Effect of calcium chloride on hydration kinetics and pore structure of hydrated tricalcium silicate

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Abstract. Chemical admixtures are frequently used to regulate the setting and strength development of concrete materials. In this study, tricalcium silicate (C₃S) was used as a model of the cement system, and the influence of calcium chloride, an extremely useful accelerator, on C₃S hydration and the pore structure of hardened C₃S paste were investigated by the combination of the techniques of differential scanning calorimetry (DSC) and the N₂ adsorption (BET). The results indicated that the addition of calcium chloride would significantly shorten the pre-induction and induction periods and enhance the specific surface area and porosity of hardened C₃S paste. However, the presence of CaCl₂ has little effect on the pores, with a width ranging from 2.5 nm to 5 nm. DSC technique has an advantage of measuring continuously the process of C₃S hydration by changes of free water in hydrated C₃S.

1. Introduction
Calcium chloride (CaCl₂) is an extremely useful accelerator of tricalcium silicate (C₃S) and cement hydration[1]. This accelerator is still frequently used in the unreinforced concrete. The higher the dosage of CaCl₂, the more significant the accelerating effect. CaCl₂ could promote the dissolution of cement, accelerate the formation of hydration products, and increase the heat flow rate of C₃S hydration [2-4].

According to the heat flow curve, the hydration of C₃S is generally divided into four stages:(1) pre-induction period; (2) induction period; (3) acceleration period; (4) deceleration period[5]. The hydration of C₃S would release abundant heat, and produce amorphous calcium silicate hydrates and crystalline calcium hydroxide[6, 7]. The evolution of hydration heat flow is frequently used to represent the hydration kinetics of C₃S [8].

Calorimetry is a commonly used and effective method to measure the exothermic properties of cement hydration reaction, including heat of solution calorimetry, semi-adiabatic/adiabatic calorimetry, isothermal conduction calorimetry and differential scanning calorimetry (DSC)[9]. The approach for DSC is to measure the changes of free water in C₃S and cement hydration, which can continuously measure the hydration regardless of the amount of heat released. In the study, with the same method, the influence of CaCl₂ on C₃S hydration was investigated.

With the progress of C₃S hydration, the number of gel pores from C-S-H gels[1, 10, 11] would increase, whereas that of capillary pores would decrease. Since the capillary pores are the main channel
of water transportation, it is closely related to the deterioration of cement-based materials caused by ingress of foreign ions [12]. Therefore, the study of the pore structure of hydrated C₃S is helpful to understand the C₃S hydration products, microstructure and performance.

2. Materials and Methods

Sample Preparation. Triclinic C₃S was purchased from CTL Group, Skokie, IL, U.S.A and C₃S particles were passed through the sieve of 45μm. Anhydrous C₃S powder was mixed with deionized water with a liquid-to-solid ratio of 0.4 and 0.5, and CaCl₂ was added with 1% wt of anhydrous C₃S. Hydrated C₃S pastes were placed into CryoTube vials (1.8mL) under N₂-gas protection at room temperature and then were sealed in a vacuum bag. The samples of hydrated C₃S without and with CaCl₂ were respectively dried in a vacuum oven at 23°C after 1, 3, 7 and 28-day hydration.

X-ray Diffraction. The X-ray diffraction tests of samples were conducted on a PNAalytical X’Pert Pro diffractometer equipped with a Co-target X-ray tube (λ=1.79 Å) and rapid X’celerator detector. The 2-theta ranges from 5° to 55° with a step of 0.02°. X-pert High Score Plus software was used to analyze the XRD patterns of the samples.

Differential Scanning calorimetry (DSC). Differential scanning calorimetry measurements were performed using a DSC Q2000 from TA Instruments. Around 50 mg of sample was mounted into an aluminum pan (φ5.4*2.0 mm), and then was sealed with the appropriate cover to avoid the leaking of water. Then, to the samples were equilibrated to -30°C and kept at this temperature for 1 min, after which the samples were heated from -30°C to -12°C at 20°C/min and -12°C to +25°C at 4°C/min. The collected data were analyzed by a Q series software (version 5.5.22).

N₂ adsorption (BET). The pore distribution of samples was measured by an accelerated surface area and porosimetry system (ASAP 2020) from Micromeritics (U.S.). The test temperature is around room temperature.

3. Results and discussion

XRD Patterns. Hydration reaction of C₃S hydration would form amorphous C-S-H and crystalline calcium hydroxide (Portlandite), which generally follows the following formula:

\[ \text{C}_3\text{S} + (3-x-y)\text{H}_2\text{O} \rightarrow \text{C}_3\text{SH}_x + (3-x)\text{Ca(OH)}_2 \]  

(1)

Allen et al. [13] determined \( x \) and \( y \) values in the above formula by using small-angle X-ray scattering and small-angle neutron scattering, and obtained the following equation:

\[ \text{C}_3\text{S} + 3.1\text{H}_2\text{O} \rightarrow 1.7\text{SH}_1.8 + 1.3\text{Ca(OH)}_2 \]  

(2)

It can be seen from Fig. 1 that CH and C-S-H (a hump at the d-spacing of 3.08 Å) are the only hydration products, and that CH was formed after 1-day hydration and the C₃S were almost consumed after 28 days. This means that the addition of CaCl₂ did not change the types of hydration products, and no new substances were produced.

Hydration kinetics of C₃S. In this paper, the evolution of free water content (Free Water Index, FWI) was chosen to represent the hydration kinetics of C₃S, by the technique of DSC which allows the quantitative analysis of free water content by integrating the melting peak of free water [9, 14]. Fig. 2 presents the heat flow curves of hydrated C₃S pastes as a function of hydration time. With these heat flow curves, FWI can be calculated according to the following formula:

\[ \text{FWI} = \Delta H_{\text{exp}}/\phi_w\Delta H_{\text{theor}} \]  

(3)

where \( \Delta H_{\text{exp}} \)——the area of the water melting peak, J/g;

\( \phi_w \)——the weight fraction of water in the paste;

\( \Delta H_{\text{theor}} \)——the theoretical value of melting enthalpy of water in the C₃S/water paste, 333.4J/g;
Fig. 1 XRD patterns of phase change from hydrated C₃S (w/c=0.5) in the presence of CaCl₂ during different hydration time[4].

The changes of free water in C₃S pastes of the melting peak of C₃S pastes with w/c of 0.4 and 0.5 over time is shown in Fig. 3. It can be seen that the addition of CaCl₂ would shorten the pre-induction and induction period, which is consistent with the results in the literature. In the absence of CaCl₂, where would be an induction period of around 3 hours, this period would almost disappear in the presence of CaCl₂. For the system with a w/c of 0.4 as shown in Fig. 3b, similar results can be found that the addition of CaCl₂ would accelerate the assumption of free water. Interestingly, it can be found that the FWI in the systems with a w/c of 0.4 are lower than those with a w/c of 0.5 regardless of the presence of CaCl₂.

CaCl₂ can significantly increase the nucleation rate of hydration products on the surface of C₃S particles and has little influence on the growth rate[15]. The addition of would shorten the pre-induction and the induction period as shown in Fig. 3. This means that CaCl₂ would promote the dissolution of C₃S particles and the release of Ca²⁺ and SiO₄ into the pore solution, and finally accelerate the saturation or supersaturation of hydration products. The critical effect of CaCl₂ is to trigger the initiation of acceleration, to accelerate the hydration products of nucleation[16].

Analysis of Pore structures. N₂ adsorption is a commonly used method to measure the specific surface area and pore size distribution of cement-based materials, especially for the determination of relatively small gel pores[17]. Hydrated C₃S paste is porous, in which there are plenty of pores with the diameters ranging from nanometers to microns, such as gel pores and capillary pores.

Fig. 4 presents the adsorption isotherm of C₃S pastes in the absence and presence of CaCl₂. From
figure 4, it can be seen that the maximum adsorption of CaCl₂-free samples reaches up to 58.8 cm³/g STP at 28 days, while the 7-day maximum adsorption amount of samples is ranging from 20 cm³/g STP to 30 cm³/g STP. C-S-H gel has a high specific surface area, and these amorphous gels stack and is rolled to form gel pores. As the hydration time increases, more foil-like and layer-structure C-S-H gel are generated, increasing N₂ adsorption. According to the International Union of Pure and Applied Chemistry (IUPAC) classification of N₂ adsorption isotherms, the shapes of hysteresis loops of the samples with different hydration time are shown in Fig. 4. It can be seen that hysteresis loop type of the pores in the hydrated C₃S sample transform from H4 type to H3 type with hydration. Hysteresis type H4 is associated with non-rigid aggregates of plate-like particles (e.g., calcium hydroxide), while hysteresis type H3 is associated with being filling with micropores, aggregated hydration product of C-S-H gels. The pores in C₃S samples hydrated for 28 days show H3 hysteresis ring, and the adsorption amount was enormous when the relative pressure was high. The slit pores formed by the accumulation of flake particles are mostly laminated Ca(OH)₂ crystals and C-S-H layered structure.

![Figure 4](image)

Fig. 4 The adsorption isotherm of C₃S in the absence (a) and presence (b) of CaCl₂

The specific surface areas of Langmuir, BET, t-plot and BJH adsorption/desorption are shown in Table 1. The specific surface area of C₃S pastes gradually increases with hydration time, which reflects the increase of C-S-H hydration products in the sample. Noticeably, the specific surface area of C₃S pastes with CaCl₂ is all larger than that without addition after the same hydration time. Also, Langmuir specific surface area is higher than the BET specific surface area. Theoretically, Langmuir adsorption is based on single-layer adsorption and focuses on measuring smaller pores, while BET specific surface area is based on multi-layer adsorption, which is suitable for testing larger pores.

In Fig. 5, the pore diameter of the hydrated C₃S is mainly distributed between 2.5 nm and 5nm at different hydration times. Furthermore, regardless of the presence of CaCl₂ or not, the average pore diameter of the gel pores in the hydrated C₃S samples are about 3.5nm. Although CaCl₂ can accelerate the hydration reaction of C₃S and produce more hydration products in the early stage, it has little effect on the size of the gel pores.

Table 1 Specific surface area of the pores in hydrated C₃S with different hydration time (m²/g)

| Samples          | BET   | Langmuir | t-plot | BJH adsorption | BJH desorption |
|------------------|-------|----------|--------|----------------|---------------|
| C₃S_1d           | 10.46 | 14.97    | 11.36  | 10.33          | 13.98         |
| C₃S_3d           | 9.16  | 12.92    | 8.88   | 7.72           | 11.61         |
| C₃S_7d           | 11.29 | 16.26    | 12.96  | 11.93          | 16.58         |
| C₃S_28d          | 33.52 | 47.19    | 34.17  | 35.72          | 56.78         |
| C₃S_CaCl₂_1d     | 16.33 | 22.96    | 16.26  | 16.673         | 24.31         |
| C₃S_CaCl₂_3d     | 10.63 | 14.94    | 10.11  | 9.97           | 15.52         |
| C₃S_CaCl₂_7d     | 14.85 | 20.65    | 12.64  | 12.59          | 19.99         |
| C₃S_CaCl₂_28d    | 46.58 | 65.72    | 48.72  | 48.30          | 65.00         |
Fig. 5 Pore size distribution of hydrated C₃S with different hydration time in the absence (a) and presence (b) of CaCl₂

4. Summary
Differential scanning calorimetry offers the possibility of studying the effect of CaCl₂ on the hydration kinetics of C₃S hydration. Changes in free water in hydrated C₃S pastes can easily be determined continuously by DSC.

The presence of CaCl₂ does not change the types of hydration products, which is mainly C-S-H gel and calcium hydroxide. CaCl₂, as an inorganic chloride salt, can shorten distinctly the pre-induction period and induction period during the hydration reaction.

As the progress of hydration, the specific surface area of hydrated C₃S pastes gradually increase due to the formation of hydration products, such as C-S-H gel and calcium hydroxide, and the addition of CaCl₂ would accelerate this increasing rate. Based on the shapes of H₄ hysteresis loops of hydrated C₃S pastes, the pores in hydrated C₃S are of slit pores ranging from macropores to mesopores due to the generation of C-S-H gel with a layer structure and plate-like crystal calcium hydroxide. However, the presence of CaCl₂ does not affect the pore width of mesopores of hydrated C₃S, which is ranging from 2.5 nm to 5 nm.

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