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Influence of superabsorbent polymers on the chloride ingress of mortar measured by chloride diffusion and a quasi-steady-state migration test

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Abstract

The ingress of chloride ions is a serious threat for concrete structures. Superabsorbent polymers (SAPs) are interesting additions to cementitious systems due to their property of absorbing water during mixing and releasing it at a later time to provide internal curing, thereby reducing shrinkage and promoting durability. In addition, SAPs can improve the regain in impermeability of cracks by swelling and blocking the crack and promoting autogenous healing. The current study investigates the influence of the addition of SAPs without additional mixing water to the chloride ingress in cracked mortar via diffusion and quasi-steady-state migration testing. Filtration tests showed that the charge-screening effect in a NaCl solution is more dominant than for cement filtrate solution during swelling of SAPs. After wet/dry cycling for a month, subsequent chloride diffusion tests with 2 and 6 weeks of exposure showed that the addition of SAPs improved the performance with respect to a reference mix with the same total water-to-cement ratio. A reference mix with the same effective water-to-cement ratio as the SAP mix had a comparable performance to the SAP mix. One set of chloride diffusion experiments showed that the SAP mix was the only one successfully preventing chloride ingress into the deepest zone of the crack. The superior performance of the series with SAPs was also confirmed by migration testing where cracked and healed specimens obtained a migration coefficient which was only 12% higher than uncracked specimens.

Keywords: self-healing, super absorbent polymers, hydrogel, filtration testing, chloride diffusion, quasi-steady-state chloride migration

1. Introduction

Due to its low tensile strength, crack formation in concrete is inevitable. These cracks form a gateway for aggressive substances to the deeper concrete matrix and the steel reinforcement. This can cause concrete deterioration and reinforcement corrosion, which increases the need for repair as otherwise the service life would be significantly shortened. Chloride-induced corrosion is one of the main causes for degradation and failure of reinforced concrete structures [1]. When chlorides penetrate the concrete up to the level of the reinforcement steel and the chloride concentration reaches a critical value, the passivation layer breaks down locally which causes pitting corrosion and a decrease of the steel cross section. Furthermore, the formation of corrosion products, which is an expansive reaction, causes stresses in the concrete, which can lead to cracking and spalling [2]. Chloride ions can penetrate into the concrete through the above mentioned crack formation or through chloride diffusion [3].

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In order to solve this problem, self-healing concrete, which has the ability to close its own cracks, is a widely studied topic. To a certain extent, concrete has the potential for self-healing without the addition of additives. This phenomenon is called autogenous healing [4, 5], and is mainly caused by the ongoing hydration reaction of unhydrated cement, pozzolanic activity, and the precipitation of calcium carbonate ($CaCO_3$) due to carbonation [5]. A model focusing on self-healing resulting from hydration of unreacted cement showed that the initial cement content, the granulometric composition of the cement and the degree of hydration at cracking significantly influence the self-healing potential [6]. To stimulate the autogenous healing of concrete, researchers have been investigating the use of superabsorbent polymers (SAPs) [7]. SAPs are cross—linked polymer networks with the ability to swell when in contact with a solution [8, 9]. The swelling, which can be 1000 times the mass of the SAP, is dependent of the osmotic pressure difference between the SAP and the external solution [10]. When a crack is formed in the concrete, and the SAPs at the crack surface come in contact with a liquid, they will block the crack and prevent further ingress, as described in the literature using water permeability tests and visualization techniques [11-15]. Besides the sealing of the crack, autogenous healing is promoted by providing water to continue the hydration reaction of cement [11, 16]. SAPs provide water in the dry conditions of the wet/dry cycle, as well as moisture in conditions of high relative humidity [7, 17, 18]. With the dissolution of carbon dioxide in the vicinity of these water sources, calcium carbonate crystals are likely to be precipitated, and the hydration of unhydrated cement particles is promoted. Compared with a reference, the use of SAP results in 40% more hydration [17]. This healing ability is maintained for at least 10 years [19, 20] in strain-hardening mixtures containing SAPs, resulting in a recovery of impermeability and mechanical properties. Even in alkali-activated mixes, the use of SAP promotes autogenous healing [21].

Other than their self-sealing and self-healing properties in concrete, SAPs can increase the durability of concrete in various ways. In the fresh state of mortar or concrete, SAPs absorb a part of the mixing water, causing them to swell. During the hardening of the material, the swollen SAPs create air voids which causes them to have an air entrainer effect. Due to this air entrainment, concrete has a better resistance against freeze-thaw damage [22-24]. SAPs can also act as an internal curing agent, reducing the autogenous and plastic shrinkage of concrete [25, 26]. Internal curing consists of providing enough water in the specimens which is released at the correct time to prevent self-desiccation. During concrete hardening, SAPs slowly release the absorbed mixing water which can be used for further hydration and ensures that the internal relative humidity remains constant [27-30]. A more detailed explanation on the influence of SAPs on rheology, internal curing to mitigate plastic and autogenous shrinkage, as well as self-sealing and self-healing of cracks, and improvement of freezing-and-thawing can be found in a recent state-of-the-art report [9, 31].

SAPs have recently been applied in the concrete of walls of an in-field large-scale testing campaign [32]. A cradle-to-gate Life Cycle Assessment linked to this large-scale testing campaign showed that the impact of the incorporation of SAPs in the mix design was negligible [33]. However, when considering a design case of 100 years and estimating the need for repair from a hemispherical corrosion pit model, the wall with SAPs had a reduction of 20% of the environmental burdens linked to the Fresh Water Aquatic Ecotoxicity impact category, showing that the inclusion of SAPs can be a sustainable option.

Several test methods have been developed and used to assess the efficiency of self-healing materials such as microscopy, gas and water permeability, ultrasonic pulse velocity, X-ray and neutron radio-/tomography, repeated mechanical testing, a wide range of non-destructive testing, absorption and/or chloride penetration [34, 35]. The promoted healing by SAPs has already been the subject of in-depth studies in the literature [7, 11-16, 19, 20], as has been described above. However, results concerning chloride penetration in cracked and healed samples are rare. This research focuses on the latter and

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evaluates the self-healing efficiency of mortar with superabsorbent polymers through a chloride diffusion and a quasi-steady-state chloride migration test. The effect of the addition of SAPs to mortar on the chloride diffusion coefficient depends on the total water-to-cement ratio. Due to the absorption of water by the SAPs during mixing, the workability of the fresh mortar decreases. Therefore, additional mixing water is sometimes added to the mixture to compensate for the absorption. Research showed that concrete specimens containing SAPs without additional mixing water, had a decreased chloride diffusion coefficient due to matrix densification [36, 37]. However, when additional mixing water is added, the diffusion coefficient increases [36, 37]. Hasholt and Jensen studied the influence of the addition of SAPs in concrete both with and without additional water on the chloride migration, measured according to NT BUILD 492 [38]. The research concluded that the chloride migration coefficient depends on the gel space ratio, which is the ratio between the volume of gel solid and the space available. The addition of SAPs to the concrete has a beneficial effect on the chloride ingress if there is an increase in gel space ratio [39]. The latter is the case when no additional water was added to compensate for the absorption of the SAPs or when extra water was added causing an increase in the degree of hydration due to internal curing, which is the case if the W/C is below 0.42, following Powers' model [39].

In previous research, the effect of SAPs on the chloride penetration is usually tested on uncracked specimens and high-strength concrete [36, 37, 39, 40]. A recent study developed a multiphysics-lattice discrete particle model to simulate the effect of autogenous and stimulated healing on the chloride ingress, which was validated on an experimental database of ultra-high performance concrete [41]. The current paper investigates the chloride diffusion and chloride migration coefficient of mortar containing SAPs with and without additional mixing water on cracked samples exposed to cyclic wet/dry conditions to stimulate autogenous healing.

2. Materials and methods

2.1. Superabsorbent polymers (SAPs)

The superabsorbent polymers (SAPs) were a commercially available cross-linked copolymer of acrylamide and acrylate (Floset 27 CC, Floerger SNF, France) produced by means of bulk polymerization (d50 = 307 µm). The particle size of the SAPs is less than 600 µm.

The swelling capacity of the SAPs was determined using the filtration method following the recommendations of RILEM TC 260-RSC [42]. A certain mass of dry SAPs (m_{SAP}) are added in a beaker to which approximately 100 mL (m_{liquid}) of test liquid is added. After a certain time interval, the SAPs are filtered from the solution and the mass of the filtered liquid is recorded ($m_{filtered}$). The sorption capacity SC can then be determined as:

$$SC = \frac{m_{liquid} - m_{filtered}}{m_{SAP}} \tag{1}$$

The sorption capacity of the SAPs was determined in four different testing liquids: (1) demineralised water, (2) NaCl solution, (3) cement filtrate solution, and (4) NaCl solution made with cement filtrate. The cement filtrate was made by mixing cement (CEM I 52.5 N) with demineralised water (W/C=5) for approximately 24 hours. The concentration of the NaCl solutions was 33 g/L solution, which is the same concentration as used for the chloride diffusion test.

2.2. Mortar mix composition

To test the chloride diffusion and chloride migration in (cracked) self-healing mortar, three different mix designs were made. The first mix was a reference mortar "REF" with a sand-to-cement ratio of 3 and a water-to-cement (W/C) ratio of 0.5 which corresponds to the standard mortar mix design described by EN 206-1 [43]. This resulted in a cement content of approximately 500 kg/m³, which was kept constant for all mix designs to account for the chloride binding capacity of cement.

For the second mix "SAP"0.7 m% of superabsorbent polymers (with respect to the mass of cement) were added without additional mixing water. Note that the total water-to-cement ratio $(W/C)_{tot}$ of the REF and SAP mix was equal to 0.5. However, the SAPs will absorb part of the mixing water. Based on pre-trials, where the workability of mortars was measured with a flow table test (EN 1015-3 [44]), it was determined that 19.4 g of additional water per g of SAPs is needed to obtain a similar workability. This value is in line with 20 g of additional water per g of SAPs reported in previous research on the same type of SAPs [45]. The loss of workability due to the addition of SAPs was compensated via the addition of a superplasticizer (MasterGlenium 51 concentration 35%, BASF, Belgium). This type of superplasticizer relies on modified polycarboxylic ether polymers to increase workability. In literature, the amount of water which the SAPs absorb is used to calculate $(W/C)_{add}$ [46]. By subtracting $(W/C)_{add}$ from $(W/C)_{tot}$ the effective ratio $(W/C)_{eff}$ can be calculated. For mixes without superabsorbent polymers the total and effective water-to-cement ratios are equal. The type of superabsorbent polymer used in this study is retentive, meaning that the water is released after final setting [47-49].

The third mix was a reference mortar (without superabsorbent particles) for which W/C was taken equal to $(W/C)_{eff}$ of the SAP mix, or in other words the amount of water was reduced by the estimated amount of water taken up by the SAPs in the SAP mix. This mix was termed "REF-low W/C". The lower volume of water per m³ was compensated by additional sand.

A dosage of 0.5 – 1.0 m% of superabsorbent polymers with respect to the cement mass has been used in literature to promote crack healing [45]. The dosage of 0.7 m% which was used in this study was based on trial tests. It was found that for dosages higher than 0.7 m% of superabsorbent polymers an increase in superplasticizer dosage could no longer compensate the loss of workability in a reference mix with a corresponding W/C ratio equal to the $(W/C)_{eff}$ of the SAP mix.

Table 1: Mix designs of three different mixes ($(W/C)_{tot}$ is the water-to-cement ratio considering all of the water, $(W/C)_{add}$ is the ratio of the water absorbed by the SAPs with respect to the cement weight, and $(W/C)_{eff}$ is the effective water-to-cement ratio)

Materials	**REF**	**SAP**	**REF-low W/C**	
CEM I 52.5 N	502.9	500.1	497.4	kg/m³
Sand 0-5 mm	1508.8	1500.3	1678.7	kg/m³
Water	251.5	250.1	182.2	kg/m³
SAPs	-	3.5	-	kg/m³
Superplasticizer	-	7.5	7.5	kg/m³
$(W/C)_{tot}$	0.500	0.500	0.366	-
$(W/C)_{eff}$	0.500	0.364	0.366	-
$(W/C)_{add}$	-	0.136	-	

Cylinders (height 200 mm, diameter 100 mm) were cast for each mix design, along with prisms (40 x 40 x 160 mm³) to test the strength. For each mix design two batches were prepared immediately one after the other to have enough mortar to produce all specimens. The workability of each batch was determined by a flow table test (according to EN 1015-3, table not lubricated with oil but with a wet cloth) [44]. The cylinders were vibrated with a vibration needle. The prims were vibrated on a vibration table. The specimens were demoulded after 1 to 2 days in a curing room (20 °C and >95 % RH). They were then stored again in the curing room until cracking.

2.3. Air void content

The air content of the hardened mortar was determined at the age of 28 days using an air void analyser according to the standard EN 480-11 [50]. This measured air content includes entrapped air voids and SAP voids created by the absorption of mixing water by the superabsorbent polymers. Capillary pores with pore sizes ranging from 10 nm until 1 µm [51, 52] are not included in this value since the air void analyser is unable to detect pores of this order of magnitude (< 1 µm).

Mortar slices with a height of 20 mm were cut from the same cylinders used for chloride diffusion and migration. After cutting, one side of the mortar slices was polished and cleaned in order to obtain a flat surface with no height difference between the paste and the aggregate. To obtain a better contrast between the pores and the cement paste, a black ink layer was applied to the polished surface using a permanent marker. Subsequently, barium sulphate ($BaSO_4$) powder was pressed into the air voids and the excess powder was removed. The air void analysis was then performed by an automatic air void analyser (RapidAir 457).

2.4. Cracking method and stimulated healing conditions

The cylinders (height 200 mm, diameter 100 mm) were sawn into discs with a height of 50 mm at an age of 21 days. At an age of 28 days these were cracked in a Brazilian splitting test. No specific measures were implemented to prevent superabsorbent polymers from falling out of the specimen due to the cracking action; therefore, a loss of some of the superabsorbent polymers at the crack wall is to be expected. Hose clamps were used to tie the two halves back together. To keep the crack open, silicon sheets with a nominal thickness of 100 µm and 200 µm were inserted at the outer ends, reducing the crack length to 70 mm [53, 54].

For each specimen three pictures were taken on each side with a microscope camera (Leica DMC 2900). The location of the pictures was not fixed in order to prevent local damage to skew the determination of the crack width, according to the guidelines proposed by Round Robin Test 5 of the EU Cost Action SARCOS [55, 56]. Five measurements of the crack width were performed on each picture, resulting in 30 measurements per specimen.

After cracking, healing was promoted in all specimens by subjecting them for 28 days to wet/dry conditions (1 h wet and 23 h dry). The wet/dry cycling occurred in an airconditioned room (20 °C and 60% relative humidity) with separate containers for each mix. The uncracked specimens were placed in the same container and were also subjected to wet/dry conditions for 28 days.

2.5. Chloride diffusion

After healing, the specimens for chloride diffusion were stored for a few days in a dry laboratory environment, after which all faces except the circular exposure surface were covered with an epoxy coating. After curing of the coating, all specimens were submerged for 2 days in demineralized water to ensure a comparable water content. Then, the specimens were submerged in containers with a solution of 33 g NaCl per litre of solution. This is significantly lower than the concentration described by NTB Build 443 [57] and is more comparable to the concentration of sea water.

Four specimens of each series were taken out of the solution after 1, 2, 4 and 6 weeks, respectively. The chloride ingress was visualized and measured by spraying silver nitrate ($AgNO_3$) on a surface perpendicular to the crack. A light grey colour indicates that there are chlorides present in the mortar. First specimens were opened along the crack. Then, one half of the cracked specimen was split in two using a Brazilian splitting test. The depth of chloride ingress was measured perpendicular to the crack every 2 mm on two quarter specimens (see Figure 1).

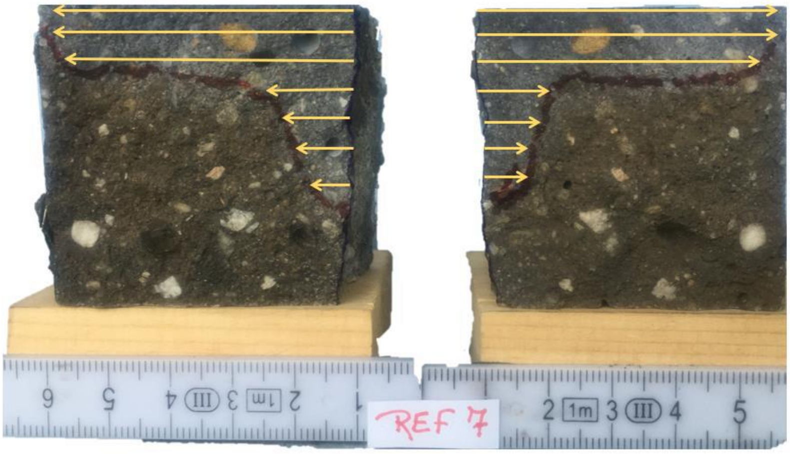

Figure 1: Measurement of chloride ingress via spraying of $AgNO_3$ solution. Arrows show the direction of the measurement.

2.6. Quasi-steady-state chloride migration

A separate set of cracked and uncracked disc specimens was used for the quasi-steady-state chloride migration method [58]. For each mix design, 4 uncracked and 4 cracked samples were tested after 28 days in stimulated healing conditions. Before placing the specimens in a cell, they were vacuum saturated in water for at least 12 h. The upstream and downstream cells were filled with a 0.5 M NaCl solution and a 0.3 M NaOH solution respectively. For 24 h, an electrical potential of 36 V was applied. In the last 6 to 8 hours the chloride concentration in the cell with NaCl solution was measured hourly by taking out a small quantity of solution and measuring it with an Ion Selective Electrode (ISE). From these measurements the chloride migration coefficient D_{ssm} was determined by means of Equation (2):

$$D_{ssm} = \frac{RTLV}{zFUA}\left|\frac{\Delta \ln\,(c_1)}{\Delta t}\right| \tag{2}$$

in which R is the gas constant (8.3145 J/mol·K), T is the temperature (K), L is the thickness of the sample, V is the volume of the cell (m³), z is the ionic valence, F is the Faraday constant (96485 C/mol), U is the applied potential (V), A is the exposure area (in m²), and $\Delta \ln\,(c_1)/\Delta t$ is the derivative of the ln of the measured chloride concentration with time in the quasi-steady-state region.

The great advantage of this test method is the short test period, allowing for a quick assessment of the healing performance. Unfortunately, it was difficult to discern any relevant trends from the initial tests on the five different mixes. This might have been caused by leaks in the migration cell; due to the Brazilian splitting test used for pre-cracking there was some crushing on the circumference which could have allowed leakage of solution. In addition, the determination of the chloride concentration with the ISE needs some time for the reading to stabilize and even then possibly fluctuates.

New REF, SAP, and REF-low W/C specimens were cast, cracked and healed similar to the diffusion specimens. In order to reduce the variability on the chloride migration coefficient, the following aspects were considered:

- The crack opening at the circumference of the cylinder was sealed using an epoxy coating. This decreased the leaking of the migration cells for cracked specimens;
- In addition, Teflon tape was used to wrap the circumference of the disc specimens prior to placement in the migration cell;
- A standardized approach was adopted for the determination of the chloride concentration: approximately 30 ml of NaCl solution is brought into a small container and the ISE is placed in this solution. The solution is stirred for 30 s and then the solution is left to settle for 2 min. After the settlement period the chloride concentration is determined.

In previous research, the migration coefficient of the cracked specimens is often determined immediately after cracking (day 0) and after placing the specimens in healing conditions to calculate the healing efficiency [58]. However, in this research it was decided to only perform a measurement of the migration coefficient after 28 days of healing and compare this to the migration coefficient on uncracked samples. The migration test was not executed immediately after cracking (and before healing conditions) as this would have resulted in the deposition of chloride ions in the crack. This would result in a different boundary condition compared to the diffusion test (where chloride contact was only after healing conditions) and a different swelling behaviour of the SAPs (see section 3.1). After the migration test, the ratio of the migration coefficient of the cracked specimens to the migration coefficient of the uncracked specimens was calculated. A smaller ratio indicates a better healing efficiency.

3. Results and discussion

3.1. Swelling behaviour of SAPs

The average sorption capacity of the SAPs in a specific solution was calculated from 4 repetitions. Table 2 gives the sorption capacity determined from four different exposure times in the respective liquids: 10 min, 1 h, 3 h, and 24 h. There is a slight increase in the values going from 10 min to 1 h, after which the sorption capacity stays approximately constant. The NaCl solution made with cement filtrate is an exception as the sorption capacity is approximately constant between 10 min and 1 h. The cement filtrate and NaCl solutions result in a much smaller sorption capacity than the demineralised water. This is caused by the charge-screening effect resulting from the presence of cations. A strong complexation of the charged groups of the polymeric chains is caused by the divalent and trivalent cations (e.g. Ca^{2+} ions) [45, 59]. A NMR study comparing SAPs in alkali-activated slag and Portland cement systems underlined that also Na^{+} ions have an important effect [60]. It is important to realise that the sorption capacity obtained in cement filtrate is higher than the additional water needed to compensate the loss in workability due to addition of SAPs (19.4 g water per g of SAPs, see section 2.2). This is caused by a higher concentration of monovalent ions [61] and physical forces exerted on SAP particles [28] limiting the swelling of SAPs in mortar compared to cement filtrate solution .

The NaCl is the most determining with regards to the sorption capacity, as evidenced by a statistical comparison of the means of the three solutions (NaCl solution, cement filtrate, and cement filtrate + NaCl) at 24 h (with a p-value <0.1% equal variances could not be assumed, a Tamhane's post-hoc test showed the pure cement filtrate solution was different from the others with a p-value <0.1%, while the two NaCl solutions could be assumed equal with a p-value of 17.6% and a significance level of 5%). This means that in a chloride-rich environment the absorption capacity of the SAPs is lower than in the cementitious matrix, which could influence the (immediate) crack sealing capacity of the SAPs. Hence, prior crack healing before exposure to chloride ions would be beneficial. A previous study by some of the authors also found that the absorption in artificial seawater was lower than in cement filtrate [7], although it needs to be mentioned that the W/C ratio of the solution used to make the cement filtrate solution was 10 (instead of 5 which was used in the current study), and that the seawater was different from the NaCl solution used in this study as it consisted of 5 g $MgCl_2$, 4 g Na_2SO_4, 0.7 g $CaCl_2$ and 0.8 g $MgBr_2$ in addition to 24 g NaCl. The actual water absorption will depend on the type of SAP investigated, as well as the synergetic effect between the osmotic pressure, charge-screening effect and strong complexation by the cations and anions present in the liquid studied.

Table 2: Sorption capacity (μ: mean calculated on four repetitions, SEM: standard error of the mean) determined in four different testing liquids: (1) demineralised water, (2) NaCl solution, (3) cement filtrate solution, and (4) NaCl solution made with cement filtrate.

	10 min		**1 h**		**3 h**		**24 h**	
	μ	**SEM**	**μ**	**SEM**	**μ**	**SEM**	**μ**	**SEM**
Demineralised water	297.83	14.53	337.59	8.51	320.51	2.11	345.56	8.27
NaCl solution	23.87	0.11	25.84	0.14	24.37	0.18	24.99	0.07
Cement filtrate	29.91	0.47	37.06	0.09	36.37	0.35	36.90	0.47
Cement filtrate + NaCl	23.49	0.27	23.17	0.10	23.17	0.24	24.62	0.13

3.2. Workability and strength

The workability as determined by flow table testing is given in Table 3. The series REF, SAP and REF-low W/C all obtain a similar flow value, which means that the dosage of superplasticizer used to compensate for the water uptake by the superabsorbent polymers, respectively the lower water content, was properly selected.

Table 3: Flow value of different series (average of single result from two different batches).

Series	**Flow (cm)**
REF	14.6
SAP	14.0
REF-low W/C	14.1

Figure 2 and Figure 3 show the flexural and compressive strength results. The highest flexural strength is obtained by the REF-low W/C series, while the lowest flexural strength is obtained by the REF series. This can be explained by the low, respectively high, water content. The addition of SAPs without additional water has improved the flexural strength in comparison with the REF mix with the same total water content. This is in contrast to previous research which stated that the macropores created by the SAPs reduce the flexural strength [7]. The latter research performed four-point bending tests; in contrast to the current study in which a three-point bending test was employed, meaning that the crack will form under the loading point, rather than at the weakest point of the prism. The SAPs have a dual effect. They cause the formation of macro pores while at the same time induce internal curing and stimulate further hydration. Both effects occur at the same time and are dependent on the water-to-binder ratio [46]. Nevertheless, it should be noted that the difference between the REF and SAP series in the current study is relatively small.

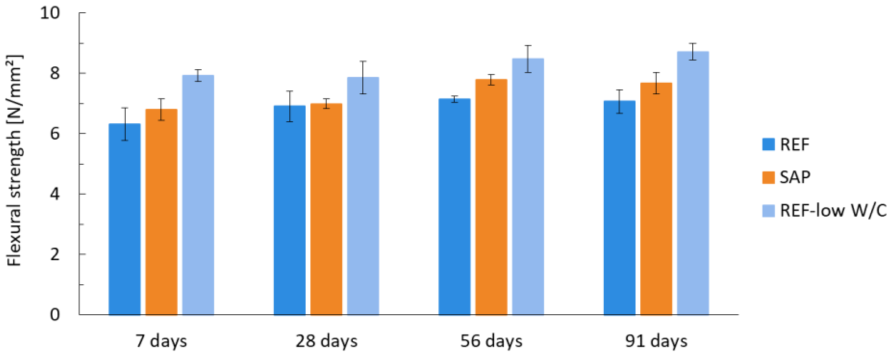

Figure 2. Flexural strength at an age of 7, 28, 56 and 91 days. Error bars represent the sample standard deviation (n = 3).

The bars in Figure 3 represent the average of six compressive tests. In case a value differed by more than ±10% from the average it was omitted and the average was calculated based on five results. Note that EN 196-1 prescribes that if there is another value which differs by more than ±10% from the average calculated from the five results, the test should be repeated. This was not possible in the current study, as there would be insufficient samples to determine the strength at the different ages; the strength was then calculated from five results. The best compressive strength is obtained for the REF-low W/C series due to its low water content. The compressive strength at 7 days does not follow the trend as the average compressive strength of the REF specimens is slightly higher than for the REF-low W/C specimens, albeit that the standard deviation is significantly larger for the latter, giving statistically insignificant differences (level of significance = 5%, p = 69.9%). Considering this uncharacteristic result, new samples were made for this specific age; the 7-days strength of the REF-low W/C specimens was 52.0 ± 3.1 MPa, compared to 47.1 ± 2.8 MPa for the REF series. Comparing the series with superabsorbent polymers to their reference series with the same total water content (SAP vs REF) there is a drop in the compressive strength of 18.4% at an age of 28 days. However, at 91 days this drops to a strength reduction of 9.8%. The decrease in strength reduction going from 28 to 91 days for the SAP series could be explained by the macropores formed by the superabsorbent polymers which allow for further hydration and porosity reduction by deposition of hydration products [62]. The strength reduction upon superabsorbent polymer addition for series with the same total water content was also established in a previous study [46]; the SAPs are irregular in shape and the formed macropores do not allow for compressive stress transfer via dome action.

When comparing the series with superabsorbent polymers to the reference series with the same effective W/C ratio (SAP vs REF-low W/C) there is a drop in the compressive strength of 33.3% at an age of 28 days. At an age of 91 days the strength reduction is 28.7%. The high strength reduction is a result of the irregular macropores formed by the superabsorbent polymers filled with water, and the fact that more water is provided than the 0.42 which is theoretically required for unrestricted cement hydration [25].

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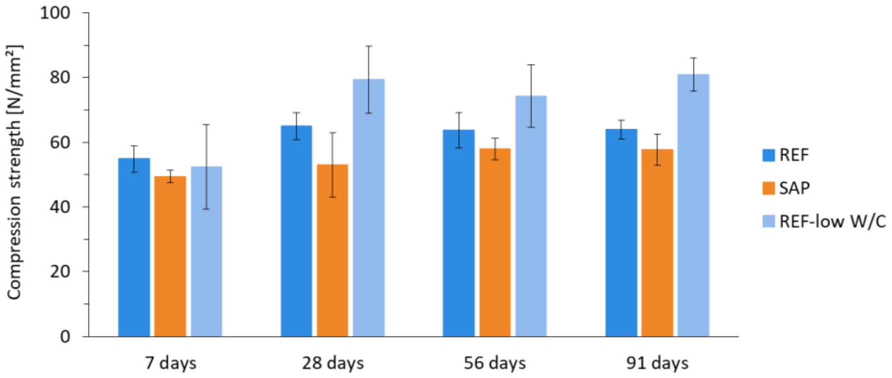

Figure 3. Compression strength at an age of 7, 28, 56 and 91 days. Error bars represent the sample standard deviation (n = 5 or 6).

3.3. Air void content

The results on the air void content determined with the air void analyser of mixes REF, SAP and REF-low W/C are shown in Figure 4. As previously mentioned, the total air void content for specimens containing SAPs is a combination of air voids and SAP voids. The amount of SAP voids can be theoretically determined by the method described in the work of Snoeck et al. [46], respectively Laustsen et al. [63] . The absorption capacity of the used SAPs in mortar was 19.4 g water/g SAP (see section 2.2), which corresponds to 68 l/m^3 water assumed to be absorbed in the fresh mortar. This results in an amount of SAP voids of 6.8 %. Therefore, in Figure 4, the total air void content is divided into two parts: the bottom part represents the air voids and the upper, lighter part represents the SAP voids. When considering only the air void content, there is no statistical difference between the mean values for REF, SAP and REF-low W/C (level of significance = 5%, p = 88.5%). This can be explained by the similar workability of the three mixes as shown in section 3.2. The ability of entrapped air to escape during compaction depends on the workability of the mix [64]. As shown in section 3.2, the formation of SAP voids reduces the strength of the mortar; however, it is expected that the permeability and therefore the durability will not be negatively affected by the SAP voids [64, 65].

Overall the values of the air void content appear to be high. Nevertheless, a Round Robin study which investigated the test method employed concrete samples with an air void content of 3.2% – 7.6% [66]. In the current study mortar samples were used, which generally have a higher air content than concrete. Figure 5 shows an overview of the samples used for the air void analysis, which shows that the measured air content corresponds with the amount of air voids (and SAP voids) that can be visually observed.

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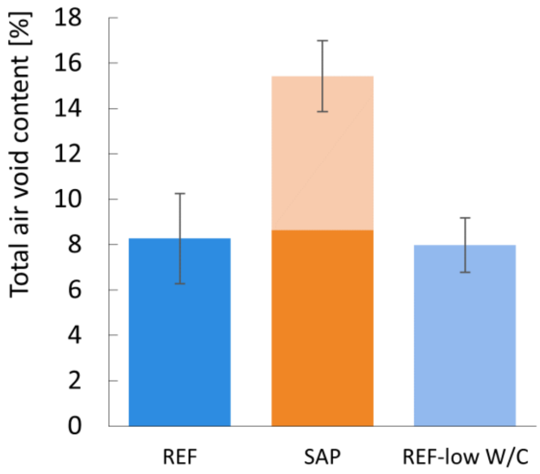


Figure 4: Air content determined using an air void analysis on REF, SAP and REF-low W/C specimens. Error bars represent the standard deviation. For the SAP mix the upper lighter part are the estimated SAP voids.

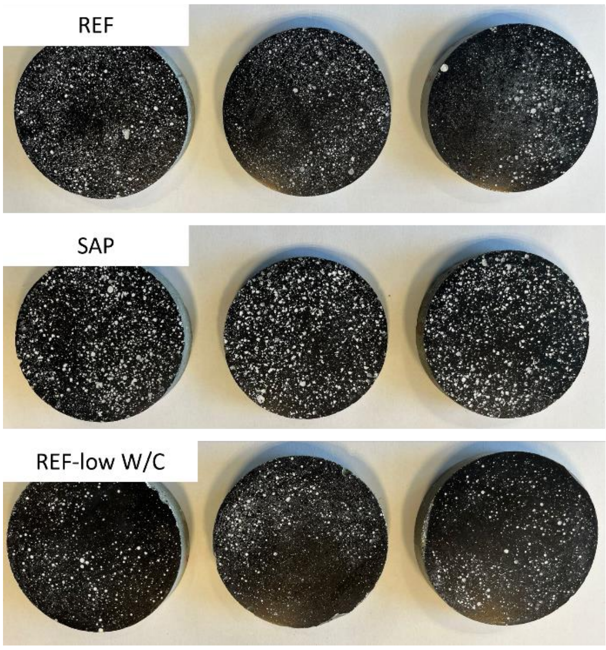


Figure 5: Overview of the specimens for air void analysis.

3.4. Chloride diffusion

After 7, 14, 28 and 42 days, at least three uncracked specimens were removed from the NaCl solution. The specimens were opened in two halves and sprayed with $AgNO_3$. Figure 6 shows the depth of the colour change boundary, indicating the depth of penetration of the chloride ions. The SAP series performs better than the REF series; both have the same total W/C ratio, yet the SAPs result in a better microstructure due to the internal curing effect. In an initial stage, superabsorbent polymers retain part of the mixing water and they release this at a later stage, providing internal curing [67, 68]. The REF-low W/C and the SAP series have a comparable performance, yet the SAP series is slightly better; e.g. after 42 days the chloride ingress in the REF-low W/C series is equal to 10.0 ± 0.6 mm compared to 8.6 ± 0.6 mm for the SAP series.

These findings are in agreement with Hasholt and Jensen [39] who stated that SAP addition is beneficial when SAPs are added with additional water for mixes with a W/C generally lower than 0.42 (which is the case here when comparing the SAP and REF-low W/C series) and in case no extra mixing water is added (which is the case here when comparing the REF and SAP series). Also Beushausen et al. [65] found a better performance for SAP addition (without additional mixing water) to blended mortars with silica fume with a water-to-binder ratio of 0.55.

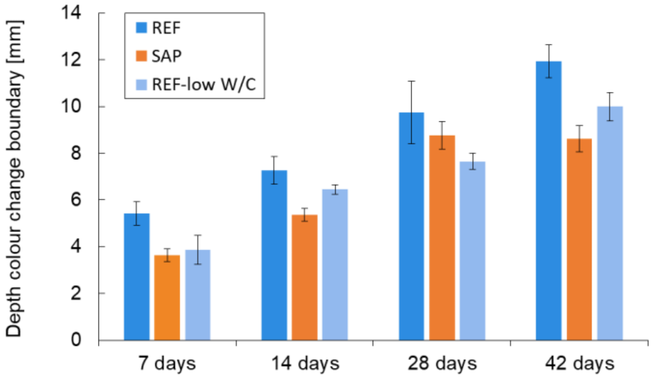
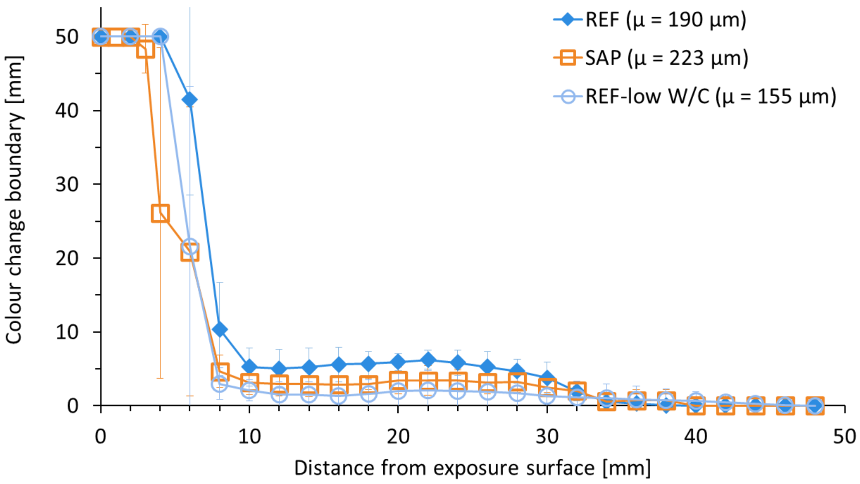


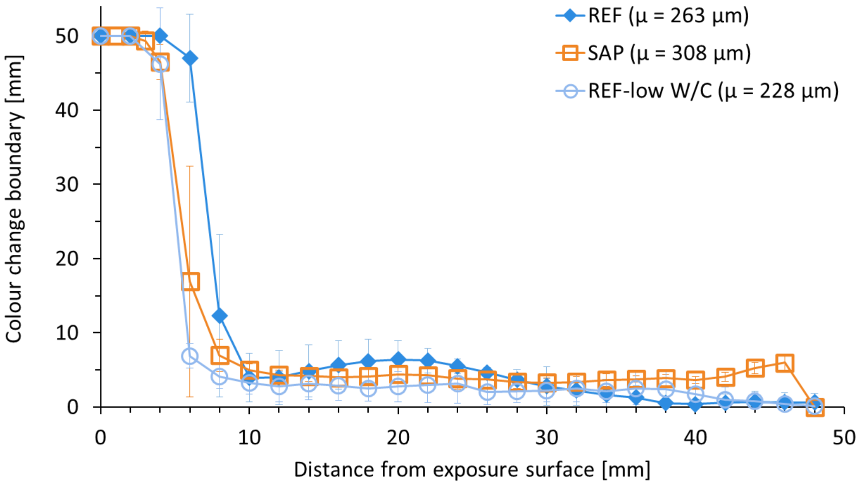
Figure 6: Depth of the $AgNO_3$ colour change boundary for uncracked specimens after 7, 14, 28 and 42 days in a chloride solution. Error bars represent sample standard deviation (n = 4, except for REF-low W/C at 28 days for which n = 3).

After 2 weeks, respectively 6 weeks, a minimum of three cracked cylindrical specimens were removed from the chloride solution and their chloride ingress profile was determined, see Figure 7 and Figure 8. The legend of each graph shows the average crack width of the specimens considered. Note that the actual crack width of the specimens was significantly larger than the thickness of the silicone spacers (100 or 200 µm) inserted after cracking to keep the crack open. The crack width of the REF-low W/C was the closest to the thickness of the silicone spacers. This series was also the strongest of the five series considered, see section 3.2. For series with SAPs it was noted that the crack walls were relatively weak, i.e. the crack walls were grainy with loose particles which could get lodged between the two halves when they were put back together after cracking via Brazilian splitting. Some SAPs may thus have gone lost during the process of recombining both halves; the SAPs sit loose within their macropores and the cracks tend to go through the macropores. The specimens in the current study were placed in a W/D environment to promote healing prior to chloride exposure. The relatively large cracks widths will have impacted the crack healing capacity [34].

Looking at 2 weeks of exposure (Figure 7 a), the SAP specimens with silicone spacers of 100 µm have the lowest ingress in the top of the crack (near the exposure surface). When looking at the chloride ingress deeper inside the crack, the SAP series has a slightly higher, yet comparable, ingress to the REF-low W/C series. For the specimens with spacers of 200 µm the performance of the REF-low W/C series is marginally better than the SAP series near the exposure surface. The SAP series performs better than the REF series, except deeper into the crack (> 36 mm from the exposure surface).



A) series with silicone spacers of 100 μm



B) series with silicone spacers of 200 μm

Figure 7: Perpendicular distance of crack wall to the boundary of colour change after 2 weeks of exposure. Error bars represent the sample standard deviation calculated from the minimum of three specimens.

The results are more pronounced looking at 6 weeks of chloride exposure, see Figure 8. While the chloride ingress was negligible near the bottom of the specimens (±40 mm away from exposure surface) in the 100 μm spacer series, this is no longer the case after 6 weeks of exposure. Table 4 compares the chloride ingress perpendicular to the crack at a distance of 40 mm away from the exposure surface to the chloride ingress in uncracked samples. For chloride diffusion it has been established that once a crack is wider than 75-125 μm the crack will not be a limiting factor for chloride ingress and the crack will behave as an exposure surface [69]. The average crack widths, which have been reported in Figure 7 and Figure 8, were consistently larger than the nominal thickness of the spacers and the 125 μm boundary value. The results in Table 4 clearly show a lower ingress inside the crack than the ingress from the exposure surface. The values indicate that even while the crack healing was not perfect -as chloride ions were still able to penetrate into the crack- there was some crack healing restricting the ingress of chloride ions into the crack and preventing it from behaving as an exposure surface, as would be expected from cracks with a crack width wider than 125 μm [69, 70]. Figure 8 shows that the SAP series performs almost identical to the REF-low W/C series and better than the REF series. This is a result of the higher chloride diffusion that the REF mix experiences, as was evidenced by Figure 6.

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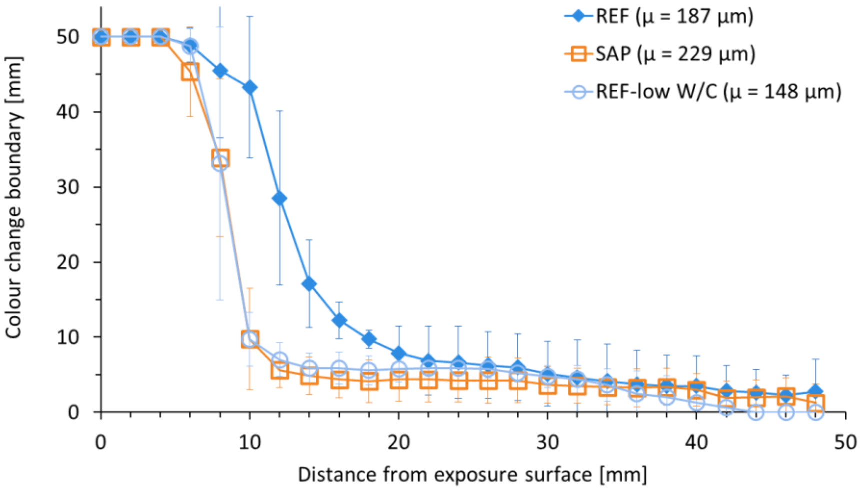
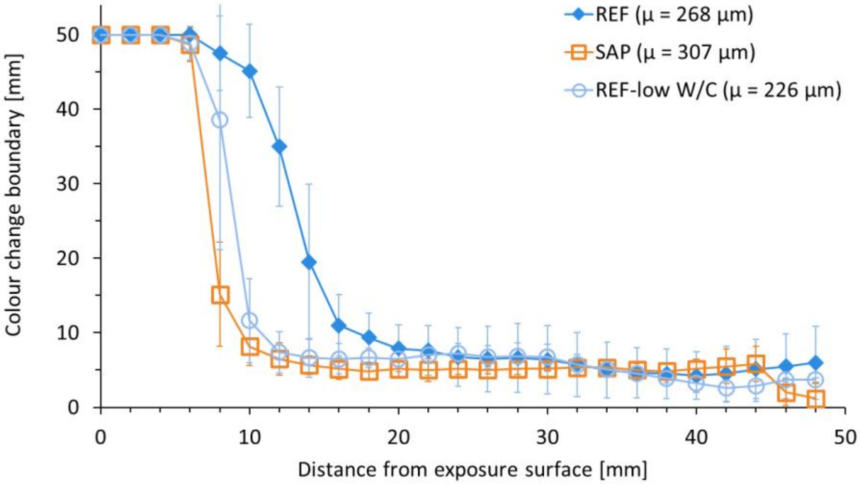


A) series with silicone spacers of 100 µm



B) series with silicone spacers of 200 µm

Figure 8: Perpendicular distance of crack wall to the boundary of colour change after 6 weeks of exposure. Error bars represent the sample standard deviation calculated from the minimum of three specimens.

Table 4: Comparison of chloride ingress after 6 weeks of exposure of uncracked specimens (UNCR) and chloride ingress perpendicular to the crack wall 40 mm away from the exposure surface for series with silicone spacers of 100 respectively 200 µm (notation: average ± sample standard deviation). Average crack widths of specimens have been reported in Figure 7 and Figure 8 and were larger than the nominal thickness of spacers.

	UNCR	100 µm	200 µm
REF	12 ± 1	4 ± 4	4 ± 3
SAP	9 ± 1	3 ± 2	5 ± 1
REF-low W/C	10 ± 1	1 ± 2	3 ± 1

Considering the relatively large crack widths which were obtained, it was decided to repeat the diffusion experiment for cracked specimens with silicone spacers with a nominal thickness of 100 µm. The reassembly of the specimens after Brazilian splitting was done more meticulously, ensuring the tightest possible fit of the hose clamps and preventing the lodging of particles inside the crack as much as possible. Figure 9 shows the results after 6 weeks of exposure on triplicates. The average crack width was smaller and closer to 100 µm. For the SAP series the average crack width of 170 ± 28 µm was considerably larger than for the REF (114 ± 6 µm) and REF-low W/C series (119 ± 21 µm). However, the SAP series was the only one in which no chlorides entered into the crack after 6 weeks of submersion in a chloride solution (one specimen showed some ingress at 45 and 50 mm away from the exposure surface but this could have been due to a failure of the coating as there was no ingress at 30, 35, nor 40 mm). The prior W/D cycling for 28 days prior to chloride exposure has resulted in a promoted healing of the crack by the superabsorbent polymers. The fact that the results of this repeated series are better than the previous one (see Figure 8) can be explained by the narrower crack width, facilitating crack healing (and in the case of the SAP series crack sealing). From this repeated experiment, it can be concluded that the addition of superabsorbent polymers can improve the performance with regards to chloride diffusion if the $(W/C)_{eff}$ ratio is equal to the W/C of the related reference mixture without SAPs.

In addition to the possible beneficial influence of SAP addition with respect to chloride ingress, findings in literature have shown that the addition of SAPs can also have a beneficial influence on the sealing efficiency of cracks [8, 11, 16], the freeze-thaw performance [22-24, 71], and the shrinkage performance [26, 27, 68].

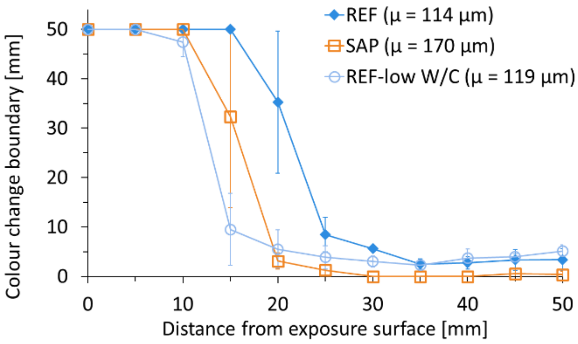


Figure 9. Perpendicular distance of crack wall to the boundary of colour change after 6 weeks of exposure for repeated experiments on cracked REF, SAP and REF-low W/C specimens with silicone spacers with a nominal thickness of 100 µm. Error bars represent the sample standard deviation calculated from the triplicates.

3.5. Quasi-steady-state chloride migration

Table 5 gives the mean value and the standard deviation of the measured crack widths for the specimens used for the chloride migration test. The larger mean crack width for the SAP specimens can possibly be explained by the more rough crack surface due to the addition of the superabsorbent polymers, which resulted in weaker crack walls (see also section 3.4).

Table 5: Mean crack width and standard deviation of REF, SAP and REF low W/C.

REF	**SAP**	**REF low W/C**
142 ± 22 µm	204 ± 19 µm	181 ± 58 µm

Figure 10 shows the mean migration coefficient for REF, SAP and REF-low W/C for uncracked samples and cracked samples after 28 days of wet and dry cycles. Each mean value is calculated from the migration coefficients of 3 samples. For the uncracked samples, the migration coefficient for the REF samples seems higher in comparison to SAP and REF low W/C. This could be explained by the higher effective W/C. However, an ANOVA analysis indicated that there is no statistically significant difference between the mean values of the three mixes (level of significance = 5 %, p = 20.5 %). Due to the higher macro-porosity determined using an air void analysis, it could be expected that the SAP specimens

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have a higher migration coefficient. However, these results show a similar average migration coefficient for SAP and REF-low W/C. This can be explained by the similar effective W/C and the fact that the majority of the pores created by the superabsorbent polymers are closed pores, which do not increase the transport of chloride ions [72]. Furthermore, these results are in line with previous research from Hasholt and Jensen [39] who found that if no extra water is added to compensate for the absorption by the SAPs, the migration coefficient decreases. Regarding the cracked and healed samples, the SAP mix has a lower migration coefficient in comparison to the reference and the reference with the same effective W/C. Although there is little information available in literature on chloride migration in cracked samples, the water permeability through a crack in specimens with superabsorbent polymers has been studied. The SAPs at the face of the crack swell during the water permeability test, causing them to block the crack and decrease the water flow through the crack [12]. In the current research, similar to the water permeability test, the swelling of the SAPs in the crack and closing of the crack due to stimulated autogenous healing can explain the obtained lower migration coefficient for cracked SAP specimens. It is unclear how the uncracked zone in the cracked specimens affects the migration coefficient measurement. Therefore, in more recent literature it is recommended to coat the uncracked surface of the specimens before testing [73].

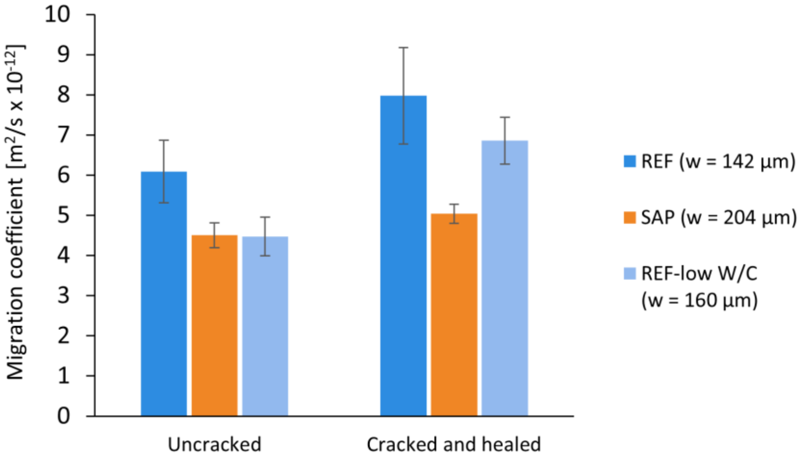

Figure 10: Migration coefficient D_{ssm} for uncracked and cracked and healed specimens of REF, SAP and REF low W/C. Error bars represent the standard deviation.

Table 6 shows the ratio of the migration coefficient of the cracked specimens to the uncracked specimens, which is an indication for the healing efficiency, calculated from the uncracked and cracked specimens for REF, SAP and REF-low W/C. As expected, the ratio of the SAP specimens is the lowest due to an increase in migration coefficient of only 12 % between the uncracked, and the cracked and healed specimens.

Table 6: Ratio D_{CR}/D_{UNCR} after chloride migration testing.

	$\frac{D_{CR}}{D_{UNCR}}$
REF	1.31
SAP	1.12
REF-low W/C	1.53

4. Conclusion

This study investigated the influence of promoted autogenous healing of cracked mortar via superabsorbent polymer addition on chloride ingress. To this end a series with SAPs was compared to two reference series: one with a W/C ratio equal to the $(W/C)_{tot}$ of the SAP series, and one with W/C ratio equal to the $(W/C)_{eff}$ of the SAP series

The chloride diffusion test on uncracked specimens confirmed the statements by Hasholt and Jensen [39] that in case superabsorbent polymers are added to the mix without additional mixing water or when they are added with additional mixing water for low W/C systems (generally W/C<0.42) the performance is improved.

Filtration tests showed that the charge-screening effect in a NaCl solution with the same concentration as the one for the diffusion testing was more pronounced than in a cement filtrate solution. This is why less immediate sealing of the crack by swollen SAP particles was expected, and the cracked specimens were subjected to wet/dry cycles to promote healing prior to chloride contact.

With regards to chloride diffusion into cracked specimens, the performance of the SAP series was comparable to the reference with W/C ratio equal to the $(W/C)_{eff}$ of the SAP series. The SAP series performed better than the reference with W/C ratio equal to the $(W/C)_{tot}$ of the SAP series. After 6 weeks of chloride exposure all three series showed chloride ingress into the crack. However, the chloride ingress perpendicular to the crack was lower than the ingress from the exposure surface which is evidence of (promoted) autogenous healing. When the test was repeated with samples with smaller crack widths, the SAP series had a superior performance with no chloride ingress into the depth of the crack, which shows the beneficial influence of the addition of superabsorbent polymers due to promoted healing capacity and sealing effect.

The better performance of the series with superabsorbent polymers was confirmed by quasi-steady-state chloride migration testing. The cracked specimens of this series showed the best restoration after wet/dry cycling with respect to the uncracked specimens (only an increase of 12 %), despite having the widest crack width. For the reference series the increase was 31 % and 53 % for the series with the W/C ratio equal to the $(W/C)_{tot}$ of the SAP series, respectively for the series with the W/C ratio equal to the $(W/C)_{eff}$ of the SAP series.

Previous studies have already demonstrated that the addition of superabsorbent polymers can improve the sealing and healing [8, 11, 16], shrinkage [26, 27, 68] and freeze-thaw performance [22-24, 71]. From the current study it can be concluded that the addition of superabsorbent polymers results in a comparable or lower chloride ingress compared to a reference with a W/C ratio (< 0.42) equal to the $(W/C)_{eff}$ of the SAP series.

Acknowledgments

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