A new self-healing agent for accelerating the healing kinetics while simultaneously binding seawater ions in cracked cement paste

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ABSTRACT

To mitigate the corrosion of steel bars and the erosion of the matrix in cracked reinforced concrete in a marine environment, a new self-healing agent was developed that can not only chemically bind the invading ions in the cracks, but also accelerate the crack closure. The closure ratio of a crack with an initial width of 400 µm can reach 80% after self-healing for 1 day when the developed CaO-NaAlO2 healing agent was added into the concrete with a dosage of 5% by volume. The value for the references without the self-healing was only about 20%. The fast sealing of cracks can rapidly stop the further ingress of these ions. Moreover, reaction products of self-healing, such as Friedel's salt, Kuzel's salt and brucite, were detected, which indicates that Cl−, SO42− and Mg2+ ions invading into the cracks were bound chemically. Therefore, the risk of steel bar corrosion was decreased.

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1. Introduction

Concrete cracks easily and aggressive ions can invade into the concrete matrix through the cracks when the concrete is exposed in marine environment. Consequently, corrosion of reinforcing bars and deterioration of the concrete take place early. In addition to repairs by using coating materials [1,2], self-healing of cracks is a potential solution for this problem [3–8]. However, once concrete cracks seawater immediately penetrates into cracks. The ions in seawater invade into the cracks as well. As a result, the efficiency of self-healing of cracks to mitigate the corrosion of steel bars and the erosion of the concrete matrix will be very limited.

In the previous study [9], a self-healing agent that can chemically bind the invading ions from seawater was developed. Nevertheless, after healing for 7 days, the closure ratio of a 400-µm-wide crack only reached 60% although the dosage of such a healing agent reached 5% by volume. The seawater ions can still invade into the matrix thereafter. In order to decrease the risk of steel bar corrosion more significantly, a new self-healing agent that can not only chemically bind the invading ions but also accelerate the healing kinetics, was proposed in this study.

2. Development of self-healing agent

According to the thermodynamics, when self-healing agent can provide Ca2+ and Al(OH)3 ions to the solution in cracks, the invading ions i.e. Cl−, SO42− and Mg2+, could be chemically bound by forming precipitates, such as Friedel’s salt (3CaO·Al2O3·CaCl2·10H2O), ettringite (3CaO·Al2O3·3CaSO4·32H2O), and hydrotalcite (Mg4Al2(OH)14·3H2O) etc. Therefore, in the previous study [9], CaO and metakaolin with a mass ratio of 3 was used to prepare artificial aggregates as self-healing agent. It was found that the reaction of metakaolin took place primarily after a healing period of 3 days since its reaction needed Ca(OH)2 to activate. Moreover, it was interesting to note that the main mineral formed on the crack mouth was brucite (Mg(OH)2), while Friedel’s salt and ettringite chemically binding Cl− and SO42− were formed in situ in the artificial aggregates. It means that the closure of cracks was mainly due to the formation of brucite, instead of Friedel’s salt and ettringite. Therefore, in order to accelerate the closure of the crack, a more
reactive chemical agent should be adopted to replace metakaolin. Moreover, the formation of Mg(OH)$_2$, which is the main reaction product blocking the crack, should be facilitated.

It is well known that NaAlO$_2$ can dissolve in water fast. Na$^+$ and Al(OH)$_4$ ions are released to the solution and the pH in the solution can increase to a high value. By using NaAlO$_2$ to replace metakaolin, Al(OH)$_4$ ions released make the binding of Cl$^-$, SO$_4^{2-}$ possible and the high pH can facilitate the formation of Mg(OH)$_2$ so that accelerate the closure of the crack.

Therefore, in this study NaAlO$_2$ was adopted to manufacture the novel self-healing agent that can not only chemically bind the invading ions, but also accelerate the healing kinetics. The encapsulation of the self-healing agents as artificial aggregates was referred to [9].

3. Specimens and experiments

Portland cement was used to prepare cement paste specimens with a dimension of 40 mm × 40 mm × 40 mm. The water to cement ratio (w/c) was 0.4 and the volume fraction of artificial aggregates added was 5%. In each specimen, a 400-μm-wide crack was generated by following the method described in [10]. Then the cracked specimens were immersed in simulated seawater for self-healing at a temperature of 20 ± 1 °C.

At different self-healing time, the surface cracks were observed by using a microscopy and the crack width was measured. In this study, 6 specimens for each series were prepared and the crack widths at more than 6 locations in each specimen were measured.

Fig. 1. Crack widths at different locations in specimens before and after self-healing for different periods in sea water: (a) reference specimens without self-healing agents; (b) specimens with a self-healing agent CaO-metakaolin; (c) specimens with a self-healing agent CaO-NaAlO2. The curves were drawn with the measured crack widths (for example, the dots in blue) at different locations in all specimens. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
After self-healing for 7 days, the reaction products of self-healing formed were characterized by means of X-ray diffraction (XRD) and Energy dispersive spectrometer (EDS) to check the binding of seawater ions.

### 4. Results and discussion

#### 4.1. Closure of cracks due to self-healing

Fig. 1 shows the crack widths at different locations in specimens after self-healing for different periods. As self-healing proceeds, the curves drawn with the crack width data close up to the centre (representing the crack width of 0 μm) of the diagram, indicating the decrease in crack widths at different locations. It can be seen that in reference specimens after self-healing for 7 days most of the crack widths decreased from 390 to 440 μm to 190–340 μm, except several values decreasing to 0 μm. In the specimens with a self-healing agent composed of CaO and metakaolin, two thirds of the values of crack width decreased to 0 μm after the same self-healing period, i.e. 7 days (see Fig. 1 (b)). It reveals that the healing agent CaO-metakaolin accelerated the healing process.

However, at many locations the crack width was still larger than 290 μm after self-healing for 7 days. In comparison, in the specimens with the healing agent CaO-NaAlO₂, almost all the crack widths were 0 μm after self-healing for 7 days (see Fig. 1 (c)). Therefore, the acceleration effect on self-healing process by the healing agent CaO-NaAlO₂ is much better than that by CaO-metakaolin.

To quantify the efficiency of self-healing, the closure ratio of cracks was defined as the average ratio between the crack width after self-healing and the original crack width. As presented in Fig. 1, the closure ratios of cracks at different self-healing time were calculated and shown in Fig. 2. It was found that self-healing of cracks in the specimens with the healing agent CaO-NaAlO₂ proceeded much faster than that in the specimens with CaO-metakaolin. At a healing time of 1 day, the closure ratio of cracks for CaO-NaAlO₂ reached 80%, while only 50% for CaO-metakaolin and 20% for the reference. At a healing time of 7 day, the closure ratio of cracks for CaO-NaAlO₂ increased to 98%, while only 60% for CaO-metakaolin. Therefore, the self-healing agent CaO-NaAlO₂ developed in this study can remarkably accelerate the kinetics of self-healing in cementitious materials immersed in seawater.

#### 4.2. Chemical binding of aggressive ions from seawater based on the mineralogy of reaction products of self-healing

Fig. 3 (a) shows XRD profiles of the reaction products of self-healing formed on the surfaces of cracks in reference specimens and the specimens with self-healing agents, while Fig. 3 (b) shows XRD profiles of the reaction products of self-healing formed inside the broken artificial aggregates carrying self-healing agents. According to the intensity of peaks in XRD profiles, no matter in which series of specimen the main mineral in the reaction products of self-healing formed on crack surfaces was brucite (Mg(OH)₂) (see Fig. 3 (a)). From Fig. 3 (b), it can be seen that there were Friedel’s salt and Kuzel’s salt in the reaction products formed in artificial aggregates that was intersected by cracks. Fig. 3 (c) also shows the distribution of elements Mg, Cl and S in the reaction products formed in the broken artificial aggregates, which corresponds to the XRD results. Fig. 3 reveals that Mg²⁺ ions from seawater were mainly bound in the reaction products formed on crack surfaces, while Cl⁻ and SO₄²⁻ were mainly bound in the reaction products formed inside the broken artificial aggregates carrying self-healing agents. Therefore, the self-healing agent CaO-NaAlO₂ developed in this study can also chemically bind the aggressive ions in cracks coming from seawater.

### 5. Conclusion

In summary, a new self-healing agent was developed for accelerating the healing kinetics and simultaneously binding the invading aggressive ions in cracked cement paste immersed in seawater. The closure ratio of a 400-μm-wide crack reached 80% after healing for 1 day and 98% for 7 days when CaO-NaAlO₂ artificial aggregates was added to the cement paste with a dosage of 5% by volume. In addition, reaction products of self-healing, such as brucite, Friedel’s salt and Kuzel’s salt, were detected, indicating the chemical binding of aggressive ions invading into the cracks from seawater.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References