

水化硫铝酸钙和水化铝酸钙对内掺、外渗氯离子的固结机理及能力

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摘 要: 为研究单硫型水化硫铝酸钙(AFm)和水化铝酸钙(C₃AH₆)的 Cl⁻ 固结能力和机理, 通过人工合成的方法采用 C₃A 制备了高纯 AFm 与 C₃AH₆, 并研究了内掺、外渗 Cl⁻ 条件下 2 种物质固结 Cl⁻ 后的产物类型、微观形貌、Cl⁻ 固结量和固结率。结果表明: C₃AH₆ 对内掺 Cl⁻ 的固结能力(最高可达 75%)远高于 AFm(稳定约为 17%), 该差异在内掺 Cl⁻ 含量相对较低的情况下尤为显著; 对比 AFm, Cl⁻ 与 C₃AH₆ 的反应更迅速且更为彻底; C₃AH₆ 的固氯产物一致为 Friedel 盐, AFm 则根据 Cl⁻ 浓度及其不同引入方式分为 Hc、Kuzel 盐、Friedel 盐以及高硫型水化硫铝酸钙(Aft)。

关键词: 单硫型水化硫铝酸钙; 水化铝酸钙; 氯离子; 固结能力; 固结机理

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Binding Mechanism and Capacity for AFm and C₃AH₆ on Premixed and Ingress Chlorides

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Abstract: To investigate the binding capacity and mechanism of AFm and C₃AH₆ with Cl⁻ ions, high purity AFm and C₃AH₆ were synthesized with C₃A. The mineralogy and morphology of the products after reaction of AFm or C₃AH₆ with premixed and ingress Cl⁻ ions, and the corresponding binding capacities were characterized. The results show that C₃AH₆ has a higher Cl⁻ ions binding ability (*i.e.*, up to 75%) with premixed Cl⁻ ions than AFm (*i.e.*, 17%), especially at a relatively low content of premixed Cl⁻ ions. A reaction between Cl⁻ ions and C₃AH₆ is faster than that between Cl⁻ ions and AFm. The binding product generated by C₃AH₆ is Friedel's salt, while those by AFm are Hc, Kuzel's salt, Friedel's salt and Aft, which depends on Cl⁻ ions concentration and its introduced manners, *via* premixed or ingress Cl⁻ ions.

Keywords: monosulfate calcium silicate hydrated; calcium aluminate hydrate; chlorides; binding capacity; binding mechanism

1 Introduction

Development of infrastructure has been consuming significant amount of aggregates resources, leading to a short supply of river sand used as fine aggregates in traditional concrete. To alleviate this problem, industry has used a relatively rich sea sand as an alternative material. Based on a great deal of fundamental study

and practical testing, sea sand has been applied in multiple countries and regions successfully, effectively release the shortage of sand resources for concrete manufacture. However, sea sand usually contains certain amount chloride salts, which may lead to corrosion of steel reinforcement embedded in structures, and is presently the core problem restricting its usage as concrete fine aggregates.

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Currently, widely used methods can effectively reducing the content of chloride ions (Cl^-) in sea sand and prohibiting the Cl^- induced corrosion include sea sand desalination^[1], anti-corrosion treatment on reinforcement^[2], using non-corrosive reinforcements^[3–4], improving concrete microstructure with supplementary cementitious materials^[5], etc. Meanwhile, using novel cementitious materials with high Cl^- binding capacity, such as calcium sulfoaluminate cement, calcium aluminate cement, Limestone calcined clay cement, is also a wide suggested manner^[6–7].

For all these novel cements, it is reported that their good Cl^- binding capacity is due to the relatively higher content in monosulfate (AFm) and hydrated calcium aluminate (with various calcium aluminum ratio and usually stabilized with a formula of C_3AH_6)^[6, 8–11]. Regarding the binding performance of AFm, it has been well accepted that Cl^- ingress into the system from environment may replace OH^- , SO_4^{2-} and CO_3^{2-} in the interlayer structure of AFm and yield Friedel's salt ($\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$) or Kuzel's salt ($\text{C}_3\text{A} \cdot 1/2\text{CaCl}_2 \cdot 1/2\text{CaSO}_4 \cdot 11\text{H}_2\text{O}$)^[12]. CAH_{10} is reported as a metastable hydration products, usually formed by hydration of high-aluminum phases within cement^[13], which will gradually transform into the stabilized C_3AH_6 crystal^[14–15]. Up to date, however, no detailed evidence has been published on verifying the Cl^- binding capacity and mechanism of the crystalline aluminum phases.

Furthermore, within the concretes manufactured with desalinated sea sands, Cl^- exists in the mixtures prior to cement hydration and influence the entire reaction process. Similarities and differences for binding mechanism and capacity of AFm and C_3AH_6 on the premixed Cl^- and the ingress ones need direct experimental support. In order to

minimize the detrimental effect of sea sand Cl^- on embedded steel reinforcement with cementitious materials of high binding capacity, it is highly needed to conduct in-depth research on the Cl^- binding mechanism in the above two scenarios.

Based on the referred background and currently existing problems, reaction process and Cl^- binding capacity of AFm and C_3AH_6 on the premixed and ingress Cl^- were studied via experiments. The detailed experimental results and discussions are presented in this paper.

2 Experimental

2.1 Materials and sample preparation

Raw materials and chemicals used in this study are all at an analytical grade. The AFm and C_3AH_6 were acquired with a controlled hydration of self-synthesized tricalcium aluminate (C_3A).

2.1.1 Synthesis of C_3A C_3A phase was synthesized following the solid phase sintering method as introduced by Ma^[16]. The brief steps are as follows: 1) $\text{Ca}(\text{OH})_2$ and Al_2O_3 were uniformly mixed at a molar ratio of 3:1 and compressed into discs with a thickness of 5–6 mm; 2) the discs were calcined from room temperature to 1 320 °C at an increasing rate of 5 °C/min in a muffle furnace (the temperature was kept still at 450 °C for 2–3 h, 1 320 °C for 3 h, and the samples were taken out of the furnace and cooled down in room environment after the sintering); 3) The process of crushing, grinding, screening, molding and sintering was repeated twice on the obtained samples. XRD pattern of the synthesized product is shown in Fig. 1(a). By comparing with that reported in literature (Fig. 1(b))^[16], it can be deduced that the yield product was high purity C_3A .

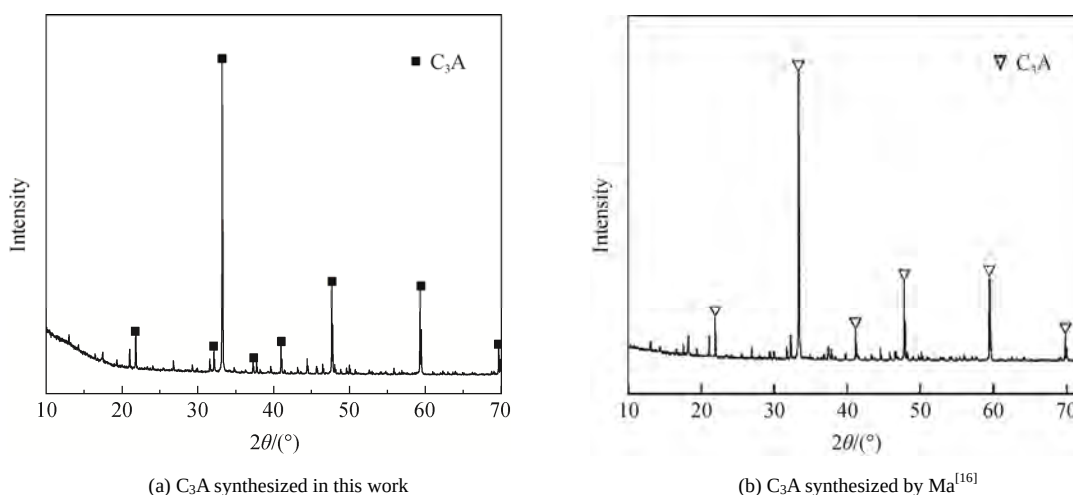


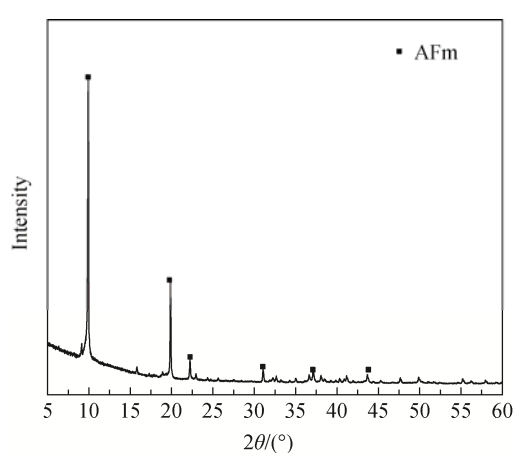
Fig. 1 XRD patterns of C_3A

2.1.2 Synthesis of AFm AFm was prepared following the method described by Jiang^[17]. In this process, C_3A and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were uniformly mixed at a molar ratio of 1:1 and deionized water was

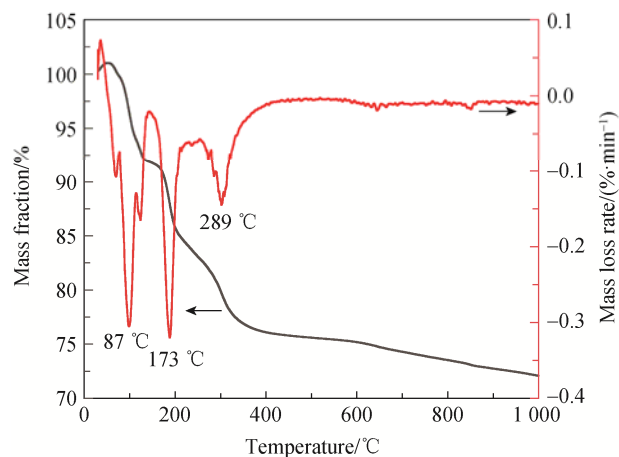
weighed accordingly at a solid-to-liquid ratio of 1:10. The suspension was transferred into a conical flask and stirred with a magnetic stirrer for continuous stirring at about 800 r/min for 14 day. Solution of the sample was

vacuum filtered and the obtained solid portion was vacuum dried in a 60 °C oven for 3 day to get the AFm phase. XRD, TG-DTG and Secondary Electron Image

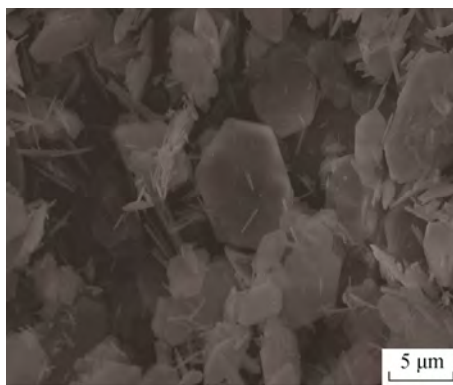
(SEI) of the obtained high purity AFm are shown in Fig. 2, which are consistent with the AFm synthesized by Isabel Baur^[18].



(a) XRD



(b) TG-DTG



(c) SEM

Fig. 2 XRD, TG-DTG and SEI results of the synthesized AFm

2.1.3 Synthesis of C_3AH_6 C_3AH_6 was synthesized following the method mentioned by Black^[19]. C_3A and deionized water were weighed at a solid-to-liquid ratio of 1:10 and the samples were stirred continuously for 3 day with a magnetic stirrer at 800 r/min. The mixture was vacuum filtered and the obtained solid phase was placed in a 60 °C vacuum dryer for 3 day to get the high purity C_3AH_6 . Results of XRD, TG-DTG and SEI of the yield products are shown in Fig. 3.

2.2 Preparation of samples with premixed Cl^-

To explore reaction mechanism of AFm and C_3AH_6 with the raw material introduced premixed Cl^- , a series of samples with different Cl^- contents were prepared following mix proportions as listed in Table 1. Detailed processes of heating, stirring and other steps for preparing the Cl^- containing samples were consistent with those described in Section 2.1 on syntheses of AFm and C_3AH_6 samples, respectively. The filtrated solution obtained after vacuum filtration was potentiometric titrated for its Cl^- content, which

was used to determine the amount and ratio of binding Cl^- in these two hydration products. The remaining solid after filtration was dried, ground and characterized by SEI, XRD and TG for its morphology and mineralogy composition.

2.3 Immersion of samples in Cl^- solution

To explore the binding capacity of AFm and C_3AH_6 on Cl^- ingress from environment, the two types of chemicals were immersed in NaCl solution with different Cl^- concentrations. Detailed proportion of the mixtures are listed in Table 2. After thoroughly manual shaken for 3 min, the samples were stand still in room temperature for 1 day and 7 day, respectively, so as to evaluate reaction rate of the two chemicals on external Cl^- . Consequently, the suspensions were vacuum filtrated and Cl^- content in the solution was determined by potentiometric titration, so as to determine binding capacity on external Cl^- ; the filtrated solids were dried and ground for mineralogy and morphology characterizations *via* the same techniques as described in

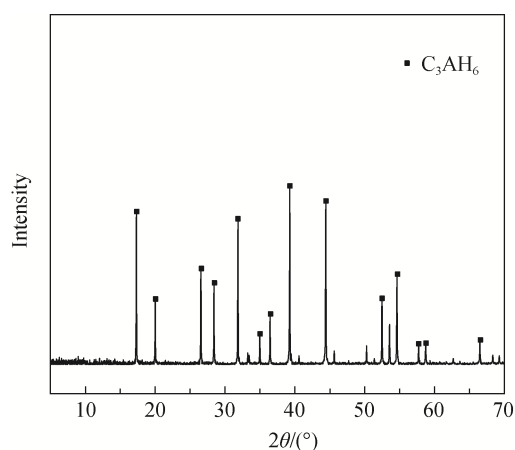
Section 2.2. To facilitate comparison and characterization on differences of AFm and C_3AH_6 on its performances of binding premixed and ingress Cl^- , same amount of AFm and C_3AH_6 was used in either the premixed or the immersion tests.

2.4 Testing methods

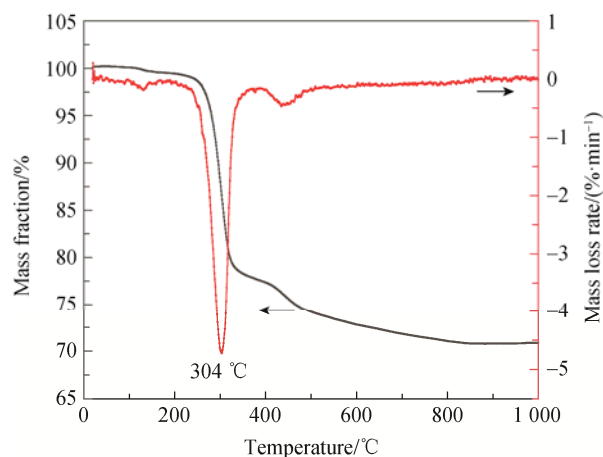
2.4.1 Mineralogy and morphology analyses During the study, SEI was used to observe morphology of

synthetic minerals and the yield products. XRD and TG were carried out on powder samples for qualitatively and quantitatively assess mineralogy of the samples. Detailed settings for each analysis were as follows:

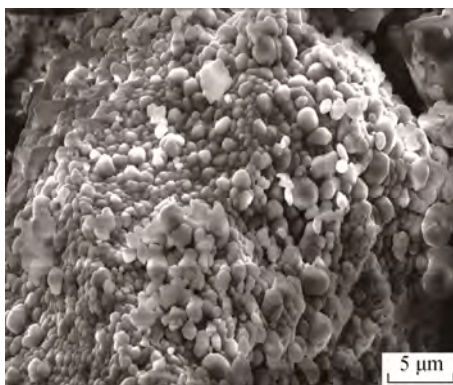
Microstructure of the samples was observed with an Environmental SEM (Quanta FEG 250, USA), with a magnification ranging from 10 to 100 000 times and an acceleration voltage of 3–10 kV.



(a) XRD



(b) TG-DTG



(c) SEM

Fig. 3 XRD, TG-DTG and SEM results of synthesized C_3AH_6

Table 1 Mix proportions of the AFm and C_3AH_6 samples with different premixed Cl^-

Sample No.	Mass/g				Molar ratio	
	C_3A	$C\bar{S} \cdot 2H$	NaCl	H_2O	Cl^-/AFm	Cl^-/C_3AH_6
A-in-0.5	3.00	1.91	0.33	52.40	0.50	
A-in-1	3.00	1.91	0.65	55.60	1.00	
A-in-2	3.00	1.91	1.30	62.10	2.00	
A-in-3	3.00	1.91	1.95	68.60	3.00	
C-in-0.5	3.00		0.33	33.30		0.50
C-in-1	3.00		0.65	36.45		1.00
C-in-2	3.00		1.31	43.05		2.00
C-in-3	3.00		1.95	49.50		3.00

For all ID presented, the notation “A” and “C” indicate AFm and C_3AH_6 , respectively; “in” indicates a premixed Cl^- scenario; the following number “0.5” indicates Cl^-/AFm or Cl^-/C_3AH_6 molar ratio. (e.g., the ID “A-in-0.5” indicates AFm sample with premixed Cl^- at a Cl^-/AFm molar ratio of 0.5.) “ H_2O ” is the water consumption required for AFm or C_3AH_6 synthesis.

Table 2 Immersion of the AFm and C_3AH_6 in different NaCl solutions

Sample No.	Mass/g		NaCl solution		Molar ratio	
	AFm	C_3AH_6	Concentration/(mol·L ⁻¹)	Volume /mL	Cl/AFm	Cl/ C_3AH_6
A-out-0.1	3.00		0.10	30.00	0.62	
A-out-0.2	3.00		0.20	30.00	1.24	
A-out-0.4	3.00		0.40	30.00	2.49	
A-out-0.6	3.00		0.60	30.00	3.73	
C-out-0.1		3.00	0.10	30.00		0.57
C-out-0.2		3.00	0.20	30.00		1.13
C-out-0.4		3.00	0.40	30.00		2.26
C-out-0.6		3.00	0.60	30.00		3.40

“A” and “C” indicate AFm and C_3AH_6 respectively; “out-0.1” indicates samples immersed in a 0.1mol/L NaCl solution. (e.g., the ID “A-out-0.4” indicates AFm sample immersing in solution with Cl^- concentration of 0.4 mol/L.)

Mineralogy of the samples was analyzed by XRD (Bruker D8 Advance, Germany) using a CuK_{α} source, operated at 45 kV and 40 mA. The 2θ scanning range was from 5° to 70° , with a step of 0.02° and an interval of 0.1 s.

Thermogravimetric experiments were performed by TG (STA-409PC, Germany). Samples were heated in alumina pans from room temperature to 1 000 $^\circ C$ at a heating rate of 10 $^\circ C/min$ under nitrogen blanket.

2.4.2 Binding capacity and binding ratio on Cl^- In testing binding capacity of AFm and C_3AH_6 on ingress and premixed Cl^- , solutions obtained from vacuum filtration, as referred in Section 2.2 and 2.3, were all moved to volumetric flasks and diluted into 250 mL solution with deionized water. Subsequently, 2.5 mL of the solution was measured with a pipette and diluted again with deionized water within a beaker and generated a 40 mL sample. Cl^- content of the 40mL samples was measured by an automatic potentiometric titrator (916 Ti-Touch, Switzerland) using $AgNO_3$ solution (0.01 mol/L), and subsequently, the content of free

Cl^- within the analyses powder samples (Q , mol) was calculated. By comparing the amount of total Cl^- content (P , mol) added during sample mixing or immersion process, the binding rate (W , %) of AFm and C_3AH_6 on premixed and ingress Cl^- can be calculated following.

$$W = \frac{P-Q}{P} \times 100\% \quad (1)$$

3 Results and discussion

3.1 Binding behavior for AFm

3.1.1 Binding behavior for AFm on premixed Cl^- Fig. 4 illustrates the results of binding content and rate for AFm on different contents of premixed Cl^- . As can be seen from Fig. 4(a) that there is an approximate linear relationship between Cl^- binding content and Cl/AFm molar ratio within the studied concentration, and about 3.6 mmol Cl^- can be bound by per mol AFm. Meanwhile, the binding rate for the studied mixes (Fig. 4(b)) showed limited difference, ranging between 16% and 20%.

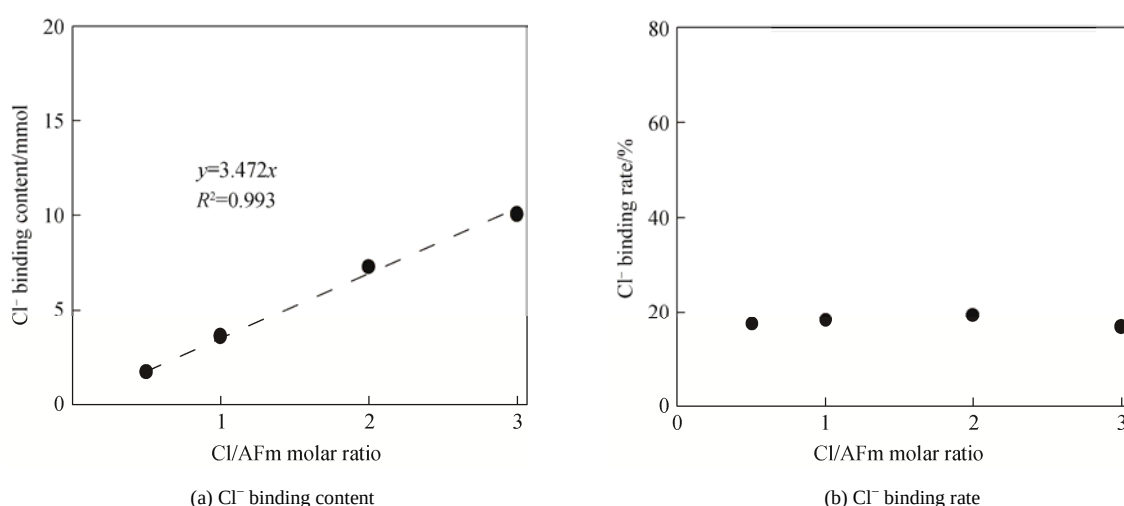


Fig. 4 Cl^- binding behavior for AFm with different premixed Cl^- contents

Fig. 5 shows the XRD patterns for AFm samples with premixed Cl^- . Different types of AFm phases are generated when AFm is on different contents of premixed Cl^- . The

patterns indicate that once content of Cl^- was relatively low (Cl/AFm ratio=0.5), hemihydrate (Hc, $C_3A \cdot Ca(OH)(CO_3)_{0.5} \cdot 11.5H_2O$, $2\theta=10.8^\circ$) was the main yielding

product. With an increase in Cl^- concentration, content of Hc decreased and Kuzel's salt ($2\theta=10.6^\circ$) increased. Once the Cl/AFm rises to 3, Kuzel's salt and small quantities of AFt were the major observed products.

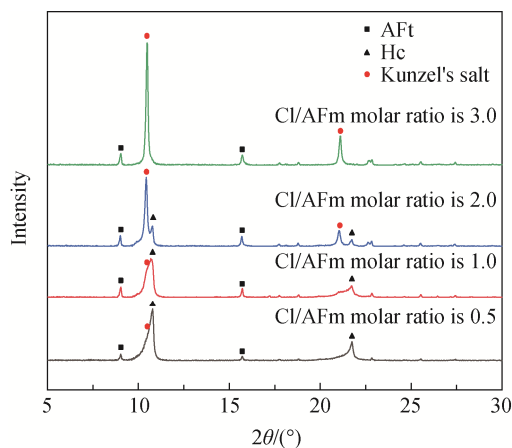


Fig. 5 XRD patterns for AFm with different premixed Cl^- contents

Fig. 6 shows TG-DTG curves for AFm samples with different premixed Cl^- contents. Based on the mineralogy results as presented in Fig. 5 and existing literatures^[20–21], weight loss and its corresponding substances are AFt (50–90 °C), Hc (150–200 °C) and Kuzel's salt (100–

150 °C, 300–400 °C), respectively. The TG results reveal that, with a higher Cl/AFm, there was an increase in AFt content and a decrease in Hc, which was consistent with that revealed from XRD. It needs to be noted that, since the characteristic peak of Kuzel's salt covers a wide temperature range, its mass change can not be accurately quantified from the TG curves.

It can be seen from the micro images (Fig. 7) that premixed Cl^- promote a morphology variation from flake

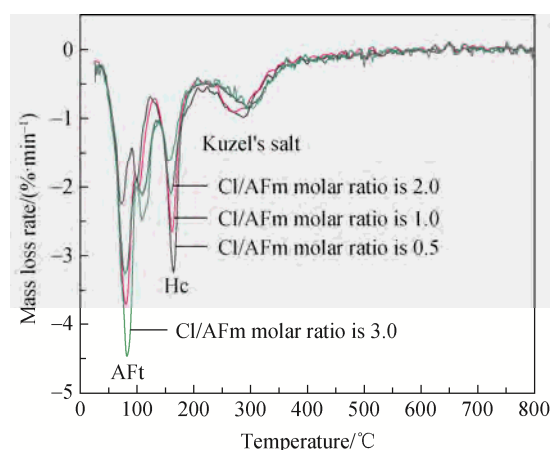
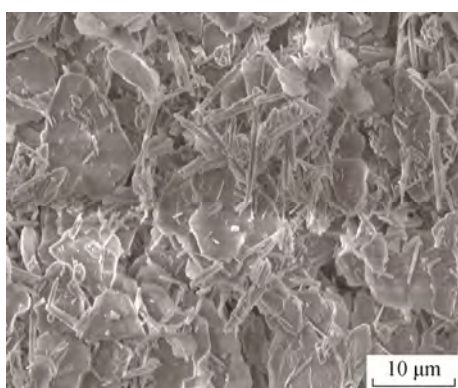
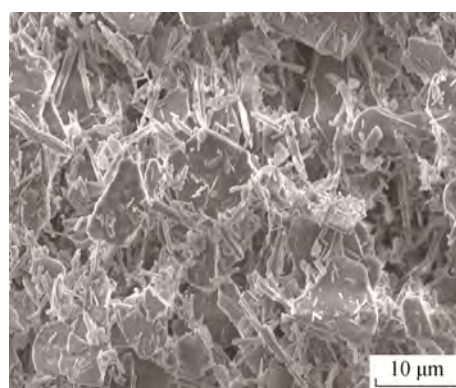


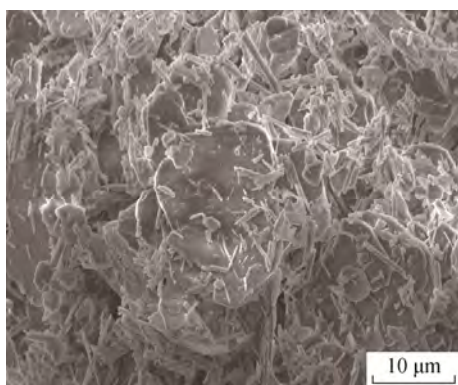
Fig. 6 TG-DTG curves for AFm with different premixed Cl^- contents



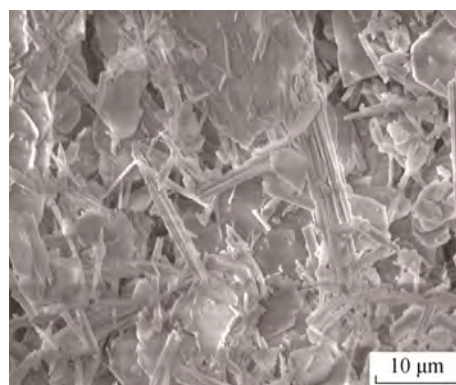
(a) Cl/AFm molar ratio is 0.5



(b) Cl/AFm molar ratio is 1.0



(c) Cl/AFm molar ratio is 2.0



(d) Cl/AFm molar ratio is 3.0

Fig. 7 SEI results for AFm with different premixed Cl^- contents

AFm (as illustrated in Fig. 2) to needle-like mineral. Based on the XRD results (Fig. 5) and references^[22], it can be inferred this needle-like substance was highly likely to be crystallized AFt.

3.1.2 Binding behavior for AFm on ingress Cl^- Fig. 8 illustrates the results of binding content and rate for AFm immersing in NaCl solution with different concentrations and durations. As shown in Fig. 8(a), with

Cl^- concentration in the solution increasing, bound chloride content for AFm showed an approximately linear increase trend (especially in 1 day). With an increasing in immersion duration, content of bound Cl^- increased obviously (the increase was 52.3% in 0.6 mol/L solution sample). The binding rate results (Fig. 8b) indicates that higher proportion of Cl^- was bound in solution with relatively lower Cl^- concentration (<0.4 mol/L).

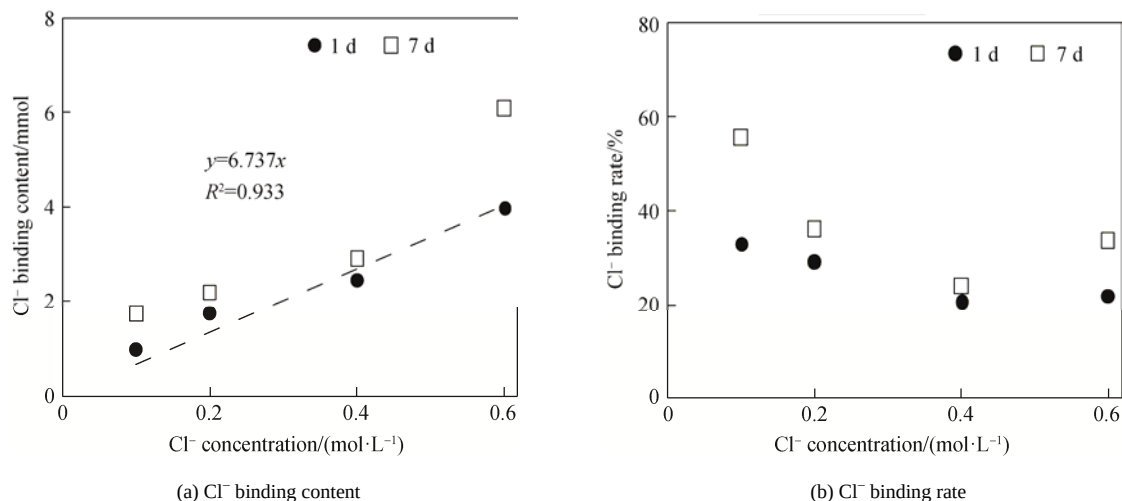


Fig. 8 Cl^- binding behavior for AFm immersing in Cl^- solutions for 1 day and 7 day

Fig. 9 shows the XRD patterns of AFm immersing in NaCl solutions for 7 day. The patterns indicate that Kuzel's salt was formed in all samples, and small quantities of Friedel's salt ($2\theta = 11.2^\circ$) was detected after immersing in 0.6 mol/L Cl^- solution for 7 day. With Cl^- concentration increasing, the AFm content decreased significantly, while Kuzel's salt increased continuously. All the above phenomenon proves that AFm has the ability to bind free Cl^- in the solution and yielding Kuzel's salt, which is consistent with the conclusions reported by Adel Mesbah^[21]. In addition, Friedel's salt appeared in 0.6 mol/L Cl^- solution situation, possibly because SO_4^{2-} in AFm or Kuzel's salt was replaced by Cl^- from the solution

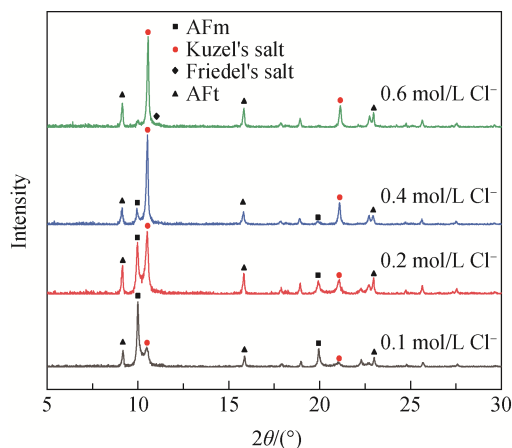


Fig. 9 XRD patterns of AFm immersing in different Cl^- concentration solutions for 7 d

3.2 Binding behavior for C_3AH_6

3.2.1 Binding behavior for C_3AH_6 on premixed Cl^- Fig. 10 illustrates the results of binding content and rate for C_3AH_6 on different contents of premixed Cl^- . As can be seen from Fig. 10(a) that content of bound Cl^- increased with the $\text{Cl}/\text{C}_3\text{AH}_6$ ratio within the studied concentration, and the increasing trend was quite steep at a lower Cl^- content and became relatively modest at a higher Cl^- content. Meanwhile, the Cl^- binding rate (Fig. 10b) was at a high extent once $\text{Cl}/\text{C}_3\text{AH}_6$ was lower than 1 (about 75%) and its value decreased obvious with a higher premixed Cl^- content.

XRD patterns (Fig. 11) for C_3AH_6 samples with premixed Cl^- indicate that Friedel's salt is the main yielding product. Furthermore, the characteristic peak of C_3AH_6 significantly weakened as $\text{Cl}/\text{C}_3\text{AH}_6$ molar ratio increased from 0.5 to 1.0, while these results showed no significant change when $\text{Cl}/\text{C}_3\text{AH}_6$ continued to increase. These rules are consistent with those revealed from results of the Cl^- binding behavior, as shown in Fig. 10.

Based on literatures, it is known that Friedel's salt has weight loss at $100\text{--}150^\circ\text{C}$ and $250\text{--}400^\circ\text{C}$ ^[23-24], while that for C_3AH_6 is $290\text{--}330^\circ\text{C}$ ^[25-26]. Therefore, relative content of Friedel's salt and C_3AH_6 in mixes can be deduced from the TG-DTG results (Fig. 12), which proved that with the $\text{Cl}/\text{C}_3\text{AH}_6$ molar ratio increased from 0.5 to 3.0, content of Friedel's salt gradually increased and C_3AH_6 decreased. The content change was extremely significant in the range of molar ratio between 0.5 and 1.0. These are also consistent with Cl^- binding behavior and XRD results mentioned above.

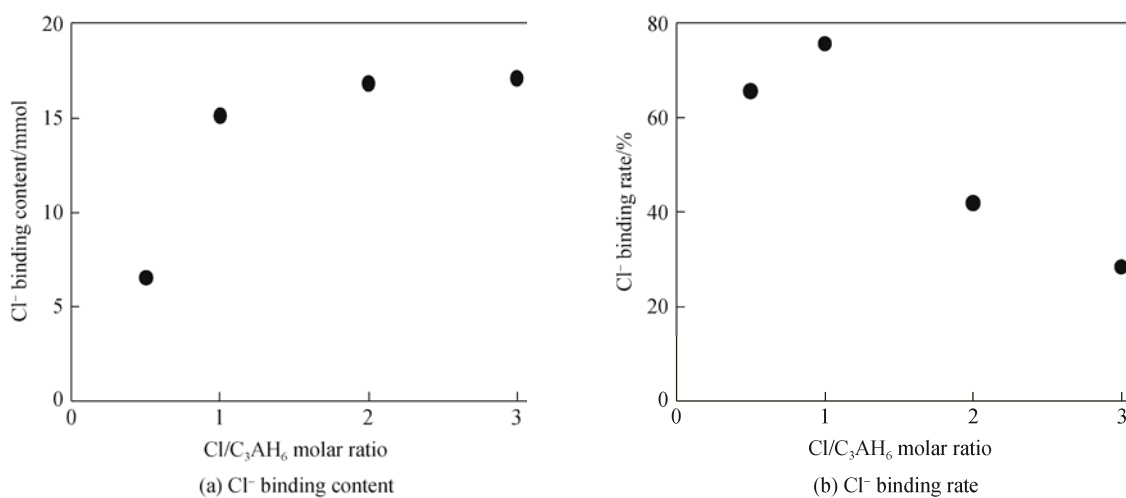


Fig. 10 Cl⁻ binding behavior for C₃AH₆ with different premixed Cl⁻ contents

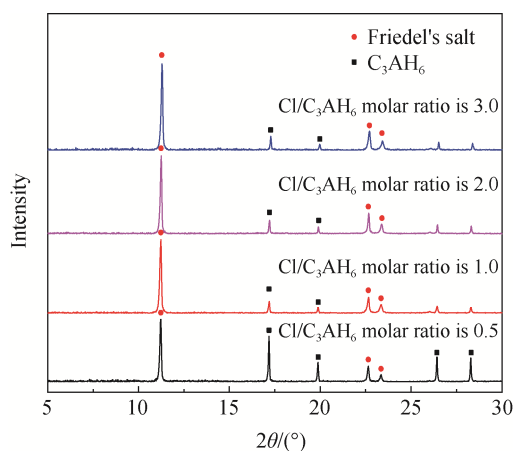


Fig. 11 XRD patterns for C₃AH₆ with different premixed Cl⁻ contents

Minerals with spherical and flake morphology can be found in SEI results with different contents of premixed Cl⁻ as shown in Fig. 13. With assistance from morphology of synthesized C₃AH₆ (Fig. 2) and the obtained XRD results (Fig. 11), it can be inferred that two observed substances in the micro graphs were highly

likely to be the unreacted spherical C₃AH₆ and yield flake Friedel's salt, respectively. Combined with the analysis of TG results (Fig. 12), it can be seen that with the Cl/C₃AH₆ molar ratio increased from 0.5 to 3.0, spherical C₃AH₆ gradually changed into flake Friedel's salt

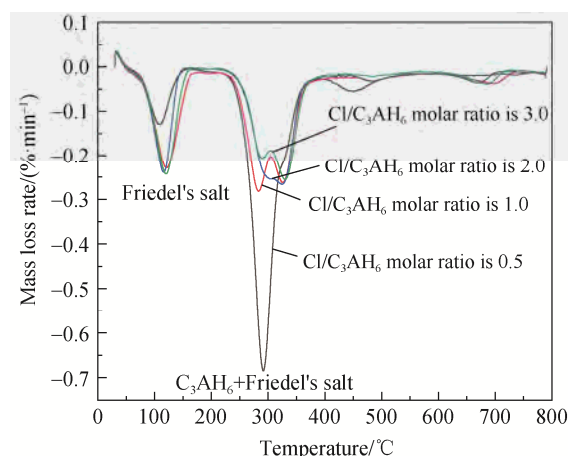
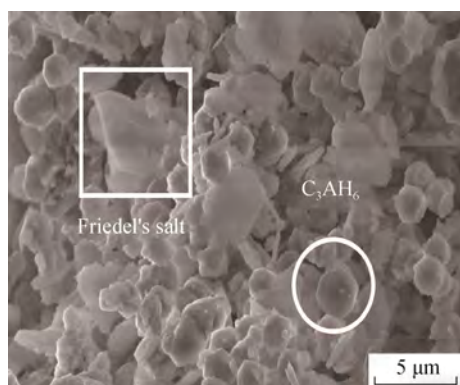
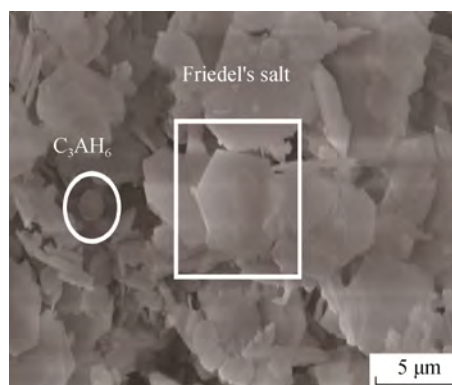


Fig. 12 TG-DTG curves for C₃AH₆ with different premixed Cl⁻ contents



(a) Cl/C₃AH₆ ratio=0.5



(b) Cl/C₃AH₆ ratio =3

Fig. 13 SEI results for C₃AH₆ with different premixed Cl⁻ contents

3.2.2 Binding behavior for C₃AH₆ on ingress Cl⁻ Fig. 14 illustrates the results of binding content and rate for C₃AH₆ immersing in different NaCl solutions within 7 day.

As presented in Fig. 14(a), content of bound Cl⁻ by C₃AH₆ increased progressively with increasing in Cl⁻ concentration at both 1 day and 7 day. The binding rate

results (Fig.14(b)) reveals the Cl^- binding capacity decreased in solution with a higher Cl^- concentration. Also, the inappreciable higher value for the 7 day of immersion than that for 1 day indicates an almost thorough reaction of C_3AH_6 with Cl^- during the 1st day of immersion.

XRD patterns (Fig. 15) of C_3AH_6 samples immersing in NaCl solutions indicate that the main yielding

product was Friedel's salt, same with that produced by C_3AH_6 and premixed Cl^- (presented in Section 3.2.1). With increasing Cl^- concentration, a trend of significantly lower C_3AH_6 and higher Friedel's salt content were observed. Almost all the C_3AH_6 samples in 0.6 mol/L Cl^- were converted into Friedel's salt after an immersion of 7 day.

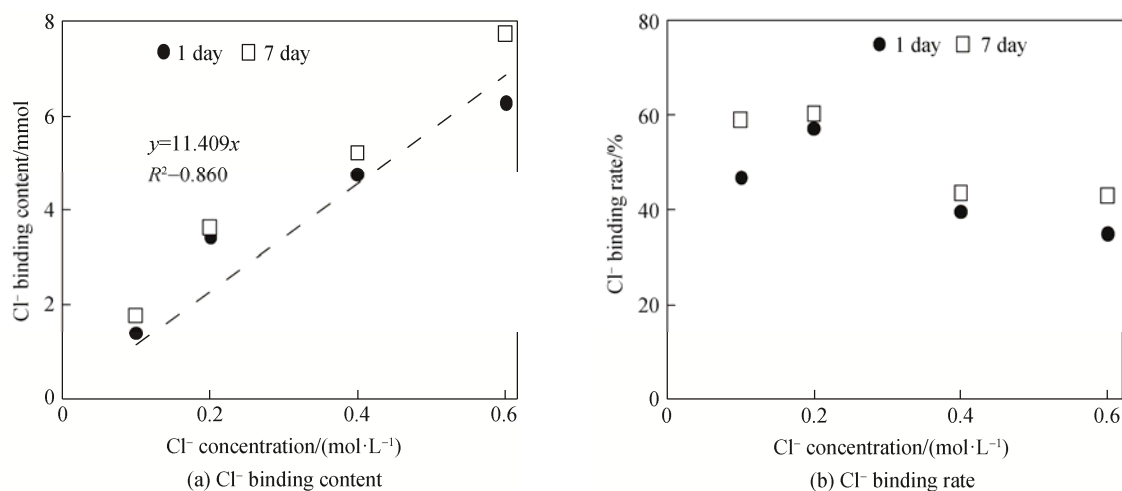


Fig. 14 Cl^- binding behavior for C_3AH_6 immersing in Cl^- solutions for 1 day and 7 day

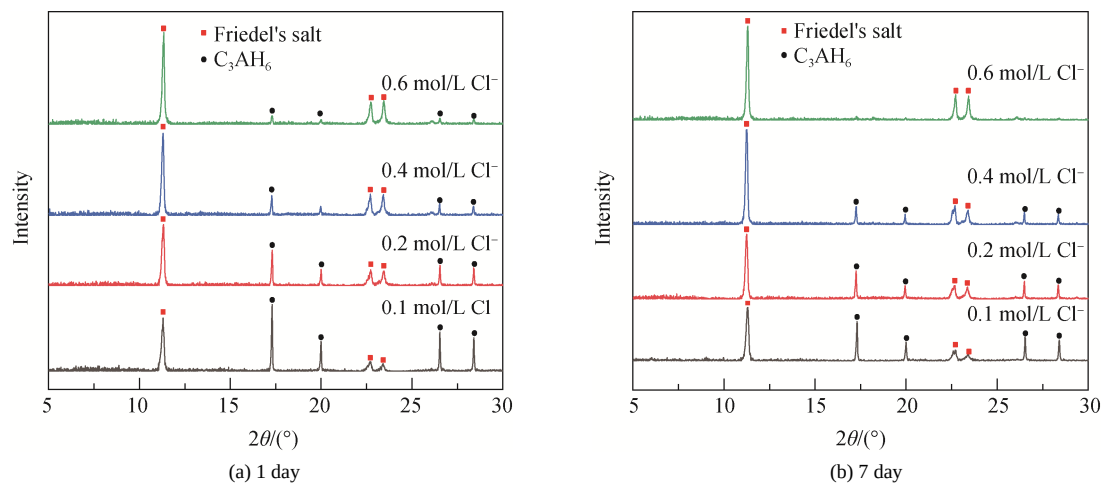


Fig. 15 XRD patterns of C_3AH_6 immersing in different Cl^- concentration solutions for 1 day and 7 day

Fig. 16 shows the TG-DTG curves of C_3AH_6 immersing in NaCl solutions for 7 day. Based on the XRD results as presented in Fig. 15 and previous literatures^[23-26], mass loss appearing at the temperature range of 100–150 °C and 250–400 °C corresponds to decomposition of Friedel's salt and C_3AH_6 , respectively. Based on the mass loss trend at 100–150 °C, it is proved that the product of binding reaction between C_3AH_6 and Cl^- is Friedel's salt. Besides, exist of higher content of Friedel's salt with an increase of Cl^- concentration can be proved, which validates promoting effect of higher Cl^- concentration on Cl^- binding ability for C_3AH_6 .

Fig. 17 shows the SEI results of C_3AH_6 immersing in NaCl solutions for 1 day and 7 day. It reveals that the spherical C_3AH_6 (shown in Fig. 2) turned to flaked Friedel's salt. Meanwhile, the generated Friedel's salt was more regular and thicker with the increase in Cl^-

concentrations and durations.

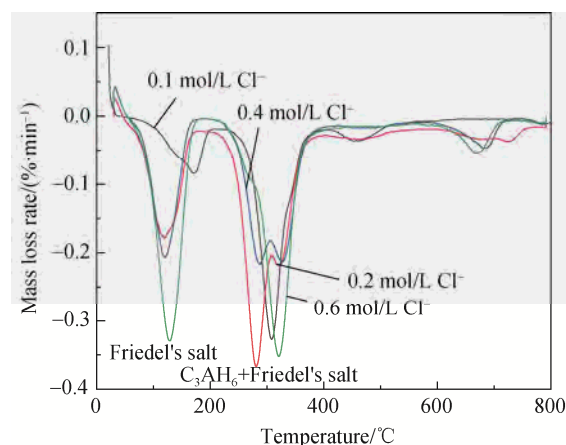


Fig. 16 TG-DTG curves for C_3AH_6 immersing in different Cl^- concentration solutions for 7 d

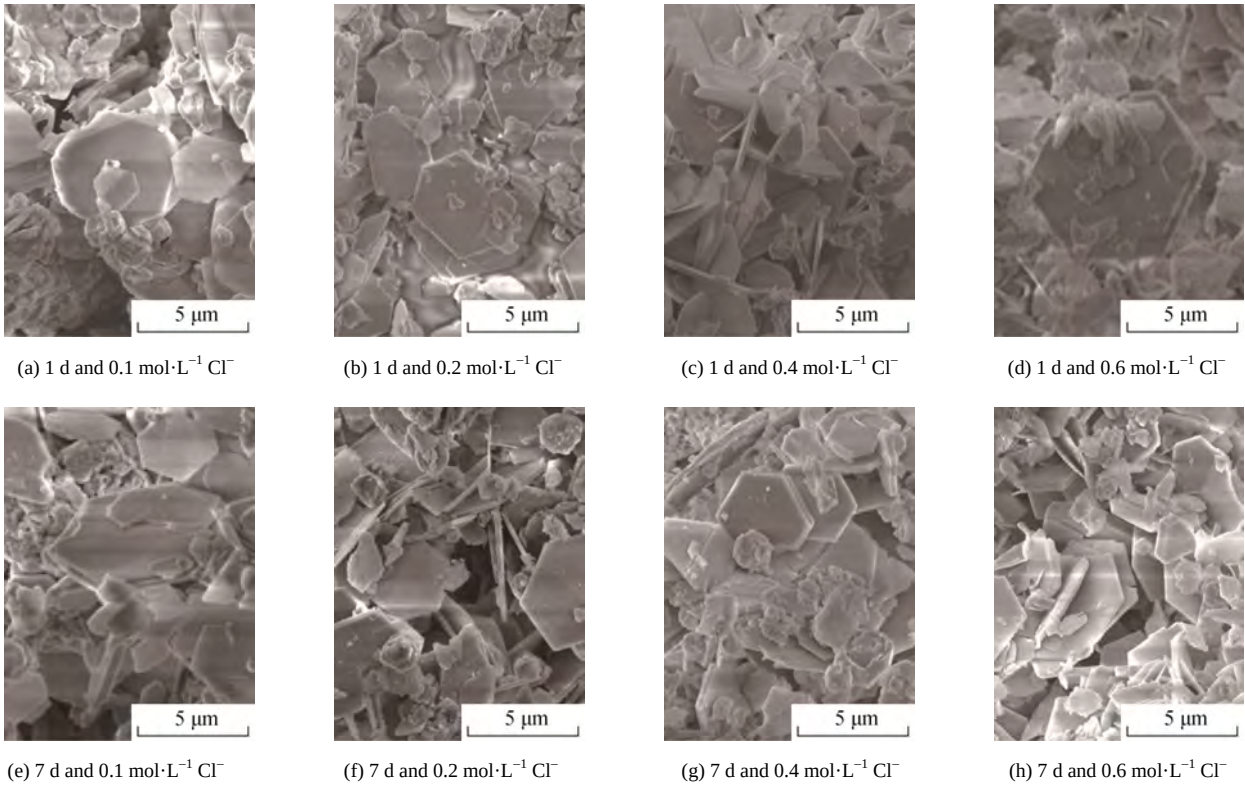


Fig. 17 SEI results for C_3AH_6 immersing in Cl^- solutions for 1 d and 7 d

3.3 Comparison on Cl^- binding behavior between AFm and C_3AH_6

The above presented results proved the binding capacity of AFm and C_3AH_6 on both premixed and

ingress Cl^- , which are quite different in extents and binding mechanisms. The important differences are summarized in Table 3 and Fig. 18 for a clear comparison and it can be seen that:

Table 3 Binding products and capacity of AFm and C_3AH_6

Samples	Product		Binding capacity	
	Premixed Cl^-	Immersion in NaCl solutions (7 day)	Premixed Cl^-	Immersion in NaCl solutions (7 day)
AFm	low Cl/AFm ratio: Hc high Cl/AFm ratio: Hc, Kuzel's, Aft	low $[Cl^-]$: Kuzel's high $[Cl^-]$: Kuzel's, Friedel's	Cl^- binding content: Fig. 18a	Cl^- binding content: Fig. 18c
C_3AH_6	Friedel's	Friedel's	Cl^- binding rate: Fig. 18b	Cl^- binding rate: Fig. 18d

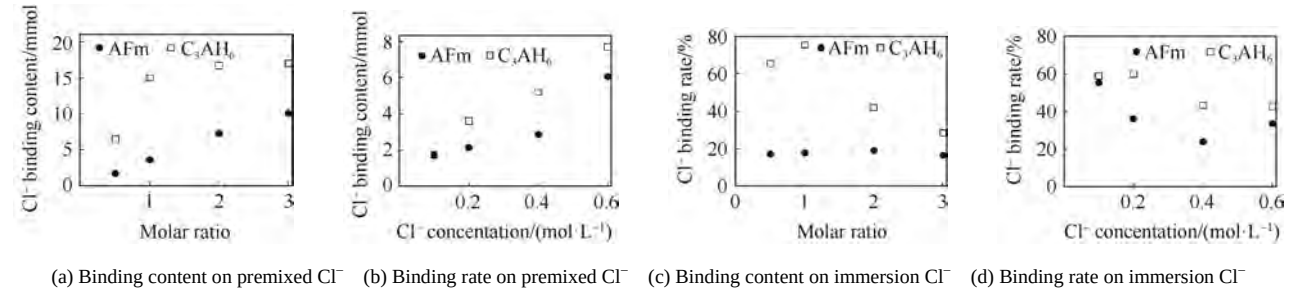


Fig. 18 Comparison on binding capacity between AFm and C_3AH_6 on premixed and immersing Cl^-

1) Based on the results of binding behavior on premixed and ingress Cl^- , it can be inferred that C_3AH_6 preforms more pronounced Cl^- binding capacity than AFm. Within the tested premixed Cl^- contents, the binding rate value of AFm was stabilized at about 17%, while the maximum value about C_3AH_6 was up to 75% (molar ratio of Cl^-/C_3AH_6 ratio=1). In addition, the binding content of C_3AH_6 is higher than that of AFm in different Cl^-

concentrations, regardless of ingress^[11] or premixed Cl^- . C_3AH_6 had excellent binding performance once content of premixed Cl^- was relatively low and the amount of reacted Cl^- was almost unchanged when the Cl^-/C_3AH_6 raised from 1 to 3, which directly proved a thorough reaction of C_3AH_6 with limited amount of Cl^- (XRD results in Fig. 11 also validated the same phenomena).

Reaction between AFm and premixed Cl^- was in a dynamic equilibrium and the binding rate was stabilized at about 17%.

2) Product of C_3AH_6 reacting with premixed Cl^- or ingress Cl^- was Friedel's salt. Whereas, those generated by AFm were Hc and Kuzel's salt, usually reported as less stabilized minerals^[27-30] because Cl^- will replace the corresponding X^- between crystal structure of Hc or Kuzel's salt, meanwhile, AFt and limited amount of Friedel's salt presented in the cases with high Cl^- concentrations. Stability of the reaction products from AFm and C_3AH_6 offers indirect evidence for the stabilized and sufficient reaction of C_3AH_6 with Cl^- .

4 Conclusions

Based on results and analysis stated in this paper, it can be concluded that except from the widely accepted AFm phases, calcium aluminate hydrates (represented by C_3AH_6) also have noticeable binding ability on premixed and ingress Cl^- . Their binding mechanism and ability are significantly different from the AFm phases. Major conducted conclusions from this study are as follows:

1) C_3AH_6 exhibits higher Cl^- binding ability than AFm. The binding rate of C_3AH_6 can be up to 75% when Cl^- is introduced from raw materials; the rate of AFm is only around 17%, regardless on content of the premixed Cl^- (about 1/4 of that for C_3AH_6). This proves C_3AH_6 has its advantages in protecting safety of reinforced concrete structures manufactured with desalinated sea sand.

2) In both premixed and ingress Cl^- scenarios, content of bound Cl^- increases with an increasing in Cl^- concentration, and the ratio of bound Cl^- descends, which is quite obvious in a relatively higher premixed Cl^- contents and concentrations of immersion solution.

3) Compared with AFm, the reaction of C_3AH_6 with Cl^- is much faster and thorough. For C_3AH_6 , when the content of premixed Cl^- is relatively low, its binding capacity can be delivered effectively and the Cl^- binding content only presents a slight increase with a higher content of premixed Cl^- . Regarding AFm, its reaction with Cl^- seems to be in a dynamic equilibrium state, as proportion of the bound Cl^- is relatively stable within different premixed Cl^- contents.

4) The Cl^- binding products formed by C_3AH_6 are more stable than that from AFm. Product of the former reaction is always Friedel's salt with relatively high stability. While products from AFm can be Hc and Kuzel's salt, which are less stabilized minerals, and turn to be AFt and Friedel's salt once concentration of premixed and ingress Cl^- is relatively high.

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References:

- [1] ZHAO M Y. Development and application of sea sand desalination technology (in Chinese) [J]. Build Mater Ind Inform, 1999(4): 9–10.
- [2] ERDOĞDU Ş, BREMNER T W, KONDRATOVA I L. Accelerated testing of plain and epoxy-coated reinforcement in simulated seawater and chloride solutions[J]. Cem Concr Res, 2001, 31(6): 861–867.
- [3] LI S, ZHU D, GUO S, et al. Static and dynamic tensile behaviors of BFRP bars embedded in seawater sea sand concrete under marine environment[J]. Compos Part B: Eng, 2022, 242: 110051.
- [4] YI Y, GUO S, LI S, et al. Effect of alkalinity on the shear performance degradation of basalt fiber-reinforced polymer bars in simulated seawater sea sand concrete environment[J]. Constr Build Mater, 2021, 299: 123957.
- [5] LI S C, YU Y, JIN Z Q. Review on mechanical properties and durability of seawater and sea-sand concrete[J]. Bull Chin Ceram Soc (in Chinese), 2020, 39(12): 3743–3752.
- [6] HIRAO H, YAMADA K, TAKAHASHI H, et al. Chloride binding of cement estimated by binding isotherms of hydrates[J]. J Adv Concr Technol, 2005, 3(1): 77–84.
- [7] SCRIVENER K, MARTIRENA F, BISHNOI S, et al. Calcined clay limestone cements (LC^3)[J]. Cem Concr Res, 2018, 114: 49–56.
- [8] BALONIS M, LOTHENBACH B, LE SAOUT G, et al. Impact of chloride on the mineralogy of hydrated Portland cement systems[J]. Cem Concr Res, 2010, 40(7): 1009–1022.
- [9] PELLETIER L, WINNEFELD F, LOTHENBACH B. The ternary system Portland cement-calcium sulfoaluminate clinker-anhydrite: Hydration mechanism and mortar properties[J]. Cem Concr Compos, 2010, 32(7): 497–507.
- [10] JEN G, STOMPINIS N, JONES R. Chloride ingress in a belite-calcium sulfoaluminate cement matrix[J]. Cem Concr Res, 2017, 98: 130–135.
- [11] ZHU Z, WANG Z, XU L, et al. Phase-dependent study of chloride binding capacity and its relation to the properties of CAC[J]. J Build Eng, 2022, 46: 103718.
- [12] MATSCHEI T, LOTHENBACH B, GLASSER F P. The AFm phase in Portland cement[J]. Cem Concr Res, 2007, 37(2): 118–130.
- [13] SON H M, PARK S, KIM H Y, et al. Effect of CaSO_4 on hydration and phase conversion of calcium aluminate cement[J]. Constr Build Mater, 2019, 224: 40–47.
- [14] SAKAI E, SUGIYAMA T, SAITO T, et al. Mechanical properties and micro-structures of calcium aluminate based ultra high strength cement[J]. Cem Concr Res, 2010, 40(6): 966–970.
- [15] PACEWSKA B, NOWACKA M. Studies of conversion progress of calcium aluminate cement hydrates by thermal analysis method[J]. J Therm Anal Calorim, 2014, 117(2): 653–660.
- [16] MA B G, SHAN Z X, TAN H B, et al. Influence of the Fineness of Tricalcium Aluminate on Chloride Ion Binding Capacity (in Chinese) [J]. J Wuhan Univ Technol-Mater Sci Ed, 2017, 39(12): 1–6.
- [17] JIANG W B. Binding mechanism of chlorides for cement minerals and their hydration products (in Chinese) [D]. Wuhan City, China: Wuhan University of Technology, 2018.
- [18] BAUR I, KELLER P, MAVROCORDATOS D, et al. Dissolution-precipitation behaviour of ettringite, monosulfate, and calcium silicate hydrate[J]. Cem Concr Res, 2004, 34(2): 341–348.
- [19] BLACK L, BREEN C, YARWOOD J, et al. Hydration of tricalcium aluminate (C_3A) in the presence and absence of gypsum--studied by

- Raman spectroscopy and X-ray diffraction[J]. *J Mater Chem*, 2006, 16(13): 1263.
- [20] QOKU E, BIER T A, WESTPHAL T. Phase assemblage in ettringite-forming cement pastes: A X-ray diffraction and thermal analysis characterization[J]. *J Build Eng*, 2017, 12: 37–50.
- [21] MESBAH A, CAU-DIT-COUMES C, RENAUDIN G, et al. Uptake of chloride and carbonate ions by calcium monosulfoaluminate hydrate[J]. *Cem Concr Res*, 2012, 42(8): 1157–1165.
- [22] NORMAN R L, DANN S E, HOGG S C, et al. Synthesis and structural characterisation of new ettringite and thaumasite type phases: $\text{Ca}_6[\text{Ga}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_6[\text{M}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4)_2(\text{CO}_3)_2$, $\text{M}=\text{Mn}, \text{Sn}$ [J]. *Solid State Sci*, 2013, 25: 110–117.
- [23] BIRNIN-YAURI U A, GLASSER F P. Friedel's salt, $\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl}, \text{OH}) \cdot 2\text{H}_2\text{O}$: its solid solutions and their role in chloride binding[J]. *Cem Concr Res*, 1998, 28(12): 1713–1723.
- [24] SHI Z, GEIKER M R, LOTHENBACH B, et al. Friedel's salt profiles from thermogravimetric analysis and thermodynamic modelling of Portland cement-based mortars exposed to sodium chloride solution[J]. *Cem Concr Compos*, 2017, 78: 73–83.
- [25] SHANG X, YE G, ZHANG Y, et al. Effect of micro-sized alumina powder on the hydration products of calcium aluminate cement at 40 °C[J]. *Ceram Int*, 2016, 42(13): 14391–14394.
- [26] PARK S M, JANG J G, SON H M, et al. Stable conversion of metastable hydrates in calcium aluminate cement by early carbonation curing[J]. *J CO₂ Util*, 2017, 21: 224–226.
- [27] WANG Y, SHUI Z, GAO X, et al. Chloride binding behaviors of metakaolin-lime hydrated blends: Influence of gypsum and atmospheric carbonation[J]. *Constr Build Mater*, 2019, 201: 380–390.
- [28] MESBAH A, FRANÇOIS M, CAU-DIT-COUMES C, et al. Crystal structure of Kuzel's salt $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1/2\text{CaSO}_4 \cdot 1/2\text{CaCl}_2 \cdot 11\text{H}_2\text{O}$ determined by synchrotron powder diffraction[J]. *Cem Concr Res*, 2011, 41(5): 504–509.
- [29] ZAJAC M, ROSSBERG A, LE SAOUT G, et al. Influence of limestone and anhydrite on the hydration of Portland cements[J]. *Cem Concr Compos*, 2014, 46: 99–108.
- [30] GEORGET F, LOTHENBACH B, WILSON W, et al. Stability of hemcarbonate under cement paste-like conditions[J]. *Cem Concr Res*, 2022, 153: 106692.