



Sorption kinetics of superabsorbent polymers (SAPs) in fresh Portland cement-based pastes visualized and quantified by neutron radiography and correlated to the progress of cement hydration



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ABSTRACT

Water sorption of two superabsorbent polymers in cement-based pastes has been characterized by neutron radiography. Cement pastes with W/C of 0.25 and 0.50 and one additionally containing silica fume (W/C = 0.42) were investigated. The SAPs differed in their inherent sorption kinetics in extracted cement pore solution (SAP 1: self-releasing; SAP 2: retentive).

Desorption from SAP 1 started very early after paste preparation. Hence, its individual non-retentiveness governs its behavior only.

SAP 2 released water into all matrices, but its kinetics were different. In the paste with the highest W/C, some moderate water release was recorded from the beginning. In the other two pastes, SAP 2 retained its stored liquid during the dormant period, i.e., up to the percolation threshold. Intense desorption then set in and continued throughout the acceleration period.

These findings explain the pronouncedly higher efficiency of SAP 2 as internal curing admixture as compared to SAP 1.

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1. Introduction

Superabsorbent polymers (SAP) have evolved as multifunctional admixtures in high-performance concrete due to their ability to absorb water quickly and release it slowly into the hydrating, cement-based matrix. They were found to be especially efficient as admixtures for internal curing to mitigate autogenous shrinkage in Portland cement-based construction materials with low water-to-cement ratios (W/C, water by weight of cement). They significantly reduce the potential of crack formation caused by self-desiccation. By now their functioning related to this effect of “internal curing” (IC) has been described well in principle [1–6]. The majority of studies have been performance-oriented and show the effects of IC from an engineering point of view. Only a few investigations have been published on the detailed mechanisms and kinetics of water migration within the cement-based material, including, for example, migrating amounts of water from SAP into the surrounding matrix or the onset and duration of water release [6–8]. Wyrzykowski et al. [6] described a so-called “demand–supply-mechanism” based on the findings with their individual SAP sample. They found that liquid was extracted from swollen SAP at that point in time coincident with the first drop in internal relative humidity.

Utilizing neutron tomography, Trtik et al. [8] visualized and quantified the water release from one SAP particle into a cement paste. They linked these kinetics to the progress of cement hydration and concluded that the onset of water release from their SAP particle coincided with the transition from the dormant to the acceleration period. In a similar study, Trtik et al. [9] characterized the release of internal curing water from two individual lightweight aggregate particles.

Utilizing nuclear magnetic resonance (NMR) relaxometry, Nestle et al. [7] monitored hydrating cement pastes containing an individually designed SAP sample. They found that the drainage of water from inside the SAP particles into the matrix started by the time of the acceleration period and was finalized one or two days after paste preparation, depending on the particle size of the SAP. However, cement hydration by itself was not assessed by an independent method such as calorimetry, for example.

Justs et al. [10] as well as Reinhardt and Assmann [11] employed isothermal calorimetry in order to characterize the impact of SAP on the hydration kinetics of cement pastes. The white Portland cement paste investigated in [10] had a basic W/C of 0.25, and the addition of SAP resulted in a slight delay in and a diminished extent of hydration within the first 30 h when compared to the SAP-free reference paste. In the long term, the degree of hydration of the SAP-containing paste conformed to that of the SAP-free paste with the same total amount of water in the sealed system. In [11] the authors utilized normal Portland

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cement and W/C between 0.30 and 0.50 but did not report in detail on the first few hours of cement hydration. However, they found as well that in the long run the degree of hydration depends only on the overall amount of water present in the system, irrespective of whether a part of it was entrapped in SAP at an early age.

None of the articles published so far has disclosed chemical details about the superabsorbers. Comparative studies investigating differently composed SAPs and focusing on their molecular sorption mechanisms in direct linkage to the specific behavior of cement-based construction materials have been quite rare to date. One approach showed how different SAPs perform individually in cement mortar depending on their cross-linking density and their density of anionic functional groups [12–15].

Indirect insight into the sorption kinetics of the two SAP samples employed in the present study during the first 90 min after concrete preparation has been gained recently [15]. The development of the two rheometric parameters, yield stress and plastic viscosity, led to the conclusion that the sorption kinetics as obtained from the so-called “tea-bag method” mirror themselves to some extent in the fresh concrete.

Pourjavadi et al. [16] synthesized one SAP sample and characterized its impacts on various properties of cement-based pastes containing nano-sized silica particles as well.

The literature survey as presented above shows that it is of essential importance to refine the knowledge of the working mechanisms of SAPs. The present study provides a new contribution to this field of research and in perspective to concrete technology, too.

Experimental data of sorption kinetics of SAPs obtained from within cement-based pastes directly are presented. The results are linked to the chemical compositions of the SAPs, the progress of cement hydration as well as performance-oriented effects of the SAPs in the cement-based materials such as modification of rheology and mitigation of autogenous shrinkage.

Neutron radiography – apart from neutron tomography – has evolved as a powerful method in observing water migration inside hardening and hardened cement-based specimens [17–20]. In particular the experimental setup and consecutive image processing are easier than in tomography. The work at hand used neutron radiography imaging both to visualize and to quantify water migration from two individual, chemically different acrylate-based SAP samples into pastes of normal Portland cement (W/C = 0.25, W/C = 0.50) and one made of normal Portland cement and silica fume (W/C = 0.42, silica fume 10 wt.% by weight of cement [bwoc]). The SAP samples are two of those used previously by Schröfl et al. [12,13] and Mechtcherine et al. [14,15]. The sorption kinetics as observed by neutron radiography imaging are linked to results of the free sorption tests (“tea-bag method”), which had quantified the intake and release of extracted cement pore solution by the SAPs. A further link has been established to cement hydration as characterized by isothermal calorimetry. The buildup process of the solid matrix is traced via ultrasonic pulse transmissivity [21, 22]. Furthermore, the experimental results of the present study are closely connected to previous investigations on rheology [15] and the efficiency of mitigating autogenous shrinkage [12–14] of the very SAP samples.

As demonstrated by Trtik et al. [8] using neutron tomography, the size of a SAP particle within the paste could be detected as well. This investigation used merely two individual SAP particles placed in a quite tiny paste volume. Hence, the spatial resolution was very high. However, the experimental setup utilized in the present study did not allow for assessing the sizes of the SAP particles for reasons of spatial resolution. Apart from [8], particle sizes of swollen SAPs to be used in cement-based materials have been quantified to date in liquids only, without the surrounding real paste. Esteves focused on the particle size assessment of hydrogels in an extracted cement-pore solution. The studies were based on observations using light microscopy [23] and laser light diffraction [24]. Consequently, the assessment of the particles sizes of various SAPs embedded in one sample of cement-based paste in the

order of magnitude of several cubic centimeters should be a core topic of a follow-up study building on the present manuscript.

2. Experimental

2.1. Raw materials

Two superabsorbent polymers were used, both of which were synthesized by means of block polymerization and crushed into small pieces after synthesis (R&D samples provided by SNF Floerger, Anrézieux Cedex/France). SAP 1 had the maximum relative anionicity; it was produced of acrylic acid as the sole main monomer. Its cross-linking density is qualitatively rather high; specifically, it is in fact higher than that of SAP 2. The relative anionicity of SAP 2 is below that of SAP 1. SAP 2 is a cross-linked copolymer composed of the two main monomers acrylic acid and acryl amide. These SAP samples had been used in previous studies: in [12, 13] the present SAP 1 was denominated as “SAP B” and SAP 2 as “SAP D”. The present SAP 1 was called “SAP 2” in [14] and SAP 2 is “SAP 4” in that study. “SAP-B” in [15] was the present SAP 1 and “SAP-DS, -DC, -DN” were individual gradings of SAP 2.

The performance of the chosen superabsorbent polymers in cement-based mortar has been discussed in [12–15] with respect to the correlation between their molecular structure and composition, impact on rheology and efficiency in mitigating autogenous shrinkage. Table 1 shows the characteristic values of their particle size distributions in the dry state (laser granulometer LS 13320, BeckmanCoulter, Krefeld/Germany; dispersive liquid: propan-2-ol). Both samples were used as obtained from the external supplier and not treated further. Future studies will be conducted with equally sized SAP samples to exclude potential influences from the different gradings.

The sorptivity of SAP 1 and SAP 2 was assessed by the so-called “tea-bag method” in accordance to the procedure described in [12–15]. Similar to those studies, the test solution was the filtrate of a slurry of the normal Portland cement used in the mortar (cf. below) prepared at the W/C of 4.3. The most crucial ions to influence the progress of absorption and potential individual desorption in time, i. e., Na^+ , K^+ , Ca^{2+} , OH^- and SO_4^{2-} are well represented in this solution. Admittedly, the distinct concentrations of these ions differ from the pore solution in the mortars, but basically, all ions relevant for the relative sorption kinetics are present. The retention ability or an inherent trend to desorb intaken liquid without any further trigger is reliably obtained from the test with this kind of ionic solution [12]. The time of recording was 24 h to cover the entire period of neutron imaging (Fig. 1).

Pastes consisting of cement, SAP, water and – where applicable – superplasticizer or silica fume were prepared immediately before beginning neutron radiography imaging, calorimetry or ultrasonic testing, as applicable. The cement was a rapid-hardening, normal Portland cement with no extra defined properties according to DIN EN 197-1 [25] (CEM I 42.5 R by Schwenk, Ulm/Germany, production site Bernburg/Germany). Its chemical and mineralogical compositions are summarized in Table 2. The silica fume was a dry powder with an average particle size of 85 nm and a purity of 97 wt.% amorphous SiO_2 (Grade 971, Elkem Refractories, Kristiansand/Norway). As a high-range water-reducing admixture a polycarboxylate-based commercial product was used as obtained in the form of an aqueous solution (Glenium 51, BASF, Trostberg/Germany).

Table 1
Particle size distributions of SAP 1 and SAP 2 in the dry state.

	SAP 1	SAP 2
d_{10} [μm]	224	386
d_{50} [μm]	586	903
d_{90} [μm]	1029	1446

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