

# Model for simulating the effects of particle size distribution on the hydration process of cement

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**Abstract.** The hydration of cement contributes to the performance characteristics of concrete, such as strength and durability. In order to improve the utilization efficiency of cement and its early properties, the particle size distribution (PSD) of cement varies considerably, and the effects of the particle size distribution of cement on the hydration process should be considered. In order to evaluate effects of PSD separately, experiments testing the isothermal heat generated during the hydration of cements with different particle size distributions but the same chemical composition have been carried out. The measurable hydration depth for cement hydration was proposed and deduced based on the experimental results, and a PSD hydration model was developed in this paper for simulating the effects of particle size distribution on the hydration process of cement. First, a reference hydration rate was derived from the isothermal heat generated by the hydration of ordinary Portland cement. Then, the model was extended to take into account the effect of water-to-cement ratio, hereinafter which was referred to as PSD hydration model. Finally, the PSD hydration model was applied to simulate experiments measuring the isothermal heat generated by the hydration of cement with different particle size distributions at different water-to-cement ratios. This showed that the PSD hydration model had simulated the effects of particle size distribution and water-to-cement ratio on the hydration process of cement with satisfactory accuracy.

**Keywords:** PSD hydration model; particle size distribution; measurable hydration depth; reference hydration rate; isothermal hydration heat generation.

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## 1. Introduction

Recently, in order to improve the utilization efficiency of cement and its early age properties (Bentz *et al.* 2008), such as early strength, the fineness of cement and its manufacturing procedure have been gradually improved. This had greatly changed the particle size distribution (PSD) of cement. PSD is one of the important parameters involved in the kinetics of the hydration of cement. This parameter is independent of fineness; cements of equal fineness can have different characteristic PSDs (Cohen 1981).

Enormous experimental effort has been directed towards evaluating the effects of the particle size distribution of cement. Some researchers (Frigioine and Marra 1976, Osbaeck and Johansen 1989, Lange 1997, Celik 2009) found that the microstructure and compressive strength of mortar were very much dependent on the particle size distribution of the cement. Some researchers (Sprung *et al.* 1985, Taylor 1997, Bentz *et al.* 1999, Bentz *et al.* 2008) found that the particle size distribution

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had great importance on the cement's performance, including characteristics such as setting time, hydration heat release, capillary porosity, diffusivity and chemical shrinkage. Zhao Fei *et al.* (1992) studied the effects of cement particle size distribution on the hydration heat released. The results showed that finer cements more rapidly generated hydration heat. These experiments have shown that the particle size distribution has considerable effect on the performance of cement and concrete. In most of the experiments, the chemical composition of cement changes with the fineness and particle size distribution, so the effect of particle size distribution on the hydration process of cement seems not be evaluated separately.

Over the past decades, many researchers have developed models to simulate the hydration process of cement, which was one of the most importance factors on the performance of cement and concrete (Bentz 2006). Among these, some models can hardly positively take the effects of PSD into account, such as Power's Model (Powers 1962), and the Avrami equation (Breugel 1991). Some models considered the effects indirectly from the specific surface area of the cement, such as the Suzuki's Model (Suzuki *et al.* 1990) and Parrott's Model (Parrott 1986). This may present some difficulties for simulating of the cement of the same fineness but with different particle size distribution.

The effects of the particle size distribution on hydration kinetics have been investigated in detail by Taplin (1968) and Knudsen (1980). Bentz (1997) developed a digital-image-based model: CEMHYD3D. In this model, each cement particle was represented as a collection of pixels in a digital image. This model permits a direct representation of multiphase, multisize and nonspherical cement particles using SEM images. However, the digital nature of the model imposes limits on resolution and applications. Particles smaller than the pixel size can not be represented. Bishnoi and Scrivener (2009) developed a new modeling platform:  $\mu ic$ . The pixel size used in this model is much smaller than CEMHYD3D, but is still large relative to the actual resolution. Kondo and Ueda (1968) assumed a monomodal particle size distribution to develop a hydration model by considering the diffusion through the inner and outer hydrate products. Pommersheim and colleagues (1979, 1986) later expanded the model, developing a model for the hydration of tricalcium silicate considering the particle size distribution. For each tricalcium silicate particle, the hydration process depended on the thickness of the hydrate layer and diffusivity through the hydrate layer. The hydrate layer was understood as consisting of three layers of products, as depicted schematically in Fig. 1: inner, middle and outer.

The rate of hydration is controlled by the diffusion of chemical species through these product layers. In this model, the parameters in the model change with the water-to-cement ratio, temperature history and other factors. It can be anticipated that fitting the model to experimental results with different

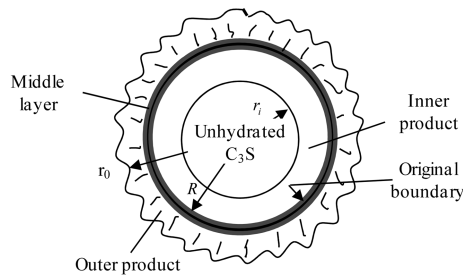


Fig. 1 Schematic of the hydration of a  $C_3S$  (tricalcium silicate) particle

water-to-cement ratios at different temperatures will probably require different parameter sets, which may result in some difficulties for the model's application.

Cohen and Cohen (1987) assumed that the hydrate layer consisted of one homogenous layer to simplify the derivation of the model, and they further assumed the growth velocities for individual particles were similar throughout hydration regardless of their particle size. Based on these assumptions, the shrink core model was incorporated. They deduced the hydrate layer's growth velocity as a function of the hydrate layer's thickness. Both the experimental data of Kondo and Ueda (1968) and Knudsen (1980) were adopted. The particle size range of Kondo's specimens was relatively narrow (2-5  $\mu\text{m}$  and 5-8  $\mu\text{m}$ ), while the particle size distribution of Knudsen's cement was characterized by Eq. (1)

$$p(r) = \frac{BC}{B-C}(e^{-Br} - e^{-Cr}) \quad (1)$$

where  $B = 0.0595$  and  $C = 1.28$ . For the specimens adopted from the experimental data of Kondo and Ueda, all three specimens possessed similar behaviours in terms of hydrate layer growth velocity. The hydrate layer growth velocity deduced from the experimental data of Knudsen showed different behavior. It can be anticipated that fitting the model to the cement with different ranges of particle size will probably result in different behavior in the hydrate layer growth velocity, which may lead to some difficulties for the model's application. Besides that, the derivation of the model considered the final hydration degree to be the same for cements with different particle size distributions.

The author of this paper found experimentally that cement with finer particle size distribution had larger final hydration degree, which led to higher utilization efficiency.

The objective of this paper is to find the effects of particle size distribution on the hydration process of cement by measuring the isothermal heat generated, and then to develop a PSD hydration model to characterize this behavior of cement hydration. Meanwhile, the model will be modified for the effects of the water-to-cement ratio on the hydration process of cement. Following this, a simulation of the PSD hydration model and the experimental results are correlated in order to verify the accuracy of the PSD hydration model.

## **2. Experiment for isothermal hydration heat generation**

The hydration reactions of cement are exothermic. As the hydration progresses, plenty of heat is liberated. Generally, the hydration process can be measured directly by the heat liberated. The degree of hydration can be thereby defined as in Eq. (2).

$$\alpha = Q/Q_0 \quad (2)$$

where  $\alpha$  : The hydration degree

$Q$  : Specific heat released during the hydration process

$Q_0$  : final hydration heat released when all the cement is hydrated, which depends on the chemical composition of cement

The isothermal heat generation was examined for the hydration process as follows.

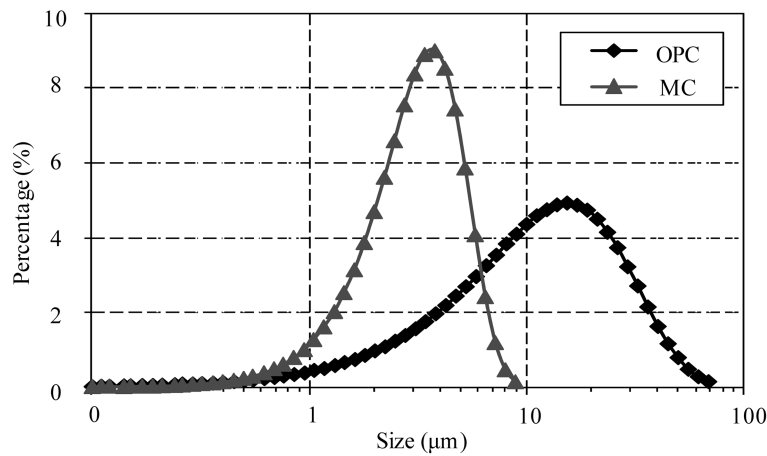


Fig. 2 The particle size distributions of the cements OPC and MC

Table 1 Chemical composition and proportions of OPC and MC

Cement label	Ignition loss (%)	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO(%)	MgO(%)	SO <sub>3</sub> (%)
OPC	0.95	21.11	5.37	2.77	64.7	1.62	1.94
MC	2.56	20.76	5.26	2.72	63.71	1.60	1.93

## 2.1 Materials

Commercial OPC (Ordinary Portland Cement) 42.5 (Beijing JinYu) was adopted and, in order to get cement with different particle size distribution but the same chemical composition, a specially designed Fluid Jet Mill was adopted for manufacturing OPC with different PSD. The cement produced by the Fluid Jet Mill was labeled as MC and had finer particle size distribution.

Fig. 2 shows the particle size distributions of OPC and MC, as examined by the Laser Particle analyzer (Bettersize-9300S).

The chemical compositions of the OPC and MC were examined by X-ray Fluorescence Analysis, as shown in Table 1.

The results showed that the chemical composition of OPC were almost the same as MC. It can therefore be assumed that MC and OPC have the same chemical composition. By experiments with cements OPC and MC, the effect of particle size distribution can be evaluated separately.

## 2.2 Experiment outline

A Differential Scanning Calorimeter (Toni CAL) was used to test the isothermal heat generated from hydration of the cement specimens. The specimens were maintained at constant temperature of 25°C during the measurement. The hydration heat was collected automatically by the data acquisition system, with a precision of 0.2 J/g. Both OPC and MC were adopted for cement specimens with different water-to-cement ratios, as shown in Table 2.

Table 2 Specimens for isothermal heat generated by hydration

Specimen No.	Water-to-cement ratio	Cement
OPC-0.7	0.7	OPC
MC-0.7	0.7	MC
Half-0.7	0.7	Mixed*
MC-0.6	0.6	MC
MC-0.5	0.5	MC

\*Mixed: the cement consists of 50% OPC and 50% MC in mass.

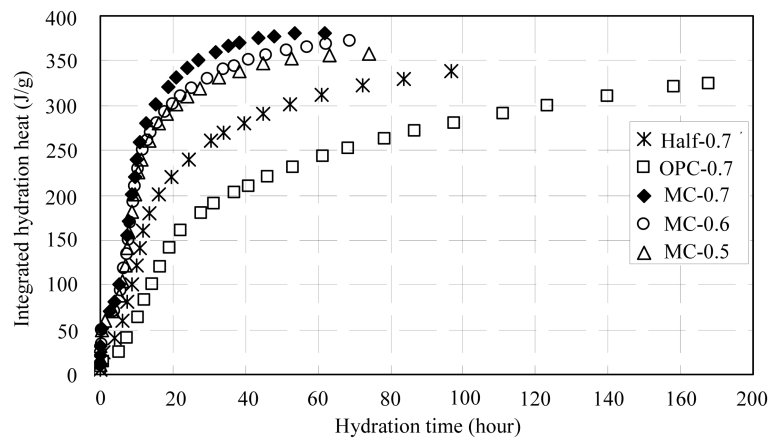


Fig. 3 The isothermal heat generated by hydration

The experiment results are shown in Fig. 3.

### 3. PSD hydration model

In the deduction, the cement particle is assumed to be spherical, as expressed in Fig. 4.

The hydration of cement occurs from outside to inside. The hydration depth refers to the depth to which hydration has arrived. For simplification, some basic assumptions are as follows:

- (1) The chemical composition is uniform from the outside to the inside of the particle;

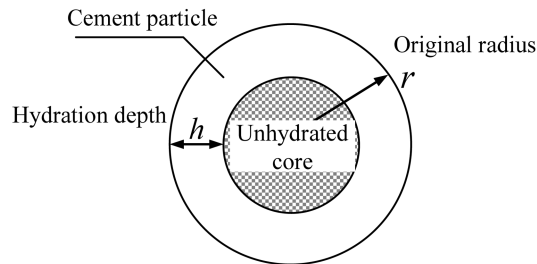


Fig. 4 Hydration of the cement particle

- (2) All of the cement compositions at the hydration depth are completely hydrated;
- (3) The hydration depth is independent of the particle size.

### 3.1 Modeling of the hydration process

Since the chemical composition is assumed to be uniform from the outside to inside, the density is also uniform from the outside to inside. The hydration degree can be expressed as the ratio of the volume of hydrated cement to the total volume of cement.

Define the  $p(r)$  as the volume proportion of the particles with radius  $r$ , which can be examined for particle size distribution. At time  $t$ , the hydration depth is  $h(t)$ . The hydration rate  $v(h)$  is a function of the hydration depth  $h(t)$ . The hydration depth can be obtained from Eq. (3)

$$h(t) = \int_0^t v(h) dt \quad (3)$$

For a particle with radius  $r$ , the hydration degree  $\alpha(r, h)$  can be obtained from Eq. (4)

$$\alpha(r, h) = \begin{cases} 1 & \text{if } h \geq r \\ 1 - (1 - h/r)^3 & \text{if } h < r \end{cases} \quad (4)$$

The total hydration degree  $\alpha(h(t))$  can be obtained from Eq. (5)

$$\alpha(h(t)) = \int_0^\infty \alpha(r, h) p(r) dr \quad (5)$$

### 3.2 Basic concepts for hydration rate

In an actual reaction, the hydration rate can be influenced by many factors, such as the temperature and the water content available for hydration. A reference hydration rate was defined as the hydration rate at constant temperature with an ample supply of water for hydration, which is not affected by the particle size distribution. By modifying the reference hydration rate, the actual hydration rate was obtained. The effect of the water content available for hydration was taken into account in the PSD hydration model, with the modified hydration rate as in Eq. (6).

$$v(h) = \eta v_0(h) \quad (6)$$

Where  $v_0(h)$ : The reference hydration rate

$\eta$  : The coefficient to express the effect of water content available for hydration

Temperature effect and other influential factors will be taken into account in further research.

### 3.3 Measurable hydration depth

From the experiment results of the isothermal heat generated by hydration, the isothermal heat from hydration of the specimens OPC-0.7 and MC-0.7 are compared, as shown in Fig. 5.

These specimens have the same water-to-cement ratio 0.7, which can supply ample water for complete hydration, since there is a general acceptance that amount of water necessary for complete hydration of ordinary Portland cement is about 40% of the total cement weight (Arai 1984). Because cements of the specimens OPC-0.7 and MC-0.7 have the same chemical composition, the

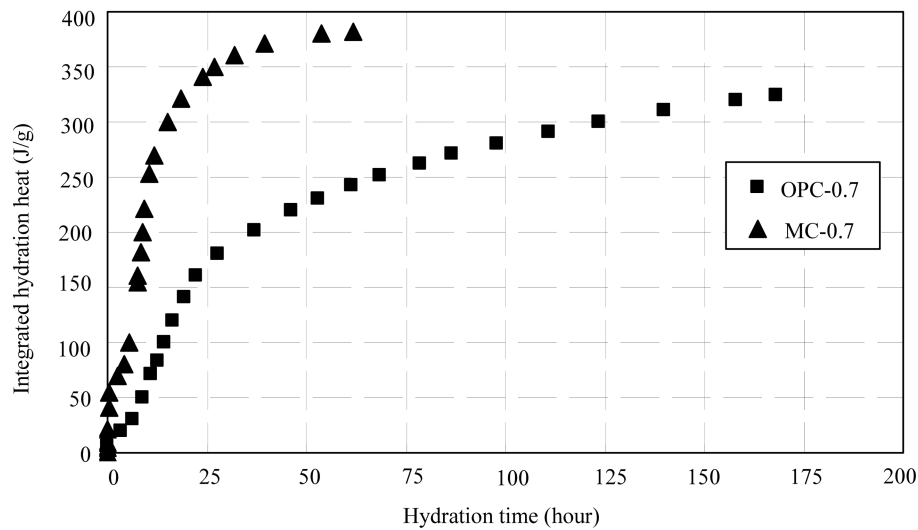


Fig. 5 The isothermal heat of hydration

final hydration heat of complete hydration should be the same. In the experiments, the hydration heat generated was examined until the heat generation rate of cement hydration approached to 0 approximately. From experimental results, final hydration heat of specimen OPC-0.7 is 324.5 J/g, which is different from the final hydration heat of specimen MC-0.7 381.1 J/g. So it can be concluded that at least one of these two specimens didn't hydrate completely.

According to Odler's research (Odler 1998), during later stage of hydration, the hydration of cement is controlled by water diffusion through internal hydrated layer. As the thickness of internal hydrated layer increases, the diffusion of water through the hydrated layer becomes more difficult, which results in slower hydration rate and hydration heat generation rate. When the hydration depth approaches to some degree, the hydration heat generation rate is less than heat generation rate that can be detected by the equipments, which cannot be examined. Hydration heat examined at this moment is the final hydration heat in usually conception, while cement didn't hydrate completely. In this study, the final hydration heat examined in the experiments defines as measurable hydration heat, while the hydration depth defines as measurable hydration depth, which depends on the accuracy of equipments.

On the final hydration heat, there are two main processing modes. Some researchers (Cohen and Cohen 1987), treat the final hydration heat examined in the experiments as the final hydration heat of complete hydration. The final hydration heats of cements with the same chemical composition are the same. This processing mode cannot consider the effects of particle size distribution on the final hydration heat examined in the experiments. Some researchers think that there is a cement core unable to be hydrated (Qiao Lingshan 2004). By examining the hydration process of cement with specific surface area  $300 \text{ m}^2/\text{kg}$ , it is founded that only 44% cement hydrates in one year (Shen Wei *et al.* 1991). Based on this, it is deduced that coarse cement particle cannot hydrate completely. This processing mode can consider the effects of particle size distribution on the hydration process of cement. But according to the development of concrete long-term performance, the hydration process lasts for a very long time. Isami Hiroi produced more than 60,000 mortar specimens for long-term performance during construction of Otaru Port since 1899, which showed that the tensile strength

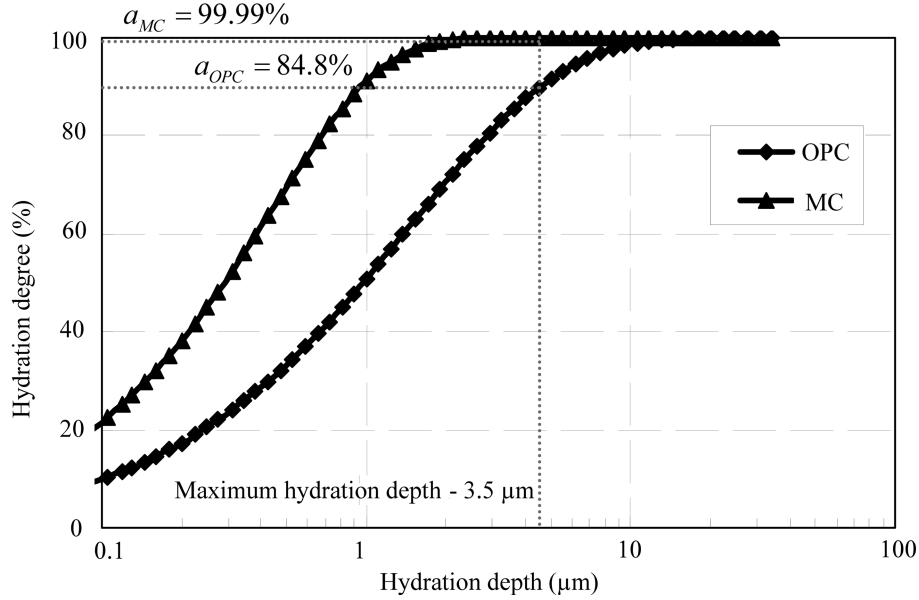


Fig. 6 Hydration degree of OPC and MC

increased with curing ages and reached maximum value until 30~40 years later (Feng 2002). This phenomenon reflects that hydration process of cement lasts for a long time, while hydration rate becomes so slow that cannot be examined by experiments. The measurable hydration depth can reflect the difference between final hydration status examined in experiments and final hydration status of complete hydration, which can represent the effects of particle size distribution on final hydration heat examined in experiments, and also the developments of concrete long-term performance as curing ages. In fact, cement can hydrate completely in the end as long as the water supply is sufficient. But for the limits of equipment accuracy, the hydration process of cement after the measurable hydration depth can not be examined.

According to the particle size distribution of the OPC and MC shown in Fig. 2, the hydration degree of the OPC and MC at different hydration depth was calculated using Eq. (4) and Eq. (5), as shown in Fig. 6.

Since the cement of these two specimens, OPC-0.7 and MC-0.7 had the same chemical composition, the maximum specific heats of hydration are also the same, labelled as  $Q_0$ . The final hydration degree of OPC-0.7  $\alpha_{OPC}$  and the final hydration degree of MC-0.7  $\alpha_{MC}$  have the relationship as in Eq. (7)

$$\alpha_{OPC}/\alpha_{MC} = \left(\frac{324.5}{Q_0}\right) / \left(\frac{381.1}{Q_0}\right) = 0.85 \quad (7)$$

As shown in Fig. 6, the corresponding hydration depth is 3.5  $\mu\text{m}$ , which is defined as the measurable hydration depth; the hydration process after measurable hydration depth cannot be examined by equipment. The final hydration heat  $Q_0$  can be obtained as in Eq. (8), which is affected by chemical composition of cement.

$$Q_0 = 324.5 / \alpha_{OPC} = 324.5 / 84.8\% = 383 \text{ J/g} \quad (8)$$

### 3.4 Reference hydration rate



Table 3 Hydration heat values of OPC-0.7

Specimen No.	Hydration heat (J/g)						
	0.5 h	3h	12 h	24 h	48 h	72 h	168 h
OPC-0.7	13.4	18.8	79.6	167.9	222.4	255.9	324.5

The reference hydration rate set in the proposed model is based on the assumption that the hydration proceeds with an ample supply of water for hydration at constant temperature. In the experiments for isothermal heat generated by hydration, above, the hydration process was measured at a constant temperature of 25°C. There is a general acceptance that the amount of water necessary for complete hydration of ordinary Portland cement is about 40% of the total cement weight. It can be assumed that water content would be ample for hydration at a water-to-cement ratio of 0.7. So, the reference hydration rate can be derived from the isothermal heat generated by hydration as examined in the experiments above. The hydration heat of the specimen OPC-0.7 was adopted for the reference hydration rate. Table 3 shows some hydration heat values.

Fig. 7 shows the process of derivation. The maximum specific hydration heat  $Q_0$  was based on the measurable hydration depth.

Fig. 8 shows the reference hydration rate derived.

The hydration process of Portland cement at ambient temperature is characterized by several distinctive stages: pre-induction stage, induction stage, acceleration stage and deceleration stage (Odler 1998). The stages are divided by the hydration time, according to a shift in the hydration rate. Generally, the pre-induction stage last for the first few minutes, the induction stage last for a few hours after the pre-induction stage, the acceleration stage is from 3 to 12 hours after mixing, and the deceleration stage is after the acceleration stage. For each hydration stage, the hydration of cement has a different mechanism. Bullard *et al.* (2010) reviewed the current state of knowledge of hydration mechanisms. However, usually a shift in

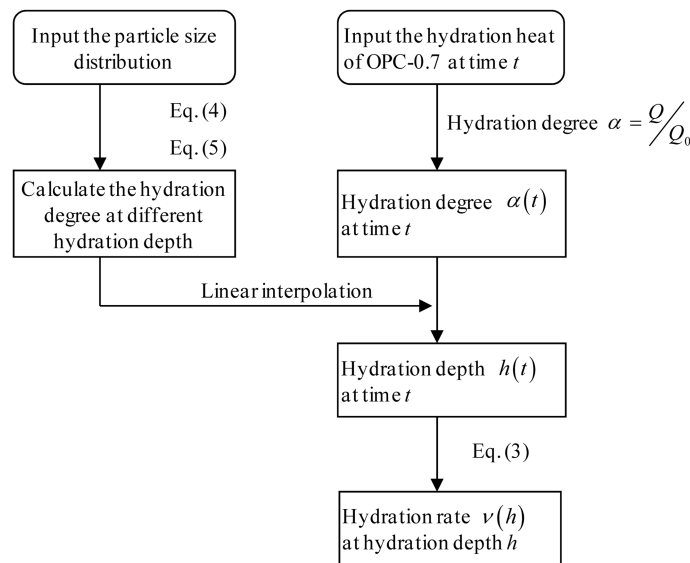


Fig. 7 The process of the derivation of the reference hydration rate

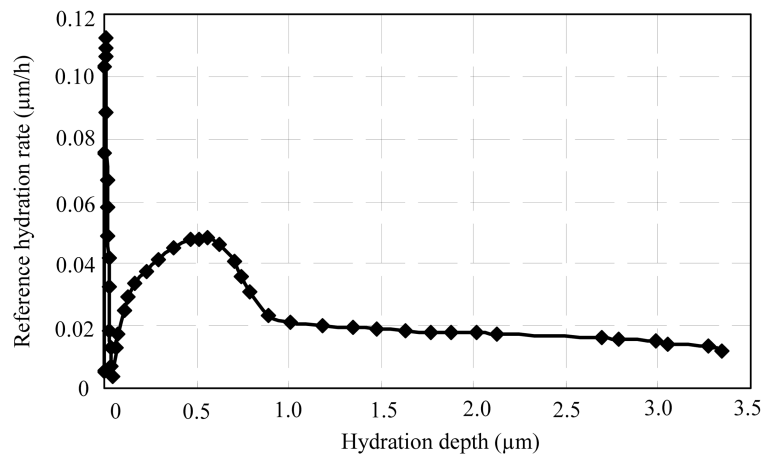


Fig. 8 The reference hydration rate

the hydration rate may not necessarily indicate a shift in the hydration mechanism. The shift may be attributed to the depletion of a particularly sized group of particles due to the variable particle size distribution of cement, or it may be attributed to both changes in mechanism and depletion, occurring simultaneously. Very frequently, the shifts are incorrectly attributed to changes in hydration mechanism; however, this can only be the case for monosized PSD.

Since the hydration depth is assumed to be independent of the particle size, the reference hydration rate as a function of deduced hydration depth is independent of the particle size distribution of cement. A shift in the reference hydration rate can indicate a shift in the hydration mechanism. Accordingly, based on the reference hydration rate, the hydration process can also be divided into four stages by the hydration depth, despite the particle size distribution of cement, as follows:

(1) Pre-induction stage. The hydration depth of this stage is from 0 to 0.04  $\mu\text{m}$ . The rapid reactions which show a larger rate of heat generation occur for a short time just after the cement comes into contact with water. This heat results from the wetting of cement and the dissolution of ions in water (Nagashima 1992).

(2) Dormant stage. The pre-induction stage is followed by a stage in which the rate of hydration slows down significantly. The rate of hydration is too small (almost 0.004  $\mu\text{m/h}$ ) and the hydration seems to be stagnant. Generally, the stagnant of hydration is thought to be caused by the formation of a protective layer on the surface of the cement particles (Nagashima 1992), and the destroy of protective layer results in the end of dormant stage, due to the formation of ettringite (Arai 1984). The hydration depth of this stage develops very slowly, from 0.04  $\mu\text{m}$  to 0.045  $\mu\text{m}$ .

(3) Acceleration stage. This stage follows the termination of the dormant stage that is induced by the increase of permeability of the protection layer. The rate of hydration accelerates suddenly and reaches a maximum at a hydration depth of 0.5  $\mu\text{m}$ . In this stage, the diffusion of water supplies ample water for hydration. The hydration rate mainly depends on the rate of reaction. According to the Avrami equation, the rate of reaction accelerates with the development of hydration depth (Odler 1998). The hydration depth of this stage is from 0.045  $\mu\text{m}$  to 0.5  $\mu\text{m}$ .

(4) Deceleration stage. The layer of cement hydrated plays a role as the diffusion area. As the rate of reaction accelerates and the thickness of hydrated layer increases according to the progress of hydration during the acceleration stage, the diffusion of water gradually can not satisfy the needs of

the reaction. After reaching a maximum the rate of hydration starts to slow gradually. In this stage, the hydration rate mainly depends on the diffusion of water, which is remarkably reduced by the development of the thickness of the hydrated layer (Maekawa *et al.* 1999). When the hydration depth is large enough, the diffusion of water through the thick hydrate layer can be ignored. The hydration depth is at the maximum mentioned above. According to the experimental results, the measurable hydration depth is 3.5  $\mu\text{m}$ .

### 3.5 Effect of water-to-cement ratio on hydration rate

As mentioned in its definition, the reference hydration rate is based on the assumption that the hydration proceeds with an ample supply of water for hydration. However, the actual hydration rate is reduced against the reference hydration rate at a low water-to-cement ratio, since it is then impossible to assume sufficient water supplied for hydration. In some research, it is assumed that the reduction of hydration rate due to a shortage of free water results from the reduction of the probability of contact between the reacting surface of particles and free water (Maekawa *et al.* 1999), which is adopted in the proposed model as Eq. (9)

$$\eta = 1 - \exp\left(-r\left(\left(\frac{w/c - 0.4\alpha}{1 - (1 - \alpha)^{1/3}}\right) \cdot s_i^t\right)^s\right) \quad (9)$$

where  $r$ ,  $s$  and  $t$  are material constants. By comparison between the experimental and analytic results, it was determined that  $r = 1.5$ ,  $s = 0.8$  and  $t = 4$ . The coefficient  $\eta$  represents the reduction of hydration rate because of reduction of free water and is simply formulated in terms of both amount of free water and the thickness of internal hydrated layer. In the equation,  $w/c$  represents the water-to-cement ratio, while  $\alpha$  represents the current hydration degree. Since the amount of water necessary for complete hydration of Portland cement is about 40% of the total cement weight as mentioned (Arai 1984), the consumed water for complete hydration is assumed to be 40% of the total cement weight of cement, though it will be affected by chemical composition of cement. So the free water can be represented as expression  $w/c - 0.4\alpha$ , while the thickness of internal hydrated layer can be defined as expression  $1 - (1 - \alpha)^{1/3}$ . The coefficient  $\eta$  is also affected by fineness of cement represented as coefficient  $s_i$ , which is the ratio of cement's specific surface area to 450  $\text{m}^2/\text{kg}$  (specific surface area of OPC in the experiments). Because the specific surface area of cement affects probability to contact with free water. The coefficient  $\eta$  above varies from 0 to 1 and hardly gives the reduction when free water is sufficient in the early ages, while it sharply reduces the hydration rate when the amount of free water is reduced for consume and water diffusion though the internal hydrated layer becomes difficult.

### 3.6 Flowchart of the computation of the PSD hydration model

Fig. 9 shows the flowchart of the computation of the PSD hydration model.

The information input into the model includes the particle size distribution of the cement and the water-to-cement ratio. For some hydration depth  $h$ , the hydration degree was calculated by Eq. (4) and Eq. (5). Based on the reference hydration rate curve, the current reference hydration rate was determined. Then the actual hydration rate was modified from the reference hydration rate according to Eq. (6) and Eq. (9), with the effect of the water-to-cement ratio on the hydration rate taken into account. Last, the hydration depth was updated for the next time step, until the setting time.

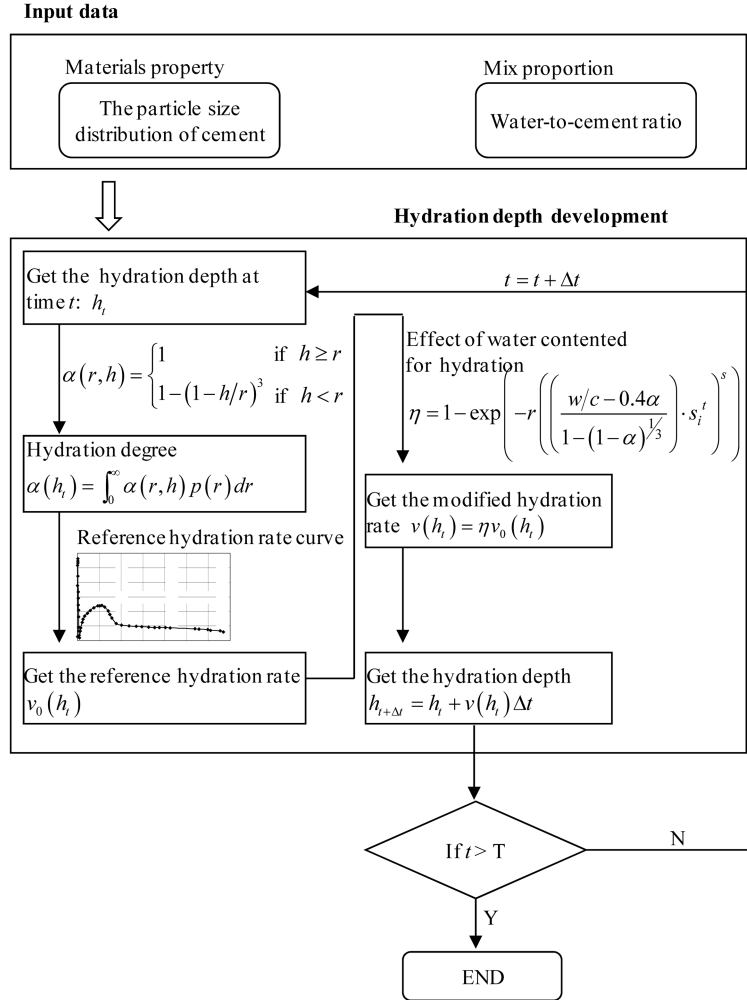


Fig. 9 Flowchart of computation of the PSD hydration model

#### 4. Simulated experiments

The PSD hydration model proposed above was applied to simulate the experimental results of the isothermal heat generated by hydration, in order to verify the accuracy of the model.

##### 4.1 Effect of particle size distribution on the hydration process

For specimens OPC-0.7, MC-0.7 and Half-0.7, their cements have different particle size distributions, while the chemical composition and water-to-cement ratio remained the same. Fig. 10 shows the simulation results for the heat of hydration of these three specimens.

From Fig. 10, it can be found that finer particle size distribution lead to higher final hydration

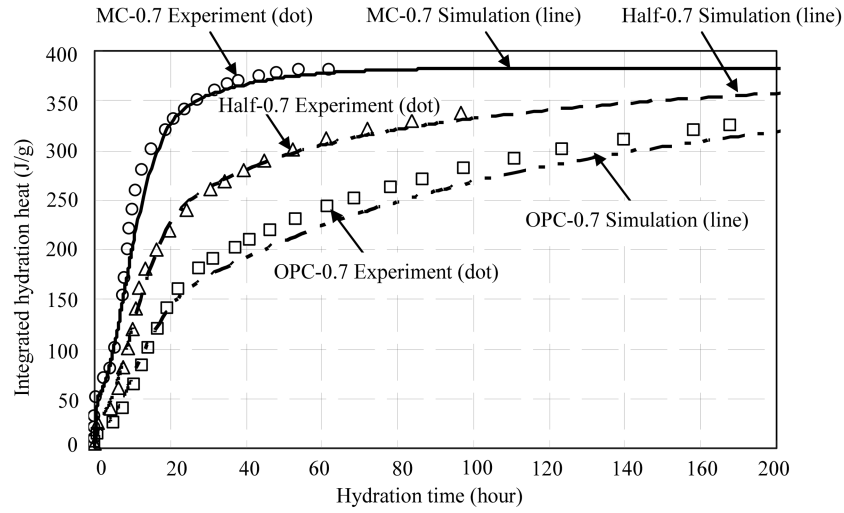


Fig. 10 Simulation for the effect of particle size distribution on the hydration process

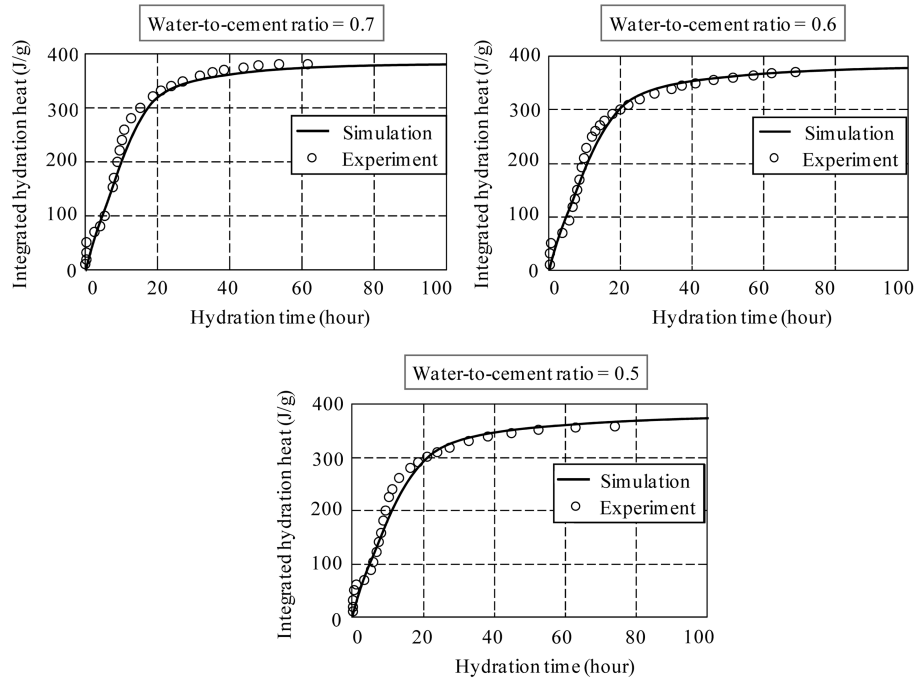


Fig. 11 Simulation for the effect of water-to-cement ratio on the hydration process

heat and faster hydration rate, which can be simulated by the PSD model very well.

#### 4.2 Effect of the water-to-cement ratio on the hydration process

For specimens MC-0.7, MC-0.6 and MC-0.5, their cements have the same particle size distribution and chemical composition, while the water-to-cement ratio is different for each. Fig. 11 shows the

simulation results for the heat of hydration of these three specimens.

From Fig. 11, it can be found that the effect of the water-to-cement ratio on hydration is weak during early hydration, gradually becoming distinct with the development of hydration. This is because, during early hydration, the hydration is in the acceleration stage. In this stage, the water is ample and the hydration rate mainly depends on the rate of reaction. As the hydration develops into the deceleration stage, the hydration rate mainly depends on the diffusion of water. According to Fick's law, the water content affects the diffusion rate, which greatly affects the hydration rate. A lower water-to-cement ratio leads to a lower hydration rate and a lower final hydration degree, which can be simulated by the PSD model with satisfactory accuracy.

## 5. Conclusions

Based on the proposed PSD hydration model and the application of the simulation to the experimental results, the following conclusions can be reached:

- In order to evaluate the effects of PSD on hydration process of cement separately, PSD of cement is changed based on Fluid Jet Mill system without changing the chemical composition. The experimental results of isothermal hydration heat show that finer particle size distribution leads to higher final hydration heat examined in experiments.
- The measurable hydration depth is proposed for representing the difference between final hydration status examined in experiments and final hydration status of complete hydration, which depends on the accuracy of equipment in experiments. By experimental results, the measurable hydration depth and measurable final hydration heat is deduced.
- The PSD hydration model is developed in this study, which can consider effect of PSD on hydration process of cement, and also the effects of water-to-cement ratio. The simulation of experimental results shows that the PSD hydration model has satisfactory accuracy to take into account both the effects of particle size distribution and water-to-cement ratio on the hydration process of cement.

In this study, the hydration heat was isothermal with constant temperature, and the cement of the specimens had the same chemical composition. Accordingly, the proposed PSD hydration model is temporarily limited to isothermal hydration of cement with the same chemical composition. In further research, the PSD model should be developed to take the temperature and chemical composition of cement into account.

## References

- Arai, Y. (1984), "Chemistry of cement materials", Dai-nippon Tosho Publishing Co., Tokyo.
- Bentz, D.P. (1997), "Three-dimensional computer simulation of portland cement hydration and microstructure development", *J. Am. Ceram. Soc.*, **80**(1), 3-21.
- Bentz, D.P. (2006), "Cement hydration: building bridges and dams at the microstructure level", *Mater. Struct.*, **40**(4), 397-404.
- Bentz, D.P., Garboczi, E.J., Haecker, C.J. and Jensen, O.M. (1999), "Effects of cement particle size distribution on performance properties of portland cement-based materials", *Cement Concrete Res.*, **29**(10), 1663-1671.
- Bentz, D.P., Sant, G. and Weiss, W.J. (2008), "Early-age properties of cement-based materials-I: Influence of cement fineness", *J. Mater. Civil Eng.*, **20**(7), 502-508.

- Bishnoi, S. and Scrivener, K.L. (2009), "µic: A new platform for modelling the hydration of cements", *Cement Concrete Res.*, **39**(4), 266-274.
- Breugel, K.V. (1991), *Simulation of hydration and formation of structure in hardening cement-based materials*, PhD. thesis, Delft.
- Bullarda, J.W., Jenningsb, H.M., Livingstone, R.A., George, W., Nonat, A., Jeffrey, S.S., Scrivener, K.L. and Thomash J.J. (2010), "Mechanisms of cement hydration", *Cement Concrete Res.*, **41**(12), 1208-1223.
- Celik, I.B. (2009). "The effects of particle size distribution and surface area upon cement strength development", *Powder Technol.*, **188**(3), 272-276.
- Cohen, M.D. (1981), *PhD Dissertation*, Stanford University, Stanford, California.
- Cohen, R.D. and Cohen, M.D. (1987), "Kinetics of depletion of a population of hydrating cement particles", *J. Mater. Sci.*, **22**(6), 2032-2036.
- Feng Naiqian (2002), "The long-term performance of cement and concrete in bay and ocean structures", *China Cement Concrete Products*, **6**, 11-14. (In Chinese)
- Frigioine, G and Marra, S. (1976), "Relationship between particle size distribution and compressive strength in Portland cement", *Cement Concrete Res.*, **6**(1), 113-128.
- Knudsen, T. (1980), *On particle size distribution in cement hydration*, 7<sup>th</sup> int. conference on the chemistry of cement, Paris.
- Kondo, R. and Ueda, S. (1968), *Kinetics and mechanisms of the hydration of cements*, 5<sup>th</sup> int. Congress on the chemistry of cements, Tokyo.
- Lange, F., Mortel, H. and Rundert, V. (1997), "Dense packing of cement pastes and resulting consequences on mortar properties", *Cement Concrete Res.*, **27**(10), 1481-1488.
- Maekawa K., Rajesh C. and Toshiharu, K. (1999), *Modelling of concrete performance: hydration, microstructure formation and mass transport*, E & FN Spon Press, London.
- Nagashima, M. (1992), "Hydration, setting and hardening", *Cement Concrete*, **544**, 36-44.
- Odler Ivan (1998), *Hydration, setting and hardening of Portland cement*, in "Lea's chemistry of cement concrete (4<sup>th</sup> edition)", edit by Peter C. Hewlett, Reed Educational and Professional Publishing Ltd, London.
- Osbaeck, B. and Johansen, V. (1989), "Particle size distribution and rate of strength development of Portland cement", *J. Am. Ceram. Soc.*, **72**(2), 197-201.
- Parrott, L.J. (1986), *Modeling the development of microstructure*, *Proceedings of engineering foundation conference on research on manufacture and use of cements*, Henniker, New York.
- Pommersheim, J.M. and Clifton, J.R. (1979), "Mathematical modeling of tricalcium silicate hydration", *Cement Concrete Res.*, **9**(6), 765-770.
- Pommersheim, J.M. and Clifton, J.R. (1982), "Mathematical modeling of tricalcium silicate hydration II. Sub-models and the effect of model parameters", *Cement Concrete Res.*, **12**(6), 765-772.
- Pommersheim, J.M. and Clifton, J.R. (1986), "Kinetics of hydration of tricalcium aluminate", *Cement Concrete Res.*, **16**, 440.
- Powers, T.C. (1962), *Physical properties of cement paste*, *Proceedings of the fourth international conference on the chemistry of cement*, Washington, D.C.
- Qiao Lingshan (2004), "Effects of particle size distribution on cement's strength", *Cement*, 1, 1-6. (In Chinese)
- Shen Wei, Huang Wenxi and Min Panrong (1991), *Cement technology*, Wuhan University of Technology Press, Wuhan. (In Chinese)
- Sprung, S., Kuhlmann, K. and Ellerbrock, H.G. (1985), "Particle size distribution and properties of cement, Part II: water demand of Portland cement", *ZKG Int.*, **9**, 275-281.
- Suzuki, Y., Tsuji, Y., Maekawa, K. and Okamura, H. (1990), "Quantification of hydration-heat generation process of cement in concrete", *Concrete Libr. JSCE*, **16**, 111-124.
- Taplin, J.H. (1968), *Kinetics and mechanisms of the hydration of cements (Discussion)*, 5<sup>th</sup> int. Congress on the chemistry of cements, Tokyo.
- Taylor, H.F.W. (1997), *Cement Chemistry (2d edition)*, Thomas Telford, London.
- Zhao Fei, Feng Xiujie (1992), "The effect of the particle size on the hydration and strength of cement", *Bull. Chinese Ceram. Soc. Bull.*, **4**, 10-14. (In Chinese)