao, China) with irregular particle shape were selected, its average particle size was 302.6 μm. The tea-bag method was used to determine that the water absorption ratio of the SAPs in deionized water was about 250 times of its own weight. The water for the cement mixing and the pre-absorbed by the SAPs were deionized water.

Table 1: Chemical composition of the white Portland cement

Component	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SO_3	Na_2O	K_2O	P_2O_5	Others
Mass fraction/ %	60.1	18.2	0.35	2.23	13.5	2.49	0.28	0.48	0.03	2.36

2.2 Preparation of AAS paste

There are two different ways of incorporation of SAPs in this study. In the first way, after mixing cement and deionized water according to the water-cement ratio of 0.3 for 30 seconds, then add the pre-absorbed SAPs (pre-absorbed water-cement ratios are 0.03 and 0.06), and continuously stirred for 30 seconds. The second is to mix the SAPs without pre-absorbed with the cement, then added deionized water according to the water-cement ratio of 0.3, 0.4 and 0.5, and stirred for 1 minute. The dosage of SAPs in all the paste samples is 0.03% (by cement mass).

2.3 ^{1}H low-field NMR test

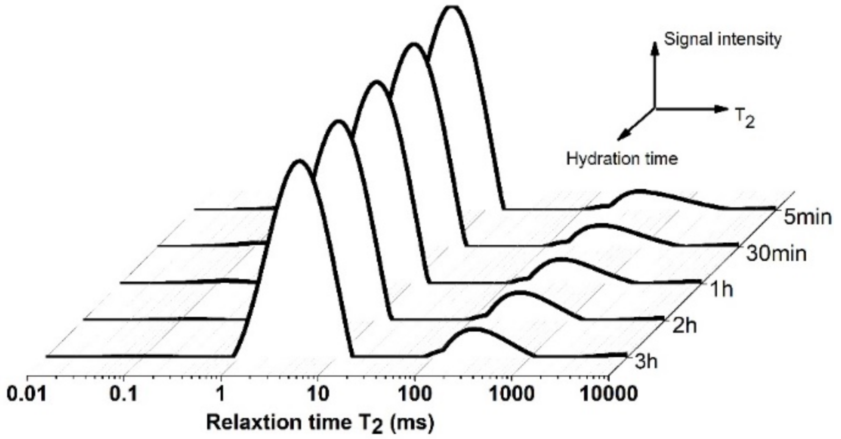
The ^{1}H low-field NMR instrument (MICRO-MR20, Niumag, Shanghai, China) used for this study has a magnetic field of 0.5 T and a 25 mm Radiofrequency (RF) coil. After mixing, about 20 g of fresh paste was poured into a small glass bottle, which was then sealed by a polytetrafluoroethylene film. The transverse relaxation time (T_2) was measured using CPMG (Carr-Purcell-Meiboom-Gill) sequence and the parameters including the echo time ($\tau1 = 0.302$ ms) and the number of scans (NS = 4) was kept constant. The T_2 relaxation curve was fitted to a multi-exponential curve by using the inverse Laplace transform algorithm.

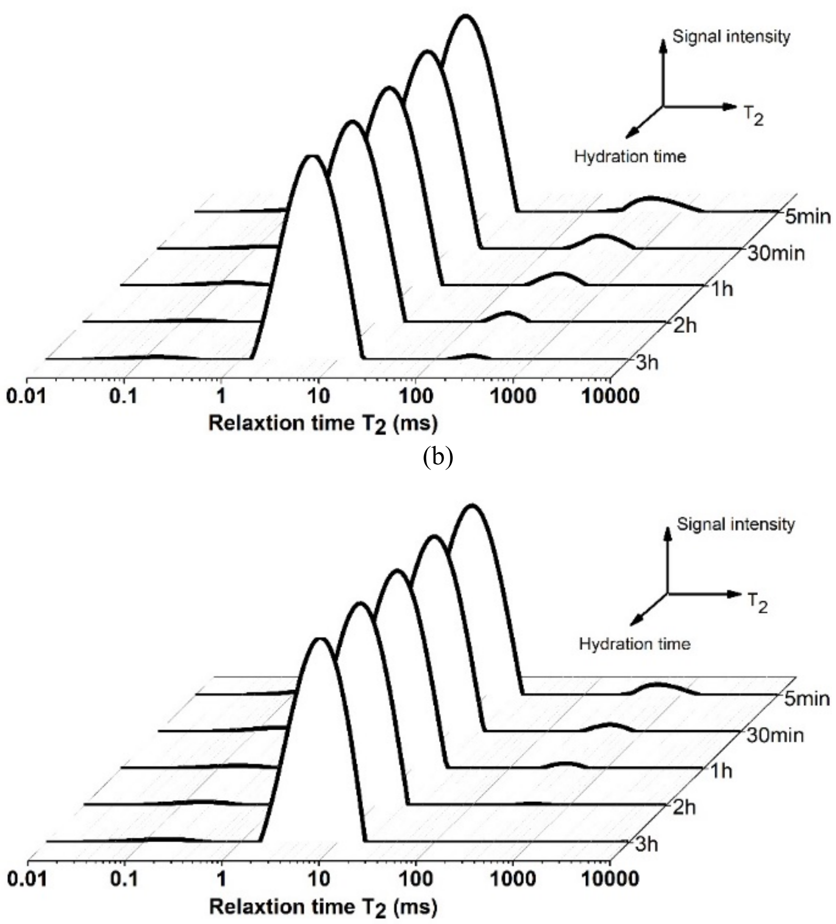
3. RESULTS

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

Figure 1 shows the transverse relaxation time (T_2) distribution of cement pastes containing the SAPs without pre-absorption (the total water-cement ratio is 0.30+0), SAPs with 0.03 water-cement ratio of pre-absorption (the total water cement-ratio is 0.30+0.03) and SAPs with 0.06 water-cement ratio of pre-absorption (the total water cement-ratio is 0.30+0.06), respectively. The broad peaks in the T_2 range of about 1-10 ms and the peaks in the T_2 range of about 100-100 ms are attributed to water in the pores of the cement paste and water contained in the SAPs[7-9], respectively.

In Figure 1a, even if the SAPs were not pre-absorbed water, it can be observed that some mixing water was absorbed in the SAPs from paste after 5 minutes after mixing. Between 5 minutes and 1 hour after mixing, the intensity of the T_2 relaxation peaks of SAPs gradually increased, indicating that SAPs continued to absorb free water. And in the following 1 hour to 3 hours, the intensity of the T_2 relaxation peaks of SAPs was relatively stable, indicating that SAPs did not undergo severe water exchange with the fresh paste. In Figure 1b and Figure 1c, the SAPs pre-absorbed a certain amount of deionized water before mixing. However, the intensity of the T_2 relaxation peaks of the SAPs at 5 minutes after mixing was not higher than that of the SAPs at the same time in Figure 1a. And with the increase of the hydration time, the intensity of the T_2 relaxation peaks of the SAPs gradually decreased. In Figure 2b, only a tiny T_2 relaxation peak can be observed at 3 hours after mixing, while in Figure 1c, the T_2 relaxation peak of SAPs was nearly disappeared at 2 hours after mixing. This is, the pre-absorbed SAPs cannot absorb the mixed water from the paste; on the contrary, the pre-absorbed water will gradually release into the paste. Comparing the results in the Figure 1b and Figure 1c, the more pre-absorbed water by the SAPs, the faster the water release in the paste after mixing.





(a)

(b)

(c)

Figure 1: The transverse relaxation time (T_2) distribution of cement pastes containing the SAPs (a: the SAPs without pre-absorption, b: the SAPs with 0.03 water-cement ratio of pre-absorption, c: the SAPs with 0.06 water-cement ratio of pre-absorption)

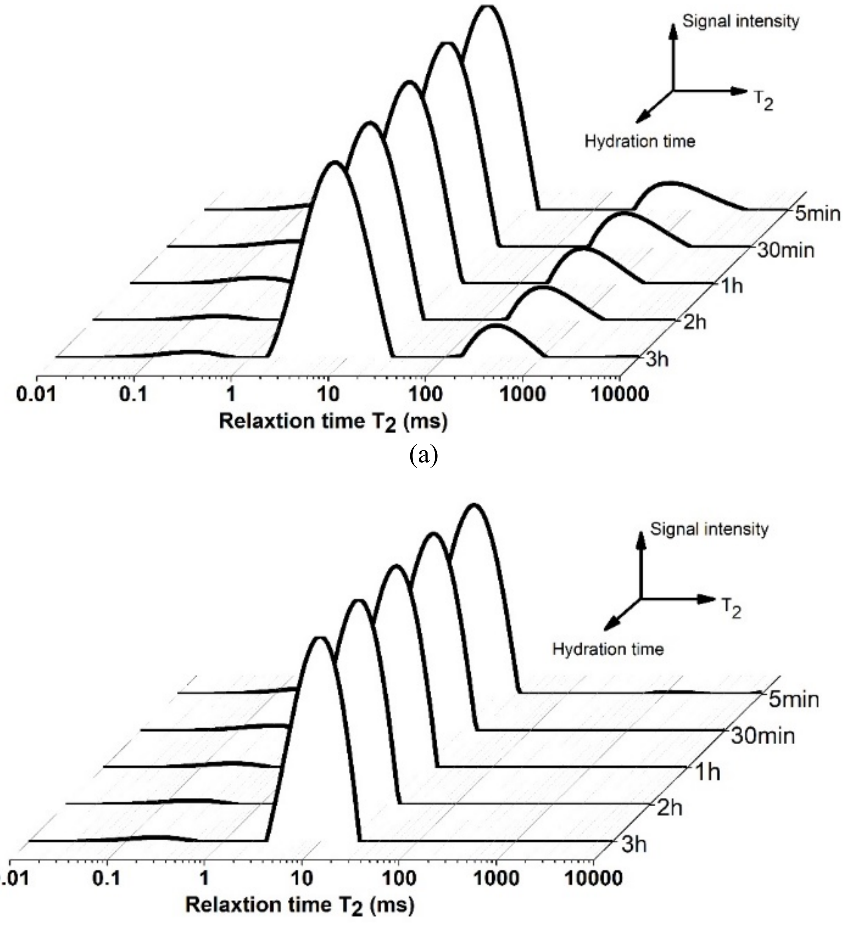
3.2 Effect of the water-cement ratio on the behavior of SAPs in the fresh paste

To achieve a better internal curing effect, sometimes the water content in the SAPs has to be adjusted. However, the above results showed that it may not be an effective method to change the water content in the SAPs by pre-absorption of a certain amount of water, because the water pre-absorbed by the SAPs before mixing will gradually release into the paste after mixing, and it cannot play a role in adjusting the water content in the SAPs. A better result may be obtained by combining the SAPs without pre-absorption with cement, and it is possible to control the water content in the SAPs by increasing or decreasing the water-cement ratio of the paste.

Figure 2 shows the transverse relaxation time (T_2) distribution of cement pastes containing SAPs without pre-absorption (the total water-cement ratio is 0.40+0) and SAPs without pre-absorption (the total water cement-ratio is 0.50+0), respectively.

When the water-cement ratio of the paste was 0.40, it can be observed that the T_2 relaxation peak of the SAPs at 5 minutes after mixing, and the intensity of this T_2 relaxation peak is higher than that of the T_2 relaxation peak at the same time in Figure 1a. Then, the SAPs continued to absorb water until the relaxation peak intensity slowly decreased after 1 hour after mixing, and the T_2 relaxation peak of SAPs at each time in the Figure 2a is higher than that at the same time in the Figure 1a, which indicates that increasing the water-cement ratio of the paste from 0.30 to 0.40 does increase the water content in the SAPs.

However, an interesting result is shown in Figure 2b. When the water-cement ratio was further increased to 0.50, except for a tiny T_2 relaxation peak of the SAPs that occurs at 5 minutes after mixing, no T_2 relaxation peak of the SAPs can be observed at other times. The results show that the SAPs do not absorb water from the paste at this water-cement ratio.



(a)

(b)

Figure 2: The transverse relaxation time (T_2) distribution of cement pastes containing the SAPs without pre-absorption (a: the water-cement ratio of paste is 0.40, b: the water-cement ratio of paste is 0.50)

4. DISCUSSIONS

The sodium polyacrylate-based SAPs ionizes in water or solvent, with the increase of ion concentration inside the SAPs, the concentration difference between the inside of the SAPs and the external solution causes reverse osmosis, so that the water enters the SAPs. This is the primary driving force for water absorption.

In the cement paste, the absorption capacity of SAPs is dependent on the external fluid composition and the chemical structure, length and crosslinking degree of the SAPs[5]. When the SAPs with pre-absorption were added to the cement paste, due to the dissolution of the cement particles, there were a considerable amount of ions (such as Ca^{2+} and Na^{+}) in the liquid phase, which improved the ion concentration of the external solution of SAPs and reduced the concentration difference inside and outside the SAPs. While when the ion concentration of the external solution of SAPs was higher than that of the internal solution of SAPs, the inner solution of the SAPs would be reversely released into the outer solution due to the osmotic pressure. These can explain why after adding the pre-absorbed SAPs to the fresh paste, the SAPs released the pre-adsorbed water instead of absorbing water from the paste. With the increase of pre-absorbed water in the SAPs, the solution in SAP can be considered to be diluted and the internal ion concentration decreased. Therefore, when the water-cement ratio of the external paste was constant, the ion concentration difference inside and outside the SAPs structure was further enlarged, and the release of pre-adsorbed water was accelerated.

It has been known that the swelling capacity of SAPs in a solution is affected by the type and concentration of ions. In the cement paste with a low water-cement ratio generally contains a higher ion concentration, while the paste with a high water-cement ratio has a lower ion concentration in the liquid phase due to dilution[10]. Therefore, when the water-cement ratio of the paste increased from 0.30 to 0.40, the SAPs absorbed more mixing water. However, a high water-cement ratio may also accelerate the dissolution of cement particles, such as accelerating the dissolution of Ca^{2+}[11], while Ca^{2+} can combine the desirable groups in the SAPs structure to form stable complexes, thus reducing the absorption capacity. Therefore, when the water-cement ratio of the paste increased from 0.40 to 0.50, the swelling capacity of SAPs was inhibited, and it could not absorb water in paste with water-cement ratio of 0.5. These results are similar to those obtained by Yang et al.[6] in the filtered slurry, the SAPs achieved the highest absorption in the filtered slurry with water-cement ratio of 0.32, and when the water-cement ratio of the filtered slurry continued to increase to 0.36 and 0.40, the absorption of SAPs decreased. As for the difference of water-cement ratio corresponding to the highest water absorption of SAPs, it may be caused by the filtered slurry and the original cement paste.

5. CONCLUSIONS

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

(1). Different mixing methods have an important effect on the water absorption-release behavior of the SAPs in the fresh paste. When the water-cement ratio of the paste was 0.30, the SAPs without pre-absorption could absorb the mixing water from the paste and stored the mixing water in the SAPs relatively stable, while the pre-absorbed water in the SAPs would quickly release into the paste within 3 hours after mixing, which cannot play an internal curing role. And the more pre-absorbed water, the faster the water release after mixing, it seems that it is not feasible to control the water content in SAPs by adjusting the amount of pre-absorbed water of the SAPs.

(2). When the water-cement ratio of the paste increased from 0.30 to 0.40, the SAPs without pre-absorption absorbed more the mixing water from the paste after mixing. However, when the water-cement ratio of the paste was further increased to 0.50, the SAPs without pre-absorption could not absorb the mixing water from the paste, which may be related to the high water-cement ratio promoting the dissolution of cement particles, increasing the ion concentration (such as Ca^{2+} and Al^{3+}) in the liquid phase and inhibiting the swelling of SAPs. The water absorption of the SAPs from the paste can be adjusted by changing the water-cement ratio of the paste. However, due to the dissolution of cement particles and the sensitivity of the swelling of SAPs to the ions in the fluid, it is necessary to pay attention to selecting an appropriate water-cement ratio.

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