

## **Enhanced durability performance of cracked and uncracked concrete by means of smart in-house developed superabsorbent polymers with alkali-stable and -unstable crosslinkers**

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### **ABSTRACT**

For the past two decades, research on the use of superabsorbent polymers (SAPs) in cementitious materials has proven that these innovative materials have the potential to become a suitable admixture in the concrete industry. Not until recently, most of the applications studied made use of SAPs originally designed to be used in other industries, such as in food, agricultural and hygiene products. In this paper, an innovative “in-house” developed SAP (SAPX) is presented, designed with a double crosslinking system specifically for applications in concrete structures. Its efficiency is compared with two commercially available SAPs (SAP1 and SAP2) for different applications. The “in-house” developed SAP promoted an immediate sealing effect of cracked concrete specimens as reflected by a reduction of 72% in the water permeability of specimens with cracks up to 250 µm against 45% for specimens with commercial SAP1, compared to specimens without SAPs. The performance against frost attack improved as a reduction of 55% in salt scaling after 28 cycles of freezing and thawing was found for specimens with SAPX, compared to 34% and 49% for specimens with SAP1 and SAP2 respectively. Although no complete mitigation of shrinkage was noticed, SAPX promoted a significant reduction in the shrinkage strain at early ages and up to 28 days. In terms of mechanical properties, SAPX reduced the strength to a comparable extent as SAP1 and less than SAP2. To conclude, SAPX showed a better performance compared to the already commercialized SAPs and has a high potential towards large-scale production to be exploited for concrete applications.

**Keywords:** SuperAbsorbent Polymers, durability, self-sealing, concrete, cracks, impermeability, crosslinkers

## 1. INTRODUCTION

Superabsorbent polymers (or hydrogels) are a natural or synthetic water-insoluble 3D network of polymeric chains cross-linked by chemical or physical bonding. They possess the ability to take up a significant amount of fluids from the environment, in amounts up to 1500 times their own weight [1-4].

The swelling and posterior water release are of great interest in the development of more durable cementitious materials. Over the past two decades a lot of attention has been paid to the topic and considerable advances have been achieved. At this point, the use of SAPs in cementitious materials is well established mainly for the purposes of internal curing to prevent shrinkage-cracking due to self-desiccation [5-7].

However, while SAPs have been primarily used as internal curing agents, some existing studies [8-10] have indicated that SAPs can also be a promising alternative for the sealing of cracks, provided that there is ingress of water. Swollen SAPs leave behind macropores after release of the stored water, increasing the fraction of voids in the matrix. Through these voids, cracks might be formed, exposing the dry SAPs to the external environment. Depending on the ionic concentration of the water that penetrates the crack, the SAPs would be able to swell more than when they were mixed in the fresh concrete. Therefore, there is the possibility for the SAP to swell beyond the size of its own macropore, filling the gap in between the crack surfaces [10].

In terms of healing and recovery of mechanical properties, the use of SAPs has also been found to increase the formation of healing products inside cracks, especially when the specimens are subjected to wet and dry cycles [11-13].

The macropores left behind after internal curing can also be beneficial for freeze-thaw resistance [14-16] as the induced macroporosity resembles an air-entraining agent system [17]. The addition of SAPs in the range of 0.10-0.34% in relation to the mass of cement has been reported to promote a reduction of at least 50% in the scaling after more than 25 freeze-thaw cycles in both cement mortars and concrete mixtures [7, 18-20].

In terms of production and market availability, until recently, the SAPs used for research in the construction industry had been developed for use in other industries, such as in food, agriculture and hygiene products. When working with such a versatile material, the possibility to fine tune

properties aiming for specific applications can be of advantage. In this paper, an “in-house” developed SAP, named SAPX, produced specifically for applications in cementitious materials is presented. SAPX has been initially designed for use as sealing agent for cracks, but it has also shown very promising results in terms of reduction of shrinkage strain and salt-scaling under frost attack. Its performance is presented and discussed in comparison with two commercial available SAPs, recently produced specifically for applications in cementitious materials.

## **2. MATERIALS AND METHODS**

The experimental program consisted of a comparative study regarding the performance in concrete of an in-house developed SAP versus two commercially available SAPs. The effects of the SAPs on the compressive strength, water permeability of cracked specimens, autogenous shrinkage and salt-scaling resistance under freeze-thaw cycles of uncracked specimens were investigated. All tests have been performed with triplicates.

### **2.1. The SAPs**

Two different commercial SAPs have been used in this study. SAP1, made by SNF Floerger (France) is a cross-linked acrylate copolymer produced through bulk polymerization and has a mean particle size ( $d_{50}$ ) of 360  $\mu\text{m}$ . SAP2, provided by BASF (Germany), is a copolymer of acrylamide and sodium acrylate, also produced through bulk polymerization, having a mean particle size ( $d_{50}$ ) of 40  $\mu\text{m}$ .

One “in-house” developed SAP, from now on named SAPX, was produced by ChemStream bv (Belgium). It mainly consists of the monomer NaAMPS (2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt) and it is based on ChemStream’s prior art EP2835385 [21]. SAPX has two different types of crosslinkers: an alkali-stable crosslinker (0.15 mol% with respect to NaAMPS monomer) and an alkali-unstable crosslinker (1 mol% with respect to NaAMPS monomer).

The idea behind this concept is to provide SAPX with an initial low absorption capacity. This will enable the use of higher dosages of SAPs without the need of higher amounts of additional water to compensate for the loss in workability. The use of additional water normally leads to a significant increase in the air content in the hardened state of the concrete (due to the formation of macropores) and a resulting decrease in compressive strength of the concrete. Once the alkali-unstable crosslinker is hydrolyzed, the SAP particles can swell more, which can be an added value for the promotion of self-sealing of future cracks, where typical high amounts up to 1 m% over the mass of binder are necessary [22].

SAPX was produced using a thermal bulk-polymerization reaction in water under inert atmosphere. After reaction, the bulky hydrogel formed was cut into smaller pieces and dried until all water was evaporated. In the final stage the dried product was ground with a RETSCH centrifugal mill. For this study three mean particles sizes were used: 100  $\mu\text{m}$ , 300  $\mu\text{m}$  and 500  $\mu\text{m}$ . The particle size distribution is shown in Table 1. SAPs with mean particles size of 100  $\mu\text{m}$  were used for the production of specimens for the monitoring of autogenous shrinkage and salt-scaling resistance under freeze-thaw cycles. For the water permeability tests, SAPs with the three mean particle sizes were used.

Table 1 - Particle size distribution of SAPX.

Mean particle size	Particle size distribution [ $\mu\text{m}$ ]		
	d10	d50	d90
100	26	93	283
300	66	262	757
500	140	473	1071

The dosage of stable and unstable crosslinkers was determined based on a preliminary study where different amounts of alkali-stable crosslinker were used. Figure 1 shows the effect of the total crosslinking amount on the absorption capacity of a NaAMPS-based SAP for both demineralized water and cement filtrate solution after three days of immersion, by means of the filtration method [23]. In the test performed with demineralized water it was noticed that an amount of crosslinking agent above 1 mol% did not promote a significant lowering in absorption capacity by the SAP. Based on that, a total crosslinking degree of 1.15 mol% was chosen for the production of SAPX.

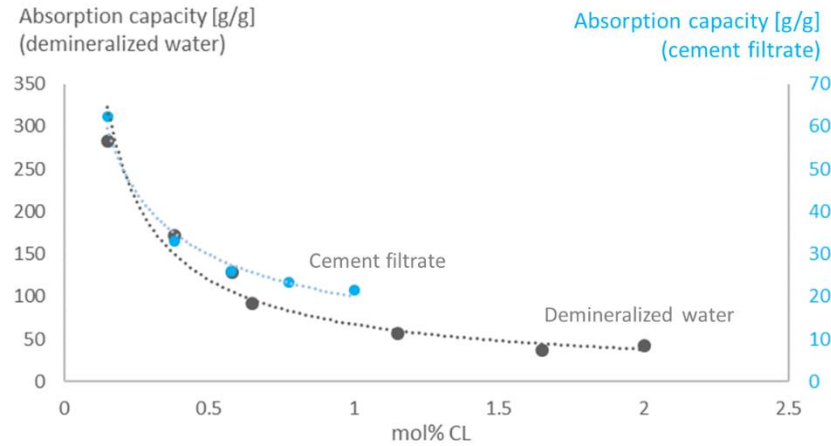


Figure 1 - Effect of the total crosslinking degree on the absorption capacity of NaAMPS-based SAP, measured after three days of immersion in the respective fluid (CL stands for crosslinker).

## 2.2. Determining the water absorption of the SAPs

The absorption capacity of all SAPs was investigated in demineralized water, cement filtrate solution, cement paste and concrete. For the absorption in demineralized water and cement filtrate solution, a filtration test was performed in accordance to [23]. The cement filtrate solution was prepared with demineralized water and cement type CEM III-B 42.5N – LH/SR (CBR, Belgium) (1:5 mass proportion of cement and demineralized water).

For the cement paste and the concrete, the absorption capacity was measured by means of workability of the fresh mixture. The flow table test was used for the pastes, in accordance with EN 1015-3 [24]. The slump test for concrete was executed in compliance with EN 12350-2 [25]. The absorption capacity of the SAPs in the cementitious mixtures was then estimated on the basis of a comparative analysis of the workability of mixtures with and without SAPs. With a fixed amount of SAPs, the amount of additional water was progressively increased until the SAP-containing mixture reached the same workability as a reference mixture without SAPs and with the same effective amount of mixing water. For the pastes a diameter of 300 mm in the flow table test was the aimed reference workability. For the concrete mixtures, the reference for workability was a slump of 160 mm.

Given the double crosslinker nature of SAPX, the absorption capacity in demineralized water was determined in two stages. In the first stage, the test was performed as described in [23]. In the second stage, SAPX was tested after the hydrolysis of the alkali-unstable crosslinker. To do so, the

SAP particles were tested in three different conditions: initial (before exposure to any alkaline environment), after 24 h and 72 h of continuous exposure to an alkaline environment (cement filtrate solution). The SAP particles exposed to the cement filtrate solution were prepared as described below:

- SAPs were immersed in cement filtrate solution for 24 h/72 h and filtered afterwards;
- After filtration, the swollen SAPs were immersed in demineralized water for 24 h and filtered afterwards. This step was executed twice;
- Then, the swollen SAPs were oven-dried at 80°C for 24 h;
- The dry SAPs were then ready for determination of the absorption capacity after hydrolysis of the alkali-unstable crosslinker.

### **2.3. Fourier-transform infrared spectroscopy (FTIR)**

The FTIR technique was used to identify changes in the chemical structure of SAPX that could indicate the degradation of the alkali-unstable crosslinker. A Frontier FTIR spectrometer from Perkin Elmer (with 'PerkinElmer Spectrum' software) and an MKII Golden gate Single Reflection ATR System (Specac) were used. The specimens were tested before exposure to the alkaline environment and after 24 h and 72 h of continuous exposure, following the steps described in 2.2.

### **2.4. Concrete mixtures**

Four concrete mixtures were studied. A reference mixture without SAPs and three mixtures containing the three different SAPs. In the mixtures tested for water permeability and freeze-thaw, the dosage for the commercial SAPs was 0.5% over the mass of cement and for SAPX, a dosage of 1% over the mass of cement was adopted. This value was chosen based on the absorption capacity of the three SAPs in concrete so that all SAP-containing mixtures would have the same effective water-to-cement ratio and workability.

All concrete mixtures were produced with cement type CEM III-B 42.5N – LH/SR (CBR, Belgium); a polycarboxylate superplasticizer (Tixo, 25% conc., BASF, Belgium, at a constant dosage of 1.8 m% in relation to the cement mass); sea sand 0/4 (absorption of 0.4% in mass); sea sand 0/3 (absorption of 0.3% in mass) and limestone 2/20 (absorption of 0.5% in mass). More details about the compositions of the concrete mixtures are given in Table 2.

Table 2 - Composition of the studied concrete mixtures, values in kg/m<sup>3</sup>.

Mixture	Cement	Sand 0/3	Sand 0/4	Limestone 2/20	Superplasticizer	SAP	w/c*
REF	356	421	343	1086	6.35	0	0.46
SAP1	340	406	331	1046	6.12	1.70	0.57
SAP2	339	405	330	1043	6.10	1.70	0.58
SAPX**	340	406	331	1046	6.12	3.40	0.57

\* Total water-to-cement ratio. The effective water-to-cement ratio was 0.46 for all mixtures.

\*\* Same mixture composition for the three studied SAPX sizes.

In the mixing procedure, the dry materials were first mixed for 1 min (including dry SAPs, when present), then the water and superplasticizer were added and mixed for an additional 2 min. When SAPs were present, the additional entrained water was added during the third minute and the mixing proceeded for an additional 2 min. The total mixing time was 3 min for the reference mixture and 5 min for the SAP-containing mixtures.

## 2.5. Characterization of the concrete mixtures in the fresh and hardened state

The workability of the concrete mixtures was assessed by means of a slump test, in accordance with the standard EN 12350-2 [25], executed 10 minutes after the first contact of water with the cement in the mixing procedure.

For each mixture, two cylindrical specimens (with a diameter of 100 mm and height of 200 mm) were molded for the preparation of specimens for the water permeability test. One extra cylinder with the same dimensions was molded for the preparation of specimens for salt scaling test under frost attack. Three cubic specimens (150 mm in dimension) were molded for the assessment of the compressive strength at 28 days of age and one cubic specimen (100 mm in dimension) was molded for the evaluation of the air void distribution and air content in the hardened state in compliance with the standard EN 480-11 [26]. All specimens were cured in a room with controlled atmosphere of  $20 \pm 2$  °C and RH > 95% until the testing day. The 100 mm cubic specimens for the air void analysis were sawn into slices with dimensions of 100 mm x 100 mm x 20 mm. The testing surface of each slice was polished, painted with black ink and dried for 24h in an oven at 35 °C. Then a layer of barium sulfate was applied to fill in the voids on the surface. An automated air void analyzer, RapidAir-3000 (Germann Instruments, Denmark) was used in the test.

Three prismatic specimens (100 mm x 100 mm x 400 mm) were also cast for the monitoring of shrinkage. They were cured for 23 h in a room with controlled atmosphere of  $20 \pm 2$  °C and RH > 95%. Right after casting, the free surface of the specimens was covered with a layer of plastic foil, attached to the mold with a thin layer of vaseline to improve the adhesion and prevent drying.

## 2.6. Water permeability test

Cracked specimens were used in order to assess the effects of the SAPs in the immediate sealing of cracks upon swelling. The water permeability setup proposed by Aldea [27] was used. In this setup, a cylindrical specimen with a diameter of 80 mm and thickness of 20 mm is placed in between two water-filled containers. On the top of the upper container, a thinner tube with a diameter of 12 mm is installed to monitor the level of water going through the crack. During the test, the amount of time that it takes for a water column with height of 280 mm to pass through the cracked specimen is recorded. The water exit point is at the same level as the bottom surface of the specimen. A schematic of the setup is shown in Figure 2.

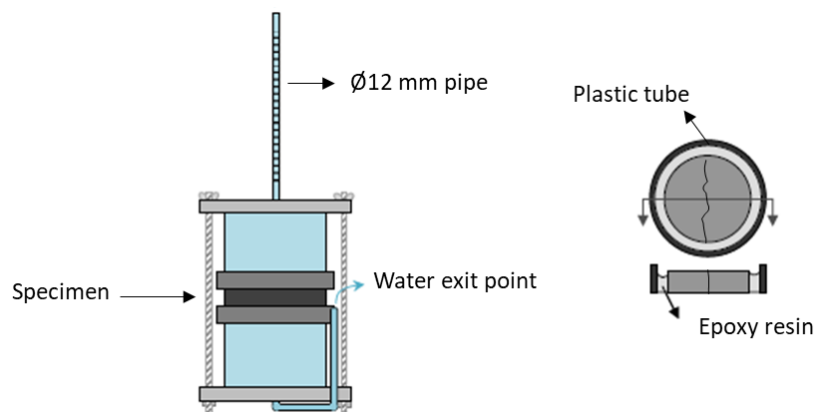


Figure 2 - Overview of the test set up with detail of the specimen on the right. Adapted from Snoeck (2015).

During the preparation of the specimens, the cylinders with a diameter of 100 mm and height of 200 mm were first cut into cylinders with a diameter of 80 mm and height of 20 mm. They were then cracked (in order to obtain a crack width upon reloading of 200-250  $\mu\text{m}$ ) at the age of 28 days, by means of a Brazilian splitting test. After cracking, the specimens were placed inside a PVC mold with a diameter of 100 mm and the gap between the specimen and the mold was filled with epoxy resin. Care was taken that no resin filled the crack by means of taping the samples. The epoxy (Figure 2, right side) also guaranteed unidirectional flow during water permeability testing. Once the resin hardened, the specimens were vacuum saturated for 24h with demineralized water. After that, the specimens were placed in the testing setup for the measurements. To account for possible unsteady



flow due to the presence of air bubbles or loose particles inside the crack, the water flow was recorded for five consecutive days.

In order to assess a possible healing of the cracks over time, the specimens were subjected to wet dry cycles after the five-days testing for the immediate sealing in order to stimulate healing. The cycles consisted of 12 h of immersion in demineralized water and 12 h of exposure of the specimens to air for a period of 28 days.

The water permeability coefficient of each series (before and after healing) was then calculated considering the average flow of the five days. For that, Darcy's law was used:

$$k = \frac{a_f \cdot T_s}{A \cdot t_f} \cdot \ln\left(\frac{h_0}{h_f}\right)$$

With,  $a_f$  = cross-sectional area of the fluid column [ $\text{m}^2$ ];  $T_s$  = specimen thickness [ $\text{m}$ ];  $A$  = surface area of the sample subjected to the flow [ $\text{m}^2$ ];  $t_f$  = measured time [ $\text{s}$ ];  $h_0$  = initial pressure head [ $\text{m}$ ];  $h_f$  = remaining pressure head [ $\text{m}$ ] and  $k$  = coefficient of water permeability [ $\text{m/s}$ ].

## **2.7. Monitoring of autogenous shrinkage**

After the curing period, the specimens were demolded and wrapped with aluminum tape to avoid moisture exchange with the environment, thus reducing the effects of drying shrinkage. Two measuring points were glued to the side surfaces of the specimens (except for the troweled surface due to the existence of shape irregularities that could hinder the measurements), placed 200 mm apart on the central line of the specimens' surface. At the position where the measuring points were placed, the tape was removed so that the points were glued on the surface of the specimen and not on the tape. Only a portion of the tape, the same size as the measuring point, was removed. The measurements were performed once per day for 28 days and started 24 h after the first contact of cement with the mixing water. The measurements were performed in a room with a controlled atmosphere of  $20 \pm 2$  °C and  $60 \pm 5\%$  RH where the specimens were kept during the complete testing period.

## **2.8. Salt scaling resistance and air void analysis**

The resistance against salt scaling under frost attack was tested following an adaptation of the standard EN 12390-9 [28] with the temperature cycle as shown in Figure 3. The freezing medium

used was a 3% NaCl solution (prepared with demineralized water), corresponding to a thin layer of 3 mm poured on the top surface of the specimens.

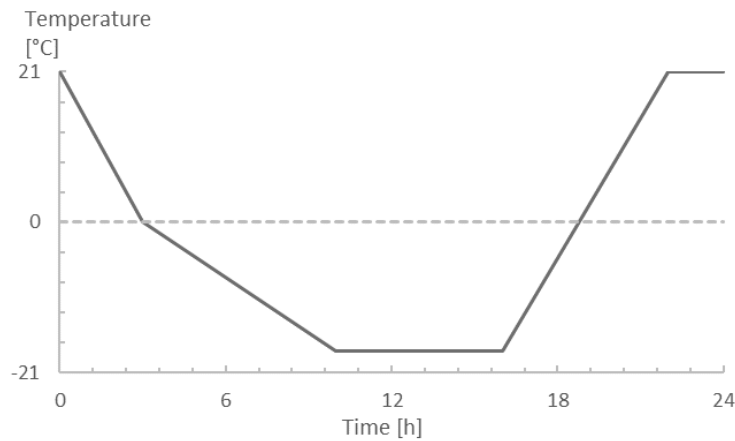


Figure 3 - Temperature cycle.

For each concrete mixture one cylinder with a diameter of 100 mm and height of 200 mm was cut into three cylinders with a diameter of 100 mm and a height of 50 mm were used. At 25 days of age, the specimens were placed into a PVC tube with an inner diameter of 100 mm and a height of 70 mm. A thin layer of epoxy was applied at the sides to prevent any leakage of the freezing fluid from the top of the surface. From the 26<sup>th</sup> till the 28<sup>th</sup> day a thin layer of 3 mm of demineralized water was poured on the top surface of the specimens to verify the existence of any leakage. On the 28<sup>th</sup> day the specimens were placed inside an insulating recipient and the freezing medium was poured on top of them. The specimens were covered with a plastic sheet and placed inside the freezing chamber. After 7, 14, 28, 42 and 56 cycles, the scaled material was collected and the freezing solution was renewed.

### 3. RESULTS AND DISCUSSION

#### 3.1. Absorption capacity of the SAPs and degradation of the crosslinker

In terms of water absorption (Table 3), SAP1 and SAP2 presented very similar values in all tested fluids and in mixing water. SAPX on the other hand, showed a lower absorption capacity in all fluids. In comparison to SAP1 and SAP2, a reduction around 50% was achieved for SAPX in terms of absorption capacity in the cementitious media while 86% less absorption was found in demineralized water. The reduced initial absorption capacity of SAPX can be related to the presence of the second crosslinker that contributes to a lower absorption capacity at initial stage. The value

obtained for SAPX in cement filtrate and demineralized water after 10 min are in accordance with the expected values shown in Figure 1. This reduced water absorption in cementitious fluids enabled the use of a dosage of SAPX twice the value of SAP1 and SAP2 for the same amount of additional water, as described in Table 2.

Table 3 - Water uptake [g/g] of the SAPs in demineralized water, cement filtrate solution, upon mixing in cement paste and in concrete, measured 10 min after first contact of the SAPs with the fluid.

SAP	Water uptake [g/g]			
	Demineralized water (n=3)	Cement filtrate solution (n=3)	Cement paste	Concrete
SAP1	297 ± 14	34 ± 6	22	21
SAP2	288 ± 5	37 ± 8	27	24
SAPX	40 ± 1	16 ± 1	13	11

Considering the degradation of SAPX in time, a significant increase in water uptake was observed after immersion in cement filtrate. After 24 h of continuous exposure to the cement filtrate solution, the absorption capacity in demineralized water increased by a factor of 2.5. At the mark of 72 h of continuous exposure the absorption capacity was 3.3 times higher than the initial one (Figure 4).

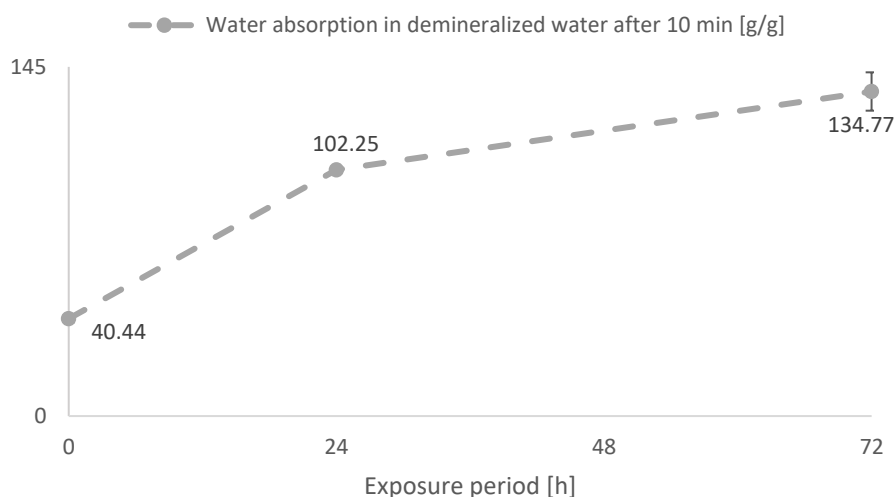


Figure 4 - Swelling capacity of SAPX after hydrolysis of the alkali unstable crosslinker at different exposure times.

The increase in the absorption capacity of SAPX is related to the hydrolysis of the alkali-unstable crosslinker. Although there is a considerable increase, the value after 72 h of exposure is still lower than the expected value for a NaAMPS-based SAP with 0.15 mol% of crosslinker (see Figure 1). This indicates that the alkali-unstable crosslinker might not have degraded completely in the cement filtrate solution within the evaluated time frame. After 72 h, the increase in the water absorption seems to develop to a lower rate, indicating that it tends to stabilize shortly after that period. This could be an indication that the crosslinker would not completely hydrolyze in the cement filtrate solution regardless of the time of exposure. Apart from that, after some time a second process might start, namely extra complexation of the sulfonic acid groups with the high concentration of  $\text{Ca}^{2+}$  ions inside the pores. With this complexation a counter reaction of extra ionic crosslinking can take place, which has the opposite effect to the hydrolysis of the second crosslinker.

The infrared spectra are shown in Figure 5. No observable difference was found in the chemical structure of SAPX after the different periods of alkali exposure, which indicates that the polymer has a very stable structure in a cementitious environment (at least with regard to the functionalities which are detectable with IR spectroscopy).

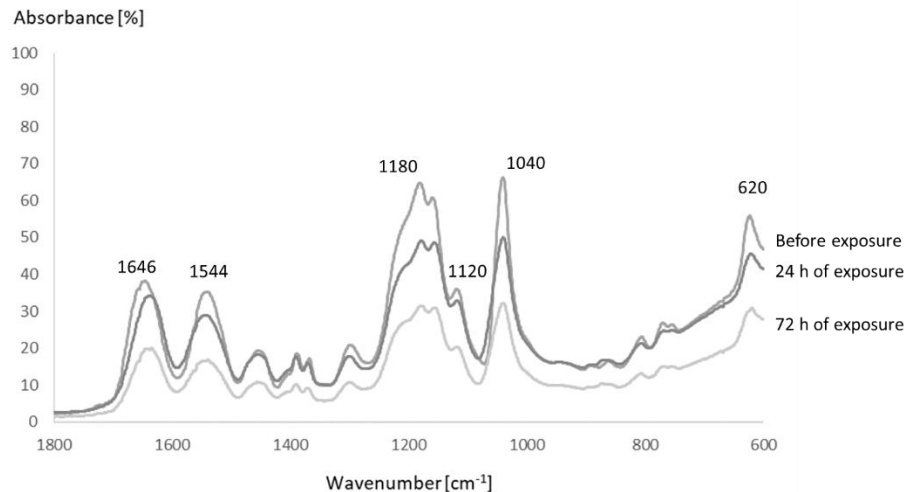


Figure 5 – FT-IR spectra of SAPX before and after alkali exposure at different times.

Some characteristic peaks for a NaAMPs-based SAP are presented in Table 4 and indicated in Figure 5. As for the degradation of the alkali-unstable crosslinker, for the type of unstable crosslinker used, the two most important peaks would be apparent between wavenumbers 1050-1150  $\text{cm}^{-1}$  and between wavenumbers 1725-1750  $\text{cm}^{-1}$ . However, these are not seen in the spectra mainly because

of the low concentration applied (1 mol%), so no degradation can be observed by analyzing these isolated peaks.

Table 4 - Characteristic peaks for a NaAMPS-based SAP.

Wavenumber [ $\text{cm}^{-1}$ ]	Characteristic peak
620	$\text{SO}_3^-$
1040	symmetric stretch of S=O
1120	S=O stretch $\text{SO}_3^-$
1180	asymmetric stretch of S=O
1544	N-H bend vibration
1646	C=O stretch amide functionality

### 3.2. Water permeability and instant sealing

During the course of the measuring time of five days, no significant differences were found for the water flow of the different specimens. In order to compare the difference in the efficiency of the SAPs, the average value of the coefficient of water permeability over the five days was considered as representative for each series (Figure 6).

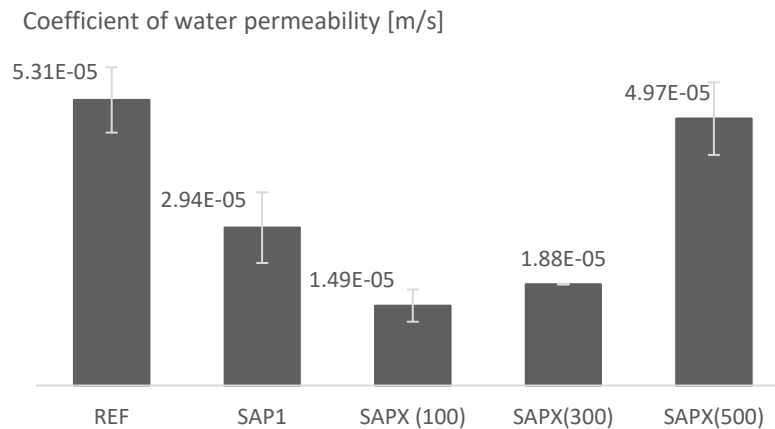


Figure 6 - Average values of water permeability coefficient for the different cracked concrete specimens.

When analyzing the average values (Figure 6), both SAPs showed a reduction in water permeability of the cracked specimens, but different rates of reduction were found. SAP1 (360  $\mu\text{m}$ ) promoted a reduction of 45% while for SAPX, the reduction was dependent of the particle size of the SAP. For a  $d_{50}$  of 100  $\mu\text{m}$  the best result was achieved with a reduction of 72% in comparison with the cracked

reference. A reduction of 65% and 7% was observed for the  $d_{50}$  of 300 and 500  $\mu\text{m}$ , respectively. The difference in performance of the mixtures containing SAPX was already expected. Considering the same dosage of SAPX, the use of bigger particle sizes will reduce the relative total number of SAP particles in the mixtures. As the SAP particles act as stress concentrators [29], more smaller SAPs will be exposed at the crack walls. Due to the increasing swelling effect by SAPX, the swelling will even further increase over time in comparison to the moment at which the SAPs were added to the mixture, leading to a lower recorded permeability.

In [30], the authors tested four different SAPs (all based on acrylic acid chemistry) with mean particle size in the range of 200 to 300  $\mu\text{m}$  and absorption capacity around 20 g/g in cement filtrate solution and around 200 g/g in demineralized water. A reduction of up to 98% in the total water flow was obtained for dosages of SAPs of 4%, 5% and 13% over the mass of cement. However, given the considerably higher amount of SAPs, a reduction of 87% was found for the compressive strength of the SAP specimens, in comparison to the reference without SAPs. In their study, a different water permeability test method was used.

The results reported in [31] showed a reduction of 34% and 52% in the water flow of cracked specimens with a crack width in the range of 250 to 350  $\mu\text{m}$  for a dosage of SAPs of 0.5% and 1%, respectively, over the binder weight. The authors used a polyacrylate-co-acrylamide spherical SAP. A reduction of 21% and 44% was found for the compressive strength at 28 days, in comparison to the reference without SAPs. In the same study, the authors have also used a different water permeability setup. In both cases, the performance of SAPX can be considered to be positive in comparison to the results reported earlier. The impact of SAPX on the compressive strength will be presented in section 3.5.

Considering the variation of results for each series, the standard deviation ranges from 11% to 23% of the mean values (depending on the series). This variation can be directly related to the geometry of the crack. The cracking method adopted does not provide a uniform crack width over the length of the crack since it simulates a realistic crack. In addition to that, the measurements of the crack width were performed at the crack mouth, on both sides of the specimens, but they might not reflect the internal geometry and tortuosity of the crack. According to [32], the internal geometry of the crack (which cannot be controlled, regardless of the chosen cracking technique) can cause a difference of more than 25% in the permeability of specimens with an identical nominal surface crack width.

Comparing the properties of the SAPs and the concrete compositions, the dosage of SAPX was double the dosage of SAP1 which means more particles of SAPX are present in the concrete mixture (for  $d_{50}$  100  $\mu\text{m}$  and 300  $\mu\text{m}$ ) and the probability of more SAPs being distributed along the crack is higher for the concrete made with SAPX.

Figure 7 shows the coefficient of water permeability after the healing regime. No significant healing was noted for any of the series, which can be explained on the one hand by the relatively high water-to-cement ratio of the concrete mixtures and on the other hand by the type of cement used (CEM III-B 42.5N – LH/SR). The high amount of water used in the mixing process and the reduced amount of clinker present in the cement are not ideal for healing purposes given the reduced amount of unhydrated binder particles available for further hydration, which is one of the main mechanisms of healing.

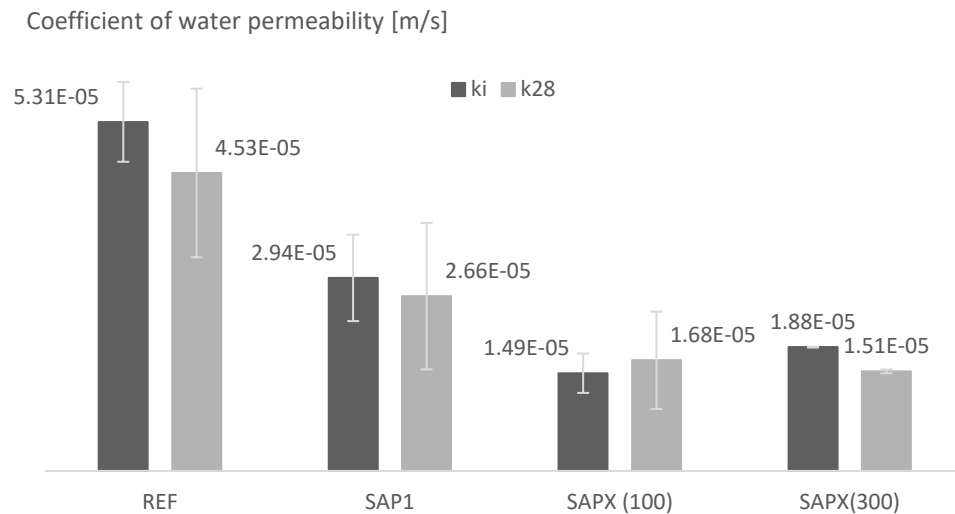


Figure 7 - Average values of water permeability coefficient for the different concrete mixtures before and after healing cycles. “ki” represents the coefficient of immediate sealing and “k28” represent the coefficient after 28 healing cycles.

A larger variability can also be noted in the results for the healed specimens in comparison with the specimens before the healing cycles. This could be an indication that possible newly formed healing products are being washed out with the ascending and descending movement of the water during the cycles. The same could be expected for dry SAP particles inside the cracks, especially with small size.

### 3.3. Reduction of autogenous shrinkage strain

All SAPs promoted a considerable reduction in the shrinkage strain over time, when compared to the reference mixture without SAPs (Figure 8). For both SAP1 and SAP2 a complete mitigation of the shrinkage was obtained. For SAPX a reduction of 66% in shrinkage strain was obtained, in comparison to the reference mixture. Although the shrinkage was not completely mitigated as in the case for SAP1 and SAP2, the reduction promoted by SAPX might be enough to prevent shrinkage cracking at the early ages. For the whole testing time, the strain for the SAPX mixture remained below  $-100 \mu\text{m/m}$ , while for the reference mixture this value was reached after three days and increased further to around  $-200 \mu\text{m/m}$  after 10 days. The difference of SAPX compared to SAP1 and SAP2 is due to the increased swelling ability over time, thus possibly partially reabsorbing the mixing water, leading to slightly less potential for internal curing. Furthermore, the rate of shrinkage levels after approximately 8 to 9 days, while the reference continues to shrink, showing the benefit of using SAPs to mitigate autogenous shrinkage.

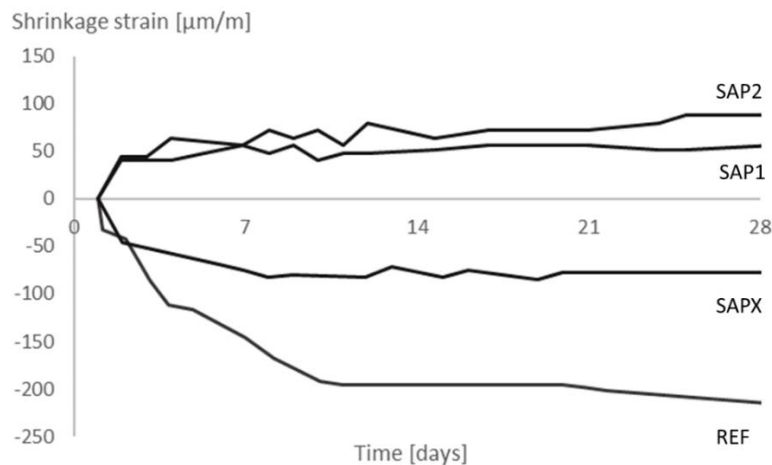


Figure 8 - Autogenous shrinkage strain of SAP-containing mixtures and reference mixture.

### 3.4. Salt-scaling resistance

Figure 9 shows the cumulative scaled material of the studied concrete mixtures up to 56 freeze-thawing cycles. All SAPs promoted a considerable reduction in the amount of scaled material over the 56 cycles in comparison with the reference mixture. After 28 cycles, the reduction was around 34%, 49% and 55% for SAP1, SAP2 and SAPX, respectively. The results are in compliance with the findings of [33, 34].



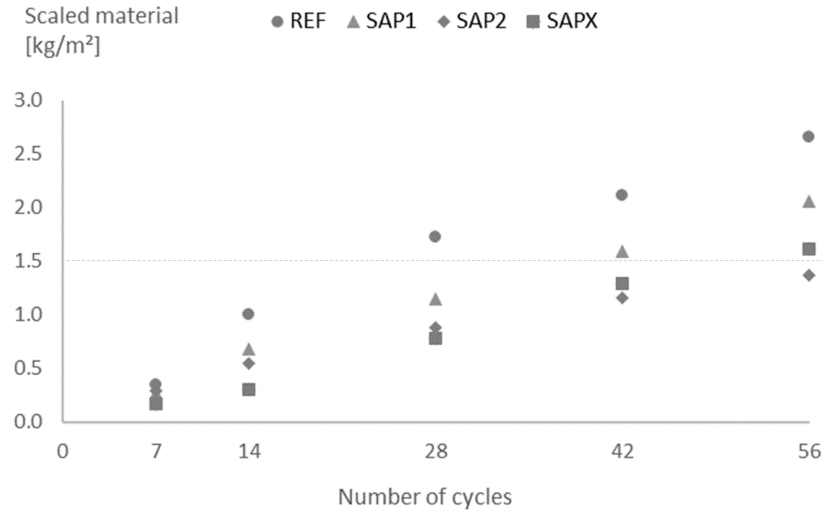


Figure 9 - Cumulative amount of scaling material for the studied concrete mixtures under freeze-thaw cycles with de-icing salts.

In literature, some failure thresholds are usually mentioned regarding the amount of scaled material. In [34] and [35] a value of  $1.5 \text{ kg/m}^2$  is cited (also indicated in Figure 9), while the Belgian standard for concrete paving flags [36] mentions a limit of  $1 \text{ kg/m}^2$ , both after conducting 28 freeze-thaw cycles. All SAPs enabled the production of a concrete mixture in compliance with both thresholds cited up to 28 freeze-thaw cycles. At the mark of 28 days the cumulative amount of scaling material (in  $\text{kg/m}^2$ ) was  $1.14 \pm 0.07$  for SAP1,  $0.88 \pm 0.18$  for SAP2,  $0.78 \pm 0.03$  for SAPX. On the other hand, the reference mixture presented a scaling around  $1 \text{ kg/m}^2$  already after 14 cycles ( $1 \pm 0.06 \text{ kg/m}^2$ ) and a value higher than 1.5 ( $1.73 \pm 0.24$ ) between the 21 and 28 cycle. In the air void analysis, the spacing factors found were  $0.45 \pm 0.01 \text{ mm}$  for the REF mixture,  $0.38 \pm 0.03 \text{ mm}$  for SAP1,  $0.29 \pm 0.01 \text{ mm}$  for SAP2 and  $0.36 \pm 0.02 \text{ mm}$  for SAPX. In fact, the SAPs promoted a reduction in the spacing factor of the concrete mixtures, which is related to an increase in salt-scaling resistance of the SAP concrete mixtures. On the other hand, no linear relation was found with the amount of scaled material and the values of the spacing factors. The test method used to determine the spacing factor (given by [26]) assumes that all air voids in the material have spherical shapes, which is not the case for the SAPs used.

Apart from that, it can be seen that SAPX performance was comparable to SAP2 during the whole testing period and slightly better than SAP1 already from 28 cycles onwards.

### 3.5. Effects on the compressive strength

The values of the average compressive strength of all concrete mixtures are shown in Figure 10. All SAP-containing mixtures presented a reduction in compressive strength in comparison to the reference mixture without SAPs, which was already expected given the macropore effect related to the water release and drying of the swollen SAP particles in time.

The reduction varied in the range of 10% (SAPX(500)) to 22% (SAP2), but considering the standard deviation it can be assumed that all SAP-containing mixtures performed in the same way. On the other hand, considering that the dosage of SAPX was twice the one used for both SAP1 and SAP2, the fact that it causes the same reduction in strength but with the achievement of many other positive features (reduction of salt-scaling, reduction of shrinkage strain and impressive reduction in water permeability of cracked specimens) is very promising.

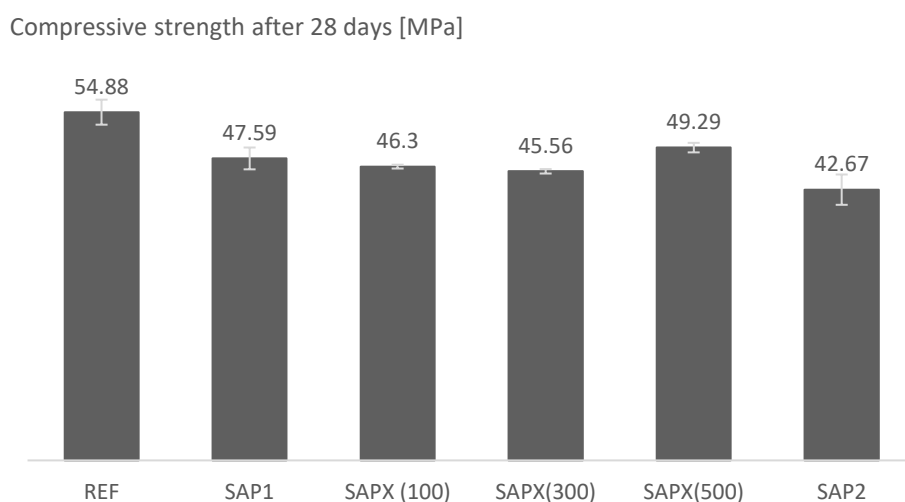


Figure 10 – Average compressive strength measured after 28 days.

#### 4. CONCLUSIONS

The use of superabsorbent polymers in cementitious materials enables the production of smart, more durable and multifunctional materials. In order to achieve the best performance, the properties of the superabsorbent polymers must be fine-tuned to the specific application of the cementitious material in question.

In this study, two commercial SAPs were able to completely mitigate the autogenous shrinkage strain and significantly reduce the scaling of material during the freeze-thaw cycles. Also, in terms of compressive strength, both SAPs showed a very similar impact on the mixtures, when compared to the reference without SAPs.

The "in-house" developed SAPX showed positive results in all tests. For the freeze-thaw attack the mixture produced with SAPX performed in a comparable way with SAP2, which was the best amongst the three SAPs in terms of reducing the salt scaling damage under freezing and thawing, and better than SAP1, which was not specially developed for that purpose. Also for the reduction in shrinkage strain a positive performance was obtained with the mixture containing SAPX. Even though a complete mitigation was not achieved, as it was the case for both SAP1 and SAP2, the reduction of shrinkage strain promoted by SAPX might as well be enough to prevent shrinkage cracking at early ages depending on the application (conditions of the structure). In terms of compressive strength, the effects of SAPX were comparable to both SAP1 and SAP2.

For the immediate sealing of cracks SAPX performed better than SAP1, reducing almost twice more the water permeability of the cracked specimens. The addition of the alkali-unstable crosslinker in the composition of SAPX enabled the use of a higher dosage of SAPX with the same effect on the compressive strength as it was observed for SAP1, for example. The higher dosage of SAPX represents a larger relative number of SAP particles in the cementitious material which is fundamental for a better sealing of cracks. As a matter of comparison, we can consider a new mixture with twice as much SAP1 (1 m% instead of 0.5 m%) in order to increase the amount of SAP particles in the mixture and by that increase the immediate sealing effects. Following the absorption capacity of SAP1, that mixture would present a total water-to-cement ratio of 0.67. The expected compressive strength for such mixture is around 40 MPa at 28 days, which represents a further reduction of 16% in comparison to the value found for the concrete with 0.5 m% of SAP1 and 27% in comparison to the reference mixture without SAPs.

With the positive performance of SAPX, with superior scaling efficiency over commercially available SAPs, this innovative material represents a promising future towards the introduction of a new type of SAP in the construction industry. Nevertheless, further improvement and research is needed. Considering the use of SAPX only for sealing purposes, additional superplasticizer without additional water to compensate the loss in workability by the addition of SAPs will be investigated. This would enable even higher amounts of SAPs without corresponding reductions in compressive strength. The microstructure may be affected and will be subject of study.

After the preliminary results presented in this paper, SAPX was used in a large-scale testing campaign where 154 m<sup>3</sup> have been produced for the construction of five reinforced concrete walls. SAPX was then applied in two of those walls, which remained crack free for over five months of monitoring. A reference wall without SAPs presented cracks five days after casting.

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