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Thermodynamics and kinetics**

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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-NaAlO₂ and CaO-metakaolin agents can have Cl⁻, SO₄²⁻ and Mg²⁺
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

24 removal of Mg^{2+} and SO_4^{2-} were hardly influenced and approximated 100%. Because
25 NaAlO_2 dissolves and releases $\text{Al}(\text{OH})_4^-$ rapidly, precipitates binding Cl^- , SO_4^{2-} and
26 Mg^{2+} were formed fast. In comparison, the reaction of metakaolin binding aggressive
27 ions occurred after 3 days. Because of the faster reaction and the capacity to make
28 $[\text{Cl}^-]/[\text{OH}^-]$ lower in the solution, CaO-NaAlO_2 would be more efficient for
29 self-healing and mitigating reinforcement corrosion than CaO-metakaolin .

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

32 1. INTRODUCTION

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

39 Self-healing of cracks in cementitious material has attracted significant attention in
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
42 was reported that autogenous self-healing of cracks in a marine environment is
43 promoted by Mg^{2+} in the sea water [6, 7]. Compared to autogenous self-healing in
44 fresh water, autogenous self-healing in sea water can enhance the closure ratio of a
45 surface crack with an initial width of $400\ \mu\text{m}$ by 37% for a healing period of 7 days
46 [7]. However, it must be emphasized that there are multiple aggressive ions in the
47 marine environments, such as Cl^- , SO_4^{2-} and Mg^{2+} . While these ions might contribute
48 to the self-healing they can also decrease the durability of reinforced concrete as they
49 lead to weakening of the concrete cover and corrosion of steel bars [8-10]. It is
50 conceivable that once cracks appear, the aggressive ions can invade faster through
51 these cracks. Therefore, an ideal self-healing agent to improve the durability
52 performance of cracked reinforced concrete in a marine environment should not only

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

56 In the presence of Ca^{2+} and $\text{Al}(\text{OH})_4^-$, Cl^- , SO_4^{2-} and Mg^{2+} are known to precipitate
57 as Friedel’s salt ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$), ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot$
58 $3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) and hydrotalcite ($4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$) [11-13], which means
59 that Cl^- , SO_4^{2-} and Mg^{2+} in the crack can be chemically bound. Simultaneously, the
60 crack can be filled by such precipitates. It is well known that calcium is one of the
61 main elements in Portland cement-based materials. According to a previous study [14],
62 unhydrated cement and portlandite with a relatively high solubility results in the
63 diffusion of Ca^{2+} ions into the crack. In addition, $\text{Al}(\text{OH})_4^-$ ions can be supplied by
64 Al-rich materials, such as slag and metakaolin, which can be added directly by
65 blending or after encapsulation. Thus in a next step the binding efficiency of Cl^- ,
66 SO_4^{2-} and Mg^{2+} , and the volume of precipitates formed in sea water need to be
67 investigated as a function of the moles of Ca^{2+} and $\text{Al}(\text{OH})_4^-$ ions, and their molar
68 ratio.

69 In this study, the appropriate moles of Ca^{2+} and $\text{Al}(\text{OH})_4^-$ ions, as well as their
70 molar ratio, were determined by thermodynamic modeling for the self-healing of
71 cracks and the chemical binding of Cl^- , SO_4^{2-} and Mg^{2+} ions from sea water. The
72 volume of relevant precipitates and the corresponding binding efficiency of the
73 aggressive ions in sea water as a function of the masses and ratio of Ca^{2+} and
74 $\text{Al}(\text{OH})_4^-$ ions were predicted. Moreover, in order to evaluate the thermodynamic
75 modeling results and obtain further information on the kinetics of the binding
76 reactions, CaO-NaAlO_2 and CaO-metakaolin , the agents that provide Ca^{2+} and
77 $\text{Al}(\text{OH})_4^-$ were reacted with simulated sea water. The mineralogy of the reaction
78 products was determined by means of X-ray diffraction (XRD). The relative content
79 of Cl, S and Mg chemically bound in the reaction products were quantified by X-ray
80 fluorescence analysis (XRF). The change in concentrations of Mg^{2+} , SO_4^{2-} , and Cl^- in
81 simulated sea water as a function of reaction time was monitored by means of Ion
82 Chromatography (IC) and Inductively Coupled Plasma (ICP). Based on these results,

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

86 **2. MATERIALS AND METHODS**

87 **2.1 Thermodynamic modeling**

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

94 The modeling simulated the reactions taking place after the self-healing agents
95 were mixed with 100 mL seawater. The ratio between the mass of self-healing agent
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
98 self-healing agents. Total moles of ions in seawater can be determined according to
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
101 temperature, at which the reactions of self-healing agents in seawater take place, was
102 assumed to be 25°C.

103

104 **2.2 Experiments for studying the reactions between the self-healing agents and** 105 **simulated sea water**

106 **2.2.1 Materials and sample preparation**

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

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

115 By following the literature [7], sea water was prepared by using the chemical agents
116 listed in Table 2. The purity of all these chemical agents was higher than 99.7%. The
117 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
119 was set to be 0.2. After the agents were mixed with simulated sea water for 1 minute,
120 the mixtures in containers were sealed with plastic sheet with very small holes so that
121 water evaporation was hindered but the air still accessed. The mixtures were cured in
122 a room with a temperature of $20 \pm 1^\circ\text{C}$. At 0.5, 1, 3, 7, 14 and 28 days, the mixtures
123 were centrifuged to separate the solid phase from the solution, respectively. After that,
124 the solid phases were washed 3 times with ethanol and dried at 40°C in an oven until
125 the weight was constant. Finally, the dried solid phases were grounded with agate
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

129 In order to determine the crystalline phases in the reaction products, X-ray
130 Diffraction (XRD) analysis was performed on a X'Pert PRO X-ray diffractometer by
131 using Cu $K\alpha$ as a radiation source. The samples were measured between $5^\circ 2\theta$ and
132 $90^\circ 2\theta$ with a step size of $0.033^\circ 2\theta$. The contents of each crystalline phases in reaction
133 products of self-healing agents reacted with seawater for 28 days were quantified based on
134 Rietveld method. In order to guarantee the accuracy of the quantification,
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.

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

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

145 X-ray Fluorescence (XRF) analysis on the reaction products were carried out using
146 Axios Pw 4400, PaNalytical B.V, with Rh as radiation source and an accuracy of
147 0.05%. According to XRF results, the binding efficiency (BE) of ions by the
148 self-healing agents can be determined with Equation 1.

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

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

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

155

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

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

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

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

169 **3. RESULTS AND DISCUSSION**

170 **3.1 Thermodynamic modelling results on the reactions between self-healing**
171 **agents and sea water**

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

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

185 For the mixture of CaO-metakaolin agent and sea water, in addition to Friedel's salt
186 and ettringite, C-S-H and straetlingite (CaAl₂Si₂O₈) are expected to be formed. It is
187 worth noting that at Ca/Al molar ratio of 3 (see Fig. 2 (a)) portlandite is absent, while
188 at Ca/Al molar ratio of 5 (see Fig. 2 (b)) portlandite is expected, as in the presence of
189 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
192 on thermodynamic modeling: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar
193 ratio of 5

194

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

198

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

211

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

215

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

219 **3.1.2 Removal efficiency of chloride, sulphate and magnesium from solution.**

220 As discussed above, thanks to the formation of Friedel's salt, ettringite and
221 hydrotalcite after the self-healing agents react with sea water, chloride, sulphate and
222 magnesium in the sea water can be chemically bound. From this point of view, they
223 are removed from the solution.

224 As shown in Fig. 5 (a), in general, the removal efficiency of chloride from sea
225 water increases linearly with the increase of the amount of self-healing agents. Only
226 for the CaO-NaAlO₂ agent with Ca/Al of 3, the removal efficiency of chloride reaches
227 a maximum of 80% when the ratio between the mass of agent and the mass of sea
228 water is 0.2. Moreover, the slope of the lines for Ca/Al of 3 is larger than that of 5,
229 indicating a higher chloride uptake at Ca/Al of 3 than at 5.

230 Fig. 5 (b) and (c) show that nearly 100% of sulphate and magnesium can be
231 removed even at a low ratio between the mass of self-healing agent and the mass of
232 sea water, indicating a higher binding efficiency of sulfate and magnesium than of
233 chloride. A “valley” is observed in the removal efficiency curves of SO₄²⁻ in the four
234 series of self-healing agent (see Fig. 5 (b)) corresponding to the transition of ettringite
235 to the Kuzel’s salt shown in Fig. 1 and 2, which demonstrates that from a
236 thermodynamic point of view ettringite binds sulfate stronger than Kuzel’s salt.

237

238 Fig. 5 Removal efficiency of ions as a function of ratio between the mass of agent
239 to the mass of sea water based on thermodynamic modeling: (a) Cl⁻; (b) SO₄²⁻; (c)
240 Mg²⁺ in sea water. C/A means Ca/Al molar ratio.

241

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

254 influenced by Ca/Al and approximates 100%.

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

259

260 Fig. 6 Removal efficiency of chloride, sulfate and magnesium in sea water as a
261 function of Ca/Al in self-healing agents based on thermodynamic modeling: (a) Cl⁻; (b)
262 SO₄²⁻; (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**

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

270

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

273

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

284

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

288

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

294 concentration of Cl^- and the concentration of OH^- ($[\text{Cl}^-]/[\text{OH}^-]$) in pore solution is
295 often used to evaluate the corrosion initiation of reinforcement, which is influenced
296 by Cl^- concentration and pH. Higher concentrations of chlorides and sulphates relative
297 to the hydroxyl concentration can increase the corrosion rate of carbon steel [21].
298 Selected thresholds for corrosion initiation are $[\text{Cl}^-]/[\text{OH}^-] > 0.6$ and $[\text{SO}_4^{2-}]/[\text{OH}^-] >$
299 1.5 [22, 23] and shown in Fig. 9. It can be seen that the ratio between the mass of
300 self-healing agent and the mass of sea water, as well as the Ca/Al molar ratio in the
301 agent, have significant influence on the $[\text{Cl}^-]/[\text{OH}^-]$ value (see Fig. 9 (a)). For
302 CaO-NaAlO₂ agent, mixed with sea water at a mass ratio of 0.2, the $[\text{Cl}^-]/[\text{OH}^-]$
303 value is lower than 0.6 when Ca/Al molar ratio is between 1 and 5. When the
304 CaO-NaAlO₂ agent mixed with sea water at a mass ratio of 0.3, the Ca/Al molar ratio
305 in the agent that leads to a $[\text{Cl}^-]/[\text{OH}^-]$ value lower than 0.6 ranges from 1 to 9. For
306 CaO-metakaolin agent mixed with sea water at a mass ratio of 0.3, when the Ca/Al
307 molar ratio is between 3 and 6, the $[\text{Cl}^-]/[\text{OH}^-]$ value is also lower than 0.6. However,
308 when the CaO-metakaolin agent mixed with sea water at a mass ratio of 0.2, the
309 $[\text{Cl}^-]/[\text{OH}^-]$ value is hardly lower than 0.6 no matter what the Ca/Al molar ratio is. In
310 term of $[\text{SO}_4^{2-}]/[\text{OH}^-]$, both agents with Ca/Al molar ratio larger than 1 can lead to a
311 value of $[\text{SO}_4^{2-}]/[\text{OH}^-]$ lower than 1.5 (see Fig. 9 (b)).

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

319

320 Fig. 9 Ratios between concentration of Cl^- or SO_4^{2-} and the concentration of OH^- : (a)
321 Cl^-/OH^- , (b) $\text{SO}_4^{2-}/\text{OH}^-$. SH/SW refers to the ratio between the mass of self-healing
322 agent and the mass of sea water.

323

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**

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

337 Also, for the CaO-metakaolin agent with Ca/Al of 5 reacting with sea water, the
338 mineral compositions of solid phases changed with reaction times. As shown in Fig.
339 10 (c), diffraction peaks of Friedel's salt and hydrotalcite were not obvious at 1 day,
340 while those of portlandite were distinct. As the reactions proceeded, the diffraction
341 peaks of Friedel's salt and hydrotalcite became more distinct. This is related to the
342 relatively slow reaction between metakaolin and the Ca(OH)₂ in the system.

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

350 The detection of Friedel's salt and hydrotalcite by XRD was consistent with the
351 thermodynamic results shown in section 3.1. However, the simulated Kuzel's salt was
352 not detected. Moreover, according to the experimental results SO₄²⁻ was not bound in
353 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
355 the late stage of reactions. It must be mentioned that the modeling was based on
356 thermodynamic theory. Mineralogy of reaction products were calculated based on the
357 chemical species from complete dissolutions of self-healing agents and related
358 thermodynamic equilibria. However, kinetics of the reactions between self-healing
359 agents and seawater was ignored. In particular, dissolution rate of each mineral in the
360 self-healing agents is different, which can lead to a different mineralogy of reaction
361 products from the thermodynamic modeling results. However, thermodynamic
362 modeling can still provide useful information for the design of such new self-healing
363 agents.

364

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

369

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

375

376 Fig. 11 EDS point analysis of reaction products of CaO-metakaolin reacted with seawater for
377 28 days. For the reaction, the ratio between the mass of self-healing agent and the mass of sea
378 water was 0.2.

379

380 3.2.2 Ion removal based on solution concentrations

381 The concentrations of sulfate and chloride in the solution obtained after the mixing
382 of self-healing agents with the simulated sea water were adopted to calculate the ion
383 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
385 reaction period of 0.5 day. After that, the removal efficiency fluctuated around this
386 value. In comparison, the removal efficiency of chloride ion by the CaO-metakaolin
387 agent with Ca/Al of 5 increased gradually and reached the maximum value, i.e. 50%,
388 at 14 days, which was due to the slower metakaolin reaction. As shown in Fig. 12(a),
389 the experimentally determined removal efficiencies were lower than the
390 thermodynamic modeling results by 5% to 10%. Nevertheless, these differences still
391 show a satisfactory agreement.

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

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

405

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

409

410 3.2.3 Ion binding observed by XRF analysis

411 By means of XRF, the mass ratio of chloride, sulfate and magnesium bound in the
412 self-healing agents were determined and plotted in Fig. 13, compared with the results
413 of thermodynamic modelling. It can be seen that although there is some difference

414 between the modeling results and the experimental results, the modeling can still
415 provide information on the difference of ion binding abilities between the various
416 self-healing agents. It should be mentioned that the relative mass percentages of ions
417 bound in the solid phases were very low, only 6% to 9% for chloride and less than 2%
418 for sulfate and magnesium. It is possible that the difference between the modeling
419 results and the experimental results are partially caused by experimental errors as the
420 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
422 value at a reaction time of 12 hours as NaAlO₂ dissolved rapidly in water and released
423 Al(OH)₄⁻ to make precipitates, i.e. Friedel's salt, AFm and hydrotalcite, formed
424 immediately. Therefore, chloride, sulfate and magnesium were bound within a short
425 period after the mixing of sea water with CaO-NaAlO₂ agent. In comparison, because
426 of the slower reactions of CaO-metakaolin, the binding of these aggressive ions
427 increased gradually until a reaction time of 14 days, which is consistent with the
428 results on ion removal efficiency in Section 3.2.2.

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

436

437 Fig. 13 Aggressive ions binding efficiency in reaction products: (a) Cl⁻; (b) SO₄²⁻; (c)
438 Mg²⁺. C/A means Ca/Al molar ratio.

439

440 **3.2.4 Volume increase of solid phases after reactions of self-healing agents with** 441 **simulated sea water**

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

444 phase increased dramatically within the first 12 hours and remained stable thereafter.
445 As mentioned above, NaAlO_2 dissolved rapidly in water and released Al(OH)_4^- . Thus
446 precipitates binding aggressive ions in synthetic water were formed very fast.
447 Therefore, the volume of the solid phase increased within the first 12 hours after
448 CaO-NaAlO_2 agent was mixed with sea water, while little change occurred afterwards.
449 The final increase ratio of CaO-NaAlO_2 agent with Ca/Al of 5 was smaller than that
450 of the agent with Ca/Al of 3, which agrees with the sequence predicted by
451 thermodynamic modelling.

452 As shown in Fig. 14, there were two stages for the volume increase of
453 CaO-metakaolin agent with Ca/Al of 5 after mixed with sea water. The solid phase
454 volume increased significantly within the first 12 hours after the CaO-metakaolin
455 agent was mixed with sea water. After that, the increase slowed down up to 3 days but
456 occurred again between 3 and 7 days. After a reaction time of 7 days, the volume
457 increase ratio reached 2.2 and remained stable. According to the XRD results in Fig. 9,
458 portlandite was the main reaction product of the CaO-metakaolin agent mixed with
459 sea water after 1 day, which seems to cause the first volume increase, as the hydration
460 of lime into Ca(OH)_2 resulted in a significant volume increase [28]. After longer
461 reaction times (> 3 days), metakaolin reacted significantly and Friedel's salt, Kuzel's
462 salt, hydrotalcite and C-S-H were formed (see Fig. 10). The formation of these
463 mineral which contain significant amounts of water in their structure was
464 accompanied by volume increase [29]. Thus, the slow reaction of metakaolin and
465 formation of Friedel's salt, Kuzel's salt, hydrotalcite and C-S-H contributed to the
466 later volume increase up to 7 days. The final volume increase ratio of CaO-metakaolin
467 agent in sea water determined experimentally compared reasonably well with the
468 thermodynamic modeling result. Moreover, the experimental finding that both
469 CaO-NaAlO_2 agents had smaller volume increases than CaO-metakaolin agent is
470 consistent with the thermodynamic modelling.

471

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

473

C/A means Ca/Al molar ratio.

474

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

477 As demonstrated above, the volume increase ratio of CaO-NaAlO₂ is lower than that
478 of CaO-metakaolin self-healing agent (see Fig. 14). However, for hindering the
479 ingress of aggressive ions into the crack, not only the crack filling, but also the
480 distribution of precipitates in the crack space is important. As addressed in a previous
481 study [7], where encapsulated CaO-metakaolin agent with Ca/Al of 3 was used as
482 self-healing agent, brucite was the main mineral formed at the crack surfaces, while
483 Friedel's salt and hydrotalcite were mainly formed inside the capsule, as the mobility
484 of Al(OH)₄⁻ (and H₂SiO₄²⁻) is much lower than that of other ions in the system.
485 Moreover, the solubility of Friedel's salt and hydrotalcite is much lower than that of
486 portlandite or brucite. Therefore, Friedel's salt and hydrotalcite were formed locally
487 inside the broken capsule, while the OH⁻ ions from the portlandite diffused outwards
488 and reacted with the Mg²⁺ ions invading inwards the crack to form brucite. At the
489 same time, the remaining Ca²⁺ ions reacted with CO₃²⁻ to form calcite, which also
490 contributes to the crack closure. To efficiently block the pathway in the crack and to
491 hinder the further ingress of aggressive ions, precipitates must form inside the crack
492 space, particularly in the crack mouth, rather than inside the broken capsules.
493 According to the mineralogy of the reaction products of these two agents (see Fig. 4),
494 the percentage of portlandite is higher in the reaction products of CaO-NaAlO₂
495 self-healing which could support an efficient distribution of reaction products in the
496 crack and in particular also the formation of calcite. Thus, although the volume
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
499 agent. Further studies will be necessary to clarify this point.

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

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

513 In this study, the reactions of self-healing agents took place directly in seawater. The
514 influence of the pore solution of the bulk matrix on the reaction process of
515 self-healing agents was ignored. Because of the higher concentrations and larger
516 diffusion coefficients, OH⁻ and Ca²⁺ are the ions from the pore solution that may
517 influence the composition of the crack solution, rather than the other ions in the pore
518 solution. It must be mentioned that, however, compared with the direct dissolution of
519 the self-healing agent, which could be stored in capsules and exposed to the crack
520 solution after the capsules were intersected by the crack, the diffusion of OH⁻ and
521 Ca²⁺ ions from the pore solution are too slow to influence the reactions of self-healing
522 agents. Therefore, the studies on the reactions of self-healing agents directly taking
523 place in seawater here can still provide useful information for understanding the
524 self-healing of cracks in cement-based materials.

525

526 **4. Conclusion**

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

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

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

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

543 (3) The kinetics of chemical reaction between self-healing agents and simulated sea
544 water was investigated via XRD and solution analysis. For CaO-NaAlO₂ agent it was
545 found that NaAlO₂ can rapidly dissolve in water and release Al(OH)₄⁻, making
546 precipitates formed very fast. For the CaO-metakaolin agent, portlandite formed
547 within the first 12 hours, while the reaction of metakaolin, which make aggressive
548 ions in sea water bound, occurred mainly after more than 3 days. Because of the faster
549 reaction and higher pH enhancement of CaO-NaAlO₂ agent, the [Cl⁻]/[OH⁻], which is
550 an indicator to corrosion risk of steel bars, would be much lower in the crack solution
551 than that for CaO-metakaolin agent. From this point of view, CaO-NaAlO₂ agent will
552 be more efficient for declining the corrosion risk of steel bars in cracked concrete.

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

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

561 In summary the investigated self-healing agents can bind chloride, magnesium and
562 sulfate very efficiently and in both cases additional volume was generated due to the
563 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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648 20 (1998) 163-170.

649 Table 1. Chemical equations and the corresponding equilibrium constants at 25°C [18,
650 19]

Minerals	Chemical equations	log K _{so}
Ettringite	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \Leftrightarrow 6\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 26\text{H}_2\text{O}$	-44.9
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	$\text{Mg}_4\text{Al}_2(\text{OH})_{14} \cdot 3\text{H}_2\text{O} \Leftrightarrow 2\text{Al}(\text{OH})_4^- + 4\text{Mg}^{2+} + 6\text{OH}^- + 3\text{H}_2\text{O}$	-56.0
CSHQ-JenD	$1.5\text{CaO} \cdot 0.6667\text{SiO}_2 \cdot 2.5\text{H}_2\text{O} + 3\text{H}^+ \Leftrightarrow 1.5\text{Ca}^{2+} + 4\text{H}_2\text{O} + 0.6667\text{SiO}_2$	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	$0.6667\text{CaO} \cdot \text{SiO}_2 \cdot 1.5\text{H}_2\text{O} + 1.3334\text{H}^+ \Leftrightarrow 0.6667\text{Ca}^{2+} + 2.1667\text{H}_2\text{O} + \text{SiO}_2$	8.3
C ₃ AH ₆	$\text{Ca}_3\text{Al}_2(\text{OH})_{12} \Leftrightarrow 3\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + 4\text{OH}^-$	-20.5
Kuzel's salt	$\text{Ca}_4\text{Al}_2\text{Cl}(\text{SO}_4)_{0.5}(\text{OH})_{12} \cdot 6\text{H}_2\text{O} \Leftrightarrow 4\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + \text{Cl}^- + 0.5\text{SO}_4^{2-} + 4\text{OH}^- + 6\text{H}_2\text{O}$	-28.5
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O} \Leftrightarrow 2\text{Na}^+ + 2\text{Al}(\text{OH})_4^- + 3\text{SiO}_2 + 2\text{H}_2\text{O}$	-30.2
Straetlingite	$\text{Ca}_4\text{Al}_2\text{SiO}_2(\text{OH})_{10} \cdot 3\text{H}_2\text{O} \Leftrightarrow 2\text{Ca}^{2+} + 2\text{Al}(\text{OH})_4^- + \text{SiO}(\text{OH})_3^- + \text{OH}^- + 2\text{H}_2\text{O}$	-19.7
Portlandite	$\text{Ca}(\text{OH})_2 \Leftrightarrow \text{Ca}^{2+} + 2\text{OH}^-$	-5.2
Cacite	$\text{CaCO}_3 \Leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$	-3.2
Brucite	$\text{Mg}(\text{OH})_2 + 2\text{H}^+ \Leftrightarrow \text{Mg}^{2+} + 2\text{H}_2\text{O}$	16.8

Monocarbonate	$\text{Ca}_4\text{Al}_2\text{CO}_9(\text{H}_2\text{O})_{11} + 4\text{H}^+ \Leftrightarrow 2\text{AlO}_2^- + \text{CO}_3^{2-} + 4\text{Ca}^{2+} + 13\text{H}_2\text{O}$	24.5
Hemicarbonate	$(\text{CaO})_3\text{Al}_2\text{O}_3(\text{CaCO}_3)_{0.5}(\text{CaO}_2\text{H}_2)_{0.5}(\text{H}_2\text{O})_{11.5} + 5\text{H}^+ \Leftrightarrow 2\text{AlO}_2^- + 0.5\text{CO}_3^{2-} + 4\text{Ca}^{2+} + 14.5\text{H}_2\text{O}$	40.9

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657 Table 2. Compounds used to prepare sea water and the main ion concentrations in the simulated
658 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
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	1.47	Mg^{2+}	1.27
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	10.57	SO_4^{2-}	2.69
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	9.02	Ca^{2+}	0.40
KCl	0.75	Na^+	10.82
NaCl	24.08	K^+	0.39
		HCO_3^-	0.14

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663 Table 3. Contents of crystalline phases in reaction products of self-healing agent
 664 reacted with seawater for 28 days

Crystals	F/H/S	Ca(OH) ₂	CaCO ₃	R _w	sig
Self-healing agents	(% b.w.)	(% b.w.)	(% b.w.)		
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

665 Note: For the reaction, the ratio between the mass of self-healing agent and the mass of sea
 666 water was 0.2.

667

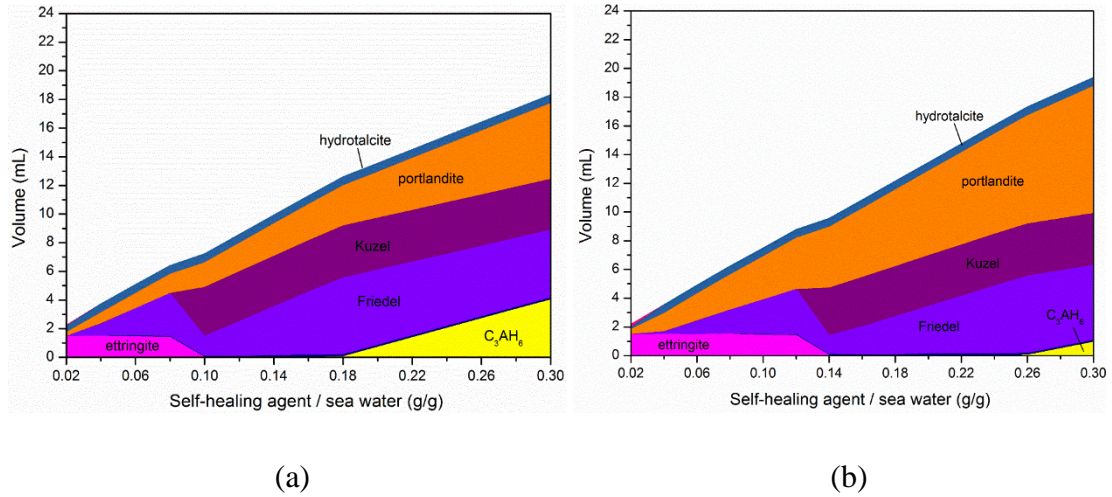


Fig. 1 Phase assemblages in the mixture of CaO-NaAlO₂ and 100 ml sea water based on thermodynamic modeling: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar ratio of 5

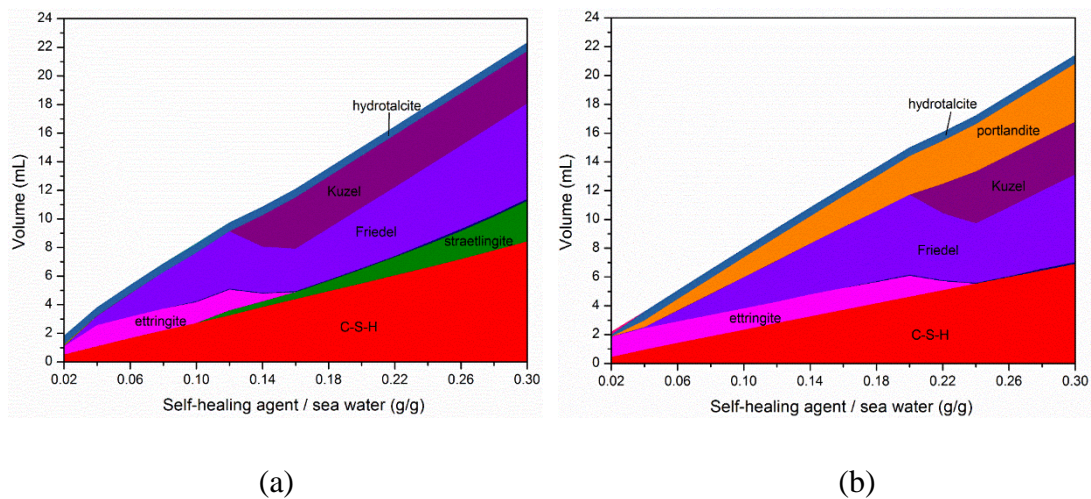


Fig. 2 Phase assemblages in the mixture of CaO-metakaolin and 100 ml sea water based on thermodynamic modeling: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar ratio of 5

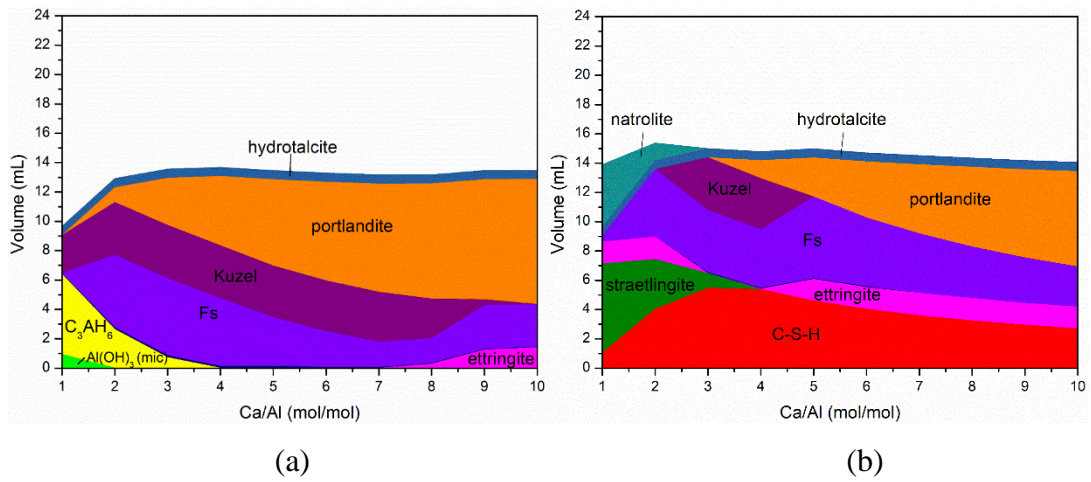


Fig. 3 Phase assemblages in the mixture of 100 ml sea water and 20 g self-healing agents with various Ca/Al based on thermodynamic modeling: (a) CaO-NaAlO₂; (b) CaO-metakaolin. Fs: Friedel's salt

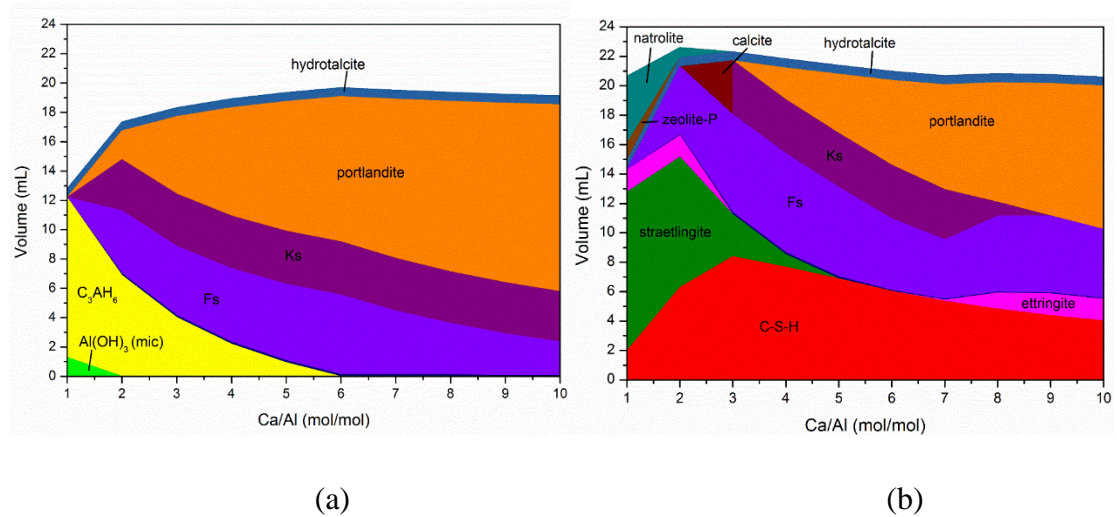
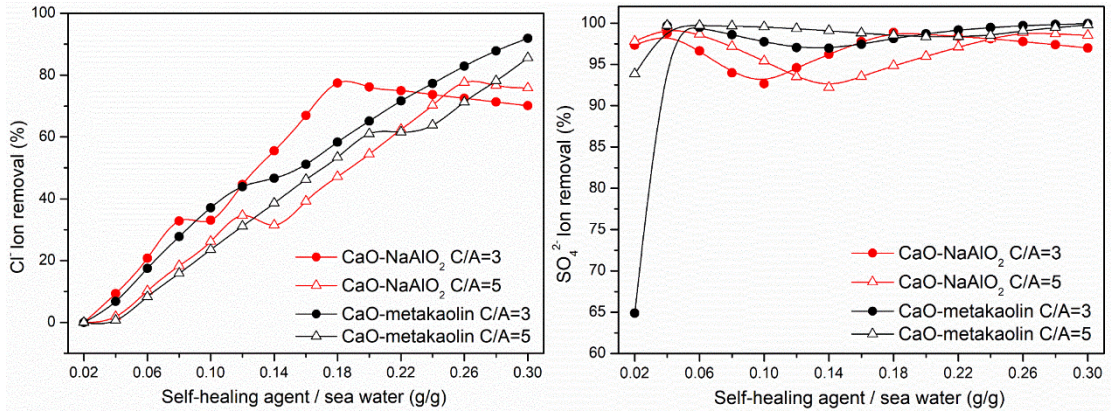
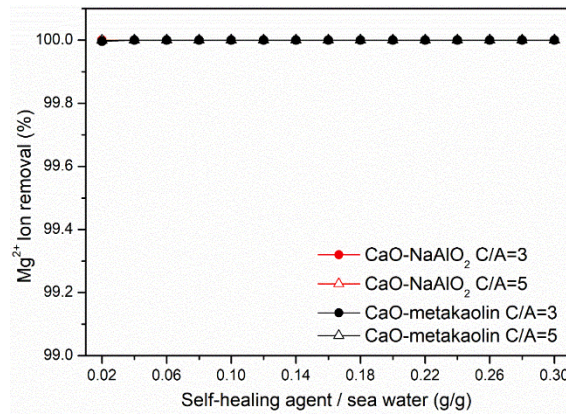


Fig. 4 Phase assemblages in the mixture of 100 ml sea water and 30 g self-healing agents with various Ca/Al based on thermodynamic modeling: (a) CaO-NaAlO₂; (b) CaO-metakaolin. Fs: Friedel's salt; Ks: Kuzel's salt



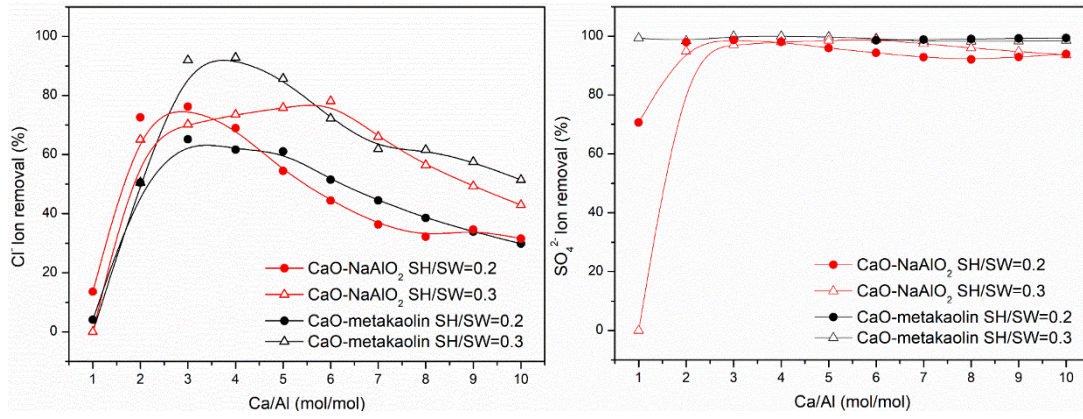
(a)

(b)



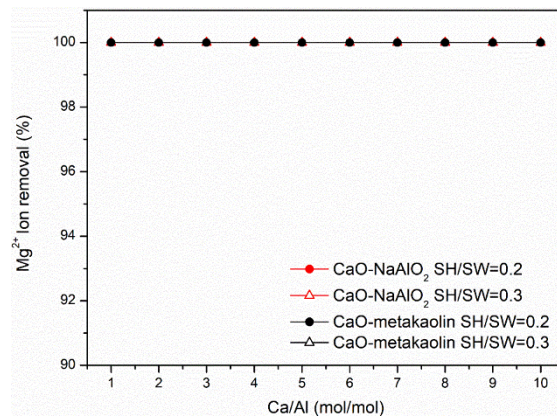
(c)

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) SO₄²⁻; (c) Mg²⁺ in sea water. C/A means Ca/Al molar ratio.



(a)

(b)



(c)

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.

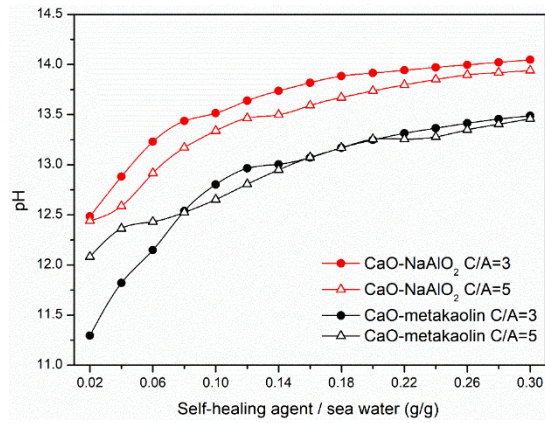


Fig. 7 pH value as a function of the ratio between the mass of agent to the mass of sea water based on thermodynamic modeling. C/A means Ca/Al molar ratio.

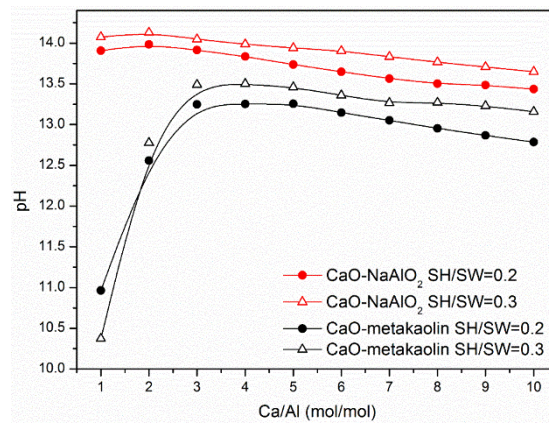
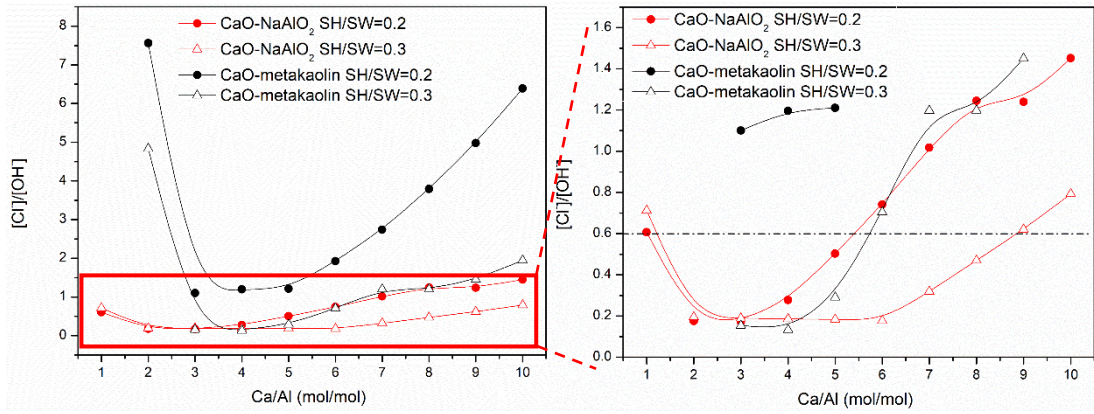
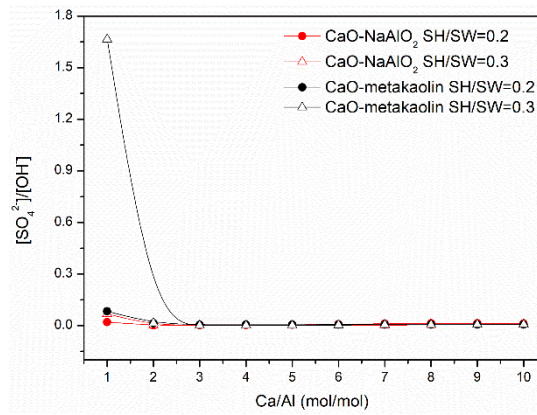


Fig. 8 pH value in sea water mixed with self-healing agent with various Ca/Al based on thermodynamic modeling. SH/SW refers to the ratio between the mass of self-healing agent and the mass of sea water.

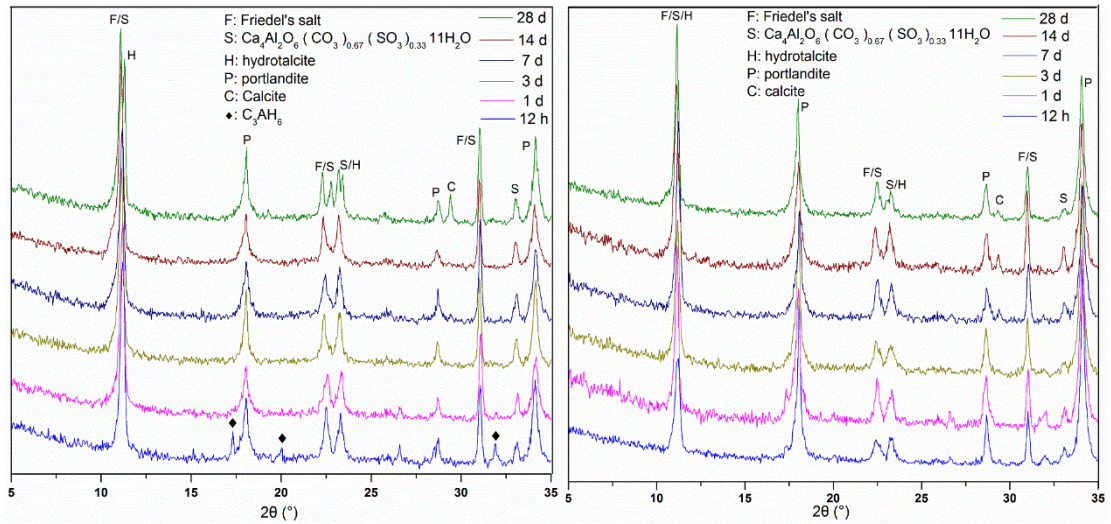


(a)



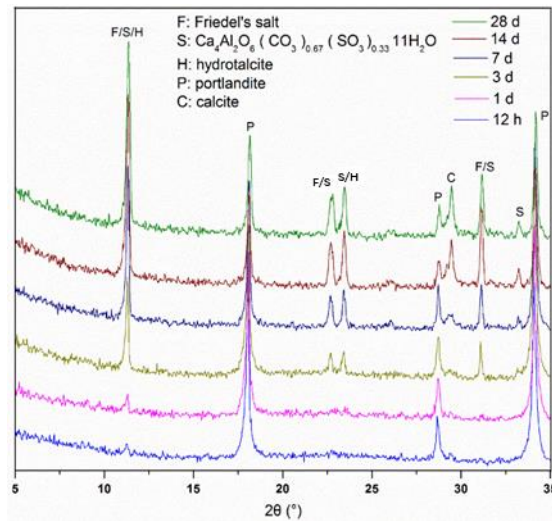
(b)

Fig. 9 Ratios between concentration of Cl^- or SO_4^{2-} and the concentration of OH^- : (a) Cl^-/OH^- , (b) $\text{SO}_4^{2-}/\text{OH}^-$. SH/SW refers to the ratio between the mass of self-healing agent and the mass of sea water.



(a)

(b)



(c)

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.

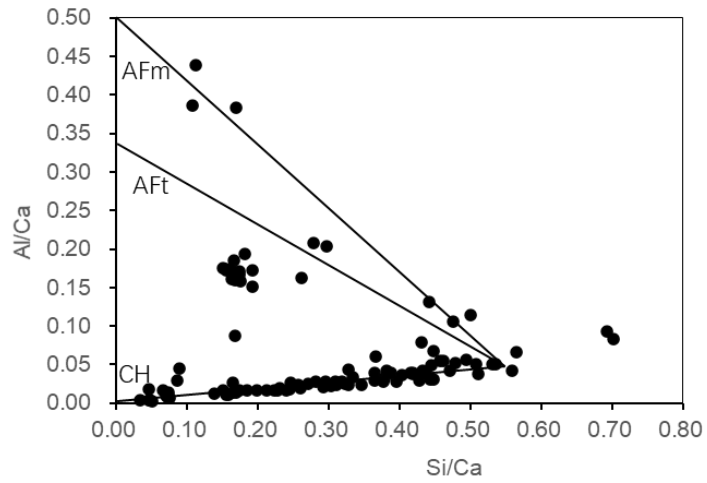
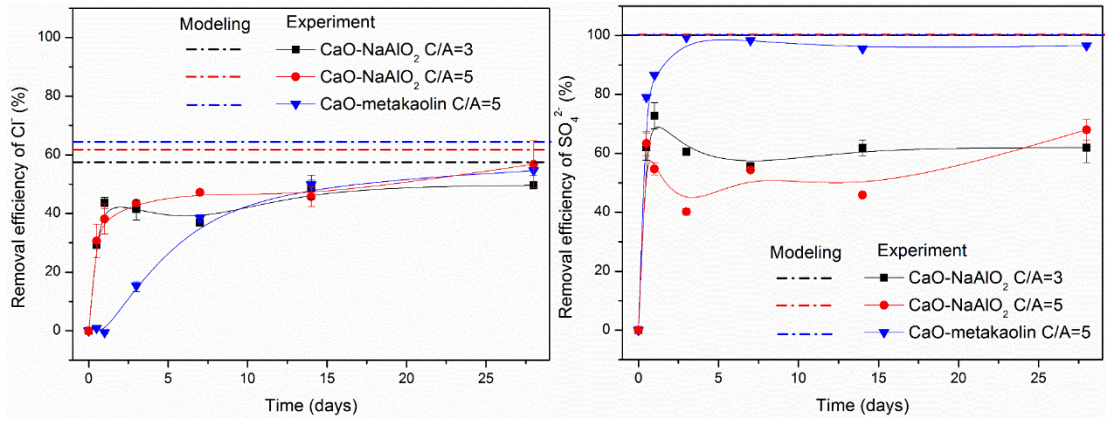
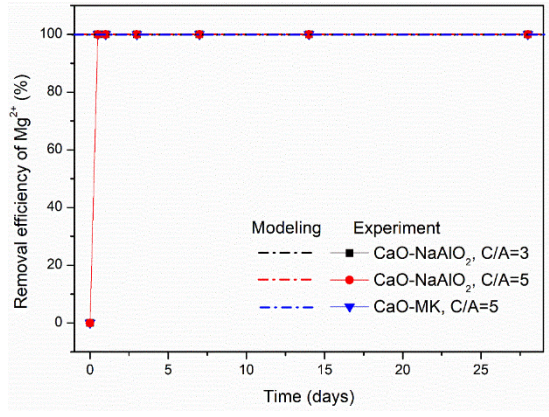


Fig. 11 EDS point analysis of reaction products of CaO-metakaolin reacted with seawater for 28 days. For the reaction, the ratio between the mass of self-healing agent and the mass of sea water was 0.2.



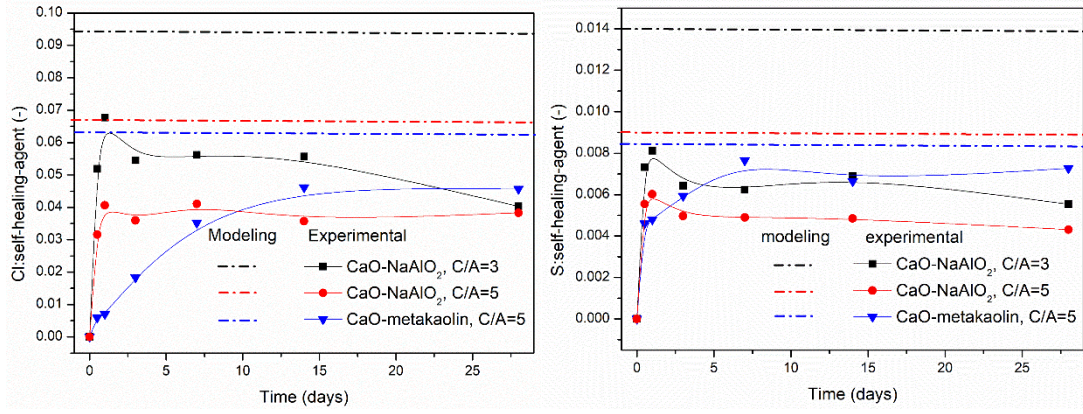
(a)

(b)



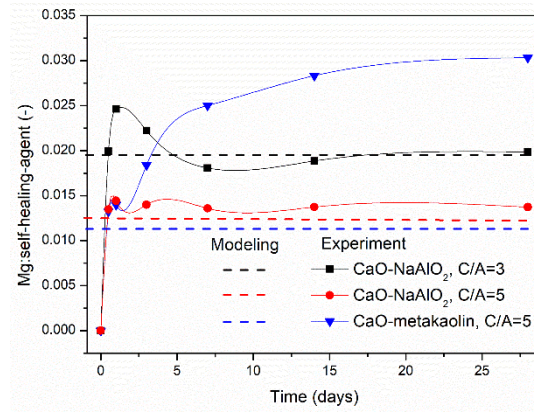
(c)

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



(a)

(b)



(c)

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.

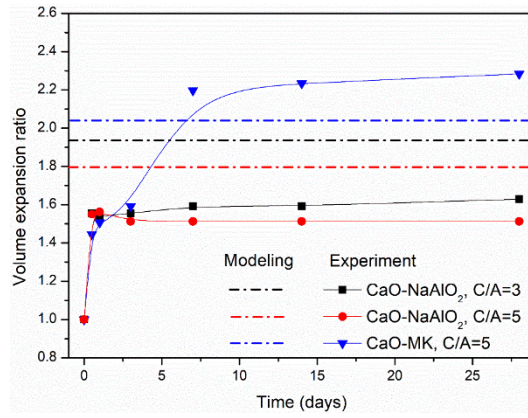


Fig. 14 Volume increase ratio of self-healing agents mixed with simulated sea water.

C/A means Ca/Al molar ratio.

Conflict of interest

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