Effect of healing agents on the rheological properties of cement paste and compatibility with superplasticizer

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Abstract. Self-healing concrete is considered as a new generation of concrete with the ability to heal cracks without human intervention. The healing agents are incorporated into the concrete to activate the healing mechanism and to improve the healing efficiency. While both lab- and large-scale projects have shown that the addition of healing agents can have a possible positive effect on the hardened concrete properties (e.g. compressive strength), unfortunately, the evaluation of fresh properties of self-healing concrete mixes is often neglected. In the current study, the effect of healing agents is clearly identified starting from the paste level. Different techniques were used to study the effect of healing agents on the consistency, viscosity and adsorption behaviour of PCE-based superplasticizer in cement paste. A crystalline admixture and bacteria were used as healing agents, and CEM III/A was used as the binder component of the paste. The results showed that the inclusion of bacteria did not influence the rheological properties of the cement paste and no incompatibility issues were found with the superplasticizer. On the other hand, the presence of the crystalline admixture in the paste interfered with the rheological properties of the cement paste as a reduction of workability, an increase of paste viscosity, and an increased adsorption of superplasticizer.

1 Introduction

Concrete has been widely used as a major material for infrastructure works. The durable character and the advantageous price-quality ratio compared to other materials has made concrete indispensable in the modern era. However, cracks in concrete structures are inevitable and are known as one of the inherent weaknesses of concrete, thereby making a threat to the durability of infrastructure which can lead to unsafe conditions. There are many repair techniques to seal and heal the cracks, but these approaches are costly and time-consuming. Therefore, during past years, many researchers searched for alternatives to solve these problems by developing a new generation of concrete, namely self-healing concrete. Self-healing technologies have proven to effectively close cracks partially or fully in concrete. This is sometimes accompanied by a recovery in mechanical properties, possibly even an improvement. Therefore, these technologies could make concrete respond to its environment and increase the lifespan of infrastructure. Crystalline admixture (CA) and bacteria are two examples of promising healing agents which have been extensively researched both at the academic and industrial levels. De Belie et al. [1] classified the functionality of CA as stimulated or improved autogenous healing and bacteria as autonomous healing. According to the research by Roig-Flores et al. [2], CA has the ability to seal large cracks with a width around 250 μm. The healing product of CA composite was found to be calcium carbonate ($CaCO_3$) under the morphology of aragonite [3]. On the other hand, the use of microorganisms allows for microbiologically induced calcium carbonate precipitation (MICP), leading to a sudden urge for the development of bacterial healing agents for concrete application. Jafarnia et al. [4] reported an increase of mechanical properties of the bacterial concrete due to the calcite precipitation. In addition, cracks up to 160 μm were completely healed and if the specimens were treated in a curing environment, a bigger crack of around 540 μm could be healed. The main goals of utilizing healing agents in the concrete are to promote the healing mechanism and to improve the healing efficiency, however, the evaluation of fresh properties of self-healing concrete mixes is often neglected [5]. Furthermore, the adsorption behaviour of superplasticizer in fresh cement paste has been previously studied [6–10], while the compatibility between cement, superplasticizer and healing agents is still unknown. Therefore, understanding the influence of healing agents in relation to the rheological properties is of great importance. Before going into the concrete level,

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the effect of healing agents should be clearly identified starting from the paste level to serve as a basic input for formulating the mix design of self-healing concrete. In this study, the effect of healing agents on the dispersing ability of PCE-based superplasticizer in the paste is analyzed to understand the adsorption behaviour.

2 Materials and methods

CEM III/A 42.5N and tap water were used to prepare fresh cement paste. This type of cement contains 52% clinker and 48% blast-furnace slag. Two commercial healing agents, named Penetron crystalline admixture and Basilisk bacteria healing agent (BAC), were used in this study. The dosages of CA and BAC were fixed at 1% and 2% by weight of powder, respectively, as recommended by the producers. The healing agents were added into the paste by changing the powder proportion of the mixture. It means the powder in CA paste comprises 99% cement and 1% CA, while the powder in BAC paste has the proportion of 98% cement and 2% BAC. Furthermore, Fluvicon 801 was used as a polycarboxylate-ether (PCE) based superplasticizer (SP) with a solid concentration of 20%. The dosage of SP was fixed in the range of 0–0.8% by weight of powder (i.e. powder means 100% cement for control paste, 99% cement + 1% CA for CA paste, and 98% cement + 2% BAC for BAC paste). This superplasticizer is mostly used for ready mix concrete application, which is in line with the target application of this study. Finally, all pastes were made with a water to powder (*w/p*) ratio of 0.40. For the mixing procedure, the dry components and water were initially mixed for 1 min in the Hobart mixer with a low speed. Then, the mixer was stopped for 30 sec and the bowl was scraped to ensure homogeneity and ensure no dry components remained on the wall and bottom part of the bowl. Next, the paste was mixed again for 2 mins in the Hobart mixer with a low speed. Thus, the total mixing time was 3 mins. In order to evaluate the fresh properties of the paste, several experimental tests were executed including:

- Mini slump test

The mini-slump test was performed to evaluate the workability of the fresh paste. Another aim of this test was to determine the critical and saturation dosage of the SP. The critical dosage (CD) is defined as the minimum SP dosage to start improving the workability, while the saturation dosage (SD) corresponds to the dosage at which the effectiveness of the SP reaches the maximum limit, as beyond this dosage, water reduction is not possible or segregation occurs. To do this test, a truncated conic mould (70 mm in top diameter, 100 mm in bottom diameter and 60 mm in height) was placed on an acrylic plate, filled with the paste and lifted upward. The resulting spread diameter of the paste was the mean value of two measurements made in two perpendicular directions. The slump tests were performed at 5, 30, 60 and 90 mins after mixing time. As a note, prior to all slump tests, the paste was pre-mixed for 30 sec. The slump spread was recorded and regarded as a consistency parameter.

- Viscosity test (visco-test)

The visco-test was carried out to measure the plastic viscosity of the paste in relation to the rheology of the fresh paste which could not be quantified in the mini slump test. The paste was poured into the cup with the constant mass of paste between 210–220 g. Then, the container was installed in the HAAKE Viscotester 550 together with a spindle. The apparatus was programmed to measure the paste viscosity at 5, 30, 60 and 90 minutes after mixing time. On each measurement, the shear rate was gradually increased from 0 to 50 s^{-1} for about one minute. In this study, the shear rate of 15 s^{-1} was considered for further analyses. This shear rate mimics the concrete mixing during rotation inside the truck mixer and pouring the fresh concrete from 1 meter height.

- Total organic carbon (TOC) test

The TOC test was executed to analyse the adsorption capacity of SP on cement and healing agent particles. After mixing the powder and water for 3 mins, the paste was poured into plastic tubes with ~50 g of paste per tube and centrifuged for 10 mins to separate the solid from the pore solution. The supernatant was then extracted and diluted with phosphoric acid (H_3PO_4). The solution was centrifuged for another 10 mins in order to allow sedimentation of the impurities. The solution was finally diluted with demineralized water to meet the calibration range of the TOC analyzer and poured into vials to be tested on the Lotix TOC Combustion Analyzer. The carbon content of pure SP and control paste without SP was also measured in order to calculate the total amount of SP reacted.

3 Results and discussions

3.1. Slump life

Figure 1 illustrates the slump changes over time on pure cement paste and cement pastes with healing agents. The first slump of pure cement paste was measured at 135 mm. The slump gradually decreased as time increased, reaching 118 mm after 90 mins. The influence of CA and BAC was noticeable. The slump values at 5 mins for CA paste and BAC paste were 120 and 145 mm, respectively. In comparison to the pure cement paste, it showed that the CA reduced the slump by 11.1% while the slump increased by 7.4% due to BAC. The tendency of slump reduction over time was also clear on these pastes. Especially for CA paste, the reduction was less significant as compared with pure and BAC pastes and was almost constant. It was attributed to the very low slump value at the beginning which almost reached the boundary of the mini slump cone. Thus, further reduction was not possible over 100 mm. In contrast, although the BAC slightly increased the slump, the slump reduction over time had a similar trend to the pure cement paste. It is interesting to observe that the initial slump of the pure cement paste corresponded to the slump of the BAC paste after 60 mins.

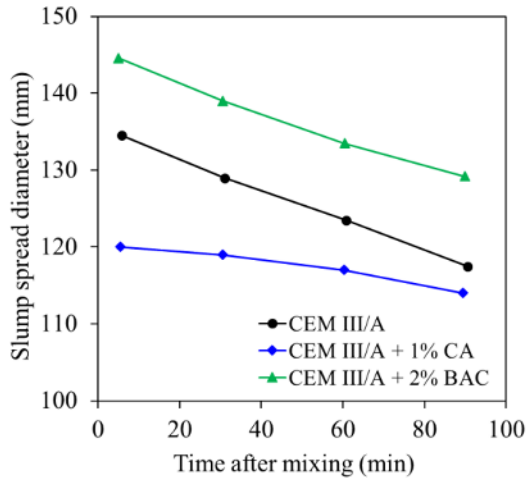

Fig. 1. Reduction of slump values over time on all pastes

3.2 Impact of SP dosage on pure cement paste

Based on Figure 1, it was evident that there is a need to introduce the SP to improve the workability of the paste. To start, the SP was initially introduced to the pure cement paste from 0.1 to 0.6% by weight of powder. Both slump spread and viscosity were simultaneously recorded as depicted in Figure 2. Initially the slump life of the cement paste with the addition of SP was evaluated as shown in Figure 2.

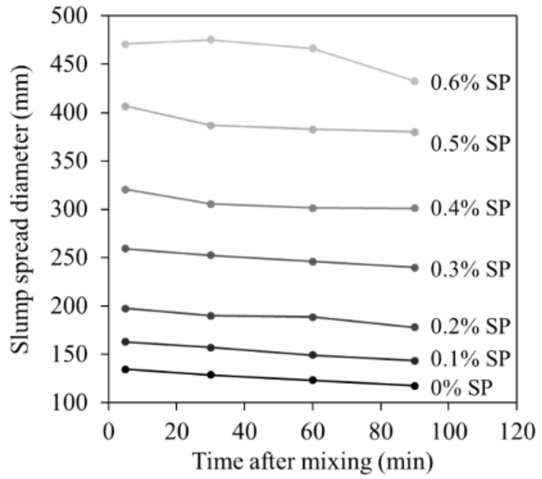

Fig. 2. Slump life of superplasticized cement paste with different SP dosage

In general, the slump spread reduction as a function of time was relatively small by the addition of SP dosage ≤ 0.3% by powder weight. The slump retention was clearly identified when the SP was introduced at the dosage of 0.4 and 0.5% by powder weight, maintaining the existing slump after a long period (in this case, from 30 to 90 minutes). Cement paste containing 0.6% SP showed segregation. Further analysis was done to establish the relationship between slump spread and SP dosage by considering the slump results from the first slump test (5 minutes after mixing). Figure 3 shows that, as expected, the slump spread diameter increases with an increasing dosage of SP. It can also be seen that increasing the SP dosage results in a decrease in the viscosity.

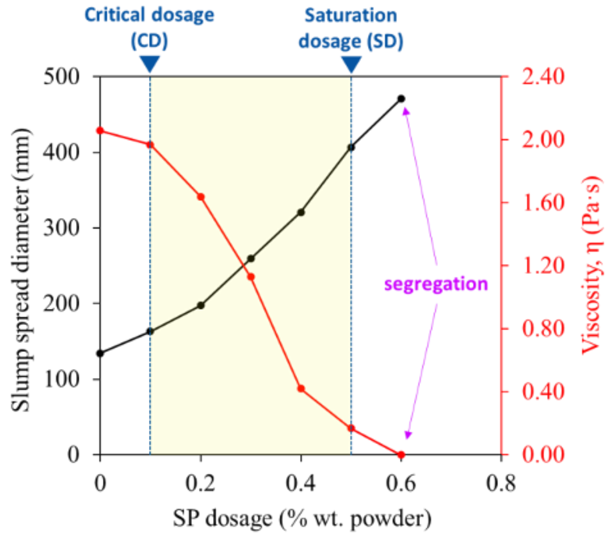

Fig. 3. Determination of CD and SD based on slump and viscosity results

As can be seen in Figure 3, when a high SP dosage (0.6% wt. powder) was introduced, segregation was observed from visual inspection. It was also clear that the slump spread still increased with a high SP dosage but the viscosity of the paste was considerably lower reaching zero value. Therefore, the CD and SD were determined at 0.1% and 0.5%, respectively. In this range between 0.1–0.5%, the addition of SP can be regarded as effective to improve the paste workability.

3.3 Impact of healing agents on superplasticized cement paste

The CA and BAC pastes were evaluated in the same way as the pure cement paste and the results are depicted in Figure 4. As can be seen in Figure 4(a), the introduction of BAC slightly increased the slump values as compared with pure cement paste. Nevertheless, both BAC paste and pure cement paste exhibited a very similar tendency in terms of workability changes by the gradual SP addition from 0 to 0.6% by powder weight. It suggests that (1) the BAC did not considerably affect the rheology of superplasticized cement paste and (2) BAC did not interfere with the dispersing ability of SP in the paste. In contrast, the incorporation of CA considerably affected the slump value. The CA paste, in fact, showed an initial improvement of the workability after 0.3% SP was introduced. Above this dosage, the slump started to increase gradually. It is noteworthy to mention that the pure cement and BAC pastes showed segregation at 0.6% SP, while for CA paste it occurred at 0.8% SP. It was clear that the CA paste needs more SP than the other two systems. On the other hand, Figure 4(b) showed that the viscosity of BAC paste was identical with the viscosity of pure cement paste, despite the minor differences which were observed at 0 and 0.1% SP. It indicates no considerable effect of bacteria on the fresh properties of the paste, which is in line with the mini slump test result. Specifically on the use of CA, the paste showed a thixotropic behaviour. In order to eliminate this behaviour, the CA paste was pre-sheared at the highest shear rate (50 s^{-1}) before testing as suggested by Wallevik et al. [11]. The viscosity of CA paste without SP was recorded at 2.5 Pa·s, which was approximately 21% higher than the viscosity of pure cement paste. However, regardless the SP dosage, the CA paste always showed a higher viscosity as compared with other pastes. All in all, the CD and SD of BAC paste were determined at 0.1% and 0.5% by powder weight, respectively. The CD and SD of CA paste showed higher values at 0.2% and 0.7% by powder weight, respectively.

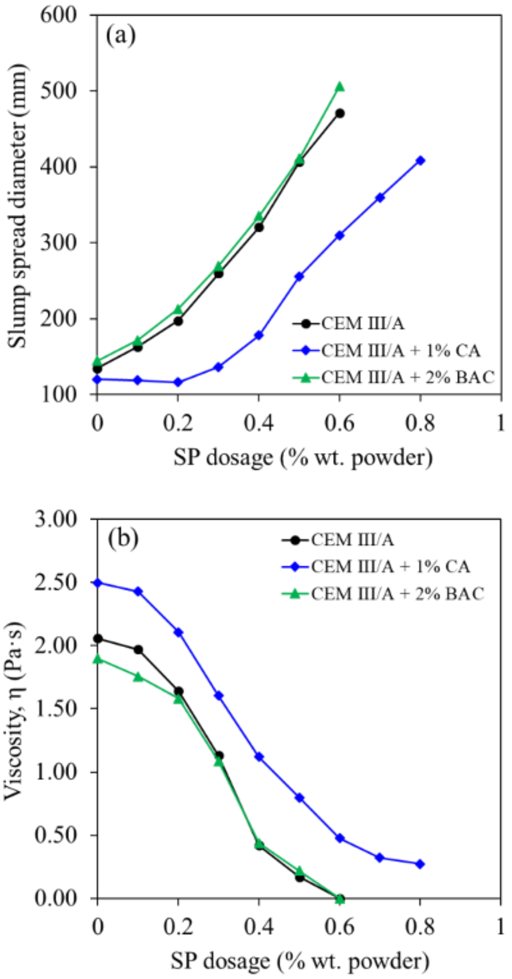

Fig. 4. Alteration of (a) slump and (b) viscosity of the cement paste with various SP dosages due to the addition of healing agents

3.4 Superplasticizer adsorption capacity of cement pastes with and without healing agents

Initially, the total organic carbon of all pastes without SP was measured. The total organic carbon of pure cement paste, CA paste and BAC paste were 161, 771 and 794 ppm C (parts per million carbon), respectively. This showed that the healing agents (CA and BAC) released a significant amount of organic carbon into the pore solution with the contribution of roughly 600 ppm C to the cement paste. The SP was then introduced to the pastes with the SP dosage between 0.1–0.5%. The result is shown in Figure 5.

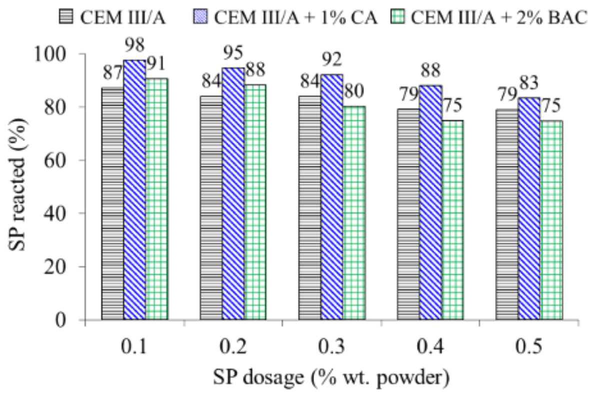

Fig. 5. Percentage of SP reacted on the paste systems

By adding 0.1% SP on pure cement paste, it showed 87% SP reacted on the paste, while 23% remained in the pore solution. The further additions of SP in the range of 0.2–0.3% and 0.4–0.5% slightly reduced the amount of SP reacted at 84 and 79%, respectively. In case of CA paste, a higher amount of SP is adsorbed indicating that the SP also adsorbs on the surface of the CA healing agent particles. XRD analysis revealed that the CA contains a significant amount of C_3A. SP is known to have a high affinity for C_3A and it determines the paste rheology. Alonso et al. [12] reported that since C_3A has a higher zeta potential than the silicate phases, the admixture tends to adsorb into the aluminate. The hydration products of C_3A such as C_4AH_{19} and calcium monosulfoaluminate hydrate (C_4AsH_{12}) are able to take up admixtures in their laminate structures. Therefore, in this case, the SP is adsorbed by the C_3A phase and a higher SP demand is needed when the CA is introduced into the cementitious system to reach the same dispersion as the system without CA. Moreover, the incorporation of BAC slightly altered the adsorption capacity of the SP. The addition of 0.1% SP dosage showed that 91% SP was reacted and a gradual reduction of the amount of SP reacted was observed as the SP dosage increased. Nevertheless, the result on BAC paste showed minor effects related to the use of BAC in terms of SP usage. The SP adsorption isotherms on powders (cement + healing agent) are illustrated in Figure 6. As a matter of fact, this relationship follows a Langmuir adsorption isotherm. After constantly introducing SP into the paste, at one point, addition of extra SP will not result in additional adsorption because all adsorption sites at the surface of cement particles are occupied, as shown by plateau curves. Thus, the non-reacted SP will stay in the pore solution. To summarize, by incorporating CA into the superplasticized cement paste, the SP was also adsorbed by the CA. It means the SP is not sufficiently available to disperse the cement particles thus lower workability and high viscosity were observed. Conversely, the utilization of BAC as a healing agent showed a comparable result with the pure cement paste.

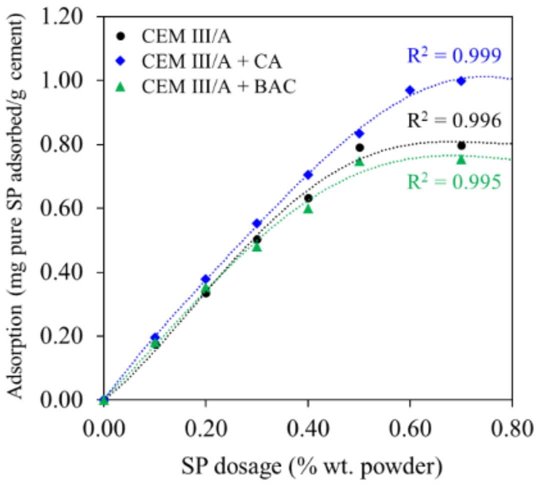

Fig. 6. Adsorption isotherms of SP on powders

4 Conclusions

This study explores the compatibility between PCE superplasticizer, cement and healing agents and their impacts on the rheological properties of cement paste. The major conclusions can be drawn as follows:

- The incorporation of BAC did not affect the rheological properties of the paste and no negative interaction with superplasticizer was found.
- The incorporation of CA considerably influenced the rheological properties of the paste by reducing the workability and increasing the viscosity of the paste.
- The CA paste showed a thixotropic behaviour and required a higher SP dosage to achieve the same workability as the pure cement paste because the SP could adsorb on CA particles.
- The critical and saturation SP dosages of pure cement paste and BAC paste were the same (0.1% and 0.5% by powder weight, respectively); while for the CA paste they were higher (0.2% and 0.7% by powder weight, respectively).

Acknowledgments

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