

# A review of characterisation methods for superabsorbent polymer (SAP) samples to be used in cement-based construction materials: report of the RILEM TC 260-RSC

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**Abstract** Superabsorbent polymers (SAPs) have proven to be a very promising admixture which can positively influence various properties of cement-based materials. SAP samples intended for such use should be pre-tested with respect to their absorptivity as well as their kinetics of ab- and desorption prior to implementation in concrete or mortar. This not only reduces workloads in concrete laboratories in pre-testing modified cement-based mixtures but in fact discloses essentials of the eventual performance of the SAP in

concrete and other cementitious materials. The review at hand outlines fundamentals of the thermodynamics of polymer chemistry as a basis for the sorptivity tests. The importance of the ionic composition of the test liquids and the interplay among expansive (swelling) and collapse-causing chemical forces in the hydrogel network are highlighted. Methods of free sorptivity testing in adequate saline solutions as well as absorptivity determined subject to the application of external forces are summarised. Advantages and drawbacks of these methods are discussed, including a validation of anticipatory evaluations of SAPs' performance as admixtures in cement-based building materials. Apart from sorptivity pre-tests several methods of instrumental analytics for the chemical characterisation of SAP samples are drawn up, which represent standard approaches of polymer-chemical analytics.

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**Keywords** Concrete technology · Superabsorbent polymer (SAP) · Cement pore solution · Hydrogel stability · Sorption kinetics · Instrumental analytics

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## 1 Introduction

Intense research has been carried out on the use and performance of superabsorbent polymers (SAPs) as a novel, multipurpose admixture in cement-based building materials. The respective state-of-the-art was summarised by, e.g., [1–3]. The most promising prospective applications of SAPs include mitigation of autogenous shrinkage of concrete and mortar with low water-to-cement ratio [3–5], enhancing freezing-and-thawing resistance of ordinary concrete [6–9], mitigation of crack formation due to plastic shrinkage in various types of mortar and concrete [3] as well as self-sealing [10] and promoted autogenous self-healing [11] of cracks. In all these and other potential applications the sorption behaviour of SAPs in highly alkaline environment of fresh cement-based mixes plays a central role.

To date, performance-oriented studies and investigations focused on the effect of SAP addition on the microstructure of the hardened cement paste prevail. Publications that focus on the chemistry of superabsorbers used in concrete are scarce, although exceptions exist [4, 12–14]. On the contrary, pure and applied polymer science have generated numerous high-quality publications on hydrogels, as SAPs are mostly called in that community. But the polymers in focus there have seldom been incorporated in cement-based systems; thus, in most cases poorly specified or characterised SAPs have been used in concrete materials. Extensive full-scale mortar or concrete testing is commonly performed to find whether a selected SAP sample is useful as an admixture in achieving the intended benefits. To mitigate the required intense workload in concrete laboratories, pre-characterisation approaches for SAP samples prior to incorporation in the cement-based systems are needed. Such pre-tests should produce targeted and concise hints in respect of the performance of SAPs in cement-based materials.

Practically oriented and rather easy pre-tests have been established to check SAP samples for their principal suitability:

- qualitative solubility testing in extracted or mimicked pore solutions;
- time-resolved quantification of ab- and desorption in extracted or mimicked pore solutions.

More sophisticated chemical and physical characterization techniques include:

- optical microscopy;
- scanning electron microscopy (SEM) most appropriately with no requirement of sputtering in, e.g., the low-vacuum or environmental modes (ESEM);
- laser diffraction to assess particle size distribution;
- conventional elemental analysis, which can be substituted by energy-dispersive X-ray analysis (EDX);
- optical emission spectroscopy (OES) and atomic absorption spectroscopy (AAS) to quantify the cations such as  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  taken in;
- infrared spectroscopy (IR) or nuclear magnetic resonance (NMR); and
- extractability of solubles in pore solution followed by qualitative and quantitative chemical analysis of the liquids.

Numerous procedures primarily focusing on compatibility with sanitary aspects have been described by nonwovens associations, e.g. the European Disposables and Nonwovens Association [15]. The listed selection summarises tests to characterise a SAP sample obtained from a commercial provider that is intended for use in cement-based construction materials. Individually synthesized SAP samples should be characterized in this manner as well, but more intense analysis should be considered from a mere polymer-chemical point of view. From a practitioner's point of view, SAP samples as provided cannot and should not be characterised entirely in chemical terms, but highly valuable hints can be obtained by analysis with respect to the prospective performance of a SAP in cement-based materials. The purpose of the manuscript at hand is, hence, to summarise and discuss critically existing characterisation methods and practice-oriented pre-tests to be applied to incoming SAP samples. Such tests are needed to obtain a first impression of their features and individual behaviour prior to incorporation in a cement-based construction material so that more elaborated tests on cement-based materials could be performed with highly promising SAP samples only.

As a prerequisite, representative sampling of aliquots of obtained SAP lots is the initial step for meaningful characterisation of the samples. Respective recommendations of common laboratory practice must be obeyed, e.g., [15, 16].



Most SAPs used in cement-based materials as yet have been made of acrylic acid and acrylamide as the main monomers, and a few structure/efficiency relationships have been explained with respect to mitigation of autogenous shrinkage and rheology [4, 12, 13, 17]. Alternatives to the acrylate-/acrylamide-based polymers which might be discussed for use in cement-based construction materials may include hydrogels incorporating or being based on sulfonate-bearing (co)monomers [18–20], poly(aspartic acid) [21], L-histidine residues [22, 23], chitosan [24], cellulose and cellulose derivatives [25–27], chitin [27], starch [28–30], alginate [14] or photo-crosslinked poly(ethylene glycol) [31]. Besides non-ionic, purely anionic or cationic SAPs, polyampholyte hydrogels have been described as well, e.g. [32–38]. As yet, no study has become public with non-ionic or the latter type of polymers as admixtures in cement-based materials.

## 2 Chemical precautionary measures and storage conditions

SAP are a chemical product, and thus careful handling in accordance with good laboratory practice is self-evident. To avoid potential dangers that may arise when the polymers are exposed to the specific chemistry of the cement environment, any potential supplier or manufacturer of SAP should be informed about the intended use of the substance and the supplier should in principle agree upon such intended use.

Any SAP samples should at all times be kept in sealed, opaque containers to avoid contact with water vapour in ambient air and direct exposure to sunlight. UV irradiation may change the molecular structure of polymers and, consequently, their adsorption and desorption properties. Depending on the chemical nature of the cross-linking, cleavage or post-crosslinking may occur and result in altered performance. Experience teaches us that a relative humidity of  $(60 \pm 5)\%$  and a temperature of  $(20 \pm 2)^\circ\text{C}$  are good conditions for safe short- and long-term storage. Under these conditions SAP samples relevant to application in concrete neither cluster nor deteriorate. Other common laboratory climates may be applied as well. Other storage conditions are possible, but the behaviour of the so-exposed polymers has to be assessed individually and

be considered when experimental results should be compared with other laboratories. Alternatively, the SAP samples can be pre-conditioned prior to testing, e.g., by drying over silica gel (3% relative humidity) under vacuum for 24 h [39].

## 3 Analysis of particle shape, particle size and elemental composition in the dry state: implications of the polymer synthesis route

SAP samples for use in cementitious building materials should be particulate and not subject to caking. The shapes of the individual particles can be made visible by light microscopy or, in more detail, by scanning electron microscopy (SEM), e.g. [40]. If a high-vacuum SEM is utilized, the SAP sample have to be sputtered with a conductive overlay, e.g., gold or carbon, in accordance with common SEM practice for non-conductive materials. Preparation artefacts due to this sputtering as well as shape deformation as a consequence of the exposure to high vacuum in the SEM may occur. Most beneficial is a SEM which allows direct observation of non-conductive specimens, e.g., an ESEM. By tuning the relative humidity in the ESEM carefully, swelling and shrinking features can be viewed. However, qualitative information on the particles' shapes should be derived from SEM and ESEM imaging only. Since the final states of the hydrogels in their fully saturated state are not feasible inside an ESEM one should refrain from quantification of swelling kinetics. Having this in mind as well as a limited availability of ESEM, light microscopy seems to be more relevant for routine analysis of practically dry SAPs and its resolution is as a rule fully sufficient (for issues of size assessment of swelling hydrogels, cf. Sect. 7.1.1).

The most common methods used to assess particle size distribution of SAP samples are based on laser diffraction. Unswollen SAP particles are individualized in an air jet stream or a dispersive liquid. In the latter medium disagglomeration is mostly supported by ultrasonication. When using ethanol or 2-propanol as the dispersing medium, there is general agreement that the polymer networks are collapsed, and hence, the results obtained yield reliable particle-size distributions of SAP particles as they would be in the dry state. Routine evaluation of the diffraction patterns implies spherical particles. Despite the SAP particles'



often having irregular shapes, no investigation is known to have dealt with the influence of such aberrations from the spherical on the measurement results of particle-size distribution of the polymers.

Recently, Esteves proposed laser diffraction to assess the size of swollen hydrogel particles after absorption of saline liquid [41]; cf. Sect. 7.1.6.

Another method in the assessment of the size fractions of dry SAP samples is sieving using metal mesh sieves as proposed for gravimetric or volumetric determination of the grading of mineral aggregates. Sieves with mesh sizes of 63, 125, 250, 500 and 1000  $\mu\text{m}$  can be used as an exemplary sequence. To allow smooth processing it is of uttermost importance to pay attention to the absence of any trace of water. Cleaning of the sieves should avoid water as well; air jet stream is recommended instead.

From the observed particle shape the mode of synthesis can be deduced. SAPs relevant to application in cement-based building materials are commonly synthesized via free radical (co)polymerization. This can be carried out in bulk, emulsion, suspension, or solution processes. From a procedural point of view, two modes of SAP synthesis are preeminent:

- Irregular, uneven particles stem from block or solution (co)polymerisation [40, 42–46]: synthesis in a macroscopic jelly block, either batch-wise or as an endless belt. Post-processing steps include drying, milling, or grinding and sieving. The grading can be easily adjusted by these post-processing sequences. Especially milling and sieving can be accomplished using rather simple laboratory standard equipment such as some manner of coffee grinder and metal mesh sieves used for fine mineral powders.
- Inverse suspension or emulsion (co)polymerisation [40, 45–49]: the (co)monomers are emulsified and polymerised within phase-separated droplets, which results in spherical particles. The particle-size distribution is adjusted via chemical and physical parameters, which include phase distribution equilibria, reactant ratios, feeding speeds, reaction times and agitation intensity. Rather narrow particle size distributions can be obtained through this method. Post-processing should not involve anything more than careful sieving in order not to vitiate the spherical particle shape. Applicants from the concrete technology branch

should contact the SAP's supplier and ask for polymers of targeted grading.

Siriwatwechakul et al. [50] studied the swelling characteristics of one solution polymerized and one microemulsion polymerized hydrogel in cement-relevant solutions. They stated that the two SAP samples differed in the strategy of synthesis only, but no chemical characterisation of the polymers was provided. The same sorption behaviour was reported for both SAP samples, which indicates that mere particle shape does not influence the sorptivity characteristics. Omidian et al. [40, 45, 46] as well found that chemical composition and particle size do in fact determine the sorption characteristics, whereas the particle shape as the result of the synthesis strategy does not play a decisive role.

In a hardened, cement-based matrix, each SAP particle causes a void. Fracture mechanics hold that spherical cavities are less worrisome than irregular ones. However, to date no scientifically integer study on cement-based materials containing SAPs has been made public which would substantiate this general prediction. Any studies comparing the performance of SAP samples has been conducted with polymers that differed at least potentially in more parameters than just that of particle shape. Thus, a discussion of the significant differences among the results relying solely on the shape of the individual SAP particles has not been possible up to now.

The chemical composition of superabsorbent products can be characterised through conventional elemental analysis, see e.g. [20, 28, 51]. Energy-dispersive X-ray analysis (EDX) as an add-on tool with SEM and ESEM devices may be applied for elemental analysis as well. Hereby the limits of detection, especially of the lighter elements, should be considered. The results can be considered as qualitatively decent, but it must be stressed that in quantitative terms they cannot be ultimately reliable. For sure, the counter-ion or combination of counterions (most likely  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$ ) to the anionic polymer network can be elucidated. But, for instance, a detected presence of nitrogen or sulphur needs further analytical methods for validation since the detected presence of these elements may indicate their implementation in the polymer chains as the hydrophilic functional groups, e.g., amide, amine, ammonium, sulfuric or sulfonic groups, respectively, but



they might as well be a fraction of the free counter-ions.

To clarify these options qualitatively, infrared spectroscopy (IR) is a good choice. The absorption bands identify typical functional groups and they can provide basic information about the principal chemistry of the polymer chains, e.g. [18]. Further methods of instrumental analytics can be applied, e.g.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, or two-dimensional NMR strategies to elucidate connectivity, functional groups, or moieties that are spatially neighbouring though not covalently bonded to each other (e.g. [29]).

#### 4 Background: thermodynamics and kinetics of ab- and desorption

The most essential feature of each SAP is the ability to take up aqueous solution in multiple amounts of their individual dry weights. These cross-linked (co)polymers can absorb and retain liquids without dissolving. The absorbable amount of liquid, absorption kinetics, potential desorption and stability of the liquid-enriched product, i.e., the swollen hydrogel, depend on several thermodynamic and kinetic determinants [52, 53]. Not just any SAP “off the shelf” is suitable and beneficial for use in cement-based building materials. Three factors are most important: (1) the molecular composition of the polymer, (2) the particle-size (distribution) of the SAP and (3) the ionic composition of the aqueous solution. Thermodynamic equilibrium at the stable, final stage is as described in Eq. 1 [53]:

$$\Delta\pi = \Delta\pi(\text{mix}) + \Delta\pi(\text{elastic}) + \Delta\pi(\text{ion}) + \Delta\pi(\text{bath}) = 0 \quad (1)$$

This equilibrium is gained stepwise in several consecutive actions. The four terms are explained in their temporal order of significance. From immediately after the first contact of polymer and solvent (water), polymer/solvent interactions give rise to osmotic pressure  $\Delta\pi(\text{mix})$  to equalize the content of water molecules outside and inside the polymer network. The hydrated polymer chains require more space than the non-hydrated ones do in the dry state. Consequently, adsorption of solvent leads to expansion. Due to their cross-linking, these primary chains

cannot move freely so that the polymer would dissolve as an entity. A counteracting elastic force  $\Delta\pi(\text{elastic})$  arises and limits the expansion. In the case of polyelectrolytes, the counter-ions linked to the functional groups along the chains become mobile in the now present solvent envelope and detach from their places of electrostatic anchorage. From anionic groups, cations are released and from cationic groups, anions are released into the solvent. Acrylic-based polymers in cement-based environment are virtually completely deprotonated, i.e. practically all carboxylic groups are negatively charged [54]. Hence, neighbouring chains become charged likewise, resulting in strong electrostatic repulsion. An expansive pressure term begins to contribute to the thermodynamic equilibrium  $\Delta\pi(\text{ion})$  [53]. Since the entire system must remain electrically neutral, the counter-ions cannot leave the network without replacement. If mobile ions are present in the surrounding liquid and the ionic strength is sufficiently high, then they can exchange with the ions inherent in the hydrogel and enter the network space. In this respect,  $\text{Ca}^{2+}$  is the most important ion with respect to anionic hydrogels in contact with cement pore fluid. As a result, electronic shielding  $\Delta\pi(\text{bath})$  occurs in the solvent envelope. This term reduces the osmotic pressure and may even be so intense as to lead to a hydrogel collapse (contraction).

During the time of swelling in a saline solution with doubly charged and strongly complexing cations three phases coexist in a SAP particle, the borders of which are progressing locally in the course of time. This was elucidated by evaluating birefringent patterns of cross-polarised transmitted light microscopy using a saline solution containing  $\text{Cu}^{2+}$  [55–57]. For chemical reasons it may be expected that the  $\text{Ca}^{2+}$  ions present in cement pore solution behave similarly in forming multidentate chelate complexes and hence, evoke the same response of zone formation and progression in the polymer network as the  $\text{Cu}^{2+}$  ions [4, 58, 59]. First, a zone of liquid imbibes progressing from the outer rim of the dry SAP particle to the centre. After a characteristic period of some seconds to minutes the dry core disappears and the hydrogel has reached its maximum size. A bit delayed but even before complete disappearance of the inner dry zone a rim becomes visible at the outer circumference of the hydrogel. This is quickly progressing but at some point it stops on its way to the centre. Such rim represents





the collapse of the hydrogel as the consequence of  $\text{Cu}^{2+}$  ions chelating the anionic groups of neighbouring polymer chains and post-crosslinking them. Synchronously, initially intaken water is released from the hydrogel to the surrounding [55–57]. The complex formation was shown to be reversible. By exchanging the salt solution by diluted HCl the  $\text{Cu}^{2+}$  ions were washed from the collapsed regions of the SAP into the surrounding liquid phase [56]. Besides divalent cations,  $\text{Al}^{3+}$  as a trivalent species was found to form stable complexes in pre-swollen acrylic-based SAPs. As the reaction front progressed into the interior of the hydrogel a shell-like barrier was created. Due to this core–shell-like structure the product body was mechanically significantly stiffer than the initially swollen hydrogel. Self-release of stored solution was prevented although such loss of swelling capacity might be expected upon the multidentate complexation [59].

The fundamental kinetics of swelling and deswelling of hydrogels have been studied intensely in terms of polymer chemistry and physics [60–66]. Beyond free swelling kinetics, modelling of swelling under spacial restraint was attempted with a special focus on chemical sensor and actuator applications [54]. However, such approaches have not regarded the specific environments and confinements in fresh, hardening and hardened cement-based matrices.

From the point of view of a practitioner in the field of construction materials, the speed of absorption of a given SAP primarily depends on the particle grading [40, 44, 59, 67]. Among different SAPs their chemical composition dominates the absorption speed and ratio [4, 40, 44]. Desorption kinetics from a hydrogel as determined in saline solution can also be regulated by the SAP's composition [4, 68, 69]. During the dormant period, the desorption kinetics of hydrogels embedded in the cement-based matrix are similar to those in saline solution and desorption during this time can occur only when the  $\Delta\pi(\text{elastic})$  and  $\Delta\pi(\text{bath})$  terms outweigh the  $\Delta\pi(\text{mix})$  and  $\Delta\pi(\text{ion})$  terms. Such characteristics depend on the chemical composition of the SAP used [12, 17]. Later on, in the first hours to days after setting, the hydration reactions give rise to desorption of water from then still water-containing hydrogels in the matrix through chemical shrinkage. In this stage, the main mechanism is the emptying of the capillary pores and the capillary suction that extract the liquid from the water reservoirs [70, 71].

As can be concluded from Eq. 1, a prerequisite for obtaining meaningful results from pre-tests of readily available SAP samples prior to implementing them in a cement-based matrix is the assessment of their behaviour in ionic solutions typical for these materials. Numerous cement-pore solution compositions as well as recipes for mimicking pore solutions have been published, cf. [59, 67, 72–79]. Modern blended, cement-based materials may vary in the ionic composition of their pore solutions [79]. However, in principle and with respect to the fundamental sorptivity, the main factors remain the same throughout all reactive powder pastes based on Portland cement: highly alkaline pH (11 to close to 14) and balanced saturation concentrations of  $\text{Ca}^{2+}$ , aluminium species,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$  and  $\text{Na}^+$  [4, 59, 69]. The roles of further dissolved ions such as silicate species (e.g.  $\text{SiO}_4^{4-}$ ), which are present in cement pore solutions only in quite minor concentrations [77, 79], have not yet been comprehensively studied.

As the ion concentration in the pore fluid is different when studying different types of cement-based mixtures (normal Portland cement, fly ash blended cement, blast-furnace blended cement), or alkali-activated materials or other types of binders, the swelling capacity of SAP samples could be expected to be different as well. However, Snoeck et al. [80] showed that no difference was found in the workability characteristics among the mixtures containing SAP and different binders based on Portland cement, and it was concluded that the absorption of pore fluids was approximately the same in all mixtures being made with a normal Portland cement or with cements containing fly ash or blast-furnace slag.

Strictly speaking, the filtrate liquid or centrifugate of each individual paste should be extracted time-resolved because the ionic composition changes considerably in time [77–79]. These changes are imposed on the SAPs. They can affect the polymers' desorption kinetics in addition to the water demand from the cement-based matrix during the acceleration period of cement hydration [12] and the capillary forces [70]. Hence, ex situ sorptivity tests of SAPs should be performed using such “fresh” ionic solutions extracted time-resolved from the hydrating cement-based materials. To date, this issue of changing pore fluid chemistry over time has not yet been covered in the field of SAP research for concrete. However, for



ordinary practice-oriented tests, the extraction of solution from only one representative paste and at only one point in time is considered to be feasible and sufficient. To get a general impression of SAP performance with respect to their use as a concrete admixture and for qualitative comparison among several polymer samples, the use of water-rich, cement-based slurries can be considered to obtain reasonable amounts of filtrate liquid without exaggerated laboratory effort, e.g.  $W/C = 4.3$  [4] or  $W/C = 10$  [39], where prior to filtration dissolution of ions from the cement should be allowed for several hours. In any case the ionic composition of the test liquid used must be detailed as thoroughly as is feasible.

Exemplary orders of magnitude provide an impression of how intense the chemistry of the absorbate liquids affects the swelling capacities of SAPs. Considering the long-term absorbency of acrylic-based SAPs, about 10–75% of a cement filtrate could be stored as compared to de-ionized water [4, 69]. The higher the co-monomer ratio acrylic acid/acryl amide and the lower the cross-linking density were in the SAP, the bigger was the extent of reduction in intake and retention capacity. Examples include reduction from 430 to 55 g liquid per g SAP (high anionicity, low cross-linking density) and from 25 to 18 g/g (low anionicity, high cross-linking density) [4]. Irrespective of these long-term values, quick absorbance of up to 35 g/g within 15 min, followed by individual desorption and a long-term retention of 5 g/g only, was measured for highly anionic SAPs [4, 69]. Another study on the same systematics of polymer parameters found that  $\text{Na}^+$  reduced the long-term swelling ratio by 25–50% in comparison to de-ionized water.  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  in the same concentrations as  $\text{Na}^+$  cut that swelling ratios by at least 80% and even more than 98% (from 125 to 1.9 g/g as the maximum reduction). Merely increasing the  $\text{Na}^+$  concentration from 0.0125 to 0.1 mol/L reduced the swelling capacity from about 70 g/g to 30 g/g, i.e. by approximately 57% [59]. A study related to physiological aqueous salt solutions reported the reduction of the equilibrium swelling degree of an acrylic acid-based, fully neutralized hydrogel from 800 to 1000 g/g with no salt in the liquid via about 150 g/g with 30 mmol/L to approximately 110 g/g with 100 mmol/L of alkali chlorides (LiCl, NaCl, KCl, CsCl). Earth-alkali-ions, in the form of their chlorides ( $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ), cut this equilibrium swelling degree to 4 g/g with 0.2 mmol/L

salt concentration [64]. In 40 mmol/L NaCl pre-swollen hydrogel with a swelling ratio of 115 reduced this to a minor extent only, i.e. to 105 upon increase of 2 mmol/L NaCl. However, divalent cations ( $\text{Cl}^-$  being their anions) affected the swelling degree pronouncedly. While up to 1 mmol/L of earth-alkali-ions reduced it to 40 g/g, any further increase of salt concentration resulted in a practically complete collapse of the hydrogel, i.e. complete loss of the swelling extent. The threshold to collapse was 0.5 mmol/L with  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ , whereas less than 0.1 mol/L of  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  had the hydrogel collapse. Immersion of the so-treated polymers in excess 40 mmol/L NaCl solution resulted in almost full recovery of the initial swelling degree of the hydrogels loaded with  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  within 150 min and  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  within 600 min, which indicates reversibility of the complex formation with the polymer chains. Contrarily, the trivalent cations of  $\text{La}^{3+}$  or  $\text{Ce}^{3+}$  featured such intense complex binding intensities that after three to four weeks the hydrogels were still in their collapsed state [65].

Internally stored cations within the hydrogels may be quantified by optical emission spectroscopy (OES) and atomic absorption spectroscopy (AAS) [64].

Besides ionic conditions of the absorbate, temperature can play a crucial role in sorption kinetics of hydrogels. To date SAP samples for use in construction materials have been pre-tested at ordinary laboratory temperatures (20–25 °C) only. However, the literature indicates that numerous temperature-related, potentially surprising effects on SAP performance may occur depending on the chemical composition of the polymers, e.g. [18, 31, 33, 81–85]. To briefly summarize the respective literature, merely the chemical composition of a polymer determines the sorption characteristics at varied temperatures if any other external stimuli are imposed. Superabsorbers which have an upper critical solution temperature (UCST) swell to a pronouncedly larger extent at elevated temperatures, whereby such temperatures are in fact reachable during concrete production and processing or the lifetime of a structural element. Other hydrogels, which feature a lower critical solution temperature (LCST), swell considerably less upon heating or even collapse completely. Furthermore, ionically, pH- or temperature-induced post-crosslinking, cleavage of cross-links or degradation of the primary chains, respectively, can take place and affect the hydrogel's



sorptivity performance. Such chemical changes can occasionally release molecules or ions from the polymer network, some of which give rise to a characteristic odour (e.g. amines).

From a concrete practitioner's point of view, temperature-controlled pre-tests as well as experiments using specific saline solutions are recommended with SAP samples subjected to prospective temperature levels and profiles as well as prospective ionic compositions of the contact liquids. Such procedures have already been established with hydrogels intended for medicine or health care applications, e.g. [31]. Besides the temperature-dependent hydrogel stabilities themselves, the composition of the cement pore solution varies considerably with the temperature [78, 79].

## 5 Analyses of solubles and extractables

Loosely bound components, residual monomers, or additive substances in a SAP material can be easily soluble. As well, freely movable counter-ions of the charged polymer chains can escape from inside the hydrogel while ions immigrate from outside. This ion exchange is explained by the discussion of Eq. 1 [53, 64]. Furthermore, the highly alkaline pH of the cement-based materials as well as imposed temperature profiles can cleave chemical bonds in the polymer network and hence cause the formation of extractable molecular fragments.

To gravimetrically quantify the solubles and extractables, a representative portion of the as-obtained SAP material should be weighed in the dry state, immersed in the respective test liquid and gently stirred or left at rest until equilibrium of swelling is obtained. After separation of excess liquid the hydrogel is dried to the initial conditions until mass constancy. The mass difference before and after immersion denotes the amount of solubles and extractables [20, 28]. Various standard methods of instrumental chemical analytics can be applied to the separated solution for qualitative and quantitative characterisation, e.g.:

- pH measurement;
- atom absorption spectroscopy (AAS), atom emission spectroscopy (AES), conventional qualitative and quantitative analysis of inorganic ions;

- ion chromatography (IC);
- total organic carbon (TOC);
- UV/VIS spectroscopy, infrared (IR) spectroscopy;
- nuclear magnetic resonance (NMR) techniques;
- high-performance liquid chromatography (HPLC), coupled with suitable detection systems, e.g. mass spectrometry (MS);
- gas chromatography (GC), coupled with suitable detection systems, e.g., mass spectrometry (GC-MS);
- size-exclusion chromatography (SEC); and
- determination of the surface tension.

Readily available SAP materials can contain surfactants as was derived from experimental results of investigations on concrete [8, 86]. They are likely to migrate into the surrounding cement-based matrix when the SAP particles are integrated into the building material. As a result, the rheological behaviour and air content of the fresh mixture, as well as the mechanical properties and the freeze-thaw resistance of the hardened cementitious material can pronouncedly be affected.

## 6 Qualitative pre-test for principal suitability for use in cement-based materials

This qualitative experiment can be fully integrated into quantitative sorption tests, but it is particularly interesting for screening, thus for obtaining a first impression about the behaviour of unknown SAP samples with respect to their potential suitability for use in cement-based materials. Basically in a collective of SAP particles each individual particle should be preserved; i.e., no dissolving, caking, or intense discolouring should occur. A qualitative impression is gained by placing some 0.2–1 g of as-obtained polymer particles in a beaker with an excess of pore solution (100–500 mL). After air-tight covering to prevent carbonation and evaporation, the experiment is visually monitored for several hours. The contents of the beaker may be gently swayed or stirred from time to time.

Every now and then the scent or other unexpected reactions (e.g., intense discolouring or visible gas generation) should carefully be checked. Obvious smell as well as any apparent and clear distinctions from what would be expected should be immediately





reported to the manufacturer, and such polymers should not be further used in laboratory or field tests.

In the common context of concrete or mortar technology, any such tests have been performed at normal laboratory temperature only (around 20 °C). But in considering heat curing, construction at elevated temperatures, or the temperature rise due to cement hydration, it may be meaningful to perform the qualitative pre-testing at the expected or intended temperature.

At temperatures above 100 °C polymer degradation sets in for most common superabsorbers. These degradation reactions can, however, be exploited purposefully in thermogravimetric (TGA) analysis for polymer characterisation [18, 39].

## 7 Recommended test procedures for assessment of ab- and desorption kinetics and absorption capacity

Numerous recognized test methods for SAPs have been agreed upon and edited over the last years. Their primary focus has been on the performance of hygiene products, such as diapers or tissues. Some of these procedures have been adopted for SAPs which are intended for use in cement-based building materials. This section will discuss such tests to assess the

- free swelling capacity
  - gravimetrically in the co-called “tea-bag method” [4, 12, 15];
  - by filtration and gravimetry without application of a vacuum [39] as well as using an aspirator [51];
  - by precipitation from acetone and vacuum drying [28];
  - by volumetric quantification of capillary suction [28, 51];
  - by the filtering and rubbing gravimetric method [40, 46, 87, 88];
  - by the vortex method [88];
  - by means of dynamic vapour sorption (DVS) [89];
  - by visual size determination based on optical microscopy [55–57, 67, 90], laser diffraction [41] or monitoring the rising horizon of the hydrogel in a beaker [68];

- centrifuge retention capacity as a modification of the tea-bag method [15, 69]; and
- absorbency against pressure [15, 25, 91]

The same statements regarding temperature as outlined in the previous section hold true for these test procedures.

Any known statistical evaluation can be applied to any obtained results. This may include averaging the results per SAP type, quantity, kinetics, liquid etc., calculating corresponding standard deviations, performing *T*-tests, or any other method to estimate the statistical significance or uncertainty of the measurements. Respective literature and calculation schemes should be regarded, but they are not part of the present review.

### 7.1 Free swelling capacity

#### 7.1.1 Gravimetric “tea-bag method” [4, 12, 15]

Before starting the sorptivity test, it must be established by qualitative pre-testing that the dry SAP particles cannot escape through the interstices of the (dry) tea-bag or similar permeable sachet.

A tea-bag is pre-wetted in the later test fluid. The tea-bag is placed on a dry cloth and gently wiped with another dry cloth for a short time to remove surplus and weakly bound liquid. The mass of the tea-bag is recorded (mass  $m_2$ ). Next a predetermined, exactly measured mass  $m_1$  of SAP particles is inserted. The tea-bag containing the SAP particles is hung in a beaker filled with the test liquid and the beaker tightly covered with a self-adhesive, plastic stretch film to avoid carbonation and evaporation. After distinct times of SAP/liquid contact, the tea-bag with the hydrogel inside is released and weighed (mass  $m_3$ ). Drip-drying is performed in the same manner as for the pre-wetting. After weighing, the tea-bag containing the hydrogel is returned to the test solution until the next time step of weighing. The amount of absorbed liquid at each particular sorption time with respect to the initial mass of SAP is calculated in accordance with Eq. 2.

$$m_{\text{absorbed per g dry SAP}} = \frac{m_3 - m_2 - m_1}{m_1} \quad (2)$$

A systematic drawback of the tea-bag method can be residual interparticle (capillary) liquid that may



remain within the samples during wiping and weighing. This topic has been postulated by, e.g., [68], and Kang et al. [69] have recently reported a systematic study on this issue (cf. Sect. 7.2). Furthermore, a Round Robin test currently being performed by RILEM TC 260-RSC should bring some clarification on that point, so that this phenomenon can be considered in the Recommendations for Practitioners, to be prepared in the framework of the TC activities. Despite these concerns, the tea-bag gravimetric method as described here is a very common and widely accepted quantification method for sorptivity assessment of superabsorbent polymers.

### 7.1.2 Filtration method

**7.1.2.1 Without vacuum according to [39], modified for time-resolved recording** In this test, an excess of the test liquid is added to the SAP particles for the hydrogels to swell freely. A recorded mass of test liquid is added to a distinct mass of dry SAP. The beaker is then tightly covered with a self-adhesive, plastic stretch film to avoid carbonation and evaporation.

To ensure that there is no influence of the filter paper, the latter is saturated with the test fluid prior to filtration. After distinct times after SAP/liquid contact, the mixture is filtered. For each time, individual containers need to be filled, as the sorption capacity can be measured once per sample only. Figure 1 sketches the steps of the procedure.

The mass increase of the SAP is gravimetrically determined as the difference between the initial mass of liquid and the filtered mass and normalised to the mass of dry SAP. Equation 3 provides the formula to calculate the absorption capacity in each time step.

$$\text{Swelling capacity} = \frac{m_{\text{fluid added}} - m_{\text{fluid filtered}}}{m_{\text{dry SAP}}} \quad (3)$$

Inter-particulate fluid may affect the results as obtained, but microscopic analysis as described by Snoeck et al. [90] revealed that this influence was negligible.

**7.1.2.2 Using an aspirator according to [51], modified for time-resolved recording** A portion of the dry SAP (exact mass  $m_1$ ) is immersed in an excess of the test fluid. At an appropriate time of equilibrium absorption the excess liquid is separated from the

hydrogel by suction filtration with an aspirator. The soaked polymer is weighed (mass  $m_2$ ) and the extent of swelling calculated according to Eq. 4.

$$\text{Swelling capacity} = \frac{m_2 - m_1}{m_1} \quad (4)$$

While Lee and Wu [51] let the polymer imbibe for several hours for equilibrium of swelling to be reached, the experiment may be conducted time-resolved by using multiple polymer portions for each distinct time step. For sure, intensity of negative pressure, time of applying the vacuum, type of filter (mesh size) as well as masses of dry SAP and volume of initial test liquid have to be adjusted individually. Any of these conditions may impact the extent of removing surplus, interparticle water or might even result in extracting absorbed liquid from inside the hydrogels.

### 7.1.3 Liquid retention capacity after precipitation of the swollen hydrogel in acetone followed by vacuum drying [28]

A portion of dry SAP is immersed in the intended test liquid and swelling is allowed for a distinct time. Then, the swollen hydrogel is placed on a sieve and weighed exactly. This polymer mass is precipitated in acetone and dried at a temperature of 40 °C while vacuum is applied. The mass of the dried polymer sample is measured. Finally, the extent of absorption is calculated as the quotient of the mass of the retained liquid divided by the initial dry mass.

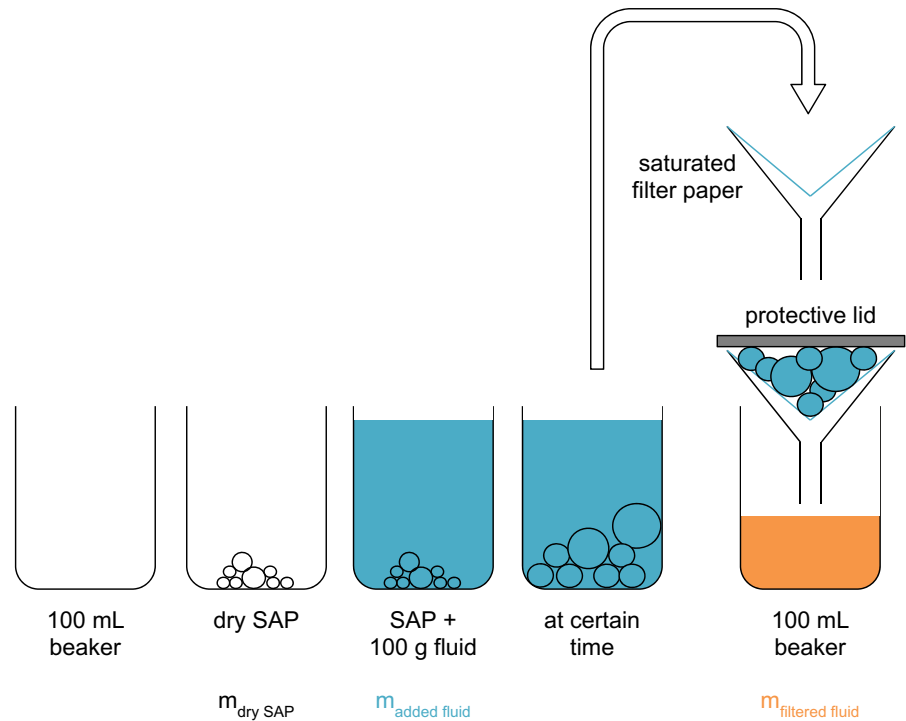
This method was proposed as a single-point measurement in time [28]. However, it can be modified to time-resolved quantification by using multiple polymer portions for each distinct time step. As well, there seems to be no obvious limitation in the aqueous test solutions because acetone precipitates the hydrogels anyway from the water phase.

### 7.1.4 Volumetric quantification of capillary suction [28, 51]

A graduated burette equipped with an air inlet at its bottom is linked to a cell which has a metal sieve at its top. The sieve is at the same height level as the air inlet. The burette is filled with the respective test fluid and then closed tightly at its top. An exactly weighed portion of dry SAP is placed on the metal mesh. Air is



**Fig. 1** Filtration method procedure



let into the system while the superabsorber is imbibing the liquid by capillary suction. Derived from the readings of the volume change in the burette the absorbency of the hydrogel is quantified.

#### 7.1.5 Filtering and rubbing gravimetric method [40, 46, 87, 88]

Some dry SAP (exact mass  $m_1$ ) is interspersed in an excess volume of test liquid and mildly agitated with a magnetic stirrer. After the planned soaking time, the sample is filtered through a metal sieve having mass  $m_2$ . The mesh has to be fine enough to retain all of the hydrogel material. Surplus liquid is extracted by rubbing a soft open-cell polyurethane foam under the meshwork and squeezing it. This agitation is performed until the hydrogel no longer slips from the metallic gauze when turned to the vertical position. Quantification of the sorptivity accords with Eq. 5; for experimental reasons, the hydrogel sample is left on the mesh for weighing.

$$\text{Sorptivity} \left[ \frac{m_{\text{absorbed liquid}}}{m_1} \right] = \frac{(m_{\text{swollen SAP}} + m_2) - m_1 - m_2}{m_1} \quad (5)$$

To date, no application of this method for testing SAPs intended for use in cement-based construction materials has been made public. Interestingly, very elaborate studies linking synthesis method, chemical composition and particle size of systematically varied SAP samples utilised this method to distinguish the sorptivities of the polymers [40, 44, 46].

#### 7.1.6 Vortex method [88]

The swelling time can easily be determined using this vortex method. Quite naturally, no time-resolved sorption kinetics are accessible herewith.

An exactly weighed mass of test solution is placed in a beaker. By stirring with a magnetic stirrer bar, a vortex is created. A portion of dry SAP is poured in and time recording begins. The time at which the vortex disappears is then read. Obviously, the geometry of the experimental setup and the stirring intensity can decisively influence the test result. Masses of test liquid, beaker size, stirrer bar dimensions and stirring speed as well as SAP amount to allow for equilibrium swelling in the selected amount of liquid must be experimentally elucidated in pre-tests. There is also a subjective notion of the time of the vortex

disappearing, which may result in some differences in time recording. This aspect has not yet been discussed in the literature.

The test must be repeated several times for statistical significance, e.g., ten times, using fresh portions of test material and solution for each run [90].

### 7.1.7 Visual size assessment by optical microscopy

**7.1.7.1 Procedure in accordance with [67]** This procedure has been demonstrated with spherical SAP particles. They are submerged in a micro-bath placed in the detection area of a stereo optical microscope. A scale bar within the bath allows straightforward size-assessment and accounts for time-dependent particle movement. Digital images are recorded through the ocular using a CCD camera. One image is recorded per minute until 10 min after the first contact of SAP with liquid, followed later by one image every 10 min. The magnification should be set to a most suitable balance among field of view, lateral resolution, depth resolution, and the general ease of determining the SAP particles. Swelling and de-swelling kinetics are evaluated with respect to the scale bar using contemporary digital image processing software.

Until now, only spherical particles have been investigated. Hence, modifications in image analysis will be required to investigate irregularly shaped SAP particles from bulk polymerisation. Due to the energy input by the intense light source, local temperature variations may occur, as well as heating over time. Effects of both aspects have not yet been assessed yet in the framework of this measurement technique.

**7.1.7.2 Procedure in accordance with [39]** A dry, spherical SAP particle is imaged using an optical light microscope at first as the reference. The test fluid is added drop-wise using a syringe and images are recorded over time. Complete saturation sets in where no additional liquid can be taken up by the particle. The absorption amount is calculated as the volume increase relative to the original volume in the dry state, divided by the relative density of the SAP and fluid and expressed as gram fluid absorbed per gram polymer; for this, the diameters are recalculated to the respective volumes.

The particle size must be well-suitable for visualisation in the optical microscope, and liquid absorption

must not be too slow, to ease the clear determination of the saturation level.

**7.1.7.3 Polarised light optical microscopy to assess immigration front of chelating cations [55–57]** Although this method used and intensely coloured, aqueous solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with diligently balanced concentration, and dates back to as early as 1998, it may be relevant for studying SAPs in the context of cement-based building materials because of the advancement of image recording and evaluation techniques.

A dry, spherical SAP particle is placed between two glass slides, whereby spacers between the glass slides thicker than the maximum swelling thickness assure free swellability and inhibit evaporation of the solvent. This setup is put in an optical transmitted light microscope. Cross-polarised light is applied instead of ordinary. After recording the initial state the test liquid is immersed while recording a movie sequence as quasi-continuous imaging. Distinct patterns of light intensity and clear borders separating different areas become visible due to birefringence (experimental details cf. [56]). For interpretation see the discussion of Eq. 1 in Sect. 4.

### 7.1.8 Visual size assessment by laser diffraction [41]

The well-known laser diffraction method in a conventional respective apparatus has recently been suggested to be applicable to swollen hydrogel collectives as well. Evaluation of the raw data follows the Mie scattering model. First, the size of the dry (collapsed) SAP particles is assessed using pure ethanol, in which the polymer network cannot swell. Then SAP particles are circulated and dispersed in a typical saline solution relevant to cement-based materials and the size distribution of the particles is determined. However, as yet only the  $D_{50}$  value has been used to calculate the hydrogel particles' volume. Spherical particle shape is assumed for evaluation of the absorbency in accordance with Eq. 6 where  $\rho_{\text{saline solution}}$  is the density of the test liquid and  $\rho_{\text{SAP}}$  is the density of the SAP.

$$k = \frac{\rho_{\text{saline solution}}}{\rho_{\text{SAP}}} \cdot \frac{V_{\text{SAP in the saline solution}} - V_{\text{SAP in the collapsed state}}}{V_{\text{SAP in the collapsed state}}} \quad (6)$$



The test gives the absorbency  $k$  in mL of absorbed saline solution per gram of dry (collapsed) SAP. While [41] provides the numbers of the density of the hydrogel as  $\rho_{\text{SAP}} = 1500 \text{ kg/m}^3$  and that of the saline medium as  $\rho_{\text{saline solution}} = 1000 \text{ kg/m}^3$  each experimenter should determine the individual densities of the substances used.

Interestingly, nothing is stated about the compatibility of the alkaline saline solution with the liquid circuit of the laser diffraction apparatus and the streaming behaviour of the swollen hydrogel entities in there.

### 7.1.9 Rising horizon of the swelling hydrogel particles [68]

To monitor swelling over time, the height of SAP settlement in a graduated cylinder can be used. While swelling, the horizon of the particles lying on the ground rises. The relationship between the volume and the mass of packed dry hydrogel particles is required. The latter is obtained by filling a cylinder to its maximum reading ( $V_1$ ) with dry particles and recording their mass ( $m_1$ ). Next, the test fluid, in excess compared to the final swelling capacity, is added in a graduated cylinder to a small amount of hydrogel particles with known mass ( $m_2$ ). During the absorption, the cylinder is softly shaken to allow free swelling of the particles. After settling due to gravity, the volume of the swollen particles is read ( $V_2$ ). The absorption capacity  $K$  (g/g) is calculated using Eq. 7 where  $\rho_{\text{hydrogel}}$  is the density of the hydrogel and  $\rho_{\text{fluid}}$  is the density of the test fluid. These densities have to be determined individually.

$$K = \frac{\rho_{\text{fluid}}}{\rho_{\text{hydrogel}}} \cdot \left( \frac{V_2}{V_1} \cdot \frac{m_1}{m_2} - 1 \right) \quad (7)$$

This test is useful to study the level of packing in time and, thus, time effects such as degradation and possible loss or gain in swelling capacity.

Due to the settling of the particles, the initial absorption value is overestimated. The most significant part of the swollen SAP collective is the fluid itself, and the density of the swollen SAPs is in turn close to that of the surrounding liquid. As a result, the packing is less dense due to a buoyant effect. There are also individual viscous drags between hydrogel particles depending on their sizes and settlement acts like

a sieve separating different sizes. Therefore, the packing of dry and saturated SAP particles may be different. After settlement and due to the potentially different packing degree, the absorption value can be different to the real absorption capacity.

To summarise, such measurement can serve as a quick estimation of total swelling behaviour, however, the test is clearly not useful when the SAP particles become buoyant in the course of swelling. Such buoyancy may occur when they swell to such a large extent that their density approaches that of the surrounding liquid.

### 7.2 Centrifuge retention capacity as a modification of the tea-bag method [15, 25, 69]

Specimen preparation, SAP and liquid proportions are the same as those of the tea-bag method; see Sect. 7.1.1. However, two aliquots of a polymer sample are placed here, each in one tea-bag, and the openings are sealed. These tea-bags are then submerged in the test liquid to allow free sorption for a specified time. Afterwards, the tea-bags are transferred to a centrifuge drum so that liquid can be freely released downwards; balancing is easiest when the two initial masses are equal. Calculation of the absorbency accords with Eq. 2.

Due to the intense centrifugal forces, inter-particle liquid is removed to a noticeable extent. Hence, the test results can be claimed to have a higher accuracy than those of other gravimetric methods [69, 88] but most appropriate conditions to remove the entire inter-particle liquid have not yet been clarified [68]. Kang et al. [69] used 1000 rpm for distinct time durations. One minute of centrifugation caused a quite considerable dewatering in comparison to the centrifugation-free tea-bag method, whereby longer centrifugation times of up to 20 min had the sorptivity readings level off at a plateau value. While their sample of cross-linked poly(acrylic acid) with irregular particle shape released 25% in average ( $\pm 13\%$ ) during the centrifugation, the poly(acrylic acid-co-acryl amide)-based sample with spherical particles lost only 16% ( $\pm 8\%$ ). A combination of the two parameters of polymer composition and particle shape caused this difference.

Finally, it has to be stated that none of these studies has yet elucidated the effect of centrifugation on the internal retention capacity of the hydrogels.





### 7.3 Absorbency against pressure

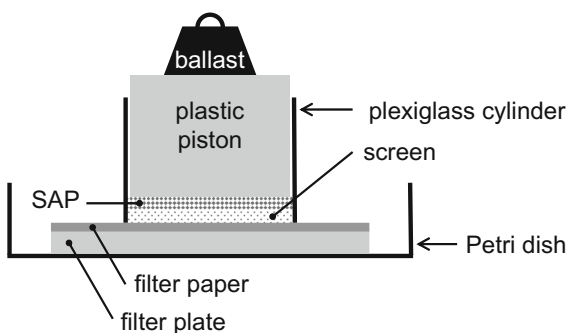
#### 7.3.1 Piston and filter plate method [15]

As the basic apparatus, a stamp filtration press such as used in the extraction of cement pore solution [72] could be used to determine absorption capacity against pressure of a SAP. However, an especially designed test setup is described in [15], which is sketched in Fig. 2. It uses a suction screen at the bottom of a cylinder and a heavy piston exerting the pressure.

A portion of dry SAP (exact mass  $m_1$ ) is placed evenly on the bottom screen of the test cylinder. The piston is inserted in this cylinder and the entire setup is weighed in its dry state (mass  $m_A$ ). In the petri dish the filter plate is positioned and the test liquid filled to such a height that its surface just reaches the upper edge of the filter plate. A filter paper is mounted atop the filter plate and thoroughly soaked, but excess surface liquid must be avoided. The test cylinder is put on this filter and the extra weight set on its top. For a specified time, the SAP sample is allowed to soak. The mass of the cylinder containing the swollen hydrogel—but without the additional ballast—is recorded as mass  $m_B$ . The absorbency against pressure (AAP) is calculated in accordance with Eq. 8. At least two runs should be performed per SAP material and point of time, respectively.

$$\text{AAP} = \frac{m_B - m_A}{m_1} \quad (8)$$

For instance, [29] applied such test setup to investigate sorption characteristics of starch-based superabsorbers cross-linked with di- and multifunctional carboxylic acids. However, no test results from this test method with respect to use of SAPs in cement-based materials have been made public to date.



**Fig. 2** Schematic view of a test setup for absorbency under pressure according to [15]

#### 7.3.2 Isotropic compression [25]

Sannino et al. presented a self-developed experimental setup for swelling of SAPs against isotropic compression in a confined volume and the evaluation strategy therefore [25]. A porous spherical mould connected to a loading cell is placed in a temperature-controlled tub. The dry SAP sample is inserted in the mould and a pressure sensor is placed in tight contact at the top of this mould, which prevents the sample holder from moving but does not exert relevant stress. The test liquid is filled into the tub and penetrates the mould. When it reaches the polymer swelling initiates and continues until the free volume of the mould is completely filled. From that point onward, volumetric expansion is inhibited and a pressure is being recorded by the load cell. When equilibrium swelling is reached the isotropic compressive stress representing the swelling stress  $\sigma$  is calculated according to Eq. 9.

$$\sigma = \frac{F}{\pi \cdot R^2} \quad (9)$$

$F$  is the recorded force and  $R$  the mould's radius. Afterwards, the hydrogel sample is taken out and weighed immediately. In parallel, the free equilibrium swelling is determined gravimetrically. The corresponding deformation  $\varepsilon$  upon the restrained swelling is calculated according to Eq. 10.

$$\varepsilon = \frac{S_{\text{restrained}} - S_{\text{free}}}{S_{\text{free}}} \quad (10)$$

$S$  represents the swelling ratio, in each case the restrained or the free one, and the numerator is the measure of the inhibited expansion. By using several moulds with individual volumes (diameters) a set of different deformations is realised so that a  $\sigma$ - $\varepsilon$ -plot is obtained as the characteristic result of this test method.

Interestingly, [25] neither discloses technical details of the developed apparatus, for example the nature of the porous mould material, order of magnitude of recorded forces, size dimensions, SAP mass nor volumetric filling ratio of the mould. Only the cited general principle is outlined.

#### 7.3.3 Diaphragm deflection [91]

This experimental setup allows determination of the swelling pressure. A gel swells in a closed chamber equipped with a porous bottom, against a flexible wall

which constitutes a diaphragm for force measurement. The chamber is filled loosely with SAP particles and test liquid starts to immerse through the porous bottom. A thin quartz disk is used as the flexible wall. Atop this diaphragm a glass plate is located which is spotlighted by a laser light beam. Diaphragm deflection as the consequence of hydrogel swelling generates Newton's rings due to interference. Compared to the height of the chamber the expansion is very small. Hence, the volume is regarded as constant all the time and the deformation of the polymer practically isotropic. Time resolved, the light intensity (photo-current) is plotted as a function of the radius from the centre of the beam. Based on reference measurements with known hydrostatic pressures with the very quartz disk the swelling pressure of a hydrogel sample is evaluated over time.

#### 7.4 Dynamic vapour sorption [89]

Apart from liquids, SAPs can absorb moisture from the humid air. DVS gravimetrically measures the moisture uptake capacity at a constant temperature of 25 °C under varying relative humidity (RH). Within a temperature-controlled housing the flow of wet and dry N<sub>2</sub> gas is monitored. With increasing RH the weight of a sample and reference container is determined by means of a microbalance during measurement inside the housing. A first step (RH of 0%) is necessary to start with a completely dry material. Afterwards, the relative humidity is increased stepwise. Every subsequent step is initiated when the change of the sample mass as a function of time is lower than a chosen change rate per minute, e.g. 0.002 wt%. To determine the equilibrium value at 98% RH, extrapolation is required for time reasons. Experience teaches us that using the drift criterion of maximum 0.002 wt% per minute the establishment of the absorption value takes a lot of measuring time. Hence, derived from such exemplary real-time measurements at this very high RH the following equation was found as an extrapolation up until that RH step, which is based on an analytical solution of the diffusion equation. In Eq. 11,  $m(t)$  is the mass of the sample at time  $t$  and the coefficients  $a$ ,  $b$  and  $c$  are determined by means of non-linear curve fitting on the data obtained before reaching equilibrium.

$$m(t) = a \cdot (1 - b \cdot e^{-ct}) \quad (11)$$

However, if DVS should be conducted in a range of 60–90% RH only, no extrapolation is required and the absorption is experimentally accessible at all RH levels during reasonable measurement times.

## 8 Conclusion and final remarks on sorptivity assessment of SAPs incorporated in cement-based materials

Any pre-test of free sorptivity in adequate saline solutions or absorbency determined under the application of external forces can give primary hints towards the in-fact behaviour of a SAP sample when embedded in cement paste, mortar or concrete. They disclose fundamental features of SAPs relevant for use in cement-based materials. Recommendations in respect of particular testing procedures will be issued by RILEM TC 260-RSC at a later date. Whatever pre-test method is selected based on the best available information, it should belong to the standard repertoire of any SAP characterisation prior to the application of this new admixture in the practice of construction.

Numerous methods have been described to quantify the kinetics of ab- and desorption of SAPs embedded in real, cement-based matrices, especially with the focus on the actually available amount of internal curing water in the decisive stages of cement hydration. They include:

- neutron tomography [92] and neutron radiography [12],
- rheometry of fresh cement pastes and mortars [17, 93],
- isothermal calorimetry [94, 95],
- back-scattered electron microscopy (BSE SEM) of polished sections [96].

Furthermore, nuclear magnetic resonance (NMR) spectroscopy has been tried as an analytical method to explain the migration of water between SAP particles and the cement-based matrix [97]. Finally, the sorption kinetics of SAPs in cracked, cement-based, solid bodies have been explained using neutron radiography with the aim of assessing the role of SAPs in the self-sealing and self-healing of concrete [10, 39].

SAP dosages in cement-based building materials have been based on performance-oriented full-scale concrete laboratory pre-tests up to date. 0.2–1.0 wt%

dry SAP by weight of cement have been found to be most beneficial throughout numerous test campaigns and for multiple benefits and applications. Practically, the dry SAP is batched into the powdery pre-blend of all dry constituents of a concrete or mortar and the SAP swells during the mixing procedure after addition of the water and dissolved or liquid chemical admixtures [1, 2, 4–9, 17, 39, 70, 71, 86, 89, 90, 93, 95–97]. To date, results from *ex situ* SAP pre-tests have not been used as the sole or primary fundament for selecting and justifying SAP dosages in the construction materials. Neither have the findings from instrumented analytics on SAP-enriched cement-based pastes been exploited for this purpose [12, 17, 92–96]. Establishing such cross-links lies ahead for the close future in this field of materials science and the outcomes are expected to reduce the work-load in concrete laboratories significantly.

#### Compliance with ethical standards

**Conflict of interest** All co-authors are members in RILEM TC 260-RSC. None of the co-authors has financial conflict of interest.

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