

HYDRATION MODEL OF CEMENT PASTE MIXED WITH EXPANSIVE ADDITIVE

Van NGUYEN DUC^{*1}, Hyeonggil CHOI^{*2} and Yukio HAMA^{*3}

ABSTRACT

Although expansive additive (EX) has been widely used in concrete as an admixture to allay shrinkage cracking, little research has been done on modeling the hydration reaction of cement paste mixed with an expansive additive. In this research, the hydration process of ordinary Portland cement (OPC) and Portland cement-expansive additive blends were evaluated by using isothermal calorimetry method. Besides, based on the shrinkage-core model, this research represents hydration model that describes the heat evolution of OPC and cement-expansive additive blends. The parameters of this model were determined by fitting to experimental results. Using the proposed model, the degree of hydration and the rate of heat evolution were predicted. A comparison between predicted and measured results was performed and shown a good agreement.

Keywords: Hydration model, Expansive additive, Kinetics, Degree of hydration, Isothermal Calorimetry.

1. INTRODUCTION

The expansive additive (EX) is an admixture having a reaction of expanding concrete by producing ettringite or calcium hydroxide due to hydration reaction when mixed with cement and water [1] and is commonly used in concrete because it reduces cracks due to drying shrinkage. Hydration of cement-expansive additive (cement-EX) blends is very important to be estimated since there is a great relation of hydration with heat evolution of hydration, strength development, and volume change, which lead to the cracks of hardened concrete. Therefore, the hydration of cement-EX blends is necessary to study clearly, but its hydration process is more complicated than the hydration process of ordinary Portland cement (OPC), due to the coexistence of OPC hydration and EX hydration.

For studying hydration of the cement, over the past few decades, a number of studies have been made on modeling of cement hydration in order to grasp the time-dependent properties of cement bases materials (Kondo 1968) [2]. In recent studies, Tomosawa et al. proposed a hydration model to estimate the rate of heat evolution of hydration of OPC and simulated hydration process using a single kinetic equation. Base on the Tomosawa's model, a hydration model of OPC was developed by Maruyama et al. [3], the volume change of cement particle during hydration process, chemically bound water and physically bound water were

considered. Besides, Park built a microstructural hydration model of Portland cement that considers the reduction in the hydration rate that occurs due to the reduction of free water and the reduction of the interfacial area of contact between the free water and the hydration products [4]. In addition, the hydration model of slag-cement blends was proposed by Xiao-Young et al. [5]; in this model, the production of calcium hydroxide in cement hydration and its consumption in the slag reaction were considered.

This paper focuses on the hydration model of cement paste mixed with expansive additive. The effects of dosages of the EX on the rate of heat evolution of cement-EX blends were considered. Firstly, the heat evolution rates of cement-EX blends were investigated using isothermal calorimetry. Secondly, based on the shrinkage-core model [6], the heat evolution rates of cement-EX blends were also predicted. Finally, a comparison between experimental and predicted results was performed.

2. MATERIALS AND EXPERIMENTAL METHOD

2.1 Materials

Table 1 shows the chemical compositions and physical properties of OPC and EX.

The mineral compositions of materials are shown in Table 2. It can be seen in this table that there are no C_2S and C_3A content in EX.

*1 Graduate Student, Course of Architecture and Building Engineering, Muroran Institute of Technology
 *2 Assistant Professor, College of Environmental Technology, Muroran Institute of Technology, JCI Member
 *3 Professor, College of Environmental Technology, Muroran Institute of Technology, JCI Member

Table 1 Chemical compositions and physical properties of materials

Oxide (%)	OPC	EX
SiO ₂	21.38	1.2
Al ₂ O ₃	5.46	16.1
Fe ₂ O ₃	2.93	0.6
CaO	64.34	-
MgO	1.53	1.1
K ₂ O	0.46	-
Na ₂ O	0.31	-
SO ₃	2	27.5
LOI	0.68	1.1
f-Cao	0.61	51.3
Blaine (cm ² /g)	3490	3010
Density (g/cm ³)	3.15	2.86

Table 2 Mineral composition of materials

Sample	C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	C ₄ AF (%)
OPC	50.33	23.41	9.51	8.92
EX	3	-	-	5

Table 3 Mixing proportions

Sample	OPC (%)	EX (%)	W/B (%)	Curing Temperature (°C)
OPC100	100	0		
OPC95+EX5	95	5		
OPC90+EX10	90	10	50	20
OPC85+EX15	85	15		
OPC80+EX20	80	20		
EX100	0	100		

The mineral composition of OPC was calculated by Bouge's equation, as given by Eq. (1) and that of EX was referred from previous research [7].

$$\begin{aligned}
 C_3S &= 4.071CaO - 7.6024SiO_2 - 1.4297Fe_2O_3 \\
 &\quad - 6.7187Al_2O_3 - 2.85SO_3 \\
 C_2S &= 2.87SiO_2 - 0.754(3CaO.SiO_2) \\
 C_3A &= 2.65Al_2O_3 - 1.692Fe_2O_3 \\
 C_4AF &= 3.0432Fe_2O_3
 \end{aligned} \quad (1)$$

2.2 Experimental method

The mixing proportions are given in Table 3. Water to binder ratio (W/B) of 0.5 was chosen. In this study, the EX was CSA (Calcium Sulfoaluminate) type. The replacement ratios of the EX were 5, 10, 15, and 20% by weight of the OPC. Isothermal calorimetry was used to evaluate the hydration process of cement-EX blends at 20°C. The mass of samples were 20g cement-EX blends and 10g water to prepare for experimental, loaded in channel calorimeter block, and

mixed within 3 minutes. The measuring process starts immediately after the contact of cement-EX blends and water. The hydration process was determined within 72 hours (3days). The results measured were the rate of heat evolution with unit to be expressed in J/hr.g

3. HYDRATION OF CEMENT PASTE MIXED WITH EXPANSIVE ADDITIVE

The fundamental modeling hydration equation was based on the shrinkage-core model and developed by Tomosawa et al. [8] and Maruyama et al. [3] to simulate the hydration reaction of single cement particle. There are three coefficients to be considered in Tomosawa's model: k_d is the reaction coefficient in induction period; D_e is the effective diffusion coefficient of water through the hydration product layer; k_r is coefficient of reaction rate per unit area of reaction front.

Based on Tomosawa's model and Maruyama's model, the hydration model of cement paste mixed with EX is simulated by the following equation.

$$\begin{aligned}
 \frac{d\alpha}{dt} &= \frac{3C_{w\infty}}{(\gamma + W_{a,g})\rho_B r_0^2} \\
 &\quad \left(\frac{1}{\frac{1}{k_d r_0 \alpha_0^{2/3}} + \frac{\alpha_0^{-1/3} - (2 - \alpha_0)^{-1/3}}{D_e} + \frac{1}{k_r r_0 \alpha_0^{2/3}}} \right) \quad (2)
 \end{aligned}$$

Where α is the hydration degree of cement-EX blends; α_0 is the non-hydration degree; r_0 is the average radius of initial OPC and EX particle ($r_0 = 3/S_B \rho_B$) [9]; ($S_B = p_{OPC} S_{OPC} + p_{EX} S_{EX}$), S_B is the average specific surface area of OPC and EX; S_{OPC} and S_{EX} are the specific surface area of OPC and EX, respectively; p_{OPC} and p_{EX} are the OPC and EX mass to the total cementitious content ratio, respectively; γ is the average chemically bound water of cement-EX blends; $W_{a,g}$ is the average physically bound water of cement-EX blends, $(\gamma + W_{a,g}) = 0.42.p_{OPC} + 0.48.p_{EX}$; ρ_B is the average density of OPC and EX; $C_{w\infty}$ is the concentration of water at outer region of the C-S-H gel.

At the induction period the coefficient of reaction k_d is determined by Eq. (3) [10].

$$k_d = \frac{B}{\alpha^{1.5}} + C(r_0 - r_t)^4 \quad (3)$$

Where B and C are the rate determining coefficient; r_t is the average radius of an unhydrated cement and EX particle [11].

The effective diffusion coefficient of water D_e in the gel which is assumed to be a function of the degree of the hydration and given by Eq. (4).

$$D_e = D_{e0} \ln\left(\frac{1}{\alpha}\right)^{1.5} \quad (4)$$

Where D_{e0} is the initial diffusion coefficient of water in the gel.

The concentration of water at the outer region of the C-S-H gel $C_{w\infty}$ is also assumed as a function of the degree of the hydration. Besides, X.Y Wang et al. reported that $C_{w\infty}$ also considers a decrease in the available capillary water for Portland cement hydration, and the item, $(w_0 - 0.42C_0\alpha)$ is the mass of capillary water [4, 5, and 12], where 0.42 is the total of chemically bound water and physical bound water. For cement-EX blends, therefore, it is necessary to calculate the concentration of water at outer region of the C-S-H gel.

Theoretically, at complete hydration, 1g of cement binds chemically approximately 0.23g of water during the cement hydration reactions, and 0.19g of strongly physical bound gel water [13]. The chemically bound water, also called non-evaporable water, which is determined by heating the specimen at about 1000°C for approximately 30 minutes, the amount of mass loss minus the ignition loss of the original cement gives the non-evaporable water content of the specimen. The physically bound water is called evaporable water to be calculated by drying the specimen in an oven at 105°C for 24 hours. According to the experimental results, the total of chemically bound water and physically bound water of expansive additive is 0.48g. Therefore, the decrease in the available water for cement-EX blends hydration must be recalculated by subtracting the amount of water used by the hydration reaction of expansive additive as shown in Eq. (5)

$$C_{w\infty} = \frac{w_0 - 0.42C_0\alpha_{OPC} - 0.48E_0\alpha_{EX}}{w_0} \quad (5)$$

Where α_{EX} and α_{OPC} are the degree of hydration of expansive additive and Portland cement, which were determined by isothermal calorimetry method; E_0 , w_0 and C_0 are the mass fraction of expansive additive, water and cement in the mix proportions, respectively.

K. van Breugel [14] assumed that the cement degree of hydration was determined by the ratio of the amount of heat evolution to the maximum heat evolution, as shown in Eq. (6).

$$\alpha_{(t)} = \frac{Q_{(t)}}{Q_{max}} \quad (6)$$

Where $Q_{(t)}$ is the heat released at time t and Q_{max} is the total heat available for cement hydration reaction.

The maximum amount of heat released at complete hydration can be determined by the following equation [14]:

$$Q_{(max)} = q_1 \cdot (\%C_3S) + q_2 \cdot (\%C_2S) + q_3 \cdot (\%C_3A) + q_4 \cdot (\%C_4AF) + q_5 \cdot (\%C) + q_6 \cdot (\%MgO) \quad (7)$$

Table 4 Relative contribution of evolution heat of clinker compounds (J/g) [14]

Author	q_1 C_3S	q_2 C_2S	q_3 C_3A	q_4 C_4AF	q_5 fr.C	q_6 MgO
Woods	570	260	840	125	-	-

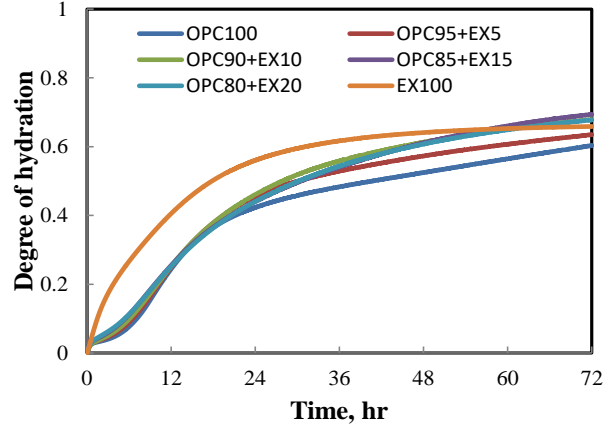


Fig.1 Degree of hydration of OPC and cement-EX blends.

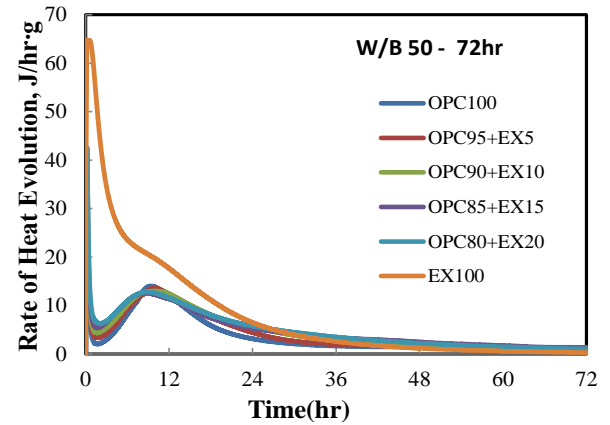


Fig.2 Heat evolution rate of OPC and cement-EX blends at 20°C

Where q_1, q_2, q_3, q_4, q_5 and q_6 are evolution heat of each composition to be predicted by Woods [14] and shown in Table 4; $\%C_3S$, $\%C_2S$, $\%C_3A$, $\%C_4AF$, $\%C$, and $\%MgO$ are the mineral composition of cement to be obtained by Bouge's equation.

According to Eq. (6), the hydration degree of the cement-EX blends is defined as the ratio between the heat released at time t to the maximum amount of heat released at complete hydration. Where Q_t is determined by isothermal calorimetry method and Q_{max} is calculated from cementitious properties in Eq. (8) [15].

$$Q_{(max)} = Q_{OPC} \cdot p_{OPC} + Q_{EX} \cdot p_{EX} \quad (8)$$

Where Q_{OPC} is the maximum amount of heat released of OPC, and is calculated by Eq. (7); p_{OPC} is the cement mass to total cementitious content ratio; Q_{EX} is the maximum amount of heat released of EX ($Q_{EX}=887.12$ J/g) [16]; p_{OPC} is the EX mass to total cementitious content ratio.

4. RESULTS AND DISCUSSIONS

4.1 Isothermal Calorimetry

Figure 1 shows the degree of hydration of OPC and cement-EX paste with various dosages of EX within 72 hours. The addition of EX increased the hydration degree of cement-EX blends at 72 hours. Increasing the dosages of EX caused an accelerating in hydration at the first 24 hours. The degree of hydration is about 0.65 at 72 hours for all cement-EX blends, while the degree of hydration of OPC is about 0.6. The sample with 100% EX shows that the hydration degree is the largest at the first 24 hours.

Figure 2 shows the heat evolution rate of OPC and cement-EX blends. It can be seen that the addition of EX reduced the height of the main peak of heat evolution curves. The heat evolution rate of sample using 100% EX is higher than that of the other sample at all ages.

4.2 Modeling hydration of cement-EX blends

In this section, to evaluate the application of our model, a comparison of the predicted hydration degree and measured hydration degree of cement-EX blends with w/b ratio of 0.5 was performed.

Figure 3 shows an example of the fitting the model to the experimental result. The fitting data was performed to determine the model parameter. Table 5 shows the model parameters value of OPC100 and blends consist of 5%, 10%, 15% and 20% EX cement replacement by weight. It can be seen in Table 5 that when the cement replacement ratio is changed, almost these parameters of blends vary; C is not changed for all cement-EX blends, B and D increase with the EX replacement ratio, while k_r decreases with EX replacement ratio. For OPC100 paste, the value of C is chosen according to the results of Maruyama's model [10]

A typical calorimetric curve for the rate of heat evolution of cement-based materials is presented in Figure 4. As shown in this figure, the hydration process is divided into four stages: Initial period, induction period (also called dormant period), acceleration period, and deceleration period [17].

Besides, the hydration degree of clinker phases is shown in Figure 5. It can be seen that the hydration of C_3A and C_4AF starts immediately after the initial contact of cement and water. The hydration of C_3S starts about 2 hours, and that of C_2S at about 30 hours [18]. Combining Figure 4 with Figure 5, the reaction period of mineral composition could be assumed as follows: at initial period, C_3A and C_4AF starts reaction; at induction period, to create the nucleation of C-S-H and C_3S starts reaction; at acceleration period, fast dissolution of C_3S to precipitation of portlandite and C-S-H; at deceleration period, the hydration of C_3A and C_2S .

As we mentioned above, the model parameters were determined by fitting the model to the experimental results. During the fitting data, the change

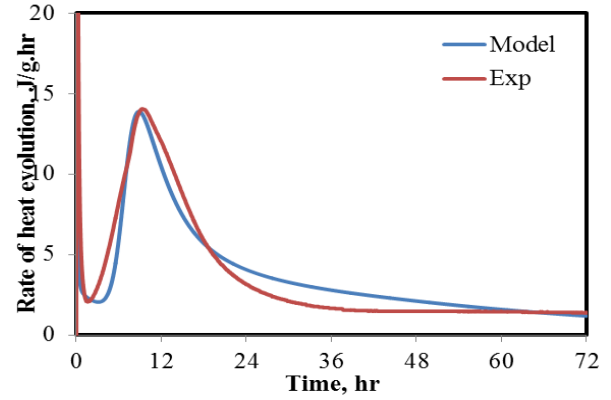


Fig.3 Fitting the model to the experimental result (Example of OPC 100%)

Table 5 Model parameters

Sample	B_{20} (mm/h)	C_{20} (mm/h)	D_{20} (mm ² /h)	K_r (mm/h)
OPC100	3.6E-11	1.0E+9	2.5E-11	6.8E-8
OPC95+EX5	1.2E-10	5.0E+8	4.0E-11	6.5E-8
OPC90+EX10	1.6E-10	5.0E+8	7.0E-11	5.9E-8
OPC85+EX15	2.5E-10	5.0E+8	9.0E-11	5.2E-8
OPC80+EX20	3.0E-10	5.0E+8	1.0E-10	5.0E-8

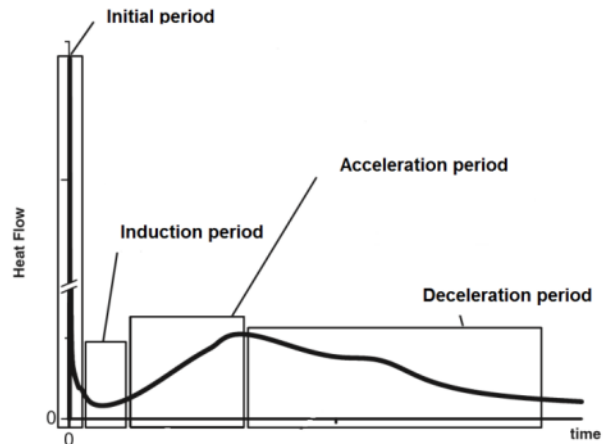


Fig.4 Changes detected in the phase composition of the OPC paste, assigned to the different periods of OPC hydration [17]

Note:

1. Initial period: the complete dissolution of bassanite and arcanite. Partial dissolution of anhydrite and C_3A . C_3A dissolution is stopped due to an amorphous $Al(OH)_3$ -layer or adsorbed sulfate ions. Initial precipitation of ettringite. No reaction of C_3S .

2. Induction period: Nucleation of C-S-H. Dissolution of anhydrite. Slow precipitation of ettringite from $Al(OH)_3$ -layer.

3. Acceleration period: the Further dissolution of sulfate carriers. Further precipitation of ettringite from $Al(OH)_3$ -layer. Fast dissolution of C_3S synchronous to precipitation of portlandite and C-S-H phase.

4. Deceleration period: Slowdown of silicate reaction. Slowed dissolution of sulfate carriers causes further dissolution of C_3A .

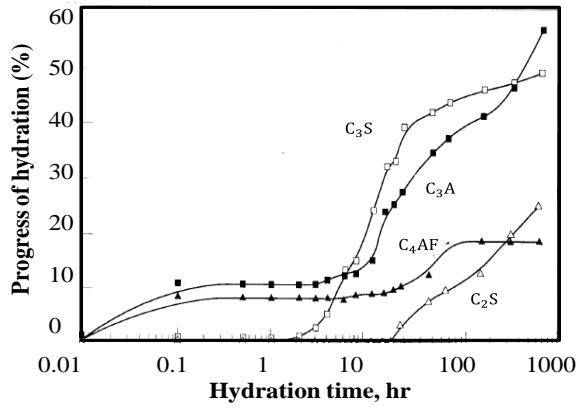


Fig.5 Hydration degree of clinker phases in Portland cement paste as a function of hydration time at ambient temperature [18]

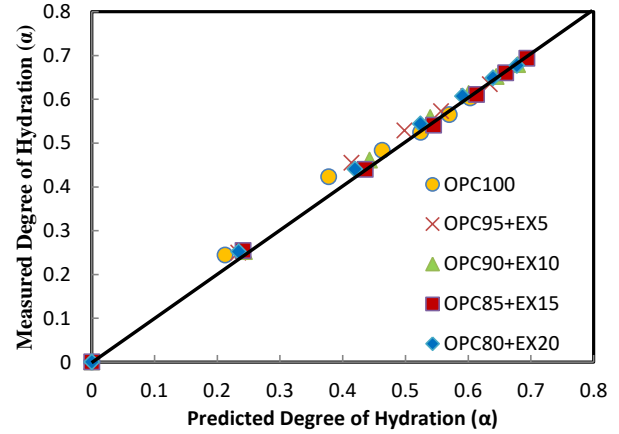


Fig.7 Comparison between predicted hydration degree and measured hydration degree.

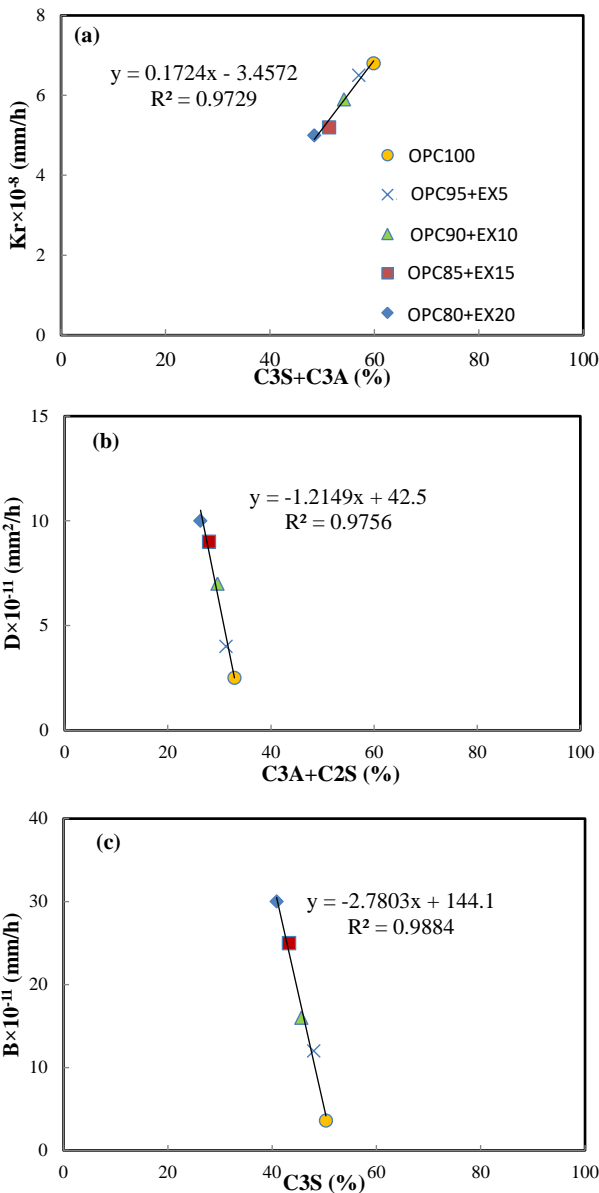


Fig.6 Relationship between the mineral composition and the model parameters: Where Fig 6 (a), (b) and (c) shows the relationship between K_r , D , B and (C_3S+C_3A) , (C_3A+C_2S) , C_3S content, respectively

of model parameters value leads to change the heat flow line of all periods. Therefore, there is a relation between the hydration of mineral composition and the model parameters; this result also has been reported by Maruyama et al. [10].

According to the fitting to the experimental results, when the value of k_r parameter changed, the heat flow line varies at acceleration and initial deceleration period. These stages are the time for the dissolution of C_3S and C_3A . It presents that there is a relation between k_r and $(C_3S$ and $C_3A)$ content. The D value change leads to the change of heat flow line at deceleration period, which the dissolution of C_3A and C_2S (after 30 hours) occur at this period. So, the value of D parameter depends on the amount of C_3A and C_2S . Similarly, B parameter depends on the amount of C_3S due to its change caused the change of heat flow line at the induction period that is the time for the dissolution of C_3S .

The relationship between the mineral compositions of cement-EX blends and the model parameters is shown in Figure 6. It can be seen, while k_r decrease with reducing (C_3S+C_3A) content, B and D increases with reducing C_3S and (C_3A+C_2S) content, respectively. These parameters are assumed to be a function of mineral composition and given by following equations:

$$C = 5 \times 10^8 \quad (9)$$

$$k_r = (0.1724 \cdot (C_3S\% + C_3A\%) - 3.4572) \cdot 10^{-8} \quad (10)$$

$$D = (-1.2149 \cdot (C_3A\% + C_2S\%) + 42.5) \cdot 10^{-11} \quad (11)$$

$$B = (-2.7803 \cdot C_3S\% + 144.1) \cdot 10^{-11} \quad (12)$$

Figure 7 shows a comparison of predicted hydration degree and measured hydration degree of OPC and cement-EX blends. It can be seen that the predicted and measured results are in good agreement for all samples. Hence, our parameters could simulate the hydration of cement-EX blends.

5. CONCLUSIONS

In this paper, hydration model of cement paste mixed with EX with W/B ratio of 0.5 was studied at the curing temperature 20°C. Based on the results obtained from the investigation the following conclusions may be drawn:

- (1) The hydration degrees of cement-EX blends were approximately 0.65, while that of OPC was about 0.6 at 72 hours. The height of the main peak of heat evolution rate decreases with increasing the dosages of EX.
- (2) The fitting to the experimental results were used to determine the model parameters. Besides, the relationship between the mineral composition of cement-EX blends and the model parameters were considered. The value of C parameter was constant for all cement-EX blends. The value of B and D parameter increases with reducing C_3S and (C_3A+C_2S) content, respectively. While the value of k_r parameter decreases with reducing (C_3S+C_3A) content. These parameters are expressed as a function of the C_3S , C_3A , and C_2S content, as given by Eq. (10), (11) and (12).
- (3) The agreement between the predicted and measured results presents that our model is effective and useful as a method to predict the hydration reaction of cement-EX blends.

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