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Effects of temperature on the hydration characteristics of free lime

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Abstract

The rate of heat evolution of hydrating CaO has been determined quantitatively by means of a conductive microcalorimetry, and the hydration kinetics of CaO has been studied. Some regularity of the influence of temperature on the hydration characteristics of free lime (f-CaO) has been discussed as well. Based on the present research, the mechanism of effects of temperature in the calcining process and the hydration process on the hydration of CaO has been illustrated. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Temperature; Calorimetry; Hydration; Kinetics; Microstructure

1. Introduction

The most outstanding characteristic of cement-based materials is that they need two technology processes (calcination and hydration) in contrast to glasses, ceramics and other inorganic nonmetallic materials. Temperature is of great importance in the calcination of cement clinker, the hydration of cement and the formation of cement stone. Free lime (f-CaO), as a composition phase of Portland cement clinker, has great effect on some properties of cement, especially on it soundness [1–7]. Besides the content of f-CaO in the cement, the soundness of the cement also depends greatly on the hydration activity of the f-CaO [6,7]. That is, it is closely related to the calcination temperature of the clinker. The hydration activity of f-CaO formed under different conditions is variable, so the soundness of the cement must be tested and cannot be predicted reliably from the f-CaO content. Industrial practice has showed that, even when produced in the same kiln and under the same conditions, the rate of disappearance of f-CaO in cement clinker is affected by the ambient temperature. In some factories with shaft kiln operated in China, the clinker produced in winter has to be stored because the dispelling rate of f-CaO is very slow. Thus, normal production and working capital are affected. In summer, the matter is not as serious. It demonstrates that the disappearance of f-CaO is closely related with the ambient temperature.

In this paper, the influence of calcination temperature on the hydration activity and microstructure of CaO crystals, the influence of environmental temperature on the hydrating rate of CaO and the hydration kinetics during its hydration process have been studied by means of conductive microcalorimetry, X-ray diffraction and other techniques. The mechanism of the effect of temperature on the hydration characteristics of f-CaO has also been investigated.

2. Experimental

2.1. Materials and preparation of samples

An analytical pure $CaCO_3$ reagent and an industrial limestone powder were used in this work. The powders were pressed into cylinders (Φ 40 × 5 mm) under a pressure of 25 MPa, fired at different temperatures for 1 h in a high-temperature electric furnace and then cooled rapidly in air to provide a series of sample of pure CaO and industrial CaO. The chemical composition of the industrial limestone is shown in Table 1.

2.2. Determination of hydration activity

The heat of hydration of CaO determined by means of an improved RD-I conductive microcalorimetry is regarded as the characteristic of hydration activity in this research.

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Table 1
Chemical composition of limestone (%)

IL	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
42.49	0.85	1.12	0.29	54.55	0.82

Generally, the fineness of each specimen was almost the same, and a fixed w/c ratio (w/c = 2.5), constant hydration temperature (± 0.1 °C) and sample mass (1 ± 0.0001 g) and internal mixing were adopted in the test. Some special cases would be illustrated separately in this paper.

2.3. Determination of crystal microstructure

Based on the X-ray diffraction line-broadening effect, approximate functional methods were used to determine the crystal grain size and crystal lattice [8]. Testing conditions were as follows: Rigaku X-ray diffractometer made in Japan, CuK_α radiation, 40 kV/100 mA, DS 1°, SS 1°, RS 0.3 mm, graphite diffracted beam monochromators, step scanning, step length 0.02°, counting time 2 or 4 s. The diffraction peaks of the following crystalline planes of CaO were determined: (111), (200), (220), (311), (222), (400), (331), (420), (511), (440) and (531). All the data were handled by special software. The crystal parameters of CaO were determined under the same conditions. The $K_{\alpha 1}$ and $K_{\alpha 2}$ doublets were separated, and the crystalline cell parameters of CaO were calculated according to the peak position 2θ of individual peak $K_{\alpha 1}$ and d of crystalline plane (531).

3. Experimental results and discussion

3.1. The influences of firing temperature

CaO and other minerals in cement clinker are unstable products of high-temperature physical and chemical reactions. When the CaO in a high-energy state comes in to contact with water, the following reaction occurs [9]:

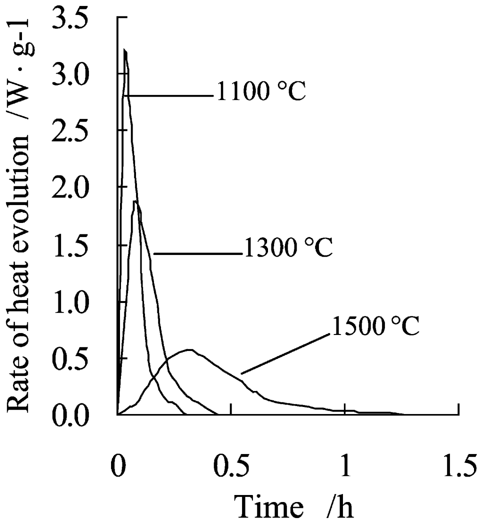

Fig. 1. Effect of firing temperature on the rate of heat evolution of pure CaO.

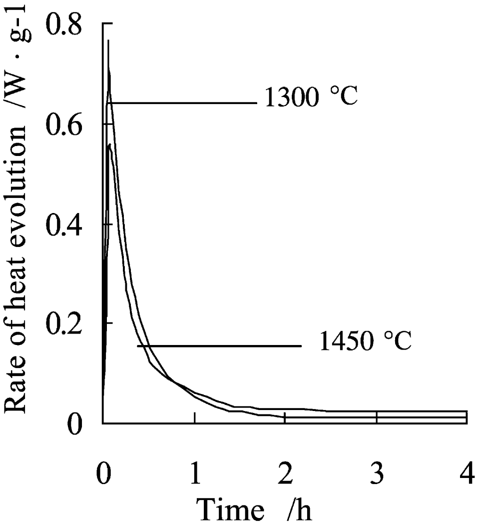

Fig. 2. Rate of heat evolution of industrial CaO calcined at 1300 and 1450 °C.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$\Delta H_{296} = -15,620\ \mathrm{cal/mol}\ (-65.40 \times 10^3\ \mathrm{J/mol})$$

Figs. 1 and 2 show the heat evolution curves during the hydration of pure CaO and industrial CaO calcined at various temperatures, respectively. The magnitude of the peaks and the times at which they were observed are presented in Table 2. As shown in Fig. 1 and Table 2, with increase of firing temperature, the rate of heat evolution of pure CaO decreases considerably. For the CaO calcined at 1100 °C, the highest rate of heat evolution was reached after only 2 min, the hydrating reaction would be completed after about 21 min and the rate of heat evolution tended towards zero at that time. In contrast, for the CaO calcined at 1300 °C, the highest rate of heat evolution was reached after 5 min. The rate of heat evolution tended to zero after 27 min. For the CaO calcined at 1500 °C, the highest rate of heat evolution is just about 1/6 of that calcined at 1100 °C. The magnitude of the largest heat evolution peak is far lower than that of the CaO calcined at lower temperature. The heat

Table 2
Rate of heat evolution of CaO fired at various temperatures and time at which

Sample	Firing temperature (°C)	Heat evolution Maximum rate (w/g)	 Time at maximum rate (min)	Time of hydration termination (min)
Pure CaO	1100	3.144	2.0	21.1
	1300	1.872	5.0	27.4
	1500	0.571	18.2	79.2
Industrial CaO	1300	0.754	3.7	> 240
	1450	0.557	5.1	>240

evolution curve becomes smoother and flat, and the duration of heat evolution becomes longer. The time for the whole heat evolution process is almost four times longer than that of CaO calcined at 1100 °C. It shows that the CaO calcination temperature has a great effect on its hydration activity. Similar to the f-CaO in clinker, the industrial CaO contains small amounts of SiO_2, Al_2O_3, Fe_2O_3 and other oxides. Consequently, the hydration activity is lower than that of pure CaO [7]. Nevertheless, the regularity of the influence of firing temperature on hydration activity is similar, which can be seen from Fig. 2 and Table 2. The highest rate of heat evolution of industrial CaO calcined at 1450 °C is remarkably lower than that calcined at 1300 °C. The study shows whether pure CaO or industrial CaO is considered. Their hydration activities have been greatly affected by the firing temperature. Raising the calcination temperature decreases the hydration activity of CaO.

The hydration activity and other properties of Portland cement depend on the microstructure of the clinker, that is, they depend on the microstructure of each phase in the clinker. The clinkers with identical chemical or mineral composition may have very different hydration activities and hydraulic characteristics because of their various microstructures. It can be seen from the study of the crystal microstructure of pure CaO that the microstructure of CaO crystals is closely related to the calcination temperature. As shown in Table 3, when the firing temperature is raised, the crystallite size of CaO increases rapidly. It is almost by an order of magnitude greater at 1500 °C than that at 1100 °C. Moreover, when the firing temperature is increased, the growth rate of CaO crystallites also increases. Over the temperature range of 1100–1300 °C, the crystallite size only increases by about 150 nm, but over the temperature range of 1300–1500 °C, it increases by about 500 nm. In addition, with the increase of firing temperature, the array of atoms in the crystal becomes more regular, the defects present in the crystal are evidently reduced and the lattice distortion also decreases. As shown in Fig. 3, the higher the calcining temperature, the denser the crystal structure and the more perfect the crystal lattice, so the smaller the cell parameter of CaO. Furthermore, from the slope of the curve in Fig. 3, one can see that the curve over the range of 1300–1500 °C is steeper than that over the range of 1100–1300 °C. It shows that the changing rate of the cell parameter increases with the rise of temperature, which is in accordance with that of the crystallite size. The higher the firing temperature, the greater the influence on the microstructure of CaO. The CaO when first decomposed from $CaCO_3$ retains the typical rhombohedral structure of $CaCO_3$, and the crystal lattice is rather imperfect. There are more vacancies and defects in the crystal structure, so the structure is loose and the crystallite size is small. With rise of temperature, the crystals of CaO grow and change to the cubic structure.

Table 3
Crystallite size and lattice distortion of CaO

Firing temperature (°C)	Firing time (h)	Crystallite size (nm)	Lattice distortion (%)
1100	1	86	0.09
1300	1	233	0.06
1500	1	738	0.04

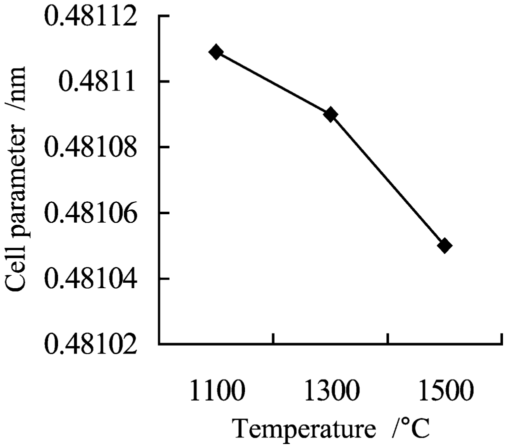

Fig. 3. Crystalline cell parameter of CaO vs. firing temperature.

The essence of crystal growth is atomic transition. Grain growth results from grain boundary removal. The difference in the free enthalpy of material on the two sides of a grain boundary is the driving force that makes the boundary move toward its center of curvature. Raising calcination temperature increases the average atomic vibration energy and accelerates the transition of atoms, resulting in a faster speed of migration of the grain boundaries. At the same time, the array of atoms in the crystal lattice tends to become more regular and the imperfections become less. Therefore, the lattice distortion and cell parameter reduce. The smaller the crystallite, the more crystal imperfections, the larger the area of crystal boundaries and the lattice distortions and the higher the free energy in the crystal surfaces, so the more

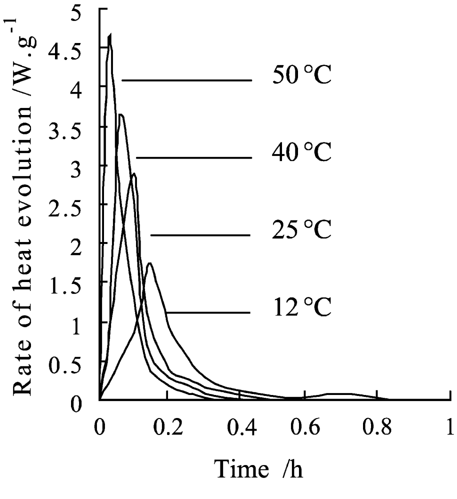

Fig. 4. Rate of heat evolution of pure CaO at various temperatures.

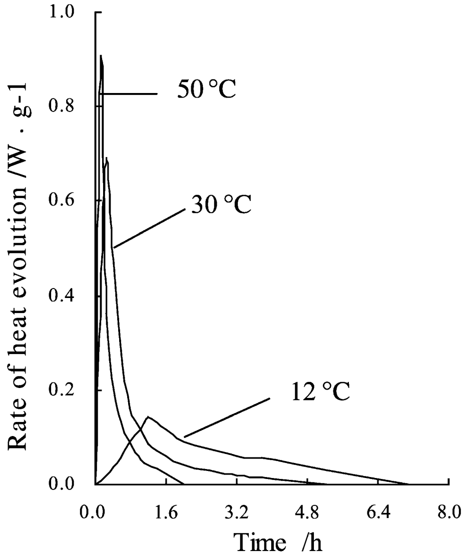

Fig. 5. Rate of heat evolution of industrial CaO at various temperatures.

unstable the crystal structure. When it reacts with water, the CaO with such structure shows higher reactivity. The essence of the effect of firing temperature on the hydration activity of CaO is to change its microstructure. The difference in the microstructure of CaO fired at various temperatures results in its different hydration activity. The hydration activity of CaO is a macroscopic reflection of its microstructure.

3.2. Hydrating temperature and hydration kinetics

Figs. 4 and 5 show the rate of heat evolution of pure CaO and industrial CaO calcined at 1500 °C at various hydrating temperatures, respectively. Table 4 gives the magnitude of the peaks and the times at which they were observed. From Figs. 4 and 5 and Table 4, one can see clearly that whether pure CaO or industrial CaO containing certain impurities. Their rate of heat evolution accelerates with the increase of hydrating temperature. The maximum rate of heat evolution of pure CaO increases from 1.736 w/g at 12 °C to 4.585 w/g at 50 °C. The increase is even more obvious for industrial CaO from 0.144 w/g at 12 °C to 0.905 w/g at 50 °C. An increase of more than sixfold is observed. The experimental results show that the influence of hydrating temperature on the rate of heat evolution of industrial CaO containing impurities is larger than that of pure CaO. With the increase of hydrating temperature, the duration of heat evolution decreases remarkably. The duration of the total heat evolution of pure CaO during hydration decreases from 0.83 h at 12 °C to 0.36 h at 50 °C, whereas that of industrial CaO decreases from 7.1 h at 12 °C to 2.0 h at 50 °C.

Table 4
Maximum rate of heat evolution of CaO at various temperatures

Sample	Temperature (°C)	Maximum rate of heat evolution (w/g)	Time at maximum rate (min)
Pure CaO	12	1.736	7.1
	25	2.892	5.9
	40	3.694	3.4
	50	4.585	1.5
Industrial CaO	12	0.144	72.0
	30	0.688	13.7
	50	0.905	6.9

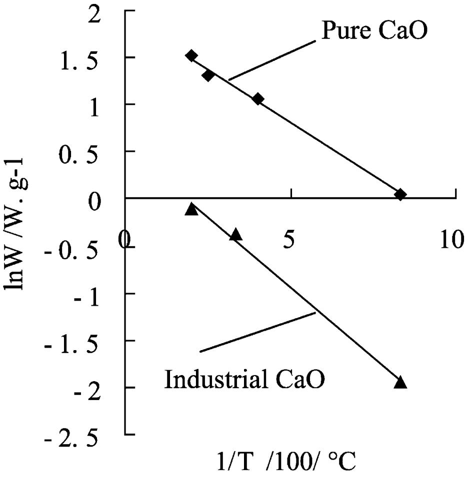

Fig. 6. Plot of maximum rate of heat evolution (ln *W*) vs. 1/*T*.

The rate of heat evolution of CaO increases with the rise of reaction temperature, which shows that the hydration reaction rate also increases with the rise of hydrating temperature. According to the Law of Boltzmann distribution, the rate in a physical or chemical reaction process has a relationship with temperature, as follows (Eq. (1)):

$$N_{\mathrm{i}} = \frac{N}{Z}\exp\left(-\frac{E_{\mathrm{i}}}{KT}\right) \tag{1}$$

where N is the total number of molecules, N_{i} is the number of molecules with energy E_{i}, K is Boltzmann's constant, T is the absolute temperature and Z is the partition function.

For $CaO + H_2O \rightarrow Ca(OH)_2$, the reaction rate also follows the Arrhenius equation:

$$\kappa = Ae^{-E_{\mathrm{a}}/RT} \tag{2}$$

where κ is the reaction rate constant, A is the Arrhenius factor, E_{a} is the activation energy, R is the universal gas constant and T is the absolute temperature.

Suppose the reaction rate is in direct proportion to the rate of heat evolution. That is

$$\kappa = BW \tag{3}$$

where B is a proportionally constant and W is the rate of heat evolution. Substituting Eqs. (2) and (3) and taking the

Table 5
Parameters of hydration kinetics of CaO at heat evolution reaction

Sample	E_{a} (R)	ln C	E_{a} (J/K mol)
Pure CaO	14.25	1.710	1.714
Industrial CaO	29.64	0.546	3.565

logarithm, we have Eq. (4):

$$\ln W = \ln C - \frac{E_a}{RT} \tag{4}$$

where $C = A/B$.

According to the maximum rate of heat evolution of CaO in Table 4, taking linear regression (see Fig. 6), we can calculate the activation energy of the hydrating reaction of CaO (see Table 5). Table 5 shows that, for the hydration reaction of CaO, the activation energy of industrial CaO containing impurities is twice as much as that of pure CaO. For the material with high activation energy, higher energy is needed for the creation and continuation of reaction. At the same temperature, the hydration rate of industrial CaO with high activation energy is lower than that of pure CaO with low activation energy. Rising reaction temperature increases the average kinetic energy of Ca^{2+} and OH^- (or CaO and H_2O molecules), accelerates their diffusion rate in solution and increases their mutual collision frequency. Besides, at higher temperature, more ions have enough energy to form an activated complex when they collide with other ions. Therefore, raising temperature can increase both collision energy and collision frequency. Thus, the reaction rate increases greatly, which has been confirmed by our experiment. With the increase of reaction temperature, the rate of heat evolution of CaO increases rapidly and the duration of the maximum rate of heat evolution and the duration of the whole reaction decrease greatly.

In the manufacturing process of Portland cement clinker, many kinds of oxides coexist and interact with each other. The f-CaO formed under this condition is bound to contain some other oxides and so has a higher hydration activation energy. Therefore, the ambient temperature of Portland cement, when stored for a long time or when it hydrates, has great influence on the dispelling and hydrating rate of f-CaO.

4. Conclusion

The hydration activity decreases with increase of calcination temperature. The essence of the effect of firing temperature on the hydration activity of CaO is to change its microstructure. The differences in the microstructure of CaO crystals formed at different temperatures result in its different hydration activity. When the firing temperature is raised, the crystallite size of CaO crystals increases, while the lattice distortion and crystal cell parameters decrease. The more perfect the lattice of CaO and the denser its structure, the lower the free energy of the crystal surfaces and the lower the hydration activity of CaO. The hydration activity of CaO is a macroscopic reflection of its microstructure.

The hydration rate of CaO is closely related to the hydration reaction temperature. Raising the hydration reaction temperature can make the reactant obtain enough energy to surmount reaction the potential barrier, thus increasing reaction rate effectively. The effect of the hydration reaction temperature on CaO with high activation energy and some impurities is more obvious than that on pure CaO. The f-CaO in Portland cement clinker forms in coexistence with many other oxides coexists. Thus, it has higher hydration activation energy, so the ambient temperature has a great influence on the disappearance and hydration rate of CaO.

Acknowledgments

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