Cement and Concrete Research 42 (2012) 865–873

Contents lists available at SciVerse ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Relation between the molecular structure and the efficiency of superabsorbent polymers (SAP) as concrete admixture to mitigate autogenous shrinkage

Christof Schröfl, Viktor Mechtcherine *, Michaela Gorges

Institute of Construction Materials, Technische Universität Dresden, 01062 Dresden, Germany

ARTICLE INFO

Article history:
Received 10 August 2011
Accepted 15 March 2012

Keywords:
Superabsorbent polymers (SAP)
Autogenous shrinkage (C)
Cement pore solution (B)
Cement hydration (A)
High-strength mortar (E)

ABSTRACT

Superabsorbent polymers (SAP) were studied as admixtures for mitigating the autogenous shrinkage of a high-strength concrete. The presence of Ca^{2+} ions in the alkaline solution modified the kinetics of the liquid uptake and release when compared to that in other saline solutions and distilled water. SAP with high density of anionic functional groups took up the cement pore solution quickly, but greatly released it subsequently. The cross-linking density had no pronounced influence on the behaviour of such SAP. SAP with lower density of anionic groups did not release the liquid over the time of experiment. All SAP counteracted autogenous shrinkage during the acceleration period of cement hydration. For the materials which released the absorbed pore solution no effect on autogenous shrinkage was found beyond the initial period. SAP materials which did not release the absorbed solution in the experiments with liquids continued the mitigation of autogenous shrinkage during the deceleration period. The internal curing had no negative effect on the compressive strength of the mortar.

1. Introduction

Autogenous shrinkage was first recognised and described more than sixty years ago by Lyman [1] when a decrease in the volume of concrete was observed without any notable change in its mass or temperature. However, since autogenous shrinkage of ordinary concrete is considerably smaller than drying shrinkage, not much attention was paid to this subject until the beginnings of the application of high-performance concrete in construction, where it was observed that HPC was prone to autogenous-shrinkage-caused cracking under restraint. Up to date, formulas for predicting autogenous shrinkage are included in a number of design codes for concrete structures, e.g., DIN 1045-1 [2], JSCE Design Code 2002 [3].

Autogenous shrinkage is typically defined as the bulk deformation of a closed (sealed), isothermal, cementitious material system not subject to external forces [4]. Before the setting of concrete, autogenous shrinkage is considered equal to chemical shrinkage, i.e., the internally occurring and the externally measurable volume changes being the same. This is attributed to the cementitious material's liquid-like state's not being able to sustain the internal voids created by chemical shrinkage. After the formation of a solid skeleton of hydration products, the outward bulk deformations of the concrete are clearly smaller than the changes in the internal volume of the material. The macroscopically measured reduction in concrete specimen volume (autogenous shrinkage) can be, therefore, only a fraction of the real material shrinkage (chemical shrinkage).

To which extent chemical shrinkage is transformed into autogenous shrinkage depends obviously on the water content of the system and the pore-size distribution resulting from hydration. In the case of ordinary concrete autogenous shrinkage is relatively small in comparison to drying shrinkage. Mainly for reasons of workability, more water is used in the production of such concrete than is needed for the complete hydration of cement. Thus, pores forming due to chemical shrinkage are either filled with water or with air of relative humidity near 100%. This means that during the entire hydration process no significant self-desiccation occurs and the thermodynamic equilibrium of the system is undisturbed to a great extent. Similar arguments can be offered with regard to the disjoining pressure between the particles of the C–S–H gel. Hence, there is no intense driving force for autogenous deformations in typical normal-strength concrete.

On the contrary, in high-strength concrete/high-performance concrete (HSC/HPC) the amount of water is insufficient for complete cement hydration due to its low water-cement ratio (w/c clearly below 0.4). This shortage of free water results in a pronounced decrease in the relative humidity within the pore system. Two mechanisms are likely to be responsible for the development of such shrinkage deformations from self-desiccation: 1) a decrease in the disjoining pressure between the particles of the C–S–H gel, and 2) a decrease in the menisci radii of the pore water, which bespeaks an increase in tension both within the pore water and at its surface. As a result of the second phenomenon, compressive stresses develop simultaneously in the solid skeleton of the cement system to restore equilibrium by compensating

---

* Corresponding author. Tel.: +49 351 463 35 920.
E-mail address: mechtcherine@tu-dresden.de (V. Mechtcherine).

0008-8846/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2012.03.011

the tensile stresses in the fluid phase. This results in a volume reduction of the entire system, i.e., autogenous shrinkage. As of today it is not clear to which extent the first or the second mechanism dominates the material behaviour observed. Further mechanisms are possibly involved as well [5,6].

Conventional methods in curing concrete cannot contribute substantially to mitigating the autogenous shrinkage of concrete with a low water-to-cement ratio, even if intensive wet curing is applied. In contrast to drying shrinkage, which occurs due to water loss at the surface of concrete members, autogenous shrinkage occurs over the entire volume of the concrete member. Consequently, mere surface treatment cannot suffice. Since the microstructure of typical HSC/HPC is very dense even at early ages, it does not allow a sufficiently rapid transport of curing water into the interior of concrete members, especially if they are thick [7,8].

With this in mind the use of internal curing (IC) by adding materials with a high water storing capacity to the mixture has been proposed, which would supply water to the surrounding matrix as soon as self-desiccation begins to occur. Several researchers have investigated the effect of the addition of a portion of water-saturated lightweight aggregate (LWA) on the properties of HSC since the 1990ies, e.g., [7,9]. As well, other materials were proposed as IC-agents, of which superabsorbent polymers (SAP) appear to be most appropriate. Following the work of Jensen and Hansen [10,11], quite a number of researchers tested various types of SAP and demonstrated that certain of them possess a very beneficial ability to mitigate autogenous shrinkage in HSC [12,13].

Superabsorbent polymers (SAP) have primarily been used in sanitary and convenience products. They can store up to 1500 g of water per gram polymer [14]. For application in concrete, covalently cross-linked polymers of acrylic acid and acrylamide, neutralised by alkali hydroxide, have been proven efficient. They have to be chemically stable and able to swell in the strong alkaline saline solution of the liquid phase of the cement paste [15,16]. This liquid is highly alkaline ($pH > 12$) and contains Ca^{2+} at its saturation level with regard to ettringite, portlandite and $CaSO_4$-species at the current pH value. Considerable amounts of K^+ and Na^+ are present as well, which are prevailingly responsible for the high pH value.

The polymers can be synthesised in two principal ways. One is bulk polymerisation (in substance), from which a block results. This is crushed into small particles of the desired size distribution. Hence, the particle shape is irregular. The other way is inverse suspension polymerisation which produces spherical particles. In both ways, different methods of cross-linking can be applied, e.g., the addition of multivalent monomers in a small amount or some post-polymerisation techniques such as intense irradiation [14].

The increasing interest in the use of SAP as a concrete admixture led to the initiation of the RILEM Technical Committee 225-SAP "Application of Superabsorbent Polymers in Concrete Construction" in 2007. This committee prepared a State-of-the-Art Report summarizing the available knowledge in the area and providing a solid basis for further research [17].

Although SAP have been used as concrete admixtures in research for several years, no systematic study of a structure-effect-relationship has been made public. As exceptions, studies on the effect of the particle size of SAP can be cited, e.g., [18,19]. It was shown that that smaller SAP particles absorb less water but much faster than larger particles [19]. It was further found that for the given amount of SAP and extra water the mitigation of autogenous shrinkage was more pronounced when SAP with larger particles were used.

In the present study, the influence of two main chemical characteristics of acrylic acid-based SAP – the level of anionicity and the degree of cross-linking – is investigated. These parameters are correlated with the kinetics of uptake and release of cement pore solution and the efficiency in mitigating autogenous shrinkage of a high strength mortar. Furthermore, the effect on the compressive strength is considered. This knowledge should provide a better background for a purposeful choice of SAP materials for internal curing of concrete and mortar.

2. Materials and methods

2.1. Superabsorbent polymers

Six SAP samples made of the main monomers acrylic acid and, potentially, acrylamide (SNF Floerger, Andrézieux Cedex/France) were considered. Fig. 1 provides information on their molecular structure with respect to the relative amount of anionic groups and the cross-linking density, both given qualitatively in relative terms. Homopolymers of acrylic acid, which only contain some initiator and cross-linker but which are free of acrylamide, correspond to the level of anionic group density of one (100%). SAP A has spherical particles produced using the inverse suspension polymerisation technique. All the other types are crushed materials produced by the bulk polymerisation technique.

The particle size distributions of the SAP samples in the dry state were characterised in a laser granulometer (LS 13320, BeckmanCoulter, Krefeld/Germany). The shape of the SAP particles was observed in an environmental scanning electron microscope (XL30 ESEM, FEI, Eindhoven/The Netherlands).

2.2. Kinetics of moisture uptake and release by SAP

Qualitatively, the absorption of cement pore solution was first observed visually. Neither should the particles form a homogenous gel nor should they dissolve. In a beaker, 0.5 g of SAP were dispersed in 100 ml of liquid and observed for eight hours and then after 24 and 48 h from the beginning of the experiment.

The cement pore solution had been obtained from a suspension of ordinary Portland cement type I according to DIN EN 197–1 with no special specifications (CEM I 42.5 R by Schwenk, Bernburg/Germany). It had a pH value of 13 and an electric conductivity of 880 µS/cm. The distilled water had a pH value of 6 to 7 and an electric conductivity of 3 to 4 µS/cm.

For the quantitative studies of the ab- and desorption, the so-called "teabag method" was applied. Distilled water and cement pore solution as well as alkaline saline solutions were employed. The latter contained the characteristic ions of cement pore solution individually. To obtain the highly alkaline pH value, 4.45 g potassium hydroxide (KOH, 99%, VEB Jenapharm Laborchemie, Jena/Germany), was dissolved in five litres of distilled water, resulting in a pH of 12.2 in the solution. For the typical concentration of 7 g of SO_4^{2-} per litre of water and the high pH value (but no Ca^{2+}), 55.28 g of sodium sulphate, Na_2SO_4 (99%, Grüssing, Filsum/Germany), and 4.45 g of KOH were dissolved in five litres of distilled water. For the characteristic concentration of 1 g of Ca^{2+} per litre and the high pH value (but no sulphate), 29.76 g of calcium nitrate tetra-hydrate ($Ca(NO_3)_2{\cdot}4H_2O$, 99%, Grüssing, Filsum/Germany), and 4.45 g of KOH were dissolved in five litres of distilled water.

The teabag method was conducted as follows. Some 0.2 to 0.3 g of SAP particles (exact mass m_1) were put in a teabag (mass m_2) which had been pre-wetted in the corresponding liquid. The teabag containing SAP was hung in a beaker filled with the liquid under consideration. The beaker was carefully and tightly covered with a plastic

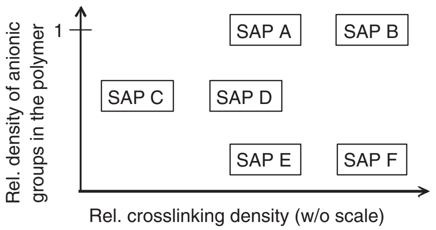

Fig. 1. SAP structures with respect to the level of density of anionic groups and cross-linking density (polymers made of acrylic acid and acrylamide).

foil to avoid carbonation of the liquid due to absorption of CO_2 from the air. Until the end of the experiments, no precipitation occurred. The foil was released only for short times to conduct the weighing procedures.

After 30 s, 2, 5, 10, 15, 30, 60 and 180 min, the teabag with the SAP was released to be weighed (mass m_3). It was put on a dry cloth and wiped with another dry cloth for a short time of approximately 30 s to remove surplus and weakly bound liquid. Some liquid held as capillary water between the SAP particles could leave the sample. However, the sample was not squeezed so as not to disturb the storage function of the polymers. In all probability some residual surface or capillary water remained in the teabags, but this was considered not to be relevant to the present study. The amount of absorbed liquid in relation to the initial mass of SAP was calculated according to Eq. (1).

$$m_{H_2O} = \frac{m_3 - m_2 - m_1}{m_1} \tag{1}$$

2.3. Mortar composition, mixing and testing

The high strength mortar was composed as given in Table 1. The cement was the same as that used in the sorption tests. The silica fume was a dry powder and exhibited an average particle size of 85 nm (Grade 971, Elkem Refractories, Kristiansand/Norway). Because the available river sand 0/4 lacked sufficient fines, the aggregate was composed of 90% by mass of this sand and 10% by mass of quartz sand 0.06/0.2, which provided a steady grading curve of the aggregate. The superplasticizer was a polycarboxylate-based aqueous solution (Glenium 51, BASF, Trostberg/Germany). Its dosage was 1.8% by weight of cement (% bwoc). It was completely pre-dissolved in the mixing water.

Six litres of mortar were produced per mix. The mixing tool was an ordinary concrete mixer (HSM 20, Hobart, Offenburg/Germany). Table 2 gives the mixing sequence and duration.

After completion of mixing, the mortar was introduced into a Hägermann cone and the flowability test specified in DIN 18555-2 was performed, but without the prescribed beats; hence the value obtained is categorised as a slump flow value. Due to the handling routine in the laboratory (stop of mixing tool, paste transfer into the cone, smoothing the surface), the paste flow was measured between 17 and 20 min after initial contact of the dry powders (including the SAP) with water. The slump flow value of the plain mortar was 19 cm ± 1 cm.

Free autogenous shrinkage tests were performed according to ASTM C 1698-09 using a dilatometer with corrugated tubes. However, instead of the manual recording scheduled in ASTM C 1698-09 automatic readings of the length changes were taken at intervals of 30 min. The measurements were started immediately after filling the tubes. They were later referenced to the time of final set which was obtained from a parallel Vicat needle test.

Compressive strength was measured according to DIN EN 1015-11.

2.4. Modification of the mortar by means of SAP

The basic mortar composition (Table 1) was modified by the addition of SAP and an extra amount of water. Due to water absorption by the SAP, the mortar consistency became significantly stiffer if no extra water was added. To keep the workability constant, a distinct amount of water was added to have the same slump flow value as in the mixture without IC agent. This procedure is a common laboratory practice, which attributes the extra water to the liquid storage capacity of the SAP in a fresh mixture at the instant of rheological testing. Due to their action as further fines in the paste, the SAP particles themselves may contribute to the ease of workability to some extent as well. This effect was not taken into account in the present study. However, in further studies it would be worthwhile to assess the liquid storage capacity of the SAP in the fresh paste using other methods, e.g., in measuring their size in the paste using non-destructive methods, as well as investigating in detail the effect of SAP addition on the rheological behaviour of fresh concrete. The state-of-the-art on this subject is described in [20].

Table 1
Mortar recipe.

Material	Unit mass [kg/m^3]	Unit volume [l/m^3]
Cement CEM I 42.5 R	700	222.9
Silica fume	70	30.0
Water, w/c = 0.30	210	210.0
Air		20.0
Aggregate (sand 0/4)	1218	459.6
Quartz sand 0.06/0.2	121.8	46.0
Superplasticizer	12.6	11.5

Table 2
Mixing sequence and duration.

Time [min]	Action	Duration of each step [min]
−04:00–00:00	Homogenise all the dry powders	4
00:00–01:00	Addition of water including the pre-dissolved superplasticizer	1
01:00–02:00	Mixing, intensity 1 (170 rpm)	1
02:00–04:00	Mixing, intensity 2 (198 rpm)	2
04:00–05:00	Manual scraping of agglomerates from the walls of the mixing drum	1
05:00–08:00	Mixing, intensity 3 (361 rpm)	3

For reasons of practicability the mortar composition was kept constant except for the amount of water; i.e., the unit amounts of solids were not adjusted, but the water was added on top of the reference mix.

As an initial dosage of SAP, 0.3% bwoc was chosen. Particular to each SAP, the amount of mixing water was adjusted for constant slump flow. Apart from this, for SAP D the polymer dosage was altered to 0.1 and 0.2% bwoc as well, including the corresponding adjustment of the water addition. Hereby as well, the potential effect of the SAP particles as fines in the paste was neglected.

3. Results and discussion

3.1. Polymer structure, particle size distribution and shape of superabsorbent polymers

For the kinetics of uptake and release of the highly ionic solutions, the density of anionic groups and that of the cross-linking are essential (for a categorisation of the SAP samples used, refer to Fig. 1).

The particle size distributions of the SAP materials under investigation are displayed in Fig. 2; Table 3 gives the corresponding d_{50} values. SAP A had the smallest average particle size, 324 μm. The d_{50} values for SAP B, C and F were close to each other at around 600 μm, whereas the sizes of SAP D and SAP E were significantly larger.

Since the particles were added in the dry state with the mineral powder components, they were homogenously distributed throughout the entire volume during mixing. The mechanical strength of the SAP particles was sufficient so as to preclude their being crushed as a result of the mixing process (optical microscopy results, not shown here).

The shape of the SAP particles was investigated in the ESEM. Fig. 3 shows the spherical shape of SAP A particles and Fig. 4 displays the particles of SAP D as an example of the irregularly shaped polymers SAP B to SAP E.

3.2. Swelling behaviour of the SAP in saline media and cement pore solution

The essential feature of SAP as a chemical admixture to mitigate the autogenous shrinkage of concrete is their ability to absorb water, store it, and eventually make it available to the hardening

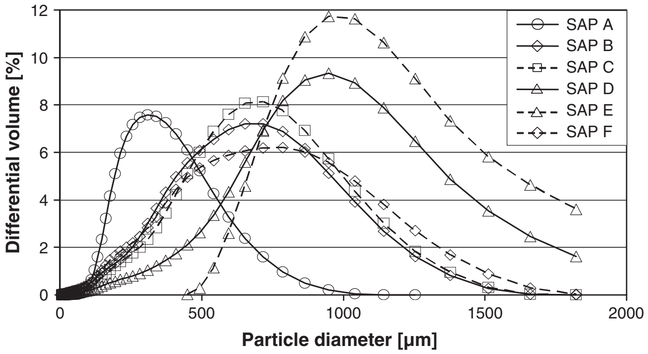

Fig. 2. Particle size distribution of the superabsorbent polymers under investigation.

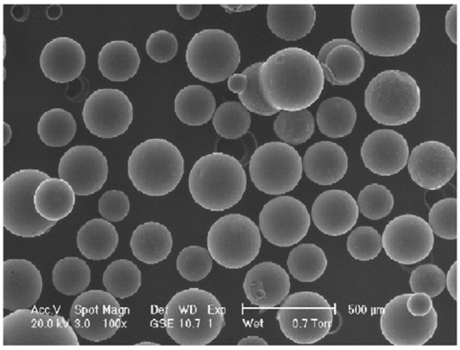

Fig. 3. ESEM picture of SAP A in the dry state.

cement matrix. The main driving force for the water absorption and swelling is osmotic pressure. Due to the uptake of water, the confined close proximity of the carboxylate groups of the SAP releases by expansion. The intrapolymerically bound water not only lets the particles swell but also increases their weight. This effect is utilised in the "teabag test". To study the distinct influences of the ions constituting the cement pore solution, various saline model solutions were considered (Figs. 5–9). Taking distilled water as a starting point, the first step was to use potassium hydroxide solution to mimic the strong alkaline pH value with monovalent cations, which behave passively in this experiment. The next steps were made by introducing the bivalent ions of sulphate and calcium, respectively. Hereby, monovalent counterions were used which do not influence the much stronger interactions between the bivalent inorganic ions and the polymers. Hence, SO_4^{2-} was used with Na^+, and Ca^{2+} was used in the presence of NO_3^-.

The absorptivity of any SAP sample was much weaker in the saline solutions (Figs. 6–9) than in distilled water (Fig. 5). The reason is a general screening of the charges of the SAP by the dissolved ions, thus reducing the osmotic pressure causing the swelling.

The principal kinetics of uptake and release were not affected in potassium hydroxide solution (Fig. 6) and in KOH solution containing sulphate but only monovalent cations (K^+ and Na^+, Fig. 7) when compared to that in distilled water. Herein, all the SAP materials took up the major part of the liquid within 20 min and stored it for at least three hours. SAP C (lowest cross-linking density of all the samples) showed the greatest but also the slowest absorption. On the contrary, SAP F (highest cross-linking density combined with the lowest anion concentration) absorbed the least amount. Furthermore, SAP F showed the most stable absorptivity, i.e., the amount of absorbed liquid was least influenced by the respective saline conditions in comparison to that of the distilled water. The maximum absorption for other SAP samples (A, B, D and E) was localised between the materials SAP C and SAP F. No conclusive trend among the molecular parameters of anion concentration and cross-linking density (and particle shape, since SAP A was the only spherical polymer) became clear with respect to the absorption kinetics in the "intermediate region".

In comparison to the results presented in Figs. 5–7, the presence of the bivalent cation Ca^{2+} in a typical concentration of cement pore solution (1 g/l) fundamentally changed the absorption behaviour of some SAP samples while for some other SAP materials the behaviour was only moderately affected (Fig. 8).

SAP A and SAP B, both of which possessed the highest density of anionic functional groups, started to release a significant portion of the initially absorbed liquid only approximately 15 min after beginning the experiment. As regards cross-linking density, SAP A, with its lower cross-linking density, showed a slightly stronger desorption of the solution than SAP B, which has a higher density. SAP D, with intermediate cross-linking density and anionicity, released some absorbed solution freely as well. However, this occurred to a much smaller extent than in the case of SAP A and SAP B. For the SAP materials designated C, E and F, the presence of Ca^{2+} in the solution did not affect the general course of the absorption/time curves. Therefore, it can be concluded that the molecular parameters that let SAP swell independently from Ca^{2+} are firstly a low cross-linking density combined with intermediate anionicity and secondly a low anionicity combined with any cross-linking density. In other words, the effect of Ca^{2+} is strong in SAP with high density of anionic groups; the cross-linking density seems to play a minor role. On the contrary, the kinetics of liquid uptake and release by SAP with a low density of anionic groups or a low cross-linking density, respectively, are not greatly affected by Ca^{2+}.

In cement pore solution (Fig. 9), the SAP samples showed principal behaviour very similar to that observed in the alkaline Ca^{2+} solution (Fig. 8). Ca^{2+} thus proved to be the most important ion in the cement pore solution with respect to the kinetics of liquid storage by SAP. The anionic functional groups (carboxylate groups) of the polymers can intensely interact with Ca^{2+} ions, as was shown by Plank and Sachsenhauser [21] for polycarboxylate-based superplasticizers. The carboxylic groups of the polymer complex the Ca^{2+} ions in a very stable way, and the efficient anionic charge density inside the SAP diminishes. As a consequence, the now apparently uncharged polymer chains experience a considerably lower osmotic pressure than the more highly charged, uncomplexed chains. The absorption capacity is thus tremendously diminished. This effect of Ca^{2+} complexation is strongly pronounced in SAP with high anionicity,

Table 3
d_{50} values of the particle size distributions of the investigated SAP.

d_{50}	SAP A	SAP B	SAP C	SAP D	SAP E	SAP F
[µm]	324	586	631	903	1065	596

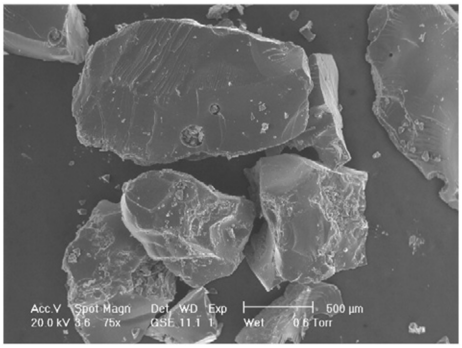

Fig. 4. ESEM picture of SAP D in the dry state.

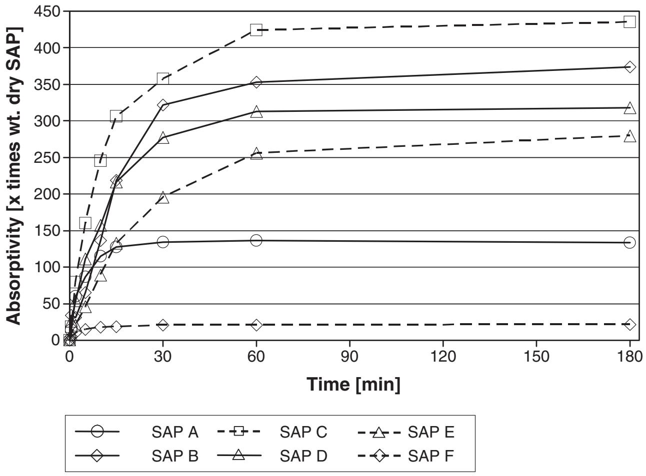

Fig. 5. Absorptivity of SAP in distilled water.

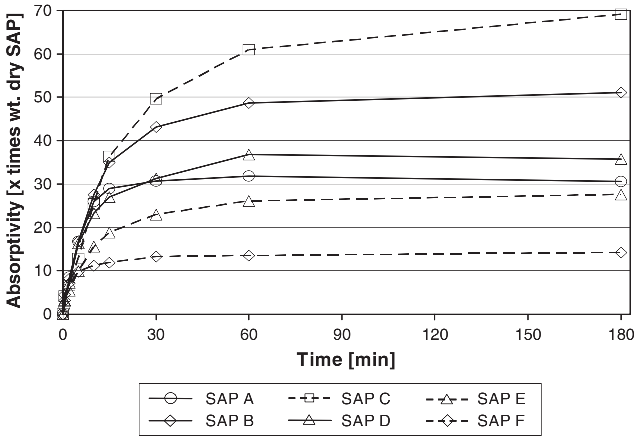

Fig. 7. Absorptivity of SAP in alkaline SO_4^{2-} solution (pH 12.2 by KOH, $c(SO_4^{2-}) = 7$ g/l by sodium sulphate).

whereas it is weaker or even below the limit of experimental detection for SAP with low anionicities.

3.3. Influence of the SAP on the workability of mortar

Since SAP absorb water or cement pore solution, respectively, they withdraw a portion of the mixing water from the paste, which is not available as free water to attain a required workability of the fresh mixture. A common practice is to compensate this water "loss" by adding just enough extra water to restore the mortar workability as it would be without SAP addition and extra water. In the first test series the addition of SAP was equal 0.3% bwoc. In earlier studies by the authors and other researchers, this dosage had proven efficient in the mitigation of autogenous shrinkage. Since the absorption behaviour was different for various SAP, the amount of water was adjusted to keep the paste slump flow constant at 19 cm ± 1 cm as with the reference mixture without SAP (cf. Fig. 10). As a starting point for the adjustment of water addition, $(w/c)_{total} = 0.36$ had been chosen for each SAP. Thus, the amount of extra water corresponded to an increase of w/c by 0.06. The corresponding slump flow values are only shown for the mixtures with SAP A, B, and C as well as, to ease comparison, for the SAP-free reference. With this dosage the required slump flow value could be attained only for the mixture containing SAP D. In the next step the dosage of water was adjusted to meet the desired slump flow value better.

The needed dosage of extra water corresponded to an increase in w/c by 0.02 for the mixture with SAP F, 0.03 for the mixture with SAP A, 0.04 for SAP B and 0.05 for SAP E.

SAP C stood out prominently. The paste was stiff and did not flow at all at w/c 0.36 and for achieving the target slump flow value, $(w/c)_{total}$ of 0.56 was necessary, which meant an increase of the original w/c by 0.26! The absorptivity of SAP C was thus much too strong for suitable application in the chosen mortar. Increasing the w/c to such a large extent fundamentally changes the macroscopic mortar parameters (cf. Fig. 13). In principle, this kind of SAP may be considered for other applications in, for example, shotcreting [22].

The absorptivity of SAP in cement pore solution (Fig. 9) had a clear effect on mortar workability (Fig. 10). Absorptivity has to be considered specifically for the time interval from 17 to 20 min after the initial contact of dry raw materials (including SAP) with water because this equals the time of the flowability test. Up to that time, SAP C had absorbed the largest quantity of pore solution of all SAP samples, and the absorption was still uncompleted at that point. This explains the extraordinary amount of additional water required by this mixture to regain the flowability. In contrast SAP F was by far the weakest absorbing polymer and its complete absorption capacity was almost reached by the time of performing the slump flow test. This explains the lowest needed increase in w/c for SAP F. The values for samples SAP D and SAP E lie between those of SAP C and SAP F. The higher absorptivity of SAP D in comparison to that of SAP E may correspond to the (slightly) higher needed increase in w/c. Between SAP C and SAP

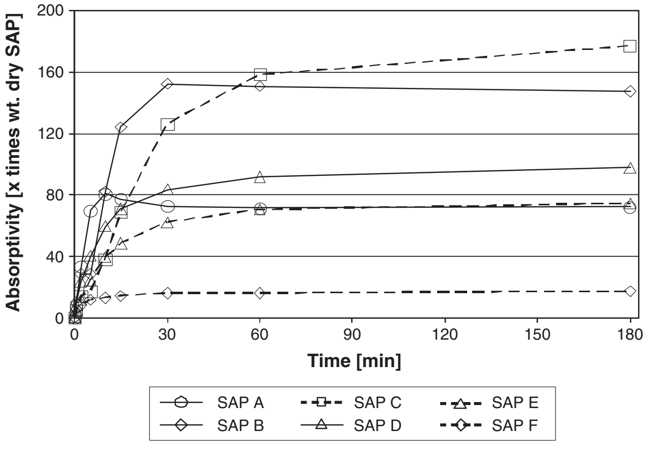

Fig. 6. Absorptivity of SAP in potassium hydroxide solution (pH 12.2).

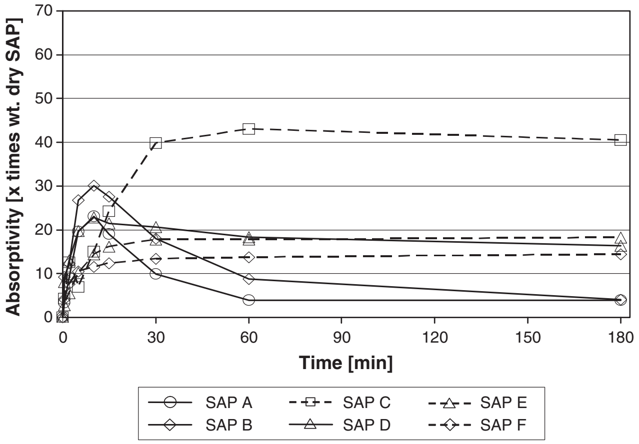

Fig. 8. Absorptivity of SAP in alkaline Ca^{2+} solution (pH 12.2 by KOH, $c(Ca^{2+}) = 1$ g/l by calcium nitrate).

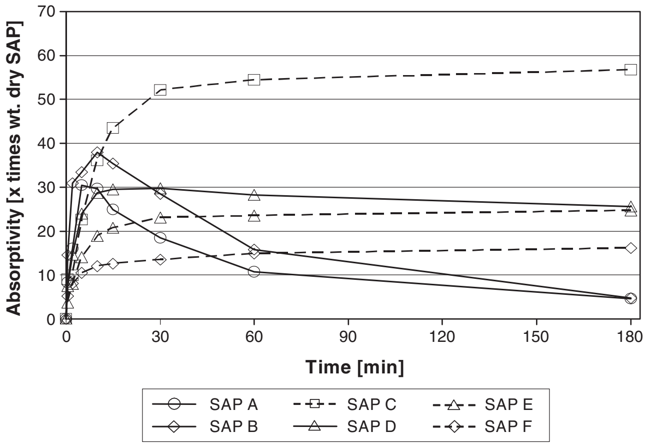

Fig. 9. Absorptivity of SAP in cement pore solution.

F, the two quickly re-desorbing SAP A and SAP B are positioned. Their delicate desorption kinetics, however, do not allow the giving of an exact dosage of extra water to compensate for the loss in workability.

3.4. Mitigation of autogenous shrinkage by addition of SAP

The predominant purpose of implementing SAP in mortar or concrete is to mitigate autogenous shrinkage. The mortar used here is considered to be a typical high strength mortar prone to significant autogenous shrinkage due to its low w/c of 0.3 and its high cement content of 700 kg/m^3 (cf. Table 1). Fig. 11 shows the results of the free autogenous shrinkage tests performed on this mortar without and with addition of SAP and extra water. Each curve gives an average result of three measurements.

Generally, when compared to the SAP-free reference mortars, any SAP addition reduced autogenous shrinkage significantly.

Due to the high absorptivity of SAP C and the w/c of 0.56, the properties of this mortar changed fundamentally. The complete content of water is much higher than needed for cement hydration and internal curing. This results in a high porosity which compromises the strength characteristics of the mortar (cf. also Fig. 13). Thus, the mixture with SAP C will not further be discussed.

All other mixtures with SAP addition exhibited a more or less pronounced expansion of the paste after final set, which is the initiation point of the curves shown. Final set was determined by the Vicat needle test method and was found to be between eight and eleven hours, mostly depending on the amount of extra water. Seven to twelve hours after this each strain-time curve reached its distinct point of unsteadiness.

In cement hydration, the point of final set coincided temporally well with the onset of the acceleration period (results of heat of hydration development are not shown here). The point of the unsteadiness of strain-time curves occurred in middle of the deceleration period shortly after the end of the acceleration period. The SAP-free mortar used as reference showed pronounced deformations due to shrinkage during the acceleration period. This can be attributed to chemical shrinkage caused mainly by the intense hydration reactions of alite to C-S-H phases in this period. At the end of the acceleration period, due to the general slowing down of the reactions, chemical shrinkage proceeds only very slowly. From this turning point on, the internal relative humidity begins to decrease significantly and causes capillary stresses, which manifest themselves externally as autogenous shrinkage.

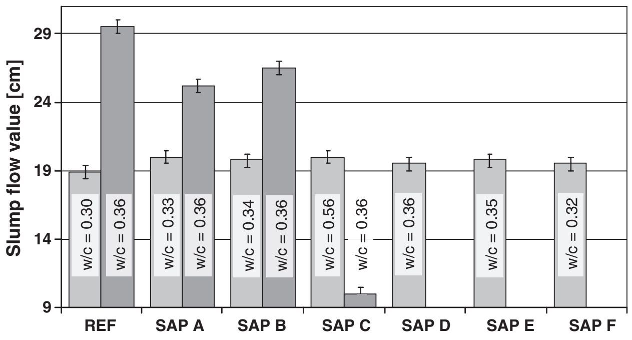

Fig. 10. Slump flow of mortars with 0.3% SAP bwoc and adjusted w/c as a measure to compensate the loss of the workability due to the water uptake capacity of the polymers (spread from the Hägermann cone, deviation ± 1 cm).

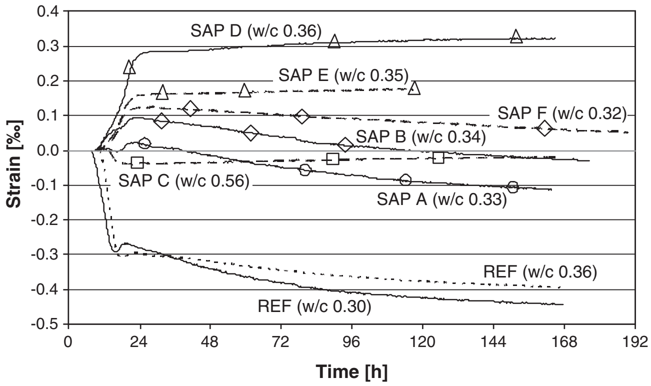

Fig. 11. Results of dilatometer tests on the reference mortar and mortar modified with SAP; dosage of SAP 0.3% bwoc and w/c adjusted to meet the slump flow value of 19 cm ± 1 cm according to Fig. 10.

In contrast to the reference mortars, mixtures with SAP addition exhibited intense expansion during the acceleration period. The reason for this could not as yet be clarified. The phenomenon of early-age expansion was previously reported by e.g. Baroghel-Bouny et al. [6] and Sant et al. [23]. Both these publications discuss portlandite formation as the reason for the early-age expansions observed. Although no superabsorbent polymers were used in those studies, it seems likely that in the present study the modification of portlandite formation by the presence of superabsorbent polymers may play a decisive role in early-age expansion as observed. Moreover, ettringite crystallisation might be taken into consideration as well. However, this topic is a subject of ongoing investigation. After the acceleration period, shortly after the transition point to the deceleration period, individual SAP materials caused particular effects on the course of the strain-time curves.

The time period covered by these experiments was by far longer than that considered in the absorptivity experiments (180 min, cf. Fig. 9). However, interestingly enough the general kinetics of liquid release or of its “permanent” storage in the pore solution as observed in the sorption tests could be well recognised as a trend in the autogenous deformations. At the present stage of research this relationship cannot be explained mechanistically, but it is worthwhile to demonstrate some correlations here in more detail.

Regarding the strain-time curves for the mortar mixtures with SAP A or SAP B, it can be concluded that here the internal curing was effective at an early stage only; after initial swelling the curves run nearly parallel the reference curve for the mortars without SAP. Note that these are exactly those SAP which exhibited a pronounced desorption in the teabag experiment (Fig. 9). The early, free desorption by SAP is sufficient to mitigate shrinkage in the first hours after the final set; even some swelling was recorded for the mixtures with these polymers. Eventually, however, after the rest of the internal curing water is consumed, the positive effect vanishes. The increase in autogenous shrinkage proceeds at the same rate as that for the SAP-free mortars.

Contrarily, the behaviour of SAP which showed stable storage in cement pore solution affected the behaviour of the high strength mortar in a way which can only be the result of the characteristic, very slow release of stored liquid into the surrounding paste volume (cf. curves in Figs. 9 and 11 for SAP D, E and F). The samples SAP D, E and F take up pore solution and keep it stored. Among these SAP, the sequence of absorptivity was SAP D > SAP E > SAP F. This order is mirrored in the amount of extra water to be added in order to compensate the workability loss (Fig. 10). It is no surprise that the dilatometer tests revealed the same succession in the intensity of counteracting autogenous shrinkage, in fact leading to different degrees of expansion (Fig. 11). The effect was most pronounced during the acceleration period. In the subsequent deceleration period the remaining amount of the IC water can be recognised qualitatively from the shape of the strain-time curves. The mixture with SAP D, the SAP with the highest water storing capacity, continued to swell. That with SAP E showed no changes in strain. The mortar with SAP F, the SAP with the lowest water absorption, exhibited very slight shrinkage.

To judge how the dosage of SAP and extra water would affect the availability of IC water at different stages of the hardening process, a series of tests on mortar with various dosages of SAP D was performed (Fig. 12). Following the approach presented above the amount of extra water was adjusted to compensate the flowability loss due to the water absorption by SAP.

As presented above, the mixture with 0.3% bwoc SAP D and w/c of 0.36 showed continuous expansion during the entire time of strain measurements (7 days). The mortar with SAP dosage reduced to 0.2% bwoc, combined with w/c = 0.34, exhibited after initial swelling no further expansion, but rather minor reversal deformation. Further decrease in SAP dosage to 0.1% bwoc (and w/c 0.32) increased this trend clearly. For the initial mortar expansion during the acceleration period, these small amounts of SAP and extra water were still enough, even if the swelling was much less pronounced in comparison with the mortar with higher dosages of IC agents. Starting at a time approximately 24 h after mixing, the reserve of the water in the mix was obviously exhausted, which led to an apparently abrupt change from autogenous swelling to autogenous shrinkage. The slope of the strain-time curve became similar to that of the SAP-free mixtures. Interestingly this was the same pattern as observed for the mixtures containing SAP A and SAP B (Fig. 11), but it should be underlined that more extra water was used in the mixtures with SAP A and SAP B.

3.5. Effect of SAP and extra water on the compressive strength of the mortar

When using SAP as an admixture in cement-based materials, in the matrix a number of voids is created, which may affect the strength of the material negatively. A decrease in strength was repeatedly reported in the majority of previous publications, e.g. [11,13], while in other investigations no negative effect was observed on mortar [24]. Regarding the importance of the strength characteristics for practical applications of high strength concrete or mortar, the compressive strength was measured in this study for all mortars under investigation (Fig. 13).

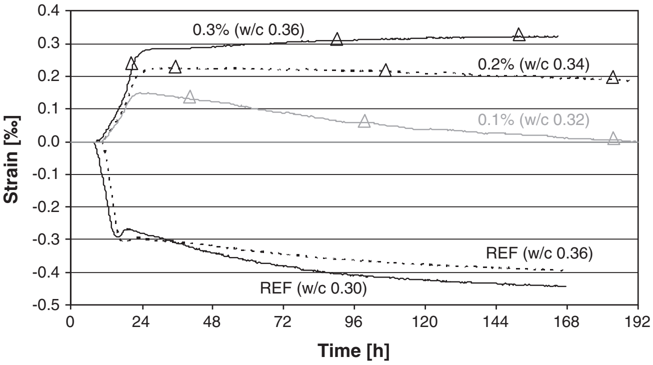

Fig. 12. Results of dilatometer tests on the mortar modified with various dosages of SAP D and extra water; the results for the reference mortars are included for comparison.

As could be expected, the reference mortar with w/c = 0.36 showed lower strength values than that with w/c = 0.30. The mixture with SAP C with its clearly exaggerated w/c of 0.56, which had been so mixed as to maintain the predefined flowability, achieved only considerably lower strength values. The other mixture with SAP C (w/c = 0.36) exhibited a slightly stronger decrease in compressive strength than the mixture with SAP D, which had the same amount of polymer and extra water. This may likely be attributed to the somewhat worse compaction of the stiffer fresh mortar containing SAP C. With regard to the other SAP modified mortars, a clear dependence on the SAP sorption kinetics could be observed. The mortars containing the readily releasing SAP A and SAP B exhibited lower values of compressive strength in comparison to the mixtures with water-retentive SAP D, SAP E, or SAP F and a comparable amount of water. The premature partial water release by SAP A and SAP B, which probably occurs before setting, results in a higher effective w/c in the corresponding mortars, and hence leads to their higher capillary porosity and lower strength. In contrast, the mixtures containing SAPs able to retain the pore solution showed either no decrease or only a very slight decrease in compressive strength when compared to the reference mortar with w/c of 0.30 if both the SAP dosage and the amount of extra water were properly chosen. These SAPs released their stored water at the proper times, which means beginning at the earliest with the setting time, when it is needed for internal curing. The positive effects on compressive strength resulting from the use of SAP and extra water evidently offset the negative effect of the additional voids introduced by SAP particles well. One likely reason for the positive influence of SAP addition on compressive strength is a higher degree of hydration of the cement and silica fume [25]. For the compositions presented this is to be clarified in subsequent related studies. Another reason might be that due to internal curing and diminished autogenous shrinkage of the cement paste no internal stresses develop from the restraint of such shrinkage deformations by stiff and non-shrinking sand particles.

4. Summary and conclusions

This study focussed on understanding the kinetics of water absorption and desorption by superabsorbent polymers (SAP) in concrete in dependence on their molecular structure and on linking this knowledge to the efficiency of internal curing.

The kinetics of liquid uptake into and release from the SAP depend on the ionic composition of the liquid. Using distilled water as a starting point, KOH and Na_2SO_4 generally reduced overall absorptivity. Ca^{2+} in alkaline solution was able fundamentally to modify the absorption and desorption behaviour of some of the polymers. SAP materials of very high anionic functional group density took up the liquid quickly and released it back into solution to a large extent over the first one to three hours. Contrarily, SAP with lower anion density stored the absorbed liquid over the entire time of the experiment. Here no desorption was observed independent of the cross-linking density. The absorption and desorption behaviour of SAP in the alkaline Ca^{2+} solution was very similar to that of the cement pore solution as extracted; thus, Ca^{2+} is responsible for specific SAP behaviour. This can be traced back to the less pronounced complex formation between the anionic functional groups of the polymers and Ca^{2+} in the case of SAP with lower anion concentration.

To keep the mortar slump flow unchanged despite the addition of SAP, extra water was added to the mixture. The amount of this extra water for the purpose of internal curing depended on the absorptivity of each distinct SAP in the cement paste environment. The chosen dosage of 0.3%

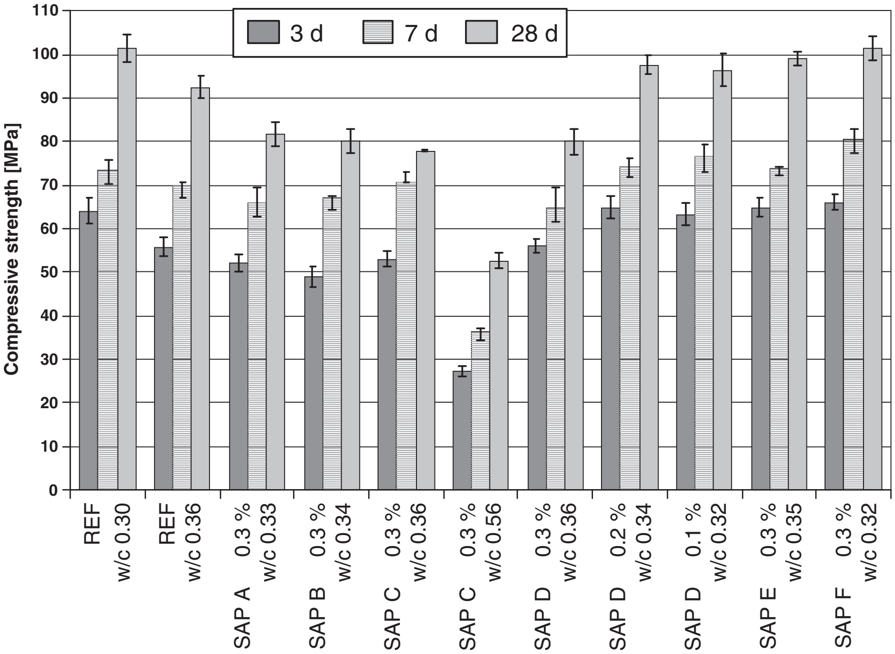

Fig. 13. Compressive strength of the reference mortars and mortars modified with SAP and extra water; measured according to DIN EN 1015–11, average values from three specimens each (REF w/c 0.30, SAP A, SAP B, SAP C, SAP D 0.3%, SAP E) or six specimens each (REF w/c 0.36, SAP D 0.2% and 0.1%, SAP F), respectively; standard deviations are indicated in the diagram.

SAP bwoc led mostly to a necessary increase of the $(w/c)_{total}$ by 0.02 to 0.06 (from 0.30 to 0.32 and 0.36, respectively). The amount of extra water required for the SAP-modified mortars corresponded with the order of absorbed cement pore solution by the SAP in teabag tests at the moment of the flowability test.

The second focus was to connect the kinetics of uptake and release of pore solution by the SAP with their ability to mitigate autogenous shrinkage in high-strength mortar. It was found that any SAP counteracts autogenous shrinkage during the acceleration period of cement hydration. Indeed the expansion of mortar volume was observed after the final set, which was used as the starting point of data recording. Shortly after transition from the acceleration to the deceleration period, SAP were divided into two groups according to their effect. For one group of SAP the course of the strain-time curve was nearly parallel to the reference curve for mortar without internal curing. This indicates that no sufficient amount of internal curing water could be provided by SAP at this stage. Such behaviour was observed for mixtures with SAP showing a pronounced liquid release after initial absorption in the teabag experiments. Different behaviour was observed for the mixtures with SAP not showing liquid release in the teabag experiments. After initial swelling these mortars could to a great extent maintain their expanded state in the decelerating period for the duration of measurements (7 days). Obviously, the SAP particles had retained enough water for a sufficiently long time. Smaller doses of an SAP of this group led to a minor reduction of the expansion after the initial swelling. For an even lower dosage of this SAP, the strain-time curve turned parallel to those of the mortars without any SAP as soon as the expansion during the acceleration period was finalized.

The amount and the time period of water release from SAP into the mortar are thus crucial to the efficient mitigation of autogenous shrinkage.

Finally, the compressive strength tests on the hardened mortars revealed that the type of SAP and, in turn, its water release kinetics are relevant to mechanical properties as well. A premature release of water, i.e., before setting, in the mixtures containing SAP with a very high density of anionic functional groups led to a significant decrease in compressive strength; this can be attributed to the increase of the effective w/c and subsequently higher porosity of the mortar. In contrast, for mixtures with SAP of lower anion concentration either no decrease or only a very moderate decrease in strength was observed. This was explained by the release of stored water at a later stage, beginning with setting as the earliest point. In this case the extra water serves truly as internal curing water. The efficient mitigation of autogenous shrinkage and the enhanced degree of hydration seem to be sufficient to balance the negative effect of voids induced by SAP particles. However, the development of the microstructure of the cement-based matrix in dependence on the type of SAP has yet to be thoroughly studied in order to develop a substantiated mechanistic explanation for the macroscopic findings.

Acknowledgements

The authors gratefully thank SNF Floerger (Andrézieux Cedex/ France) for the generous supply with superabsorbent polymers and for the permission to publish the data in the paper at hand.

References

[1] G.C. Lyman, Growth and Movement in Portland Cement Concrete, Oxford University Press, London (Great Britain), 1934.
[2] DIN 1045–1, Tragwerke aus Beton, Stahlbeton und Spannbeton – Teil 1: Bemessung und Konstruktion (in German), Beuth Verlag, Berlin (Germany), 2008.
[3] JSCE Standard Specifications for Design and Construction of Concrete Structures, , 2002.
[4] Internal Curing of Concrete. State-of-the-art Report of RILEM Technical Committee 196-ICC, in: K. Kovler, O.M. Jensen (Eds.), RILEM Report 41, RILEM Publications S.A.R.L, Bagneux (France), 2007.
[5] C. Hua, P. Acker, A. Ehrlacher, Analyses and models of the autogenous shrinkage of hardening cement paste, I. Modelling at macroscopic scale, Cem. Concr. Res. 25 (7) (1995) 1457–1468.
[6] V. Baroghel-Bouny, P. Mounanaga, A. Khelidj, A. Loukili, N. Rafai, Autogenous deformations of cement pastes, Part II. W/C effects, micro–macro correlations, and threshold values, Cem. Concr. Res. 36 (1) (2006) 123–136.
[7] S. Weber, H.W. Reinhardt, A new generation of high performance concrete: concrete with autogenous curing, Adv. Cem. Based Mater. 6 (2) (1997) 59–68.
[8] G. Ye, X. Liu, G. de Schutter, L. Taerwe, Y. Yuan, The microstructure of self-compacting concrete compared with high performance concrete and traditional concrete, RILEM Proceedings PRO 042, 1st International symposium on design, performance and use of self-consolidating concrete, RILEM Publications S.A.R.L, Bagneux (France), 2005, pp. 383–394.

[9] A. Bentur, S. Igarashi, K. Kovler, Prevention of autogenous shrinkage in high-strength concrete by internal curing using wet lightweight aggregates, Cem. Concr. Res. 31 (11) (2001) 1587–1591.

[10] O.M. Jensen, P.F. Hansen, Water-entrained cement-based materials: I. Principle and theoretical background, Cem. Concr. Res. 31 (4) (2001) 647–654.

[11] O.M. Jensen, P.F. Hansen, Water-entrained cement-based materials: II. Experimental observations, Cem. Concr. Res. 32 (6) (2002) 973–978.

[12] V. Mechtcherine, L. Dudziak, J. Schulze, H. Staehr, Internal curing by Super Absorbent Polymers (SAP) — effects on material properties of self-compacting fibre-reinforced high performance concrete, in: O.M. Jensen, P. Lura, K. Kovler (Eds.), International RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation, RILEM Proceedings PRO 052, RILEM Publications S.A.R.L, Bagneux (France), 2006, pp. 87–96.

[13] S. Igarashi, A. Watanabe, Experimental study on prevention of autogenous deformation by internal curing using super-absorbent polymer particles, in: O.M. Jensen, P. Lura, K. Kovler (Eds.), International RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation, RILEM Proceedings PRO 052, RILEM Publications S.A.R.L, Bagneux (France), 2006, pp. 77–86.

[14] F.L. Buchholz, A.T. Graham, Modern Superabsorbent Polymer Technology, WILEY-VCH, New York (USA), 1998.

[15] A. Pourjavadi, R. Soleyman, G.R. Barajee, Novel nanoporous superabsorbent hydrogel based on poly(acrylic acid) grafted onto salep: synthesis and swelling behavior, Starch-Starke 60 (2008) 467–475.

[16] X.-P. Chen, G.-R. Shan, J. Huang, Z.-M. Huang, Z.-X. Weng, Synthesis and properties of acrylic-based superabsorbent, J. Appl. Polym. Sci. 92 (2004) 619–624.

[17] V. Mechtcherine, H.W. Reinhardt (Eds.), Application of superabsorbent polymers in concrete construction, in: State-of-the-art Report prepared by the RILEM TC 225-SAP, Springer, Heidelberg (Germany), 2012.

[18] P. Lura, F. Durand, O.M. Jensen, Autogenous strain of cement pastes with superabsorbent polymers, in: O.M. Jensen, P. Lura, K. Kovler (Eds.), International RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation, RILEM Proceedings PRO 052, RILEM Publications S.A.R.L, Bagneux (France), 2006, pp. 57–66.

[19] L.P. Esteves, On the absorption kinetics of superabsorbent polymers, in: O.M. Jensen, M.T. Hasholt, S. Laustsen (Eds.), International RILEM Conference on Use of Superabsorbent Polymers and Other New Additives in Concrete, RILEM Proceedings PRO 074, RILEM Publications S.A.R.L, Bagneux (France), 2010, pp. 77–84.

[20] R.D. Toledo Filho, E.F. Silva, A.N.M. Lopes, V. Mechtcherine, L. Dudziak, Effect of superabsorbent polymers on the workability of concrete and mortar, in: V. Mechtcherine, H.W. Reinhardt (Eds.), Application of Superabsorbent Polymers in Concrete Construction. State-of-the-art Report of the RILEM TC 225-SAP, Springer, Heidelberg (Germany), 2012, pp. 39–50.

[21] J. Plank, B. Sachsenhauser, Experimental determination of the effective anionic charge density of polycarboxylate superplasticizers in cement pore solution, Cem. Concr. Res. 39 (2009) 1–5.

[22] O.M. Jensen, Use of superabsorbent polymers in construction materials, in: W. Sun, K. van Breugel, C. Miao, G. Ye, H. Chen (Eds.), 1st International Conference on Microstructure Related Durability of Cementitious Composites, RILEM Proceedings PRO 061 (vol. 2), RILEM Publications S.A.R.L, Bagneux (France), 2008, pp. 757–764.

[23] G. Sant, B. Lothenbach, P. Juillant, G. Le Saout, J. Weiss, K. Scrivener, The origin of early age expansions induced in cementitious materials containing shrinkage reducing admixtures, Cem. Concr. Res. 41 (2011) 218–229.

[24] P. Lura, F. Durand, A. Loukili, K. Kovler, O.M. Jensen, Strength of cement pastes and mortars with superabsorbent polymers, in: O.M. Jensen, P. Lura, K. Kovler (Eds.), International RILEM Conference on Volume Changes of Hardening Concrete: Testing and Mitigation, RILEM Proceedings PRO 052, RILEM Publications S.A.R.L, Bagneux (France), 2006, pp. 117–126.

[25] L.P. Esteves, On the hydration of water-entrained cement-silica systems: combined SEM, XRD and thermal analysis in cement pastes, Thermochim. Acta 518 (1–2) (2011) 27–35.