

## Apparent Activation Energy of Cement Blended with Rice Husk Ash

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### ABSTRACT

The hydration kinetics of cement depends on the reaction temperature. An issue related to the effects of curing temperature on cement hydration is the apparent activation energy ( $E_a$ ). The effect of Rice husk ash (RHA) on  $E_a$  is still not clear. This paper studies the  $E_a$  of Portland cement blended with RHA using isothermal calorimetry.

Based on the experimental data, the  $E_a$  of RHA blended cement was first calculated with the hydration process. Besides, the mean  $E_a$  was also calculated according to the modified ASTM C 1074 method.

In this study, it was observed that the  $E_a$  depends on the degree of hydration, water to binder ratio, temperature, and the RHA replacement. The variation of  $E_a$  along with the degree of hydration reflects the change in the mechanism during the hydration process.

### INTRODUCTION

The apparent activation energy ( $E_a$ ) of Portland cement is the minimum amount of energy needed for this material to hydrate.

By using the Arrhenius function with a proper value of  $E_a$ , the influence of temperature on the hydration rate of Portland cement can be described. Thus, the relative influence of the temperature on the development of any concrete property, which is in turn related to the degree of cement hydration, could be estimated. This approach has been used to predict compressive strength as a function of curing temperatures [P. Freiesleben Hansen and E.J. Pedersen 1977].

The determination of  $E_a$  is usually carried out by means of mechanical or calorimetric tests. The mechanical strength, not like the heat of hydration, doesn't reflect a purely chemical mechanism. From heat evolution curves the effect of the cement chemistry is clearer. The isothermal test has the advantage of fixing the temperature parameter on which the apparent activation energy is likely to depend [H. Kada-Benameur et. al. 2000].

In calculations of temperature distributions in concrete structures  $E_a$  can be considered a constant [Ma W. et. al., 1994]. Several studies, however, reveal  $E_a$  not to be constant at all. Schindler [Schindler A.K. 2004] proposed an equation for  $E_a$  that considers the chemical

composition and fineness of cement. Hansen and Pedersen [P. Freiesleben Hansen and E.J. Pedersen 1977] recommended that  $Ea$  is only a function of curing temperature. Van Breugel [K. van Breugel 1991] proposed an equation for  $Ea$  as a function of chemical composition of cement, curing temperature and the degree of hydration.

RHA constitutes about one fifth of the 690 million metric tons of rice paddy produced annually in the world [Rice market monitor, 2009]. Rice husk ash obtained after complete combustion of the husk in controlled conditions contains 90-96% silica in amorphous forms. The average particle size of RHA ranges in general from 5 to 10  $\mu\text{m}$ , much larger than that of silica fume. However, due to its extremely porous structures, it possesses a very high surface area (even more than 250  $\text{m}^2/\text{g}$ ) [Bui, D.D. 2001]. RHA have been classified as “highly active pozzolans” [Mehta, P.K. 1983]. RHA when incorporated in cement affects the rate and the extent of heat generation [Quigge Feng 2003]. However, the effect of RHA on the activation energy in all subsequent cement hydration stages is still not clear.

The objective of this work is to study the effect of the hydration degree, temperature, water to binder ratio (wbr) and RHA replacement amount on  $Ea$ . Isothermal calorimetry has been used to study heat evolution when the reaction temperature was set from 10 to 40°C.

## **EXPERIMENTAL INVESTIGATION**

### **Materials**

Materials for the cement paste to be tested are Portland cement (CEM I 52.5N); Rice husk ash and superplasticizer (Glenium 51). The mineral composition calculated by the Bogue formula [K. van Breugel 1991] was 63.9%  $\text{C}_3\text{S}$ , 9.2%  $\text{C}_2\text{S}$ , 8.2%  $\text{C}_3\text{A}$ , and 9.1%  $\text{C}_4\text{AF}$  by weight.

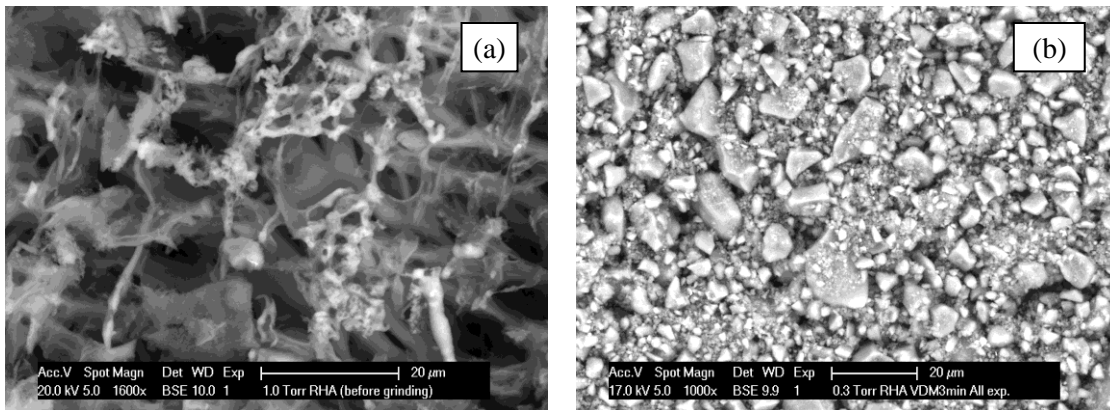
Rice husk, an agricultural waste material from Vietnam, was burnt by a drum incinerator developed by Pakistan Council of Scientific & Industrial Research [UNIDO, Vienna. 1984] under uncontrolled combustion conditions (Figure 1). Details of the oven and rice husk combustion process were described elsewhere [Bui, D.D. 2001]. The ash obtained was finely pulverized by using a vibrating ball mill. The ash contains 87.96%  $\text{SiO}_2$  and its mean particle size is 9.07  $\mu\text{m}$ . The SEM images of RHA are shown in Figure 2. It can be seen that RHA is porous (Figure 2a). Its particles are angular (Figure 2b).

### **Experiment description**

To study the effect of temperature on the hydration process, the isothermal heat was measured by TAM Air isothermal calorimeter on cement pastes at 10, 20, 30 and 40°C. The duration of all tests was seven days. Before mixing, all the materials were placed in an oven for at least one night at the desired testing temperature. The weight of the cement paste for the isothermal measurements was  $10 \pm 0.01\text{g}$ . Water to binder ratios (wbr) of 0.40 and 0.25 were chosen. The amounts of cement replacement by RHA were 0, 5, 10, 20, 30% by weight. The amount of superplasticizer was constant for all mixtures.



**Fig. 1. View of drum incinerator used for ashing the rice husks**



**Fig. 2. SEM images of RHA before grinding (a) and after grinding (b)**

## RESULTS AND DISCUSSIONS

### Heat evolution

Cement hydration is an exothermic process. The isothermal calorimeter records the heat release or the thermal power. The degree of hydration at time  $t$  can be approximated by the heat released at time  $t$  divided by the maximum heat [K. van Breugel, 1991], viz.

$$\alpha(t) = Q(t) / Q_{max} \quad (1)$$

where  $Q(t)$  is the heat liberated at time  $t$ ,  $Q_{max}$  is the maximum heat when all the cement has hydrated. The maximum heat of the binder (cement + RHA) is calculated as follows:

$$Q_{max} = P_{Cem} \cdot Q_{Cem} + P_{RHA} \cdot Q_{RHA} \quad (2)$$

$P_{\text{Cem}}$ ,  $P_{\text{RHA}}$  is the percentage of cement and RHA, respectively;  $Q_{\text{Cem}}$  is the maximum heat of cement calculated according to Bogue [see K. van Breugel 1991];  $Q_{\text{RHA}}$  is the maximum heat of RHA calculated from the amount of amorphous  $\text{SiO}_2$  in RHA, where  $Q_{\text{SiO}_2} = 780 \text{ J/g}$  [Waller V. et. al. 1996].

### Activation Energy

The activation energy is calculated from the heat rate results [H. Kada-Benameur et. al. 2000, L. D'Aloia et. al. 2002]:

$$Ea(\alpha) = R \left[ \frac{T_1 T_2}{T_1 - T_2} \cdot \ln \left( \frac{\frac{d\alpha_1}{dt}}{\frac{d\alpha_2}{dt}} \right) \right] \quad (3)$$

with  $R$  the gas constant ( $8.314 \text{ J/mol K}$ );  $T_1$  and  $T_2$  the curing temperatures (K);  $d\alpha_1/dt$ ,  $d\alpha_2/dt$ : the rate of hydration at  $T_1$  and  $T_2$ , respectively.

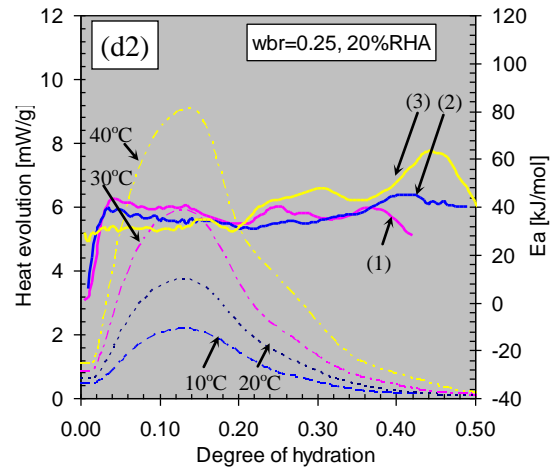
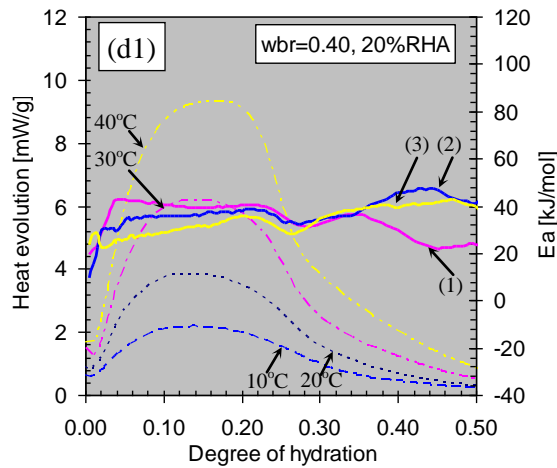
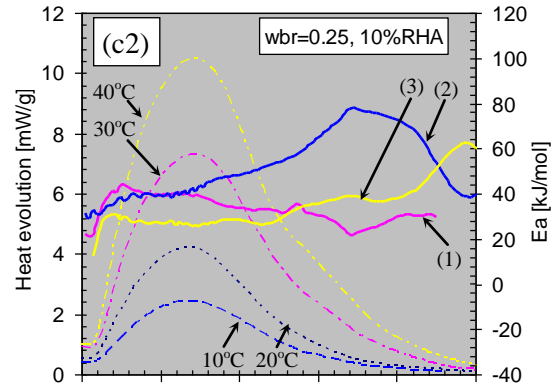
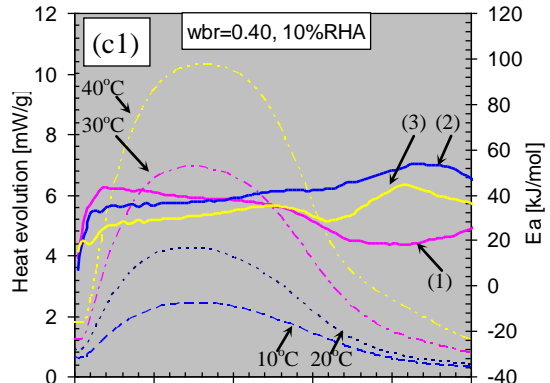
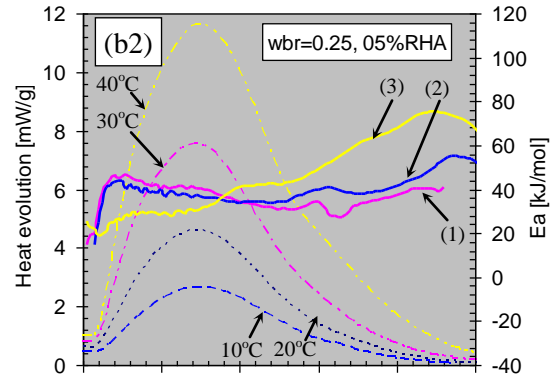
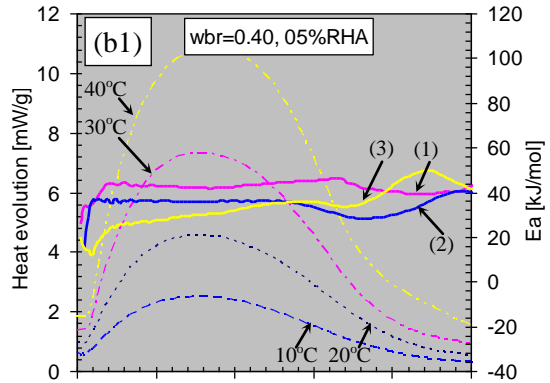
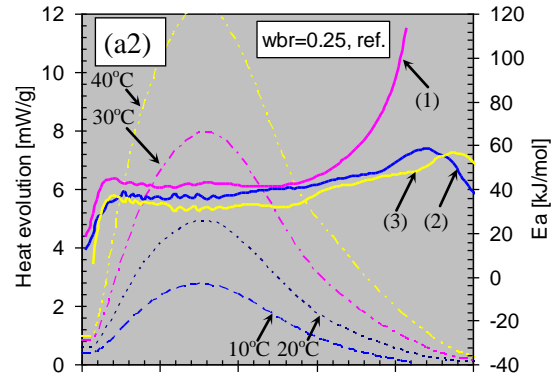
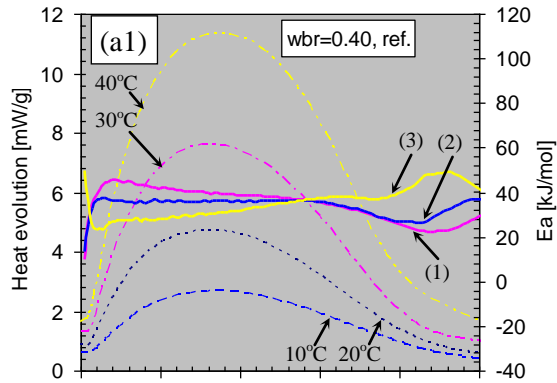
### Results and Discussion

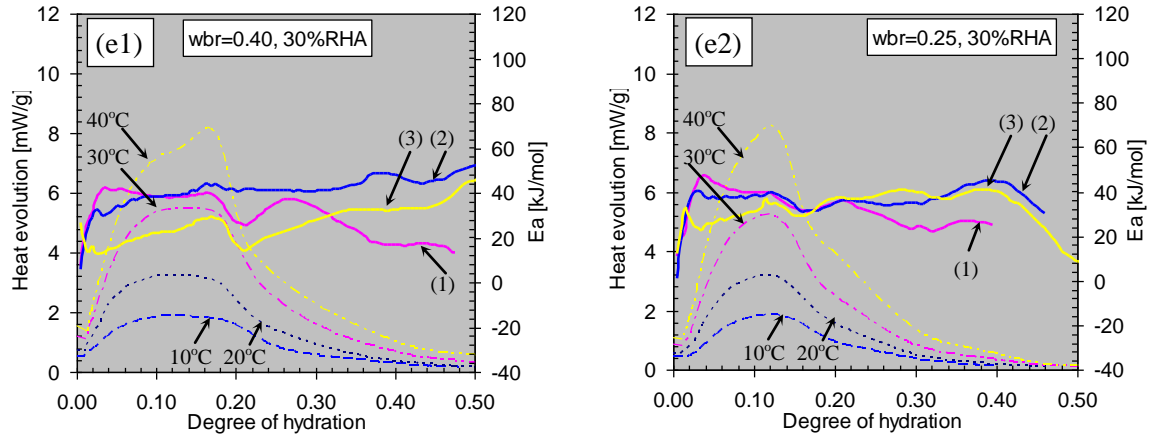
The results of heat evolution and the calculated  $Ea$  for the samples with  $wbr = 0.40$  and  $0.25$  are shown in Figure 3 (left. 0.4; right, 0.25).  $Ea$  for different amount of cement replacement by RHA are shown from top to bottom. The three ranges of temperature studied were 10-20, 20-30, 30-40°C.

Figure 3 shows that for both  $wbr$ 's  $Ea$  is almost "constant" in the range of values of the hydration degree from 0.05 to 0.20-0.40. Furthermore, the mean value of  $Ea$  seems almost independent of the amount of RHA as long as one temperature range is considered. For example, for the 0.40  $wbr$  mixture, the  $Ea$  is around 38 kJ/mol within the temperature range of 10-20°C, which is independent of the RHA-replacement percentage. However, at higher temperature range, lower values for  $Ea$  are found. For example, for the 0.40  $wbr$  mixtures with 5 % RHA replacement, the  $Ea$  reduces from 43.37 to 31.44 kJ/mol in the temperature ranges from 10-20°C to 30-40°C respectively (Table 1).

Table 2 shows mean values of  $Ea$  of mixtures for increasing RHA replacement percentages. These mean values of  $Ea$  are almost constant for both  $wbr$  of 0.40 and 0.25.

It was found that in the deceleration period, there is a shoulder in the heat evolution curve at 20°C from 10 to 16 hours, corresponding to the hydration degree from 0.40 to 0.50 (Figure 4a). This is attributed to the renewed formation of ettringite [H.F.W. Taylor 1990]. This shoulder is clearer at higher temperature (Figure 4a) or at lower  $wbr$  (Figure 4b).





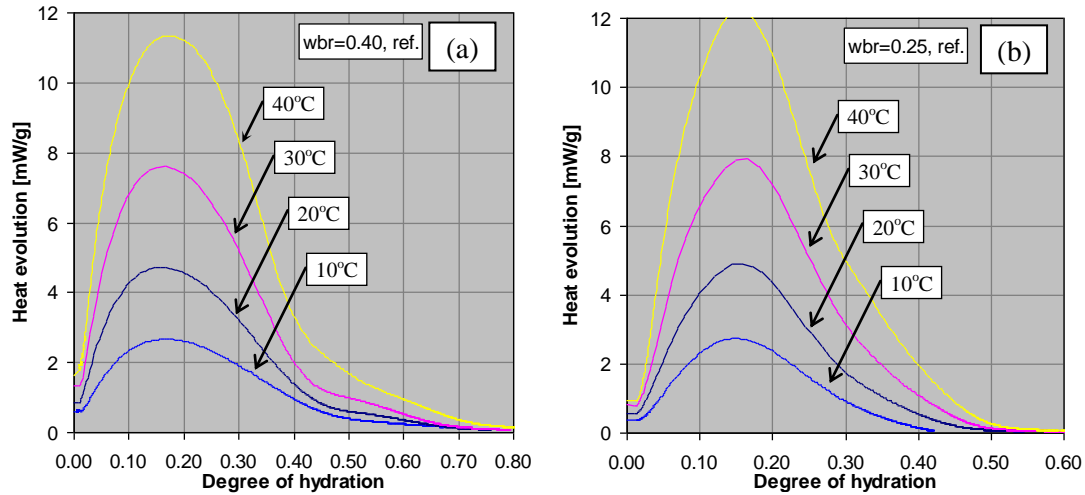
**Fig. 3.** The calculated  $E_a$  according to equation (3) with  $wbr = 0.40$  (left column) and  $wbr=0.25$  (right column); (1)  $E_a(10-20^\circ\text{C})$ , (2)  $E_a(20-30^\circ\text{C})$ , (3)  $E_a(30-40^\circ\text{C})$

**Table 1.** The  $E_a$  calculated by equation (3) obtained for degree of hydration  $\alpha$  from 0.05 to 0.2-0.4 for three ranges of temperature (10-20, 20-30, 30-40°C)

% RHA	wbr = 0.40				wbr = 0.25			
	$\alpha$ from 0.05 to	10-20°C	20-30°C	30-40°C	$\alpha$ from 0.05 to	10-20°C	20-30°C	30-40°C
0	0.380	37.82	35.04	32.81	0.285	41.87	37.57	32.39
5	0.365	43.37	34.55	31.44	0.270	37.93	36.71	34.81
10	0.335	36.10	38.59	31.01	0.250	37.38	44.07	27.34
20	0.285	38.90	35.71	30.73	0.205	38.00	34.43	31.52
30	0.220	36.60	39.63	22.12	0.175	37.77	36.39	30.55
	$\overline{E}_a$	<b>38.56</b>	<b>36.70</b>	<b>29.62</b>	$\overline{E}_a$	<b>38.59</b>	<b>37.83</b>	<b>31.32</b>
	$R^2$	0.9710	0.9774	0.9573	$R^2$	0.9815	0.9633	0.9727

**Table 2.** Mean values of  $E_a$  for different RHA replacement percentages calculated from values in Table 1 over the total temperature range from 10 to 40°C

wbr	Percentage of RHA replacement				
	0%	5%	10%	20%	30%
0.40	<b>35.22</b>	<b>36.45</b>	<b>35.23</b>	<b>35.12</b>	<b>32.79</b>
$R^2$	0.9749	0.9381	0.9614	0.9588	0.9064
0.25	<b>37.28</b>	<b>36.48</b>	<b>36.26</b>	<b>34.65</b>	<b>34.90</b>
$R^2$	0.9525	0.9843	0.9158	0.9676	0.9616



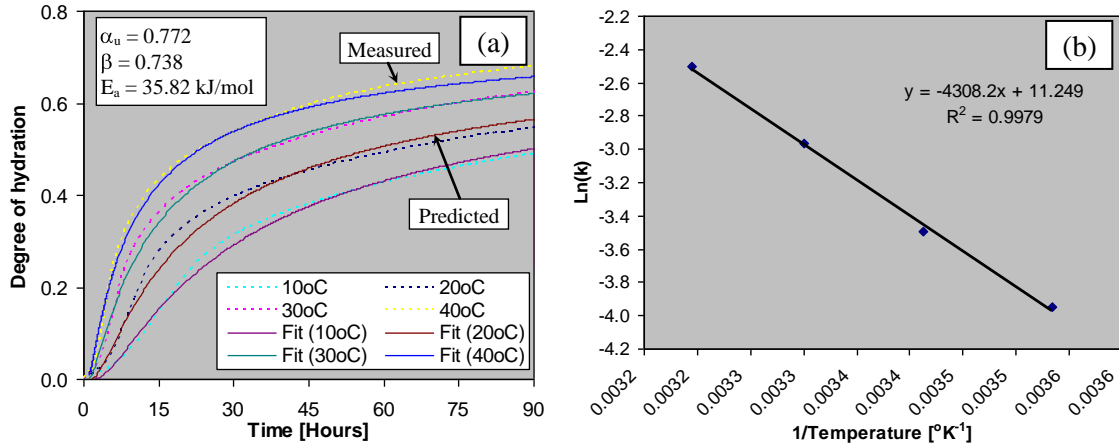
**Fig. 4. The hydration rate of cement at the temperature from 10 to 40°C, wbr = 0.40 (left) and wbr = 0.25 (right)**

When the renewed formation of ettringite appears, the  $E_a$  varies considerably and then decreases gradually (Figure 3). Kjellsen *et. al.* [Knut O. Kjellsen *et. al.* 1992] suggested that the rate controlling mechanism changes from chemical controlled to diffusion controlled in this period and that the cement hydration is a diffusion controlled process when  $E_a$  reaches the value of 20 kJ/mol. In that case applying the Arrhenius law becomes complicated. This was also mentioned by [H. Kada-Benameur *et. al.* 2000].

From the experimental results, it can be seen that the higher the percentage of RHA replacement, the earlier the phenomenon of renewed ettringite formation will appear (Figure 3 from b1 to e1 or from b2 to e2). This phenomenon occurs at a hydration degree from 0.40 (wbr=0.40, 0%RHA) to 0.20 (wbr=0.40, 30%RHA), or from 0.30 (wbr=0.25, 0%RHA) to 0.18 (wbr=0.25, 30%RHA).

More interestingly, an extra peak caused by the pozzolanic reaction of RHA is clearer with increasing cement replacement (Figure 1 d1, e1). The value of  $E_a$  shows a decreasing tendency and after that decreases again at the hydration degree of 0.17 corresponding to this reaction (Figure 3 e1).

Based on these analysis, the  $E_a$  is assumed constant from the very early period ( $\alpha=0.05$ ) to the point at which the renewed formation of ettringite occurs. The calculation of the mean  $E_a$  includes the effect of pozzolanic reaction. These mean values of  $E_a$  for the 0.40 wbr mixtures (Table 2) were similar to those calculated according to the modified ASTM C 1074 method [Jonathan L. Poole *et. al.* 2007] (Table 3).



**Fig. 5. (a) Predicted degree of hydration versus actual heat of hydration; and (b)  $E_a$  from plot of  $\ln(k)$  versus  $1/T$  for the sample with wbr of 0.40, 20% RHA (according to the modified ASTM C 1074 method)**

**Table 3. The  $E_a$  calculated by the modified ASTM C 1074, wbr = 0.40**

	Percentage of RHA replacement, wbr = 0.40				
	0	5	10	20	30
$\alpha_u$	0.8408	0.8782	0.8096	0.7720	0.6998
$\beta$	0.8059	0.7141	0.7527	0.7379	0.7087
$\tau(10^\circ\text{C})$	22.89	28.72	26.04	28.86	31.74
$\tau(20^\circ\text{C})$	14.32	16.64	17.48	18.59	21.14
$\tau(30^\circ\text{C})$	9.38	10.67	10.18	11.39	12.61
$\tau(40^\circ\text{C})$	5.76	6.77	6.77	7.52	9.07
$E_a$	<b>36.13</b>	<b>38.51</b>	<b>36.95</b>	<b>35.82</b>	<b>34.70</b>
$R^2$	0.9982	0.9968	0.9999	0.9979	0.9952

## CONCLUSIONS

The main conclusions derived from this investigation are:

- From isothermal calorimetry studies, it was observed that the  $E_a$  depends on the degree of hydration, the water to binder ratio, the temperature and the RHA replacement.  $E_a$  is considered constant from the early stage ( $\alpha = 0.05$ ) until the renewed formation of ettringite occurs (roughly  $\alpha = 0.20$  to  $0.40$ )
- When the renewed formation of ettringite appears, the apparent activation energy varies considerably and then reduces gradually. This change shows that the hydration kinetics change of rate controlling mechanism.
- The renewed formation of ettringite occurs earlier at higher percentages of RHA replacement.
- The pozzolanic reaction of RHA causes an extra peak on the heat evolution curve, especially with the higher cement replacement amounts. This reaction creates one jump of  $E_a$ .
- The mean values of activation energy for the 0.40 wbr mixtures are similar to those calculated by the modified ASTM C 1074.



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