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Measuring absorption of superabsorbent polymers in cementitious environments

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Abstract Prior to implementing superabsorbent polymer (SAP) in cement-based materials, the absorption capacity in this environment needs to be known. Two simple methods, the tea-bag method and the filtration method, are often used to measure the SAP absorption capacity in liquid environments. Typically, the two methods give results that do not agree. The scope of this work is to explain the discrepancy between results from the two methods and to examine how well the methods predict the SAP absorption capacity in concrete. The tea-bag method is modified with different convection conditions during the test, and with various water/cement ratios and hydration times during preparation of cement slurry filtrate that is used as test liquid. The filtration method is modified with different liquid/SAP ratios. Air void analyses of cement paste and concrete are used to assess the SAP absorption capacity in hardened samples. The results reveal that a decrease in absorption capacity observed with the tea-bag method is due to properties of the test liquid and ion exchange between SAP and test liquid. The difference in 24-hour absorption capacities given by the two simple methods is likely due to unequal amounts of interstitial water. It is advised not to use these simple methods as means of estimating SAP absorption capacity in concrete, since the results from these methods do not properly represent the absorption behavior in concrete. Instead, air void analysis of hardened cement paste seems to be a reliable method to register the SAP absorption capacity in cement-based materials.

Keywords *Superabsorbent polymers, absorption capacity, tea-bag method, filtration method*

1 Introduction

Two decades ago, water entrainment by superabsorbent polymer (SAP) particles was reported to be a means of mitigating self-desiccation in cementitious materials, and it was suggested that this additive might be useful for a number of other purposes [1, 2]. Since then, numerous confirmative studies have been published, and attention has been given to the application of SAP as an additive in a broad context. Such uses include, among others, plastic shrinkage prevention [3], freeze-thaw damage mitigation [4, 5], and self-sealing of cracks [6]. Whatever the reason for implementing SAP into cementitious materials, it is fundamental to know its absorption capacity and ability to release water. Incorrect estimation of this may compromise the properties of cementitious materials (typically concrete) [7, 8].

Water absorbency is often measured by tests methods where SAP is exposed to an entirely liquid environment [9]. These results may not satisfactorily represent the cementitious systems where SAP in addition to pore solution is surrounded by aggregate particles, cement and other solid components. Furthermore, exposure liquids used in these tests (e.g. cement slurry filtrate) may not properly represent the ionic composition of the pore solution in cement-based materials, including its time-dependent change. Such tests, however, are quick and simple to perform and are used e.g. to predict the development of water retention capacity and to make a quantitative comparison between different types of SAP.

The tea-bag method and the filtration method are two examples of this kind and they are both recommended by RILEM for the purpose of determining whether a certain type of SAP is suitable for a cementitious material [10]. When using cement slurry filtrate as test liquid in the tea-bag method, some types of SAP show a development of absorption capacity, where the absorption capacity increases in the first 5–10 minutes after first contact with the test liquid. Thereafter it declines within hours [11–19] by various factors ranging up to fifteen [18], and the absorption capacity does not recover at later testing times (up to 24 h). The decline is especially prominent when the tested polymers have a high density of anionic groups [13, 14]. With the high variation of absorption capacity value depending on measuring time, it is unclear which value should be used to determine the dosage of SAP for e.g. mitigating autogenous shrinkage [15]. However, when using the filtration method, and using the same batch of SAP and identical test liquid as used in the tea-bag method, a decrease in absorption capacity is hardly observed [16]. Furthermore, the long-term absorption capacity

(12–24 h) is usually higher when it is measured with the filtration method compared with the tea-bag method. As variables regarding materials in the two methods are carefully controlled, there must be some inherent differences in the two methods. Without identification of the reason for the discrepancy, it is questionable to recommend either of them as test methods.

Several reasons have been suggested as causes for the declining absorption capacity observed with the tea-bag method (see Section 3.2), but there seems to be no consensus on it. Furthermore, none of the proposed reasons explains why a similar decrease is not observed with the filtration method.

One objective of this study is to explain the inconsistency in absorption capacity results given by the two simple methods. This is reported in Part I of the paper. In one test series SAP is replaced by non-absorbent glass beads, giving a rough estimate on the amount of interstitial water in either method.

Another objective of this study is to evaluate how well the simple test methods done in liquid can predict the absorption capacity in cement-based materials. This is done by comparing results from Part I with those from Part II where the absorption capacity is measured by air void analyses of hardened cement paste and concrete.

2 Materials

2.1 Solid materials

The SAP is a covalently crosslinked acrylamide/acrylic acid copolymer. It was produced by suspension polymerization with mainly spherical particles. The SAP was rinsed with ethanol following the procedure described by Laustsen et al. [20] to remove possible surfactant. Prior to each test, the SAP was oven dried at 50 °C for 24 h to ensure a well-defined, almost-dry moisture state [21]. At this state, the water content of SAP is 1.3% by mass, as determined by subsequent vacuum-drying over silica gel. Particles were used in their originally produced size distribution (0–250 µm in diameter), except for measurements presented in section 3.2.1, which were based on a mesh sieved range of 50–75 µm validated by optical microscopy. The density of the dry particles is approximately 1500 kg/m³.

Dense glass beads (Potters A-glass 1922#, size range 150–250 µm) with a density of 2500 kg/m³ were sieved to the mesh size range 180–250 µm. This material was used for determining the amount of interstitial water.

Portland cement (CEM I 52.5 N) from Aalborg Portland was used to prepare cement slurry filtrate, cement paste and concrete. The cement has a density of 3140 kg/m³, Blaine fineness 420 m²/kg, and Bogue composition (by mass): C₃S: 63%, C₂S: 12%, C₃A: 8%, C₄AF: 12%, Na₂O eq.: 0.6%.

Sea dredged sand in the size range of 0–4 mm was used as fine aggregates (density: 2640 kg/m³; suitable for exposure class XF4 according to EN 206-1). Two size fractions of crushed granite, 4–8 mm and 8–16 mm, were used as coarse aggregates (densities: 2710 kg/m³ and 2720 kg/m³; both suitable for exposure class XF4 according to EN 206-1). Both fine and coarse aggregates have absorptions less than 1%.

2.2 Test liquids

In its basic form, cement slurry was prepared from cement and deionized water with $w/c=5$, as recommended by [10]. 300 g cement and 1500 g deionized water were added to a 2-liter beaker and maintained as a suspension by continuous magnetic stirring at a speed of 300 rpm for 24 hours. After that, the slurry was filtered (Macherey-Nagel filter paper, pore size 4–12 µm). The produced filtrate was colorless and transparent. During stirring and filtering, both the beaker and the funnel were covered with lids to reduce carbonation and evaporation, and the temperature was kept at 20±1 °C. The pH of the produced cement slurry filtrate was measured to be 12.8±0.1.

Saturated calcium hydroxide solution was prepared in the following way: an excess amount of Ca(OH)₂ (Alfa Aesar, purity >95%) was shaken with deionized water. The liquid was later filtered.

3 Part I: SAP absorption in test liquid – tea-bag method and filtration method

3.1 Methods

3.1.1 The tea-bag method and its adaptations

In this study, the reference tea-bag method was carried out according to the RILEM recommendation [10]. Moreover, two modified versions were developed from this basis. The decrease in absorption capacity measured by the tea-bag method is reported to be caused by ionic exchange [14, 22]. As ionic exchange is related to the bulk fluid motion (i.e.

convection), it is relevant to study how convection conditions influence absorption capacity changes. All tests were done in a climate room at a temperature of 20 ± 1 °C. The liquid/SAP mass ratio was 900.

Reference tea-bag method: A dry tea-bag was weighed (m_{TB1}). Then SAP was inserted into the tea-bag. The tea-bag containing SAP (total mass m_{TB2}) was put into a beaker containing test liquid. The beaker was immediately covered with a LDPE cling film to reduce carbonation and evaporation. 1, 5, 10, 30, 60 min, 3 and 24 h after the SAP/liquid contact, the tea-bag with swollen SAP was taken out, gently wiped with a dry gauze, and weighed (mass m_{TB3}). The mass of liquid (m_{TB0}) that can be absorbed by a tea-bag is determined beforehand. As such, absorption capacity (AC) of SAP was calculated by Eq. 1.

$$AC = \frac{m_{TB3} - m_{TB2} - m_{TB0}}{m_{TB2} - m_{TB1}} \quad \text{Eq. 1}$$

The whole test procedure followed the RILEM recommendation with the following exceptions: (1) Approximately 0.1 g dry particles was used for each sample because of the relatively small tea-bags available (the recommendation suggests 0.2–0.3 g); (2) instead of 200 ml cement slurry filtrate, approx. 100 ml was used for each sample in order to keep the liquid/SAP ratio in accordance with the RILEM recommendation; (3) one tea-bag was only used for one measurement at a point in time, i.e. it was never put back into the beaker to be used for further measurements; (4) some test series included measurements of absorption capacity at 6 h and 12 h after liquid contact, which are not part of the RILEM recommendation.

Dipping method: At certain time intervals, the tea-bag immersed in cement slurry filtrate was lifted with a steel thread attached to it and kept above the liquid for 5 seconds, during which liquid on the surface of the tea-bag would drip into the liquid in the beaker. The tea-bag was then again submerged into the liquid. The dipping action was repeated every minute during the first 10 minutes after test start, every 5 minutes 10–60 minutes after test start, every 15 minutes 1–3 hours after test start, and every 30 minutes 3–12 hours after test start. No dipping was conducted from 12 hours after first contact to exposure liquid until the test was ended. During the whole experiment, a plastic enclosure with a tiny, pierced hole at its top covered the beaker to reduce carbonation and evaporation. Fig. 1 illustrates the set-up.

Stirring method: In this method, the test liquid (cement slurry filtrate) was stirred with a magnetic rod at a rotation speed of 250 rpm throughout the experiment. The tea-bag was hung at a height where it was not colliding with the rotating rod beneath it while it was still

fully submerged in the liquid. Some magnetic stirrers develop heat, and this is a potential problem if the absorption capacity is temperature dependent. About 1 cm of thermal insulation material was placed between the beaker and the magnetic stirrer to reduce heat transfer. The temperature of the liquid was checked and maintained at 20±1 °C. The insulation material did not influence the stirring.

Precision of the methods: According to the RILEM recommendation [10], measurements with the tea-bag method should be carried out in triplicate. This was done in a pre-test for the reference tea-bag method, where the absorption was registered at 9 different absorption times (1 minute – 24 h), i.e. the experiment comprised 27 tea-bags. The coefficients of variance for the 9 absorption times were in the range 1.5–7.4% (no systematic differences between early and later measurements, as shown in Fig. 2). Due to the low coefficient of variance, it was decided to carry out tests with the reference tea-bag method, the dipping method, and the stirring method with only one tea-bag for each absorption time. This was a matter of priority as it made it possible to carry out the three measuring series in parallel (same operator, almost simultaneous test start on the same day, etc.), thereby ruling out other uncertainties such as temperature differences between test series.

3.1.2 The filtration method

The filtration method followed the RILEM recommendation [10]. Dry SAP (mass m_{FT1}) was put into an empty beaker. The beaker was then filled with cement slurry filtrate (approx. 100 mL, exact mass m_{FT2}). The beaker was immediately covered with a LDPE cling film to reduce carbonation and evaporation. 1, 5, 10, 30, 60 min, 3, 6 and 24 h after the SAP/liquid contact the liquid was filtered using pre-wetted filter paper (same filter paper as described in section 2.2). Filtered liquid was m_{FT3} in mass. The absorption capacity (AC) of SAP was determined by Eq. 2.

$$AC = \frac{m_{FT2} - m_{FT3}}{m_{FT1}} \quad \text{Eq. 2}$$

When the liquid/SAP mass ratio is 100 (in accordance to RILEM recommendation [10]), SAP at the bottom layer of the beaker has a hindered access to test liquid, when the SAP particles have settled due to gravity. The hindering effect is assumed to be weakened by a thinner layer of SAP particles. This assumption was examined by reducing the amount of SAP while the volume of test liquid remained constant. In addition to the recommended liquid/SAP mass ratio (100), liquid/SAP mass ratios 300 and 900 were tested.

Precision of the method: According to the RILEM recommendation [10], measurements should be carried out in triplicate when using the filtration method. This was done in a test series with 9 absorption times (1 minute – 24 h). The coefficients of variance for the 9 registered absorption capacities were in the range 3.2–10.8%. There is a tendency to larger variance at the earliest and the latest measurements. It takes approx. 10–15 minutes to finish the filtration. During the filtration time, the SAP is still to some extent exposed to liquid, so when the filtration time is significant compared to the absorption time, the measurement becomes uncertain. Despite the uncertainty, it was decided to do measurements with different liquid/SAP ratios without triplication, as this made it possible to perform the measurements in parallel.

3.1.3 Estimation of amount of interstitial water

Both the tea-bag method and the filtration method were additionally carried out with glass beads instead of SAP, using deionized water as test liquid. As the glass beads do not absorb water, any mass gain during testing was interpreted as retention of interstitial water. To make the simulation as representative as possible, two parameters are crucial: size and amount of glass beads. For SAP the absorbency changes with time, and so do its diameter and total volume. Therefore, it was impossible to set a certain value of size for glass beads to mimic the behavior of SAP. However, as the goal was to obtain the volume of water relative to swollen SAP volume, it was permissible to assume a certain absorption capacity, and $AC = 25 \text{ g/g}$ was chosen as a rough estimate (which is in reasonable agreement with the actual absorption capacity shown later). This absorption capacity and a density of dry SAP $\rho_{SAP} = 1500 \text{ kg/m}^3$ correspond to that the diameter of a spherical SAP particle increases by a factor of 3.4 during swelling. Based on this, glass beads in the diameter range of 180–250 μm were used to mimic swollen SAP with a diameter of 50–75 μm in the dry state. As regards the amount of glass beads, it was chosen so that the volume of glass beads corresponded to the volume of swollen SAP. For example in the tea-bag method, where 0.1 g dry SAP is the usual amount used, 2.5 cm^3 glass beads was used to mimic the swollen SAP.

In the tea-bag method, the mass of a tea-bag containing dry glass beads was recorded (m_{TB2}) as was done in the reference method, and the tea-bag was submerged in deionized water for 24 h, which according to [23] is sufficient time for water to penetrate into the interstices between the glass beads. The tea-bag was taken out, surface dried with gauze, and

weighed (m_{TB3}). The difference ($m_{TB3}-m_{TB2}$) consisted of two parts: (1) water absorbed by tea-bag paper (m_{TB0}), and (2) water that occupied the interstices between the glass particles.

Eq. 3 can be used to calculate the relative volume of interstitial water:

$$\alpha_{TB} = \frac{\rho_g}{\rho_w} \cdot \frac{m_{TB3}-m_{TB2}-m_{TB0}}{m_{TB2}-m_{TB1}} \quad \text{Eq. 3}$$

where α_{TB} is the volume of interstitial water relative to the volume of glass beads, ρ_g is the density of glass beads, ρ_w is the density of water.

Similarly, the filtration method was also used to give the relative volume of interstitial water. Due to the higher density of glass compared to swollen SAP, pouring all the glass beads out of the beaker was difficult. Therefore, a plastic wash bottle was used to rinse the beaker wall and release the glass beads into the funnel. The rinsing water was taken into account as part of m_{FT2} . Interstitial water was estimated by Eq. 4:

$$\alpha_{FT} = \frac{\rho_g}{\rho_w} \cdot \frac{m_{FT2}-m_{FT3}}{m_{FT1}} \quad \text{Eq. 4}$$

where α_{FT} is volume of interstitial water relative to the volume of glass beads, ρ_g is the density of glass beads, ρ_w is the density of water.

3.2 Results and discussion

The absorption capacity of SAP in cement slurry filtrate is measured with the reference tea-bag method and the filtration method. The results are compared in Fig. 3. From 1 minute up to 30 minutes upon liquid contact, an increase by 25% is observed with either method despite some fluctuations. From then on, absorption measured by the tea-bag method decreases. At 24 h, only about 60% of the maximum amount is retained. On the contrary, absorption measured with the filtration method was relatively stable. In the time range of 3–24 h, there is hardly any change in absorption within the accuracy of the method. At 24 h, the absorption measured with the filtration method was approximately 75% larger than that measured with the reference tea-bag method.

Initially, it was examined if the tea-bag material was a cause of the decreasing absorption. This was ruled out by an experiment involving extra tea-bag material in the liquid. Likewise, the mesh size of tea-bags did not seem to be relevant, because the decrease in absorption was observed even when “tea-bags” made of tight laboratory filter paper were used. Some types of SAP may degrade and dissolve in the surrounding liquid [24, 25].

However, this does not seem to account for the marked absorption capacity decrease in this

study, as confirmed by mass change of SAP-containing tea-bags before test start and after post-test drying in a 50 °C oven until constant mass.

To date, several explanations have been suggested for the noticed decrease in absorptivity with progression of time. Pourjavadi et al. [11], for example, reported precipitation of portlandite in the beaker, which was proposed to be the cause of the drastic change. However, in the present study, there was no observation of precipitation in any of the samples.

Crust formation noticed by a number of researchers involved in the RILEM round-robin test was regarded as a possible barrier for absorption [16]. Contrary to this, findings by Zhu et al. [26] suggested that shell-like incrustation played a role in preventing the SAP from further desorbing liquid. As the crusts reported in these works are not necessarily identical in composition, and the fact that no crust was observed in the present study, it is difficult to conclude whether crusts surrounding SAP particles should impede or promote liquid exchange.

3.2.1 Influence of convection

Fig 4(a) compares the absorption development of SAP in cement slurry filtrate during different convection conditions. When measuring absorption capacity of SAP with the reference tea-bag method, a noticeable drop in absorption capacity is not observed before 3 hours after test start. By regularly dipping the tea-bags or by stirring the liquid, the decrease is observed much earlier, 1 hour or 30 minutes respectively after test start. Interestingly, despite differences in development history, all three measurement conditions result in approximately the same 24 h absorption capacity. Apparently neither dipping nor stirring makes a difference on long-term absorption capacity of SAP.

Similar observations are made when saturated $\text{Ca}(\text{OH})_2$ solution is used as test liquid, see Fig. 4(b). The difference in absorption between 1 minute and 24 h is even more pronounced. Again, different versions of tea-bag methods end up in the same 24 h absorption.

In the literature, the decreasing absorption capacity over time is only observed when multivalent cations are present in the test solution, not if the test solution is pure water or if cations are all monovalent [11–13, 17]. Previous research using the tea-bag method [14] and the filtration method with slight suction [22] has shown that the absorption capacity loss over time was more pronounced, when the concentration of multivalent cations was higher. However, a high total ionic concentration [14] or a high alkalinity [22] restricted the loss of

absorption capacity over time. It therefore seems that there is an ionic exchange between multivalent cations present in the test liquid (typically Ca^{2+} , Al^{3+}) and monovalent cations (e.g. Na^+ , K^+) present in the crosslink structure of anionic SAP. If this is the case, the more intense the ionic exchange, the quicker the desorption of SAP. This explanation fits the observations shown in Fig. 4, i.e. ionic exchange is intensified by increasing the liquid convection and this accelerates the absorbency decrease. The reason for a lack of decrease with the RILEM filtration method is discussed in Section 3.2.2.

It should be noted that the observed maximum and subsequent decrease of absorption capacity is not an artefact of the tea-bag method. Similar behavior of SAP has also been observed, when SAP is mixed in e.g. mortar [27].

3.2.2 Influence of liquid/SAP ratio

Fig. 5 shows the development of absorption capacity measured with the filtration method with various liquid/SAP ratios. By increasing liquid/SAP from 100 to 300, the absorption capacity at 1 minute increases by approx. 20%, followed by a steady decrease in the following 9 minutes. This decrease is not seen when the same method is used where liquid/SAP ratio is 100. When the liquid/SAP ratio was elevated to 900, the absorption capacity at 1 minute is further increased. Hereafter, the absorption capacity drops even more steeply during the following 9 minutes. Despite the pronounced difference in short-term absorption capacity, the long-term absorption capacity does not seem to be influenced as much by the variance of liquid/SAP ratio, considering the uncertainty of this method.

The influence of the liquid/SAP ratio at the early stages can be explained by the “delayed” access to test liquid. It takes time for test liquid to diffuse into the interstices between SAP particles. When liquid/SAP ratio is higher (e.g. 900), it takes less time for all SAP particles to get access to test liquid, resulting in a higher apparent absorption capacity at an early stage (e.g. 1 min). As the delay of access does not affect absorption capacity at later stages, short-term absorption capacity looks higher than long-term absorption capacity when liquid/SAP ratio is 900, while such difference is not visible when liquid/SAP is 100.

Furthermore, when the tea-bag method is used, a consistent decrease in absorption capacity does not take place until 30 minutes after liquid contact. On the contrary, such a decrease is captured much earlier, as soon as 1 minute after liquid contact, when using the filtration method where liquid/SAP is 300 or 900.

The difference in the commencement of decrease in absorption can be explained by the fact that filtering takes time and delays weighing of the flask that contains filtered liquid. During the filtering process, SAP is still immersed in liquid, so its absorption can change within this period. For example, a nominal 5-minute absorption measurement may in reality be a 20-minute absorption measurement due to 15 minutes of filtering. Accordingly, the peak value seems to occur earlier, and if it is in the very beginning, a continuous decrease is seen instead of an increase followed by reduction after the peak.

3.2.3 Influence of test liquid

Fig. 6(a) shows the effect of changing the w/c of the cement slurry filtrate on the absorption capacity development of SAP tested with the tea-bag method. While the w/c changes from 2.5 to 10, the hydration time is constant (24 h). The effect of various hydration times when preparing the cement slurry filtrate with $w/c = 5$ is shown in Fig. 6(b).

It can be seen from Fig. 6 that even an apparently minor modification of the cement slurry filtrate has a significant impact on the test outcome, both in terms of when the decrease of absorption capacity occurs and in terms of the magnitude of the final absorption capacity (24 h). This may not be surprising. The composition of pore solution in concrete, among other things, depends on w/c (see e.g. Lothenbach [28, 29]), so cement slurry filtrate prepared at $w/c = 5$ is a poor representation of pore solution in concrete. When the composition of the test liquid strongly influences the test result, the implication is that a test carried out with cement slurry filtrate cannot be expected to properly predict the SAP absorption in fresh concrete. Besides w/c , the hydration time of the cement slurry before it is filtered also makes a difference. It is known that the total ionic concentration as well as the concentration of calcium ions in cement pore fluid are both relatively stable during the first 6 hours after mixing, but can change considerably during the following 18 hours [30]. Cement slurries prepared with different hydration times might have such variances in ionic concentration, while the magnitude of such variances might not be the same as it is in concrete pore solution. This may explain why the absolute values of absorption capacity are altered when the hydration time of cement slurry is reduced to 6 h or less.

As previously mentioned, multivalent cations are regarded as a necessary condition for the decrease in absorption capacity with time. However, not all test liquids containing multivalent cations result in the decrease. For example, artificial pore fluid is another commonly used test liquid prepared by dissolving into water compounds containing elements

typically present in cement paste pore fluid [31, 32]. Based on different types of SAP and different cation concentrations in artificial pore fluid where calcium ions are present, no significant decrease in absorption capacity over time was observed with the tea-bag method by e.g. Tabares Tamayo [33].

It is not possible to foresee the absorption capacity of SAP in cementitious environments based on measurements in saturated $\text{Ca}(\text{OH})_2$ solution. However, saturated $\text{Ca}(\text{OH})_2$ solution as test liquid does have advantages when the aim is quality assurance of a SAP production. For example, it is easier to prepare saturated $\text{Ca}(\text{OH})_2$ solution than cement slurry filtrate, and it can still reveal differences between batches. It also makes it more straightforward to compare results from different laboratories, which is not possible if the individual laboratories use cement slurry filtrate based on their local cement types.

3.2.4 Estimation of interstitial water

There is a considerable gap between long-term absorption capacities measured by the tea-bag method and the filtration method. The reason for this gap needs to be examined. The volume of interstitial water relative to the volume of glass beads is measured in triplicate ($n = 3$) according to the methods described in Section 3.1.3, see results in Table 1 and Table 2.

The results indicate that for the tea-bag method, the water in the particle interstices is 0.64 relative to glass bead volume. This agrees well with expectations based on random close packing of unisized spheres [34]. The amount of interstitial water involved in the filtration method is 1.16, i.e. much larger than for the tea-bag method. A possible explanation is that when the glass beads were transferred from the beaker to the filter, they were influenced by capillary forces, so they did not flow freely and therefore they did not attain random close packing. This led to a looser packing and thus more interstitial water. The problem is likely to be worse with swollen SAP particles as the density of swollen SAP is lower than the density of glass, and gravity therefore may not compact the swollen SAP particles as much as glass beads. Potentially, one could apply a slight negative pressure (mild vacuum) [22] to examine this supposition.

If $\alpha_{TB} = 0.64$ and $\alpha_{FT} = 1.16$ are respectively applied to correct the 24 h measurements shown in Fig. 3, the apparent absorption capacities is reduced from 18.8 g/g to 11.1 g/g for the tea-bag method, and from 33.0 g/g to 14.7 g/g for the filtration method. The difference in amounts of interstitial water in the two methods seems to explain a large part of the

1 difference in the long-term absorption capacities measured by the tea-bag method and the
2 filtration method.

3 The calculated water held in interstices between glass beads is only an estimate of water
4 held in SAP interstices. The measured values for interstitial water concerned relatively
5 unisized spheres, and would have been smaller, if the spheres had presented a broader size
6 range. Potentially, SAP and glass beads may also pack differently due to difference in surface
7 properties. However, the measurements seem reasonable, as α_{TB} is quite close to expectations
8 based on random close packing of unisized spheres, and the correction using α_{TB} and α_{FT}
9 considerably reduces the gap between absorption capacities measured with the two methods.
10

11 4 Part II: SAP absorption in cement paste and concrete

12 4.1 Methods

13 4.1.1 Absorption capacity of SAP in cement paste

14 A reference cement paste (CP-0) with $w/c = 0.45$ was made by vacuum mixing cement
15 and deionized water for 3 minutes. A similar cement paste (CP-1) was made except that it
16 contained SAP that was dry-mixed with the cement before water was added. Extra water was
17 added at an amount of 18.8 times the mass of SAP (absorption capacity according to the tea-
18 bag method, 24 h measurement). Table 3 shows the compositions of the two cement pastes.
19 The fresh cement paste was filled into 250 ml plastic bottles with care to avoid air bubbles.
20 The bottles were sealed and rotated for 24 h to prevent bleeding. At the age of 7 days, the
21 specimens were cut lengthwise. For either specimen, a 25 cm² section was ground with
22 silicon carbide abrasive papers with grit sizes of 75, 35, 17.5 and 12.5 μm successively and
23 analyzed in optical microscopy by the modified point-count method following ASTM C457
24 [35]. It is a reliable method with documented accuracy, as confirmed by interlaboratory tests
25 [36, 37]. The magnification used was 50 $\times$. The traverse length was 1730 mm and the
26 translation distance between stops was 200 μm .

27 4.1.2 Absorption capacity of SAP in concrete

28 Four concrete mixes were made. Basic w/c ratio was 0.45 for all mixes. The SAP
29 dosages were 0, 0.2%, 0.4%, 0.8% relative to cement mass. For the three SAP-containing
30 mixes, extra water was added in an amount of 17.8 times that of SAP mass (based on the
31

result from the SAP-containing cement paste, see Section 4.2.1). The concrete mix

compositions are given in Table 4.

Solid materials were dry mixed in a free-fall mixer for 2 minutes before adding mixing water. After addition of water, 5 minutes of mixing was done. Immediately after mixing, slump, density and air content of the fresh concrete were measured according to EuroNorms [38–40]. One Ø150×300 mm cylindrical specimen was cast for each mix. At the age of 7 days, a 20 mm disc was saw-cut from the center part of each cylinder. After that a 65×65×20 mm³ specimen was cut from the center of the disc. The two quadratic surfaces of each specimen were ground and analysed in the same way as previously mentioned for cement paste. An example of a ground section of concrete containing SAP is shown in Fig. 7. The wall effect for aggregate was negligible, since the minimal distance of any point on the test surface to the moulded surface of the cylinder was 2.9 cm, corresponding to ~1.8 times the diameter of the largest aggregate particles. The translation distance between stops was 2 mm. The total length of traverse and total number of points were 4356 mm and 2178, where the minimum requirements according to the standard are 2286 mm and 1350, respectively.

4.2 Results and discussion

4.2.1 Absorption capacity of SAP in cement paste

Since no stops were found in air voids in the reference mix, it was assumed that all voids in the mix containing SAP were SAP voids, i.e. voids initially occupied by swollen SAP particles. The absorption capacity was measured to be:

$$AC = \frac{\rho_w \left(V_{cp} \frac{S_v}{S_t} - V_{SAP} \right)}{m_{SAP}} = \frac{1.0 \left(442.6 \cdot \frac{1080}{8650} - 2 \right)}{3.0} = 17.8 \text{ g/g} \quad \text{Eq. 5}$$

where S_v is the number of points in voids, and S_t is the total number of points. Mix design cement paste volume V_{cp} , SAP mass m_{SAP} and SAP volume V_{SAP} are given in Table 3. Fig. 8 shows void content versus SAP content in cement paste (together with results for concrete given in the following section). The slope, k , of the dashed line in Fig. 8 linking the two points that correspond to the two mixes is related to absorption capacity through Eq. 6 (ρ_{SAP} is the dry SAP density):

$$k = 1 + \frac{\rho_{SAP}}{\rho_w} \cdot AC \quad \text{Eq. 6}$$

4.2.2 Absorption capacity of SAP in concrete

The air content in the fresh concrete is, within the accuracy of the test method, on the same level for all concrete mixes, see Table 5. There is no indication of a systematic dependence on the SAP dosage. Table 5 also shows measured slump. It is seen that the slump is reduced when SAP is incorporated, but there is no general trend (i.e. a clear relation between slump and SAP dosage).

Assuming that the amount of entrapped air is identical for all mixes and that the volume of SAP increases proportionally with its dosage, the total void content (sum of entrapped air and SAP voids) should be a linear function of SAP dosage relative to concrete volume. As shown in Fig. 8, the measuring points for concrete can be represented by a solid line with a slope k of 25.8, equivalent to an absorption capacity of 16.6 g/g, according to Eq. 6. Comparing the slopes of lines linking any two points, the largest slope and smallest slope give absorption capacities of 18.5 g/g and 12.8 g/g, respectively.

4.2.3 Comparison between cement paste and concrete

The measured absorption capacity is 17.8 g/g in cement paste, and 16.6 g/g in concrete. Potential reasons for this minor difference may include uncertainty in the measurement method, physical restraint by aggregates or discrepancy in pore liquid composition between cement paste and concrete. More experiments are needed to conclude on this. In any case, judged from images such as Fig. 7, breakdown of SAP by grinding aggregate forces is not a likely cause, as no irregularly shaped voids are observed.

Obviously, for SAP used in concrete, the SAP absorption capacity measured in concrete is the “true” absorption capacity. However, the absorption capacities measured in cement paste and in concrete are apparently close. If similar absorption capacities are measured in both materials, then it is advantageous to register the value in cement paste samples:

- It is less time- and resource consuming to mix and cast cement paste.
 - It is easier to prepare good quality plane sections of paste specimens; it is more challenging with concrete specimens, especially if the hardness of cement paste and aggregates are very different.
 - In the specimens made from cement paste, 100% of the volume is cement paste and SAP.
- In our study, the content of paste (including SAP) in the concrete was approx. 40%, i.e. considerably less, and for industrially produced concrete, the paste content is typically even lower. This means that the test area of the plane section needs to be approx. 3 times larger when

analyzing concrete instead of cement paste to obtain the same accuracy.

• Entrapped air in cement paste can be avoided by vacuum during preparation of the mix, simplifying the SAP void identification and thereby increasing result precision. Vacuum mixing is normally not possible in industrial production of concrete. Also because of entrapment of air during mixing, transportation and placement, measurements of absorption capacity in concrete is more uncertain than similar measurements for paste.

5. Implication from Part I and Part II

The 24 h absorption capacity measured with the tea-bag method (18.8 g/g) is relatively close to the absorption capacity measured in concrete (16.6 g/g). However, as demonstrated in Section 3.3.4, the absorption capacity measured with the tea-bag method includes a large amount of interstitial water. With interstitial water taken into account, the absorption capacity measured by the tea-bag method (11.1 g/g) is significantly lower than what is measured in concrete. It is a complete coincidence that the interstitial water involved in the tea-bag method is compensated by factors such as differences in ionic strength and composition of pore solution and cement slurry filtrate, earlier setting of the concrete than 24 h, etc. Therefore, even though the present study apparently shows partly agreement between measured 24 h absorption capacity with the tea-bag method and air void analysis of hardened concrete, this will definitely not be the case in general. As regards the filtration method, there are the same reservations as for the tea-bag method with respect to that the test liquid does not reflect the conditions for absorption in concrete. SAP absorption capacity, measured either with the tea-bag method, or the filtration method, is highly time dependent. There is no basis for taking the 24 h measurement as a prediction of absorption capacity in cement paste, a system which typically takes much less than 24 h to set. Accordingly, neither the tea-bag method nor the filtration method can be recommended as methods to estimate SAP absorption capacity for mix design of mortar or concrete. In contrast, the absorption capacity can apparently be reliably measured by point counting in a sample of hardened cement paste. This technique, which is well-proven for air void analysis, better reflects the authentic state in concrete. It is a disadvantage that the result is not ready until days after the concrete is placed, so air void analysis is not useful for routine production control, where acceptance or rejection has to be decided before placement. However, the tea-bag method and the filtration method are not useful in any case. The air void analysis can be used for pre-testing, when introducing

new mix designs, just as it is used for pre-testing in relation to frost resistance, and it can be used for production control of SAP.

Even for determining the suitability of a certain SAP product to be implemented in cement paste or concrete, the tea-bag and filtration methods seem to be problematic. As seen from the results, the sorption kinetics of SAP in a test liquid can be significantly altered due to a single variance of e.g. w/c of cement slurry filtrate. As there are even more differences in properties between test liquid and concrete pore fluid, measuring SAP sorption kinetics in test liquid can hardly be a trustworthy indication of whether a type of SAP is appropriate for use in cement-based materials. Despite appearing to be simple and transparent, the tea-bag method is in reality a complex and misleading technique. However, the tea-bag method might be useful for qualitative assessments of the absorption behavior of SAP, e.g. for production control of SAP to register changes from one batch to another. The filtration method is more misleading than the tea-bag method, especially at exposure times up to 1 h, because the SAP is still in contact with test liquid during the 10–15 minutes it takes to filter a sample. Additionally, more than half of the retained water may be interstitial water – even more than what is found in the tea-bag method.

All experiments and results in this work are based on SAP from suspension polymerization and with a certain chemical composition. Obviously, the results of absorption measurement in liquid will depend on SAP type. However, the dominant problem that renders the quick methods inappropriate is the difference in conditions given by a test liquid and that of a true pore solution inside a concrete (w/c and hydration time, convection, etc.).

The practical implication of the study is that neither the tea-bag method nor the filtration method can be recommended as a standard test method to assess the absorption capacity of SAP to be used in concrete.

6. Conclusions

This study investigates two simple test methods to register SAP absorption capacity, i.e. the tea-bag method and the filtration method, and makes a comparison between results obtained by these two methods and results from air void analyses on cement paste and concrete.

(a) The tea-bag method initially showed an increase followed by a marked decrease in absorption capacity. The marked decrease in absorption capacity was not observed with the

1 filtration method, where absorption capacity was relatively constant in the interval 1 minute
2 to 24 h.

3
4 (b) At 24 h the absorption capacity registered with the filtration method was 75% higher
5 than the absorption capacity registered by the tea-bag method.

6
7 5 The primary cause of the absorption decrease registered by the tea-bag method (a)
8 seemed to be ionic exchange, where multivalent cations from the test solution substitutes
9 monovalent cations in the SAP crosslink structure. Crust formation, portlandite precipitation,
10 or degradation as suggested in the literature were unlikely to be the cause of the absorption
11 decrease in the present study. The conditions for ionic exchange could be modified by
12 changing the convection of the test liquid or by changing the test liquid (e.g. cement slurry
13 filtrate based on different w/c ratios). Such ionic exchange should also be present for the
14 filtration method, but the absorption decrease is not prominent, perhaps because the early-
15 stage absorption is underestimated due to a delay of access to test liquid for the SAP.

16
17 10 The measured absorption capacities by the tea-bag method as well as the filtration
18 method were highly influenced by interstitial water, which does not reflect the absorption in
19 cement-based materials. In the present study, higher amounts of interstitial water were
20 involved in the filtration method compared to the tea-bag method. This can to a high extent
21 explain the difference in long-term absorbency (b).

22
23 Neither the tea-bag method nor the filtration method properly predicts the absorption of
24 SAP in a concrete mix, and thus none of them can be recommended as test methods for
25 determining the absorption capacity of SAP in concrete. Contrary to this, air void analyses
26 showed an agreement between the absorption capacities of SAP in cement paste (17.8 g/g)
27 and in concrete (16.6 g/g). As such, among the methods examined in the present study, only
28 measurement of void structure in hardened cement paste can apparently be used as a reliable
29 alternative to measurement in concrete.

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Fig. 1 Sketch of the set-up for the dipping method, a modification of the reference tea-bag method

Fig. 2 Development of SAP absorption in saturated Ca(OH)_2 solution measured with the tea-bag method in triplicate by the same operator. The solid line denotes the average of absorption measured at each test time. The broken lines indicate the average absolute deviation. The time axis is logarithmic.

Fig. 3 Development of SAP absorption in cement slurry filtrate, measured with the reference tea-bag method (liquid/SAP=900) and the filtration method (liquid/SAP=100), where liquid/SAP ratios are according to [10]. The time axis is logarithmic.

(a)

(b)

Fig. 4 Absorption development of SAP in (a) cement slurry filtrate and (b) saturated Ca(OH)_2 solution. Dipping method and stirring method are used as well as reference tea-bag method. The time axis is logarithmic.

Fig. 5 Absorption development of SAP in cement slurry filtrate, measured with the filtration method where various liquid/SAP ratios are used. Measurements given by the reference tea-bag method are also shown for comparison. The time axis is logarithmic.

(a)

(b)

Fig. 6 Effect of modifications of the cement slurry filtrate regarding (a) w/c and (b) hydration time before the slurry is filtered. The tests are carried out with the tea-bag method. The time axis is logarithmic.

Fig. 7 A ground section of concrete (CO-2) observed by optical microscopy. The image is a merge of 49 images each captured at 50× magnification.

Fig. 8 Relations between void contents and dry SAP volumetric contents in concrete and cement paste

Table 1 Measurements of the relative volume of interstitial water captured between glass beads with the tea-bag method. α_{TB} is defined by Eq. 3.

Sample No.	m_{TB0} [g]	m_{TB1} [g]	m_{TB2} [g]	m_{TB3} [g]	ρ_g [kg/m ³]	ρ_w [kg/m ³]	α_{TB} [-]
1	0.222	0.093	6.320	8.096	2520	1000	0.63
2	0.217	0.091	6.368	8.181	2520	1000	0.64
3	0.217	0.091	6.318	8.136	2520	1000	0.65
Mean							0.64

Table 2 Measurements of the relative volume of interstitial water captured between glass beads with the filtration method. α_{FT} is defined by Eq. 4.

Sample No.	m_{FT1} [g]	m_{FT2} [g]	m_{FT3} [g]	ρ_g [kg/m ³]	ρ_w [kg/m ³]	α_{FT} [-]
1	6.230	120.716	117.844	2520	1000	1.16
2	6.258	135.528	132.839	2520	1000	1.08
3	6.252	150.307	147.247	2520	1000	1.23
Mean						1.16

Table 3 Mix design of cement pastes with SAP (CP-1) and without SAP (CP-0)

Constituent	Density ρ [g/cm ³]	Mass m [g]		Volume V [cm ³]	
		CP-0	CP-1	CP-0	CP-1
Cement	3.14	500.0	500.0	159.2	159.2
Water	1.00	225.0	281.4	225.0	281.4
SAP	1.50	0.0	3.0	0.0	2.0
Sum, cement paste	—	725.0	784.4	384.2	442.6

Table 4 Composition of 1 m³ concrete (assuming 0.015 m³ entrapped air) with different dosages of SAP. Densities of aggregates refer to the saturated, surface dry state (SSD). Aggregate and water masses were adjusted for deviations from SSD.

Constituent	Density [kg/m ³]	Mass [kg]			
		CO-0	CO-1	CO-2	CO-3
Cement	3140	500	491	482	466
Water	1000	225	238	251	276
Fine agg.	2640	633	622	611	590
Coarse agg. (4–8 mm)	2710	195	192	188	182
Coarse agg. (8–16 mm)	2720	783	769	755	729
SAP	1500	0.0	1.0	1.9	3.7
Sum	—	2336	2313	2289	2246

Table 5 Fresh concrete properties

	CO-0	CO-1	CO-2	CO-3
Slump [mm]	155	65	90	85
Density [kg/m ³]	2374	2347	2321	2274
Air content [%]	1.0	1.3	1.1	1.4