An investigation of the compatibility of different approaches to self-healing concrete: The superabsorbent polymers and microbially induced calcite precipitation

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Abstract. The concept of the self-healing concrete, thus an improvement of the durability of concrete structures, has become a widely investigated topic in recent decades. The aim of this study is to examine a possible combination of two existing approaches to the spontaneous crack-sealing – the biologically driven calcite precipitation and the addition of superabsorbent polymers (SAP) into the concrete matrix. Firstly, the paper compares the absorption rate of SAP in various solutions, including a nutrient-based solution which is used in the bio-concrete. The results show that the ionic composition of the liquid influence the swelling capacity greatly. In this study, the absorption rate of SAP in the nutrient-based solution is as low as 6% of the rate in distilled water. Thus, this finding could indicate a possible drawback of the combination of the proposed self-healing approaches. Further, this paper determines the impact of the SAP addition to cement paste with different water/cement ratios. In this experiment, the SAP is applied in various dosages (1% and 0.5% by c. w.) and states (a dry state or a fully swollen state). The conducted flowability and mechanical properties tests indicate a profound, generally negative, impact of the SAP addition on the cement paste characteristics. The paper then discusses possible adjustments of the SAP-cement paste composition and compares the present results with previous studies.

1. Introduction

The susceptibility of concrete to cracking and the resulting need for regular repairs are fundamental issues which significantly influence the durability of concrete structures. The early microcracks formation does not endanger the structure load-bearing capacity directly; however, if the crack widths exceed a certain level, the cracking might result in a failure of the reinforcement cover layer, thus possibly to a total failure of the structure.

This durability endangerment has led researchers to the idea of self-healing concrete. For the past decades, numerous studies have focused on the amplification of the natural autogenous crack-sealing capacity of concrete – a phenomenon when delayed cement grains hydration leads to crack closure [1]. This paper deals with a combination of two previously proposed approaches to self-healing concrete: the biologically driven calcification and incorporation of superabsorbent polymers.

The firstly mentioned method, the bio-based self-healing concrete, is based on the ability of certain microorganisms to produce calcium carbonate (CaCO3) when supplied with appropriate compounds. In this novelty material, the crack sealing is a result of metabolic activity of bacteria which is incorporated
in the concrete matrix. For the past two decades, numerous studies identified suitable bacterial genotypes and described their limitations [2–5]; they proposed different types of bacteria protection [2,6–10]; and they examined the self-healing efficiency through in-vitro [2,8–14] and in-situ experiments [12,15].

The second mentioned approach to self-healing concrete relies on the ability of superabsorbent polymers (ionic monomers with a lower cross-linking density than hydrogels) to absorb fluids up to a hundred times their own weight [16].

As summarized in a RILEM technical letter by V. Mechtcherine [17], superabsorbent polymers (SAP) have been extensively investigated in the last decade as a new and promising chemical admixture for concrete. In the overview [17], several proposed applications of SAP in concrete are presented: an application of SAP for mitigation of autogenous shrinkage [18–20] (i.e., internal curing by water absorbed in SAP), an application of SAP to improve frost resistance [21–23] (i.e. a replacement of air-entering agents to create air voids), rheological modification of shotcrete [24], waterproofing (i.e. blocking of water-flow by swollen SAP), and an application of SAP for self-healing.

The possible self-healing mechanism of concrete with SAP is multilayered [16,25,26]. Firstly, the swollen SAP present in cracks is blocking the outside water with harmful aggressive substances from penetration. Secondly, the barrier from SAP maintains the products of the autogenous healing inside the crack, thus promoting the crack-closing potential. Thirdly, the rate of autogenous healing is closely related to water/humidity presence. The water absorbed by SAP then provides the needed supply of moisture for the healing action. Furthermore, the SAP can be used as a carrier for healing substances. This SAP application combined with the biological concrete principles could be developed into a profitable technology as SAP possess a remarkable variety of features: great absorption and retention potential, sensitivity to different pH, temperature, light, and pressure which affect the release of the absorbed substance [16].

The possible effect of the application of SAP in the bio-based self-healing concrete is multiple. The SAP particles could be used as a carrier for the bacterial healing agent or to create air voids in the cement matrix in which bacteria would be protected from the destructive crystalline pressures. Further, the swollen SAP could serve as a needed water reservoir for bacterial metabolic activity.

A similar combination of the microbially induced calcite precipitation (MICP) and standard hydrogels, a significantly less absorbent material than SAP, has been investigated in several studies. Some of them performed experiments with bacterial spores encapsulated in hydrogel sheets [27,28]. These pilot studies proved the compatibility of the selected bacteria with hydrogels and reported successful encapsulation process and significantly promoted crack-sealing. However, the effect of the applied hydrogels to the compressive strength turned out to be unsatisfactory as the hydrogel addition led to a drastic drop of the strength [28]. Wang et al. [29] limited this drawback by an application of pH-responsive hydrogels which increase their swelling at lowering pH, thus the creation of voids after the swollen hydrogel was limited.

The combination of SAP and MICP as investigated in this paper has been also already proposed [30]; however, this novelty approach must be examined in further detail as numerous questions remain unanswered. This paper primarily focuses on the absorption rate of the selected SAP in different solutions (distilled water, tap water, and solutions with a nutritional part of the biological healing agent), the impact of SAP to cement flowability and mechanical properties and discusses the aspects which might influence the SAP and bio-concrete compatibility.

2. Materials and methods

2.1. The absorption rate of SAP in various substances

In the previous research, it has been demonstrated that the absorption rate of SAP is closely related to the ions present in the soaking solution [31]. In our study, the swelling capacity of SAP was measured in several different solutions to outline the possible applications of the material in the bio-concrete production.
The known quantities of SAP (a cross-linked acrylamide/acrylic acid copolymer, potassium salt obtained from Evonik Industries AG, Germany) were submerged in containers with tap water (TW), distilled water (DW), and two solutions with different concentrations of nutrients (CLYA and CLYB), which have been used as a part of the biological healing agent, description can be seen in Table 1. The SAP have been left to soak in the solutions for 24 h in sealed containers in 25 °C. After the end of the absorption period, the swollen SAP was filtered from the solutions using a fine sieve. Subsequently, the unabsorbed solutions and the swollen SAP were carefully measured, and the absorption capacity was evaluated.

Table 1. Solutions for the SAP immersion – an investigation of absorbency in different conditions.

|       | TW  | DW  | CLYA | CLYB |
|-------|-----|-----|------|------|
|       | tap water | distilled water | distilled water, 80 g/l calcium lactate, 1 g/l yeast extract | distilled water, 60 g/l calcium lactate, 17 g/l yeast extract |

2.2. Mix design of cement paste with SAP and nutrients

As outlined in the Introduction, SAP have a striking absorption capacity. Although it has been shown that the liquid uptake in cement paste is decreased significantly when compared to water immersion [19,32], the effect of the SAP addition to concrete/cement paste workability is still pronounced. For this reason, researchers have been determining and testing various "extra" water-cement (w/c) ratios [19,20,33–36] which would make up for the water entrained by SAP particles and provide the needed moisture for the targeted internal curing. In our study, a variety of cement pastes with different composition was prepared and examined in greater detail.

In the conducted experiment, Portland cement CEM I 42.5 R and tap water were used (Table 2) for the cement paste preparation. The SAP was applied in the dosage of 1% by c. w. in the case of dry particles (S1 and S2) and approximately 0.5% by c. w. of particles which were immersed in tap water for 24 h prior to the mixing process (i.e. 456 g swollen SAP, S3).

Table 2. Mix designs for flowability test – the groups with CEM I and tap water.

|       | REF  | S1  | S2  | S3  |
|-------|------|-----|-----|-----|
|       | [g/l] | [g/l] | [g/l] | [g/l] |
| CEM I 42.5 R | 586 | 586 | 586 | 586 |
| tap water | 293 | 293 | 293 | 0 |
| w/c | 0.5 | 0.5 | 0.5 | 0 |
| extra tap water | - | - | 87.9 | - |
| w/c_e | - | - | 0.15 | - |
| sand (PR 0.1-2) | 1758 | 1758 | 1758 | 1758 |
| SAP dry | - | 5.86 | 5.86 | - |
| SAP wet (tap water) | - | - | - | 456 |

In all cases, the SAP has been firstly added and mixed with dry cement prior to any other additions. As mentioned, the SAP has been applied in two forms – in a dry state and in a swollen state. In the case of the swollen SAP, no mixing water was further added into the cement paste.

2.3. The flowability test

A cement flow test was performed in an attempt to determine the impact of the investigated additions (SAP and nutrients) to the rheology of fresh cement paste and further optimize their content based on the workability of the pastes. Immediately after the mixing process, the cement pastes of all the series were submitted to the cement flow test using a cement flow table according to relevant standards.
2.4. The tensile and compressive strength tests
After the flowability tests, the prepared cement mortars were cast in molds to produce 40x40x160 mm mortar specimens. After 24 hours, the specimens were demolded and kept in room temperature and humidity for further examinations. After 7 days from casting, all of the series were submitted to mechanical testing. Firstly, a three-point bending test was performed. The bending tests were run in a deflection-controlled mode, and the maximal load values were recorded and analyzed using a controlling software.

Further, the compressive strength was determined on the specimen halves that were created after the three-point bending test. The specimens were evenly loaded with pressure, and the mode of failure was observed to exclude incorrectly damaged specimens. The maximum applied load was recorded and analyzed using a controlling software.

2.5. Dynamic modulus of elasticity
To further determine the effect of SAP (with/without the extra water addition) on mechanical properties of cement paste, non-destructive measurements of the dynamic modulus of elasticity ($E_d$) were performed on the prepared cement paste specimens at 7 days from casting.

3. Results

3.1. The absorption rate of SAP in various substances
As discussed previously, the ionic composition of the soaking solution may have a dramatic impact on the SAP absorbance capacity. It is evident from our results (Table) that they have a strong concordance with this prediction. The SAP immersed in distilled water (DW) could retain up to 246 g of the liquid per gram of the material, whereas in other solutions the absorption potential decreased dramatically. In tap water, the absorbance reached 157 g/g SAP, and in the nutritional solutions (CLY A and CLY B) the values were as low as 15 g/g SAP, which is only about 6% of the capacity of SAP immersed in distilled water.

| Solution type | Absorption [g solution/g SAP] |
|---------------|------------------------------|
| TW            | 157                          |
| DW            | 246                          |
| CLY A         | 15                           |
| CLY B         | 16                           |

3.2. The flowability test
In order to determine the impact of the SAP addition on the flowability of cement pastes with different compositions, the flowability tests were performed and the results compared with reference pastes. In general, the addition of dry SAP to cement paste dramatically affected the workability in all cases.

As it can be observed from Figure 1, the addition of dry SAP (1% by c. w.) without any increase of the mixing water (S1) resulted in a much drier mixture when compared to the reference sample (REF). Furthermore, even a considerable increase of the mixing water ($w/c_e = 0.15$, S2) did not make up for the water uptake by SAP in our experiment. On the other hand, the addition of a swollen SAP (0.5% by c. w.) with approximately 453 g of absorbed tap water (S3) resulted in a slightly more flowable mixture when compared with the reference paste (REF).
3.3. The tensile and compressive strength test

It was suggested in the Introduction that the SAP addition to concrete may have a pronounced impact on the material's mechanical properties. To evaluate the effect, series of compressive and bending tests were performed.

Considering the results of flowability presented above, the impact of SAP addition on both the compressive and tensile strength is not surprising as the mechanical test results overall correspond with the paste consistency (Figure 2 and Figure 3). The paste S1 with dry SAP 1% by c.w. and no water addition showed drastic drops of both strengths. The compressive strength fell down to 27% of the reference paste strength and the tensile strength to 45%. The extra water in the case of the S2 paste partially limited the negative impact of the SAP addition. The paste S2 reached 40% of the reference paste compressive strength and 60% of the reference paste tensile strength. The paste S3 (wet SAP 0.5% by c. w.), which had the closest consistency to reference paste, reached lower but not as severely decreased strengths values as the other pastes (73% of the reference compressive strength and 69% of the reference tensile strength).

3.4. Dynamic modulus of elasticity

As it can be seen in Figure 4, the obtained dynamic modulus of elasticity of the cement pastes with various SAP and water additions are in line with the compressive strength values presented above. The findings suggest that the addition of wet SAP in the dosage 0.5% by c. w. (S3) had the lowest negative impact on the examined property (a decrease of 26% compared to the reference paste). The addition of dry SAP in the dosage 1% by c. w. with no water addition (S1) resulted in a 71% drop. However, the added extra water in the group S2 lowered the negative effect on $E_d$ significantly (49% of the reference paste value).
4. Discussion

The results describing the limits of the absorbance capacity of SAP in solutions with different ionic composition presented in this paper are in line with the existing studies [25,31]. The results of the significantly decreased absorption rates of SAP in nutritional solutions, used as a part of the healing agent in self-healing bio-based concrete, provide a valuable framework for future research of the SAP and bio-concrete combination. Possibly, the nutrients incorporated in the matrix could limit the effect of the SAP addition. Not only its internal-curing potential but also the role of SAP as a provider of the needed moisture for a bacterial activity could be restrained. However, more detailed knowledge of the SAP absorption kinetics in bio-based self-healing concrete should be explored and described in future studies.

The cement flow table tests verified the prediction that the dry SAP addition would lead to a significantly drier mixture as reported by previous studies [19,36]. In this paper, even the addition of 30% of mixing tap water (w/c_e = 0.15, i.e. 15 g/g SAP) to cement paste (1% SAP by c. w.) did not result in a mixture with a similar flowability as the reference paste, thus the amount of extra water did not make up for the moisture absorbed by SAP. This finding strongly contradicts with the most frequently considered value of SAP absorbency in cement paste between 12-13 g/g SAP [19,22,23,37]. However, in the majority of the experiments which dealt with cement composites with SAP, a certain amount of superplasticizer was applied into the mixtures. When no superplasticizer was added, the needed extra water ratio was as high as w/c_e = 0.2 in the case of 1% SAP by c. w. [34].

In our experiment, the addition of fully swollen SAP (0.5% by c. w. in a dry state) lead to similar flowable paste as the reference. It seems that the majority of the absorbed water by SAP was gradually released from the swollen particles during the mixing process, thus no further mixing water was needed.

It should be, however, noted that there are numerous possible sources of error when searching for a sufficient cement paste mix design with SAP. As presented earlier, the ions present in solution affect the absorbency greatly. Numerous studies also proved that the absorption kinetics significantly depends on the size of SAP particles [25,38]. Furthermore, we must keep in mind that the flowability of the cement paste with SAP would in all probability shift considerably in time, thus, in future studies, time-dependent flowability measurements are needed for deeper understanding of the mechanisms.

The results obtained from mechanical measurements show a distinctive tendency of SAP to decrease both the compressive and tensile strength of the material. With increasing SAP content, the negative effect seems to be more pronounced. This behavior was also reported by previous studies [19,33,34,36]; however, in our study, the mechanical tests were conducted at 7 days from curing only. This strength drop may decrease with time as the water captured inside SAP particles would be released at later ages, thus the internal curing process would be activated [19]. Furthermore, a number of researchers reported
an effect of a curing mode (i.e. wet/air curing) on the strength development [35,36]. In our experiment no other method of curing was used except air curing; however, the phenomenon should be further explored as it seems to influence the material properties significantly.

5. Conclusion
In this section, the main observations gained from the conducted experiments and future proposes will be briefly concluded:

- The absorption capacity of SAP is dramatically reduced in solutions with a nutritional part of the healing agent used in bio-based concrete. This finding suggests that a sufficient encapsulation of the nutrients in SAP by simple soaking is not realistic.
- The absorption rate of SAP in different mortars (different cement types, nutrients additions, distilled/tap mixing water, etc.) should be further determined.
- The addition of soaked SAP seems to be also an applicable approach. Future research should explore the possibility of SAP with an absorbed bacterial solution (bacterial spores scattered in water). This impregnated SAP incorporated into the mortar could then provide both water for cement hydration and the needed protection of the spores against harmful crystalline pressures by creating of air voids.

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