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1	REACTIONS OF SELF-HEALING AGENTS AND THE
2	CHEMICAL BINDING OF AGGRESSIVE IONS IN SEA WATER:
3	THERMODYNAMICS AND KINETICS
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16	
17	Abstract: New self-healing agents that can chemically bind seawater ions invading
18	cracked cementitious materials were proposed. The potential of self-healing and
19	binding of seawater ions were investigated by thermodynamic modeling. It was found
20	that CaO-NaAlO ₂ and CaO-metakaolin agents can have Cl ⁻ , SO_4^{2-} and Mg^{2+}
21	chemically bound by reacting with sea water to form Friedel's salt, Kuzel's salt,
22	ettringite and hydrotalcite. The removal of Cl ⁻ from seawater firstly increased and
23	then decreased with the increase of Ca/Al molar ratio in both agents, while the

removal of Mg^{2+} and SO_4^{2-} were hardly influenced and approximated 100%. Because NaAlO₂ dissolves and releases Al(OH)₄⁻ rapidly, precipitates binding Cl⁻, SO_4^{2-} and Mg²⁺ were formed fast. In comparison, the reaction of metakaolin binding aggressive ions occurred after 3 days. Because of the faster reaction and the capacity to make [Cl⁻]/[OH⁻] lower in the solution, CaO-NaAlO₂ would be more efficient for self-healing and mitigating reinforcement corrossion than CaO-metakaolin.

30 Keywords: self-healing, thermodynamic modeling, ion binding, marine
31 environment, cementitious materials

32 1. INTRODUCTION

The occurrences of cracks usually take place in reinforced concrete elements. In the concrete structures in marine environments, such cracks can become pathways for ingress of different ions, such as Cl^- , SO_4^{2-} and Mg^{2+} , causing deterioration of the concrete structures. Actually, concrete is able to heal cracks autogenously to some extent. A potential solution to improve the durability of reinforced concrete in marine environments is to support the self-healing of cracks by using chemical agents.

Self-healing of cracks in cementitious material has attracted significant attention in 39 40 recent years [1-5]. It was found that environmental factors, in particular the ions from 41 the environment, significantly affected the self-healing process and efficiency [1]. It was reported that autogenous self-healing of cracks in a marine environment is 42 promoted by Mg^{2+} in the sea water [6, 7]. Compared to autogenous self-healing in 43 fresh water, autogenous self-healing in sea water can enhance the closure ratio of a 44 surface crack with an initial width of 400 µm by 37% for a healing period of 7 days 45 [7]. However, it must be emphasized that there are multiple aggressive ions in the 46 marine environments, such as Cl⁻, SO₄²⁻ and Mg²⁺. While these ions might contribute 47 to the self-healing they can also decrease the durability of reinforced concrete as they 48 lead to weakening of the concrete cover and corrosion of steel bars [8-10]. It is 49 conceivable that once cracks appear, the aggressive ions can invade faster through 50 these cracks. Therefore, an ideal self-healing agent to improve the durability 51 performance of cracked reinforced concrete in a marine environment should not only 52

promote the self-healing of cracks (to prevent the further ingress of aggressive ions),
but also be able to "capture" these aggressive ions that have already invaded the
cracks.

In the presence of Ca^{2+} and Al(OH)₄⁻, Cl⁻, SO₄²⁻ and Mg²⁺ are known to precipitate 56 as Friedel's salt (3CaO · Al₂O₃ · CaCl₂ · 10H₂O), ettringite (3CaO · Al₂O₃ · 57 3CaSO₄ · 32H₂O) and hydrotalcite (4MgO · Al₂O₃ · 10H₂O) [11-13], which means 58 that Cl⁻, SO₄²⁻ and Mg²⁺ in the crack can be chemically bound. Simultaneously, the 59 crack can be filled by such precipitates. It is well known that calcium is one of the 60 main elements in Portland cement-based materials. According to a previous study [14], 61 unhydrated cement and portlandite with a relatively high solubility results in the 62 diffusion of Ca^{2+} ions into the crack. In addition, $Al(OH)_4^-$ ions can be supplied by 63 Al-rich materials, such as slag and metakaolin, which can be added directly by 64 blending or after encapsulation. Thus in a next step the binding efficiency of Cl⁻, 65 SO4²⁻ and Mg²⁺, and the volume of precipitates formed in sea water need to be 66 investigated as a function of the moles of Ca^{2+} and $Al(OH)_4^{-}$ ions, and their molar 67 ratio. 68

In this study, the appropriate moles of Ca^{2+} and $Al(OH)_4^{-}$ ions, as well as their 69 molar ratio, were determined by thermodynamic modeling for the self-healing of 70 cracks and the chemical binding of Cl^- , SO_4^{2-} and Mg^{2+} ions from sea water. The 71 volume of relevant precipitates and the corresponding binding efficiency of the 72 aggressive ions in sea water as a function of the masses and ratio of Ca^{2+} and 73 $Al(OH)_4^-$ ions were predicted. Moreover, in order to evaluate the thermodynamic 74 modeling results and obtain further information on the kinetics of the binding 75 reactions, CaO-NaAlO₂ and CaO-metakaolin, the agents that provide Ca^{2+} and 76 Al(OH)₄ were reacted with simulated sea water. The mineralogy of the reaction 77 products was determined by means of X-ray diffraction (XRD). The relative content 78 of Cl, S and Mg chemically bound in the reaction products were quantified by X-ray 79 fluorescence analysis (XRF). The change in concentrations of Mg²⁺, SO₄²⁻, and Cl⁻ in 80 simulated sea water as a function of reaction time was monitored by means of Ion 81 Chromatography (IC) and Inductively Coupled Plasma (ICP). Based on these results, 82

appropriate self-healing agents can be developed and used to manufacture artificial
aggregates [15] or encapsulated in polymeric capsules [16, 17] and added into
concrete deliberately.

86 2. MATERIALS AND METHODS

87 2.1 Thermodynamic modeling

Thermodynamic modeling was performed with the software GEMS 3.5, in which Gibbs energy minimization was adopted to calculate the mass and volume of equilibrium phase assemblages and the equilibrium ion concentrations from the total bulk elemental composition. The CEMDATA18 database [18] for cementitious materials was used. The related chemical reactions and the corresponding equilibrium constants K_{so} are listed in Table 1.

94 The modeling simulated the reactions taking place after the self-healing agents were mixed with 100 mL seawater. The ratio between the mass of self-healing agent 95 96 and the mass of seawater ranged from 0.02 to 0.3. Total moles of ions released from 97 self-healing agents can be calculated according to the chemical compositions of the self-healing agents. Total moles of ions in seawater can be determined according to 98 99 the ion concentrations of seawater given in Section 2.2. These ion compositions 100 should be input into GEMS 3.5 as initial conditions. Moreover, in the simulation the temperature, at which the reactions of self-healing agents in seawater take place, was 101 assumed to be 25° C. 102

103

2.2 Experiments for studying the reactions between the self-healing agents and simulated sea water

106 2.2.1 Materials and sample preparation

In order to evaluate the thermodynamic modeling results and obtain further
information on the kinetics of the reactions, the self-healing agents were directly
mixed with simulated sea water for reactions. Two types of self-healing agent, i.e.
CaO-NaAlO₂ and CaO-metakaolin, were prepared from CaO, NaAlO₂ and metakaolin.

The purity of these chemical agents was higher than 99.7%. By changing the mass percentages of CaO in the self-healing agent mixtures, the Ca/Al molar ratios can be modified. According to the thermodynamic results in Section 3.1, the Ca/Al in the self-healing agents used for experimental studies was set to be 3 and 5.

By following the literature [7], sea water was prepared by using the chemical agents listed in Table 2. The purity of all these chemical agents was higher than 99.7%. The concentration of the main ions in simulated sea water is presented in Table 2.

118 The ratio between the mass of self-healing agents to the mass of simulated sea water was set to be 0.2. After the agents were mixed with simulated sea water for 1 minute, 119 the mixtures in containers were sealed with plastic sheet with very small holes so that 120 water evaporation was hindered but the air still accessed. The mixtures were cured in 121 a room with a temperature of $20 \pm 1^{\circ}$ °C. At 0.5, 1, 3, 7, 14 and 28 days, the mixtures 122 were centrifuged to separate the solid phase from the solution, respectively. After that, 123 the solid phases were washed 3 times with ethanol and dried at 40°C in an oven until 124 the weight was constant. Finally, the dried solid phases were grounded with agate 125 126 mortar and pestle set to pass 200-mesh sieve.

127

128 2.2.2 Characterization of the reaction products of the self-healing agents

In order to determine the crystalline phases in the reaction products, X-ray 129 Diffraction (XRD) analysis was performed on a X'Pert PRO X-ray diffractometer by 130 using Cu K α as a radiation source. The samples were measured between 5°2 θ and 131 90°20 with a step size of 0.033°20. The contents of each crystalline phases in reaction 132 133 products of self-healing agents reacted with seawater for 28 days were quantified based on Rietveld method. In order to guarantee the accuracy of the quantification, 134 135 the analysis was not accomplished until a sig parameter was between 1-2 and, simultaneously, 136 the R_w parameter was less than 15.

For self-healing agent CaO-matakaolin XRD can hardly provide information for gel
reaction products, i.e. C-S-H. Therefore, reaction products of CaO-matakaolin, which was
mixed and reacted with seawater for 28 days, were characterized by means of EDS. Before

testing, powders of reaction products were impregnated with epoxy. After the epoxy was
hardened, the samples were sequently ground with sandpapers P320, P500, P1200 and P4000.
To analyze the chemical elements of the reaction products, random points on the surfaces of
the reaction products were tested by EDS. For the analysis, a beam with accelerating voltage
of 20 kV was used and the magnification was 400X and 500X.

X-ray Fluorescence (XRF) analysis on the reaction products were carried out using
Axios Pw 4400, PaNalytical B.V, with Rh as radiation source and an accuracy of
0.05%. According to XRF results, the binding efficiency (BE) of ions by the
self-healing agents can be determined with Equation 1.

149
$$BE = \frac{m(Cl,S,Mg)}{m(CaO + SiO_2 + Al_2O_3)} \times 100\%$$
(1)

150 where m refers to the mass percentage of compositions determined by XRF.

The volume increase of the healing agents facilitates the self-healing of cracks. Thus, the volume of solid phases as a function of reaction time was measured with pycnometer to evaluate the potential healing capacity of the self-healing agents and compared with the thermodynamic modeling results.

155

156 2.2.3 Evaluation on the removal of aggressive ions from simulated sea water by the157 self-healing agents

The concentrations of sulfate and chloride in the solution obtained after the mixing 158 of self-healing agents with the simulated sea water were measured by using ion 159 chromatography (IC). For the measurements, 1mM NaHCO₃ solution at a flow rate of 160 161 1mL/min was used as eluent. The volume of the sample injection loop was 1mL. In addition, the concentrations of magnesium in the solutions at different reaction time 162 were measured by inductively coupled plasma optical emission spectrometry 163 (ICP-OES). Based on the concentrations at different reaction times, the removal 164 efficiency of the self-healing agents was determined as follows: 165

166
$$IR = \frac{C_i - C_t}{C_i} \times 100\%$$
 (2)

where C_i is the initial concentration in simulated sea water and C_t is the concentration in the solution after a reaction period of t.

169 3. RESULTS AND DISCUSSION

3.1 Thermodynamic modelling results on the reactions between self-healing agents and sea water

172 **3.1.1** Phase assemblages of the self-healing agents mixed with sea water

For the CaO-NaAlO₂ agent, Friedel's salt, ettringite, hydrotalcite and portlandite 173 174 are the main precipitates formed at low dosages of self-healing agent as shown in Fig. 1. Ettringite is only present if the ratio between the mass of CaO-NaAlO₂ agent and 175 the mass of sea water is less than 0.1 at molar Ca/Al = 3 and 0.14 at molar Ca/Al = 5. If 176 the ratio between the mass of CaO-NaAlO₂ agent and the mass of sea water increases, 177 178 the volume of precipitates also increases and the mineralogy changes. Ettringite disappears and the volume fraction of Friedel's salt decreases, while Kuzel's salt 179 180 forms. Moreover, for the CaO-NaAlO₂ agent with Ca/Al of 3, C₃AH₆ is formed when the ratio between the mass of CaO-NaAlO₂ agent and the mass of sea water is larger 181 than 0.18 at molar Ca/Al=3 and larger than 0.26 at Ca/Al of 5. The percentage of 182 portlandite in the mixture of sea water and CaO-NaAlO₂ agent with Ca/Al of 5 is 183 larger than that with Ca/Al of 3, due to the higher availability of CaO at Ca/Al of 5. 184

For the mixture of CaO-metakaolin agent and sea water, in addition to Friedel's salt and ettringite, C-S-H and straetlingite (CaAl₂Si₂O₈) are expected to be formed. It is worth noting that at Ca/Al molar ratio of 3 (see Fig. 2 (a)) portlandite is absent, while at Ca/Al molar ratio of 5 (see Fig. 2 (b)) portlandite is expected, as in the presence of metakaolin C-S-H and strätlingite can bind additional calcium.

- 190
- 191 Fig. 1 Phase assemblages in the mixture of CaO-NaAlO₂ and 100 ml sea water based
- on thermodynamic modeling: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar

ratio of 5

193

Fig. 2 Phase assemblages in the mixture of CaO-metakaolin and 100 ml sea water
based on thermodynamic modeling: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al
molar ratio of 5

198

As discussed above, the Ca/Al in the ion-binding agent, related to the mass 199 percentage of CaO in the agent, has a significant effect on the mineralogy of the phase 200 201 assemblages, and thus a significant effect on the binding of sulfate, chloride and magnesium present in sea water. Thus, the effect of changing Ca/Al on the phase 202 assemblages was investigated. Fig. 3 and 4 show that the mineral composition of the 203 reaction products changes with Ca/Al molar ratio in the self-healing agents. In 204 205 general, an increase of Ca/Al provides more CaO and less Al₂O₃. Therefore, the volume percentage of phases containing Al decreases and the volume of portlandite 206 increases with the increase of Ca/Al. By comparing Fig. 4 with Fig. 3, it can be seen 207 that at a higher ratio, i.e. 0.3, between the mass of self-healing agents and the mass of 208 209 sea water, the total volume of reaction products is significantly larger than the volume at 0.2. 210

211

Fig. 3 Phase assemblages in the mixture of 100 ml sea water and 20 g self-healing agents with various Ca/Al based on thermodynamic modeling: (a) CaO-NaAlO₂; (b) CaO-metakaolin. Fs: Friedel's salt

215

Fig. 4 Phase assemblages in the mixture of 100 ml sea water and 30 g self-healing
agents with various Ca/Al based on thermodynamic modeling: (a) CaO-NaAlO₂; (b)
CaO-metakaolin. Fs: Friedel's salt; Ks: Kuzel's salt

3.1.2 Removal efficiency of chloride, sulphate and magnesium from solution.

As discussed above, thanks to the formation of Friedel's salt, ettringite and hydrotalcite after the self-healing agents react with sea water, chloride, sulphate and magnesium in the sea water can be chemically bound. From this point of view, they are removed from the solution. As shown in Fig. 5 (a), in general, the removal efficiency of chloride from sea water increases linearly with the increase of the amount of self-healing agents. Only for the CaO-NaAlO₂ agent with Ca/Al of 3, the removal efficiency of chloride reaches a maximum of 80% when the ratio between the mass of agent and the mass of sea water is 0.2. Moreover, the slope of the lines for Ca/Al of 3 is larger than that of 5, indicating a higher chloride uptake at Ca/Al of 3 than at 5.

Fig. 5 (b) and (c) show that nearly 100% of sulphate and magnesium can be removed even at a low ratio between the mass of self-healing agent and the mass of sea water, indicating a higher binding efficiency of sulfate and magnesium than of chloride. A "valley" is observed in the removal efficiency curves of SO_4^{2-} in the four series of self-healing agent (see Fig. 5 (b)) corresponding to the transition of ettringite to the Kuzel's salt shown in Fig. 1 and 2, which demonstrates that from a thermodynamic point of view ettringite binds sulfate stronger than Kuzel's salt.

237

Fig. 5 Removal efficiency of ions as a function of ratio between the mass of agent to the mass of sea water based on thermodynamic modeling: (a) Cl^{-} ; (b) SO_4^{2-} ; (c) Mg²⁺ in sea water. C/A means Ca/Al molar ratio.

241

Fig. 6 plots the removal efficiency of chloride, sulfate and magnesium in sea water 242 as a function of Ca/Al molar ratio of the self-healing agent. It can be seen that the 243 chloride removal increases to a maximum when the Ca/Al molar ratio of self-healing 244 agents ranges from 3 to 5, while decreases when the Ca/Al increases further (see Fig. 245 6 (a)). In case the ratio between the mass of self-healing agent and the mass of sea 246 247 water equals to 0.2 or 0.3, the maximum chloride removal efficiency is less than 90% 248 for both self-healing agents. In contrast, as shown in Fig. 6 (b), the removal efficiency of sulfate is very high for both agents, near 100% for the CaO-metakaolin and slightly 249 lower for CaO-NaAlO₂ when the Ca/Al ratio is higher than 3. It is interesting to note 250 that for CaO-NaAlO₂ agent this sulfate removal efficiency becomes much lower when 251 252 the Ca/Al is smaller than 2, which is important information for designing the self-healing agent. Fig. 6 (c) shows that the removal efficiency for magnesium is not 253

influenced by Ca/Al and approximates 100%.

It must be mentioned that in the modeling regarding the agents with metakaolin, the physical binding of chloride by C-S-H was not considered. To target at an optimization on the self-healing agent that can bind these ions as stably as possible, only chemical binding was taken into account in the thermodynamic modeling.

259

Fig. 6 Removal efficiency of chloride, sulfate and magnesium in sea water as a

function of Ca/Al in self-healing agents based on thermodynamic modeling: (a) Cl⁻; (b)

 SO_4^{2-} ; (c) Mg²⁺. SH/SW refers to the ratio between the mass of self-healing agent and

263

the mass of sea water.

264

265 **3.1.3** The pH in the sea water mixed with the self-healing agents

Fig. 7 shows the calculated pH values in the sea water mixed with different amount of self-healing agents based on thermodynamic modeling. The pH value increases with the amount of self-healing agents and is generally higher for the CaO-NaAlO₂ than for CaO-metakaolin agent.

270

- Fig.7 pH value as a function of the ratio between the mass of agent to the mass of sea
 water based on thermodynamic modeling. C/A means Ca/Al molar ratio.
- 273

The pH value plotted as a function of Ca/Al for the CaO-NaAlO₂ agent decreases 274 from 14 to 13.5 with an increase of Ca/Al from 1 to 10 (see Fig. 8). With an increase 275 of Ca/Al, less Na⁺ is provided to the system by the self-healing agent, resulting in a 276 decrease of pH value. For the sea water mixed with CaO-metakaolin agent, the pH is 277 lower than that with CaO-NaAlO₂ agent and increases strongly when Ca/Al increases 278 279 from 1 to 3, and remains higher than 12.5 at Ca/Al > 3. The solid phase assemblages shown in Fig. 3 (b) and 4 (b) indicate the absence of portlandite in the mixture of 280 CaO-metakaolin agent at Ca/Al < 3 and sea water. Moreover, strätlingite and Ca/Si 281 C-S-H are able to bind some alkali ions, also leading to an lower pH value for Ca/Al 282 ranging from 1 to 3. 283

284

Fig. 8 pH value in sea water mixed with self-healing agent with various Ca/Al based on thermodynamic modeling. SH/SW refers to the ratio between the mass of self-healing agent and the mass of sea water.

288

The pH value, together with the chloride concentration, has a significant influence on corrosion of reinforced concrete. In a non-damaged concrete, steel reinforcements remain passive due to high alkalinity of pore solution (pH>13) [20]. In cracked concrete, the easy ingress of Cl⁻ can cause depassivation of reinforcement even at a high pH in pore solution. Therefore, a critical corrosion ratio between the

concentration of Cl^{-} and the concentration of $OH^{-}([Cl^{-}]/[OH^{-}])$ in pore solution is 294 often used to evaluate the corrosion initiation of reinforcement, which is influenced 295 by Cl⁻ concentration and pH. Higher concentrations of chlorides and sulphates relative 296 to the hydroxyl concentration can increase the corrosion rate of carbon steel [21]. 297 Selected thresholds for corrosion initiation are $[Cl^{-}]/[OH^{-}] > 0.6$ and $[SO_4^{2-}]/[OH^{-}] >$ 298 1.5 [22, 23] and shown in Fig. 9. It can be seen that the ratio between the mass of 299 self-healing agent and the mass of sea water, as well as the Ca/Al molar ratio in the 300 301 agent, have significant influence on the [Cl⁻]/[OH⁻] value (see Fig. 9 (a)). For CaO-NaAlO₂ agent, mixed with sea water at a mass ratio of 0.2, the $[Cl^{-}]/[OH^{-}]$ 302 value is lower than 0.6 when Ca/Al molar ratio is between 1 and 5. When the 303 CaO-NaAlO₂ agent mixed with sea water at a mass ratio of 0.3, the Ca/Al molar ratio 304 in the agent that leads to a $[Cl^-]/[OH^-]$ value lower than 0.6 ranges from 1 to 9. For 305 CaO-metakaolin agent mixed with sea water at a mass ratio of 0.3, when the Ca/Al 306 molar ratio is between 3 and 6, the [Cl⁻]/[OH⁻] value is also lower than 0.6. However, 307 when the CaO-metakaolin agent mixed with sea water at a mass ratio of 0.2, the 308 309 [Cl⁻]/[OH⁻] value is hardly lower than 0.6 no matter what the Ca/Al molar ratio is. In term of [SO₄²⁻]/[OH⁻], both agents with Ca/Al molar ratio larger than 1 can lead to a 310 value of $[SO_4^{2-}]/[OH^{-}]$ lower than 1.5 (see Fig. 9 (b)). 311

Note that the use of such threshold values is a simplification as the corrosion rate and extent is influenced by many factors. Based on those ratios as an indicator for the corrosion risk of steel bars, a higher pH value and chloride/sulfate removal efficiency can decrease the rebar corrosion risk. Therefore, according to the thermodynamic results, the self-healing agents should not only remove the chloride and sulfate from the crack solution, but also increase the pH, so as to have potential to protect rebar from corrosion induced by the chloride and sulfate from sea water.

319

Fig. 9 Ratios between concentration of Cl^- or SO_4^{2-} and the concentration of OH^- : (a) Cl⁻/OH⁻, (b) SO_4^{2-} /OH⁻. SH/SW refers to the ratio between the mass of self-healing agent and the mass of sea water.

324 **3.2** Experimental results on kinetics of the reactions between self-healing agents

325 and simulated sea water

326 **3.2.1** Mineralogy of the reaction products based on XRD results

Fig. 10 shows the XRD patterns of the solid phases obtained after reactions of 327 the self-healing agents with simulated sea water for different periods. After the 328 reaction of CaO-NaAlO₂ agent with sea water, the solid phases mainly contained 329 Friedel's salt, SO₄-CO₃-AFm, hydrotalcite and portlandite (see Fig. 10 (a) (b)). It can 330 331 be seen that C₃AH₆ occured at 12 hours of the reaction between CaO-NaAlO₂ agent and sea water. However, it disappeared thereafter and the mineral composition in the 332 solid phases did not change with reaction times anymore, indicating that self-healing 333 agent can completely react with sea water before 1 day. By comparing Fig. 10 (a) with 334 (b), it is found that change of Ca/Al in CaO-NaAlO₂ agent had no influence on the 335 mineral composition of the reaction products. 336

Also, for the CaO-metakaolin agent with Ca/Al of 5 reacting with sea water, the mineral compositions of solid phases changed with reaction times. As shown in Fig. 10 (c), diffraction peaks of Friedel's salt and hydrotalcite were not obvious at 1 day, while those of portlandite were distinct. As the reactions proceeded, the diffraction peaks of Friedel's salt and hydrotalcite became more distinct. This is related to the relatively slow reaction between metakaolin and the Ca(OH)₂ in the system.

Table 3 lists the contents of the crystalline phases in reaction products of self-healing agents reacted with seawater for 28 days. It was found that for CaO/NaAlO₂ agent, the total content of AFm phases decreased as the Ca/Al increased from 3 to 5, while the content of Ca(OH)₂ by about 75%. For CaO/metakaolin agent, AFm phases accounts for about 50% of the reaction products. It should be mentioned that the high content of CaCO₃ in the reaction products of CaO/metakaolin agent was due to the carbonation of Ca(OH)₂ during the sample preparation.

The detection of Friedel's salt and hydrotalcite by XRD was consistent with the thermodynamic results shown in section 3.1. However, the simulated Kuzel's salt was not detected. Moreover, according to the experimental results SO_4^{2-} was not bound in Kuzel's salt, but in SO₄-CO₃ AFm (Ca₄Al₂O₆ (CO)_{0.67} (SO₃)_{0.33}·11H₂O, see Fig. 10), 354 which was not predicted by thermodynamic modeling. Calcite was also detected in the late stage of reactions. It must be mentioned that the modeling was based on 355 thermodynamic theory. Mineralogy of reaction products were calculated based on the 356 chemical species from complete dissolutions of self-healing agents and related 357 thermodynamic equilibria. However, kinetics of the reactions between self-healing 358 359 agents and seawater was ignored. In particular, dissolution rate of each mineral in the self-healing agents is different, which can lead to a different mineralogy of reaction 360 361 products from the thermodynamic modeling results. However, thermodynamic modeling can still provide useful information for the design of such new self-healing 362 agents. 363

364

Fig. 10 XRD patterns of solid phases obtained after the reaction of the self-healing
agent with sea water: (a) CaO-NaAlO₂ agent with Ca/Al of 3; (b) CaO-NaAlO₂ agent
with Ca/Al of 5; (c) CaO-metakaolin agent with Ca/Al of 5. For reactions, the ratio
between the mass of self-healing agent and the mass of sea water was 0.2.

369

Fig. 11 shows point analysis results of the samples obtained by plotting atomic ratio of Si/Ca against Al/Ca. Tie lines were drawn from the cloud of C-S-H points and different phases of known theoretical compositions. The points near the tie lines correspond to a binary mixture of C-S-H and phase along the line [24]. Therefore, it can be deduced that in addition to AFt and AFm, C-S-H appears in the reaction products of CaO-matakaolin.

375

Fig. 11 EDS point analysis of reaction products of CaO-metakaolin reacted with seawater for
28 days. For the reaction, the ratio between the mass of self-healing agent and the mass of sea
water was 0.2.

379

380 3.2.2 Ion removal based on solution concentrations

The concentrations of sulfate and chloride in the solution obtained after the mixing of self-healing agents with the simulated sea water were adopted to calculate the ion removal efficiency according to Equation 2. Fig. 12(a) shows that the removal 384 efficiency of chloride from sea water by the CaO-NaAlO₂ agent reached 45% for a reaction period of 0.5 day. After that, the removal efficiency fluctuated around this 385 value. In comparison, the removal efficiency of chloride ion by the CaO-metakaolin 386 agent with Ca/Al of 5 increased gradually and reached the maximum value, i.e. 50%, 387 at 14 days, which was due to the slower metakaolin reaction. As shown in Fig. 12(a), 388 389 the experimentally determined removal efficiencies were lower than the thermodynamic modeling results by 5% to 10%. Nevertheless, these differences still 390 391 show a satisfactory agreement.

Fig. 12(b) shows that the removal efficiency of sulfate by the CaO-metakaolin 392 agent with Ca/Al of 5 can reach 100% at a reaction time of 3 days, which is consistent 393 with the modeling results. In contrast, the experimentally observed sulfate removal 394 efficiency of the CaO-NaAlO₂ agent with Ca/Al of 3 and 5 only reached 60% at 0.5 395 396 day and longer. This is clearly lower than the modeling result. This could be related to a suppression of sulfate uptake by Kuzel's salt and SO₄-AFm at very high pH values 397 up to 14, which is not sufficiently accounted for in the available thermodynamic 398 399 models developed based on the data measured under a pH of 11 to 12.5 [25]. In fact, for the metakaolin sample with a lower pH value, i.e. about 13 (see Fig. 7), the 400 prediction and measurements agree well. 401

In addition, as shown in Fig. 12(c), the removal efficiency of magnesium by self-healing agents reached 100% rapidly at the reaction time of 0.5 day, which compares well with the modeling result.

405

Fig. 12 Removal efficiency of aggressive ions in sea water after reaction with self-healing agents for different periods: (a) Cl^- ; (b) SO_4^{2-} ; (c) Mg^{2+} . C/A means Ca/Al molar ratio.

409

410 **3.2.3 Ion binding observed by XRF analysis**

By means of XRF, the mass ratio of chloride, sulfate and magnesium bound in the self-healing agents were determined and plotted in Fig. 13, compared with the results of thermodynamic modelling. It can be seen that although there is some difference between the modeling results and the experimental results, the modeling can still provide information on the difference of ion binding abilities between the various self-healing agents. It should be mentioned that the relative mass percentages of ions bound in the solid phases were very low, only 6% to 9% for chloride and less than 2% for sulfate and magnesium. It is possible that the difference between the modeling results and the experimental results are partially caused by experimental errors as the relative mass percentages of ions in the solid phases are relatively low.

421 For the CaO-NaAlO₂ agent, the binding of aggressive ions reached the maximum value at a reaction time of 12 hours as NaAlO₂ dissolved rapidly in water and released 422 $Al(OH)_4$ to make precipitates, i.e. Friedel's salt, AFm and hydrotalcite, formed 423 immediately. Therefore, chloride, sulfate and magnesium were bound within a short 424 period after the mixing of sea water with CaO-NaAlO₂ agent. In comparison, because 425 of the slower reactions of CaO-metakaolin, the binding of these aggressive ions 426 increased gradually until a reaction time of 14 days, which is consistent with the 427 results on ion removal efficiency in Section 3.2.2. 428

It is interesting to notice that the binding of aggressive ions by CaO-NaAlO₂ agent decreased slightly after 3 days, and then remained at the similar level. This phenomenon was more obvious for the Ca/Al molar ratio of 3. This may be caused by the fast precipitation in these systems, which can lead to a strong co-precipitation of different ions, while a ripening of the solids with time can result in a partial release of such co-precipitated ions [26, 27]. No such phenomenon was observed for the slower reacting CaO-metakaolin agent.

436

Fig. 13 Aggressive ions binding efficiency in reaction products: (a) Cl^{-} ; (b) SO_4^{2-} ; (c) Mg²⁺. C/A means Ca/Al molar ratio.

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3.2.4 Volume increase of solid phases after reactions of self-healing agents with simulated sea water

The volume of the solid phase at different reaction periods was measured by a pycnometer. For the CaO-NaAlO₂ agent mixed with sea water, the volume of the solid

phase increased dramatically within the first 12 hours and remained stable thereafter. 444 As mentioned above, NaAlO₂ dissolved rapidly in water and released $Al(OH)_4$. Thus 445 precipitates binding aggressive ions in synthetic water were formed very fast. 446 Therefore, the volume of the solid phase increased within the first 12 hours after 447 CaO-NaAlO₂ agent was mixed with sea water, while little change occurred afterwards. 448 The final increase ratio of CaO-NaAlO₂ agent with Ca/Al of 5 was smaller than that 449 of the agent with Ca/Al of 3, which agrees with the sequence predicted by 450 451 thermodynamic modelling.

As shown in Fig. 14, there were two stages for the volume increase of 452 CaO-metakaolin agent with Ca/Al of 5 after mixed with sea water. The solid phase 453 volume increased significantly within the first 12 hours after the CaO-metakaolin 454 agent was mixed with sea water. After that, the increase slowed down up to 3 days but 455 occured again between 3 and 7 days. After a reaction time of 7 days, the volume 456 increase ratio reached 2.2 and remained stable. According to the XRD results in Fig. 9, 457 portlandite was the main reaction product of the CaO-metakaolin agent mixed with 458 459 sea water after 1 day, which seems to cause the first volume increase, as the hydration of lime into Ca(OH)₂ resulted in a significant volume increase [28]. After longer 460 reaction times (> 3 days), metakaolin reacted significantly and Friedel's salt, Kuzel's 461 salt, hydrotalcite and C-S-H were formed (see Fig. 10). The formation of these 462 mineral which contain significant amounts of water in their structure was 463 accompanied by volume increase [29]. Thus, the slow reaction of metakaolin and 464 formation of Friedel's salt, Kuzel's salt, hydrotalcite and C-S-H contributed to the 465 later volume increase up to 7 days. The final volume increase ratio of CaO-metakaolin 466 467 agent in sea water determined experimentally compared reasonably well with the thermodynamic modeling result. Moreover, the experimental finding that both 468 CaO-NaAlO₂ agents had smaller volume increases than CaO-metakaolin agent is 469 470 consistent with the thermodynamic modelling.

471

Fig. 14 Volume increase ratio of self-healing agents mixed with simulated sea water.

473

C/A means Ca/Al molar ratio.

475 3.2.5 Discussion on the self-healing efficiency: crack closure and binding of 476 aggressive ions

As demonstrated above, the volume increase ratio of CaO-NaAlO₂ is lower than that 477 of CaO-metakaolin self-healing agent (see Fig. 14). However, for hindering the 478 ingress of aggressive ions into the crack, not only the crack filling, but also the 479 distribution of precipitates in the crack space is important. As addressed in a previous 480 481 study [7], where encapsulated CaO-metakaolin agent with Ca/Al of 3 was used as self-healing agent, brucite was the main mineral formed at the crack surfaces, while 482 Friedel's salt and hydrotalcite were mainly formed inside the capsule, as the mobility 483 of $Al(OH)_4^-$ (and $H_2SiO_4^{2-}$) is much lower than that of other ions in the system. 484 Moreover, the solubility of Friedel's salt and hydrotalcite is much lower than that of 485 portlandite or brucite. Therefore, Friedel's salt and hydrotalcite were formed locally 486 inside the broken capsule, while the OH⁻ ions from the portlandite diffused outwards 487 and reacted with the Mg²⁺ ions invading inwards the crack to form brucite. At the 488 same time, the remaining Ca^{2+} ions reacted with CO_3^{2-} to form calcite, which also 489 contributes to the crack closure. To efficiently block the pathway in the crack and to 490 hinder the further ingress of aggressive ions, precipitates must form inside the crack 491 space, particularly in the crack mouth, rather than inside the broken capsules. 492 According to the mineralogy of the reaction products of these two agents (see Fig. 4), 493 the percentage of portlandite is higher in the reaction products of CaO-NaAlO₂ 494 self-healing which could support an efficient distribution of reaction products in the 495 crack and in particular also the formation of calcite. Thus, although the volume 496 497 increase of CaO-NaAlO₂ agent reacting with sea water is lower, the effect of 498 CaO-NaAlO₂ agent on crack closure could be better than that of CaO-metakaolin agent. Further studies will be necessary to clarify this point. 499

Moreover, the volume increase of the self-healing agents in simulated sea water underline the slower reaction of metakaolin compared to the NaAlO₂ agent and this will also affect the kinetics of the binding of aggressive ions. In fact, the kinetic of the volume increase of the self-healing agents (Fig. 14) agree well with the kinetics of ion

binding, i.e. the removal efficiency (Fig. 12) and the mass percentages of ions 504 chemically bound in the reaction products (Fig. 13). The aim of this study was to 505 design a self-healing agent that is not only able to close cracks, but also to chemically 506 bind chloride, sulfate and magnesium in sea water. The faster reactions of 507 CaO-NaAlO₂ agent lead to faster chemical binding. In addition, the corresponding pH 508 in the solution is higher than that with CaO-metakaolin agent, which more efficiently 509 lowers the [Cl⁻]/[OH⁻] ratio. From this point of view, as discussed in Section 3.1.3, 510 511 CaO-NaAlO₂ agent will be more efficient for mitigation on corrosion of steel bars, although its chloride binding is slightly lower than that of CaO-metakaolin. 512

In this study, the reactions of self-healing agents took place directly in seawater. The 513 influence of the pore solution of the bulk matrix on the reaction process of 514 self-healing agents was ignored. Because of the higher concentrations and larger 515 diffusion coefficients, OH^- and Ca^{2+} are the ions from the pore solution that may 516 influence the composition of the crack solution, rather than the other ions in the pore 517 solution. It must be mentioned that, however, compared with the direct dissolution of 518 519 the self-healing agent, which could be stored in capsules and exposed to the crack solution after the capsules were intersected by the crack, the diffusion of OH⁻ and 520 Ca^{2+} ions from the pore solution are too slow to influence the reactions of self-healing 521 agents. Therefore, the studies on the reactions of self-healing agents directly taking 522 place in seawater here can still provide useful information for understanding the 523 self-healing of cracks in cement-based materials. 524

525

526 **4. Conclusion**

In this study, thermodynamics and kinetics of the reaction of Ca-Al self-healing agents and chemical binding of aggressive ions in sea water were investigated. Based on the experimental and thermodynamic modeling results, following conclusions can be drawn:

(1) According to the thermodynamic modeling, the formation of Friedel's salt, Kuzel's
salt, ettringite and hydrotalcite indicates that Ca-Al self-healing agents can chemically
bind aggressive ions in sea water. Moreover, the Ca/Al molar ratio of self-healing

agents has significant effects on the mineralogy of the phase assemblages.

(2) Both for CaO-NaAlO₂ and CaO-metakaolin agents the removal efficiency of Cl⁻ 535 ions firstly increases and then decreases with Ca/Al, while the removal efficiency of 536 Mg²⁺ and SO₄²⁻ ions are hardly influenced by Ca/Al and near to 100%. The molar 537 Ca/Al ratios corresponding to the maximum removal efficiency of Cl- ion in 538 CaO-NaAlO₂ and CaO-metakaolin agents was approximately 3 as determined by 539 means of thermodynamic modeling. The pH of the solutions with CaO-NaAlO₂ and 540 541 CaO-metakaolin agents at Ca/Al = 3, respectively, is higher than 13 when the agent to water ratio is larger than 0.2. 542

(3) The kinetics of chemical reaction between self-healing agents and simulated sea 543 water was investigated via XRD and solution analysis. For CaO-NaAlO₂ agent it was 544 found that NaAlO₂ can rapidly dissolve in water and release $Al(OH)_4$, making 545 precipitates formed very fast. For the CaO-metakaolin agent, portlandite formed 546 within the first 12 hours, while the reaction of metakaolin, which make aggressive 547 ions in sea water bound, occurred mainly after more than 3 days. Because of the faster 548 549 reaction and higher pH enhancement of CaO-NaAlO₂ agent, the [Cl⁻]/[OH⁻], which is an indicator to corrosion risk of steel bars, would be much lower in the crack solution 550 than that for CaO-metakaolin agent. From this point of view, CaO-NaAlO₂ agent will 551 be more efficient for declining the corrosion risk of steel bars in cracked concrete. 552

(4) For magnesium and chloirde, the removal efficiencies determined by solution
analysis compared well with those determined via thermodynamic modeling, while
for sulfate⁻ the experimental removal efficiency was lower than predicted by
thermodynamic modeling.

(5) For CaO-NaAlO₂ agent mixed with sea water, the volume of the solid phase
increases dramatically within the first 12 hours. For the CaO-metakaolin agent,
volume increase experiences two stages due to the hydration of lime and the
pozzolanic reaction of metakaolin, respectively.

In summary the investigated self-healing agents can bind chloride, magnesium and sulfate very efficiently and in both cases additional volume was generated due to the hydration reaction; the NaAlO₂ based agent showed a faster kinetic than the 564 CaO-metakaolin agent.

565

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574

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Table 1. Chemical equations and the corresponding equilibrium constants at $25^{\circ}C$ [18, 649 <u>19</u>] 650

Minerals	Chemical equations			
Ettringite	ingite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \Leftrightarrow 6\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 26\text{H}_2\text{O}$			
Friedel's salt	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O} \Leftrightarrow 4\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 2\text{Cl}^- + 4\text{OH}^- + 4\text{H}_2\text{O}$	-27.3		
Hydrotalcite	$Mg_4Al_2(OH)_{14} \cdot 3H_2O \Leftrightarrow 2Al(OH)_4^- + 4Mg^{2+} + 6OH^- + 3H_2O$	-56.0		
CSHQ-JenD	$1.5CaO \cdot 0.6667SiO_2 \cdot 2.5H_2O + 3H^+ \Leftrightarrow 1.5Ca^{2+} + 4H_2O + 0.66667SiO_2$	28.7		
CSHQ-JenH	$1.3333 \text{CaO} \cdot \text{SiO}_2 \cdot 2.1667 \text{H}_2\text{O} + 2.6666 \text{H}^+ \Leftrightarrow 1.3333 \text{Ca}^{2+} + \\3.5 \text{H}_2\text{O} + \text{SiO}_2$	22.2		
CSHQ-TobD	$0.6667(1.25 \text{ CaO} \cdot \text{SiO}_2 \cdot 2.75\text{H}_2\text{O}) + 1.66675\text{H}^+ \Leftrightarrow$ $0.833375\text{Ca}^{2+} + 2.6668\text{H}_2\text{O} + 0.6667\text{SiO}_2$	13.7		
CSHQ-TobH	0.6667 CaO·SiO ₂ ·1.5H ₂ O + 1.3334H ⁺ $\Leftrightarrow 0.6667$ Ca ²⁺ + 2.1667H ₂ O + SiO ₂	8.3		
C ₃ AH ₆	$Ca_3Al_2(OH)_{12} \Leftrightarrow 3Ca^{2+} + 2Al(OH)_4 + 4OH^{-}$	-20.5		
Kuzel's salt	$Ca_{4}Al_{2}Cl (SO_{4})_{0.5} (OH)_{12} \cdot 6H_{2}O \Leftrightarrow 4Ca^{2+} + 2Al(OH)_{4}^{-} + Cl^{-}$ $+ 0.5SO_{4}^{2-} + 4OH^{-} + 6H_{2}O$	-28.5		
Natrolite	$Na_2Al_2Si_3O_{10} \cdot 2H_2O \Leftrightarrow 2Na^+ + 2Al(OH)_4^- + 3SiO_2 + 2H_2O$	-30.2		
Straetlingite	$Ca_{4}Al_{2}SiO_{2}(OH)_{10} \cdot 3H_{2}O \Leftrightarrow 2Ca^{2+} + 2Al(OH)_{4} + SiO(OH)_{3} + OH^{-} + 2H_{2}O$	-19.7		
Portlandite	$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^{-}$	-5.2		
Cacite	$CaCO_3 \Leftrightarrow CO_3^{2-} + Ca^{2+}$	-3.2		
Brucite	$Mg(OH)_2 + 2H^+ \Leftrightarrow Mg^{2+} + 2H_2O$	16.8		

	Monocarbonate	$Ca_{4}Al_{2}CO_{9}(H_{2}O)_{11} + 4H^{+} \Leftrightarrow 2AlO_{2}^{-} + CO_{3}^{2-} + 4Ca^{2+} + 13H_{2}O$	24.5
	Hemicarbonate	$(CaO)_{3}Al_{2}O_{3}(CaCO_{3})_{0.5}(CaO_{2}H_{2})_{0.5}(H_{2}O)_{11.5} + 5H^{+} \Leftrightarrow$ $2AlO_{2}^{-} + 0.5CO_{3}^{2-} + 4Ca^{2+} + 14.5H_{2}O$	40.9
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Table 2. Compounds used to prepare sea water and the main ion concentrations in the simulated

sea water with pH=7.3

Compounds used to synthesize sea water	Dosage [g/L]	Ions in simulated sea water	Concentration [g/L]	
NaHCO ₃	0.19	Cl-	19.36	
$CaCl_2 \cdot 2H_2O$	1.47	Mg^{2+}	1.27	
MgCl ₂ ·6H ₂ O	10.57	SO4 ²⁻	2.69	
$Na_2SO_4 \cdot 10H_2O$	9.02	Ca ²⁺	0.40	
KCl	0.75	Na ⁺	10.82	
NaCl	24.08	K ⁺	0.39	
		HCO ₃ -	0.14	

Table 3. Contents of crystalline phases in reaction products of self-healing agentreacted with seawater for 28 days

Crystals	F/H/S	Ca(OH) ₂	CaCO ₃	R _w		
Self-healing agents	(% b.w.)	(% b.w.)	(% b.w.)		sig	
CaO/NaAlO ₂ (Ca/Al=3)	66±3.3	28 ± 1.4	6±0.3	9.56	1.82	
CaO/NaAlO ₂ (Ca/Al=5)	47 ± 2.4	50 ± 2.5	3 ± 0.1	11.05	2.02	
CaO-metakaolin (Ca/Al=5)	52 ±2 .6	28 ± 1.4	20 ± 1.0	12.12	2.12	

Note: For the reaction, the ratio between the mass of self-healing agent and the mass of sea

666 water was 0.2.



Fig. 1 Phase assemblages in the mixture of CaO-NaAlO₂ and 100 ml sea water based on thermodynamic modeling: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar ratio of 5



Fig. 2 Phase assemblages in the mixture of CaO-metakaolin and 100 ml sea water based on thermodynamic modeling: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar ratio of 5



Fig. 3 Phase assemblages in the mixture of 100 ml sea water and 20 g self-healing agents with various Ca/Al based on thermodynamic modeling: (a) CaO-NaAlO₂; (b) CaO-metakaolin. Fs: Friedel's salt



Fig. 4 Phase assemblages in the mixture of 100 ml sea water and 30 g self-healing agents with various Ca/Al based on thermodynamic modeling: (a) CaO-NaAlO₂; (b) CaO-metakaolin. Fs: Friedel's salt; Ks: Kuzel's salt





Fig. 5 Removal efficiency of ions as a function of ratio between the mass of agent to the mass of sea water based on thermodynamic modeling: (a) Cl^{-} ; (b) SO_4^{2-} ; (c) Mg^{2+} in sea water. C/A means Ca/Al molar ratio.





Fig. 6 Removal efficiency of chloride, sulfate and magnesium in sea water as a function of Ca/Al in self-healing agents based on thermodynamic modeling: (a) Cl⁻; (b) SO₄²⁻; (c) Mg²⁺. SH/SW refers to the ratio between the mass of self-healing agent and the mass of sea water.



Fig. 7 pH value as a function of the ratio between the mass of agent to the mass of sea water based on thermodynamic modeling. C/A means Ca/Al molar ratio.



Fig. 8 pH value in sea water mixed with self-healing agent with various Ca/Al based on thermodynamic modeling. SH/SW refers to the ratio between the mass of selfhealing agent and the mass of sea water.



(b)

Fig. 9 Ratios between concentration of Cl^- or SO_4^{2-} and the concentration of OH^- : (a) Cl^-/OH^- , (b) SO_4^{2-}/OH^- . SH/SW refers to the ratio between the mass of self-healing agent and the mass of sea water.



Fig. 10 XRD patterns of solid phases obtained after the reaction of the self-healing agent with sea water: (a) CaO-NaAlO₂ agent with Ca/Al of 3; (b) CaO-NaAlO₂ agent with Ca/Al of 5; (c) CaO-metakaolin agent with Ca/Al of 5. For reactions, the ratio between the mass of self-healing agent and the mass of sea water was 0.2.

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20 (°)

(c)

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Fig. 11 EDS point analysis of reaction products of CaO-metakaolin reacted with seawater for 28 days. For the reaction, the ratio between the mass of self-healing agent and the mass of sea water was 0.2.



Fig. 12 Removal efficiency of aggressive ions in sea water after reaction with selfhealing agents for different periods: (a) Cl⁻; (b) SO₄²⁻; (c) Mg²⁺. C/A means Ca/Al molar ratio.



Fig. 13 Aggressive ions binding efficiency in reaction products: (a) Cl^{-} ; (b) SO_4^{2-} ; (c) Mg^{2+} . C/A means Ca/Al molar ratio.



Fig. 14 Volume increase ratio of self-healing agents mixed with simulated sea water. C/A means Ca/Al molar ratio.

Conflict of interest

The authors declared that they have no conflicts on interest to this work.