Delaying Effect of NaCl on The Conversion of Hydrates of Calcium Aluminate Cement

Zhong Ping Wang¹²*, Hao Yu Yang¹, Ya Ting Zhao¹, Ling Lin Xu¹², Jiang Wang¹ and Da Li Jia¹

¹ School of Materials Science and Engineering, Tongji University, Shanghai 201804, China
² Key Laboratory of Advanced Civil Engineering Materials, Ministry of Education, Tongji University, Shanghai 201804, China

* wangzpk@tongji.edu.cn

Abstract. The effect of NaCl on the conversion of hydration products of calcium aluminate cement (CAC) was determined by means of MIP, XRD, DSC-TG and SEM. Results show that the addition of NaCl promotes the formation of CAH₁₀ at early hydration stage. The total porosity and proportion of harmful pore in hardened CAC paste with NaCl are lower and the 7d-strength is 40% higher than that of the control. The later curing at 40°C accelerates the conversion from metastable C₂AH₈, CAH₁₀ to C₃AH₆, and the strength decreases with the increasing of curing age. After 90 days, there is no metastable hydrate detected in CAC paste. However, the addition of Niacin CAC paste can prominently delay the conversion of C-A-H. Massive CAH₁₀ still exists in the paste with NaCl, resulting in a slower retraction of late strength.

1. Introduction
Calcium aluminate cement (CAC) was originally famous for its resistance to sulfate attack, however it was initially applied primarily due to its rapid strength gain properties [1]. In the First World War, CAC was applied to build fortifications by Germans, and started to be used to build tunnel lining systems in the late 1920s [2]. By 1940, the material was permitted to serve for structural concrete in the United Kingdom and was being applied in precast concrete buildings for its early strength in the 1950s [2]. However, CAC experienced a heavy blow in the 1970s due to the three terrible structural collapses of pre-stressed concrete beams, which changed the overall perception of CACs. As a result, the use of CAC was limited in structural applications [2, 3]. Since then, researchers worldwide began to aware of the seriousness of the late strength retraction of CAC. It was found that the strength retraction was derived from the conversion from metastable hydration products such as CAH₁₀, C₂AH₈ to stable C₃AH₆ and AH₃, accompanying with the increase of porosity in hardened cement paste [4-6]. When 1 mL CAH₁₀ converts to C₃AH₆, only 0.25 mL C₃AH₆ and 0.22 mL AH₃ were formed (Equations (1) and (2)). The total volume of solid phase was 0.47 mL and the precipitated water was as high as 0.55 mL, and the porosity of the paste reached 53.7%. The conversion rate increases significantly with temperature [7-9]. Based on the transition rate determined by the Arrhenius equation, Revay [10] calculated the time required to convert 75% CAH₁₀ and C₂AH₈ to C₃AH₆ from 10°C to 90°C. At 10°C, it takes 76 years and 67 years, respectively. At 20°C, it takes 7 years and 6...
years, and it takes only a few minutes at 90 °C. Gosselin [9] confirmed that when the CAC was hydrated at 70 °C for 30 min, the main products is C2AH8, but all of them converted into C3AH6 within the following 3 hours.

\[
2\text{CAH}_{10} \rightarrow \text{C}_2\text{AH}_8 + \text{AH}_3 + 9\text{H} \quad (1)
\]

\[
3\text{C}_2\text{AH}_8 \rightarrow 2\text{C}_3\text{AH}_6 + \text{AH}_3 + 9\text{H} \quad (2)
\]

The conversion rate also can be affected by the proportion of different hydration products. Rashid et al [11] found the conversion from CAH10 to C2AH8 is always converted to C2AH8 firstly and then to C3AH6 at 90°C. Scrivener [3] further stated that the crystal structures of C2AH8 and C3AH6 are similar, and the conversion from CAH10 to C3AH6 always firstly converts to C2AH8. Lothenbach et al. [12] confirmed that the impetus of phase conversion between CAH10 and C3AH6 at around 20°C is very small, and these two phases can coexist for several years. It means that the conversion from CAH10 to C3AH6 is more difficult, which needs longer time than that for C2AH8. Therefore, adjusting the proportion of CAH10 in CAC paste can be regarded as a good way to delay the retraction in compressive strength. Taking the service life of the building system itself and other parts into account, if the time required for the occurrence of the harmful conversion can be extended to an acceptable range, the intractable problem of CAC may be solved indirectly. The application perspective of CAC will be broaden significantly.

Our previous study found that the appropriate amount of NaCl (3%) can significantly promote CAH10 production in CAC paste. Based on this, the influence of NaCl on the strength of CAC and the conversion of hydrates was studied by mercury intrusion porosimeter, X-ray diffractometer, scanning electron microscope and differential thermal analyzer.

**Table 1.** Chemical composition of calcium aluminate cement(%).

| SiO2  | CaO  | Al2O3 | Fe2O3 | MgO  | SO3  | K2O  | TiO2 | P2O5 | MnO |
|-------|------|-------|-------|------|------|------|------|------|-----|
| 7.43  | 37.77| 48.35 | 1.90  | 0.58 | 0.44 | 0.46 | 2.51 | 0.15 | 0.05|

**Table 2.** Mineral composition of CAC(%).

| CA  | CA2 | C2AS | CT  |
|-----|-----|------|-----|
| 53.12| 5.81| 35.95| 5.12|

2. Experimental

2.1. Raw materials

The calcium aluminate cement we used was CA50 grade produced by Kerneos Alumina Cement Company. Its chemical composition and mineral composition were shown in Table 1 and Table 2, respectively. ISO standard sand was applied, and the mixing water was tap water. The water to cement ratio was fixed at 0.6. Chloride salts were chemically pure NaCl reagents.

2.2. Samples preparation

The accurately weighed raw materials were poured into a stirring pot and slowly stirred for 5 minutes in an NJ-160A cement paste mixer to promote uniform mixing of the raw materials. Then mixing water was added and the water to cement ratio was 0.6. The size of the formed test block is 20 mm × 20 mm × 20 mm for strength testing and microscopic analysis. The samples were demoulded after 24 hours and cured at (20±1)°C and relative humidity of (60±5)% for 7 days firstly. Then the samples were divided into two groups, one group continued to be cured under the original condition, and the other group was maintained at (40±1)°C with a relative humidity around (60±5)% to speed up the conversion. The two groups were compared respectively at 28 days and 90 days.
2.3. Compressive strength

A pressure tester was used to test the compressive strength. The load was uniformly applied at a speed of 0.5 kN·s⁻¹ to 1.5 kN·s⁻¹ until the test piece was broken, and then the failure load $N_u$ was recorded. Each group had six test blocks to take the arithmetic mean, accurate to 0.1 MPa.

2.4. Microstructure analysis

The XRD data were recorded by Japanese Rigaku D/max 2550 X-ray powder polycrystalline diffractometer. Continuous scan mode was used, the $2\theta$ scanning range was 5 to 75° and the scanning speed was 2°/min. In addition, an accelerating voltage of 40 kV and a current of 250 mA were selected. A DSC-TG study was carried out by the German NETZSCH company STA 449C type DSC-TG combined thermal analyzer at the range of 30-600 °C under nitrogen atmosphere, with a heating rate of 10°C/min. SEM analysis was performed with a QUANTA 200FEG-ESEM produced by FEI Corporation with an acceleration voltage of 20 kV and low vacuum mode. The samples were coated with gold by sputtering. The pore structure of the cement paste sample was tested by Quantachrome AUTOSCAN-60.

3. Result and discussion

3.1. Compressive strength

Figure 1 shows the compressive strength development of CAC paste with different NaCl content under different curing conditions. Regardless of the curing conditions or age, when the content of NaCl increases from 0.5% to 5%, the compressive strength of hardened paste first increases and then drops significantly. When the dosage of NaCl is 3%, the strength reaches the maximum, which is 40% higher than the control. It shows that appropriate amount of NaCl is beneficial to the development of early strength of CAC, but excessive NaCl does harm to the strength development. After the samples were further cured for 28 days at 20°C, there was only a slight increase in strength, and the strength retraction take place until 90 days. While there was an obvious decline of strength at 28 days at 40 °C, and the content of retraction was even greater than that of 90 days at 20°C. Obviously, elevated temperature greatly contributes to the strength retraction.

![Figure 1. Compressive strengths of CAC pastes with different NaCl content under different curing conditions.](image)

**XRD patterns.** Figure 2 is XRD pattern of samples under different curing conditions. As shown in Figure 2a, for pure CAC, the main hydration products are metastable CAH₁₀, C₂AH₆, and steady
C3AH6, AH3 after cured at 20°C for 7 days. Consistent with Figure 1, the position of peaks changes slightly after cured at 20°C for 28 days and 90 days. Only the intensity of peaks of metastable products has a significant decrease resulting from crystal conversion after 90 days. However, the XRD pattern of samples cured at 40°C changes much more severely. Once cured at 40°C for 28 days, the amount of CAH10 declines obviously. Even no CAH10 and C2AH8 can be detected after 90 days, while the amount of C3AH6 and AH3 increased significantly. It means that metastable hydration products have almost completely undergone crystal conversion, which can be responsible for the retraction of strength. By contrast, high temperature curing at 40°C significantly accelerates the conversion of hydration products. Combing Figure 2 with Figure 1, it can be concluded that high temperature promotes the conversion, thus accelerates the strength retraction of hardened CAC paste.

![Figure 2](image)

Figure 2. XRD patterns of samples under different curing conditions.

Figure 2b shows that with addition of 3% NaCl in CAC paste, only CAH10, C3AH6, and AH3 are detected at 20°C. There is no diffraction peak of C2AH8, and the amount of CAH10 increased significantly compared with the control. This indicates that the incorporation of NaCl promotes the formation of CAH10 and massive CAH10 greatly enhances the early strength of hardened CAC cement paste. After cured at 40°C for 28 days and 90 days, the overall peak shape of the specimens do not change significantly, only the peak intensity of CAH10 decreases. After cured at 40°C for 90 days, no metastable hydration product was detected in the blank sample, while massive CAH10 still can be detected in the NaCl-doped sample. And the strength of NaCl containing specimen is also higher than the control. Therefore, the incorporation of NaCl delays the crystal conversion of hydrates to some extent.

**DSC-TG curves.** Figure 3 & 4 are DSC-TG curves of samples under different curing conditions. It is easy to see that there are significant differences in the DSC curves, especially between 100 and 200 °C assigning to the water loss of CAH10 and C2AH8 at high temperature [5]. Therefore, the formation amount of CAH10 and C2AH8 can be calculated by the mass loss rate of this interval (Figure 4). The higher the amount of water loss, the higher the amount of metastable hydration products.

Figure 5 shows the mass loss rate for each sample between 100 and 200 °C. When 3% NaCl is incorporated, the mass loss rate of samples which pre-cured for 7 days are much higher than that of the control. It mainly results from the increasing of the amount of CAH10 at early hydration stage. After cured at 40°C, the metastable hydration products CAH10 and C2AH8 rapidly convert to C3AH6. Therefore, the mass loss rate of the NaCl-doped samples and blank samples at 100~200°C gradually decreases. When cured at 40°C for 90 days, the mass loss of the NaCl-doped samples is still 3.47% much higher than the control, and the diffraction peak of CAH10 is also clearly observed in the XRD patterns (Figure 2). This indicates that the incorporation of NaCl can effectively delay the crystal conversion of the hydration products of CAC hardened cement paste.
In summary, the addition of NaCl can significantly accelerate the formation of CAH$_{10}$ and reduce the formation of C$_3$AH$_6$. Since the stability difference between CAH$_{10}$ and C$_3$AH$_6$ is very small\cite{11} and the impetus of phase conversion between them is less, therefore, CAH$_{10}$ firstly converts to C$_2$AH$_8$ and then to C$_3$AH$_6$. It takes longer time than the direct conversion from C$_2$AH$_8$ to C$_3$AH$_6$\cite{3,12}. The
incorporation of proper amount of NaCl directly promotes the formation of CAH\textsubscript{10}, which delays the conversion of the hydrates within the hardened CAC paste, thus delays the strength retraction subsequently.

![Figure 6. Pore size distribution of hardened CAC pastes with different age.](image)

![Table 3. Porosity of hardened CAC pastes under different curing conditions(\%).](image)

| Temperature  | Curing Time | Porosity (%)|
|--------------|-------------|-------------|
| 20°C-7d      | 0% NaCl     | 23.13       |
| 20°C-7d      | 3% NaCl     | 19.81       |
| 40°C-28d     | 0% NaCl     | 24.45       |
| 40°C-28d     | 3% NaCl     | 21.16       |
| 40°C-90d     | 0% NaCl     | 26.97       |
| 40°C-90d     | 3% NaCl     | 23.92       |

3.2. Pore structure

Based on the effect of the pore, Wu Zhongwei\cite{13} classified the pores in hardened cementitious materials into four categories: non-harmful pores with a pore size less than 20 nm, and less harmful pores with pore sizes between 20 and 100 nm. Harmful pores exist at 100–200 nm, and multi-harmful pores with pore sizes larger than 200 nm. Table 3 and Figure 6 show the porosity and pore size distribution of the CAC pastes under different curing conditions. The longer the curing time is at 40°C, the higher porosity and more harmful pores. Obviously, the conversion of the hydrates accelerated by the high-temperature curing at 40°C was accompanied by the formation of a large amount of harmful pores with pore diameters exceeding 100 nm. The porosity of the hardened cement pastes also increases significantly, thus the compressive strength decreases. However, compared with the control, the NaCl-doped samples not only have lower porosity but also less harmful pores. It means that the incorporation of NaCl optimizes the pore structure of CAC, which is beneficial to the strength of the hardened paste. As a result, the deterioration of the pore structure and the strength retraction caused by the hydration conversion are improved.

3.3. SEM

Figure 7 shows the natural fracture morphology of the samples after curing at 40°C for 90 days. As shown in Figs. 7a and 7b, massive C\textsubscript{3}AH\textsubscript{6} are generated in the pure CAC paste, accompanying with numerous pores under low magnification. When NaCl is added (Figure 7c and 7d), massive acicular crystals can be observed. Combined with XRD patterns, those crystals are mainly CAH\textsubscript{10}. With a lower magnification (Figure 7d), the microstructure is much denser than that of pure CAC. It can be further confirmed that the incorporation of NaCl effectively retards the conversion of CAC hydrates and improves the compaction of hardened pastes.
Figure 7. SEM pictures of samples after curing at 40°C for 90 days.

4. Conclusion

(1) Curing at elevated temperature accelerates the conversion between the hydration products of CAC and thus speeds the compressive strength retraction.

(2) The incorporation of proper amount of NaCl promotes the formation of CAH$_{10}$, resulting in the decreasing of the porosity and the amount of harmful pore of hardened CAC paste, thus significantly improves early strength.

(3) At 40°C, the time required for the conversion of CAH$_{10}$ to C$_3$AH$_6$ is longer than that of C$_2$AH$_8$. The incorporation of NaCl delays the conversion between the hydration products and further suppresses the strength retraction.

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