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Testing SAP characteristics prior to implementation in concrete: results of a RILEM round-robin test

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Abstract

This article presents the results of a round-robin test performed by 13 international research groups in the framework of the activities of the RILEM Technical Committee 260 RSC “Recommendations for use of superabsorbent polymers in concrete construction”. Two commercially available superabsorbent polymers (SAP) with different chemical compositions and gradings were tested in terms of their kinetics of absorption in different media; demineralized water, cement filtrate solution with particular cement distributed to every participant and local cement chosen by the participant. Two absorption test methods were considered; the tea-bag method and the filtration method. The absorption capacity was evaluated as a function of time. The results showed correspondence in behaviour of the SAPs among all participants, but also between the two test methods, even though high scatter was observed at early minutes of testing after immersion. The tea-bag method proved to be more practical in terms of time dependent study, whereby the filtration method showed less variation in the absorption capacity after 24 hours. However, absorption followed by intrinsic, ion-mediated desorption of a respective SAP sample in the course of time was not found by the filtration method. This SAP-specific characteristic was only displayed by the tea-bag method. This demonstrates the practical applicability of both test methods, each one having their own strengths and weaknesses at distinct testing times.

Keywords

Absorption capacity, filtration method, kinetics, round-robin test, superabsorbent polymer, tea-bag method

The study reported in this paper was performed within the framework of the RILEM TC 260-RSC "Recommendations for Use of Superabsorbent Polymers in Concrete Construction". The paper was reviewed and approved by all members of the RILEM TC 260-RSC.

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TC Secretary: Mateusz Wyrzykowski

Members: Fernando C.R. Almeida, Alexander Assmann, Billy Boshoff, Daniel Cusson, João Custódio, Nele De Belie, Igor De la Varga, Kendra Erk, Vyatcheslav Falikman, Eugenia Fonseca Silva, Stefan Friedrich, Michaela Gorges, Kazuo Ichimiya, Shin-Ichi Igarashi, Agnieszka J. Klemm, Konstantin Kovler, Pietro Lura, Juhyuk Moon, Hans W. Reinhardt, António Bettencourt Ribeiro, Klaus-Alexander Rieder, Christof Schroefl, Didier Snoeck, Konstantin Sobolev, Romildo D. Toledo Filho, Nikolajs Toropovs, Chiara Vilani, Guang Ye.

1. Introduction

Significant interest in superabsorbent polymers (SAPs) as a class of chemical admixtures for concrete has arisen in the past few years due to their multiple functionalities. SAPs can be applied for mitigation of autogenous and plastic shrinkage [1-3], improvement of freeze-thaw resistance [4], steering of rheological properties of fresh mixes [5,6], self-sealing [7,8] as well as self-healing [9,10]. Therefore, the RILEM Technical Committees (TCs) 225 SAP "Application of Superabsorbent Polymers in Concrete Construction" and 260 RSC "Recommendations for use of superabsorbent polymers in concrete construction" were formed to coordinate research efforts and to compile results of SAP studies. These studies mainly address the effects of SAPs on properties of concrete in its fresh and hardened states in order to prepare recommendations for its use in construction industry. In the context of these Technical Committees, a state-of-the-art report was published in 2012 [11], an international conference held in 2014 [12] and two inter-laboratory studies on mitigation of autogenous shrinkage [1] and the improvement of the freeze-thaw resistance [4] were performed.

SAP samples should be characterized by their sorptivity as a pre-test to estimate their performance when embedded in cement-based construction materials. The reasoning for performing this Round Robin Test (RRT) was to promote the use of SAPs in concrete construction by presenting simple and efficient pre-tests for practitioners and researchers. These pre-tests performed on SAP samples can disclose long-term effects of these admixtures on the properties of cement-based construction materials. By compiling the results from numerous international laboratories this paper intends to evaluate the consistency of these pre-tests independently of the particular choice of raw materials, laboratory equipment and local staff. Furthermore, it is expected that the experience from the RRT would form an integral part of the base knowledge essential for formulation of Recommendations for Practitioners, the ultimate target document of TC 260 RSC.

Depending on their molecular structure SAPs may differ significantly and characteristically in terms of swelling kinetics and final long-term storage capacity [13,14]. Besides initial intake followed by extraction due to sucking forces from the hydrating matrix [15,16], SAP samples may inherently release absorbed ionic liquid for chemical reasons [17]. Both intrinsic properties may be beneficial for use in cement-based materials, i.e. to steer rheological characteristics [5,6] or affect early-age drying and related plastic shrinkage. The latter topic is currently under investigation in the form of an RRT initiated by TC 260 RSC. Various test methods have been described in literature to estimate sorption kinetics of SAPs in relevant media and a recent review has been issued by members of TC 260 RSC [18]. Taking into account simplicity of tests and no need for any sophisticated lab facilities, two main test methods have evolved: the *tea-bag method* and the *filtration method*. Both methods were adopted in this round-robin test. The aim was to verify the applicability of both testing methods and the variability amongst different laboratories. Furthermore, the attempt was made to refine whether the tea-bag method systematically overestimates the sorption capacity at a specific time as compared to the filtration method. In the course of quantifying the sorption capacity, forces causing the extraction of capillary water may be much weaker in the tea-bag method in comparison to those acting in the filtration method. This means that more inter-particle liquid may remain in the sample, which is only physically retained but not chemically adsorbed to the polymer chains in the polymer network of the particles [19]. By conducting and carefully evaluating the present RRT, this long-standing uncertainty in the community of SAP-engaged researchers should be clarified.

Besides these two methods numerous other procedures have been applied for characterization of SAP samples for use in cement-based construction materials. These two procedures as well as other experimental protocols, which have not yet been regarded in the field of concrete technology, can be found in the recent review paper [18] prepared by the TC 260 RSC.

Table 1 presents all participants of the RRT. The numbers listed in table serve as reference numbers for data obtained from the corresponding laboratories. All data was summarized and evaluated by the RRT conveners at Ghent University and TU Dresden, where also the draft of this article was prepared. The article was comprehensively discussed and agreed upon by all participants of the round-robin test prior to the manuscript submission.

Table 1: Participants of the round-robin test

No.	Participating institution	Principal investigator	Country
1	Ghent University	Didier Snoeck	Belgium
2	Technische Universität Dresden	Christof Schröfl	Germany
3	National Institute of Technology Oita College	Kazuo Ichimiya	Japan
4	National University of Singapore	Juhyuk Moon	Singapore
5	Empa	Mateusz Wyrzykowski	Switzerland
6	BCSG Trostberg	Alexander Assmann	Germany
7	Kanazawa University	Shin-ichi Igarashi	Japan
8	Turner-Fairbank Highway Research Center	Igor De La Varga	USA
9	Glasgow Caledonian University	Agnieszka J. Klemm	United Kingdom
10	Purdue University	Kendra Erk	USA
11	National Laboratory for Civil Engineering	António Bettencourt Ribeiro	Portugal
12	Universität Stuttgart	Hans Wolf Reinhardt	Germany
13	Moscow State University	Vyatcheslav Falikman	Russia

2. Materials, pre-characterization of SAP and testing liquids

Six SAP samples, one cement sample for producing a particular test solution, tea bags and filter paper were organized and shipped to all participants by TU Dresden.

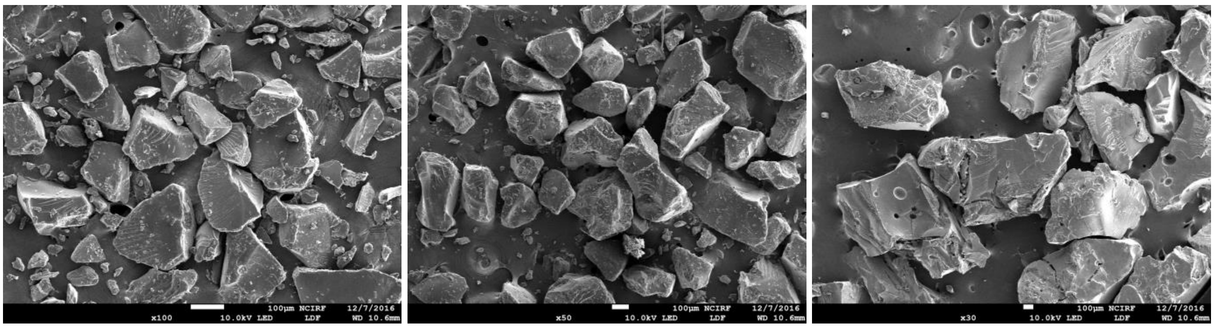
Two types of SAPs called SAP 1 (crosslinked poly(acrylate-*co*-acrylamide) with qualitatively intermediate crosslinking density) and SAP 2 (crosslinked polyacrylate with qualitatively intermediate crosslinking density) were studied in their 'as-delivered', original grading as well as in two different particle size distributions: < 200 µm and 200 µm to 500 µm. The SAPs in their original grading were already used in previous tests. Respective nomenclatures of these polymer samples in those publications have been as follows:

- Present SAP 1 (original grading) was the one SAP used in [6], it was denominated SAP 2 in [16], SAP-DN in [5], and SAP D in [13];
- Present SAP 2 (original grading) was called SAP 1 in [1,4], SAP 1 in [16], SAP B in [5], and SAP B in [13].

In order to obtain specific required gradings the original samples were gently milled by a customary grinder (KM1310S, Tarrington House/METRO, Düsseldorf, Germany) and sieved at TU Dresden so that no such action was required by any other participant. Metal mesh sieves were used in the form of a sieve tower consisting of bottom, 200 µm and 500 µm grids. Sieving was performed until constant masses were achieved on the 200 µm and the 500 µm sieves, respectively. Although this procedure should result in distinct gradings, practical experience from sieving of powders in a similar way revealed that minor portions of undersize and oversize particles might still be present. As was internally confirmed by the polymer provider, the milling did not affect the fundamental chemical characteristics of the SAP samples since the particles had not been subject to post-synthesis surface treatments and temperature was below 50 °C at any time. As agreed by all participants as well as the polymer provider, no details on the SAP samples were disclosed throughout the entire TC and RRT action. After delivery of the SAP samples to the participant, all SAP samples and other involved materials were put in a relative humidity condition of 65 % and 20 °C for a minimum of two weeks. This way, any false dry weight reading should be excluded due to a possible absorption of moisture at high relative humidity.

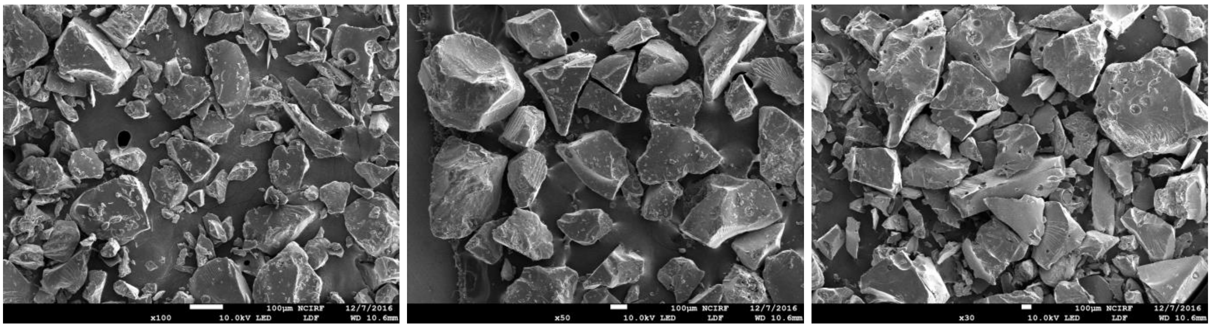
Scanning electron microscope (SEM) images of the polymers under investigation are shown in Figure 1, the respective cumulative particle size distributions are presented in Figure 2. The SEM (JSM-7800F Prime from JEOL Ltd., Tokyo, Japan) was used to obtain the SAP images. SAP particles in dry state were distributed in double-side carbon tape and 10 kV was used to take 30 images with x30 magnification for each SAP type under high vacuum condition. The particle size distributions in the dry state were assessed classically using laser granulometry using an LS 13320 by BeckmanCoulter, Krefeld, Germany.

Furthermore, two laboratories determined the particle size distribution of each SAP. The calculations were based on size measurement of around 500 SAP particles to obtain reliable results. One lab used the above mentioned SEM equipment and the other lab used an FEI Quanta 650 environmental scanning electron microscope (ESEM). The specimens were examined using a large field detector at 5 kV of voltage under low vacuum (50Pa). The obtained results were consistent. They indicated only minor portions of oversize or undersize grains in the respective size fractions, which can be regarded an acceptable outcome for the adopted procedures.



SAP 1

< 200 µm | 200 µm to 500 µm | Native grading



SAP 2

< 200 µm | 200 µm to 500 µm | Native grading

Figure 1: Scanning electron images of the SAP samples; the scale bars amount to 100 µm.

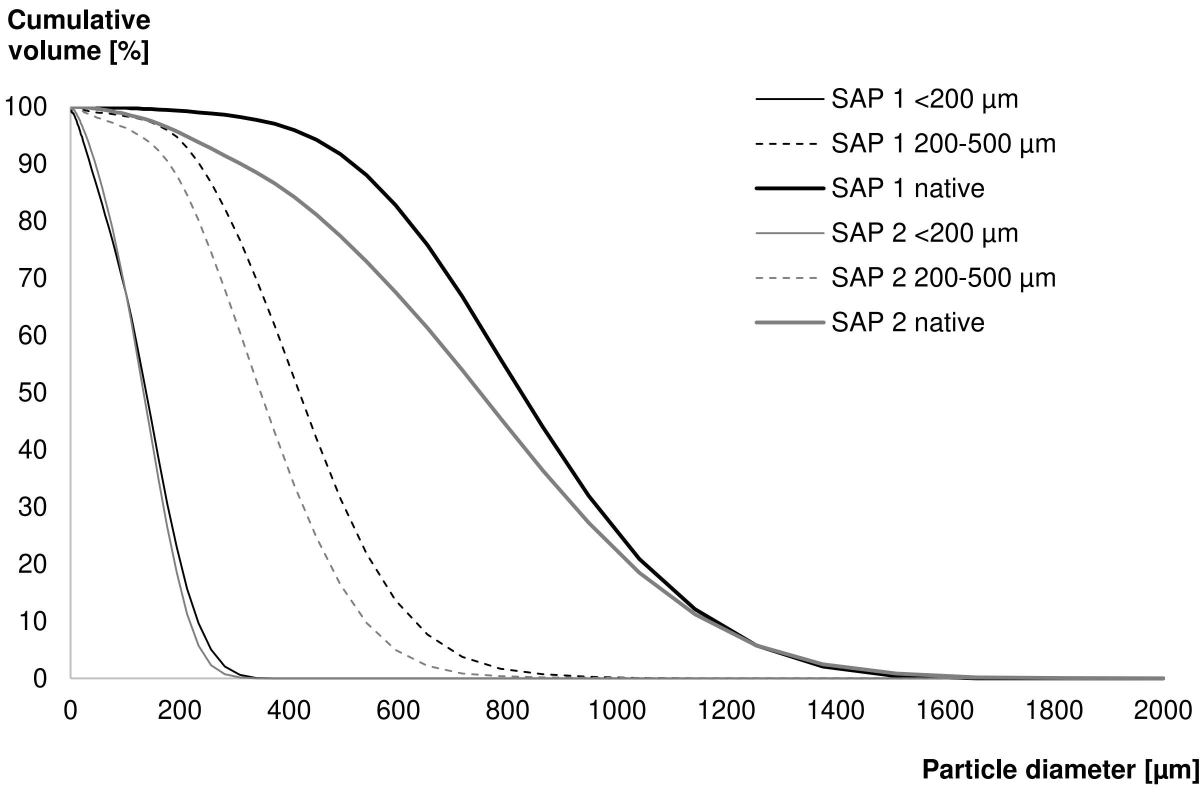


Figure 2: Cumulative particle size distribution of the studied SAPs.

The sorptivity tests were performed for three test liquids, among which two were mandatory:

1) Mandatory: DI water: de-ionized by ion exchange or distillation;
2) Mandatory: Filtrate of cement slurry: Portland cement was shipped to each participant (CEM I 42.5 R according EN 197-1 provided by Schwenk, Bernburg/Germany). A slurry of

this cement in DI water with water-to-cement ratio (W/C) of 5 (wt/wt), immersion time 24 hours with continuous automated stirring, followed by separation of the liquid (most recommended: filtration);

3) Optional: Filtrates of other cement slurry: Each participant could select a local representative cement (Portland cement or standardized blended cement), produce a slurry of paste with W/C = 5 (wt/wt), immersion time 24 hours with continuous automated stirring, followed by separation of the liquid (most recommended: filtration).

3. Testing methods

3.1 Tea-bag method

Although the tea-bag method is described in several internationally renowned specifications exist [20-23], a distinct prescription was followed in the present RRT. From a practical point of view, this procedure was based on individual experience and common practice in participating laboratories. In the course of the RRT it turned out that it should be slightly modified prior to issuing as the RILEM recommended test procedure.

A tea-bag was pre-wetted in test fluid and its mass determined (mass m_2). Approximately 0.2 g of SAP particles were inserted, which represent the exact mass m_1. To ensure the reliability of the results, three individual tea-bags were prepared per one SAP sample. The tea-bag containing the SAP was hung in a beaker filled with the fluid (about 200 mL). The beaker was tightly covered with a self-adhesive plastic stretch film quickly to avoid carbonation and evaporation. It should only be removed as shortly as feasible for each weighing. After 1 minute, 5, 10, 30, 60 minutes, 3 and 24 hours after the contact time SAP/liquid the tea-bag (with the hydrogel inside) was removed and weighed (mass m_3). The tea-bag was placed on a dry cloth and gently wiped with another dry cloth for a short time of approximately 30 seconds to remove surplus and weakly bound liquid. However, in order to not disturb the sorption degree, the sample should neither be squeezed nor come into contact with the cloths longer than necessary. After weighing, the tea-bag containing the hydrogel was returned into the stock solution until the next time step of mass recording. Equation 1 provides the formula to calculate the absorption capacity (AC) at each time of reading. This primary raw data evaluation was automated in an Excel file which was provided to each participant and was returned to the conveners for further processing.

$$AC = \frac{m_3 - m_2 - m_1}{m_1} \qquad (1)$$

where m_1 is the mass of the dry SAPs, m_2 is the mass of the pre-wetted tea-bag and m_3 is the mass of the tea-bag (with the hydrogel inside) at a specific time.

3.2 Filtration method

This method has been previously documented in publications [24,10] and was also applied in this RRT. Similarly to the tea-bag method, during the course of the RRT it turned out that it should be slightly modified prior to issuing as a RILEM recommended test procedure. The amount of dry SAP should depend on the actual absorption capacity; there should be an excess in liquid for the polymers to freely swell to full extent. It was recommended to perform a dummy test to estimate the amount needed to take up approximately 40-50 mL in every studied fluid. This amount of dry SAP added was to be used in further testing.

The specific amount of dry SAP (m_1) was inserted in a 100 mL beaker and approximately 100 g of test fluid was added (m_3). After 1 minute, 5, 10, 30, 60 minutes, 3 and 24 hours after the contact time SAP/liquid, the whole solution was filtered. To ensure that there was no influence of suction by the filter paper the latter was pre-saturated with the test fluid prior to filtration. During measurement, a lid was put on top of the filter to ensure no evaporation in time. Filtration was continued till no drops of liquid fell down anymore in subsequent intervals of one minute. The mass of filtered fluid was determined at the end (m_2). The mass increase of the SAP was measured as the difference between the added water and the filtered water. This mass increase is a measure for the total absorption (obtained value is divided by the dry mass of the studied SAP particles). Equation 2 provides the formula to calculate the absorption capacity (AC) at each time of reading. This primary raw data was evaluated in an Excel file which was provided to each participant and should be returned to the conveners for anonymous further processing. A single measurement required different container since the absorption capacity can be measured only once per sample. All measurements were performed in triplicate (n=3) and neither the filtered solution nor the hydrogels were re-used.

$$AC = \frac{m_3 - m_2}{m_1} \quad (2)$$

where m_1 is the mass of the dry SAPs, m_2 is the mass of filtered fluid at a specific time and m_3 is the mass of added test fluid.

3.3 Post-processing raw data

A time-resolved recording of the absorption capacities is interesting in terms of the time-dependent influences of the SAP, i.e. a slow or fast internal curing of the cement paste or a constant or in-/decreasing sealing effect in time. All data was collected and re-calculated towards the absorption capacities. These were plotted as a function of time. Furthermore, the repeatability of the results was investigated by comparing the mean of the standard deviations of all participants. The reproducibility was investigated as the standard deviation on the obtained averaged results per participant.

To investigate the different testing methods, the absorption value at 24 h of testing was used, as after this time a potential human error is negligible. At earlier times, a possible spread in actual testing time could also lead to a higher scatter in absorption capacities as the polymers may still absorb a high amount of testing fluid. At 24 h, the absorption should become constant. The authors would like to mention that this 24 h testing value might differ for different applications. Depending on the required property, different times of swelling should be recorded; i.e. influence on porosity and autogenous shrinkage where absorption capacities of several hours are of interest, and self-sealing where absorption capacities within minutes are of importance. Depending on the application, the investigator should use the appropriate absorption capacities

All data was combined and analysed as averages and 5-25-50-75-95% intervals. All standard deviations shown are deviations on individual results. A statistical analysis was performed using the program SPSS® in order to compare the obtained results. Multiple averages were compared using an analysis of variance (ANOVA) test with a significance level of 5%. The homogeneity of the variances was controlled with a Levene's test. The post hoc test for data with homogenous variances was a Student-Newman-Keuls test and if no homogenous variances were obtained, a Dunnett's T3 test was used.

The statistical analysis was performed at Ghent University. All testing procedures and data evaluation was performed in accordance with the ASTM E691-14 standard. The following parameters were discussed: the standard deviation of the complete data set per test method and testing time $s_{\bar{x}}$, the repeatability standard deviation s_r, the between laboratory variance s_L, the reproducibility standard deviation s_R, and the consistency statistics h and k. Following equations were used, where p is the total amount of participant's per test, $\bar{x}$ the participant's average, $\bar{\bar{x}}$ the overall data average, s the participant's standard deviation and n the number of repetitions:

$$s_{\bar{x}} = \sqrt{\sum_{1}^{p} \frac{(\bar{x} - \bar{\bar{x}})^2}{(p-1)}} \tag{3}$$

$$s_r = \sqrt{\sum_{1}^{p} \frac{s^2}{p}} \tag{4}$$

$$s_L = \sqrt{s_{\bar{x}}^2 - \frac{s_r^2}{n}} \quad (5)$$

$$s_R = \sqrt{s_L^2 + s_r^2} \quad (6)$$

$$h = \frac{(\bar{x} - \bar{\bar{x}})}{s_{\bar{x}}} \quad (7)$$

$$h = \frac{s}{s_r} \quad (8)$$

4. Experimental results

Both SAP types were able to visually swell as shown in Figure 3. Two particles belonging to 200-500 µm fractions swelled in demineralized water and cement filtrate solution [to be added]. The fluid was added dropwise till full saturation of the particle was achieved. The process was monitored for 24 h by means of a stereo microscope (Leica S8 APO with DFC 295 camera).

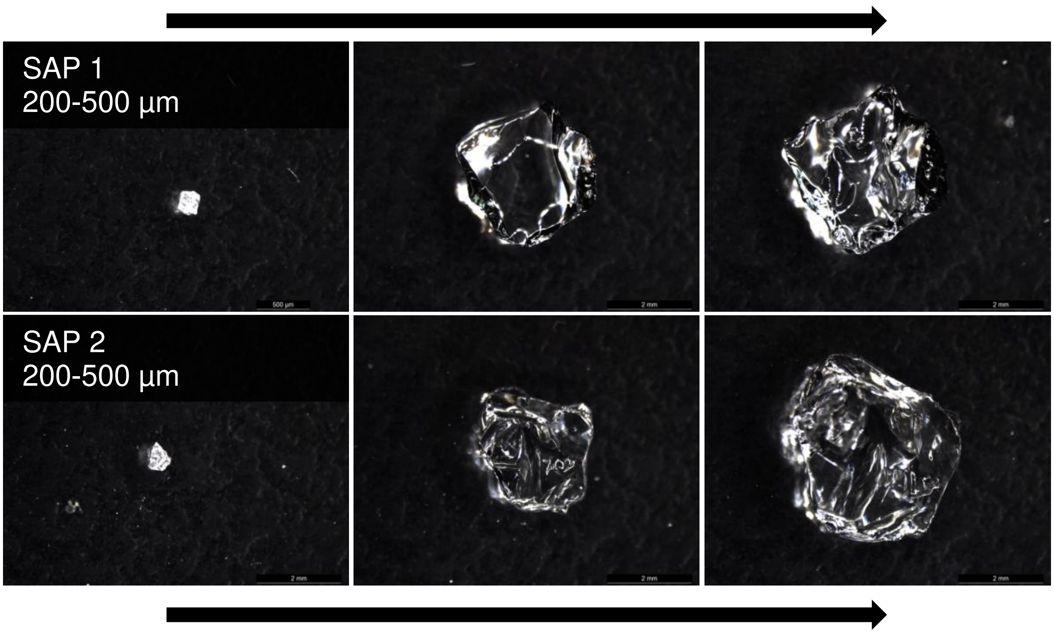
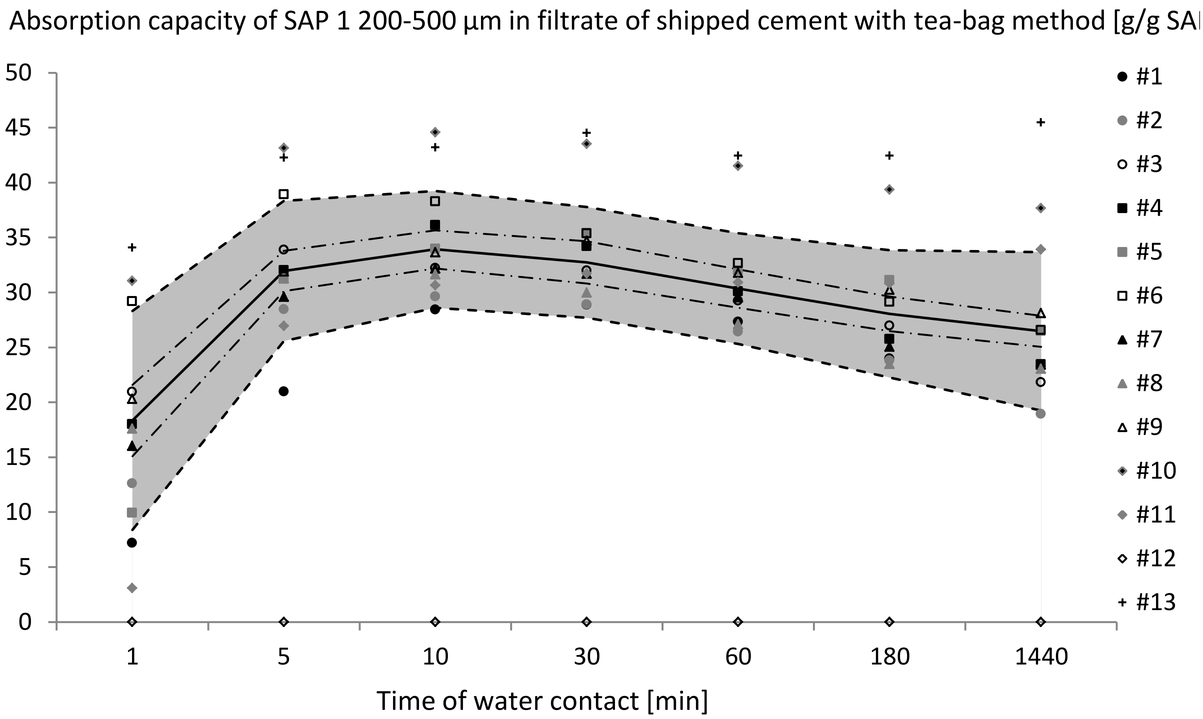
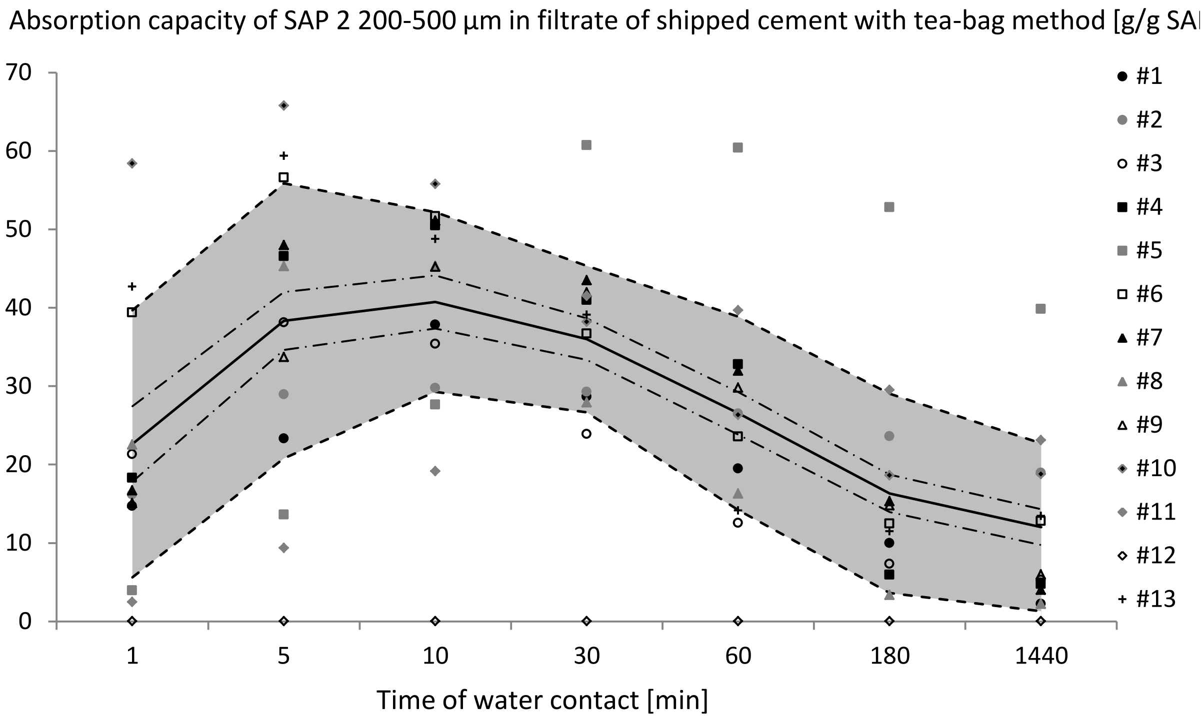


Figure 3: Swelling of the particles in demineralized water and cement filtrate solution [to be added] up to full extent as studied by means of microscopic analysis.

Typical time-resolved absorption curves in cement filtrate solution by the tea-bag method are shown in Figure 4 for SAP 1 and SAP 2 for the range of 200 to 500 µm. Figure 5 shows a comparison of the tea-bag method and the filtration method in demineralized water for SAP 2 with a range of 200 to 500 µm. All other graphs for the respective testing methods and SAP types and gradings can be found in Appendix A.

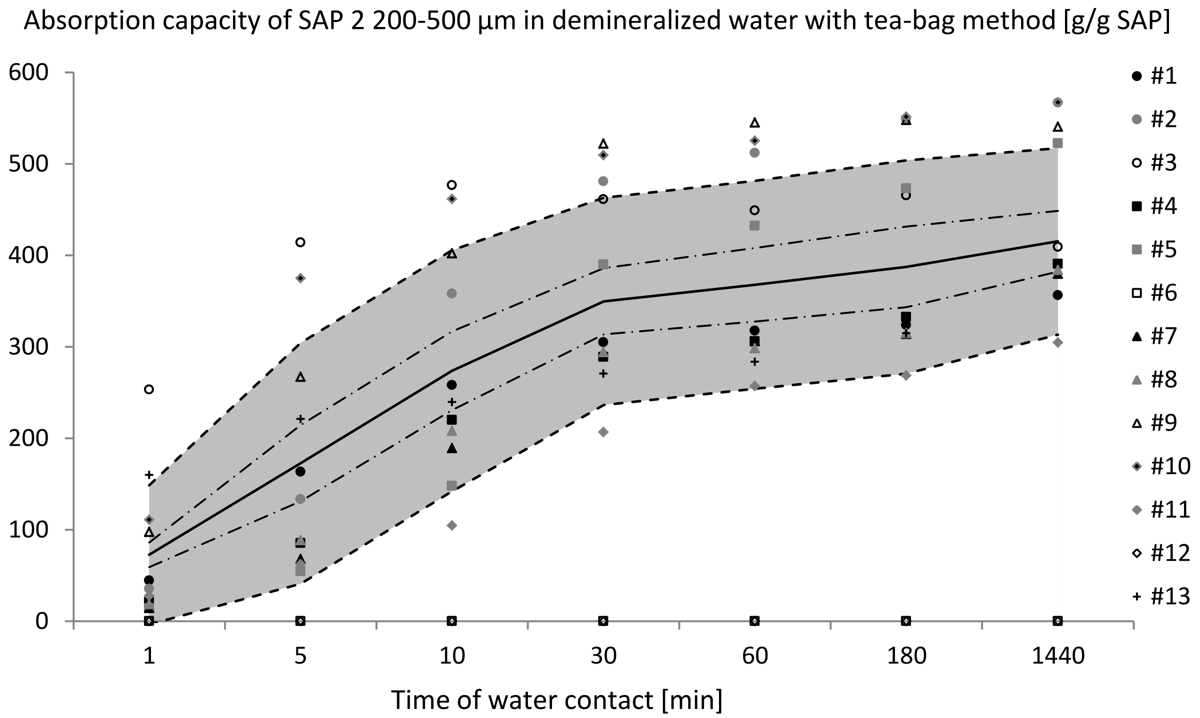


(a)

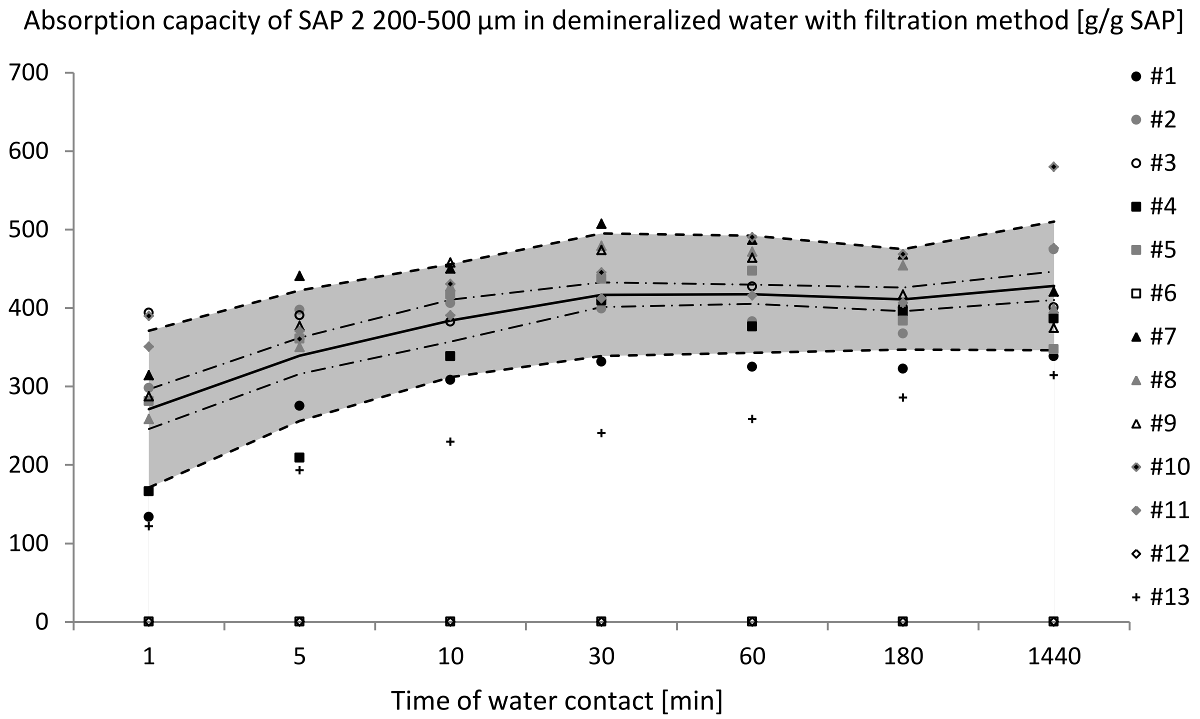


(b)

Figure 4: Absorption capacity results in cement filtrate solution by means of the tea-bag method as a function of time steps showing the average (solid lines) +/- the repeatability (dashed dotted lines) and the reproducibility (dashed lines) of SAP 1 (a) and SAP 2 (b) with 200 to 500 µm grading.



(a)



(b)

Figure 5: Absorption capacity results of SAP 2 graded from 200 to 500 µm in demineralized water by means of the tea-bag method (a) and the filtration method (b) as a function of time steps showing the average (solid lines) +/- the repeatability (dashed dotted lines) and the reproducibility (dashed lines).

In time, the SAPs were able to swell. The absorption capacity of all tested SAP samples was approximately an order of magnitude larger in demineralized water compared to that in pore solution, as previously reported by others [10,13]. All SAP samples exhibited an increasing absorptivity trend in demineralized water and the results for both methods are comparable. Stable swelling properties in demineralized water were found when monitoring the swelling capacity in time. However, this is not the case in the pore solution, where all the SAP samples reached a maximum of their absorption capacity after about 10 min to 30 min of contact with the fluid, followed by gradual decrease or polymer-intrinsic self-release (for details cf. Figure 9 and related discussion at that place). SAP 1 released a smaller portion of absorbed cement pore solution than SAP 2. After 24 h of testing SAP 1 still had a considerable portion of cement pore solution retained while desorption was much more pronounced for SAP 2. The maximum absorption capacity of SAP 1 was lower than that of SAP 2 in demineralized water after 24 h of testing.

Besides desorption of cement filtrate from intact SAP 2 particles, partial dissolution of SAP 2 in cement filtrate solution was likely to occur as the sorption curves shifted downward as a function of time. A whitish glow came out of the tea-bag and a whitish product was formed as well and could clearly by observed in the tea-bag and filter paper. A cloudy product was observed when performing the filtration method test. However, this was filtered as well during filtration measurement. This could point to a possible instability of the SAP particles in time. The phenomena reported by most of the participants:

SAP 1 - after 24 h a transparent gel was inside the tea-bag;

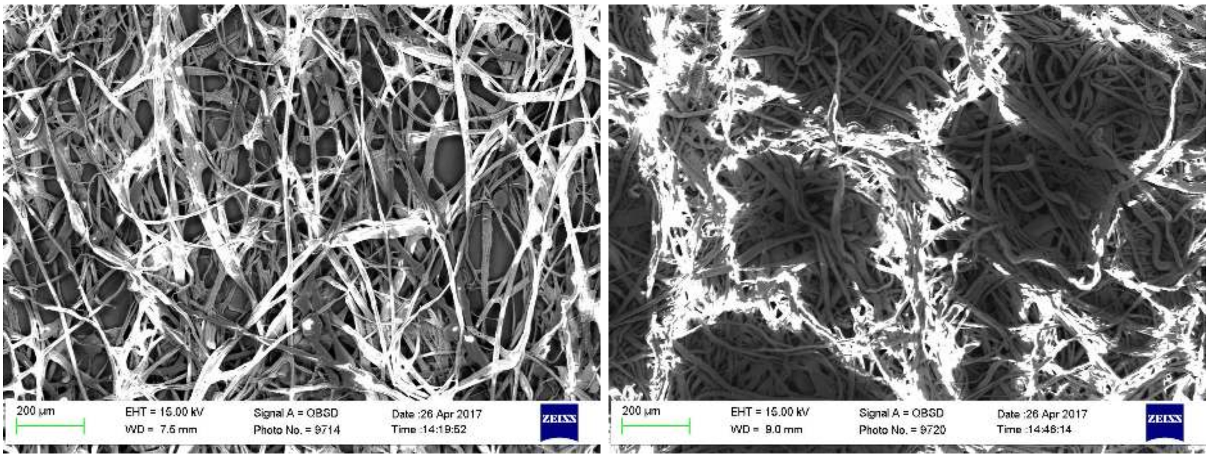
SAP 2 - after 24h a white hard incrustation was inside the tea-bag (see also Figure 6).

a) b)

Figure 6: Exemplary images made during testing of SAP 2, native grading, a) partial dissolution during the tea-bag test and b) formation of hard white particles.

Generally such a crust formation might be due to carbonation, but all test containers were sealed to minimize this effect. Only SAP 2 (all size fractions) showed this kind of reaction in the cement filtrate solution in time as reported by most participants. One participant found no decrease in absorption capacity and two found only a partial decrease. SAP 1 did not show this feature. In the short term (when SAP particles were not completely saturated, SAP 2 might have escaped from tea-bag and dissolved in the cementitious solution to minor extent. However, in long term (after 10 minutes), a predominant dissolution of SAP 2 might have taken place. When SAP 2 is placed in a highly alkaline fluid with a high ion concentration (especially with calcium ions), a hard egg-shell type of crust can be formed. Interestingly, none of these phenomena occurred in the previous studies of participant number 2 with the respective polymers [1,4-6,13,16]. This will be a subject of further investigation. For the time being, no chemical analyses have been performed since this would reach beyond the scope of the RRT intention. Any formulations of "dissolution" as well as "escape" of the SAPs are based on visual examination only and hence they do not provide mechanistic explanations from a chemical point of view.

However, as a first step towards clarifying the observations on a microstructural or physico-chemical basis, SEM micrographs were obtained for tea-bag and filter paper used in the experimental program (Figure 7). Samples were not coated and observations were carried out with Carl Zeiss EVO 50 microscope (United Kingdom) in high vacuum mode. Images were obtained with magnification of 250x, accelerating voltage (EHT) of 15 kV and working distance (WD) ranges from 7.5 to 9 mm.



a) b)

Figure 7: SEM micrographs of the a) tea-bag fabric and b) filter paper used, showing a difference in mesh openings.

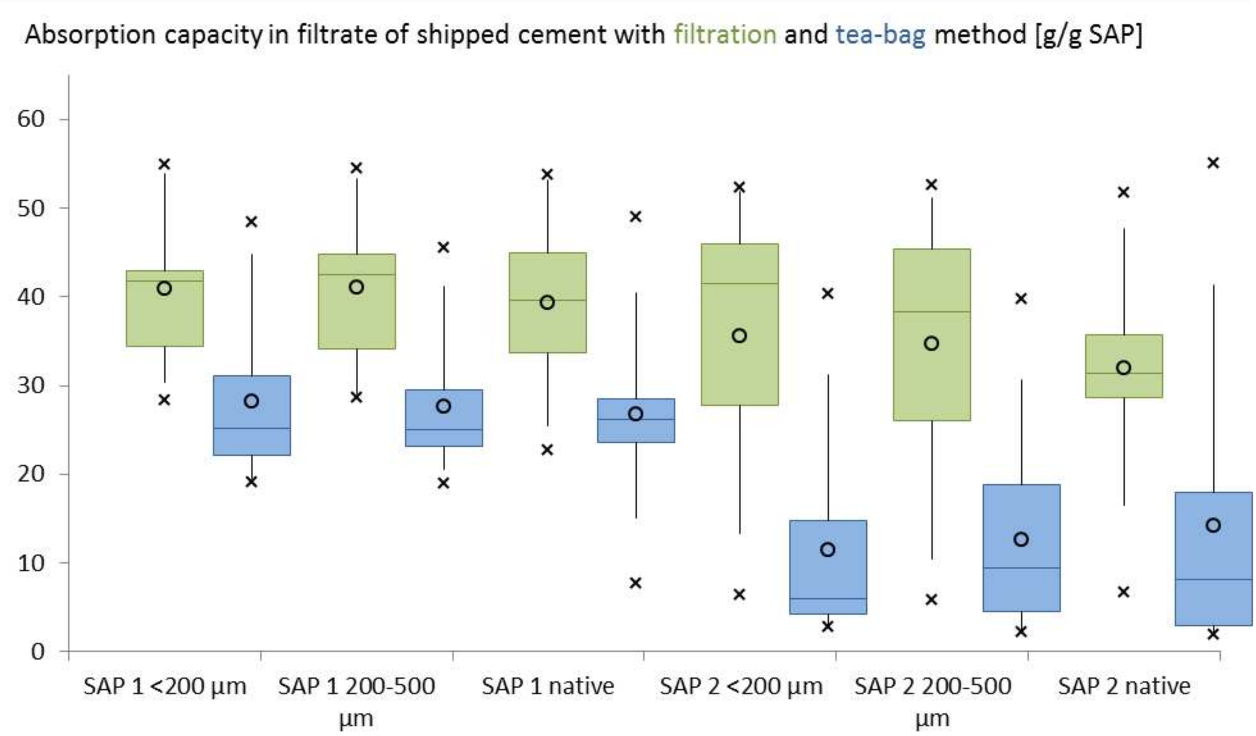
From the SEM images, it is clear that the tea-bags had a less dense mesh compared to the filter paper. This can partly explain the differences observed in swelling behaviour: the smallest particles may still be retained upon filtration, in case there is a partial dissolution. The escaping of the SAP 2 particles in the tea-bag can be explained by the larger meshes. However, upon swelling, these particles should be larger compared to the mesh size. As such, these larger particles would not escape.

High scatter in reproducibility was observed for both tests. In cement filtrate solution the scatter for both tests is in the range of 20-25 g/g. In demineralized water, the reproducibility scatter of the results was in the order of magnitude of (172 ± 89) g/g SAP for the tea-bag method and (121 ± 54) g/g SAP for the filtration method. Most likely this is due to the different operators in the different laboratories. The high scatter indicates the risk that, when testing SAPs prior to their incorporation into cementitious materials, different values obtained depending of the particular operator would lead to different concrete or mortar mixture compositions.

The repeatability per participant is again comparable per test method in cement filtrate solution; approximately 5 g/g. In demineralized water this was 57 ± 26 g/g SAP for the tea-bag method and 33 ± 24 g/g SAP for the filtration method.

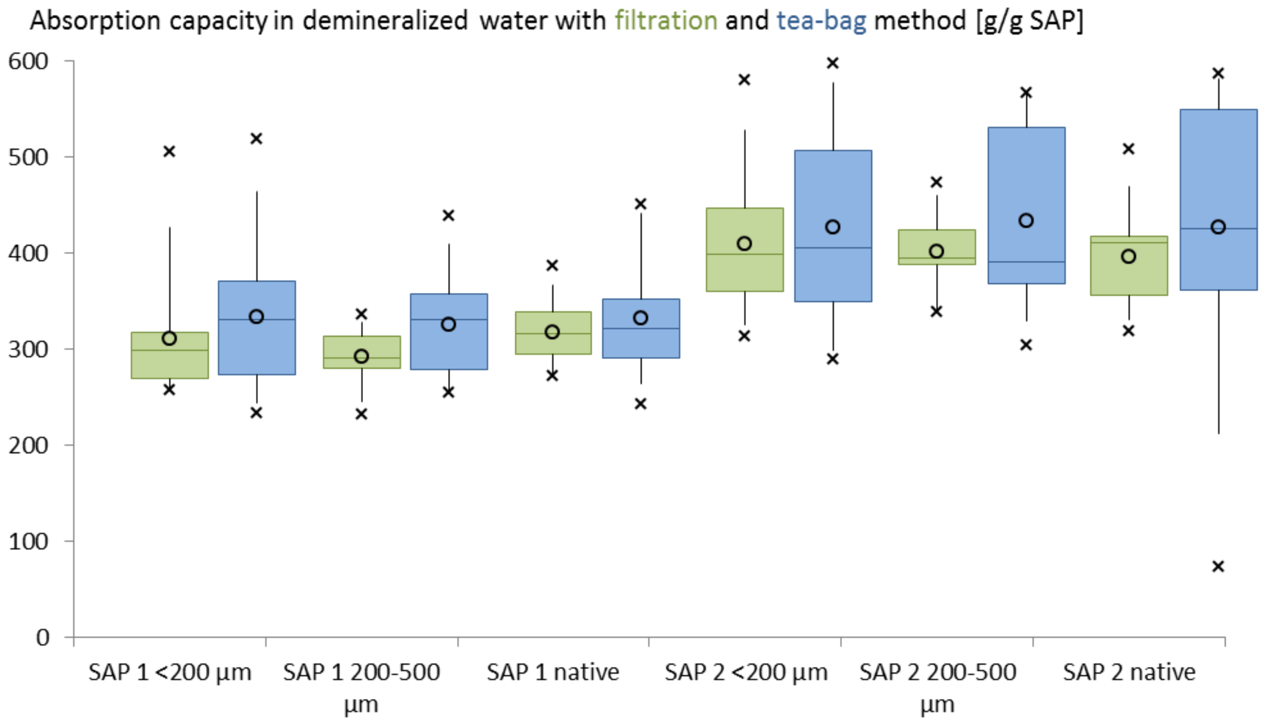
The same trends with respect to ab- and desorption behaviour of SAPs in time were observed when testing the shipped and the locally available cement types. However, as expected the scatter of the results was larger in case of local cements.

The comparison of both test methods is shown in Figure 8 for the values obtained after 24 hours of testing. In this figure, the data is represented in box plots showing the average (middle circle 'o' in box), 25-75 % quartile intervals (box), 5-95 % intervals (whiskers) and maxima and minima (crosses 'x'). Beneath the respective graphs for the absorption in the shipped cement filtrate and demineralized water, the number of participants is given (n). The results for the local cements are given in Appendix B.



n = 9 12 10 12 10 12 9 12 9 12 10 12

a)



n = 12 11 12 11 11 11 11 11 11 11 11 11

b)

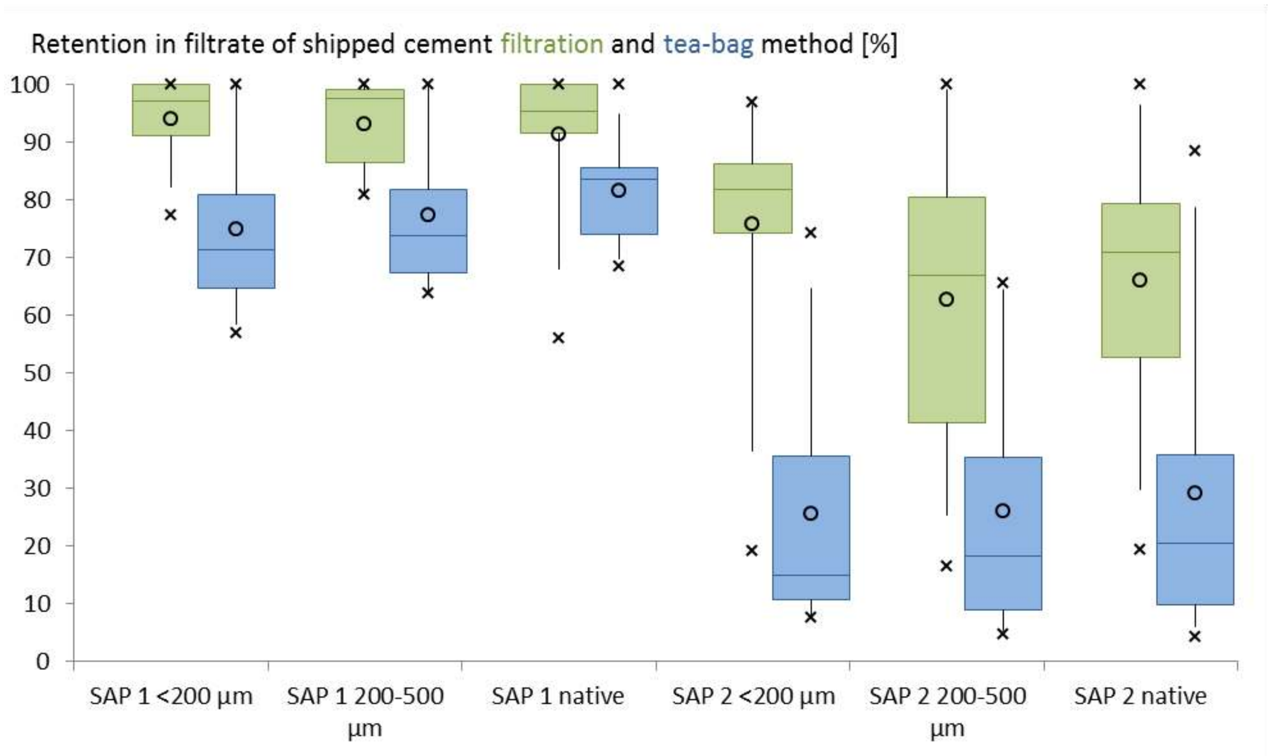
Figure 8: Absorption capacity after 24 hours of testing by means of the filtration and tea-bag methods as shown as box plots grouped per SAP type and grading: the average values (middle circle 'o' in box), 25-50-75 % quartile intervals (box), 5-95 % intervals (whiskers) and maxima and minima (crosses 'x'). Beneath the respective graphs for the absorption in a) the shipped cement filtrate and b) demineralized water, the number of participants is given (n).

Interestingly, the 24 hours sorptivity results in any cement filtrate solution with any SAP substance were systematically higher for the filtration method than for the tea-bag method. For SAP 1 the tea-bag results were roughly 25 to 35 % below those obtained from the filtration method. This difference was even more pronounced for SAP 2 where the tea-bag results varied by approximately 25 to 45 % from the filtration data.

In demineralized water, there was a very good agreement between the results from both test methods. The filtration tests showed a narrower range in obtained results and the standard deviation was smaller. A larger scatter was observed when using the tea-bag method. The values measured using the tea-bag method were on average 5 to 15 % higher for SAP 1 and approximately 5 to 10 % higher for SAP 2.

The same conclusions can be drawn from the tests in which different locally available cements were used for producing cement filtrate (results in Appendix B). The scatter is still very high, even for a lower number of participants (n).

The retention capacity was calculated based on the results of sorption experiments. It was defined as the mean swelling capacity at 24 hours divided by the maximum mean swelling capacity and first calculated for each participant/SAP/testing fluid. The results are shown in Figure 9, which presents the data in box plots showing the average (middle circle 'o' in box), 25-75 % quartile intervals (box), 5-95 % intervals (whiskers) and maxima and minima (crosses 'x'). Beneath the respective graphs for the absorption in the shipped cement filtrate and demineralized water, the number of participants is given (n). The results for the local cement can be found in Appendix B.



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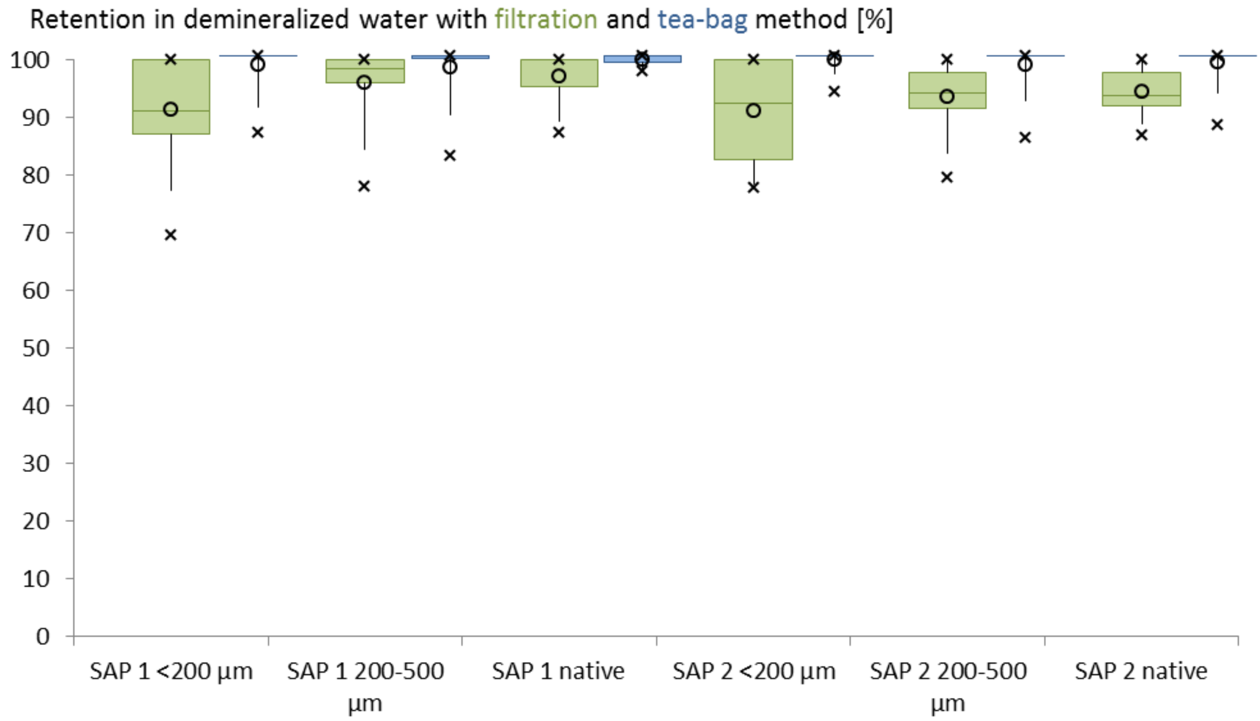
a)



n = 12 11 12 11 11 11 11 11 11 11 11 11

b)

Figure 9: Retention results (the 24 hours mean absorption capacity related to the maximal recorded mean absorption capacity) obtained by means of the filtration and tea-bag methods as box plots grouped per SAP type and grading: the average values (middle circle 'o' in box), 25-50-75 % quartile intervals (box), 5-95 % intervals (whiskers) and maxima and minima (crosses 'x'). Beneath the respective graphs for the absorption in a) the shipped cement filtrate and b) demineralized water, the number of participants is given (n).

From the retention results, it is clear that SAP 1 is able to retain the fluid for 24 hours while SAP 2 is releasing the absorbed cement filtrate solution in time. Interestingly, the extent of polymer-inherent desorption was much more pronounced in the tea-bag method opposite to the filtration method. From a point of view of polymer chemistry, the qualitative trends are as expected, i.e. SAP 1 being fairly retentive whereas SAP 2 is clearly self-releasing in the cement-derived solution. These expectations were mirrored in the tea-bag results unambiguously. On the other hand, the results from the filtration method are significantly less explicit. In demineralized water, there was practically no release of fluid by any of the SAPs under investigation.

5. Discussion – interpretation of the participants' individual and averaged results

A high variance in operator's sensitivity was observed in the cement filtrate solution for both tests. The obtained results on the swelling capacity show a large scatter, especially for SAP 2. For the latter, most of the participants found a decrease in swelling over time. Most likely, the acrylate groups undergo complex formation with Ca^{2+}, resulting in a) advancing the cross-linking of the primary polymer chains and b) decrease of the efficient charge density of likewise anionic groups. Such action does prominently reduce the swelling capacity in time as has previously been reported in e.g. [6,13,14] and the mechanism was explained in e.g. [17]. Furthermore, chemical bonds in the polymer network may cleave, which can result in dissolution of the SAP. Most of the participants noticed a drop in absorption capacity but, interestingly, some found a steady swelling behaviour and hence, a contrary trend.

With respect to a long-lasting field of discussion, a potentially systematic drawback of the "tea-bag method" had to be clarified in the course of the Round Robin Test. For many years it has been postulated by several researchers, that residual inter-particle (capillary) liquid may remain in the samples during the wiping and weighing steps of this procedure, e.g. [19]. However, no quantification and scientifically sound proof of this critical aspect has been published up to date. Hence, the aim of this Round Robin Test was to quantitatively verify that hypothesis based on experimental results.
Considering the results obtained from the participating labs and their scatter, it can be concluded that no significant difference was found on the swelling capacity in demineralized water. The values from the tea-bag test yielded a larger scatter and were slightly (5 to 15%) higher in comparison to the results obtained from the filtration method. Hence it is still not possible to formulate a solid conclusion on the residual inter-particle liquid discussion due to the high variability.
If both testing methods were compared to microscopic analysis (the data can be found in Appendix C), it was found that in cement filtrate solution, the tea-bag method yielded lower absorption values. In demineralized water, the tea-bag method gave slightly higher values compared to the values obtained by means of microscopic analysis. The filtration method showed values around the values obtained by means of microscopic analysis.

One particular feature of the tea-bag method is the high variability observed in the absorptivity results. This, along with particle agglomeration issues (especially in the fine fraction) at only several tens of minutes of time, makes it difficult to properly assess the kinetics of the absorption process. Even so, the final total (within the first 24 hours) absorption capacity seems to be independent of the SAP fraction size, as both fine and coarse fractions exhibited similar absorption values in all cases.

In between different tea-bag measurements, the time interval should be recorded and subtracted from the total measuring time. A possible error may occur as the contact times with water are changing. Even larger scatter at later ages is observed when using the tea-bag method compared to the filtration method.

During the experiments it became apparent that using a maximum of 0.1 g in the tea-bag test with DI water aided in preventing possible over-swelling of the particles. Also, the tea-bags can be sealed using a tape, which weight should be included in the dead weight during testing. The insertion of dry SAP samples in the wet tea-bag turned out to be difficult. It was more practical to put dry SAPs in dry tea-bags. The mass of water or solution absorbed by an empty tea-bag can be accounted for by calculation (i.e. considering absorption of tea-bag that came from additional measurements on 10 tea-bags).

For the filtration method, a large polymer sample is needed to conduct tests on sorption as a function of time as the sample cannot be directly reused. A possibility is to combine the method with the rising water-head test [19]. With this test, which is only usable for non-buoyant SAP particles in a testing fluid, the settlement height of the particles is recorded in time. Using the final height measurement and the absorption capacity at 24 h, the absorption capacities at other swelling times can be estimated. However, if one needs to record a swelling capacity at a certain time, the filtration method is preferred as the settlement may differ in time.

For some participants, the filtration method was less suitable for the determination of absorption capacity within the required filtration time. The total contact time with water should be recorded and used as the total absorption time. This time, however, is dependent on the filtration speed, SAP chemical composition, type of solution, particle size distribution, filter paper, use of vacuum filtration etc. Furthermore, the shape and size of the funnel may have an influence on the time needed to drain the mixture. This problem can be mitigated by accelerating the rate of filtration. Different strategies can be adopted to accelerate filtration such as increasing the size of the funnel and filter, use of ribbed funnels, or vacuum filtration with large surface area funnels. The filtration time required for filtering the small SAP particles is too long. Filtration can take sometimes up to 1 hour (one minute interval of consecutive drops as a criterion of filtration completion); during this time the SAP could still absorb the water or solution in the filter. Slow percolation of water through the fine particles (< 200 µm) of gel and potential clogging of the filter pores may lead to certain inaccuracies of the procedure. Therefore, the readings of filtered fluid mass cannot be precise, especially for measurements with short contact times of SAP and fluid. In the procedure, it was proposed that the filter paper would not make contact with the funnel. However, some participants made such contact, increasing the filtration time considerably. It was concluded that a hoovering filter paper or the use of a ribbed funnel could be effective in reducing filtration times. The difference in filtration (contact filter paper and funnel compared to no contact at all) amongst the participants accounted for the observed high scatter and the practical problems. These were taken into account in the overall recommendation, as prepared within this TC.

The decrease in swelling behaviour for SAP 2 was clearly observed in the tea-bag method and not in the filtration method. This could be potentially attributed to inadequately sealed condition during the tea-bag method compared to the filtration method. However, all participants were instructed to properly seal the containers during storage. Another reason could be the difference in mesh size of the tighter filtration paper compared to the more open tea-bag, leading to clogging. A further reason can be cleavage of chemical bonds in the polymer structure due to the high alkaline pH value or other ions present in the test liquid. As an example, some ester bonds can be prone to hydrolysis when exposed to cement filtrate for a longer time. Although not verified instrumental chemical analysis, visual observations by numerous participants indicate that the hydrogel particles in fact dissolve over time. This clearly indicates that the hydrated polymeric networks disintegrate into solutes. Such dissolution results in practically invisible polymer and the suspensions with the swollen SAPs look like clear solutions.

Apart from this, partial carbonation during measuring and dampening the tea-bags might give reason to the de-swelling. As carbon dioxide dissolves in the highly alkaline solution, the pH value drops to a small but still notable extent. Consequently, potentially intermediately precipitated Ca^{2+} ions re-dissolve, enter the hydrogels, bind intensely to the carboxylate moieties and in this way promote and support the principal de-swelling mechanism that was explained at the beginning of the Discussion Section. SAP 2, due to its higher density of carboxylate groups along the primary chains as compared to SAP 1, may be expected to be more prone to such behaviour.

Irrespective of the chemical mechanisms behind de-swelling or potential partial dissolution, care should be taken to minimize the contact time of SAPs with the environmental conditions. This way, hydrogel-inherent characteristics can be elucidated without producing interfering products.

By using the statistical analysis as described in ASTM E691-14, following values for the different standard deviations, repeatability and reproducibility could be found. Table 2 shows that the results per grading are comparable to each other so the average for individual SAPs in a distinct fluid could be calculated.

Table 2: The standard deviation of the complete data set per test method and testing time $s_{\bar{x}}$, the repeatability standard deviation s_r, the between laboratory variance s_L and the reproducibility standard deviation s_R for both tests following ASTM E691-14.

	Tea-bag method				Filtration method			
	$s_{\bar{x}}$	s_r	s_L	s_R	$s_{\bar{x}}$	s_r	s_L	s_R
Cement filtrate solution SAP 1	8.6	1.9	8.6	8.8	10.7	4.8	10.2	11.6
Cement filtrate solution SAP 2	12.7	3.1	12.5	12.9	15.1	9.9	14.0	17.2
Demineralized water SAP 1	68.0	22.8	66.7	70.6	43.9	14.6	43.0	45.5
Demineralized water SAP 2	124.9	62.8	119.1	135.6	57.4	17.1	56.6	59.1

In cement filtrate solution, both methods show approximately the same repeatability and reproducibility. In demineralized water, however, the scatter in the tea-bag method is higher compared to the filtration method. This is due to both a higher scatter in obtained averages per participant $s_{\bar{x}}$ and the participants own repeatability standard deviation s_r. This is reflected in the laboratory variances $s_L$and the reproducibility standard deviation s_R. The same conclusions as stated above following from a visual study of the obtained graphs can be made.

If zooming into the individual results, the graphs of the consistency statistics h and k can be found in Appendix D. From the consistency statistics results, it is clear that most of the participants show coherent data when performing both tests. The standard deviations are acceptable and comparable. This data shows the relative position of each participant in the RRT test and is thus disclosed as complementary data.

6. Summary and conclusions

In this Round Robin Test, the absorption capacity of two different SAP types was tested in different solutions and by two testing methods in order to assess the suitability of these methods to estimate quality of SAP as concrete admixture. The testing methods were the tea-bag method and the filtration method. The tests were performed within the framework of the activities of the RILEM Technical Committee 260 RSC “Recommendations for use of superabsorbent polymers in concrete construction” by 13 laboratories.

The results obtained from all participants were found to be consistent with respect to the sorption behaviour of the SAPs even though high scatter was observed at early ages. The tea-bag method proved to be more practical in terms of time, while the filtration method showed less variation in the absorption capacity after 24 hours. Furthermore, polymer-inherent desorption of cement pore solution (as compared to long-term retention) could be estimated by the tea-bag method clearly, whereas the filtration method could not disclose such behaviour to the same extent within the time frame of the testing period up to 24 hours of testing. The chemical mechanisms behind these observations will be subject to further research, which may include cleavage of chemical bonds in the polymeric network or different extents of cross-linking the primary polymer chains by calcium cations.

Interestingly, the absorption values in cement filtrate solution were systematically higher when the filtration method was used in comparison to those obtained using the tea-bag procedure. These results seem to contradict the earlier postulates that remaining inter-particle liquid in the tea-bag test results in systematic overestimation of swelling capacity (20 to 40 %), whereas the sucking forces during the filtration procedure remove such liquid and should give more truthful absorption values. In demineralized water, however, the results obtained with the tea-bag method are slightly higher (5 to 15 %) in comparison to the results obtained using the filtration method. No solid conclusion on this matter can be drawn.

The following conclusions are made based on the statistical analysis. A high scatter in reproducibility was observed for both tests. In cement filtrate solution the scatter for both tests is in the range of 20-25 g/g. In demineralized water, the reproducibility scatter of the results was in the order of magnitude of (172 ± 89) g/g SAP for the tea-bag method and (121 ± 54) g/g SAP for the filtration method. The repeatability per participant is again comparable per test method in cement filtrate solution; approximately 5 g/g. In demineralized water this was (57 ± 26) g/g SAP for the tea-bag method and (33 ± 24) g/g SAP for the filtration method.

As a final statement, both test methods were assessed as applicable in the context of use of SAP in concrete construction.

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Appendix A

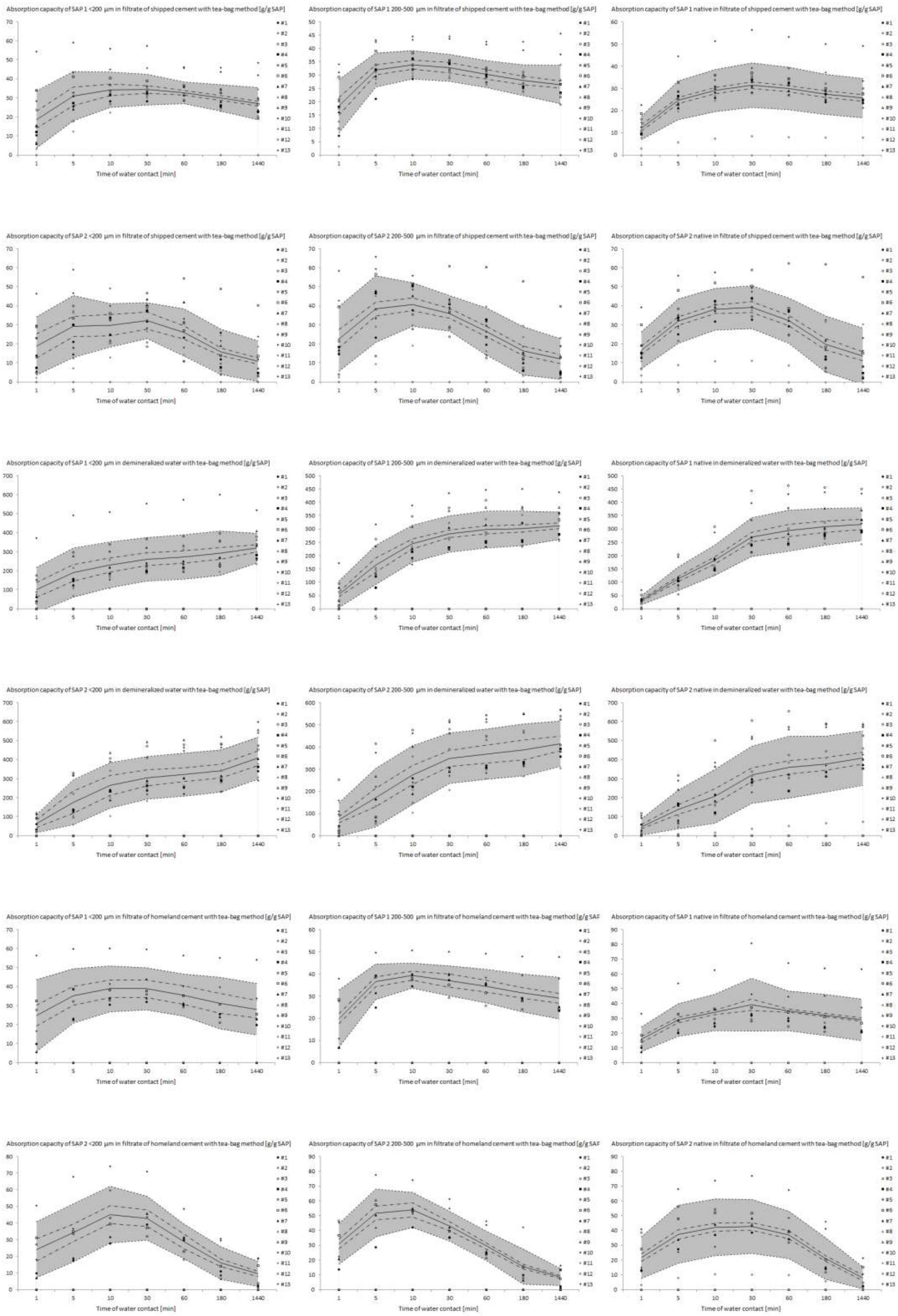


Figure 10: Absorption capacity results by means of the tea-bag method as a function of time steps showing the average and the average (solid lines) +/- the repeatability (dashed dotted lines) and the reproducibility (dashed lines).

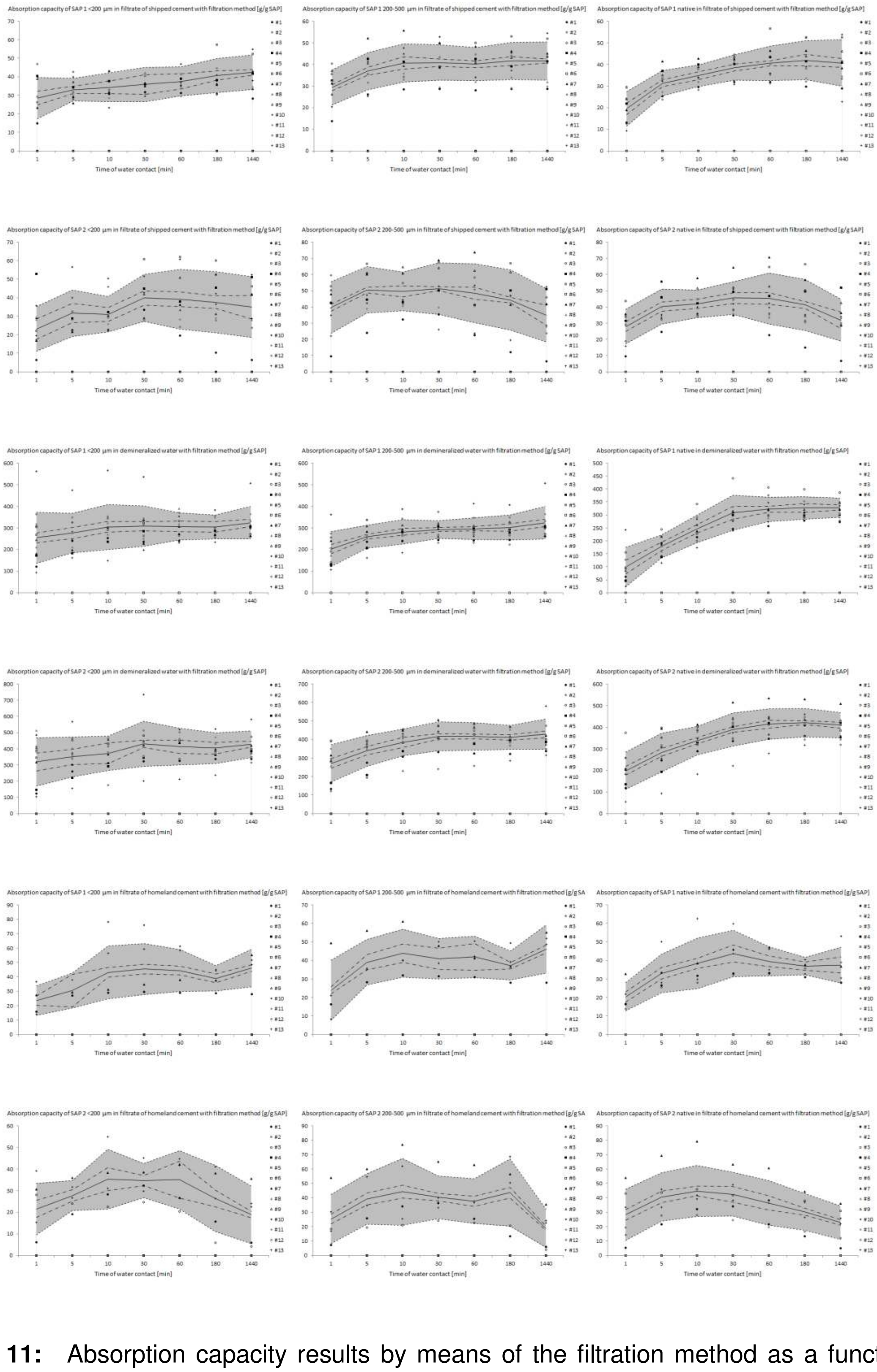
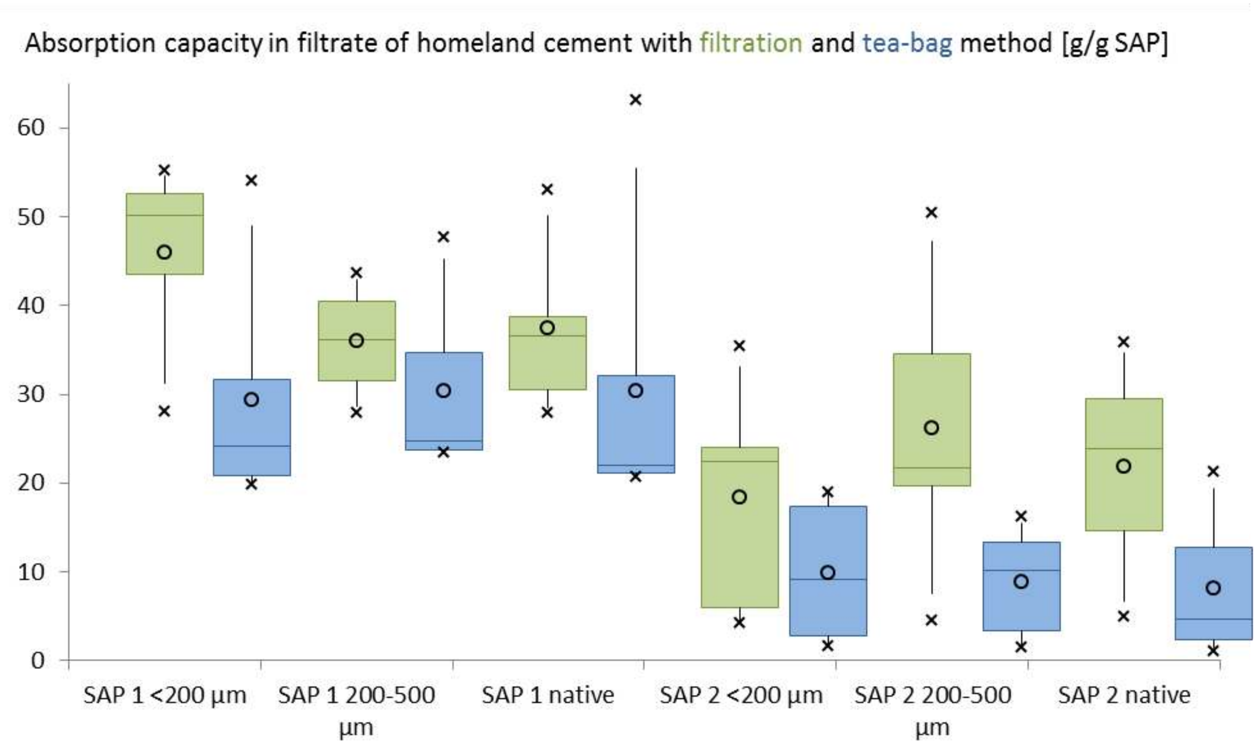


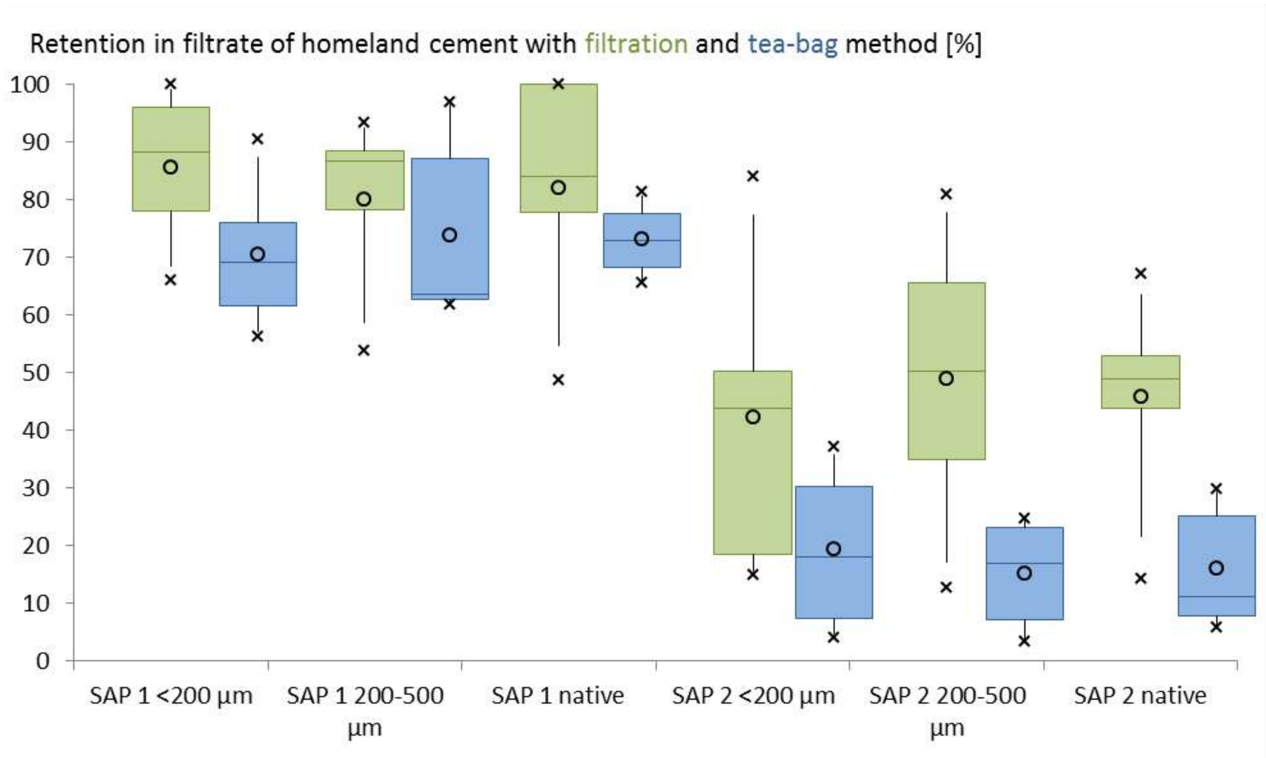
Figure 11: Absorption capacity results by means of the filtration method as a function of time steps showing the average and the average (solid lines) +/- the repeatability (dashed dotted lines) and the reproducibility (dashed lines).

Appendix B



n = 4 6 4 6 5 7 5 6 5 6 6 7

Figure 12: Absorption capacity after 24 hours of testing by means of the filtration and tea-bag methods as shown as box plots grouped per SAP type and grading: the average values (middle circle 'o' in box), 25-50-75 % quartile intervals (box), 5-95 % intervals (whiskers) and maxima and minima (crosses 'x'). Beneath the respective graphs for the absorption in the homeland cement, the number of participants is given (n).



n = 4 6 4 6 5 7 5 6 5 6 6 7

Figure 13: Retention results (the 24 hours mean absorption capacity related to the maximal recorded mean absorption capacity) obtained by means of the filtration and tea-bag methods as box plots grouped per SAP type and grading: the average values (middle circle 'o' in box), 25-50-75 % quartile intervals (box), 5-95 % intervals (whiskers) and maxima and minima (crosses 'x'). Beneath the respective graphs for the absorption in the homeland cement, the number of participants is given (n).

Appendix C

Different methods could be compared. These were the tea-bag method, the filtration method, the rising head method [19] and the microscopic analysis. Assuming perfect spherical SAPs and estimating the average diameter of the dry and saturated particle, the absorption capacity could be determined by microscopic analysis. It is true that the estimated diameter of a spherical particle is not the size of the irregular particle, but a first estimation of the swelling capacity can be made. Another estimation was the density, which was put at 1400 kg/m³ of SAP. The results are found in Figure 14 and Figure 15 for the filtrate of the cement slurry of the shipped cement and demineralized water, respectively. The values shown are the ones after 24 hours of testing.

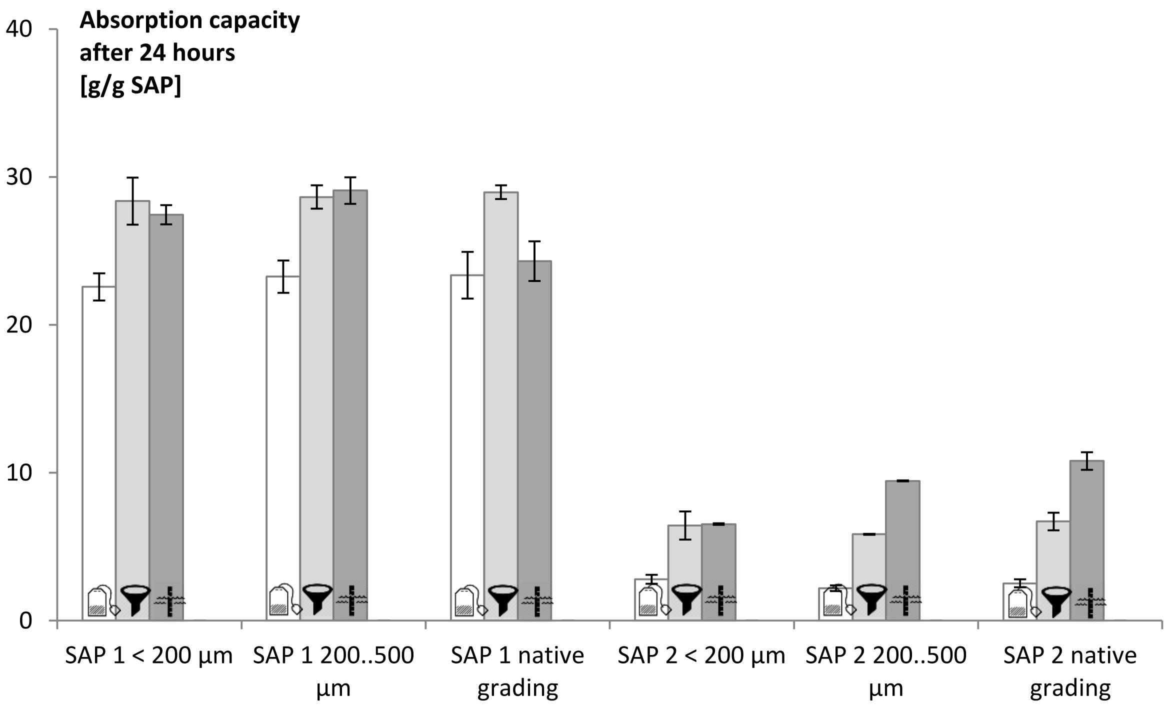


Figure 14: Comparison of the results obtained by participant 1 in the series with filtered cement slurry of the shipped cement using different testing methods: tea-bag method, filtration method, rising water-head test and microscopic analysis.

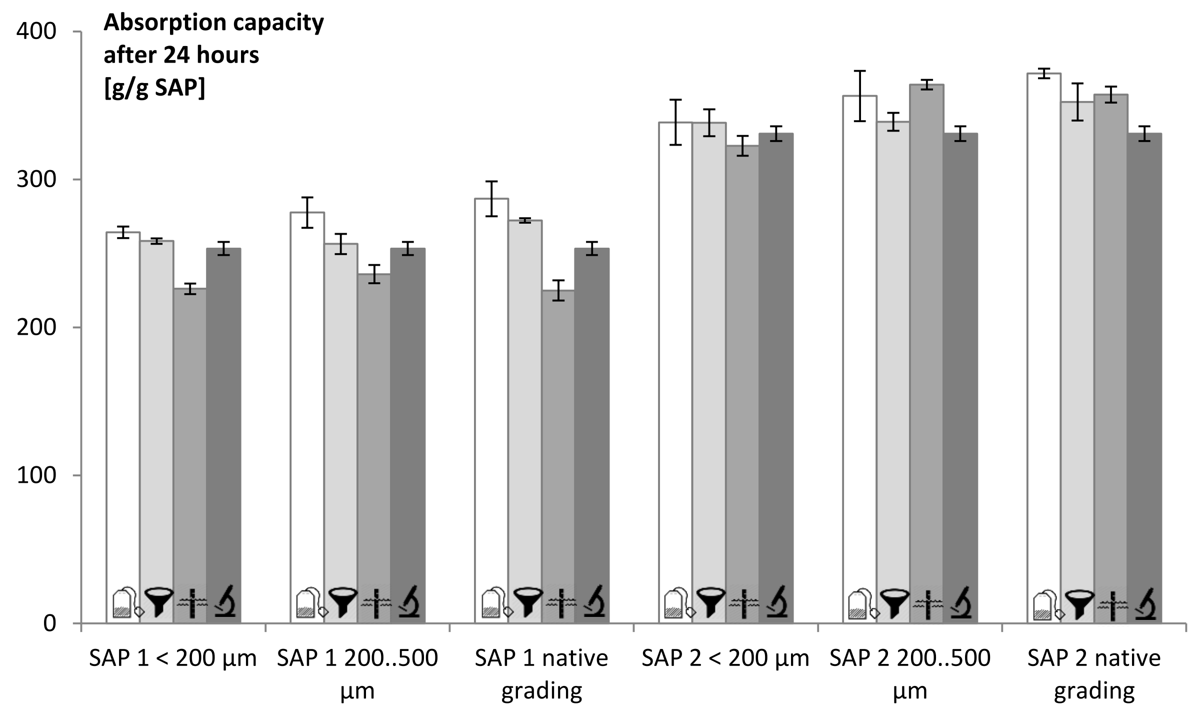
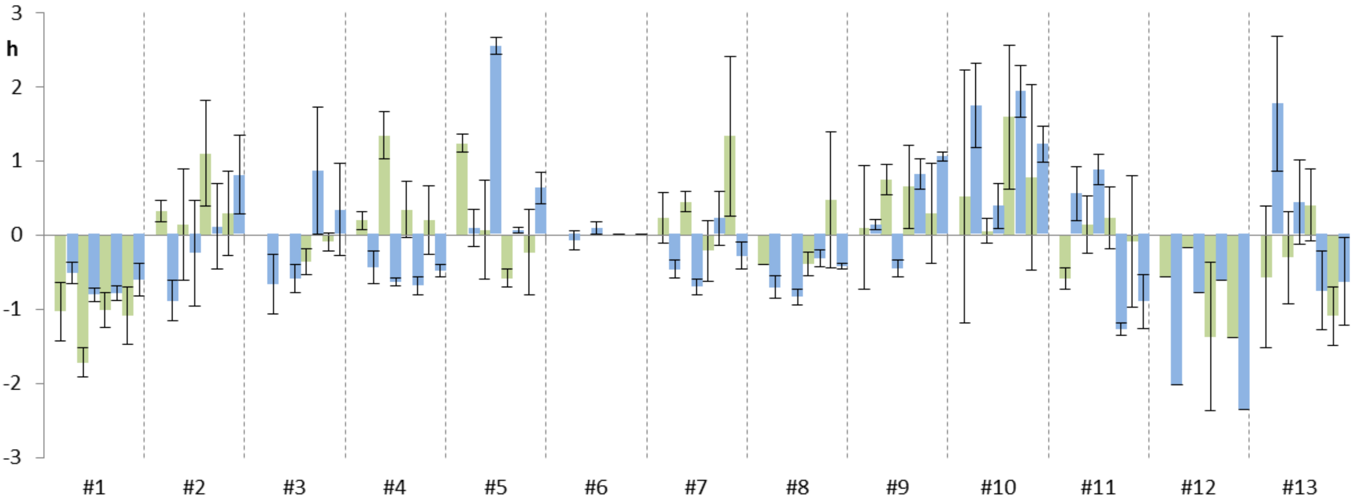
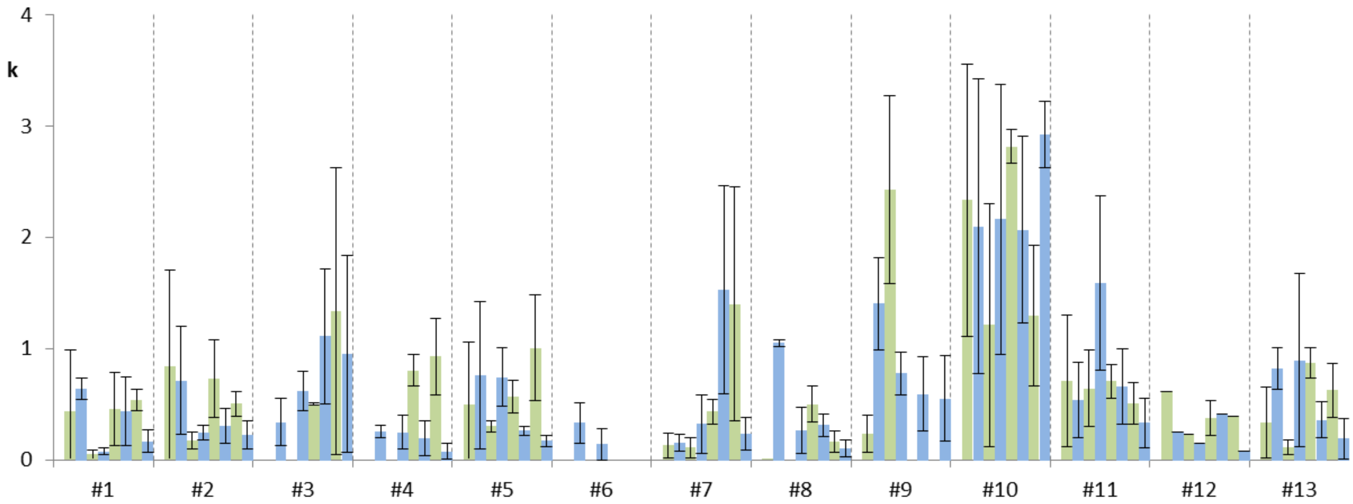


Figure 15: Comparison of the results obtained by participant 1 using different testing methods in in the series with demineralized water using different testing methods: tea-bag method, filtration method, rising water-head test and microscopic analysis.

Appendix D



a)



b)

Figure 16: Consistency statistics a) $\boldsymbol{h}$ and b) $\boldsymbol{k}$, showing the deviation from the overall average divided by the overall standard deviation and the participants standard deviation compared to the overall standard deviation of SAP 1 and SAP 2 in cement filtrate solution and demineralized water with the filtration method (green) and the tea-bag method (blue). No values shown means no tests performed and no standard deviation means no repetitive testing was performed.