

Dehydration kinetics of Portland cement paste at high temperature

Qi Zhang · Guang Ye

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Abstract Portland cement paste is a multiphase compound mainly consisting of calcium-silicate-hydrate (CSH) gel, calcium hydroxide (CH) crystal, and unhydrated cement core. When cement paste is exposed to high temperature, the dehydration of cement paste leads to not only the decline in strength, but also the increased pore pressure in the paste. In this article, the dehydration kinetic was characterized in term of the combination of kinetics of CSH and CH. The dehydration kinetics data of cement paste at different heating rates was collected by thermogravimetry. The influence of temperature on the reaction rate is analyzed by Arrhenius equation. The Arrhenius parameters of CSH and CH, activation energy, and pre-exponential factor are determined by isoconversional method. The calculated kinetics parameters were validated by further experimental data finally.

Keywords Kinetics · Dehydration · Cement paste · High temperature · TG · Isoconversional method

Introduction

The dehydration of Portland cement paste plays an important role in the concrete structure explosive spalling at fire. Calcium silicate hydrate (CSH) and calcium hydroxide (CH) are the main hydration phases which dominate the properties of Portland cement paste. The temperature range corresponds to the dehydration of CSH is about from 105 to 1,000°C [1]. The temperature range corresponds to the dehydration of CH is about from 400 to

550°C. The dehydration of cement paste, together with evaporation of capillary water, has a great influence on the build-up of high pore pressure, which can result to explosive spalling of concrete.

The dehydration analysis of cement paste can be facilitated by the use of thermal analysis techniques, including thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The dehydrations of different cement pastes [1–4] were investigated by TG at given heating rates. The chemical meanings of peaks of TG/DTG curve were qualitatively described [2–4]. The dehydration kinetics of cementitious materials were usually characterized by the modified Arrhenius equation [5], where the cementitious materials were considered as pure substance.

However, the dehydration kinetics of Portland cement paste is too complex to be described by a single Arrhenius equation. The dehydration of Portland cement paste is comprised by dehydration of CSH and CH [4]. Moreover, the dehydration of CSH itself is a multi-step reaction [6, 7], in which the Arrhenius parameters (activation energy and pre-exponential factor) vary with dehydration degree. Therefore, it's difficult to use a single pair of Arrhenius parameters to reveal the chemical mechanism and to predict the dehydration process of cement paste accurately.

In this study, the dehydration kinetics of Portland cement paste was characterized as the combination of two parallel kinetics processes, i.e., kinetics of CSH and CH. To confirm that these two reactions dominate the dehydration process, the crystalline composition of cement paste sample was characterized by X-ray diffraction. The dehydration mass losses (TG curves) of cement paste at different heating rates were collected by thermogravimetry for the parameters determination. The TG curves of cement paste were separated into the TG curves of CSH and CH by a graphic method. The dehydration kinetics parameters of

Q. Zhang (✉) · G. Ye
Stevinweg 1, 2628 CN Delft, The Netherlands
e-mail: zhangqi731@gmail.com

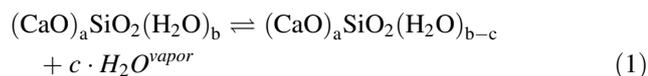
CH and CSH were computed, respectively, based on the TG data. The isoconversional method [8] was performed to calculate the reaction-degree-dependent activation energy of CSH and CH. This kinetics model and calculated parameters were verified by further experimental data.

Material

The experiment were carried out by using an ordinary Portland cement (OPC) CEM I 42.5N. The water/cement ratio was 0.5. The cement paste was cast in small plastic bottles. After curing in closed bottles for 28 days, the hardened paste were removed from the plastic bottles. Before measurement, the cement paste samples were stored in the oven at 105°C for 24 h to remove the free water. The cement paste samples were milled into powders (<50 μm) for thermogravimetric analysis.

Method

Because the cement paste with age of 28 days was investigated in this study, the possible carbonation in samples is assumed to be negligible. The dehydration process of Portland cement paste is considered as the reactions as following:



the Friedman model [9] was used for kinetics of nth-order reaction in this study.

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

where n is the reaction order, α is the reaction degree. Arrhenius equation is used to describe the influence of temperature.

$$K(T) = A_0 \exp -E_a/RT \quad (4)$$

where A_0 , the pre-exponential factor and E_a , the activation energy are referred to as the Arrhenius parameters. Given attention to the reaction order and temperature, the kinetics of dehydration of each phase can generally be expressed as following equation:

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (5)$$

Equation 5 characterizes the dehydration kinetics of CSH and CH. Hence, the global dehydration kinetics of cement paste is considered as the combination of the dehydration kinetics of CSH and CH. The kinetics analysis of CSH and CH is carried out by following four steps:

Crystalline phase identification

Portland cement paste is a complex material that might contain some minor hydration products and calcium carbonate (CaCO_3). These minor phases can effect the total mass loss of cement paste at high temperature. Therefore, before thermal analysis, the crystalline composition of cement paste must be identified to make sure that the minor phases are negligible in samples, and that dehydration of CSH and CH is the main reaction during heating. The mineral composition of cement paste sample was measured by powder X-ray diffraction (XRD). The X-ray source of Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) was used. The scan step size was 0.02° in the range 2θ from 5° to 70° .

Mass loss data collection by thermogravimetric analysis

The simultaneous thermogravimetry analyzer was used to measure the TG curves. The purge gas was nitrogen, and the gas velocity was 20 ml/min. The sample was heated from 30 to 1,100°C with different rates: 1, 2, 5, 10 and 30°C/min.

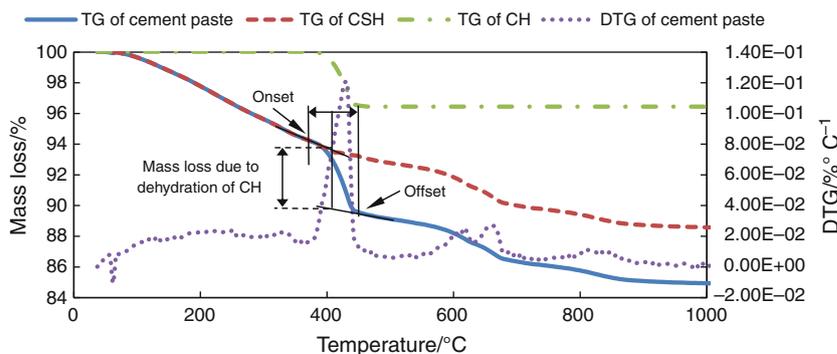
Separation of TG curve

To study the dehydration kinetics of hydrates separately, the TG curves of cement paste are divided into TG curves due to dehydration of CSH and CH respectively. As Fig. 1 shown, the derivative of mass loss (DTG) has a large peak at around 450°C, which stands for the dehydration of CH. The onset and offset point of dehydration of CH can be determined by the edge of that peak. The mass loss at this segment between the onset and offset is contributed by both the dehydration of CH and CSH. It is assumed that the rate of dehydration of CSH in this segment was the same with the neighbored segments in this study. Therefore, two tangent lines are made through onset and offset, which stand for the mass loss of CSH. The mass loss due to dehydration of CH can be known by calculating the vertical distance of these two trend lines at the midpoint between onset and offset (Fig. 1). By this graphic method, the TG curve of cement paste is separated into TG curves of CSH and CH in Fig. 1.

Determination of kinetics parameters by isoconversional method

Kinetics parameters vary with extent of conversion at the multi-step kinetics, such as dehydration of CSH. Isoconversional methods employ multiple heating rates in order to obtain data on varying rates at a constant extent of conversion. Thus, isoconversional methods allow multi-step processes to be detected via a variation of E_a with α . The dehydration degree is calculated from TG curves first:

Fig. 1 Separation of TG curve of cement paste into TG curves of CSH and CH



$$\alpha = \frac{w_i - w_0}{w_{\text{final}} - w_0} \tag{6}$$

where w_i is the mass during dehydration, w_0 is the initial mass, w_{final} is the final mass after dehydration. In this study, isoconversional Friedman method was performed [10], and the reaction order is assumed to be one:

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E_a}{RT} + \ln A + \ln(1 - \alpha) \tag{7}$$

by plotting $\ln(dx/dt)$ against $1/T$, one directly obtains the slope $-E_a/R$ for a fixed α . And the $\ln A$ can be determined by the intercept $\ln A + \ln(1 - \alpha)$.

Results and discussion

The XRD pattern of dried Portland cement paste is shown in Fig. 2. The crystalline phases are determined. Alite, belite, quartz and brownmillerite are ingredients of unhydrated clinker. Portlandite (CH) is the hydration product. Due to amorphous structure of CSH, the peaks of CSH gel can't be found in the XRD pattern. Because the samples are isolated with air during curing, the calcite (CaCO_3) is not detected in the samples. Therefore, decarbonation of samples during heating is neglected.

The mass loss curves of samples under different heating rates were shown in Fig. 3a. A rapid mass loss at around 450°C was observed in each TG curve, that was caused by dehydration of CH. By using the graphic method in Section

“Separation of TG curve”, the mass loss curves of CH and CSH at different heating rate are determined subsequently in Fig. 3b, c. Both dehydration of CH and CSH were significantly affected by the heating rate, which are shown in Fig. 3b, c. In these figures, it was found that at the same temperature the dehydration degree of the sample with low heating rate is larger than that of the sample with high heating rate. This is because the sample with lower heating rate has more time to dehydrate.

It was also found that the temperature range corresponding to the dehydration of CH varies with the heating rate (Fig. 3c). For the samples with different heating rate, the dehydration starts at the same temperature, but ends at different temperature. This is because the samples with higher heating rate need less time to reach target temperature, and its dehydration time is less.

The curves of $\ln(dx/dt)$ against $1/T$ of CSH and CH at fixed dehydration degrees range from 0.1 to 0.9 were plotted and showed in Fig. 4. It was observed that the plots of $\ln(dx/dt)$ against $1/T$ of CSH and CH were linear. The trend of $\ln(dx/dt)$ against $1/T$ plots of CSH varies with dehydration degree (Fig. 4a). In the contrast, all $\ln(dx/dt)$ against $1/T$ plots of CH at different dehydration degrees overlap together (Fig. 4b).

By making trend lines of the $\ln(dx/dt)$ against $1/T$ plots in Fig. 4, the E_a and $\ln A$ are determined and showed in Fig. 5. It is showed that the E_a and the $\ln A$ of CSH develop with α obviously. And the the E_a and the $\ln A$ of CH almost keep the same during the dehydration process. The average E_a of dehydration of CH is 151.82 kJ/mol.

Fig. 2 XRD pattern of dried Portland cement paste (oven dried by 105°C)

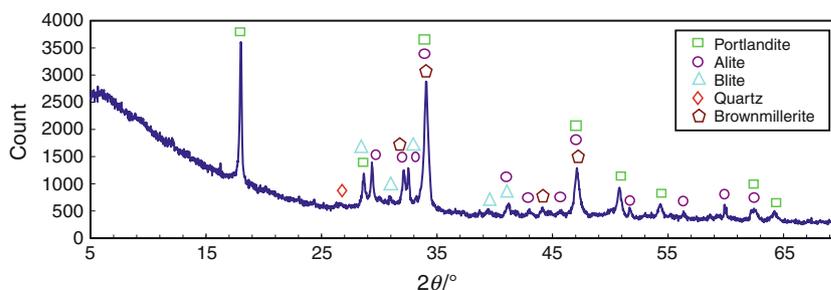


Fig. 3 TG curves of cement paste, CSH and CH

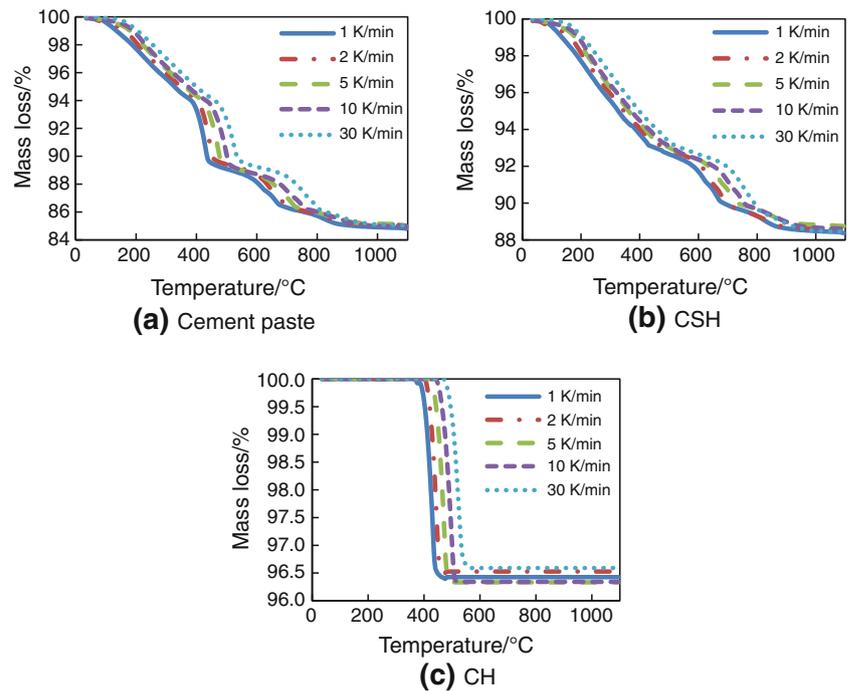


Fig. 4 Plots of $\ln(dx/dt)$ against $1/T$ of CSH and CH

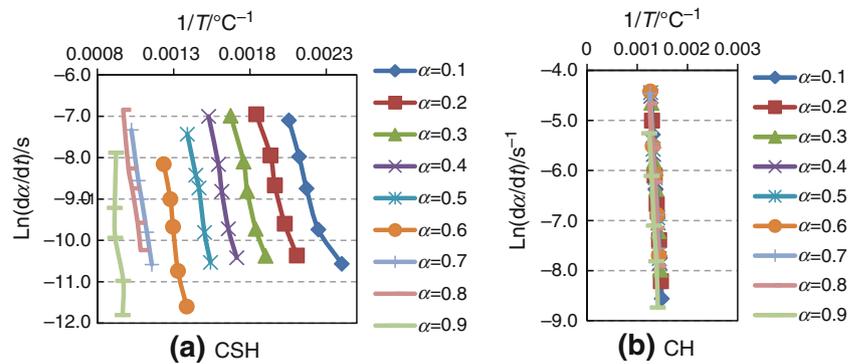
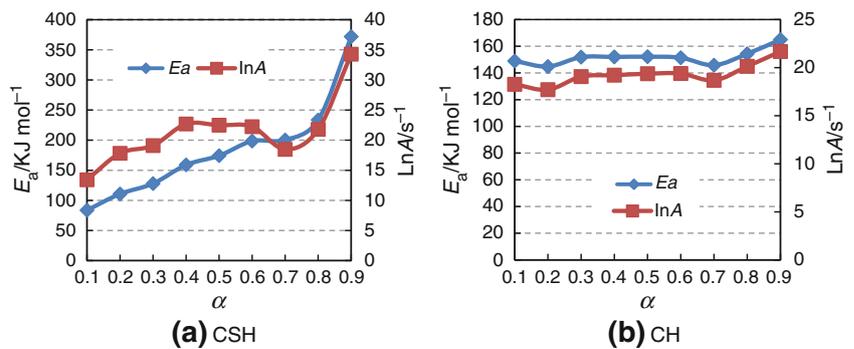


Fig. 5 Activation energy and $\ln A$ determined by isoconversional method



Discussion on variation of E_a with progress of reaction

The activation energy E_a is the average excess energy that a water molecule must possess to release [11]. A variation of E_a with reaction process implies that systematic change

of reactivity takes place during the progress of a reaction. The possible reasons of a variation of E_a were discussed by Galwey [12].

The variation of E_a of CH with α is very small (relative standard deviation = 3.85%). This can be explained that

the dehydration of CH is a single step reaction. During the reaction process, the energy barrier to bond redistribution of CH almost keep the same. The small variation of E_a might be caused by computational error.

The large variation of E_a of CSH with α can be explained by that the dehydration of CSH is a multistep reaction. The CSH gel in hydrated cement paste has consists of many small globules with a disordered layered structure [13]. There are some water molecules absorbed in the interlayer space and surrounding globule (Fig. 6). Because of the complexity of gel structure, different water molecules requires different energy to be released. At high temperature, the monolayer water molecules that surrounds globule are released first, when the interlayer water molecules keep the same. When temperature is sufficiently high, the interlayer water molecules are released finally. Moreover, the CSH structure varies with temperature rising. As Taylor [7] pointed out, the interlayer spacing shrunk with release of water molecule. The smaller the spacing between CSH layer is, the more energy could be required to dehydrate.

Verification

In order to verify the measured kinetics parameters, the above kinetics model is compared with further experimental data. The above kinetics parameters are computed from the data under different heating rate. But in principle, they are intrinsic parameters, which are applicable for the case under any temperature profile. If an arbitrary temperature–time relation is given, the total mass loss of cement paste at any time can be calculated. The dehydration degrees of CSH and CH can be calculated by numerical method first. The numerical forms of dehydration degree of CH and CSH are showed as following:

$$\alpha_{i+1,CSH} = \alpha_{i,CSH} + (1 - \alpha_{i,CSH})^n A_{0,i,CSH} \exp(-E_{a,i,CSH}/RT_i) \Delta t \tag{8}$$

$$\alpha_{i+1,CH} = \alpha_{i,CH} + (1 - \alpha_{i,CH})^n A_{0,i,CH} \exp(-E_{a,i,CH}/RT_i) \Delta t \tag{9}$$

where t is time, i is the time step, Δt is the time step length. Combining the dehydration of CSH and CH, the mass loss in the total dehydration process of cement paste can be characterized as following:

$$W_{cem} = W_{CSH}\alpha_{CSH} + W_{CH}\alpha_{CH} \tag{10}$$

where W_{cem} is the total mass loss of cement paste, W_{CSH} is the maximum mass loss caused by dehydration of CSH, W_{CH} is the maximum mass loss caused by dehydration of CH.

To validate both the kinetics of isothermal and nonisothermal process, the cement paste was heated under a multi-segment temperature program. The sample was heated with rate 5°C/min first. When temperature reached 200°C, the temperature programmer was switched from dynamic heating mode to the isothermal condition for 60 min. At the end of the 60 min, the temperature programmer was switched again to dynamic heating until 400°C. Then the sample was kept in 400°C for another 60 min. At the end of the isothermal process, the sample was heated again with heating rate 15°C/min until 1,000°C. Figure 7 illustrated that the simulated results agreed with the experimental data very well not only in non-isothermal segments but also in isothermal segments. When the heating method was switched from dynamics heating mode to the isothermal condition, the equilibrium state of CSH was not reached immediately. Therefore, the dehydration reaction proceeded at both isothermal segments and non-isothermal segments. Because the activation energy increased along with extent of dehydration, the reaction rate decreased gradually in the isothermal segment.

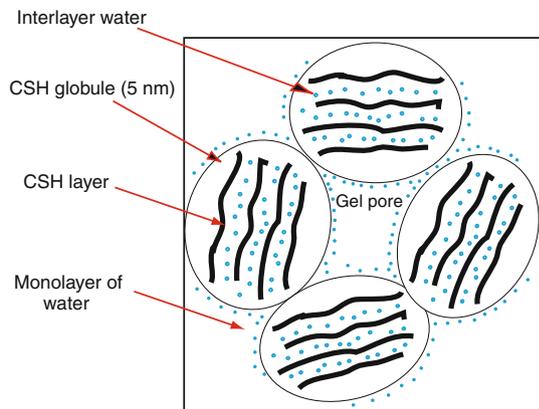


Fig. 6 A schematic of globulous structure of CSH gel

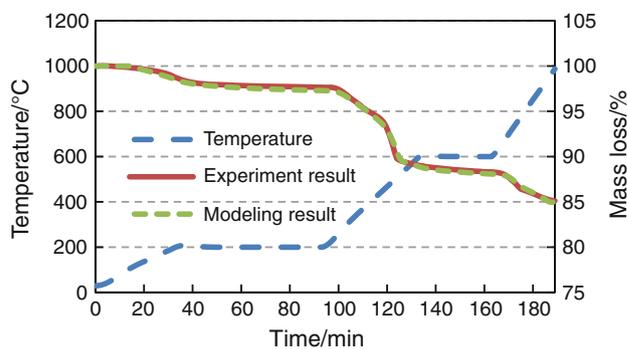


Fig. 7 Comparison of mass loss measured by thermogravimetry and mass loss curve predicted by kinetics model under complex temperature program

Conclusions

In order to characterize the kinetics of the dehydration of different phase in cement paste, a global kinetics of cement paste was considered as the combination of kinetics of CSH and CH. The phases in cement paste was identified by powder XRD. Isoconversional methods [8, 10] were performed to study the dehydration kinetics of CSH and CH. The E_a and the $\ln A$ of the dehydration of CSH and CH were determined, respectively. The following conclusions can be drawn:

- In the fresh Portland cement paste that has been oven dried at 105°C, CSH and CH are the main hydration products. The minor crystalline phase (like CaCO_3) can be neglected during the dehydration.
- The E_a of the dehydration of CH is about 151.82 kJ/mol. The variation of E_a of the dehydration of CH is very small.
- The E_a of the dehydration of CSH varies from 83.69 to 371.93 kJ/mol. The variation of E_a of the dehydration of CSH is explained by its complex globulous structure at high temperature.
- The global kinetics model of cement paste and its measured parameters were verified by comparing the simulated mass loss with experimental data.

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