

A novel way of estimation of the apparent activation energy of cement hydration using microwave technique

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The apparent activation energy of cement hydration is normally measured using the time-consuming calorimetric method. In this work, a new, quick method of estimating the apparent activation energy of cement hydration using a microwave technique is proposed. The result of the apparent activation energy of the Ordinary Portland Cement (OPC) hydration measured by the microwave method is in good agreement (5% difference) with that obtained by the conventional calorimetric method, indicating that the microwave method can be used as an alternative in the estimation of apparent activation energy of the OPC hydration. The good agreement between the results measured by microwave method and calorimetric method further helps to establish the validity of microwave measurement as a new technique for studying cement hydration proposed in our previous work. © 1999 Kluwer Academic Publishers

1. Introduction

The modeling of cement hydration has always been a goal of research on cement chemistry. The data of the kinetics of hydration such as the apparent activation energy of individual hydration reaction is of special importance in modeling the hydration process. However, since the cement properties are the outcome of all the complex reactions that involve the various phases forming cement-water systems, the data of the reactions of any single phase are far from enough to explain the hydration processes. The hydration processes, therefore, should be treated as an entity. The activation energy of the hydration of the whole cement system is therefore called the apparent activation energy [1] in order to be differentiated from that of the individual reaction.

Owing to the complexity of the cement-water system, it is difficult to measure the kinetic data of cement hydration such as the reaction rate constant and the apparent activation energy of cement hydration reactions. These kinetic data are usually measured using the calorimetric method [2]. The calorimetric measurement of the apparent activation energy of the cement hydration is based on the kinetic model describing the formation of hydrates from the reactants. Several models [3–7] have been suggested and many of them are obtained by modifying the approach proposed by Avrami *et al.* [8–11]. As a period of about half an hour or longer is required to allow the calorimeter to achieve equilibrium, thus the information about the induction period is often missed, especially when the hydration temperature is high, leading to difficulty of accurate measurement of the apparent activation energy of cement hydration reaction.

We have established a good correlation between the hydration results obtained through microwave measurement and calorimetric measurement and found that the microwave method is a good alternative of the calorimetric method in monitoring the cement hydration process [12–17]. As the microwave measurement can start just a few minutes after the cement is mixed with the water, the induction period is easily determined from the microwave measurement. We, in this study, attempt a new approach of measuring the apparent activation energy of cement hydration using the microwave method.

2. Experimental

Investigation of the hydration of the OPC using a microwave technique was conducted by filling a rectangular wave-guide section with a sample of the material and then the variation of the complex dielectric constant with time was measured at microwave frequency of 9.5 MHz. The details of the measurement are shown in references [14, 15]. The OPC samples were prepared by mixing the required amounts of solids with de-ionized water at water to cement ratio (W/C) of 0.4. The first microwave measurement was made about 5 minutes after mixing with water. Further measurements were made at intervals of 5–10 minutes during the first 5 hours and then at intervals of 0.5–2 hours over the next 25 hours. The composition of the OPC used in this work is given in Table I. For comparison, the apparent activation energy of OPC was also measured using a calorimetric method through the measurement of the heat evolution rate during hydration. The heat evolution rate was

TABLE I Component oxides (wt %) of OPC and PFA

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
OPC	21.2	5.5	3.2	63.4	1.7	2.4	0.13	0.68

measured using JAF Conduction calorimeter. Both the microwave measurements and calorimetric measurements were made at various temperatures.

3. Results and discussion

3.1. Estimation of the apparent activation energy of early hydration of OPC by microwave measurement

The rate of cement hydration is highly dependent upon the temperature and it is accelerated at an elevated temperature. It is well known that the reaction rate constant changes with temperature in a form given by the Arrhenius equation:

$$k = A \exp(-Q/RT) \quad (1)$$

where k is the reaction rate constant, Q the activation energy, R the universal gas constant (8.314 J/mol K) and T the absolute temperature. For each reaction, the activation energy Q is a constant, which can only be changed by the changes in the reaction mechanism.

Ideally, the Arrhenius equation should be applied to a single reaction. Since the hydration of cement paste comprises of several simultaneous reactions of clinker phases, the application of the Arrhenius equation to the cement hydration is not very ideal. However, according to the study of the kinetics of cement hydration, all hydration reactions taking place in the early hydration period of OPC, and the reactions of C₃S dominate in the early hydration period. Thus it is reasonable to simply treat all the hydration reactions as a whole and analyze it using classical kinetic theories such as the Arrhenius equation 2.

According to the Arrhenius equation, for each chemical reaction the ratio between the reaction rate constants k_1 and k_2 corresponding to two different temperatures T_1 and T_2 can be expressed as

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (2)$$

If the reaction rate constant k_i at different hydration temperature T_i is obtained, one reaction rate constant and the corresponding temperature can be chosen as the reference k_{ref} and T_{ref} and the plot of $\ln\left(\frac{k_i}{k_{ref}}\right)$ against $\left(\frac{1}{T_i} - \frac{1}{T_{ref}}\right)$ allow the determination of Q .

Firstly, however, a model of cement hydration should be set up. Instead of measuring k_i , the time t_i taken by the cement paste to reach a certain degree of hydration at temperature T_i is measured. As our experimental results show that the higher the temperature, the shorter the time t_i for the cement paste to reach the same hydration, i.e., the larger the reaction rate constant k_i (see Figs 1 and 2), we therefore assume that the time t_i for

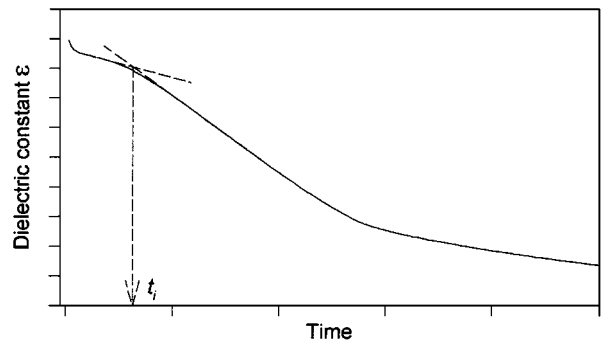


Figure 1 Determination of the reference hydration degree and the corresponding time t_i .

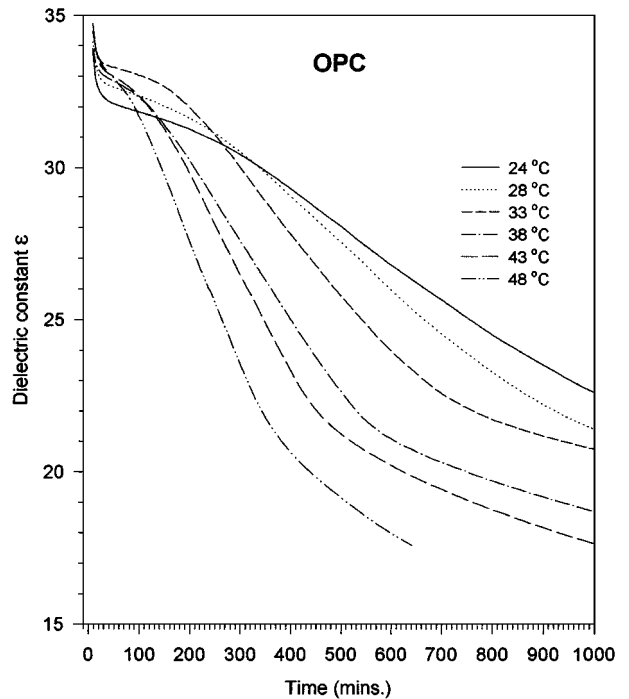


Figure 2 Variation of the dielectric constant with time for OPC paste with W/C of 0.4 measured at different temperatures.

the cement paste to reach the same hydration at different temperatures T_i is in inverse proportion to the reaction rate constant k_i , i.e.,

$$\frac{k_i}{k_{ref}} = \frac{t_{ref}}{t_i} \quad (3)$$

Equation 2 can then be written as:

$$\ln\left(\frac{t_{ref}}{t_i}\right) = -\frac{Q}{R}\left(\frac{1}{T_i} - \frac{1}{T_{ref}}\right) \quad (4)$$

In order to calculate the value of $\ln\left(\frac{t_{ref}}{t_i}\right)$, we have to determine how to choose the t_i , the time taken by the cement paste to reach a certain degree of hydration at temperature T_i . We consider that in the induction period of cement hydration, a protective layer on the cement grains formed by the product of the initial cement hydration reaction prevents water from reaching the cement grains. The induction period ends when this protective layer is destroyed or rendered more permeable by aging or phase transformation. When this protective

layer is destroyed the water reach the cement grains easily, leading to accelerated dissolution of the cement grains. In this acceleratory period of cement hydration, both the dielectric constant and heat evolution rate of cement are rapidly changed. If we assume that the apparent activation energy of cement hydration reaction is related to the energy needed to destroy the protective layer on the cement grains, then the longer the induction period the greater the apparent activation energy of cement hydration reaction. As ending time of the induction period is the time taken by the cement paste to reach a degree of hydration where the protective layer on the cement grains starts to destroy, which is related to the apparent activation energy of the cement hydration. We therefore use the ending time of the induction period as the t_i . As it is difficult to determine the ending time of the induction period t_i accurately, the t_i in this work is determined using intersection between the tangent lines of the slow change stage and the rapid decrease stage in the $\varepsilon-t$ curve, as shown in Fig. 1. When the t_i at hydration temperature T_i is obtained, the apparent activation energy Q of cement hydration can be determined from the plot of $\ln(\frac{k_i}{k_{ref}})$ against $(\frac{1}{T_i} - \frac{1}{T_{ref}})$ according to Equation 4.

The dielectric constant measurement was performed at evaluated temperatures of 24, 28, 33, 38, 43 and 48 °C on the OPC pastes with the water-cement ratio (W/C) of 0.4. The $\varepsilon-t$ curves of the hydrating OPC pastes measured at various temperature are shown in Fig. 2. The values of t_i of the OPC samples at different T_i are estimated using the method shown in Fig. 1 and listed together with the calculated values of $\frac{1}{T_i} - \frac{1}{T_{ref}}$, and $\ln(\frac{k_i}{k_{ref}})$ in Table II, where the T_{ref} is chosen as 24 °C (297.15 K) and the t_{ref} is hence 272 min. The plot of the values of $\ln(\frac{k_i}{k_{ref}})$ against $\frac{1}{T_i} - \frac{1}{T_{ref}}$ (Fig. 3) is a straight line with the correlation coefficient r^2 of 0.978 and the apparent activation energy Q of the hydration of OPC is determined as 38.44 KJ/mol using Equation 4.

3.2. Estimation of the apparent activation energy of early hydration of OPC by calorimetric measurement

In order to verify the reliability of our proposed new method of estimation of the apparent activation energy of OPC hydration using the microwave measurement, the measurement of the apparent activation energy of OPC hydration using the conventional calorimetric method is also conducted and the results from the two different methods are compared.

The calorimetric measurement of the apparent activation energy of the cement hydration is based on the

TABLE II The values of t_i and T_i of OPC samples

T_i (K)	t_i (min)	$\frac{1}{T_i} - \frac{1}{T_{ref}}$	$\ln\left(\frac{t_{ref}}{t_i}\right)$
297.15	272	0.0000	0.0000
301.15	227	4.4699×10^{-5}	-0.1809
306.15	176	9.8931×10^{-5}	-0.4353
311.15	121	1.5142×10^{-4}	-0.8100
316.15	117	2.0225×10^{-4}	-0.8436
321.15	84	2.5149×10^{-4}	-1.1750

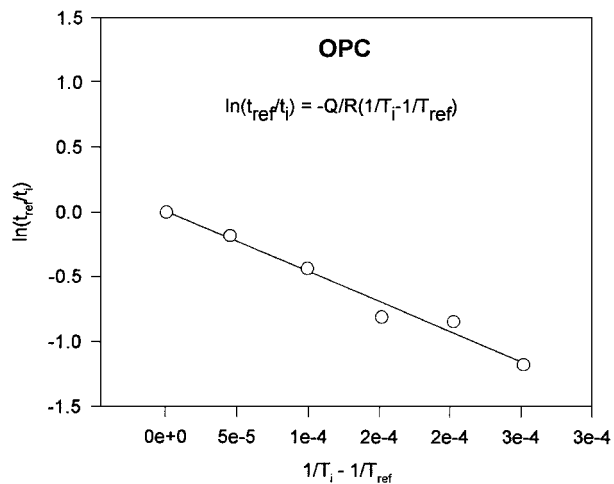


Figure 3 Plots of $\ln(\frac{t_{ref}}{t_i})$ against $\frac{1}{T_i} - \frac{1}{T_{ref}}$ for OPC.

Avrami equation

$$d\alpha/d\tau = nk\tau^{n-1}(1 - \alpha) \quad (5)$$

where α is the hydration degree, k the reaction rate constant, τ the time with the time-zero close to the end of the induction period, and n a constant. Integrate (5) to get

$$-\ln(1 - \alpha) = k\tau^n. \quad (6)$$

In the calorimetric measurement the hydration time t of cement paste is recorded immediately after mixing with water. Supposing the time of the end of the induction period is t_0 , thus

$$\tau = t - t_0. \quad (7)$$

From (6) and (7) we get

$$\ln(-\ln(1 - \alpha)) = \ln k + n \ln(t - t_0). \quad (8)$$

In order to calculate the values of the exponent n and the reaction constant k , the values of α , t and t_0 should be determined first. The hydration time t can be directly measured from the heat evolution curve. But in many cases the t_0 is hard to be measured directly, especially at high hydration temperature where a period of about one hour or longer is required to allow the calorimeter to achieve equilibrium, thus the information about the induction period might be missed in calorimetric measurement. However, the microwave measurement can start just a few minutes after the cement is mixed with the water, the t_0 is easily determined from the corresponding $-\delta\varepsilon/dt-t$ curve.

The values of α is determined by the expression $\alpha = H_t/H_f$, where H_t is the hydration heat at the time t and H_f is the final hydration heat when the hydration is completed. Since it is hard to measure the value of H_f and most of the hydration heat is evolved within the first 72 hours, the total heat evolved during the first 80 hours of OPC hydration is measured and used as the H_f for calculation of the hydration degree α .

TABLE III The values of H_t , α and t of OPC samples at different temperatures

23 °C	H_t (KJ/Kg)	284	50	100	150	200	250
	α	1	0.1761	0.3521	0.5282	0.7042	0.8803
	t (h)	80	7.75	12.42	18.11	28.88	53.16
28 °C	H_t (KJ/Kg)	304	50	100	150	200	250
	α	1	0.1645	0.3289	0.4934	0.6579	0.8224
	t (h)	80	6.35	9.90	13.80	21.84	39.86
33 °C	H_t (KJ/Kg)	311	50	100	150	200	250
	α	1	0.1608	0.3215	0.4823	0.6431	0.8039
	t (h)	80	5.03	7.68	10.93	18.21	32.12
43 °C	H_t (KJ/Kg)	353	50	100	150	200	250
	α	1	0.1416	0.2832	0.4249	0.5666	0.7082
	t (h)	80	4.28	5.76	7.88	12.56	20.05

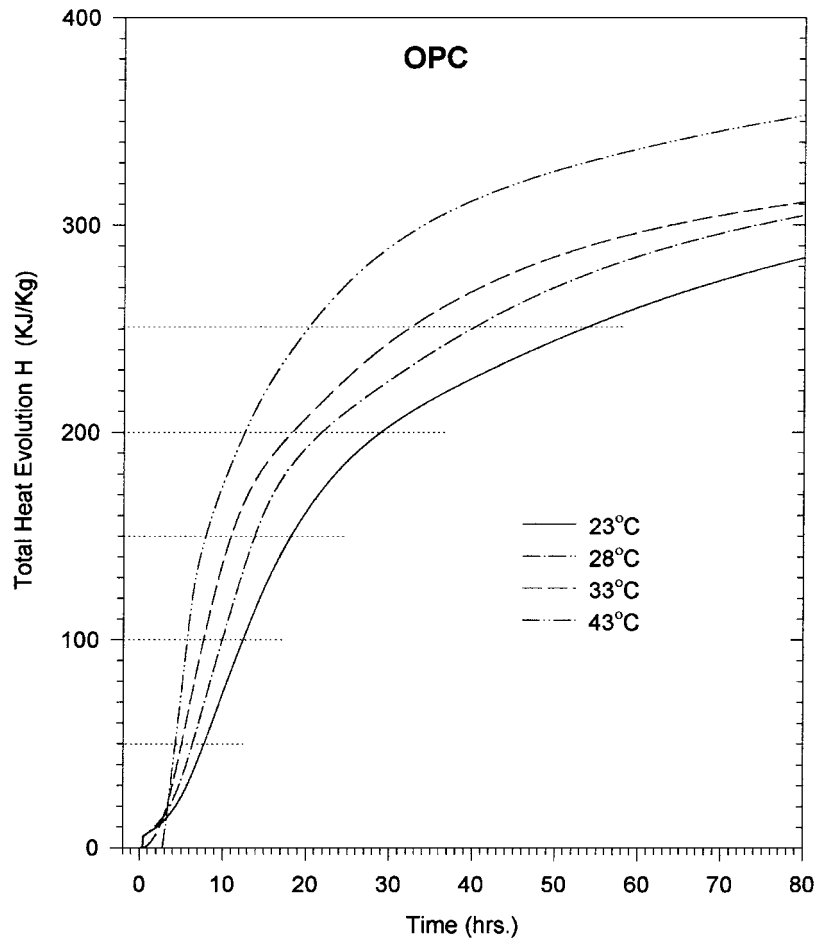


Figure 4 Heat evolution of OPC hydrating at different temperatures.

The total heat evolution curves ($H-t$ curve) of OPC hydration at different temperatures of 23, 28, 33 and 43 °C are shown in Fig. 4. Several values of H_t are chosen and the corresponding values of t and α are determined and listed in Table III. When plotting the values of $\ln(-\ln(1-\alpha))$ against $\ln(t-t_0)$ at each temperature, the linear relationship is obtained for each temperature (see Fig. 5). From this plot the values of the $\ln k$ and n for each temperature are determined (Table IV) using Equation 8 and plot of $\ln k$ against $1/T$ is made (Fig. 6). The equation of the straight line of $\ln k$ against $1/T$ is regressed with the correlation coefficient r^2 of 0.9691 and the apparent activation energy Q of the OPC is determined as 40.20 KJ/mol.

It is found that the apparent activation energy Q (38.44 KJ/mol) of OPC hydration measured using

TABLE IV The values of the $\ln k$ and n of OPC samples at different temperatures

T (°C)	$\ln k$	n	r^2
23	-9.9409	0.8890	0.9983
28	-9.5742	0.8664	0.9933
33	-9.2189	0.8461	0.9915
43	-8.8837	0.8318	0.9808

r^2 : the correlation coefficient.

the microwave method is similar to the value of Q (40.20 KJ/mol) measured using the conventional calorimetric measurement. This result suggests that it is reasonable to use the microwave method as the alternative of the calorimetric method to measure the apparent activation energy of cement hydration. This result further

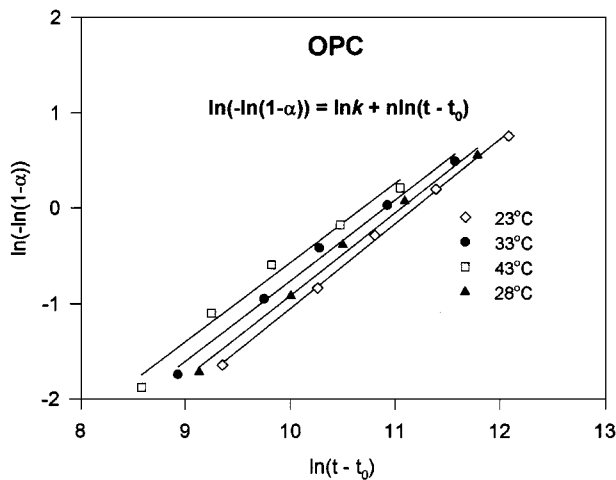


Figure 5 The relationship between $\ln(-\ln(1 - \alpha))$ and $\ln(t - t_0)$ for OPC at different temperatures.

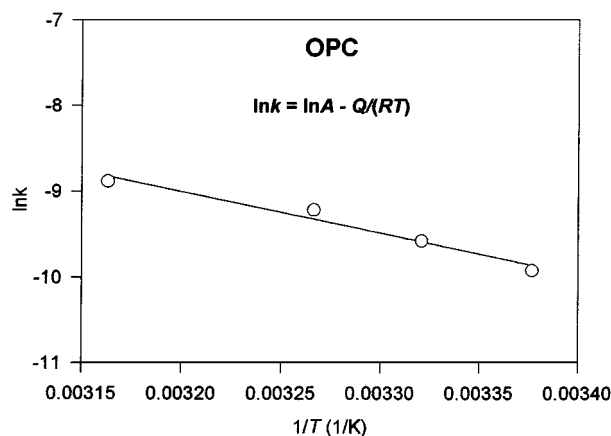


Figure 6 The relationship between the reaction rate constant k and the temperature T for OPC.

helps to establish the validity of microwave measurements as a new technique for studying cement hydration.

In the calorimetric method, the value of heat evolution H at later time is used as H_f . Even though we used the first 80 hours H as H_f in this work, the result will not be accurate enough as the heat evolution curve at 80 hours still goes up (see Fig. 4). For a more accurate estimation of the apparent activation energy of OPC using the calorimetric method, a measurement of heat evolution rate for a long length of time is needed. However, using the microwave method we can determine the apparent activation energy of OPC hydration in reasonable accuracy by doing the measurements in less than 20 hours. Hence, the microwave method exhibits an

obvious advantage in saving time used for the estimation of the apparent activation energy of cement hydration and it can also be used as a quick method for studying the kinetics of cement hydration.

4. Conclusion

A new method of estimation of the apparent activation energy of OPC hydration using microwave technique is proposed. The result of the apparent activation energy of OPC hydration measured by the microwave method has only a 5% difference from that obtained by the conventional calorimetric method. This indicates that microwave method can be used as an alternative method in estimation of apparent activation energy of the OPC hydration. The good agreement between the results measured by microwave method and calorimetric method further helps to establish the validity of microwave measurements as a new technique for studying OPC hydration. Further work is required to ascertain whether this new technique can be applied to other cementitious binders.

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