

# Isothermal Calorimetry Study of Blended Cements and its Application in Numerical Simulations

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Apparent activation energy ( $E_a$ ) is generally used to consider the effect of temperature on the kinetics of cement hydration in the numerical simulation of cement hydration processes. This paper deals with an experimental study on the kinetics of Portland cement and blast furnace slag cement using isothermal Calorimetry at 20, 30, and 40 °C. Two different water/cement ratios were used, viz. 0.4 and 0.6. Based on the experimental data,  $E_a$  for Portland cements and blast furnace cement was calculated dynamically with the progress of hydration. It was found that  $E_a$  exhibits dependence on degree of hydration, water/cement ratio, and temperature. Variation of  $E_a$  along with degree of hydration may suggest a change in the mechanisms of hydration. Numerical simulation was done using HYMOSTRUC model with a new expression of  $E_a$  and good agreement with experimental data was found.

**Key words:** Isothermal calorimetry, Apparent activation energy, Numerical simulation, Blended cements

## 1 Introduction

Cement hydration is accompanied by the release of heat and therefore, isothermal calorimeter can be used to record the thermal power of the hydration processes and by integrating the thermal power over time, the amount of released heat can be obtained. In order to describe the kinetics of the hydration processes of cement, especially to study the temperature dependence of the hydration processes, the Arrhenius equation is generally used, which can be written as

$$K(T)=A*\exp(-E_a/RT) \quad (1)$$

Where A is the collision number constant, R is the ideal gas constant, 8.314 J/(mol·K) and  $E_a$  is the activation energy.

Because cement hydration is composed of several simultaneous chemical reactions and physical processes, the term apparent activation energy is used here instead. Obviously, apparent activation energy ( $E_a$ ) is an experimentally obtained value from its definition. To determine the  $E_a$ , several methods can be used, for example by measuring the mechanical properties and by calorimetric methods. In this paper, the isothermal calorimetry method is used.

Isothermal calorimetric measurement was carried out using Portland cement (PC) and blast furnace slag cement (BFSC) cement pastes. Thereafter, apparent activation energy was calculated based on the heat released during the hydration processes and was simplified into an easily operable expression and incorporated in the HYMOSTRUC model [1] to carry out numerical simulation for concrete cured under adiabatic conditions. Comparison between measured adiabatic temperature raise and simulated results shows that a better result is obtained using the simplified expression of apparent activation energy.

## 2 Experiment Description

### *Experimental Instruments*

The isothermal calorimeter used is the 3114/3236 TAM Air isothermal calorimeter, Figure 1, manufactured by Thermometric AB, Sweden. It is an eight-channel calorimeter operating in the milliwatt region. The capacity chosen in this research was 600 mW. It can operate in the temperature range from 5 to 60°C with a fluctuation of only  $\pm 0.02^\circ\text{C}$ .

The calorimeter is located in a room where temperature was set to 20°C and RH 75%. At measurement temperatures higher than the environment temperature, in order to prevent as much as thermal shock to the calorimeter due to the temperature difference between the sample and calorimeter, both cement and water are kept in the oven for 24 hours at the desired mixing temperature before mixing and isothermal measurement. Heat of hydration in the first 7 days was recorded by the industrial computer.

### *Materials*

The cements used are all manufactured by ENCI B.V., The Netherlands and CEM I 52.5R (referred as PC later) is produced in ENCI Maastricht and CEM III/B 42.5 LH HS (referred as BFSC later) is produced in ENCI IJmuiden. The oxide composition of the cement can be found from Table 1.

The mineral content of CEM I 52.5R was calculated using Bogue equation as 60.57%  $\text{C}_3\text{S}$ , 11.37%  $\text{C}_2\text{S}$ , 8.43%  $\text{C}_3\text{A}$  and 8.79%  $\text{C}_4\text{AF}$ . The content of blast furnace slag is 68% and clinker 28%, fly ash 4% in CEM III/B 42.5 LH HS.

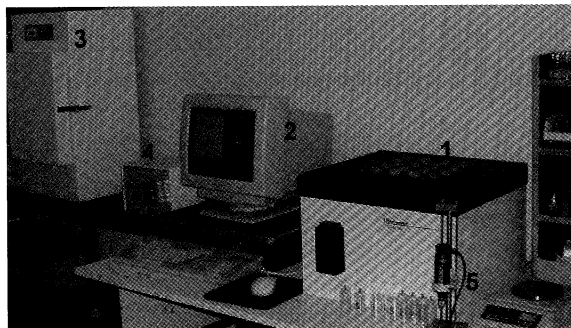


Figure 1. Experimental setup, where 1: isothermal calorimeter, 2: industrial computer, 3: oven, 4: shaking machine, 5: mixer, 6: electronic scale

Table 1. Chemical Composition of the Cements

	CEM I 52.5R wt%	CEM III/B 42.5 LH HS wt%
CaO	62.860	45.270
SiO <sub>2</sub>	19.630	30.790
Al <sub>2</sub> O <sub>3</sub>	5.020	9.880
Fe <sub>2</sub> O <sub>3</sub>	3.310	1.400
K <sub>2</sub> O	1.230	1.170
Na <sub>2</sub> O	0.301	0.221
SO <sub>3</sub>	3.010	2.820
MgO	2.280	6.590
TiO <sub>2</sub>	0.363	0.477
MnO	0.119	0.216
P <sub>2</sub> O <sub>5</sub>	0.449	0.140
LOI	1.060	0.760

Particle size distribution of the cement was also measured using laser diffraction. The equipment used was Coulter LS 230 and the result is shown in Figure 2. The Blaine number for PC is found to be 550 m<sup>2</sup>/kg and that for BFSC is 440 m<sup>2</sup>/kg.

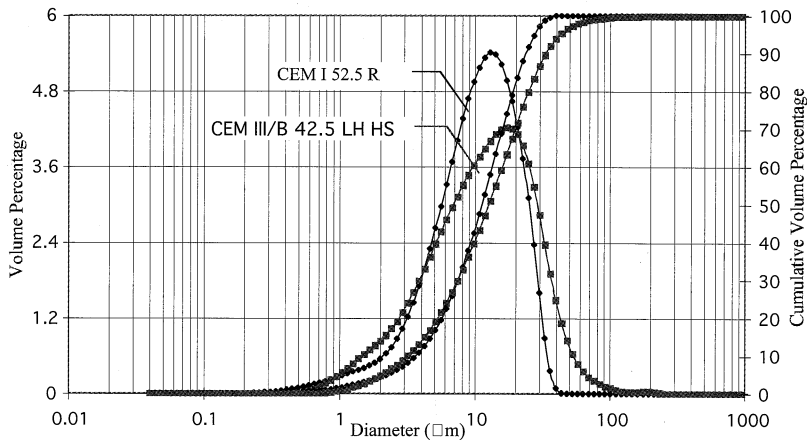


Figure 2. Particle size distribution of the two cements

#### Cement Paste Composition

Table 2 shows the compositional details of the samples. The weight of the sample cement paste for the isothermal measurement is 10 ± 0.01 gram. For each mixture composition, the measurement of the isothermal heat release was done at temperatures 20, 30 and 40°C, respectively.

Table 2 Mixture Composition

Code	W/C	Water (gram)	Cement (gram)	Cement used
R4I	0.40	2.86	7.14	CEM I 52.5 R
R6I	0.60	3.75	6.25	
R4H	0.40	2.86	7.14	CEM III/B 42.5 LH HS
R6H	0.60	3.75	6.25	

### 3 Experiment Results

#### *Thermal Power and Heat of Hydration*

Cement hydration is an exothermic process and an isothermal calorimeter records the rate of the heat release or the thermal power. By integrating the thermal power with time, we can obtain the heat of hydration. Thereafter, the degree of hydration at time  $t$  can be defined as the heat released at time  $t$  divided by the potential heat that can be released at complete hydration, viz.

$$\alpha = Q(t) / Q^{\text{pot}} \quad (2)$$

It can be seen in Figure 3 that the rate of hydration of PC is quite fast and has two peaks. The first peak appears immediately after cement is mixed with water. The second peak appears generally at about 5 to 9 hours. The higher the temperature, the earlier the second peak will appear. However, BFSC exhibits another shoulder after the second peak. The higher the temperature, the shorter the interval between the second and third peak is.

From the experimental data, a dependency of  $E_a$  on  $\alpha$  was observed. The higher the curing temperature, the higher the degree of hydration is at early age while the final degree of hydration will be lower. For Portland cement, after 1 day, the degree of hydration at higher temperature is lower than that at lower temperature. However, for slag cement, lower values of degree of hydration are found after about 2 to 3 days. The time of the lower value of the degree of hydration is also influenced by the water/cement ratio. At  $w/c=0.4$ , the time is shorter than that at  $w/c=0.6$ .

If we have a look at the experiment done with ultrasonic measurement of concrete [5], the wave speed is also lower at higher curing temperatures at later stage. In addition, lower 7 and 28 days compressive strength are also found for concrete cured at higher temperatures.

Garcia and Sharp [2] also reported that higher curing temperature will decrease the degree of hydration of both Portland cement and blended cement at the later stages.

#### *Activation Energy*

From Eq. (1) and (2), taken the rate of hydration at two isothermal curing temperatures  $T_1$  and  $T_2$  ( $T_1 > T_2$ , absolute temperature) as  $K_1$  and  $K_2$ , the apparent activation energy can be calculated using the formula below:

$$E_a(T, Q) = -R * T_1 * T_2 / (T_2 - T_1) * \ln(K_2 / K_1) \quad (3)$$

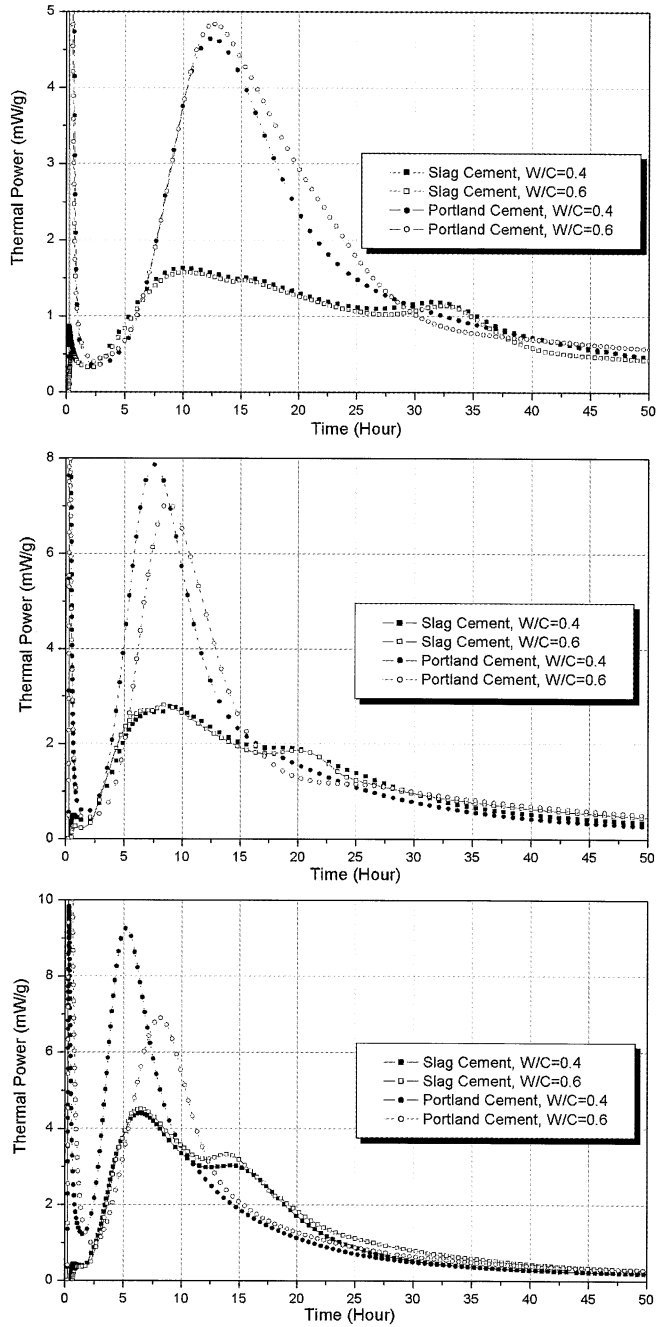


Figure 3. Thermal power of PC and BFSC at 20, 30 and 40 °C, W/C=0.4 and W/C=0.6 using isothermal calorimeter, only first 50 hours are shown for a better view

The calculated  $E_a$  is shown in Figure 4 and in order to use the obtained  $E_a$  in numerical simulation, a simplification similar to [4] was made and the following expression for  $E_a$  is obtained:

$$E_a(\alpha(t), T) = (44.92 - 0.043 * T) * \exp(-0.00017 * T) e^{-\alpha(t)} \quad \text{kJ/mol} \quad (4)$$

Where  $\alpha$  is the degree of hydration and  $T$  is temperature (K).  $\alpha$  can be expressed as a function of time.

Freiesleben et al. proposed a general bi-linear apparent activation energy, which claims that  $E_a$  remain constant for temperature above 20 °C [1, 6]. However, van Breugel [1] calculated the activation energy based on isothermal Calorimetry data on Portland cement carried out by Lerch and Ford and suggested that  $E_a$  is a function of temperature, degree of hydration and  $C_3S$ . D'Aloia [3] confirmed that the  $E_a$  shows dependence on the degree of hydration based on isothermal calorimetry study, which is also found in our experiments.

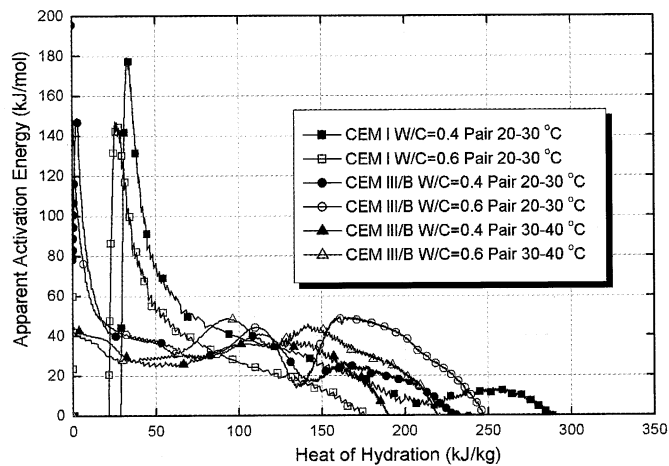


Figure 4. Calculated apparent activation energy for PC and BFSC using Eq. (3)

## 4 Application

In order to validate the effectiveness of Eq. (4), we used the equation in the HYMOSTRUC model and made several simulations using experimental data of [6], where adiabatic curing data was reported.

It can be seen from Figure 5 that numerical simulation using HYMOSTRUC with Eq. (4) gives closer results to the measured adiabatic temperature raise. Figure 5 also shows that at the very beginning of the hydration (< 24 hours), HYMOSTRUC with Eq. (4) predicts a quite acceptable adiabatic temperature raise, which is quite important because this provides the basis for more accurate calculation of the thermal stress in massive concrete at early age and has beneficial effect on the control of cracks and durability.

In addition, the predicted adiabatic temperature raise at later periods (around 1000 hours) is also decreased in the direction of experimental data in comparison with the HYMOSTRUC, with its originally implemented expression of  $E_a$ .

## 5 Conclusions

Isothermal calorimeter measurements were done using Portland cement (PC) and blast furnace slag cement and the apparent activation energy was obtained and a simplified expression for  $E_a$  was found. Numerical simulation using HYMOSTRUC with this new form of activation energy agrees quite well with experiment adiabatic data, especially at early age. This is quite important for the calculation of thermal stress, control of thermal crack and associated durability.

It is also found that  $E_a$  changes along with hydration and a significant change in the value of  $E_a$  may suggest a change in the mechanisms of the hydration processes.

In order to get a more reliable numerical simulation result of cement blended with fly ash, silica fume, and limestone powder, a systematic isothermal calorimetry study of these pastes is needed and simulation results can be guaranteed by the better understanding of the apparent activation energy.

It has to be admitted that the exact value or expression of activation energy may be less important in the real engineering practice, for example, in the case of the calculation of risk of crack. However, it is quite necessary in the fundamental study, especially on the kinetics of cement hydration processes.

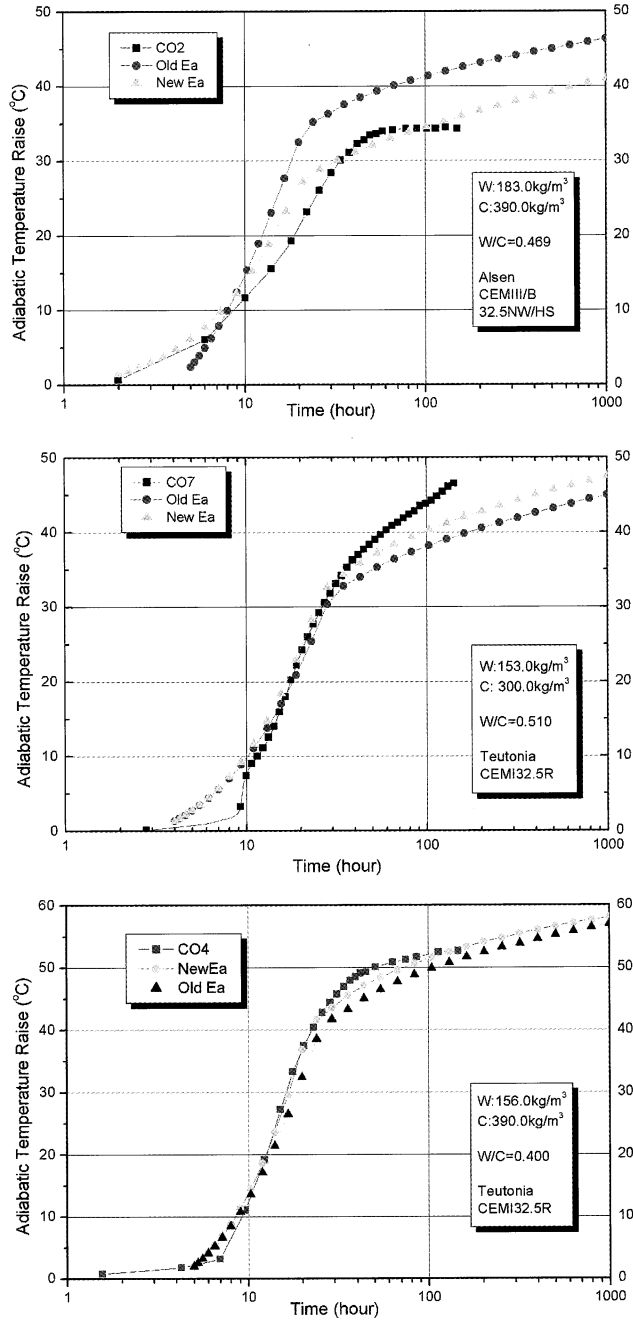


Figure 5. Comparison among experimental values, where simulations using HYMOSTRUC with Eq. (4) are denoted as "New  $E_a$ " and simulations using HYMOSTRUC with the original implementation in HYMOSTRUC are denoted as "Old  $E_a$ "



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