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Cement Hydration Rate of Ordinarily and Internally Cured Concretes

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Abstract

In the present paper, adiabatic temperature rise test was used to evaluate the effect of internal curing on cement hydration rate and final degree of hydration in normal and high strength concretes. In the experiments, emphases were placed on the impacts of internal curing and water to cementitious material ratio on the adiabatic temperature rise characteristics. Two kinds of concrete, ordinarily cured concrete and internally cured concrete were used in the experiments. In each kind, four concrete mixtures with water to cementitious material ratios of 0.20, 0.30, 0.43 and 0.62 were used. The test results show that internal curing with PSLWA increases temperature rise of concrete, whatever the concrete strength is low or high. Internal curing can not only increase the ultimate temperature rise, but also increase the rate of temperature rise. Internal curing can obviously improve the cement hydration behavior compared with the concrete without internal curing. The improvements on cement hydration may present in two. One is the hydration rate in the second stage is increased; another is the final cement hydration degree is increased. For internally cured concrete, the water used to calculate the water to binder ratio can be simply summing the mixing water and internal curing water together when calculate the final cement hydration degree. The proposed cement hydration rate model can well predict developing of cement hydration degree for both ordinarily and internally cured concretes.

1. Introduction

Shrinkage and thermal deformation occurred in concrete are thought to be the major sources of the formation of cracks in concrete. Cracks allow water and chemical agents, such as deicing salt, to go into concrete and contact with the reinforcement, leading to reinforcement corrosion and rupture in steel reinforced concrete. The progress of shrinkage since set of concrete is normally derived by chemical shrinkage of cement paste in the first short beginning stage with moisture saturation, displayed as internal relative humidity close to 100%, and capillary force developed in the capillary pores due to forming empty curved capillary pores in the following stage of relative humidity decreasing. Therefore, to fill the empty capillary pores in time should reduce the capillary force, which in turn decreases shrinkage of concrete. This is the basic principle of internal curing using pre-wetted lightweight aggregates or super absorbing polymers for shrinkage reduction. Number of existing tests shows positive affects of internal curing with lightweight aggregates or super absorbing polymers on shrinkage decrease not only for high strength concrete, but also for normal strength concrete (Zhang et al. 2016). This technique may allow high strength concrete to be used in more fields, including those structures more sensitive to shrinkage cracking, such as bridge decks, industrial floor, subway segments. However, most of the existing studies on internally cured concrete are focused on shrinkage performance. The following properties of internally cured concrete, including mechanical properties, permeability and long term durability are critically needed to be investigated as well apart from shrinkage performance, due to the inclusion of porous materials in concrete.

To well understand the effect of internal curing on mechanical and durability properties of concrete, possible impact of internal curing water on cement hydration rate during hardening of concrete has to be learnt first. Concrete is a multiphase system where the voids of the skeleton formed by aggregates and cement powders are filled with hydration products of cement, liquid water and partly with a gas mixture composed of air and water vapor. After mixing with water, the volume of hydration products of cement, liquid water and partly with a gas mixture composed of air and water vapor. After mixing with water, the volume of hydration products gradually increases with time and the total volume of pores is gradually decreased. Developing concrete strength and other mechanical properties is principally influenced by the degree of reaction between cement and water, which in turn is controlled by water to cement ratio and temperature in place. Therefore, it is reasonable to expect the extra water released from LWA or SAP should take part in cement hydration and enhance mechanical or durability properties of the internally cured concrete. This positive effect may be partly composite the negative effect of porous particles on the mechanical or durability properties of the concrete. About the determination cement hydration degree of concrete, several methods have been developed in the past. The direct determination of the degree of cement hydration degree
cured concrete and internally cured concrete was evaluated cement hydration rate in two kinds of concrete, normally estimate the degree of cement hydration by measuring TCE1 1997; ASTM C1702-09a 2009) and to indirectly determination in massive concrete (RILEM Recommendation test, which has been utilized to investigate the heat generated by means of optical microscopy or quantitative X-ray diffraction analysis. For CSH gel, it is almost impossible to obtain the accurate content. For concrete with addition of silica fume, slag or fly ash, the single measurement on content of calcium hydroxide may not well reflect the actual cement hydration degree due to pozzolanic reaction. Further, for continuously monitoring cement hydration degree, especially for concrete at very early age, and/or under varied temperature history, the optical microscopy or quantitative X-ray diffraction analysis may not be convenient. The indirect determination of degree of cement hydration may be carried out by measuring some properties of hardening concrete, for example the compressive strength, the amount of non-evaporable water, and the heat release of hydration (Parrotta et al. 1990). For in-place monitoring of cement hydration status, most of the above methods are not applicable because it cannot determine the content of specific material continuously. In such case, the indirect method, adiabatic temperature test, which has been utilized to investigate the heat generation in massive concrete (RILEM Recommendation TCE1 1997; ASTM C1702-09a 2009) and to indirectly estimate the degree of cement hydration by measuring the temperature rise, may be suitable. In present work, cement hydration rate in two kinds of concrete, normally cured concrete and internally cured concrete was evaluated by adiabatic temperature rise tests. In each kind of concrete, four concrete mixtures with water to cementitious material ratios (w/b) of 0.20, 0.30, 0.43 and 0.62 were designed, which represents low, middle, high and extra high strength concretes in practice, respectively. The effects of water to binder ratio, and internal curing, on temperature rise and cement hydration rate were analyzed.

2. Experimental programs

To study the effects of internal curing and water to binder ratio on cement hydration rate of concrete, first, four basic concrete mixtures with water to cementitious materials ratio (w/b) of 0.62, 0.43, 0.30 and 0.20 are designed to form four concretes with compressive strength at 28 days around 30 MPa, 50 MPa, 80 MPa and 100 MPa respectively, labeled as C30-OC, C50-OC, C80-OC and C100-OC, representing normal cured low, middle, high and extra high strength concretes in practice. Based on above four basic mixtures, another four mixtures were designed with some of normal aggregates replaced by PSLWA to form four additional corresponding concretes with internal curing, labeled as C30-IC, C50-IC, C80-IC and C100-IC respectively. The mixture of concrete containing lightweight aggregate is designed according to the amount of internal curing water needed based on each normal cured concrete (Zhang et al. 2013). Slightly lower water to cement ratios compared to the reference was used in the mixture with PSLWA to maintain a similar compressive strength between the two concretes with and without internal curing of each strength grade. In this study, fly ash based lightweight aggregate with particle size of 2 to 5 mm, porosity of 0.27, water absorption of 21% after 7 days of soaking, dry density of 1375 kg/m³ was used as carrier of internal curing water. Figure 1 is the photograph of the lightweight aggregate used in experiments. All concrete mixtures were made with the same type of Portland cement called ordinary Portland cement with Grade of 42.5 in Chinese standard. Oxide and compound compositions of the cement are listed in Table 1. Natural sand and crushed limestone with a maximum particle size of 5 mm and 25 mm, respectively, were used as fine and coarse aggregates. The concrete mixture proportions used in the present work are listed in Table 2. A superplasticizer admixture was used in these mixtures to guarantee the fresh concretes have a similar slump of 90-120 mm. For concrete mixing, first, the fine and coarse aggregates were mixed together. Next, the cement was added followed by the required water with the superplasticizer mixed in advance and the mixing was continued for 3 min. Then the fresh concrete was cast into the 50 liter container and compacted on a vibrating table for 1.5 min. After finishing the surface, the test sample was moved into the adiabatic temperature rise testing machine for temperature rise test until 7 days. Equipment used for the adiabatic temperature rise test is illustrated in Fig. 2. The outside heater starts to work only when the difference between the center temperature of the concrete sample and the average temperature of the three sensors fixed outside the sample achieved a pre-designed value of 0.1°C. The power of an external heat source may be adjusted according to the actual temperature difference.

Fig. 1 Lightweight aggregate used in experiments.
and the increasing rate of the sample center temperature to prevent overheating. The larger the temperature difference becomes, the longer and the more intense the heater needs to work. In such way, the heat loss during the test may be eliminated or minimized and adiabatic temperature rise may well be maintained.

3. Results and analyses

3.1 Effect of internal curing on the adiabatic temperature rise of concrete

The adiabatic temperature rise test results of the eight mixtures are presented in Figs. 3a to 3d in terms of temperature rise versus age diagrams, where the results of the mixtures with similar strength grade are presented in one figure to clearly watch the effect of internal curing on adiabatic temperature rise of concrete. From these results, we can first find that all the temperature rise-age diagrams obey a three-stage promoting under adiabatic condition, a relative slow developing stage, followed by a fast developing stage and a nearly steady-state stage, in which a constant temperature rise is gradually approached. The higher the concrete strength, the higher the temperature rise. Second, internal curing with PSLWA increases temperature rise of concrete, whatever the concrete strength (or water to binder ratio) is low or high. Based on present tests, the temperature rise at end of test of 7 days since casting is 32.7°C, 45.0°C and 49.7°C for normal concretes, C30-OC, C50-OC and C80-OC respectively, and 39.4°C, 49.7°C and 54.8°C for

Table 1 Oxide of cement, silica fume, fly ash and compound compositions of cement.

| Oxide | Percentage | Cement Compound | Percentage | Silica Fume Percentage | Fly Ash Percentage |
|-------|------------|------------------|------------|------------------------|-------------------|
| CaO   | 60.28      | C_3S             | 49.58      | 0.81                   | 5.08              |
| SiO₂  | 23.47      | C_2S             | 28.04      | 90.56                  | 47.02             |
| Al₂O₃ | 7.41       | C₆A              | 7.28       | 0.41                   | 35.06             |
| Fe₂O₃ | 2.97       | C₆AF             | 8.57       | 0.52                   | 3.88              |
| MgO   | 1.97       |                  |            | 0.95                   | 1.36              |
| K₂O   | 0.62       |                  |            | 1.59                   | 1.30              |
| Na₂O  | 0.14       |                  |            | 0.63                   | 1.18              |
| SO₃   | 2.39       |                  |            | 0.89                   | 0.89              |
| Loss  | 2.8        |                  |            | 3.72                   | 1.85              |

Table 2 Mix proportions of concrete and compressive strength and elastic modulus at 28 days.

| No.  | Cement (kg/m³) | Silica Fume (kg/m³) | Fly Ash (kg/m³) | Water (kg/m³) | Sand (kg/m³) | Stone (kg/m³) | Dry LWA (kg/m³) | Water provided by LWA (kg/m³) | Compressive Strength (MPa) | Elastic modulus (GPa) |
|------|----------------|---------------------|-----------------|---------------|--------------|---------------|----------------|-----------------------------|---------------------------|-----------------------|
| C30-OC | 240            | -                   | 60              | 186           | 750          | 1150          | 0              | 0                           | 37.9                      | 34.3                  |
| C30-IC | 252            | -                   | 63              | 181           | 473          | 1090          | 0              | 0                           | 54.7                      | 42.1                  |
| C50-OC | 345            | -                   | 85              | 185           | 685          | 1090          | 0              | 0                           | 82.1                      | 48.1                  |
| C50-IC | 367            | -                   | 92              | 175           | 409          | 808           | 0              | 0                           | 85.8                      | 38.7                  |
| C80-OC | 450            | 50                  | -               | 150           | 580          | 1140          | 0              | 0                           | 105.6                     | 53.5                  |
| C80-IC | 494            | 55                  | -               | 134           | 309          | 864           | 281.3          | 59.3                        | 108.9                     | 43.6                  |
| C100-OC | 540           | 60                  | -               | 119           | 590          | 1156          | 0              | 0                           | 108.9                     | 43.6                  |
| C100-IC | 550           | 64                  | -               | 94            | 310          | 900           | 310            | 65.1                       | 108.9                     | 43.6                  |

![Heat compensation device](image1.png)

![Heat-insulation material](image2.png)

Fig. 2 Set-up for adiabatic temperature rise test of concrete.
internal cured concretes, C30-IC, C50-IC and C80-IC respectively. Meanwhile, from the figures, it can be observed that internal curing cannot only increase the final temperature rise, but also increase the rate of temperature rise. This means that internal curing may promote cement hydration, which may present either in hydration rate, or final hydration degree, even though the thermal capacity of the concretes may vary because of the change of mixture proportion. This positive effect on cement hydration may improve microstructures of cement paste, which in turn, impact the long-term performance of concrete.

3.2 Determination of cement hydration degree from adiabatic temperature rise test
The reaction between Portland cement and water is an exothermic process. If adiabatic condition between the test sample and environment is satisfied, the temperature inside the concrete sample should gradually increase with hydration age, and finally goes into steady state with a nearly constant temperature. Thus, from concrete adiabatic temperature rise test, the degree of cement hydration, $\alpha$ at given time $t$ may be defined as the ratio of the heat released up to time $t$ of the given volume or weight of concrete, $H(t)$ to the total heat as the cement is completely hydrated, $H_\infty$ as:

$$\alpha = \frac{H(t)}{H_\infty}$$

(1)

If assume the heat capacity of concrete during hardening is a constant, the above expression may rewrite as

$$\alpha = \frac{\Delta T(t)}{\Delta T_\infty}$$

(2)

where $\Delta T(t)$ is the adiabatic temperature rising at time $t$ and $\Delta T_\infty$ is the adiabatic temperature rise as the cement is completely hydrated.

Each of the cement constituents has a unique heat of hydration (Bogue 1947). The total heat of cement hydration per unit weight of portland cement can be estimated from their composition (Table 3) by (Schindler et al. 2005):

![Fig. 3 Temperature rise versus curing age diagrams of three series of concretes, (a) C30, (b) C60, (c) C90 and (d) C100 series.](image-url)
Maekawa (1995) and Maekawa heat into account in the present study. Additional cementitious materials on cement hydration equation (3) is revised as (4) to take the effect of the cement in kJ/kg.

\[ H_0 = 500p_{C_S} + 260p_{C_S} + 866p_{C_A} + 420p_{C_A} + 624p_{SO_3} + 1186p_{FA} + 850p_{MgO} \]  

\[ H_c = M_c H_0 \]  

where \( H_0 \) is total heat of hydration of per unit weight of cement in kJ/kg. \( P_i \) is the weight ratio of each contributing component to cement hydration heat. Constant behind each constituent in equation (3) is the hydration heat per unit weight of the constituent that was determined directly with pure material (Bogue 1947). For concrete with additional cementitious materials used, the total hydration heat of cement may differ from (3). Existing studies show that the use of silica fume (SF) and fly ash (FA) will influence the total hydration heat of cement (Kishi and Maekawa 1995; Schindler et al. 2005; Maekawa et al. 2009; Wang et al. 2012). Based on the results of the contribution of fly ash and silica fume to the total hydration heat of cement presented by Kishi and Maekawa (1995) and Maekawa et al. (2009), for concrete with fly ash and silica fume used respectively, equation (3) is revised as (4) to take the effect of the additional cementitious materials on cement hydration heat into account in the present study.

\[ H_0 = 500p_{C_S} + 260p_{C_S} + 866p_{C_A} + 420p_{C_A} + 624p_{SO_3} + 1186p_{FA} + 850p_{MgO} \]  

\[ H_c = M_c H_0 \]  

where \( M_c \) is the mass of cement used in the concrete sample. From (3) and (4), the complete hydration heat per kilogram of cement in C30, C50 (cement and fly ash system) and C80, C100 (cement and silica fume system) used in present work is estimated as 400.8 kJ/kg and 450.0 kJ/kg respectively. For pure cement, without any extra cementitious materials, the value is 448.7 kJ/kg.

Considering the dispute on the slight variation of the heat capacity of concrete during the hydration process (De Schutter et al. 1995, 1996; Van Breugel 1991; Larrard 1999), present work assumes the heat capacity of concrete is only a function of the initial constituents and is estimated as:

\[ c = 1.05(p_c c_w + p_f c_f + p_s c_s + p_a c_a + p_{FA} c_{FA} + p_{LWA} c_{LWA}) \]  

where \( c \) is the specific heat capacity of concrete in kJ/(kg°C). \( c_w, c_s, c_a, c_f, c_{FA} \) and \( c_{LWA} \) are the specific heat capacity of cement, water, sand, stone, fly ash or silica fume and lightweight aggregate respectively, they are equal to 0.86, 4.19, 0.82, 0.82, 0.86 and 0.86 kJ/(kg°C) respectively. \( p_c, p_f, p_s, p_{FA} \) and \( p_{LWA} \) are the mass fraction of cement, water, sand, stone, fly ash or silica fume and lightweight aggregate respectively in concrete. Thus, the total temperature rise expected in the adiabatic temperature rise test as cement is completely hydrated, \( \Delta T_c \), can be calculated by:

\[ \Delta T_c = \frac{W_c H_0}{W_c c} \]  

where \( W_c \) is the mass of cement (kg) in the concrete sample used in the adiabatic temperature rise test. \( W_t \) is the concrete mass in the temperature rise test (kg). The specific heat capacity, expected total temperature rise of all concretes used in the present test program is listed in Table 4. Using the temperature measured in the adiabatic temperature rise test in equation (2), cement hydration degree at a given age can be obtained.

**Table 3 Composition of cementitious materials in each concrete.**

| No. | C_A | C_S | C_4A | C_4AF | SO_3 | MgO | FA | SF |
|-----|-----|-----|------|-------|------|-----|----|----|
| C30-OC | 38.54 | 6.23 | 23.30 | 6.42 | 1.71 | 1.66 | 20.0 | 0 |
| C50-OC | 38.66 | 6.25 | 23.37 | 6.44 | 1.72 | 1.66 | 19.8 | 0 |
| C80-OC | 43.36 | 7.01 | 26.22 | 7.23 | 1.93 | 1.86 | 0 | 10.0 |
| C30-IC | 38.54 | 6.23 | 23.30 | 6.42 | 1.71 | 1.66 | 20.0 | 0 |
| C50-IC | 38.54 | 6.23 | 23.30 | 6.42 | 1.71 | 1.66 | 20.0 | 0 |
| C80-IC | 43.36 | 7.01 | 26.22 | 7.23 | 1.93 | 1.86 | 0 | 10.0 |
| C100-OC | 43.36 | 7.01 | 26.22 | 7.23 | 1.93 | 1.86 | 0 | 10.0 |
| C100-IC | 43.36 | 7.01 | 26.22 | 7.23 | 1.93 | 1.86 | 0 | 10.0 |

**Figures 4a to 4d** display the diagram of cement hydration degree and age of the four groups of concretes from C30 to C100 respectively. From these results, first we can observe that the progress of cement hydration degree under adiabatic condition follows a similar trade
as the temperature rise does, which includes a first relative slow stage, then a fast developing stage and next a nearly steady-state stage, in which a constant cement hydration degree is almost approached finally. Second, the effects of concrete strength or water to binder ratio, on cement hydration, either in cement hydration rate or in final hydration degree, are significant. With increase of concrete strength or decrease of water to binder ratio, cement hydration rate in the highly developing stage is gradually increased. The higher the concrete strength or the lower the water to binder ratio, the lower the final cement hydration degree that is approached at the end of the adiabatic temperature rise test. From the present study, the final cement hydration degree at the end of the test is 0.89, 0.81, 0.60 and 0.48 respectively for C30, C50, C80 and C100. This is coincident with existing results about the effect of water to cement ratio on cement hydration degree (Zhang et al. 2014). Third, as internal curing with pre-wetted lightweight aggregate is used in concrete, cement hydration behavior is obviously enhanced compared to the corresponding concrete without internal curing. These enhancements on cement hydration may present in two aspects. One is the hydration rate in the second stage is raised. Another is the time used to

Table 4 Calculation result of total temperature rise of all concretes.

| No. | c (kJ/kg°C) | $H_\infty$ (kJ/kg) | $\Delta T_\infty$ (°C) | $\alpha_u$ | $\Delta T_{\text{max}}$ (°C) |
|-----|-------------|--------------------|----------------------|------------|-----------------------------|
| C30-OC | 1.0877     | 400.819            | 44.86                | 0.8853    | 39.71                       |
| C50-OC | 1.0881     | 401.377            | 61.94                | 0.8106    | 50.21                       |
| C80-OC | 1.0417     | 460.397            | 89.26                | 0.6014    | 53.69                       |
| C100-OC | 0.9702    | 460.397            | 116.31               | 0.4394    | 51.10                       |
| C30-IC | 1.1911    | 400.819            | 46.26                | 0.9222    | 42.66                       |
| C50-IC | 1.1715    | 400.819            | 62.21                | 0.8412    | 52.33                       |
| C80-IC | 1.1053   | 460.397            | 91.28                | 0.6299    | 57.50                       |
| C100-IC | 1.0379   | 460.395            | 113.27               | 0.5210    | 59.02                       |

Fig. 4 Cement hydration degree versus age diagrams of four concretes.
achieve the final steady-state is reduced. And, the third is the final cement hydration degree is increased. Based on the present study, the final cement hydration degree at the end the test is 0.92, 0.84, 0.63 and 0.52 respectively for C30-IC, C50-IC, C80-IC and C100-IC. Clearly, the extra water provided by the pre-wetted lightweight aggregate can not only reduce the shrinkage that is the normally purpose of internal curing (Han et al. 2014), but also can improve cement hydration performance, which may enhance the mechanical properties of concrete as well.

3.3 Simulation of cement hydration rate in internally cured concrete

The above degree of cement hydration, and its variation with age is obtained based on a specific temperature developing history. To know the degree of cement hydration under different temperature histories, such as different construction seasons or curing conditions, the effect of temperature on cement hydration must be taken into account. Therefore, a concept called equivalent age was introduced (Kjellsen et al. 1993). The equivalent age concept assumed that samples of a concrete mixture of the same equivalent age will have the same mechanical properties or degree of cement hydration, regardless of the temperature history. Based on the above definition, the equivalent age \( t_{eq} \) can be expressed as

\[
t_{eq} = \int_{0}^{t} \frac{K(T)}{K(T_{ref})} dt
\]  

(8)

where \( t_{eq} \) is the equivalent age at the reference temperature \( T_{ref} \). \( K(T_{ref}) \) and \( K(T) \) are the rate constants of cement hydration at reference temperature \( T_{ref} \) and the actual temperature \( T \). According to the Arrhenius law, the rate constant can be expressed as

\[
K(T) = Ae^{\frac{U_{a}}{R(T+273)+T}}
\]  

(9)

where \( U_{aT} \) is the apparent activation energy (J/mol). \( R \) is the universal gas constant, 8.314 J/molk and \( A \) is a constant. \( T \) is temperature in Celsius (°C). Replacing \( K(T) \) and \( K(T_{ref}) \) with (9) in (8) yields

\[
t_{eq} = \int_{0}^{t} \frac{1}{e^{\frac{U_{as} - U_{st}}{R(T+273)+T}}} dt
\]  

(10)

where \( T_{ref} = 20°C \) is assumed. Regarding apparent activation energy, a number of researchers have concluded that it could not be considered as a constant independent of time except during the beginning of cement hydration (Kjellsen et al. 1993; Kim 2001). Based on these studies, the apparent activation energy of cement is expressed as a function of temperature and curing time as (Pane and Hansen 2002):

\[
U_{a} = (42830 - 43T)e^{(-0.000177)t}
\]  

(11)

where \( T \) is curing temperature (°C) and \( t \) is curing time in days. Due to the varying curing temperature \( T \) inside of concrete, it is convenient to solve \( t_{eq} \) in the matrix form instead of integrating. If the curing time is divided into \( n \) sections and the temperature in each time interval is assumed to be a constant, then we have

\[
t_{eq} = \sum_{i=1}^{n} e^{\frac{U_{as} - U_{st}}{R(T_{i}+273)+T_{i}}} (t_{i}-t_{i-1})
\]  

(12)

The section number \( n \) may depend on the required accuracy. Thus, the relationship between degree of cement hydration and equivalent age can then be obtained from the test results of adiabatic temperature rise test and which may serve as a standard curve for solving the cement hydration status of concrete under different curing conditions and at any curing age as well. Figures 5a and 5b present the relationship of cement hydration degree and equivalent age of normal concretes and internal curing.
cured concrete respectively. After taken the effect of temperature into account, the shape of the curve changes from a three-stage mode into a simply two-stage manner, which means the first slowly progressing stage is just due to the low temperature of the fresh concrete.

From above test results of cement hydration degree in different concretes ring from compressive strength at 28 days of 30 MPa to 100 MPa, we may be obviously noted that the final cement hydration degree is less than 1, and is dependent on concrete strength or water to cement ratio, which was found by Mills (1966) with pure cement paste and Schindler et al. (2005) and Luzio et al. (2009) with additional cementitious materials apart from cement used. Mills (1966) measured the degree of cement hydration in cement paste of different water to cement ratios (w/c) by weighting the nonevaporable water and found that most cement paste stops hydrating before the cement are completely consumed. To characterize the ultimate state of the hydration reaction of cement in different concretes, a parameter called ultimate degree of hydration, $\alpha_u$ was introduced. Existing studies show that $\alpha_u$ is mainly controlled by water to cement ratio and the relationship between $\alpha_u$ and water to cement ratio are investigated. Mills (1966) proposed a relationship between $\alpha_u$ and water to cement ratio (w/c) for pure Portland cement concrete as:

$$\alpha_u = \frac{1.031(w/c)}{0.194 + (w/c)}$$  \hspace{1cm} (13)

In the view of micro mechanisms, above relationship means that the final cement hydration degree in concrete is principally controlled by the amount of water by that each cement particle is surrounded. For concrete with fly ash addition, such as C30 and C50 concrete used in the present work, above equation is revised as (Schindler and Folliard 2005):

$$\alpha_u = \frac{1.031w/(c + f) + 0.50f/(c + f)}{0.194 + w/(c + f)} \leq 1.0$$  \hspace{1cm} (14)

For concrete with silica fume, such as C80 and C100 concrete used in the present paper, $\alpha_u$ can be expressed as (Luzio and Cusatis 2009):

$$\alpha_u = \frac{1.031w/(c + s) + 0.50s/(c + s)}{0.194 + w/(c + s)}$$  \hspace{1cm} (15)

where $w$, $c$, $f$ and $s$ are mass content of water, cement, fly ash and silica fume in concrete. Above revising takes the effect of the addition of additional cementitious materials reducing the water surrounding cement particles, and the effect of activity of fly ash into account.

To further verify the validation of above equations, isothermal calorimetric tests on pure cement, cement and fly ash (weight percentage: 80% cement + 20% fly ash), cement and silica fume (weight percentage: 90% cement + 10% silica fume) systems with relatively large variation of water to binder ratio from 0.3 to 1.2 were carried out. The value of $\alpha_u$ of each mixture is estimated by the ratio of the released heat as steady state of heat releasing is closed to the total heat at complete hydration of cement. The test results of isothermal calorimetric tests in terms of heat generation in joule per gram of cement and age since mixing with water of the three cementitious systems are presented in Figs. 6a to 6c respectively. From Fig. 6, the final cement hydration degree corresponding to each of water to binder ratio in each cement system can thus be estimated. Meanwhile, for given water to binder ratio, the value of $\alpha_u$ can also be calculated from (13) to (15) respectively for pure cement, cement and fly ash, and cement and silica fume systems respectively. The model and test results on the relationship between $\alpha_u$ and water to binder ratio of each series are presented in Fig. 7. It can be seen that the model and the test results are agreeing with each other well, which indicates the model can be used for prediction of ultimate cement hydration of cement in different cementitious systems.

For internally cured concrete, it is an issue if the above model can still be used. Due to the internal curing water is provided by the relatively coarse lightweight aggregate. The impact of internal curing water on heat releasing performance cannot be determined from above isothermal calorimetric tests. However, from the results of adiabatic temperature rise tests of internal cured concrete (see Fig. 3), it can be seen that a steady-state value of the temperature rise is almost achieved. Therefore, the final cement hydration degree is simply estimated using the finial temperature at the end of the adiabatic temperature rise test. While the corresponding water used to calculate the water to binder ratio is simply summing the mixing water and internal cured water together as:

$$\frac{W}{B} = \frac{W_c + W_{ic}}{B}$$  \hspace{1cm} (16)

Thus, the determined $\alpha_u$ of internal cured concrete (C30-IC, C50-IC, C80-IC, C100-IC) are displayed in Fig. 7 as well. Obviously, the determined $\alpha_u$ (red marks) is close enough to the model, which means the internal curing water provided by the lightweight aggregate used in the present work can simply be considered as a part of mixing water. This is understandable because as internal relative humidity of concrete decrease from 100% to 97%, about 90% water contained in the lightweight aggregate should be released and flowed into the capillary pores. The cement hydration degree is therefore increased due to its actual higher water to cement ratio.

Based on the experimental results displayed in Fig. 5, the relationship between $\alpha$ and $t_0$ is simulated using the modified model based on Pane et al. (2002) as:

$$\alpha = \alpha_{exp} \left[ \frac{\left( \frac{A}{t_0 + t_0} \right)^n}{B} \right]$$  \hspace{1cm} (17)

where $A$, $B$ and $t_0$ are constants determined by fitting the experimental results with the model. The comparison between model and test results are displayed in Figs. 8 and 9 respectively for ordinarily cured concrete and
internally cured concrete, in which figure (a) displays the complete results and figure b displays the beginning part of the results. The corresponding values of $A$, $B$ and $t_0$ of each series of concrete are listed in Table 5. Clearly, the model can correctly predict the development of the degree of cement hydration with equivalent age of the four series of concrete with water to binder ratio of 0.20, 0.30, 0.43 and 0.62. From Table 5, we may observe that the constant $A$, $B$ and $t_0$ are mainly used to describe the progress of cement hydration in a given concrete, which is obviously dependent on water to binder ratio. Parameter $A$ decreases a bit with the increase of water to binder ratio. While, parameter $B$ increases a little with increase of water to binder ratio. Parameter $t_0$ increases a little with increase of water to binder ratio as well. For internally cured concrete, similar variation trend of $A$, $B$ and $t_0$ are observed. However, a higher value of $A$, $B$ and $t_0$ are used for the internally cured concrete than that of ordinarily cured concrete for the same water to binder ratio. These differences may well reflect the development of cement hydration degree of the two kinds of concrete.

### 4. Conclusions

In this paper, cement hydration degree in concrete is evaluated indirectly by adiabatic temperature rise tests. In the experiments, emphases were given to the impacts of internal curing on the adiabatic temperature rise characteristics and the development of degree of cement hydration. Two kinds of concrete, normally cured concrete and internal cured concrete were used in the experiments. In each kind, four concrete mixtures with
water to cementitious material ratios (w/b) of 0.20, 0.30, 0.43 and 0.62 were used. To further verify the validation of the existing models for predicting the ultimate degree of cement hydration, additional isothermal calorimetric tests on pure cement, cement and fly ash, cement and silica fume systems were carried out as well.

The test results show that internal curing with PSLWA increases temperature rise of concrete, whatever the concrete strength is low or high. Internal curing cannot only increase the final temperature rise, but also increase the rate of temperature rise. Meanwhile, internal curing can obviously improve the cement hydration compared to the concrete without internal curing. The improvements on cement hydration may present in two. One is the hydration rate in the second stage is increased, the time used to achieve the final steady-state is reduced; another is the final cement hydration degree is increased. For internal cured concrete, the corresponding water used to calculate the water to binder ratio may be simply by summing the mixing water and internal cured water together as it was used to calculate the final cement hydration degree. For normal and internal cured concrete, the development of degree of cement hydration with equivalent age can be described as an initially fast developing stage, followed by a stage with a gradually reduced rate and finally close to a steady-state stage. The proposed cement hydration degree model can well predict the development of cement hydration degree in both normal and internal cured concretes.

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