Chloride Binding Capacity of Portland Cement System with Different Content of Tricalcium Aluminate

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Abstract. The binding of chloride ion has been reported as an effective way to reduce the risk of steel corrosion induced by the utilization of marine sources. In this study, effect of tricalcium aluminate (C₃A) on chloride binding capacity of Portland cement paste was investigated; the setting time, compressive strength, and fluidity of cement-C₃A system were also examined. The reaction mechanism of C₃A and chloride ions was studied by X-ray diffraction (XRD) and thermo gravimetric analysis (TGA). The results showed that addition of C₃A in cement paste could increase the compressive strength not only at the early age but also at the late age. The setting time was shortened obviously and the fluidity was reduced. The main reason was that fast hydration of C₃A could hasten the formation of ettringite to consume free water, and also promote the hydration of the system. Furthermore, addition of C₃A in cement paste could greatly promote the chloride binding capacity, and the main reason was due to the promoted formation of FS in hydrates. The investigation was expected to provide experience in promoting the chloride binding capacity of cement system.

Keywords. Chloride binding, tricalcium aluminate, Friedel’s salt.

1. Introduction

Currently, ocean development has attracted attention in both research and industrial fields. Sea construction was also increasingly increased in past decades [1]. Reinforced concrete was one of most popular construction materials used in sea construction. Generally, the raw materials, such as cement and aggregates, and even water, were transported from mainland. This not only brought high cost but also resulted in long time for transportation. If the sea resources, such as coral aggregate, sea water, or sea sand, enable to be used, the cost for sea construction would be greatly cut down. However, the most concerned issue of the using the sea resources in reinforced concrete was the chloride ion which showed high potential risk to cause the steel bar corrosion. In the literature, this issue was widely studied, and the most popular measure was to combine the chloride ions by chemical binding.

It was reported that the chemical binding of chloride in cementitious materials was related to the formation of Friedel’s salt (FS, 3CaO·Al₂O₃·CaCl₂·10H₂O) and Kuzel’s salt (KS, 3CaO·Al₂O₃·0.5CaCl₂·0.5CaSO₄·10H₂O). The chloride presenting in FS and KS showed little risk for steel bar corrosion [2], and therefore, many studies in the literature focused on the mechanism behind formation of FS and KS. It was found that the pozzolanic reaction of supplementary cementitious materials (SCM) released aluminum into the system, and some could form [Ca₂Al(OH)₆·2H₂O]⁺ to bind chloride ion to form FS or KS [3-5]. Accordingly, the generation of FS and KS could be facilitated by accelerating the pozzolanic reaction of SCM. Furthermore, the aluminum dissolved from tricalcium aluminate (C₃A) in Portland cement clinker could generate FS [6-8]. Generally, at the very beginning of cement hydration reaction, C₃A could hydrate to produce the AFm structure.
(\text{[Ca}_2\text{Al(OH)}_6\cdot2\text{H}_2\text{O}]^{+}) [9], and then chloride and sulfate can be absorbed by [Ca_2Al(OH)_6\cdot2H_2O]^+ to form FS, KS, ettringite (AFt) or calcium monosulfoaluminate hydrate (AFm). It was inferred that addition of C_3A could promote the chloride binding capacity.

In this study, effect of C_3A on chloride binding capacity of Portland cement paste was investigated; the setting time, fluidity, and compressive strength of cement-C_3A system were also examined. The mechanism behind reaction between chloride and C_3A was discussed by X-ray diffraction (XRD) and thermo gravimetric analysis (TGA).

2. Materials and Methods

2.1. Materials

2.1.1. Cement. A 42.5 Portland cement conforming to GB175-2007 Chinese standard was used in this experiment. Table 1 showed the chemical composition of Portland cement obtained by XRF. And figure 1 revealed the particle size distribution of cement.

Table 1. Chemical composition of cement [wt. %].

| LOI   | SiO_2 | Al_2O_3 | Fe_2O_3 | SO_3 | CaO   | MgO   | K_2O   | Na_2O   |
|-------|-------|---------|---------|------|-------|-------|--------|---------|
| 3.56  | 22.18 | 5.88    | 3.57    | 2.00 | 59.41 | 1.80  | 0.64   | 0.13    |

Figure 1. Particle size distribution of cement.

2.1.2. Tricalcium Aluminate. Tricalcium aluminate (C_3A) is fabricated by solid-phase sintering. Calcium hydroxide (Ca(OH)_2, AR) and aluminum oxide (Al_2O_3, AR) were mixed in a ceramic mill at a molar ratio of 3:1. The mixture was pressed into slices with the thickness of 6-8 mm, and then calcined in a muffle furnace. Thereafter, the sample was cooled rapidly in air, followed by being ground into powder. And then, the mixture was pressed and calcined again. The calcining process was repeated three times, and C_3A powder was obtained. The XRD pattern and Scanning Electron microscopy image (SEM) was adopted to characterize the prepared C_3A, and the results are shown in figure 2 and figure 3. The particle size distribution was characterized, and the result is shown in figure 4. C_3A with D50=19.31 \mu m was observed.
2.2. Sample Preparation

In order to investigate the chloride binding capacity, chloride ions were introduced into cement paste by adding sodium chloride (NaCl). As shown in table 2, the binders composed of C₃A (0-2 wt.%) and
cement was designed. 1.17 g NaCl was added and water/binder weight ratio was 0.35. The paste was prepared conforming to Chinese standard GB 8076-2008. And then, the samples were cast into 40 mm × 40 mm × 40 mm cubic metallic moulds. The pasted was cured for 24 h at 20 °C and 90± 5 R.H.%. The hardened pastes were demoulded and then continue to be cured at the same condition. The compressive strength was tested at 3 d, 7 d, 28 d and 60 d. The tested sample were also broken into small pieces and soaked in alcohol to terminate the hydration reaction. After being dried in vacuum at 30 °C for 6 hours, one part of the sample was ground into particles with a size of less than 0.15 mm to test the CBR, and the particles pass the sieve of 45 μm was for phase analysis.

| Sample ID | Cement [g] | C₃A [g] | NaCl [g] | water/binder |
|-----------|------------|---------|----------|--------------|
| C0        | 100        | 0       | 1.17     | 0.35         |
| C1        | 99.5       | 0.5     | 1.17     | 0.35         |
| C2        | 99.0       | 1.0     | 1.17     | 0.35         |
| C3        | 98.5       | 1.5     | 1.17     | 0.35         |
| C4        | 98.0       | 2.0     | 1.17     | 0.35         |

The chloride binding capacity of C₃A was also considered. 0.8 mol/L NaCl solution was prepared in advance. 3.0 g C₃A was weighted, and C₃A suspension was prepared with water/C₃A weight ratio of 10. The suspension was oscillated continuously in an oscillator at room temperature. At the age of 3 h, 8 h, 1 d, 3 d and 7 d, the suspension is centrifuged by a centrifuge at a rate of 3800 r/min. The upper supernatant was used for further measurement. The precipitate was dried under a vacuum at 25 °C and ground into power for further analysis.

2.3. Test Methods

2.3.1. Chloride Binding Capacity. The hardened cement paste was ground into particles with size less than 0.15 mm. And 20 g dried particle was immersed in 200 mL deionized water for 24 h. The centrifuged solution was neutralized by dilute sulfuric acid (5 vol.%). The content of free chloride ion in the neutralized solution was determined according to Mohr method, with the main chemical reactions displayed as equation (1) and equation (2). Firstly, 20 mL neutralized solution was titrated by 0.02 mol/L AgNO₃ solution with K₂CrO₄ solution (5 wt.%, 0.5 g) as the indicator. The appearance of brick red precipitate Ag₂CrO₄ represents the titration endpoint [10]. The titration result was the average of repeated tests.

\[
\text{AgNO}_3 + \text{Cl}^- \rightarrow \text{AgCl} \downarrow + \text{NO}_3^- \quad (1)
\]

\[
2\text{AgNO}_3 + \text{K}_2\text{CrO}_4 \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow + 2\text{KNO}_3 \quad (2)
\]

The concentration of free chloride ion in upper supernatant (C) could be calculated as shown in equation (3):

\[
C = C_A \frac{V_A}{V} \quad (3)
\]

where, C is free chloride ion concentration in upper supernatant, mol/L; Cₐ is AgNO₃ concentration, mol/L; Vₐ is volume of the consumption of AgNO₃ solution, mL; V is the volume of the solution used for titration, mL.

The chloride binding ratio (CBR) was calculated according to equation (4):

\[
\text{CBR} = \frac{(C_0 - C)V_0}{m_{C_3A}} \quad (4)
\]
C₀ is the initial total chloride content, 0.8 mol/L; C is the free chloride ion concentration in upper supernatant, mol/L; V₀ is the volume of the sodium chloride solution (0.03 L), L; M is the mole mass of chloride (35.45 g/mol), g/mole; m₃A is the mass of C₃A used in this experiment (3.0 g), g.

2.3.2. Setting Time. Conforming to the Chinese National Standard GB/T 1346-2011, the test of setting time of the fresh cement paste was examined for every five minutes.

2.3.3. Fluidity. The fresh cement paste was prepared with a water/cement weight ratio of 0.29 (deionized water: 87 g; Portland cement 300 g; polycarboxylate superplasticizer: 2.4 g), conforming to Chinese standard GB 8076-2008. According to Chinese standard GB/T 8077-2012, a cone (height 60 mm, top diameter 36 mm and bottom diameter 60 mm) was filled with the fresh paste on a glass plate. After the removal of cone from the paste, the diameter of the spread paste was measured, which was defined as the fluidity value of the fresh cement paste.

2.3.4. Phase Analysis. Phase assemblages in hardened cement pastes were characterized by scanning electron microscope (SEM), thermo gravimetric analysis (TGA), and X-ray diffraction (XRD). XRD was conducted with Cu (Kα) radiation, with the speed of 4 °/min. The test range of XRD was from 5° to 70°. SEM was supplied by FEI Co, USA, used for the observation of micromorphology. TGA was conducted with the rise of the temperature rate of 10 °C/min from 40 °C to 1000 °C, using N₂ atmosphere. The TGA equipment was made by Netzsch Instruments, Germany.

3. Results and Discussion

3.1. Chloride Binding Capacity

Figure 5 shows the chloride binding capacity of cement-C₃A system. It was found that with the increase of C₃A dosage, the chloride binding capacity (CBC) was increased, and with the increasing age, CBC was also increased. These results indicate that in cement system, increase in dosage of C₃A phase could promote the CBC, which agreed with the results in the literatures.

![Figure 5. Chloride binding capacity of Cement-C₃A system.](image)

In order to examine the effect of C₃A on chloride binding capacity, CBC of C₃A slurry cured at different ages was measured, and the results are shown in figure 6. As revealed in figure 6, at 3 h the CBC was 0.05 g/g-C₃A, and at the age of 7 d, it was 0.17 g/g-C₃A. This result illustrated that C₃A could react with chloride ions with in liquid phase. This implied that chloride ion could be combined with C₃A, and this combination was increased with time going on.
3.2. Compressive Strength
Effect of C₃A on compressive strength of cement paste was investigated, and the results are presented in figure 7. From the figure, it is found that with the rise of the dosage of C₃A, the compressive strength at the age of 3 d was increased. However, it seemed that no obvious difference among the strength at 7 d, 28 d, and 60 d. This result suggested that C₃A with the dosage less than 2.0% had obviously negative effect on compressive strength of cement paste.

\[
3CaO \cdot Al₂O₃ + 3CaSO₄ \cdot 2H₂O + 26H₂O \rightarrow 3CaO \cdot Al₂O₃ \cdot 3CaSO₄ \cdot 32H₂O
\]  

3.3. Fluidity
Figure 8 shows the effect of C₃A on fluidity of cement paste. From the figure, it was found that C₃A reduced the fluidity of cement paste, and more dosage resulted in less fluidity. The reason was that C₃A in cement paste could immediately react with sulfate ions from gypsum to produce ettringite, consuming water and superplasticizer, as shown in equation (5). In this case, the free water and effective superplasticizer was cut down quickly, and the fluidity was reduced obviously.
In order to mitigate the negative effect of C₃A on fluidity, the borax was introduced as retarder to control the fluidity loss. The fluidity of cement pastes with various dosage of borax and 2% C₃A were examined as shown in Figure 9. From the figure, it was observed that the initial fluidity (at 5 min) was improved with the rising dosage of borax. Furthermore, the fluidity at 60 min was also increased with the higher dosage of borax; the fluidity loss from 5 min to 60 min was greatly improved by adding borax, and more dosage resulted in great effect. These results indicated that borax could greatly improve the fluidity loss of the cement paste added with C₃A [11]. This was because borax could obviously retard the hydration of aluminate, and hinder the consumption of free water and superplasticizer [11].

3.4. Setting Time
Effect of different dosages of C₃A on the setting time of cement paste was examined, and the results are presented in Figure 10. It was seen in Figure 10 that the increase in dosage of C₃A in cement paste prolonged the setting time, and the reason was that the addition of C₃A could react with sulfate ions, as shown in equation (5), to produce ettringite, resulting in consumption of free water, which could shorten the setting time. With time going on, ettringite further reacted with C₃A to produce AFm (3CaO·Al₂O₃·CaSO₄·12H₂O), as shown in equation (6), and this also consumed the free water and accelerated the setting process.

\[
3CaO·Al₂O₃·3CaSO₄·32H₂O+2(3CaO·Al₂O₃)+4H₂O → 3(3CaO·Al₂O₃·CaSO₄·12H₂O)
\] (6)
Figure 10. Effect of C₃A on setting time of cement paste.

3.5. Mechanism

3.5.1. Reaction between Chloride and C₃A. Hydration products of C₃A paste hydrating in the presence of NaCl was evaluated by XRD, and the XRD patterns are shown in figure 11. From the figure, the characteristic peak of Friedel’s was seen clearly, and with the increasing curing age, the peak intensity was increased. It was also found that the peak intensity of C₃A was reduced. This result indicated that C₃A could react with NaCl to produced Friedel’s salt, and the reaction was shown in equation (7).

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 2\text{Cl}^- + \text{Ca}^{2+} + 10\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}
\] (7)

Figure 11. XRD pattern of C₃A hydrates.
In the literature, it was reported that the two decomposition peaks of Friedel’s salt near 120-160°C and 250-330 °C resulted from the dehydration of main layer and interlayer, respectively [12, 13]. In this study, the hydrates were also analyzed by TG-DSC, and the results are presented in figure 12. From figure 12(a), the peak at 147.2 °C and 284 °C was seen clearly, and this was attributed to the decomposition of Friedel’s salt. It indicated that at the age of 12 h, the generation of Friedel’s salt happened. From figure 12(b), the same result was observed. Furthermore, it was also found that the weight loss at 50-200 °C and 200-400 °C was 7.89% and 14.89% at the age of 12h, and that for 3 d was 10.42% and 15.72%. This was because hydration process of C₃A continuously happened with time going on, and the content of Friedel’s salt was also increased in hydration products, which agreed with the results in XRD.

Figure 12. TG-DSC curve of C₃A hydrates.

Figure 13. SEM and EDS images of C₃A hydrates.
The hydrates were further analyzed by SEM-EDS, and the results are revealed in figure 13. The sheet-typed hydrates were seen clearly in figure 13. The element analysis was conducted by EDS, and the results are shown in table 3. Calcium, aluminum, and chloride were detected. Based on SEM and EDS, it was confirmed that the hydrate was Friedel’s salt.

Table 3. Element distribution detected by EDS.

| Point number | Atomic percentage [%] |  |
|--------------|-----------------------|---|
|              | Ca                    | Al| O  | Cl |
| 1            | 16.38                 | 10.96  | 66.87 | 5.79 |
| 2            | 15.80                 | 10.26  | 68.63 | 5.31 |
| 3            | 16.82                 | 9.39    | 69.04 | 4.74 |

3.5.2. Chloride Binding of Cement-C₃A System. During the hydration reaction of the ordinary Portland cement, C₃A reacted with sulfate ion to produce ettringite as shown in equation (5); then due to the reduction of consumption of sulfate ion, calcium monosulfoaluminate was generated as revealed in equation (6). However, in the presence of chloride ion, C₃A could directly react with chloride ions to form FS, as shown in equation (7). Because of the competition between sulfate ion and chloride ion in the binding with AFm structure ([(Ca₂Al(OH)₆-2H₂O)⁺]) in system, whether this reaction would happen obviously or not depended on the mole ratio of C₃A/sulfate.

With addition of C₃A in cement paste, the early hydration process could be altered. The formation of ettringite could be accelerated, and the water demand was increased and the content of superplasticizer added was also increased; this also shortened the setting time. However, these would be improved by adding chemicals. Furthermore, the addition of C₃A increased the C₃A/sulfate mole ratio. In the presence of chloride ion, reaction between C₃A and chloride ion took place immediately to produce FS, as shown in equation (7), and this could promote the amount of FS in hydrates, which increased the chloride binding capacity of the cement system. On the other hand, addition of C₃A could also react with ettringite to produce AFm. And AFm could react with chloride ions, as shown in equation (8), which could also increase the chloride binding capacity of the cement system.

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$$

4. Conclusion

(1) The addition of C₃A into cement paste could increase the compressive strength not only at the early age but also at the late age. The setting time was shortened obviously and the fluidity of the paste was reduced. The main reason was that addition of C₃A could hasten the formation of ettringite to consume free water, and also promote the hydration of the system.

(2) The addition of C₃A into cement paste could greatly improve the chloride binding capacity, and the main reason was attributed to the promoted formation of FS in hydrates.

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