

THERMODYNAMIC MODELING OF THE REACTIONS OF SELF-HEALING AGENTS AND THE CHEMICAL BINDING OF AGGRESSIVE IONS IN SEA WATER

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Abstract

In this study, a new concept on self healing of cracks that the ingressive ions in the crack is chemically bound to improve the self-healing efficiency was proposed for cracked cementitious materials in a marine environment. Thermodynamic modeling was performed to determine the appropriate masses and ratio of Ca^{2+} and Al^{3+} provided by chemical agents for a good efficiency of self-healing and chemical binding of Cl^- , SO_4^{2-} , and Mg^{2+} ions from sea water. It was found that when CaO-NaAlO_2 and CaO-metakaolin are used as self-healing agents, Friedel's salt, kuzel's salt, ettringite and hydrotalcite can be formed and, thus, Cl^- , SO_4^{2-} and Mg^{2+} from sea water are chemically bound. Moreover, the volume of phase assemblages becomes larger, which facilitates the self-healing of cracks. For a ratio of 0.3 between the mass of self-healing agent to the mass of sea water, the removal efficiency of Cl^- ions for CaO-NaAlO_2 agent with a Ca/Al of 5 reaches the maximum value, i.e. 87%, while for CaO-metakaolin agent the removal efficiency of Cl^- ions reaches the maximum when the Ca/Al is 3. The chemical binding of Mg^{2+} and SO_4^{2-} ions is hardly influenced by Ca/Al when it is larger than 2 and the removal efficiency approximates 100%.

Keywords: thermodynamic modeling, ion binding, marine environment, self-healing

1. INTRODUCTION

In order to make rebars withstand bending loading appropriately, occurrence of cracks with a certain width is usually expected in reinforced concrete elements. In the concrete structures in marine environments, cracks usually become pathways for ingression of ions, such as Cl^- , SO_4^{2-} , and Mg^{2+} , and cause deterioration of reinforced concrete structures. It was encouraging to find that concrete was able to heal cracks autogenously. Self-healing of cracks can be a potential solution to the durability problem caused by cracks in reinforced concrete in marine environments.

Self-healing of cracks in cementitious material has attracted great attention in recent years

[1-5]. It was found that environmental factors, in particular extra ions from the environment, presented significant impacts on the self-healing process and efficiency[1]. It was reported that autogenous self-healing of cracks in a marine environment was promoted by Mg^{2+} in the sea water [6, 7]. Compared to autogenous self-healing in fresh water, the closure ratio of a surface crack with an initial width of 400 μm increases by 37% for a healing period of 7 days in sea water [7]. However, it must be emphasized that there are multiple aggressive ions in the marine environments, such as Cl^- , SO_4^{2-} , and Mg^{2+} . These aggressive ions can obviously decrease the durability performance of reinforced concrete, particularly cracked reinforced concrete [8-10]. It is conceivable that once cracks appear, aggressive ions immediately invade through the cracks. Therefore, in order to improve the durability performance of cracked reinforced concrete in a marine environment, the self-healing of cracks not only can block the crack to prevent from the further ingress of aggressive ions, but also be able to “capture” the aggressive ions already exist in the cracks .

According to the literature [11-13] , Cl^- , SO_4^{2-} , and Mg^{2+} in concrete can be chemically bound in Friedel’s salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), and hydrotalcite ($4MgO \cdot Al_2O_3 \cdot 10H_2O$) in cement paste respectively. It can be seen that these minerals are composed of calcium and aluminum. From the thermodynamics point of view, if adequate concentrations of Ca^{2+} and Al^{3+} are present in the crack solution, Friedel’s salt, ettringite and hydrotalcite can be formed, which means that chemical binding of Cl^- , SO_4^{2-} , and Mg^{2+} in the crack can take place. Simultaneously, the crack can be filled by the precipitates. Calcium is one of the main elements in cement-based materials. According to the previous study [14], when portlandite having a high solubility is present in the matrix, there will be quantities of Ca^{2+} ions diffusing into the crack. In addition, Al^{3+} ions can be supplied by Al-rich materials, such as slag and metakaolin, which can be added by directly blending or after encapsulation. It is interesting to quantify the binding efficiency of Cl^- , SO_4^{2-} , and Mg^{2+} and the volume of precipitates formed in sea water as a function of the masses and the ratio of Ca^{2+} and Al^{3+} ions.

In this study, in order to determine the appropriate masses and ratio of Ca^{2+} and Al^{3+} ions for the self-healing of cracks and the chemical binding of Cl^- , SO_4^{2-} , and Mg^{2+} ions from sea water, thermodynamic modeling was performed. The volume of relevant precipitates and the corresponding binding efficiency of the aggressive ions in sea water as a function of the masses and ratio of Ca^{2+} and Al^{3+} ions were predicted. The Ca^{2+} and Al^{3+} ions are supposed to be provided by $CaO-Al_2O_3$ and $CaO-SiO_2-Al_2O_3$ agents with various masses and Ca/Al ratios.

2. THERMODYNAMIC MODELING

Thermodynamic modeling was performed with software GEMS 3.5, in which Gibbs energy minimization was used to calculate the mass and volume of equilibrium phase assemblages and the equilibrium ion concentrations from the total bulk elemental composition. The databases used were CEMDATA18 database [15] particularly for cementitious materials.

In this study, two series of self-healing agents, $CaO-NaAlO_2$ and CaO -metakaolin, were chosen to provide additional Ca^{2+} and Al^{3+} ions for the binding of aggressive ions in sea water and the self-healing of cracks. These agents can be used to manufactured artificial aggregates and added into concrete deliberately, as described in previous study [7]. The concentration of the main ions in synthetic sea water was listed in Table 1. In the calculation in this study, the

volume of sea water was set as 100 ml.

Table 1: Ions concentrations in synthetic sea water

Ion	Concentration [g/L]
Cl ⁻	19.36
Mg ²⁺	1.266
SO ₄ ²⁻	2.69
Ca ²⁺	0.40
Na ⁺	1.34
K ⁺	0.39

3. RESULTS AND DISCUSSION

3.1 Phase assemblages of self-healing agents mixed with sea water

As shown in Fig. 1, Friedel's salt, ettringite, hydrotalcite and portlandite are the main precipitates formed when the ratio between the mass of CaO-NaAlO₂ agent to the mass of sea water was less than a criteria, i.e. 0.08 for Ca/Al (by mole) =3 and 0.12 for Ca/Al (by mole) =5, respectively. As the ratio between the mass of CaO-NaAlO₂ agent to the mass of sea water increases, the volume of precipitates increases and the mineralogy changes. For the CaO-NaAlO₂ agent has a Ca/Al of 3, ettringite disappears and the volume of Friedel's salt decreases while kuzel's salt forms as the ratio between the mass of CaO-NaAlO₂ agent to the mass of sea water increases from 0.08 to 0.24. Similar phenomenon occurs in the mixture of sea water and CaO-NaAlO₂ agent with a Ca/Al of 5. Moreover, for the CaO-NaAlO₂ agent has a Ca/Al of 3, C₄AH₁₉ is formed when the ratio between the mass of CaO-NaAlO₂ agent to the mass of sea water is larger than 0.18 and SO₄-OH-AFm also presents when the ratio increases to 0.22. The percentage of portlandite in the mixture of sea water and CaO-NaAlO₂ agent with a Ca/Al of 5 is larger than that with a Ca/Al of 3.

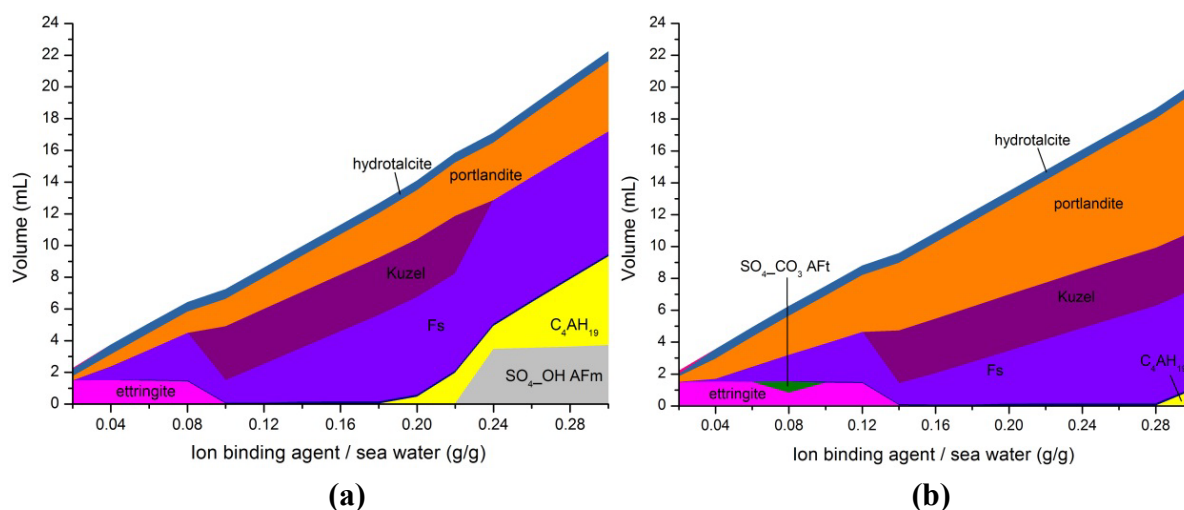


Figure 1: Phase assemblages in the mixture of CaO-NaAlO₂ and 100 ml sea water: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar ratio of 5

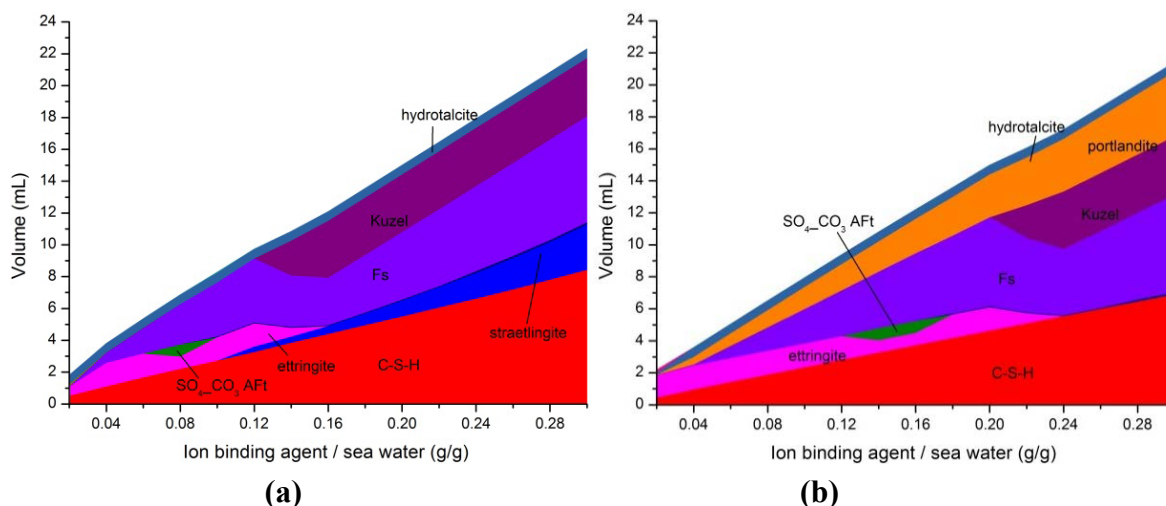


Figure 2: Phase assemblages in the mixture of CaO-metakaolin and 100 ml sea water: (a) with Ca/Al molar ratio of 3; (b) with Ca/Al molar ratio of 5

For the mixture of CaO-metakaolin agent and sea water, besides Friedel's salt and ettringite, C-S-H and straetlingite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) can be formed as well. It is worth noting that when the Ca-to-Al molar ratio is 3 (see Fig. 2 (a)) portlandite is absent, while when the Ca-to-Al molar ratio increases to 5 (see Fig. 2 (b)) portlandite occurs.

According to the results discussed above, the Ca/Al in the self-healing agent has significant effect on the mineralogy of the phase assemblages, thus on the binding of aggressive ions in sea water. Therefore, it is of significance to determine the phase assemblages changing with the Ca/Al in the self-healing agents. From Figure 3, it can be seen that the mineral composition of the reaction products changes with Ca/Al molar ratio in the self-healing agents. In general, the increase of Ca/Al means a larger amount of Ca and smaller amount of Al provided to the system. Therefore, the volume percentage of phases containing Al decreases and the volume of portlandite increases with the increase of Ca/Al. For CaO-NaAlO₂, the volume of reaction products reaches the maximum when Ca/Al = 3. In comparison, for CaO-metakaolin the volume of reaction products reaches the maximum when Ca/Al = 2.

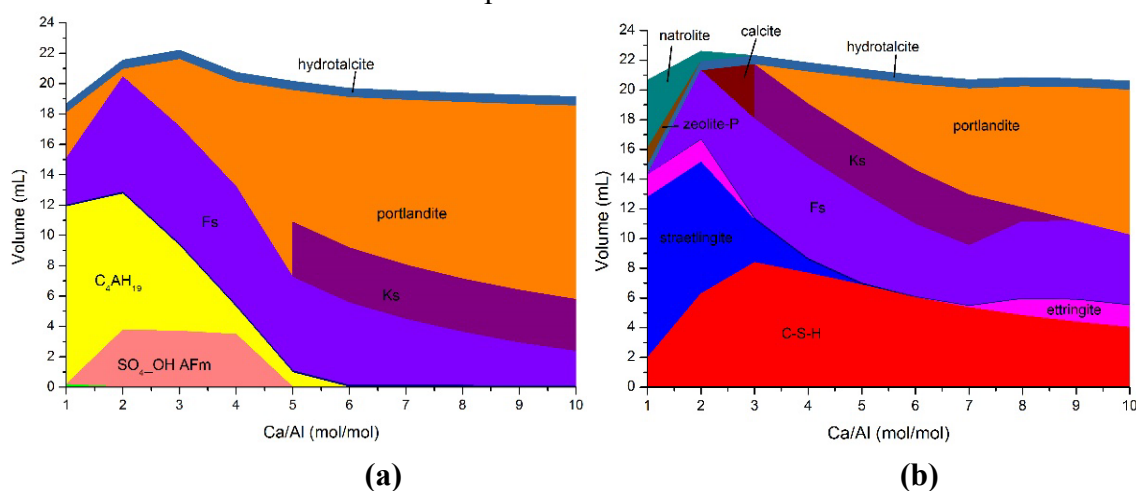


Figure 3: Phase assemblages in the mixture of 100 ml sea water and 30 g self-healing agents with various Ca/Al: (a) CaO-NaAlO₂; (b) CaO-metakaolin

3.2 Mass ratios of ingressive ions to self-healing agent.

Figure 4 shows the ratio between the mass of ingressive ions bond and the mass of self-healing agent as a function of the ratio between the mass of agent to the mass of sea water. The relative content of Cl^- for unit mass of binding agent keeps increasing significantly when the ratio between the mass of binding agent to the mass of sea water ranges from 0.02 to 0.12. When the ratio between the mass of binding agent to the mass of sea water increases further, the relative content of Cl^- becomes stable or even decreases for CaO-NaAlO₂ agent with Ca/Al of 3. In comparison, the relative contents of SO_4^{2-} and Mg^{2+} decrease with the increase of the ratio between the mass of binding agent to the mass of sea water. This is because SO_4^{2-} and Mg^{2+} are of low concentrations in sea water. As a result, they are almost chemically bond even the ratio between the mass of binding agent to the mass of sea water is very low. Therefore, with further addition of the binding agents, the relative contents of SO_4^{2-} and Mg^{2+} decrease.

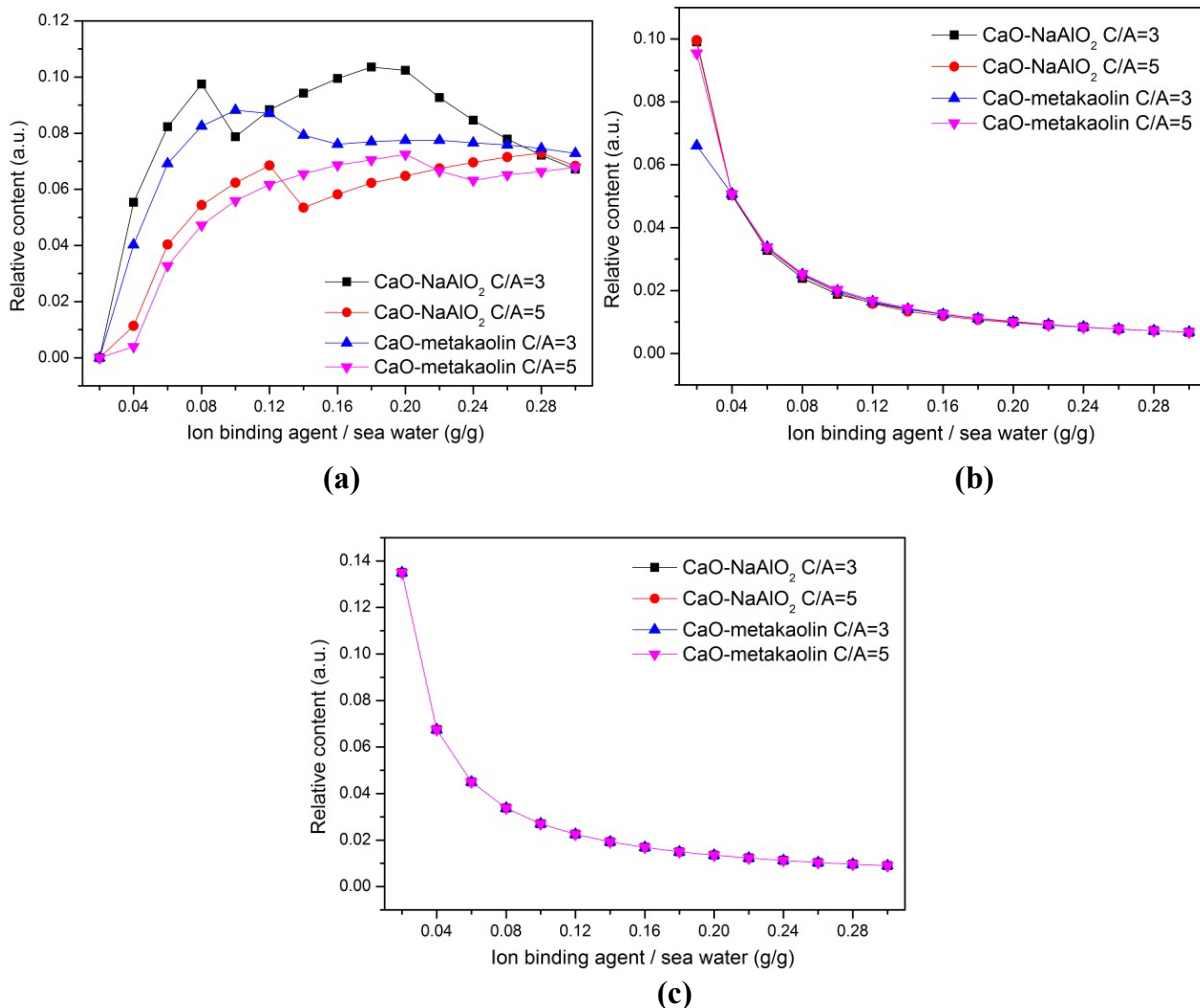


Figure 4: Ratio between the mass of ingressive ions and the mass of the self-healing agent: (a) Cl^- ; (b) SO_4^{2-} ; (c) Mg^{2+} .

3.3 Ion removal of Cl^- , SO_4^{2-} , and Mg^{2+} in solution.

As shown in Figure 5 (a), the removal efficiency of Cl^- ions from sea water increases linearly with the increase of the amount of self-healing agents. The slope of the lines corresponding to the Ca/Al of 3 is larger than that of 5. It means that the increase rate of the removal efficiency of Cl^- ions by these two self-healing agents with Ca/Al of 3 is larger than that with Ca/Al of 5. It should be mentioned that the removal efficiency of Cl^- ions reaches the maximum, i.e. 80%, when the ratio between the mass of CaO-NaAlO_2 agent with Ca/Al of 3 to the mass of sea water reaches 0.2.

As shown in Figure 5 (b) and (c), the removal of SO_4^{2-} and Mg^{2+} can reach 100% even with a low ratio between the mass of self-healing agent and the mass of sea water. It reveals that SO_4^{2-} and Mg^{2+} show greater potential to be bond compared with Cl^- . Besides, there is a “valley” in the removal efficiency curve of SO_4^{2-} in the four series of self-healing agent (see Figure 5 (b)). It is interesting to find that the positions of valleys are always consistent with that of transition of ettringite to the Kuzel’s salt shown in Figure 1 and 2, which demonstrates that when ettringite is transferred to kuzel’s salt a part of SO_4^{2-} is released to the solution again.

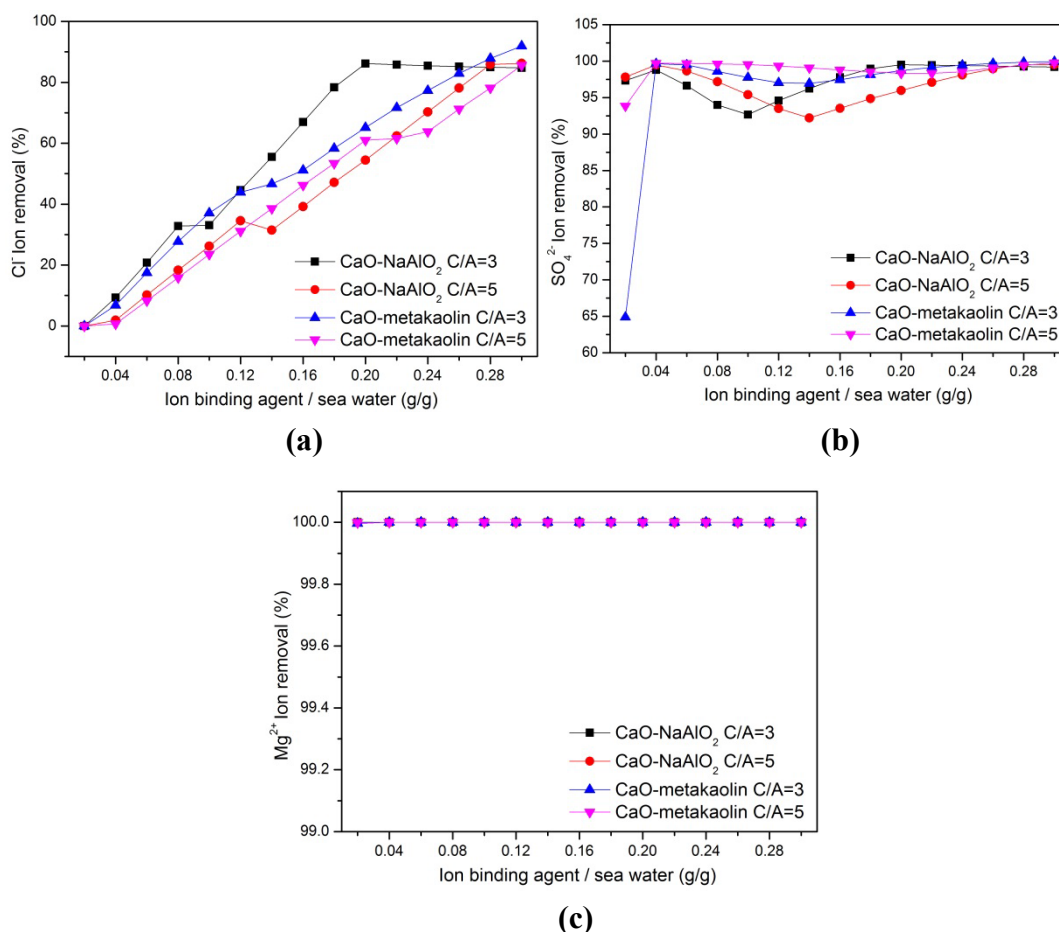


Figure 5: Removal efficiency of ions: (a) Cl^- ; (b) SO_4^{2-} ; (c) Mg^{2+} in sea water. C/A means Ca/Al molar ratio.

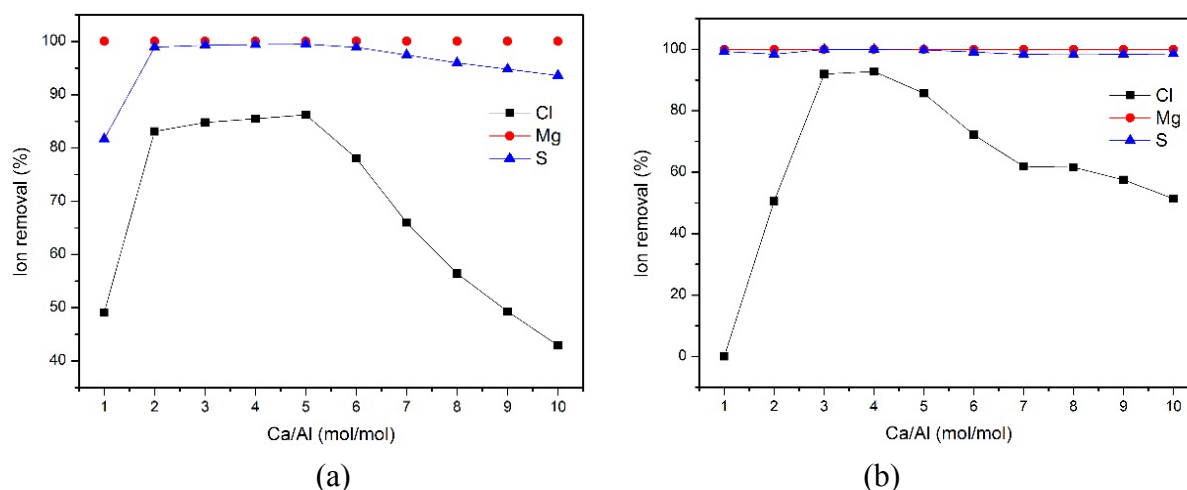


Figure 6: Removal efficiency of ions in sea water as a function of Ca/Al in self-healing agent: (a) CaO-NaAlO₂ agent; (b) CaO-metakaolin. The ratio between the mass of self-healing agent and the mass of sea water is 0.3.

Figure 6 presents the removal efficiency of ions in sea water as a function of Ca/Al molar ratio in CaO-NaAlO₂ and CaO-metakaolin agents. The ratio between the mass of self-healing agent and the mass of sea water is 0.3. It is found that both for CaO-NaAlO₂ and CaO-metakaolin agents the removal efficiency of Cl⁻ ions firstly increases and then decreases with Ca/Al, while the removal efficiency of Mg²⁺ ions is hardly influenced by Ca/Al and approximates 100%. The removal efficiency of Cl⁻ ions for CaO-NaAlO₂ agent reaches the maximum value, i.e. 87%, when the Ca/Al is 5, while for CaO-metakaolin agent the removal efficiency of Cl⁻ ions reaches the maximum when the Ca/Al is 3. The removal efficiency of SO₄²⁻ ions for CaO-NaAlO₂ agent increases from about 80% to 100% when the Ca/Al increases from 1 to 2, and decreases slightly when the Ca/Al increases further to be larger than 6. In comparison, the removal efficiency of SO₄²⁻ ions for CaO-metakaolin agent is hardly influenced by Ca/Al.

4. CONCLUSIONS

In this study, thermodynamic modeling was performed to determine the appropriate masses and ratio of Ca²⁺ and Al³⁺ ions for the self-healing of cracks and the chemical binding of Cl⁻, SO₄²⁻, and Mg²⁺ ions from sea water. Based on the thermodynamic modeling results, the following conclusions can be drawn:

(1) As the ratio between the mass of self-healing agent to the mass of sea water increases, the volume of precipitates increases and the mineralogy changes. Due to the formation of Friedel's salt, kuzel's salt, ettringite and hydrotalcite, Cl⁻, SO₄²⁻ and Mg²⁺ in sea water are chemically bound when the self-healing agents provide Ca²⁺ and Al³⁺ ions.

(2) The relative content of Cl⁻ for unit mass of binding agent keeps increasing when the ratio between the mass of binding agent to the mass of sea water ranges from 0.02 to 0.12.

(3) For a ratio of 0.3 between the mass of self-healing agent to the mass of sea water, the removal efficiency of Cl⁻ ions for CaO-NaAlO₂ agent reaches the maximum value, i.e. 87%, when the Ca/Al is 5, while for CaO-metakaolin agent the removal efficiency of Cl⁻ ions reaches the maximum when the Ca/Al is 3. The removal efficiency of Mg²⁺ and SO₄²⁻ ions is

hardly influenced by Ca/Al when it is larger than 2 and the removal efficiency approximates 100%.

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