Early hydration and setting process of cement-hydrated lime system at different curing temperatures

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Abstract. This paper investigated the hydration and setting process of the cement-hydrated lime system at the temperatures of 30°C, 40°C and 50°C with Vicat test, FTIR and TG-DTA. To obtain sufficient time resolution a freeze-dry procedure is used to instantaneously cease the hydration process. The results illustrate that a shorter initial and final setting time can be observed with a higher curing temperature. The thickening time is the same at the curing temperatures of 40°C and 50°C and is half as that at 30°C. The dissolution of C₃S, the formation of C-S-H and the hydration product of C₄AH₁₃ from the reaction of C₃A and Ca(OH)₂ are the main causes of the thickening of the cement-lime system.

1. Introduction
Autoclaved aerated concrete (AAC) is widely applied in energy saving buildings due to waste using, lightweight, high strength, heat insulation, fire resistance and construction convenience. In the production of AAC, cement, lime and quartz are mixed to be the slurry and aluminum powder is the gas generator. During the rising process and curing period, lime and cement consume and absorb the free water, which leads to the loss of workability, setting and hardening of the slurry. During this period, the green cake is prone to all kinds of quality problems, such as bad pore structures caused by faster or slower setting process. However, the increase of temperature and the variation of the slurry viscosity due to a large hydration heat of cementitious material, especially lime, make the investigation on setting and hardening process of slurry difficult. A large amount of pilot productions needs to be done before commercial operation. Besides, the quality of AAC products is uneven mostly due to the instability of produce technique owing to the difference of raw material.

There is limited research on the mixture of cement and CaO or Ca(OH)₂ [1]. Cement-Ca(OH)₂ system is mostly applied to the restoration of cultural heritage [2,3]. M. Fourmentin [4] and Uchikawa [5] both show the accelerate hydration reaction moves forward and a shorter setting time of the system of cement-hydrated lime.

However, the addition portion of lime in cement is very small in most researches. There is almost no research on setting process and influence factors on the cement-hydrated lime system when lime addition proportion is very large, and even plays the dominated role, which is very important in AAC production.
2. Materials and Method

2.1. Materials

Hydrated lime and grey cement P-II 52.5 were used. The chemical components of hydrated lime and the cement were analyzed by X-ray fluorescence (XRF) shown in table 1. The specific surface area of cement and hydrated lime are 0.83 m$^2$/g and 12.45 m$^2$/g respectively, measured for both materials by N$_2$ adsorption according to the Brunauer–Emmett–Teller theory (BET).

| Chemical Components | Na$_2$O | MgO | Al$_2$O$_3$ | SiO$_2$ | SO$_3$ | K$_2$O | CaO | TiO$_2$ | MnO | Fe$_2$O$_3$ |
|---------------------|---------|-----|------------|--------|--------|--------|-----|--------|-----|-----------|
| Cement              | 0.09    | 1.02| 4.66       | 21     | 2.41   | 0.57   | 62.8| 0.25   | 0.09| 3.48      |
| Hydrated lime       | 0.09    | 0.76| 0.63       | 0.87   | 0.78   | 87.2   | 0.04| 0.02   | 0.29|           |

2.2. Method

The sample was prepared with cement to hydrated lime ratio of 1 and water to solid ratio of 1.05. Thickening time, initial setting time and final setting time were recorded by a Vicat apparent according to a Chinese test standard GB/T 1346-2011. Thickening time is a time when the surface of the sample appears plastic, the hole on the surface is not recovered when the Vicat needle is pulled up and a clear trace remains. Thickening time is significant in AAC production, which indicates the paste starts to loss its fluidity under the deadweight. Different from initial setting time, the paste does not loss workability. It also can be reshaped if an outside force is applied.

The samples for micro measurement were hydrated in sealed centrifuge tubes, to avoid water loss and carbonation, between 5 min and 270 min in the corresponding curing temperature, then frozen by immersion in liquid nitrogen and subsequently placed in the freeze drier overnight. The sample was ground and FTIR and TG-DTA were used to characterize the micro morphology on the following day.

The FTIR spectrometer used was EQUINOX 55. The measurement range lies between 400 and 4000 cm$^{-1}$. Simultaneous TG-DTA analyses were carried out by a thermal analyser NETZSCH. The samples were heated from 25 to 1000 °C at a constant rate of 10 °C/min. XRD Rietveld was used to calculate the content of phases.

3. Results and discussion

3.1. Thickening and setting time of cement-hydrated lime system

The thickening and setting time of paste at a curing temperatures of 30°C, 40°C and 50°C is displayed in table 2. It shows that the thickening time of paste is the same at the curing temperatures of 40°C and 50°C, which is half of that at 30°C. A shorter setting time is observed with a higher curing temperature and the influence of curing temperature on the final setting time is more obvious. That is, the influence of the curing temperature is strongest on final setting time, intermediate on initial setting time and least on thickening time. Moreover, when the curing temperature is over 40°C, the thickening time does not become shorter indicating the early reaction of paste is not accelerated.

| Curing temperature | 30°C | 40°C | 50°C |
|--------------------|------|------|------|
| Thickening time/min| 110  | 60   | 60   |
| Initial setting time/min| 290  | 140  | 170  |
| Final setting time/min  | 360  | 150  | 200  |

3.2. FTIR analysis

The hydration process was monitored for the first 2~3 hours by applying the freeze dry method, grinding of sample and subsequently acquiring the FTIR spectra. To enhance the changing characteristics of micro phases and make the spectroscopic features clearer, the difference spectra were calculated subtracting the spectrum from the dry cement-hydrated lime powder (figure 1).
The dip-hump feather in the 900–1200 cm\(^{-1}\) region is taken to the hydration of paste and simultaneously the polymerization of silica to form calcium silicate hydrate C-S-H[6].

The dip in the region of 800–970 cm\(^{-1}\) displays the dissolution of C\(_3\)S. In figure 1a, there is no obvious dip until 60 min, while in figure 1b and figure 1c, the dip displays between 30–60 min. It is consistent with the thickening time of cement-lime system at corresponding curing temperature. The evidence points to the probability that the thickening of cement-lime system is caused by the dissolution of C\(_3\)S in cement.

![Figure 1](image1.jpg)

Figure 1. Difference spectra where the absorbance spectrum of the dry cement-lime has been subtracted from the absorbance spectra of the cement-lime hydrated for 5, 20, 40, 60, 120 and 270 min at 30°C and 5, 10, 20, 30, 60 and 120 min at 40°C and 50°C. (a) 30°C; (b) 40°C; (c) 50°C.

The peak at 3644 cm\(^{-1}\) corresponds to Ca(OH)\(_2\), which is from the cement dissolution and the raw material. In figure 1, the peak grows firstly and is followed by a decrease, which means the amount of Ca(OH)\(_2\) in paste increases in the beginning and then decreases. Figure 1a shows that the amount of Ca(OH)\(_2\) increases in the first 5 min and then Ca(OH)\(_2\) starts being consumed before 20 min. It keeps consuming between 20–40 min, but afterwards, there is some formation again at 40 min. In figure 1b, the Ca(OH)\(_2\) content grows slowly in the first 5 min and is followed by a sharply increase between 5–10 min, but decreases at 20 min. however, there is some formation at 30 min and then again Ca(OH)\(_2\) is consumed at 60 min and 120 min. In figure 1c, there is a slight increase at 5 min and 10 min, followed by a progressive decrease from 20 to 120 min.

It is suggested that in the early hydration, the dissolution of C\(_3\)S results in the growth of Ca(OH)\(_2\). However, the lower solubility of Ca(OH)\(_2\) at higher temperature restricts the dissolution of cement in water, which delays the growth of Ca(OH)\(_2\). The C\(_3\)A in cement could react with water and Ca(OH)\(_2\) as follows:

\[
C_3A + CH + 12H \rightarrow C_4AH_{13}
\]
If gypsum exists in the system, $C_4AH_{13}$ can react with gypsum as follows:

$$C_4AH_{13} + 3CSH_2 + 14H \rightarrow AFt + CH$$

The $Ca^{2+}$ and $OH^-$ are always saturated because of the large amount of $Ca(OH)_2$ in paste, which results in the restriction of the transformation from $C_4AH_{13}$ into $AFt$[7]. Therefore, the product of $C_4AH_{13}$ could make the system thicken due to the formation of network structure.

The peak at 1350~1550 cm$^{-1}$ is related to $Ca^{2+}$. The dip-hump suggests that the decrease and increase of $Ca^{2+}$ in the system with the hydration of cement-lime system. In figure 1a, $Ca^{2+}$ increases in the first 5 min and then decreases at 20 min. It keeps decreasing at 60~120 min. While in figure 1b and figure 1c, $Ca^{2+}$ content grows before 20 min and starts to decrease at 30~120 min. It is consistent with the change tendency of the peak at 3644 cm$^{-1}$.

As hydration progresses there is a broad feature forming with its center at ~1658 cm$^{-1}$, caused by the bending vibration $\nu_2$ of irregularly bound water.

Above all, the thickening of cement-hydrated lime system is mainly caused by the dissolution of $C_3S$, the formation of C-S-H and the formation of the hexagonal $C_4AH_{13}$ from the reaction between $C_3A$ and $Ca(OH)_2$. It is affected by the hydration rate and the contend of $Ca(OH)_2$. Higher curing temperature could reduce the solubility of $Ca(OH)_2$ in water but increase the hydration rate inversely. Therefore, the influence of curing temperature on the thickening time is conflict from this point. Considering the lower solubility and higher hydration rate at a higher temperature, the thickening time does not shorten at the curing temperature over 40°C and there might exist a shortest thickening time.

3.3. Thermal analysis

The hydration process was monitored for the first 2~3 hours by applying the freeze dry method, grinding of sample and subsequently acquiring the DTG-DTA curves shown in figure 2 and figure 3.
The data concerning the mass losses are presented into three temperature regions: (I) from 40° C to 200° C; (II) from 430° C to 510° C and (III) from 600° C to 830° C, which are analysed separately.

Region (I) is from 40 to 200° C. In this region, the mass loss is attributed to the crystal water dehydration of the new-formed C-S-H[8,9] and the deformation of AFt. The weak signatures in figure 2~3 indicate that the hydration products are not dominating. However, the deeper dips in figure 2~3 indicate that the content of C-S-H grows as the hydration of paste.

Region (II) is from 430° C~510° C. In this region, the dehydration of Ca(OH)₂ dominates. The peak is the largest due to the existence of Ca(OH)₂ in raw material as a large portion.

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Figure 2. DTG curves of cement-lime system at different curing temperatures. (a) Curing temperature is 30° C; (b) Curing temperature is 40° C; (c) Curing temperature is 50° C.

Figure 3. DTA curves of cement-lime system at different curing temperatures. (a) Curing temperature is 30° C; (b) Curing temperature is 40° C; (c) Curing temperature is 50° C.

Figure 4. The content of Ca(OH)₂ of the hydration of cement-lime system at curing temperatures of 30° C, 40° C and 50° C.

Figure 5. The content of C₃A of the hydration of cement-lime system at curing temperatures of 30° C, 40° C and 50° C.

Figure 4 shows the content of Ca(OH)₂ which is calculated from the DTG results (figure 2). It shows that Ca(OH)₂ firstly decreases sharply and starts to grow after 10 min hydration. While Ca(OH)₂ begins to decrease at about 30 min at the curing temperatures of 40° C and 50° C, Ca(OH)₂ starts to decrease at about 100 min at 30° C. The content of C₃A is determined by XRD-Rietveld of paste is shown in figure 5. It indicates that C₃A decreases at the first 10 min and then a stable period is followed. While C₃A restarts a decrease at about 50 min at curing temperatures of 40° C and 50° C, C₃A begins to decrease at about 120 min at 30° C. The results are consistent with the change of Ca(OH)₂ in thermal analysis and thickening time, but are different from that in FTIR in first 10 min.
hydration. It may be assumed that there is formation of $\text{Mg}_3[(\text{OH})_2\text{Si}_2\text{O}_5]\[\text{10}\]$ in the hydration of cement-lime system which overlaps $\text{Ca(OH)}_2$ in FTIR spectra. Above all, the thickening of cement-lime system could be ascribed to the reaction between $\text{Ca(OH)}_2$ and $\text{C}_3\text{A}$. Furthermore, the nearly consistent tendency of $\text{Ca(OH)}_2$ in the paste from FTIR and DTG results indicates the $\text{Ca(OH)}_2$ plays an important part during the hydration process. Different from the cement system, the hydration process of the paste only produces portlandite in the first 20 min and after 30 min, and then portlandite is consumed during the hydration process.

Region (III) is from 600°C to 800°C. In the region of 550–680°C, the chemical combined water dehydration of $\text{CSH}$ is dominated. The peak at 660~740°C is attributed to the decomposition of dolomite, calcite and calcium carboaluminates.

4. Conclusion

In this paper, the influence of curing temperature on the hydration and setting process were analysed and the following conclusions were obtained:

1. Higher curing temperature shortens the initial setting time and final setting of cement-hydrated lime system. The thickening time of paste at 40°C and 50°C is half as that at 30°C.

2. The dissolution of $\text{C}_3\text{S}$ and the formation of $\text{C}-\text{S}-\text{H}$ become obvious at about 30~60 min at curing temperature of 30°C and at about 60 to120 min at curing temperatures of 40°C and 50°C, which is consistent with the thickening time of cement-lime system at each curing temperature.

3. At the curing temperature of 30°C, the decrease of $\text{Ca(OH)}_2$ starts at about 60~120 min while it begins to decrease at 30~60 min at 40°C and 50°C in both FTIR and DTG-DTA. The variation trend of $\text{C}_3\text{A}$ is the same as that of $\text{Ca(OH)}_2$. The turning points are consistent with the thickening time of paste at the corresponding curing temperature. The evidences point to the probability that the thickening of paste is mainly caused by the reaction of $\text{Ca(OH)}_2$ and $\text{C}_3\text{A}$.

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