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5 Superabsorbent polymers as a solution for various problems in construction engineering

Abstract: One of the most-used man-made materials is concrete, a mixture of cement, sand, aggregates, water, and admixtures. It can be seen everywhere: in tunnels, bridges, and high-rise buildings. Ever since concrete was rediscovered two centuries ago, it has been studied in detail in order to optimize the material and to solve its inherent problems. Most people know that concrete is gray, hard, and strong, and expect it to last decades and even centuries. Unfortunately, this is not always the case. Concrete is a material which can cope with high compressive forces but when it is subjected to tensile forces, it may crack. This cracking is based on several environmental and loading conditions, but the fact that concrete is prone to crack is a big issue. When cracking occurs and potentially harmful substances enter the interior of concrete, the concrete matrix may be damaged and even be destroyed. That is the reason why a lot of maintenance and repair works are due in order to increase the durability and lifetime of structures in civil engineering. One way of dealing with these issues is the modification of the material itself, making it less prone to cracking and the durability-related consequences. An example is the use of reinforcements, coping with the tensile forces when concrete cracks. Cracks are not harmful but intruding substances may trigger the corrosion of the iron rebars leading to structural failure, which is again unwanted. In consequence, along the history, different materials were investigated and added to concrete to solve the previous adverted problems. So, why not try adding the white powder superabsorbent polymers in the cementitious material in order to solve these issues?

5.1 Introduction

Almost two decades ago [1, 2], superabsorbent polymers (SAPs) found their way into concrete technology and ever since were investigated in detail [3–7]. The typical SAPs used have the feature to absorb up to several hundred times their own weight in aqueous solutions due to osmotic pressure, resulting in the formation of a swollen hydrogel. Typically, SAPs made by polyacrylates (using acrylic acid and acryl amide as main chains) or natural polymers (such as alginates) [3, 6] are added dry to a cementitious mixture and used to solve various problems, which will be discussed in the following sections. SAPs could have different shapes. The use of SAPs with irregular shapes obtained by bulk polymerization or spheres obtained by suspension polymerization are the most studied and used in this area. Moreover,

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grape-shaped and fiber types are studied as well [8]. As SAPs swell, they will absorb part of the mixing water causing the loss in workability of the fresh cementitious mixture. It is commonly accepted to add additional water to compensate for this loss in workability [3, 9–11]. How much they swell and which tests could be performed to quantify the swelling ability are found in literature [5, 9, 12]. The main tests to determine the swelling characteristics upon application in concrete are the filtration test and tea bag test. For the filtration test, a predetermined amount of SAPs is weighed. Next, an amount of liquid (water, seawater, sulfate solution, cement filtrate solution, etc.) is added. The SAPs are then able to absorb the liquid. At a certain time interval, the whole is filtered and the amount of liquid not absorbed by the SAPs is determined. Using the weight difference of the added liquid and the remaining liquid over the initial mass of the SAPs, the absorption capacity is determined. When looking at the tea bag method, a predetermined amount of dry SAPs is added in a sealed tea bag, which is submerged in the testing liquid. By weighing the tea bag at regular time intervals, the amount of liquid absorbed can be determined and used to calculate the absorption capacity. In case the swelling time is needed, a vortex test can be used [5, 13]. This test uses a magnetic stirrer in a cup and a predetermined amount of SAPs to exactly absorb the amount of testing fluid. By measuring the time for a vortex created by magnetic stirring to disappear, the swelling time can be estimated. The swelling characteristics, next to the absorption and desorption kinetics, are important parameters for the application in a cementitious material. Furthermore, the stability of the polymer over time must be used during the service life of a concrete structure [14].

In the following sections, various problems occurring in cementitious materials are addressed. The first one is the control of rheology and the second is the occurrence of shrinkage cracks. Third, concrete is susceptible to freeze-thawing and scaling in general. Fourth, it is permeable and, at last, it cracks. In all these cases, the addition of SAPs to the cementitious mixing could solve these issues and their application will be discussed in detail.

5.2 Changing the rheology by absorbing mixing water

As SAPs are mixed in, they will absorb a fluid they may encounter. In this way, they may change the interaction in a cementitious system, due to partial absorption of the mixing water. The SAPs cause a change in rheology due to their swelling ability [1, 2, 15–17]. This swelling capacity is dependent on the composition of the mixture and the composition of the SAPs. The resulting osmotic pressure is dependent on the external fluid composition and the chemical structure, length, and cross-linking degree of the SAP [14, 16–18]. Due to the uptake of mixing water by the SAPs, the workability decreases as less water is available in the cementitious matrix itself. Later on, this water will be released for mitigating shrinkage, as will be discussed in the next section.

In addition, the workability can be controlled, which is interesting for 3D printing technologies using cementitious materials [19, 20]. Linked to shrinkage- and durability-related issues, the 3D printing of cementitious materials still faces some problems such as autogenous shrinkage, which may be counteracted using SAPs. Continuous layering of printed specimens with SAPs (Figure 5.1) already proved to be successful [19]. This is a recent field of study and many parameters may be investigated.

Figure 5.1: Three-dimensional printing of cementitious materials with SAPs by continuous layering.

5.3 Shrinkage mitigation by internal curing

The first application of SAPs in cementitious materials was the use of their swelling behavior and water-retention capability to induce internal curing in order to counteract occurring shrinkage cracks [1, 2, 21–25]. Concrete, composed of the hydrating cement and water, possesses the problem of shrinking when water is receding, especially in systems with low water-to-binder ratios. The latter systems, such as (ultra)high-performance concrete [26, 27], are used more often due to their denser matrix, high strength, and featured workability. In the following sections, the different forms of shrinkage, the role that they play in a cementitious material and the use of SAPs for its mitigation are discussed.

5.3.1 Plastic shrinkage mitigation

Shrinkage occurs from the start, due to drying and harsh environmental conditions. This so-called plastic shrinkage may cause cracking during the first few hours after casting [28]. Due to the quick drying and bleeding of concrete, high capillary pressures are exerted in the cementitious matrix. If deformations are restrained, for example, due to the formwork or the reinforcements, the concrete will show cracking [29]. That is why concrete is postcured when possible. External curing, for example, by (fog-)spraying or covering with a plastic sheet, is not as sufficient as an internal curing approach. By using SAPs, internal curing is possible. The approach is still new and a lot of research needs to be performed in order to optimize the mitigation of plastic shrinkage. Currently, the SAPs were only able to partially mitigate this type of shrinkage. It was found that by adding 0.6 m% of SAPs (versus cement weight), the capillary pressures and plastic deformations were reduced, while the settlement deformations increased [27]. A study using nuclear magnetic resonance (NMR) to monitor the water kinetics with SAPs when plastic shrinkage conditions were imposed showed that 0.22 m% of SAPs were able to reduce plastic settlement and reduced plastic shrinkage cracking but were not able to completely mitigate it [30]. The SAPs were able to protect the cement paste internally from the harsh ambient drying conditions and were able to sustain the internal relative humidity (RH) below 5 mm of the cementitious surface. Results by the RILEM TC-260 RSC support these findings in an international round robin test [31]. In this study, concrete slabs were subjected to harsh drying and wind conditions in order to stimulate plastic shrinkage. SAPs were added during mixing in amounts of 0.15 and 0.3 m%. The results on plastic shrinkage mitigation seemed to be dependent on the type of SAP and whether they possess retentive properties. The water can be released early to influence the bleeding characteristics or can be released after setting to aid with internal curing. Both effects seem to play a role. No additional information on the SAPs was disclosed, and the main difference seemed to be the cross-linking degree [31, 32].

5.3.2 Autogenous shrinkage mitigation

Other forms of shrinkage include autogenous shrinkage as a result of cement hydration, thermally induced shrinkage, drying shrinkage due to the loss of water to the surroundings, and shrinkage due to carbonation. As cement reacts with water, hydration products precipitate in the water-filled spaces between the solid particles in the cementitious material. The water in the remaining small capillaries forms menisci and exerts hydrostatic tension forces. These capillary forces reduce the distance between the solid particles, leading to autogenous shrinkage. Chemical and

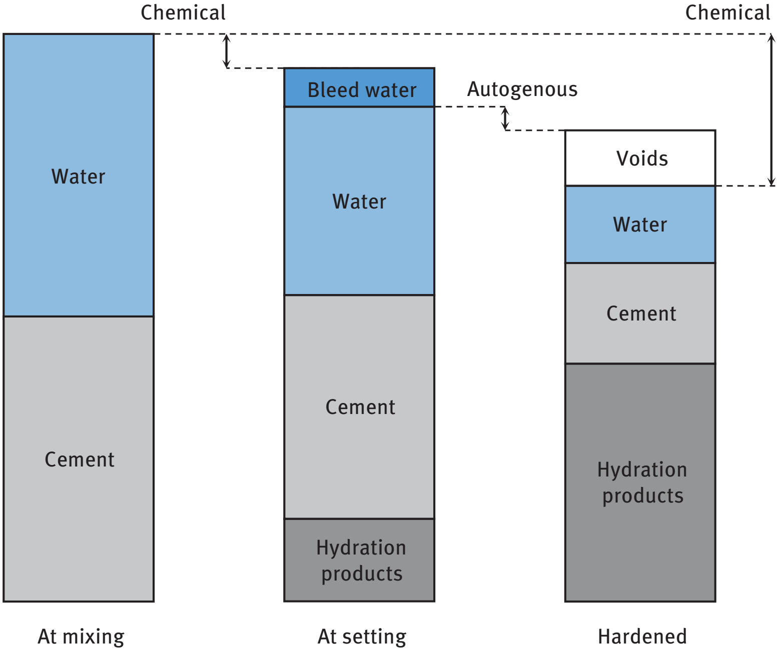

Figure 5.2: Definition of chemical and autogenous shrinkage.

autogenous shrinkage are theoretically shown in Figure 5.2 and autogenous shrinkage will be the focus point in this section.

The formed hydrostatic tensile forces, especially in systems with a low water-to-binder ratio, induce cracking. At first, these small and narrow cracks do not seem to impose such a big problem but intruding substances may cause failure of the material. The shrinkage is caused by the lowering of the internal RH [1, 2, 33] and self-desiccation when no external water source is present. The internal microcracks may interconnect flow paths for penetrating water and gases, possibly containing harmful substances during the service life of concrete structures. By maintaining the internal RH, this can be counteracted. That is why SAPs were first used to mitigate autogenous shrinkage due to their internal curing effect. The application of SAPs for this purpose proved to be successful as autogenous shrinkage was reduced and even counteracted in time [1, 2, 21–25].

The principle of the SAPs for internal curing is found in Figure 5.3. During preparation of a cementitious mixture, the SAPs will take up mixing water. The SAPs will form water-filled inclusions, useful for internal curing [21] as the water is released again in time. The water released due to self-desiccation during cement hydration can be used for further hydration and reduction of the autogenous shrinkage [22]. The water present in the SAP will hereby be released into the cementitious matrix due to the imminent drop in RH. Due to this water release, the internal

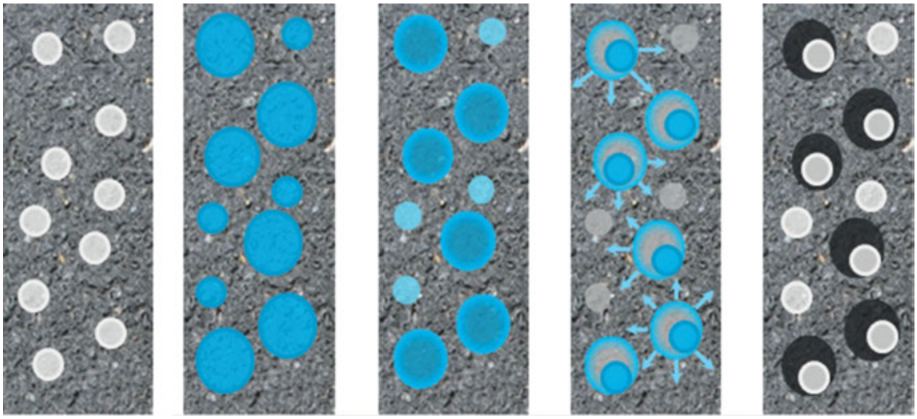

Figure 5.3: Different steps for internal curing when SAPs are used in cementitious materials [8].

RH is maintained. The SAP particles shrink and an empty macropore remains as shown by means of neutron tomography measurements [34–38]. The macropore showed a densification around its perimeter [39–41]. Due to the internal curing the autogenous shrinkage can be completely mitigated in systems with pure cement, combined with silica fume, fly ash, and blast furnace slag [10, 23, 24, 42–44].

For internal curing, the water kinetics of the SAPs are important [45]. If this water is released too soon, it leads to a significant decrease in compressive strength. But if this water is released at the ideal stage (beginning of concrete setting as the earliest point), this water would serve as internal curing water [18]. It is very important to use a SAP with the ideal properties. If the water is released too fast (i.e., before setting), the microstructure will be completely different and if the water is released too late (i.e., after a couple of days onwards), the purpose of internal curing vanishes. This was studied in detail using NMR where the entrained water signal was distinguishable from the free water in the cementitious system. In time, the water released from the SAPs toward the cementitious matrix could be studied [45]. More recently, elastic wave nondestructive testing may also be a way to monitor the water kinetics by the SAPs [46].

Typical amounts of 0.2–0.6 m% of cement weight of SAPs are used [3]. The amounts are based on the theory of powers [47] stating the amount of additional water needed to counteract autogenous shrinkage. Again, the type of polymer is important, as the absorption and release kinetics in a cementitious environment are different [33, 48, 49]. The type of polymer and the interaction with specific ions and cations play a role in terms of the absorption and release kinetics and were less related to the cross-linking density [18].

5.4 Changing the microstructure to increase the freeze–thaw resistance by the formation of an internal void system

As soon as cement and water come into contact, hydration reactions start. The hydration of a concrete mixture determines the microstructural development and SAPs influence this formation. This was already extensively studied. Hardened mixtures with SAPs showed less capillary porosity at later ages if additional water was used (compared to if no additional water was used). The water released from the SAPs resulted in continued hydration, decreasing the microporosity at later ages [23, 50], except from the macropores created by the SAPs. A reduction of the amount of smaller capillary pores was seen [51]. This is due to two effects: (1) the filling of the existing pores with hydration products due to internal curing [26] and (2) the reduction of the initial microcracks in the interior of a cementitious matrix, as autogenous shrinkage is partially reduced. Mixtures with the same effective water-to-cement ratio (ratio of the mixing water not held by the SAPs over the cement content) showed the same capillary porosity [52–55]. The microstructure in between SAPs was denser due to internal curing and the possible stimulated additional hydration caused by this release of water. The structure of a cementitious material was affected by the apparent water-to-cement ratio. As SAPs take up the mixing water, the apparent water-to-cement ratio appears lower, resulting in a closely packed matrix and subsequent hydration due to the release of the stored water. Samples without SAPs do not have access to this stored water. Therefore, the permeability was lower in between SAP macropores in samples containing SAPs than of reference samples. This was also shown by using neutron radiography [35, 36] and supported by modeling on mesoscale level [56, 57].

As can be expected due to the swollen size of the SAPs and the remaining macroporosity, mixtures with SAPs showed a higher total porosity due to macropore formation when additional water was used [21, 39, 58]. If no additional water was added, the total porosity may be lower for mixtures with SAPs [39] as the overall porosity decreased due to the densification even though macropores remain.

Microstructural properties, and especially the macropore formation, directly affect the strength characteristics of the cementitious material. The flexural and compressive strength decrease when SAPs and additional water are added [2, 3, 21–23, 36, 48, 53, 59–63]. Internal curing leads to further hydration and the effect of SAPs on strength loss is reduced at later ages. The further hydration improves the mechanical properties but is mostly counteracted by the strength loss caused by macropore formation due to the absorption of mixing water by the SAPs [64]. SAPs thus have both a positive and a negative effect on the mechanical properties. A decrease in strength is observed at earlier testing ages (<7 days) while sometimes increases are obtained at later ages [65], especially in systems with supplementary cementitious materials where the internal curing reservoirs are available for the longer term pozzolanic reactions. These characteristics depend on the polymer, mixture composition, water-to-binder ratio, amount of additional water, concrete versus mortar or paste, amount of SAPs added, curing conditions, testing age, and so on. For example, an amount of 0.2–0.6 m% versus cement weight of SAP was used to reduce the autogenous shrinkage [3], while for sealing and healing purposes, this amount was up to 1 m% [35, 66, 67]. This will influence the impact on the observed mechanical properties. Generally, in literature, a decrease in compressive strength is found [18, 26, 48, 68–73] as there is a change in microstructure [53, 55, 58, 68, 71, 72, 74–76]. When no additional water is added, there is a shift in effective water-to-cement ratio and a possible densification of the cementitious matrix. One should be very careful when comparing the mechanical properties of these different cementitious systems. Typical values are a decrease of 10–20% for acrylate SAPs with a size of 300–500 µm and 30–50% for smaller SAPs with a size of 50–150 µm [53, 68] when 0.2–0.5 m% of SAPs are added. Even though the system of macropores reduces the mechanical properties, this property is interesting considering the improvement of the impact strength in strain-hardening mixtures [60]. The macropores serve as stress activators, increasing the ductility [77] and impact absorbing features [60].

To limit the influence of the swelling SAPs on the mechanical properties, pH-sensitive SAPs [78–82] or coated SAPs [83, 84] may be used. Alginates, for example, do not reduce the strength due to their low absorption capacity [82, 85]. This lower swelling capacity is interesting in order to limit the absorption in the initial stage and aiming at other applications such as sealing and healing, needing a later swelling capacity at later ages [66, 79, 80, 82, 83]. The strength can also be compensated by the use of colloidal silica nanoparticles upon addition of SAPs [86–88]. The strength-loss due to the macropore formation is compensated by incorporating these nanomaterials which strengthen the overall cementitious matrix.

As SAPs create an internal void system (Figure 5.4), they increase the freeze–thaw resistance if properly designed [39, 40, 58, 89–94]. The voids act in the same way as if an air-entraining agent is added. In case of this internal void system, the freezing water has a pathway to expand, limiting the formation of cracks, scaling, and general expansion of the cementitious matrix. Compared to a system with an air-entraining agent, the SAP mixtures increase the freeze–thaw resistance without extreme strength loss [89] and with proper mix stability. When using an air-entraining agent, the air bubbles may migrate upon long mixing times. The SAPs are thus an interesting material to add to the cementitious matrix. As the absorption capacity in the cementitious matrix is known, the formed macroporosity can be designed to have the optimal sizes and spacing factors for a specific application. 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 [95, 96]. Not only the amount of SAPs but also their particle size and production process might have

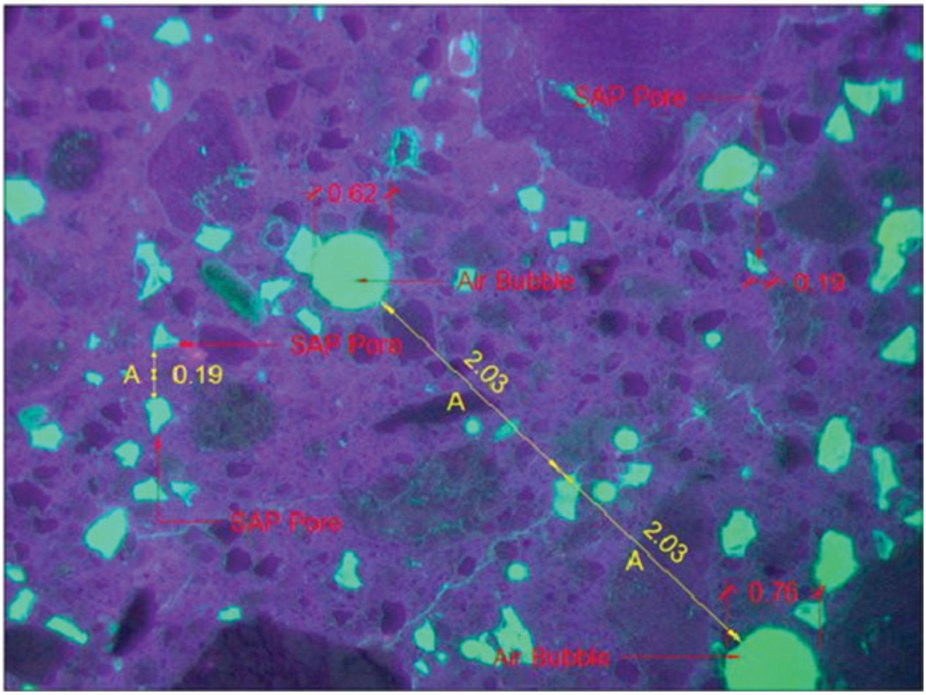

Figure 5.4: Internal void system with air bubbles and SAP pores, for increasing the freeze–thaw resistance, using a thin section and fluorescent light microscopy. This picture has been partly redrafted with (CC BY) license from [94].

an impact on the scaling resistance. In addition, the time of adding the polymers during plant-scale mixing is of importance. The addition of SAPs directly in the truck, after the mixing procedure at the plant mixer, showed no significant impact on the compressive strength of the concrete but an agglomeration of air void particles and an inferior performance in terms of shrinkage reduction occurred [33, 49, 97]. Adding SAPs on the materials' belt, along with the dry materials, or in water-soluble bags has shown promising results. This is of importance when using a specific concrete for road construction applications.

5.5 Regaining the water impermeability through self-sealing of cracks

Due to their swelling capacity upon contact with fluids, SAPs may cause a decrease in permeability of cracked cementitious materials. When liquids enter a crack, SAP particles along the crack faces will swell and block the crack [7, 8, 35, 36, 38, 66, 98–105].

In this way, the impermeability of cracked cementitious materials can be regained (Figure 5.5). Application of a superabsorbent resin in situ to repair concrete leakage can also be used, but this is rather considered to be manual applications [7, 106] while mixed in SAPs are always present to immediately seal the occurring cracks. In 100–300 µm wide cracks, SAPs with a size of approximately 500 µm were better in terms of sealing compared to 100-µm-sized SAPs as the latter were washed out and were not able to fill cracks, even though high amounts (1 m% of cement weight) were used [8, 35, 67]. It was also found that due to the swelling effect of the SAPs, the reduced water movement speed, which was critical to obtain autogenous healing, was optimal as cracks were able to close due to deposited crystals. In reference specimens, the amount of autogenous healing – inherent part of a cementitious system, see later on – was less compared to the specimens with SAPs. In water-retaining structures like quays or cellars the SAPs may prove to be useful as the flow will be reduced, sealing the cracks, but the crack may be sealed by deposited crystals as well. This is also the case in large-scale specimens or observed underneath bridges and in tunnels [107]. As studied by cryofracture scanning electron microscopy, SAPs swell across voids including cracks, causing a sealing of the cementitious material [103].

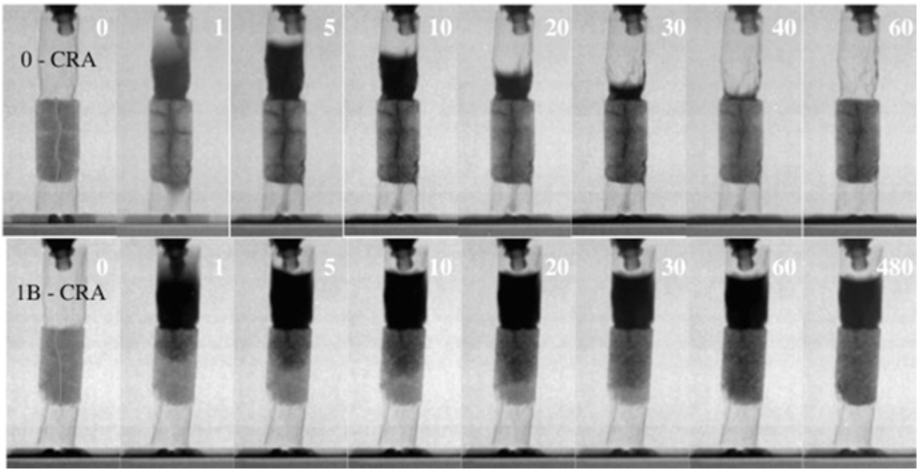

Figure 5.5: Self-sealing concrete showing a cracked cementitious material with a 1 cm diameter and 20 mm height without SAPs (**top**) and with SAPs (**bottom**). The imposed water head is not stopped in the reference material while a sealing effect is noticed with SAPs due to their swelling ability. The time is mentioned in the upper right corner in seconds. This picture has been partly redrafted with permission from Elsevier from source [35].

Self-sealing is related to the initial decrease in permeability and is not permanent. This is important to know, as a possible temporal self-sealing effect may not lead to a regain in mechanical properties. This regain, on the other hand, is the result of self-healing.

5.6 Regaining the mechanical properties due to promoted autogenous healing

Concrete already possesses the natural capacity of autogenous crack healing [4], as first found by the French Academy of Science in 1836 (as stated in [108]). It seems strange that this solid and gray material possesses this feature, but it can be seen everywhere around us. When passing underneath a concrete bridge or through a concrete tunnel, whitish crystals can be seen near and on cracks throughout the material. This is considered to be healing. One can design a concrete material to include an additional healing capacity, the so-called autonomous healing (such as polymeric foams and vascular systems) but autogenous healing is also inherent to concrete. This latter term means that concrete is able to heal its own crack, using its initial constituents or already formed products.

Four main mechanisms and their combined effect contribute to autogenous healing of concrete cracks [108–117] (as shown in Figure 5.6):

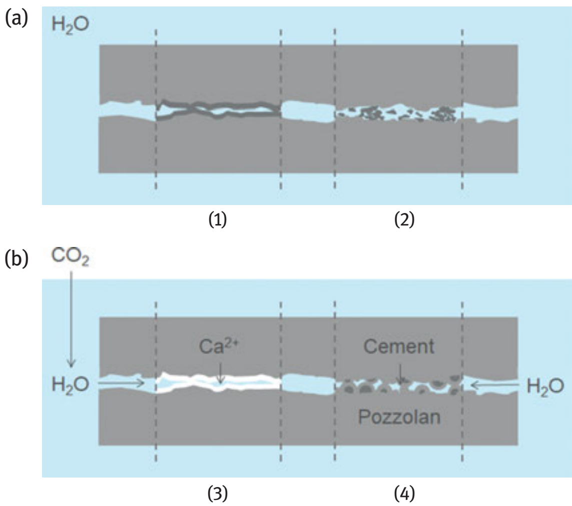

Figure 5.6: The four different healing mechanisms responsible for autogenous crack healing: **(1)** expansion of calcium silicate hydrates, **(2)** blockage by loose particles, **(3)** crystallization of calcium carbonate, and **(4)** further hydration combined with pozzolanic activity [8].

1) The matrix may expand due to swelling of calcium silicate hydrates (C-S-H) as the layering system of the gel becomes wider.
2) Loose and broken-off particles or impurities in the matrix, fluid, or surroundings may block the crack.

3) Dissolved carbon dioxide from the ambient air in water may react with Ca^{2+} ions present from hydration products in the concrete matrix to form the often observed white calcium carbonate ($CaCO_3$) crystals.
4) Unhydrated cement grains present in the matrix and on the crack surfaces may further hydrate when these particles are exposed to water. In addition, supplementary cementitious materials such fly ash or blast furnace slag can still react through pozzolanic or latent hydraulic activity. Pozzolans promote further hydration as these materials react with water and $Ca(OH)_2$ to form C-S-H.

The first two mechanisms (C-S-H expansion and blockage by impurities and other particles) are the inferior ones while the further hydration and calcium carbonate crystallization are the dominant mechanisms in order to receive a strength regain. The strength is mainly gained by further hydration as $CaCO_3$ crystals do not have sufficient strength compared to the cementitious hydration material [118]. However, the white crystals are most often observed, in combination with the grayish further hydration [111, 112, 119, 120], providing an aid in sustained promoted autogenous healing, even up to several years [118]. In high-strength concretes showing a low water-to-cement ratio, the healing is mainly due to the hydration of unhydrated cement grains on the crack surfaces as more unhydrated cement remains present [113, 121, 122]. Also, the younger the material is, the more healing will occur due to the higher amount of unhydrated particles [118]. As the cement further hydrates in time, the healing material formed at early ages is a combination of $CaCO_3$, C-S-H, and $Ca(OH)_2$. At later ages, the healing material is mainly $CaCO_3$ [110, 114, 118].

Assuming that specific chemical substances (Ca^{2+}, CO_2, etc.) are present in the mixture composition or from the specific hydration products, the exposure to humid environmental conditions (wet/dry cycles, submersion in water, etc.) and restricted crack widths up to 30–50 µm for strain-hardening mixtures [67, 109] are the main areas of focus. Only when building blocks, abundant water, and restricted crack widths are present, the material may show optimal healing. In dry conditions, that is, without the presence of liquid water such as at 95% RH, there was no healing visible and it was concluded that the presence of water as a curing medium was essential. As water is needed in all mechanisms [109, 111, 113, 123, 124], the role of SAPs becomes clear [67, 125]. Of course, the crack width and mixture composition play a huge role. Pozzolanic fly ash [126, 127], blast-furnace slag [128], lime [129], or alkaline activators [130] can be added to receive more autogenous healing. Additives like expandable geomaterials [131] or crystalline admixtures [132–136] stimulate the crack-healing capacity even further. The use of SAPs has also been explored in combination with expansive agents such as calcium sulfoaluminate in sulfur composites [137]. The stimulated autogenous healing has also been studied in specimens containing pH-sensitive SAPs or natural polymers in combination with a synthetic backbone [79, 80, 82, 85, 138]. In order to further increase the amount of calcium carbonate precipitation in a wide crack of several hundreds of micrometers, SAPs can be combined with bacteria [139, 140]. The cross-linking of the SAPs is performed after addition of carbonate-precipitating bacterium, such as *Bacillus sphaericus*, in order to properly entrap them and protect them from the harsh alkaline environment.

As the cementitious material has a problem with healing large “fractures” or “cuts” like the human body, the crack width should be restricted. This can be achieved by adding synthetic microfibers to the cementitious mixture [4, 67, 109, 123, 141–148], or by using natural fibers as a greener solution [149, 150]. The use of glass fibers can even be combined to have additional translucent properties of the gray cementitious material [151]. So, as mentioned, SAPs can be added to further stimulate the autogenous healing [8, 38, 60, 61, 66, 67, 107, 118, 125, 152–155], due to their retentive capacity as shown in Figure 5.7. Closely resembling bone healing, the links are made toward cementitious healing of narrow cracks. When a crack occurs, the SAPs will be exposed to the environment. They will start to absorb a fluid upon contact and/or the SAPs will start to adsorb moisture from the environment. This will cause a physical sealing of the crack, slowing down the fluid flow through a crack. This is related to the bleeding and clogging found in the human body. The SAPs will release their absorbed water for stimulating the autogenous healing mechanisms, especially during the drier periods. This process, like human bone reconstruction, continues until the complete crack is closed or the building blocks are consumed or exhausted. In the end, and the ideal case, a healed cementitious material is obtained with the same or even better mechanical properties compared to an uncracked material. SAPs will remain present at their location and will be available for subsequent healing if the conditions are again optimal with sufficient building blocks, water or moisture, and narrow healable cracks.

When not completely submerged in water, only samples containing SAPs showed self-healing properties due to moisture uptake [36, 67]. Even in an environment with RH > 90%, there was noticeable healing, due to their moisture uptake capacity. If reference samples were stored in a climate room with a certain RH, there was almost no autogenous healing, as water was not present to form the healing products. The samples with SAPs showed a regain in strength when stored in an RH of more than 90%. The moisture uptake by SAPs (up to four times their own weight in moisture [55]) seemed to be sufficient to promote a certain degree of autogenous healing, especially in the interior of the crack in the form of further hydration. In the RH condition of more than 90%, the material with 1 m% showed a regain of 60%. At the crack mouth, the crack was still clearly open and only at some distinct places, there was some bridging of a crack by healing products.

Cracks smaller than 30 µm exposed to wet/dry cycles healed completely both with and without SAPs after a healing period of 28 days. SAPs can contribute to the internal healing of a crack after performing wet/dry cycles [67, 125]. Cracks between 50 and 150 µm healed partly in samples without SAP, but sometimes even some cracks closed completely after 28 wet/dry cycles in a specimen containing SAPs [67], as shown in Figure 5.8. Cracks larger than 200 µm showed almost no healing.

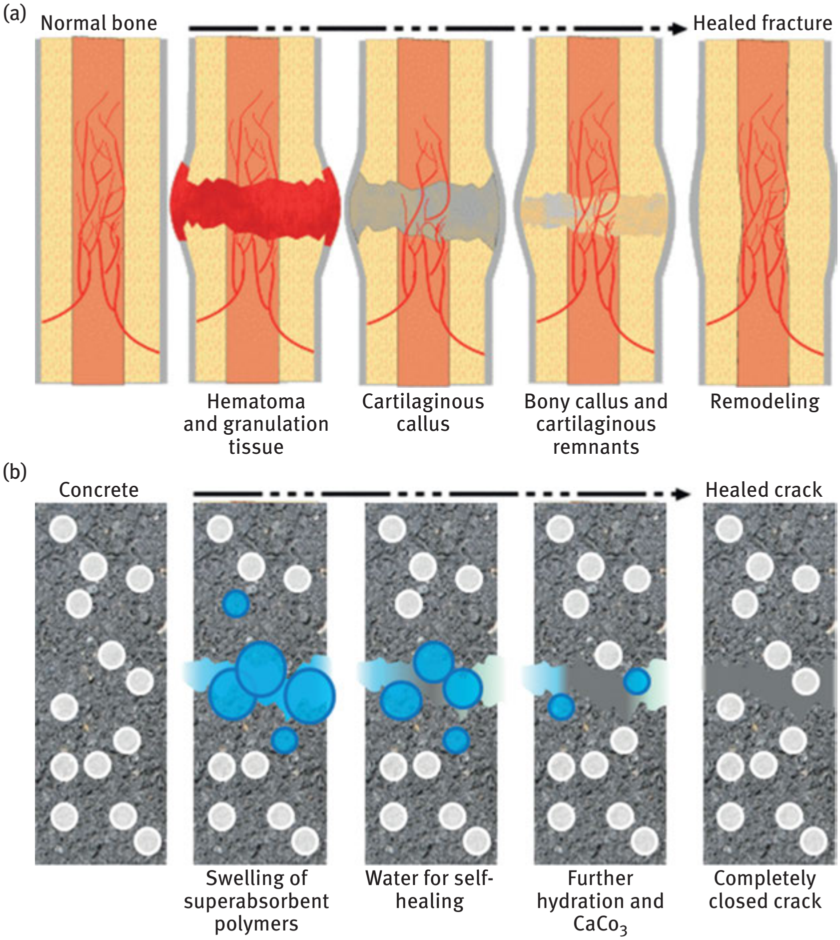

Figure 5.7: Use of superabsorbent polymers in cementitious materials to stimulate autogenous healing, as a biomimicry of bone healing found in living creatures [8].

The cracks are considered too wide to be healed properly within a 28-day period, even though SAPs are promoting autogenous healing.

This healing product formation could be visualized by means of X-ray microtomography [155], as shown in Figure 5.9. The figure shows horizontal slices of small 6 mm wide samples without (top) and with SAPs (bottom), stored at high RH (>90%, left) and in wet/dry cycling (right). The cracks are clearly seen in black, together with the spherical air porosity. The irregular-shaped voids in the bottom part of the figure are macropores formed by the swollen SAP right after final setting. The yellow colors in the figure show the material that is adhered after performing the 28-day healing cycle. This information was obtained by comparing the microtomograms prior and

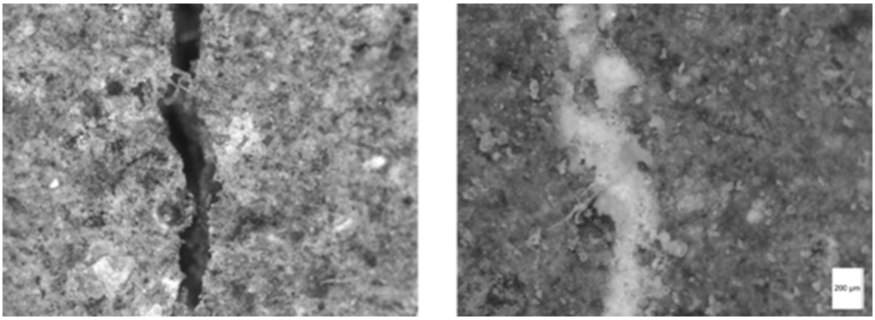

Figure 5.8: Example of a specimen containing 1 m% of SAP after performing 28 days of wet/dry cycling. The whitish healing products are mainly calcium carbonate with some further hydration [8].

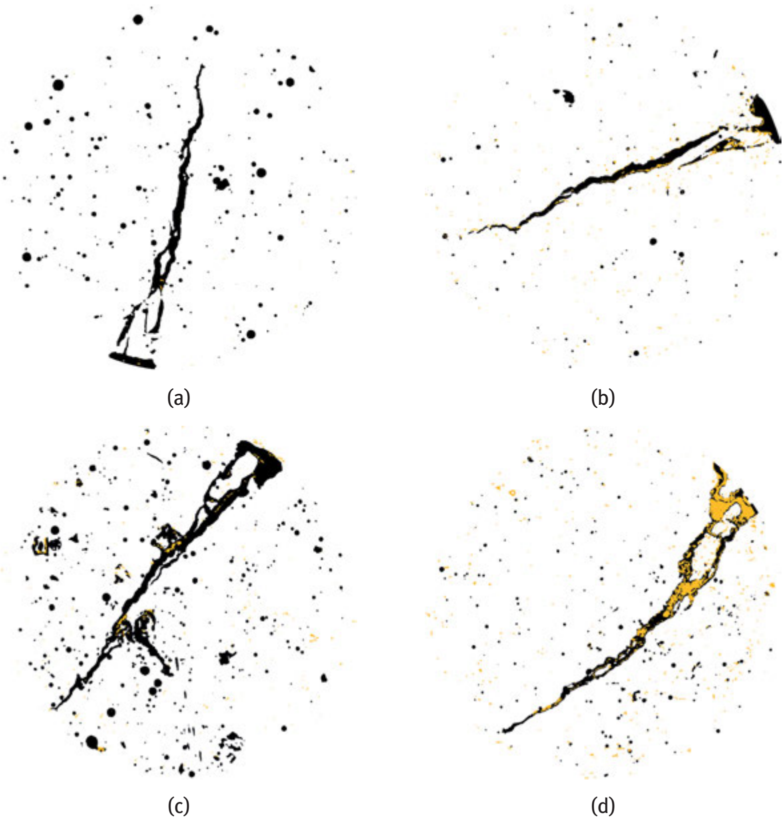

Figure 5.9: (a, b) Cross sections of the specimens without (c, d) and with (a, c) superabsorbent polymers stored at more than 90% RH (b, d) and in wet/dry cycling. Black depicts the porosity and the crack, and yellow visualizes the formed healing products. The diameter of the specimen is 6 mm. This picture has been partly redrafted with permission from Elsevier from source [155].

after healing. No healing was observed in specimens without SAPs when no liquid water is present (Figure 5.9a), while some crystal formation was present near the vicinity of SAPs in SAP specimens (Figure 5.9c). This amount of healing was comparable to the amounts found in SAP-less specimens healed in wet–dry cycling (Figure 5.9b). The largest amount of healing was observed in specimens with SAPs and stored in wet/dry cycling (Figure 5.9d). Almost the complete crack was closed. Some other conclusions could also be drawn in the research performed. The largest amount of healing was found in the region 0–100 μm below the surface. In the interior of a crack, the amount of healing products was less and only at some distinct places, the healing products bridge a crack, probably in the vicinity of a fiber (as they act as a nucleation site for the calcium carbonate crystals [8, 118]). The healing at high RH occurred in the vicinity of the SAP particles, stitching the crack at distinct locations [155]. This healing, as well as in wet/dry cycling, was still stimulated in samples with 8 years of age [118].

The autogenous healing capability of cementitious materials was maintained during subsequent loading cycles to a certain degree. SAP particles promote the self-healing ability by renewed internal water storage upon crack formation and this leads to regain mechanical properties such as the first cracking strength. In wet/dry cycles, the plain material without SAPs was able to regain 45% of its first cracking strength after a first healing cycle. After the second healing cycle, this regain was 28%. When SAPs were used, the regain was 75% and 66%, respectively [61]. The better healing in specimens containing SAPs during first and second loading and healing was also confirmed by natural frequency analysis [60]. Possible explanations are the storage of a calcium-rich fluid (i.e., the pore solution) in the swollen SAPs, and the reduced permeation through the crack. This provides the possibility of the formation of the $CaCO_3$ crystals in the crack. This caused the ideal conditions for promoted autogenous healing. The regain in mechanical properties was noteworthy.

The promoted healing capacity in systems with SAPs was also studied by means of NMR testing [156]. This will prove to be essential for model verification and to increase the simulations for this new type of material in future research. Adding 1 m% of SAP to a cementitious material stimulated further hydration with nearly 40% in comparison with a cementitious material without SAPs, in wet–dry cycling. At 90% RH, no healing was observed in reference samples while specimens with SAPs showed up to 68% of further hydration compared to a reference system without SAPs healed in wet/dry cycling, due to the uptake of moisture by the SAPs. This proved the differences in observed regain in mechanical properties.

5.7 Practical applications of SAPs in the construction industry

In 2006, a pavilion was built for the FIFA World Cup [3, 157]. It was a thin-walled structure with very slender columns without conventional reinforcement. The low water-to-binder structure did not show any kind of cracks due to the prevention of autogenous shrinkage cracks by the included SAPs and the sustained internal curing.

In China, SAPs have already been applied in several civil engineering construction projects. Examples are the Lanzhou–Urumqi railway where SAPs were used to prevent massive concrete slabs from cracking. The concretes with SAPs were less sensitive to moisture loss because of evaporation [63, 158]. Two other field applications were performed in southern China [159]. A shear wall structure that had dimensions of 20 × 50 x 0.85 m cast in one time did not show surface cracks after 7 days when SAPs were added. A cast-in-place concrete floor slab was cast in one time and had dimensions of 12 × 8 x 0.12 m^3 and no curing methods were used. No cracks were observed and the used gel-type SAP showed potential to mitigate early-age cracking.. SAPs were also applied in the China Zun tower [160]. It was found that the SAPs reduced shrinkage by 46% and that the later age compressive strength was not affected when 0.56 m% of SAP was added to the mixture.

A project on large-scale tunnel elements in Belgium, iSAP, will include the application of large-scale elements for tunnel construction [97]. SAPs will hereby be added as a mitigation measure for autogenous shrinkage. In this way, occurring shrinkage cracks may be avoided. The SAPs will also possess self-sealing and self-healing properties. In this way, some remaining shrinkage cracks may be sealed and healed and the structure will possess some sealing potential for observed cracking during its lifetime. This is interesting for the application in tunnels and other ground-retaining structures, as the flow of harmful substances is stopped [33, 49].

5.8 Conclusions

In conclusion, there is still a lot of unraveling to do in order to apply SAPs into practice. Possible applications of the self-sealing and self-healing material are widely spread. Water-retaining structures may benefit and construction companies may be interested. The principle of using SAPs has its possible applications for the industry. Contractors are searching for a way to decrease shrinkage cracks and to obtain a watertight structure. This is especially important for tunnel elements, underground parking garages, basements, liquid containing structures, pavements, and so on. Nowadays, contractors are often forced to apply crack repair right after construction, due to the formation of shrinkage cracks and thermal cracks at early age. The shrinkage could be overcome by using SAPs as they may provide internal curing to the construction element: they absorb water in the fresh concrete mix, and provide it to the cement particles at the right moment in the hydration process, in this way reducing the autogenous shrinkage. In hardened concrete, they may seal occurring cracks, as they swell in contact with intruding water. This may reduce the uptake of harmful substances, most likely leading to an enhanced long-term durability and service life. The SAPs will subsequently promote autogenous healing of the crack since they provide water for further hydration of yet unhydrated cement particles and calcium carbonate precipitation, leading to even more tight structures and possible regain of the mechanical properties. More research is needed in terms of the long-term durability of these novel cementitious materials with SAPs [161].

Microfiber-reinforced strain-hardening cementitious composites possess the qualities of a high-strength concrete combined with tensile ductility and crack width control. Their small cracks are interesting in terms of autogenous healing where only small cracks are able to heal completely, further stimulated by SAPs. Combined with (promoted) self-healing it is a durable material and very promising to use in the future. In regions with wet/dry cycles, water remains present in the SAPs during the dry periods. Therefore, self-healing can prevail at all times. However, performance-based durability concepts are still required to get a durability design framework for these strain-hardening materials [162].

Furthermore, due to the self-compacting properties of the strain-hardening mixture, thin forms are achievable [120]. Nature fits form to function. This is also true for this material; the accretion of material to places where it is most needed, resulting in adaptive structures. The form should be ideal to transfer loads, so that an excess of material can be removed. This material will result in lighter and safer structures, leading to a reduced safety factor as the structure may reach its optimal design.

The role of autogenous healing on corrosion prevention will also be important in the future. If cracks are not sealed, water containing aggressive substances will break down the passive film on the reinforcements. This aspect needs to be considered when autogenous healing is used in real-life structures. The maintenance and longevity of these structures is hereby very important. The close investigation on plastic shrinkage mitigation and other promising pathways for inclusion of SAPs in cementitious materials are also key for the near future. This white powder thus will be more accepted in the conservative building industry.

One general conclusion can be made; one should continue to build with nature's rules. The bleeding (water for SAPs), blood cells (building blocks), blood flow vascular network (porous concrete), blood clothing (formation of healing products near synthetic microfibers), skeleton and bone healing (crystallization) are only a few properties studied in the field of construction healing. By mimicking nature to enhance performance, constructions that are more durable will be designed, leading to a higher service life and better overall life quality.

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