Chemical Kinetics Analysis of Strength Development of Mortar Containing Fly Ash Based on Various Curing Temperatures

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Abstract. Due to large size and high internal temperature of hydraulic dams, the strength development process of damming materials is often faster than those under standard curing conditions. In order to further study the strength development features of damming materials under internal temperature conditions, two kinds of fly ash mortars were investigated, of which fly ash content is 40% and 30%. The compressive strength of mortars under three curing temperatures containing 20, 30 and 38℃ was tested at 3 days, 7 days, 14 days, 28 days, 56 days and 90 days, respectively. Then chemical kinetics equation was employed to describe the strength development features under different temperature conditions. The results show that the compressive strength of fly ash mortar increases with the increase of curing temperature in the range of 20 to 38 ℃. The main reason is that the chemical reaction rate of cementitious materials is accelerated by increasing curing temperature. For example, the hydration rate at 30℃ is 1.6 to 1.9 times of that at 20℃, and the hydration rate at 38℃ is 3.1 to 3.9 times of that at 20℃. In addition, the hydration rate of mortar with higher fly ash content is accelerated more. It can be seen that the apparent activation energy of mortar containing 40% of fly ash is 1.2 times of that with 30% of fly ash, and its chemical reaction barrier is higher. Therefore, the equivalent age of mortar with 40% of fly ash is longer and its compressive strength is improved more greatly under temperature-raising conditions.

1. Introduction
Large size and poor thermal conductivity are two prominent problems of hydraulic dams. The internal temperature often rises sharply due to lacking of timely heat release, generally as high as 40 to 50℃ [1]. It is obviously higher than the standard curing temperature, which is about 20 ℃. The mechanical properties of damming materials under internal temperature will also be different from those under standard curing conditions. It can be seen that it is unscientific to evaluate the actual service performance of dams based on the mechanical properties under standard curing conditions. Therefore, studying the mechanism that temperature affecting development features of mechanical properties is very important.

In terms of the influence of temperature on the mechanical properties of damming materials, Kim et al [2] accessed the effect of temperature on the compressive strength of concrete based on three actual temperature curves, of which temperature peaks were 40, 50 and 60°C, respectively. It was pointed out that the compressive strength, splitting tensile strength and elastic modulus of concrete increased with the increase of average temperature. Zhang et al [3] got similar conclusions drawn by Kim et al by testing the compressive strength, axial tensile strength and modulus of elasticity of concrete cured at 10, 25 and 40 ℃. It could be illustrated that the compressive strength, axial tensile strength and modulus of elasticity would increase with the increase of temperature in the range of 10 to 40°C. Topu1 et al [4]
further studied the effect of curing temperature at early age (at 9 hours) on the mechanical properties of concrete. It was pointed out that the compressive strength of concrete at 40 and 60 °C was 2.7 times and 3.7 times of that at 20 °C, respectively. The above research revealed a fact that increasing curing temperature could improve the mechanical properties of damming materials. However, how the compressive strength is improved and the relation with the composition of cementitious materials under higher curing temperature are still unknown.

In order to solve the above problems, two kinds of fly ash mortars were studied, and the compressive strength of mortars under three curing temperatures including 20, 30 and 38 °C was tested at 3 days, 7 days, 14 days, 28 days, 56 days and 90 days. Based on chemical kinetics, the strength development characteristics of mortars under temperature-rising conditions were analyzed.

2. Materials and mix compositions

2.1. Materials
A moderate heat Portland cement classified as P·MH 42.5 was employed. Its specific surface area was about 282 m²/kg. The strength of mortars tested according to Chinese standard specification GB 17671-1999 at 28 days, 90 days sand 180 days were 47.8 MPa, 57.4 MPa and 63.3 MPa, respectively. A fly ash with water requirement ratio of 104% and loss of ignition of 4.2% was used. Its activity indices at 7 days, 28 days, 90 days and 180 days were 59%, 83%, 85% and 91%, respectively. The fine aggregate was manufactured by crushing the rock into sand with a fineness modulus of 2.2 and a stone powder content of 21.5%. The water reducing agent was made of naphthalene, of which water reducing rate was 22% at mass content of 1.0%.

2.2. Mix compositions
Two fly ash mortars marked as F4050 and F3050 were investigated in this study, of which the mix compositions detailed in table 1.

| Mixtures | Cement | Fly ash | Water | Fine aggregate | Water reducer agent |
|----------|--------|---------|-------|----------------|---------------------|
| F4050    | 304    | 202     | 253   | 1459           | 2.5                 |
| F3050    | 354    | 152     | 253   | 1475           | 2.5                 |

3. Methodologies

3.1. Compressive strength experiments
The specimen dimension of mortars was 40mm×40mm×160mm. After fabricated, the specimens were cured at 20, 30 and 38°C, respectively. At the first 24 hours, air curing was used using a specific instrument. After that, the moulds were removed. The way to cure specimen was changed from air curing to water curing. All the specimens were immersed into the water. It would terminate at specified ages, which contained 3 days, 7 days, 14 days, 28 days, 56 days and 90 days. Among these three temperatures, 20°C represented standard curing temperature, 30 and 38°C were both regarded as typical internal temperatures of dam.

3.2. Chemical reaction rate constant, apparent activation energy and equivalent age

3.2.1. Chemical reaction rate constant calculation. Chemical reaction rate constant is an important parameter of chemical kinetics equation. It can reflect the hydration rate of cementitious material and reveal the influence of temperature on the strength of fly ash mortar. Based on the compressive strength and initial setting time at three curing temperatures, the chemical reaction rate constant $k$ can be obtained by fitting formula (1).
\[ S = S_u \frac{k(t-t_0)}{1 + k(t-t_0)} \]  

\(^1\)

\( S \) is the compressive strength at any time; \( t \) is the curing time; \( S_u \) is the ultimate compressive strength; \( t_0 \) is the initial setting time; \( k \) is the chemical reaction rate constant.

The initial setting time of mortars was tested by penetration resistance meter. During the tests, mortar was cured at the temperature of 20, 30 and 38 °C.

3.2.2. Apparent activation energy calculation. According to the Arrhenius equation marked as \(^2\), the natural logarithm of chemical reaction rate constant \( \ln(k) \) has linear relation with reciprocal of thermodynamic temperature \( 1/K \). Assume \( \ln(k) \) is a dependent variable and \( 1/K \) is an independent variable, therefore, \( E_a/R \) is the negative number of sloping, from which the apparent activation energy \( E_a \) can be obtained.

\[ \ln(k) = \ln(A) - \frac{E_a}{R} \times (1/T) \]  

\(^2\)

In equation \(^2\), \( k \) is the chemical reaction rate constant; \( R \) is the molar gas constant; \( T \) is the thermodynamic temperature; \( E_a \) is the apparent activation energy; \( A \) is the pre-exponential factor.

3.2.3. Equivalent age calculation. Equivalent age was calculated according to ASTM C1074 “Standard practice for estimating concrete strength by the maturity method”. The calculation of equivalent age is shown in equation 3. It can be seen that as long as the activation energy \( E_a \) is substituted, the expression of equivalent age can be obtained.

\[ t_e = \int_0^t \exp\left(\frac{E_a}{R} \left(\frac{1}{273 + T_r} - \frac{1}{273 + T}\right)\right) \, dt \]  

\(^3\)

In the formula, \( t_e \) is the equivalent age; \( E_a \) is the apparent activation energy; \( R \) is the molar gas constant; \( T_r \) is the reference temperature; \( T \) is the actual temperature; \( t \) is the curing time.

4. Results and discussions

4.1. Development features of compressive strength of fly ash mortars under various temperatures

The compressive strength of fly ash mortars is shown in Fig.1 and Fig.2. Curing temperatures including 20, 30 and 38 °C were considered as key factors for each mortar. It can be seen that the compressive strength of the two mortars both increase with the increase of curing temperature in the range of 20 to 38 °C.

The situations in which compressive strength of mortars are enhanced under higher temperature are shown in Fig.3. It could be seen that the maximum percentage of strength improvement of mortars at
30 °C was about 40%, while it was around 80% at 38 °C. As was also known that the compressive strength of mortar with 40% of fly ash was accelerated more than that of mortar with 30% of fly ash whatever the curing temperature was raised from 20 to 30 °C or from 20 to 38 °C. In other words, it was easier to promote the compressive strength of mortar with 40% of fly ash by raising temperature. It is closely related to hydration characteristics of fly ash. Because the hydration of fly ash requires enough alkaline environment usually provided by calcium hydroxide, which is the hydration product of cement.

Increasing curing temperature can accelerate the formation of calcium hydroxide, provide sufficient alkaline environment for fly ash hydration, and promote the early hydration of fly ash. Moreover, the higher the fly ash content, the stronger the hydration acceleration and the greater the compressive strength enhancement.

4.2. Chemical kinetics analysis of strength development considering curing temperature

4.2.1. Analysis of strength development based on chemical reaction rate constant and apparent activation energy. Compressive strength and initial setting time at three temperatures are needed as basic data for calculating chemical reaction rate constants. The compressive strength is shown in Fig. 1 and Fig. 2, and the initial setting time \( t_0 \) is shown in Table 2. The chemical reaction rate constants obtained by fitting formula (1) are shown in Table 3. It can be seen that it increases with the increase of curing temperature whatever the fly ash content is 40% or 30%.

| Table 2. Initial setting time of mortars under different temperatures \( t_0 \) (d) |
|-------------------------------|---|---|---|
| Mixtures | 20°C | 30°C | 38°C |
| F4050 | 0.50 | 0.46 | 0.42 |
| F3050 | 0.49 | 0.45 | 0.41 |

The chemical reaction rate constants of mortar with 40% of fly ash at 20, 30 and 38 °C were 0.02447, 0.04735 and 0.09631, respectively. The chemical reaction rates at 30 and 38°C were 1.9 and 3.9 times as those at 20 °C. The chemical reaction rate constants of mortar including 30% of fly ash at 20, 30 and 38 °C were 0.03787, 0.06085 and 0.11901, respectively. The chemical reaction rates at 30 and 38°C were 1.6 and 3.1 times as those at 20 °C. As is known that the hydration rate of mortars containing 30% to 40% of fly ash at 30 and 38°C is 1.6-1.9 times and 3.1 to 3.9 times of those at 20 °C.

It can be found that the chemical reaction rates of mortars with 30% of fly ash and 40% of fly ash at 30 °C are 1.9 times and 1.6 times of those at 20 °C, respectively, and 3.9 times and 3.1 times at 38 °C, respectively. As curing temperature increases by the same extent, the chemical reaction rate of mortar with 40% of fly ash increases faster and is more sensitive to the temperature-raising conditions.
Apparent activation energy can be calculated according to chemical reaction rate constant $k$ and formula (2). The correlation curve between $\ln (k)$ and $1/K$ is shown in Fig. 4. There was a good linear relationship between them. The calculated apparent activation energy is shown in Table 3. The apparent activation energy $E_a$ of mortar with 40% of fly ash, mortar with 30% of fly ash were 57.2 kJ/mol and 47.5 kJ/mol, respectively. The former was 1.2 times as much as the latter. This is because the activity of fly ash is low, and the total molar energy required for elementary reaction will be increased with the increase of fly ash content, and the chemical reaction barrier will be increased [5]. Low barrier mortar is relatively easy to be stimulated, while high barrier mortar is more difficult to stimulate. Therefore, increasing temperature is more significant for mortar with 40% of fly ash.

| Mixtures | Curing temperatures (℃) | $k$ | $E_a$ (kJ/mol) |
|----------|-------------------------|-----|----------------|
| F4050    | 20                      | 0.02447 | 57.2          |
|          | 30                      | 0.04735 |
|          | 38                      | 0.09631 |
| F3050    | 20                      | 0.03787 | 47.5          |
|          | 30                      | 0.06085 |
|          | 38                      | 0.11901 |

Figure 4. Linear relation between $\ln(k)$ and $1/K$

4.2.2. **Analysis of the compressive strength development of based on equivalent age.** As mentioned above, the apparent activation energies of mortar with 40% of fly ash and mortar with 30% of fly ash are 57.2 kJ/mol and 47.5 kJ/mol, respectively. By introducing the apparent activation energy into formula (3), the equivalent age expressions of these two mortars can be obtained, as shown in formula (4) and formula (5). Equivalent age can quantitatively reflect the rapid hydration characteristics of mortar by increasing curing temperature. Equivalent ages of mortars at 20, 30 and 38 ℃ are shown in Fig. 5.

$$t_e = \int_0^t \exp(6880 \times \frac{1}{273+20} - \frac{1}{273+T}) \, dt$$  \hspace{1cm} (4)

$$t_e = \int_0^t \exp(5713 \times \frac{1}{273+20} - \frac{1}{273+T}) \, dt$$  \hspace{1cm} (5)
Figure 5. Equivalent age for mortars with 30% or 40% of fly ash

It can be seen that the equivalent ages of mortar with 40% of fly ash, mortar with 30% of fly ash are 195 days and 171 days at 30 °C, respectively. 350 days and 278 days at 38 °C, respectively. The equivalent ages of mortars were 1.9 to 3.9 times of the testing age at 20 °C. It showed that raising curing temperature can significantly accelerate the hydration process of cement and fly ash.

In addition, the equivalent age of mortar with 40% of fly ash is greater than that of mortar containing 30% of fly ash no matter the curing temperature is 30 ℃ or 38 ℃. That’ why its increase of compressive strength is greater.

5. Conclusions
The compressive strength of fly ash mortar increases with the increase of curing temperature in the range of 20 to 38°C. The compressive strength improvement of mortar with 40% of fly ash is higher than that of mortar including 30% of fly ash.

For the composite cementitious materials containing 30% to 40% of fly ash, the hydration rate is 1.6 to 1.9 times at 30°C, and 3.1 to 3.9 times at 38°C as those at 20°C.

The apparent activation energy of mortar with 40% of fly ash is 1.2 times as that of mortar with 30% of fly ash under the water-binder ratio of 0.50. Its chemical reaction barrier is higher and the activity is more difficult to activate. Increasing curing temperature is an important means to break through the barrier, which is more significant for mortar with 40% of fly ash.

Acknowledgments
This work was financially supported by National Key research and development plan (Grant No. 2016YFC0401610), National science fund project (Grant No. 51739008) and Natural Science Foundation of Jiangsu Province (Grants No. BK 20181516).

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