

Effect of Temperature on Hydration of Cementitious Materials

by Anton K. Schindler

The activation energy defines the temperature sensitivity of a concrete mixture and it is used in the equivalent age maturity method to convert concrete properties that are determined at the reference temperature to any other curing temperature. Currently, contradictory activation energy values are recommended for use in literature. This paper emphasizes the difference in behavior of cementitious materials with regard to the effect of temperature on the development of mechanical (strength) properties and hydration products (hydration). The objectives of this paper are to provide guidance on the selection of an appropriate activation energy value and to present a model to account for the effect of temperature on the rate of hydration when different cement types and mineral admixtures are used. An activation energy model is presented that is a function of the cement composition and the type of mineral admixtures used in the concrete mixture.

Keywords: hydration; maturity; temperature.

INTRODUCTION

The curing temperature of concrete is arguably the one variable that has the most significant effect on the rate of hydration. The maturity method is an approach used to account for the combined effect of temperature and time on the development of concrete mechanical properties and the development of hydration. The nonlinear maturity function based on the Arrhenius definition, also known as the equivalent age function, is considered the most accurate as it better represents the effect of temperature on strength development over a wide range of temperatures (Carino 1991).

Freiesleben Hansen and Pedersen (1977) developed the equivalent age maturity function, shown in Eq. (1), based on the Arrhenius rate theory for chemical reactions. The equivalent age maturity function converts the chronological curing age t of a concrete cured at any concrete temperature T_c to an equivalent curing age t_e for a specimen cured at a specific reference temperature T_r .

$$t_e(T_r) = \sum_0^t \exp\left(\frac{E}{R}\left(\frac{1}{273 + T_r} - \frac{1}{273 + T_c}\right)\right) \cdot \Delta t \quad (1)$$

where

- $t_e T_r$ = equivalent age at reference curing temperature, h;
- Δt = chronological time interval, h;
- T_c = average concrete temperature during time interval Δt , °C;
- T_r = reference temperature, °C;
- E = activation energy, J/mol; and
- R = universal gas constant, 8.3144 J/mol/K.

The Arrhenius rate theory states that the variation of the specific rate of reaction with temperature may be expressed by an equation of the following form (Glasstone, Laidler, and Eyring 1941)

$$\ln(k) = \ln(A) - \frac{E}{R \cdot T} \text{ or equivalently } k = A \cdot \exp\left(\frac{-E}{R \cdot T}\right) \quad (2)$$

where

- k = specific rate of reaction;
- A = parameter that is independent or varies little with temperature; and
- T = absolute reaction temperature, °K.

The Arrhenius formulation shown in Eq. (2) is the basis of the procedure prescribed in ASTM C 1074 (1998), "Standard Practice for Estimating Concrete Strength by the Maturity Method," in which the mixture-specific activation energy is experimentally determined from the linear plot of the observed values of $\ln(k)$ against $1/T$. Based on the Arrhenius formulation, the activation energy E defines the temperature sensitivity of the concrete mixture in the equivalent age maturity function.

The further the curing temperature is removed from the reference temperature, the more important the assumed value of the activation energy becomes. Currently, mechanistic models to characterize the behavior of concrete exposed to in-place conditions are becoming common, and a model to quantify the effect of temperature on the hydration process is therefore needed. An accurate activation energy value is especially required when adiabatic calorimeter test results are converted to hydration at isothermal conditions, as the reaction temperature may be 60 °C or more. An accurate estimate of the activation energy is also required to achieve accurate in-place strength predictions. The following section will show that there are contradictory recommendations in literature regarding the selection of an activation energy value.

Activation energy values recommended in literature

Freiesleben Hansen and Pedersen (1977) proposed the activation energy formulation shown in Eq. (3), which is a function of the concrete temperature T_c . Figure 1 presents the results reported by Freiesleben Hansen and Pedersen (FHP) when they developed Eq. (3). The FHP activation energy formulation was thus developed by calibrating the equivalent maturity method to produce the best fit results of compressive strengths ($t_e < 100$ h) performed at isothermal curing temperatures ranging between -10 °C and 80 °C.

$$\text{for } T_c \geq 20 \text{ °C (68 °F): } E(T_c) = 33,500 \text{ J/mol} \quad (3)$$

$$\text{for } T_c < 20 \text{ °C (68 °F): } E(T_c) = 33,500 + 1470(20 - T_c) \text{ J/mol}$$

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ACI member **Anton K. Schindler** is an assistant professor of civil engineering at Auburn University, Auburn, Ala. He received his PhD from the University of Texas at Austin, Austin, Tex. He is a member of ACI Committees 231, Properties of Concrete at Early Ages, and E 803, Faculty Network Coordinating Committee. His research interests include nondestructive testing, hydration modeling of cementitious materials, concrete properties, early-age behavior of concrete structures, and concrete pavement performance modeling.

The FHP formulation for the activation energy is one of the most commonly used definitions, and it is even used in the equivalent age maturity method to account for the temperature sensitivity of the hydration reaction. In many cases, the FHP formulation is used, irrespective of the cement type or mineral admixtures used in the mixture (Radjy and Vunic 1994; Tritsch 1994). Carino (1991) reports, however, that the value of the activation energy depends on the cement chemistry, cement fineness, type and quantity of cement, and admixtures used in the mixture. Other authors have indicated that the activation energy is a function of the water-cement ratio (w/c), but it has been shown that it does not have a consistent effect on the activation energy (Jonasson, Groth, and Hedlund 1995).

Jonasson, Groth, and Hedlund (1995) proposed the formulation in Eq. (4) to quantify the activation energy of Standard Swedish cements. At a concrete temperature of 20 °C, this formulation produces an activation energy that is 32% higher than that produced by the FHP formulation. This formulation is also a function of the concrete temperature and produces a decreasing activation energy value with an increase in curing temperature T_c .

$$E(T_c) = 44,066 \left(\frac{30}{10 + T_c} \right)^{0.45} \quad (4)$$

The FHP activation energy formulation was recently recommended for use in the following draft RILEM test method, "Adiabatic and Semi-Adiabatic Calorimetry to Determine the Temperature Increase in Concrete Due to Hydration Heat of Cement" (RILEM 119-TCE 1999). Due to the nature of the test, it should be re-emphasized that this definition of the activation energy is in this instance recommended to define the temperature sensitivity of the hydration process. RILEM 119-TCE recommends the same activation energy irrespective of the cement type; however, a higher constant value of 48,804 J/mol is recommended when ground-granulated blast-furnace slag (GGBFS) is used.

Carino (1991) summarized a wide range of constant activation energy values obtained by different research efforts. These values range from 41,000 to 67,000 J/mol and the values vary depending on the type of cementitious materials used in the mixture. Contrary to the FHP activation energy definition shown in Eq. (3), all the activation energy values summarized by Carino were constant and independent of the concrete temperature, which is in agreement with the original Arrhenius formulation.

ASTM C 1074 (1998) recommends a constant activation energy in the range of 40,000 to 45,000 J/mol for strength prediction applications when a Type I cement with no admixtures is used. Should any other cement type or admixtures be used, ASTM C 1074 provides no guidelines for the selection of an appropriate activation energy value. In ASTM C 1074, however, a test procedure is provided to determine the mixture-specific activation energy based on

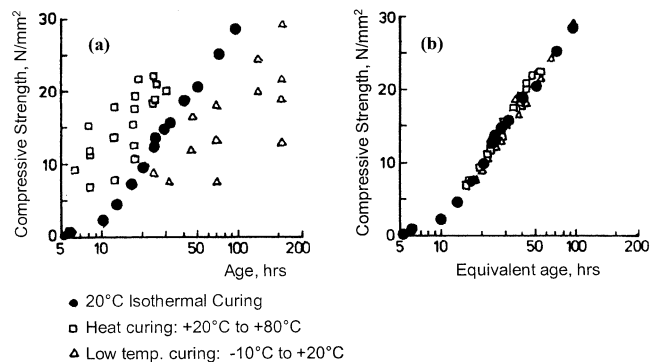


Fig. 1—Results obtained by Freiesleben Hansen and Pedersen (1977) converting strength data at various temperatures and actual ages (a) into equivalent ages (b).

the development of mortar compressive strengths at different curing temperatures. The ASTM C 1074 procedure is based on strength tests, and the question becomes whether or not these test results are valid for use during hydration prediction.

Kjellsen and Detwiler (1993) recommended an activation energy that is a function of the hydration temperature and relative strength development. The relative strength is defined in terms of the compressive strength at 28 days reached through isothermal curing at the reference temperature. This method also defines the activation energy as a function of the concrete temperature, which is not consistent with the original Arrhenius definition point of view. The authors, however, provide a detailed discussion why this effect is possible when the development of mechanical properties is considered. Recently, Pane and Hansen (2002) also presented an activation energy formulation that is a function of the curing temperature and the degree of hydration development.

After all the previous factors are considered, some of the disparity that exists in the literature concerning the selection of an appropriate activation energy value may be identified. The primary points of disagreement can be summarized with the following three key questions that will be investigated in this paper:

1. Should the same activation energy be used for the prediction of the development of mechanical properties and degree of hydration?;
2. Does the activation energy change as a function of temperature or degree of hydration?; and
3. Should the same activation energy be used for all types of cementitious materials?

RESEARCH SIGNIFICANCE

Currently, when the equivalent age maturity method is used, contradictory activation energy values exist in literature. This paper provides guidance on the selection of an appropriate activation energy value for different cement types and when mineral admixtures are used. The paper emphasizes the difference in behavior of cementitious materials with regard to the effect of temperature on the development of mechanical (strength) properties and hydration products (hydration). This paper further presents a model to accurately account for the effect of temperature on the rate of hydration of cementitious materials. An accurate estimate of the activation energy is an essential component of the mechanistic modeling of the hydration of cementitious materials.

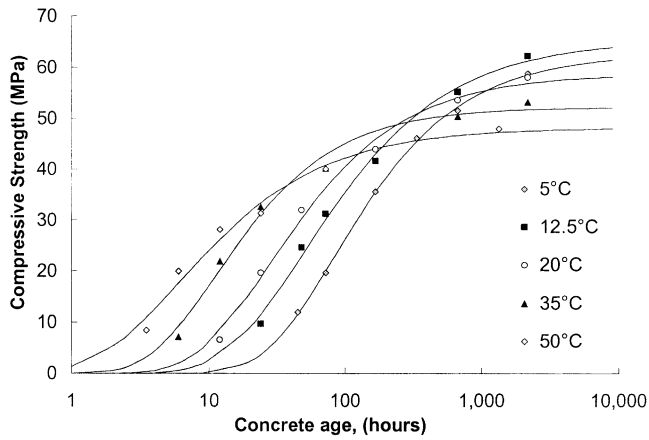


Fig. 2—Compressive strength results for mortar, 0.5 w/c (Kjellsen and Detwiler 1993).

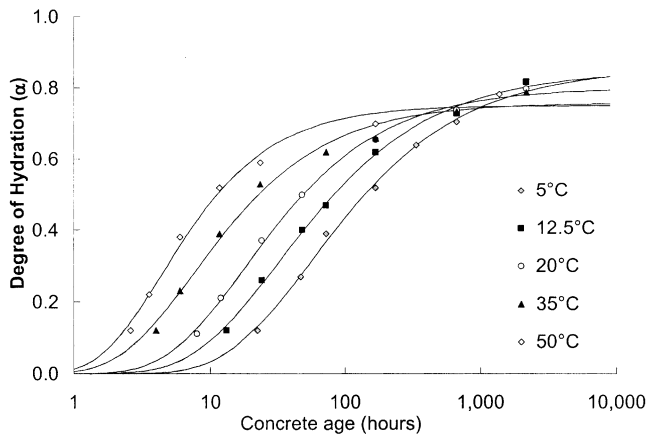


Fig. 3—Degree of hydration results for mortar, 0.5 w/c (Kjellsen and Detwiler 1992).

TEMPERATURE SENSITIVITY OF CEMENTITIOUS MATERIALS

Figure 2 presents the development of compressive strength for mortar specimens cured at isothermal temperatures of 5, 12.5, 20, 35, and 50 °C (Kjellsen and Detwiler 1993). It may be seen that the strength of the samples cured at 50 °C start to cross over the strength of the sample cured at 35 °C after only 40 h. The long-term strength loss at 50 °C was about 17% as compared with the specimens cured at room temperature. This behavior has been widely documented for the development of mechanical properties (Neville 1996). Carino (1991) termed this loss of strength due to curing at high temperatures the cross-over effect. When the shapes of these curves are compared, it may be seen that the curves do not remain affine, which may be due to the presence of the cross-over effect.

Figure 3 presents the degree of hydration development for mortar specimens cured at isothermal temperatures of 5, 12.5, 20, 35, and 50 °C (Kjellsen and Detwiler 1992). The same materials and mixture proportions were used to determine the strength data shown in Fig. 2 and hydration data shown in Fig. 3. The data in Fig. 3 were determined based on the nonevaporable water content as a means to estimate the degree of hydration. Figure 3 indicates that a minimal difference of 2% in the final degree of hydration between the samples cured at 5 °C versus 50 °C. When shapes of the hydration development curves in Fig. 3 are compared with the shapes

of the strength development curves in Fig. 2, it may be seen that the hydration curves converge at a much later age (after about 600 h) and that the hydration curves appear only to be translated in time (affine). Based on this data, it may be concluded that there is little or no reduction in the final degree of hydration (or heat released) due to curing at different temperatures. Cervera, Oliver, and Prato (1999) came to a similar conclusion and state that the final degree of hydration is the same for samples cured at any temperature, and that the final degree of hydration only depends on the initial water content of the mixture. Furthermore, Chanvillard and D'Aloia (1997) mention that by "...defining the hydration degree in terms of relative quantity of heat already generated, it can be noted that the relative quantity of generated heat versus age curves are affine, whatever the isothermal curing temperature of the concrete is, and that the affinity ratio follows the Arrhenius law."

From the data and literature evaluated in this section, it may be concluded that the cross-over effect only develops for mechanical properties and not when the development of the degree of hydration is considered. This suggests that the maturity method will be applicable over most of the hydration period when the degree of hydration needs to be predicted at temperatures other than the reference temperature. Kada-Benamure, Wirquin, and Duthoit (2000) commented that "...the mechanical strength, unlike the heat of hydration, does not reflect a purely chemical mechanism and cannot, therefore, fully abide by the Arrhenius law."

Determining activation energy from degree of hydration test results

This section will indicate how the activation energy can be determined from the degree of hydration test results based on basic principles. The exponential function shown in Eq. (5) can be used to effectively characterize the development of the degree of hydration (Freiesleben Hansen and Pedersen 1985; Pane and Hansen 2002).

$$\alpha(t_e) = \alpha_u \cdot \exp\left(-\left[\frac{\tau}{t_e}\right]^\beta\right) \quad (5)$$

where

- $\alpha(t_e)$ = degree of hydration at equivalent age t_e ;
- τ = hydration time parameter, h;
- β = hydration shape parameter; and
- α_u = ultimate degree of hydration.

To determine the activation energy, the slope of the Arrhenius plot needs to be determined between the test temperature and the reference temperature. The traditional maturity formulation shown in Eq. (1) was derived through the use of the age conversion factor, which can be defined as follows

$$f(T_c) = \frac{k(T_c)}{k(T_r)} \quad (6)$$

where

- $f(T_c)$ = age conversion factor determined at concrete temperature T_c ;
- $k(T_c)$ = rate constant at concrete temperature T_c ; and
- $k(T_r)$ = rate constant at isothermal reference temperature T_r .

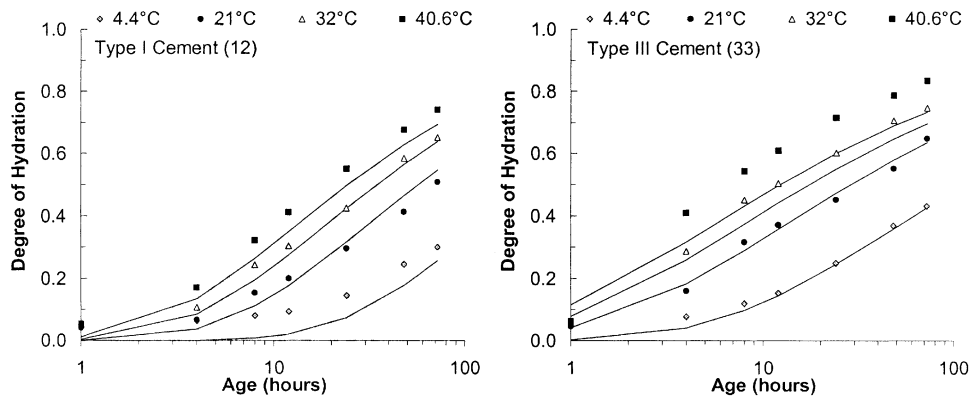


Fig. 4—Results after applying FHP activation energy to Lerch and Ford data set.

The age conversion factor defined in Eq. (6) permits the conversion of the chronological concrete age into the equivalent age. The relation between the chronological concrete age t and the equivalent age t_e is as follows (Carino 1991)

$$t_e = f(T_c) \cdot t \quad (7)$$

When the age conversion factor is known, Eq. (5) can be defined in terms of the chronological age as shown in Eq. (8). If experimental data are available at temperatures other than the reference temperature, the best-fit hydration time parameter can be determined at each of the temperatures. Note that only time can be adjusted by the maturity method and only the hydration time parameter τ may therefore be altered. When the exponential equation is used, it is assumed that the slope parameter β is independent from the curing temperature.

$$\alpha(t) = \alpha_u \cdot \exp\left(-\left[\frac{\tau}{f(T_c) \cdot t}\right]^\beta\right) \quad (8)$$

where $\alpha(t)$ = degree of hydration at chronological age t .

From Eq. (8), it may be seen that the relationship between the hydration time parameter at the reference temperature τ and at any other temperature τ_T is similar to the relationship between chronological age and equivalent age shown in Eq. (7). The age conversion factor may thus be determined as shown in Eq. 9, by dividing the hydration time parameter obtained at a temperature with the hydration time parameter obtained at the reference temperature.

$$\tau_T = \frac{\tau}{f(T_c)} \Rightarrow f(T_c) = \frac{k(T_c)}{k(T_r)} = \frac{\tau}{\tau_T} \quad (9)$$

where τ_T = hydration time parameter obtained for curing at temperature T_c , h.

Based on the fundamental definition of the activation energy (Eq. (2)) and Eq. (9), an expression to estimate the activation energy from the hydration time parameters can be derived as shown in Eq. (10). This formulation may be used on degree of hydration test data obtained at different temperatures to calculate an apparent activation energy value.

$$\frac{E}{R} = \frac{\ln k(T_r) - \ln k(T_c)}{(1/T_r - 1/T_c)} = \frac{\ln(k(T_r)/k(T_c))}{(1/T_r - 1/T_c)} \quad (10)$$

$$\frac{E}{R} = \frac{\ln(\tau_T/\tau)}{(1/T_r - 1/T_c)} \quad (\text{Note: All temperatures in K})$$

Evaluation of activation energy for hydration development

In this section, the validity of applying the Arrhenius rate theory to heat of hydration test data will be reviewed by evaluating the linearity of Arrhenius plots statistically. If the heat of hydration data obeys the Arrhenius principle, then a constant activation energy that is independent of the hydration temperature may be used. To evaluate the nature of the activation energy for the development of the degree of hydration of portland cement, experimental data presented by Lerch and Ford (1948) will be analyzed. The Lerch and Ford data set represents one of the largest data sets available on the development of heat of hydration for different U.S. cements. Although the chemical composition and fineness of cement in the United States has changed since the 1950s, the effect of each of the different cement components on the temperature sensitivity will still be applicable today. The results for the nonair-entraining cements test by Lerch and Ford will be analyzed, which include eight Type I cements, three Type II cements, three Type III and IV cements, and one Type V cement. Lerch and Ford performed heat of hydration tests on pastes through conduction calorimetry and heat of solution test methods. With the conduction calorimeter, pastes were cured for 72 h at isothermal temperatures of 4.4, 23.9, 32.2, and 40.6 °C. Through the heat of solution method, pastes were cured for 1 year at 21.1 °C. The heat of solution and the condition calorimetry tests have been shown to produce comparable results (Bogue 1947; van Breugel 1997).

A reference temperature of 21.1 °C (70 °F) was used during the analysis of this data set. Because the conduction calorimeter tests were performed at 23.9 °C, only the test results at 23.9 °C were converted to equivalent results at 21.1 °C through the equivalent age maturity concept. Because the activation energy was not known, an iterative procedure was followed throughout the analysis until the assumed and final calculated activation energy values converged.

The accuracy of the equivalent age method as applied to the degree of hydration development may be evaluated from the Lerch and Ford data set. Figure 4 presents the results

Table 1—Hydration parameters for exponential degree of hydration model (Eq. (5))

ID	Isothermal curing temperature									Maximum heat of hydration H_u , J/g*
	21.1 °C			4.4 °C		32.2 °C		40.6 °C		
	β	τ , h	r^2	$\tau_{4.4}$, h	r^2	$\tau_{32.2}$, h	r^2	$\tau_{40.6}$, h	r^2	
Type I cements										
11	0.479	25.9	1.00	87.4	0.96	10.3	0.98	7.1	0.99	488
12	0.588	30.5	0.99	83.3	0.77	16.8	0.99	10.1	1.00	475
13	0.394	33.5	0.99	87.8	0.98	17.8	0.99	12.6	0.97	471
14	0.482	17.8	1.00	53.3	0.97	8.1	1.00	6.5	0.98	440
15	0.537	18.5	0.99	64.5	0.96	8.0	0.97	6.1	1.00	508
16	0.462	23.2	0.99	62.9	0.97	11.8	0.98	4.9	0.92	469
17	0.515	23.0	0.99	68.3	0.82	11.2	0.99	7.1	0.99	474
18	0.533	24.3	0.99	85.5	0.94	12.7	0.99	8.8	0.99	475
Type II cements										
21	0.440	38.7	1.00	133.8	0.81	21.6	1.00	14.3	1.00	430
22	0.500	41.8	0.99	101.6	0.76	22.7	0.98	13.2	1.00	438
23	0.427	38.7	0.99	110.1	0.95	21.4	0.98	16.3	1.00	441
24	0.379	27.8	1.00	92.0	0.97	13.6	1.00	10.1	0.99	437
25	0.405	30.3	1.00	66.7	0.96	15.5	0.99	9.1	0.99	407
Type III cements										
31	0.485	11.1	0.99	33.0	0.97	4.1	0.97	2.5	0.93	504
33	0.451	11.6	1.00	44.9	0.98	5.1	0.98	2.8	0.93	504
34	0.397	15.4	0.99	47.6	0.96	7.0	0.98	4.9	0.95	498
Type IV cements										
41	0.369	30.2	1.00	93.3	0.94	16.4	0.99	10.5	0.99	478
42	0.370	48.2	0.99	128.3	0.96	30.4	0.97	20.9	0.97	370
43	0.409	30.3	0.99	83.0	0.75	12.7	0.99	8.2	0.99	389
Type V cement										
51	0.401	34.7	0.99	98.2	0.96	23.2	0.99	14.7	0.99	410

* $H_u = 500 \cdot p_{C_3S} + 260 \cdot p_{C_2S} + 866 \cdot p_{C_3A} + 420 \cdot p_{C_4AF} + 624 \cdot p_{SO_3} + 1186 \cdot p_{FreeCaO} + 850 p_{MgO}$ (Bogue 1947), where p_i = mass ratio of i -th component in terms of total cement content.

obtained after applying the equivalent age maturity method with the activation energy as formulated by FHP (Eq. (3)) to Type I and Type III cements. From the results of the Type I cement shown in Fig. 4, it may be seen that the age conversion factor calculated with the FHP activation energy is too high at low temperatures and too low at high temperatures. The results for the Type III cement indicate that the age conversion factor calculated with the FHP activation energy provides an accurate prediction at low temperatures but is too low for the higher temperatures.

To determine the activation energy for the 20 cements, the best-fit degree of hydration curve as defined in Eq. (5) for the experimental data obtained at the reference temperature of 21.1 °C was determined. The best-fit degree of hydration parameters obtained for all the cements are shown in Table 1. In Table 1, the coefficient of determination r^2 is also provided, and it may be noted that the r^2 values are either 0.99 or higher. This indicates that the exponential function (Eq. (5)) provides an accurate representation of the degree of hydration data at the reference temperature.

Next, the hydration shape β parameters, determined at the reference temperature, were used as constants to determine the best-fit degree of hydration curves at the other test temperatures. This is necessary because this parameter cannot be changed when the maturity method is used. Next, the best-fit hydration time parameters τ_T at the remaining test temperatures are determined. Table 1 presents the best-fit hydration time parameter and r^2 values obtained. The regression analysis for the temperature of 32.2 and 40.6 °C produced a good fit of the data because the r^2 values ranged between 0.92 and 1.00.

The lowest r^2 values were obtained for the degree of hydration at the low curing temperature (4.4 °C), and they ranged between 0.75 and 0.98. The reason for the less accurate curve fit may be explained by the fact that the model assumes that the early-age degree of hydration values will start from zero; however, this does not occur in the experimental results. This phenomenon may be attributed to the accuracy of the conduction calorimeter when low amounts of heat are being developed. These points will be used in the analysis because r^2 values of 0.75 and higher are still considered acceptable.

With the data shown in Table 1, the Arrhenius plot can now be constructed by plotting the natural logarithm of the hydration time parameters versus the inverse of the corresponding absolute curing temperatures. This concept was previously shown to be true for the exponential function and was derived in Eq. (10). Figure 5 presents the Arrhenius plot for the Type I cement (12) and Type III cement (33). Figure 5 indicates that the Arrhenius plot is indeed linear ($r^2 > 0.99$) for the heat of hydration data and that the activation energy is independent from the curing temperature. On Fig. 5, the slope of the Arrhenius plot is different for the two cements, which indicates that the activation energy is influenced by the cement type. From Fig. 5, activation energy values of 42,171 and 54,467 J/mol may be determined respectively for the Type I and Type III cements.

The constant activation energy values obtained from the Arrhenius plot in Fig. 5 were used to evaluate the accuracy of the equivalent age maturity concept with regard to the prediction of the degree of hydration at different temperatures.

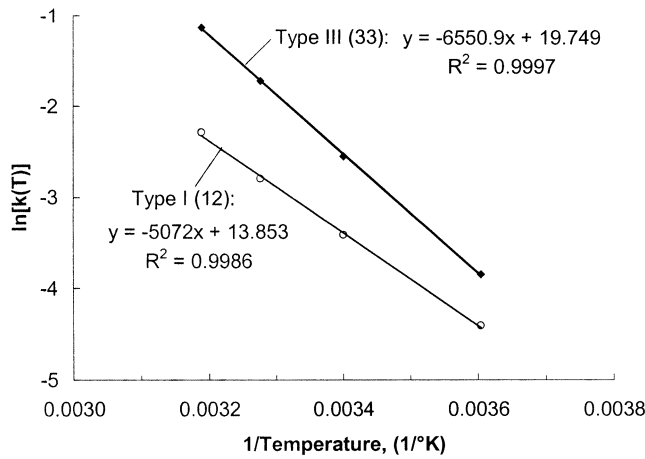


Fig. 5—Arrhenius plot for Type I cement (12) and Type III cement (33) of Lerch and Ford data set.

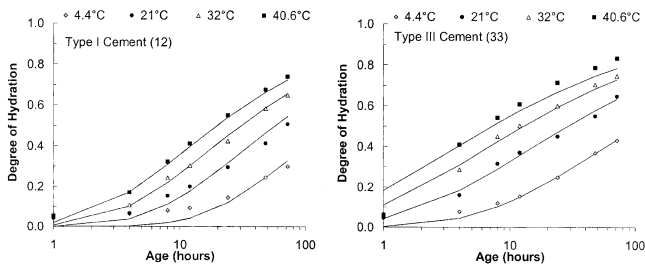


Fig. 6—Results after applying constant activation energy to Lerch and Ford data set for Type I cement (12) and Type III cement (33).

Figure 6 presents the results obtained for the Type I and Type III cements, and these results should be compared with the results obtained with the variable FHP activation energy shown in Fig. 4. Figure 6 indicates that an accurate estimate of the degree of hydration at high and low temperatures can be obtained through the use of a constant activation energy that is independent of the curing temperature.

Table 2 presents the activation energy, the r^2 value for the linear regression line, and the average activation energy obtained for the cements in the Lerch and Ford data set. From Table 2, it may be seen that the activation energy values range from 36,132 to 54,467 J/mol, which is within the range reported by other authors as discussed previously. The lowest r^2 value obtained for the 20 cements was 0.976 for cement 16 (Type I). From the high r^2 values for the linear regression line of the Arrhenius plot shown in Table 2, it may be concluded that a constant activation energy value may be used to characterize the degree of hydration development at different temperatures. Chanvillard and D'Aloia (1997) came to a similar conclusion, as they mention that by "...defining the hydration degree in terms of relative quantity of heat already generated, it can be noted that the relative quantity of generated heat versus age curves are affine, whatever the isothermal curing temperature of the concrete is, and that the affinity ratio follows the Arrhenius law."

From Table 2, the order of the average activation energy per cement type, arranged from high to low, is as follows: Type III, Type I, Type II, Type IV, and Type V. This is significant because this order is similar to what one would assign the rate of early-age heat of hydration development. This indicates that the activation energy is influenced by the

Table 2—Activation energy values for cements tested by Lerch and Ford

ID	r^2 value	Activation energy, J/mol	Average activation energy, J/mol
Type I cements			
11	0.994	51,861	45,271
12	0.999	42,171	
13	0.999	38,926	
14	0.989	44,039	
15	0.990	47,315	
16	0.976	46,795	
17	1.000	44,810	
18	0.995	46,256	
Type II cements			
21	0.995	44,899	41,788
22	0.994	40,369	
23	0.994	39,000	
24	0.993	45,185	
25	0.988	39,487	
Type III cements			
31	0.993	49,686	49,955
33	1.000	54,467	
34	0.997	45,711	
Type IV cements			
41	1.000	43,824	39,978
42	0.997	36,132	
43	0.994	46,676	
Type V cement			
51	0.993	37,329	37,329

composition and fineness of the cement, which provides a firm answer to one of the questions of disparity identified in the literature.

Concluding remarks on activation energy

In the Introduction, it was mentioned that a disparity in the literature exists regarding the selection of the most appropriate activation energy value or function. The primary points of disparity were summarized by questions, which will now be addressed:

1. Should the same activation energy be used for the prediction of the development of mechanical properties and degree of hydration?

From Fig. 5, it may be concluded that the Arrhenius rate theory for chemical reactions applies to the hydration of portland cement. A similar conclusion was reached by Ma et al. (1994), Kada-Benameur, Wirquin, and Duthoit (2000), and Cervera, Oliver, and Prato (1999). From the data evaluated in this paper, it was concluded that the cross-over effect develops only when mechanical properties are considered and not when the degree of hydration is considered. For the prediction of the degree of hydration at temperatures other than the reference temperature, the appropriate activation energy should be determined based on heat of hydration tests. The use of an activation energy determined from strength tests (ASTM C 1074) is not recommended for the purpose of predicting the progress of hydration;

2. Does the activation energy change as a function of temperature or degree of hydration?

Ma et al. (1994) performed isothermal calorimeter tests at a wide range of curing temperatures, and the Arrhenius plot

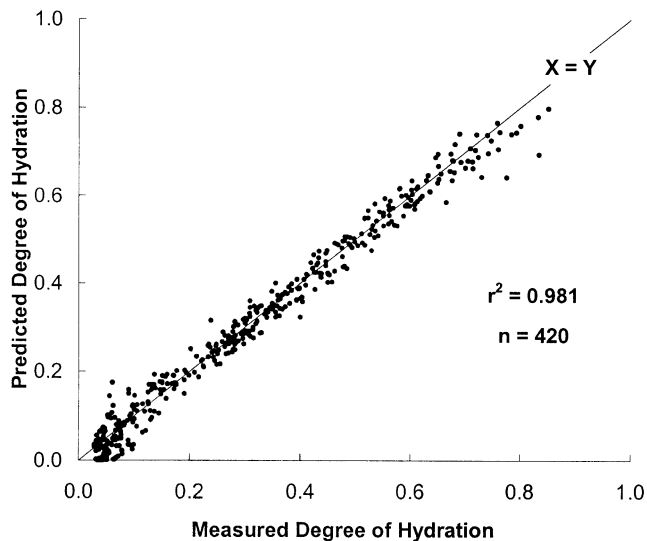


Fig. 7—Plot of measured versus predicted degree of hydration.

from the data showed no temperature dependency. After the analysis on the Lerch and Ford (1948) data set, it was shown that the Arrhenius rate theory for chemical reactions applies to the hydration of portland cement. The activation energy for hydration prediction may be formulated independent from the curing temperature and degree of hydration.

The activation energy formulation proposed by Freiesleben Hansen and Pedersen (1977) was developed to predict early-age strength results at different temperatures. The fact that the cross-over effect occurs at high curing temperatures, causes a reduced rate of strength gain, and it is the author's opinion that this is the reason why the apparent activation energy for strength prediction is lower at high temperatures and higher at low temperatures; and

3. Should the same activation energy be used for all types of cementitious materials?

Some authors presented different activation energy values for different cementitious materials (Carino 1991), and others recommend the use of the same value for all cementitious systems. Due to the difference in mechanical behavior of different cementitious materials, more variation in activation energies for strength prediction may be expected. The results obtained from the analysis of the Lerch and Ford (1948) data set showed that the activation energy varied with the cement composition. It is recommended to select an activation energy value based on the chemical composition and fineness of the cement.

DEVELOPMENT OF ACTIVATION ENERGY MODEL FOR HYDRATION

In this section, a general activation energy model will be developed based on a multivariate regression analysis of the Lerch and Ford (1948) hydration data set. The following variables that may characterize the hydration of cement were considered during the statistical analysis: C_3A , C_3S , C_2S , C_4AF , SO_3 , MgO , free lime, and specific surface area (Blaine Index).

The explanatory variables for the nonlinear model were selected by developing a regression model to predict the activation energy value for each cement type as listed in Table 2. This allows the development of a simple linear model based on 20 data points. The significance of individual

and combinations of explanatory variables was evaluated, and it was found that with the use of three explanatory variables, an r^2 of 0.68 could be achieved. This coefficient of determination was considered appropriate only to identify the most significant parameters. The chosen model was a function of the C_3A content, the Blaine Index, and the C_4AF content.

Both high C_3A and Blaine Index are associated with cements with high early-age strength gains such as Type III cements and are thus appropriate. The role of the C_4AF compound, however, is unexpected. With only the C_3A content and the Blaine Index as variables, an r^2 of 0.57 could be achieved. The statistical analysis revealed that as an individual parameter the C_4AF content does not provide a good estimate of the activation energy ($r^2 = 0.09$). When the interaction of C_4AF with the other two parameters was incorporated, however, an improved activation energy model was obtained. It was further determined that the three explanatory variables were uncorrelated and that the use of all three variables is statistically significant.

To develop the best-fit activation energy model, the response variables of the data set were comprised of the degree of hydration values versus concrete age, for each cement type, at the isothermal curing temperatures of 4.4, 32.2, and 40.6 °C. With seven test points at each curing temperature, 20 different cements, and three temperatures, the data set consisted of 420 degrees of hydration response variables. Because the Arrhenius maturity function is a nonlinear function, a nonlinear regression analysis was performed. This iterative method required that the form of the nonlinear regression model be defined and values determined from the multivariate linear regression analysis be used as initial estimates of the regression coefficients. Based on 420 response variables, the best-fit multivariate regression of the model shown in Eq. (11) was obtained. An r^2 value of 0.981 was achieved for this model. Note that the final regression parameters shown in Eq. (11) were rounded for ease of use.

$$E = 22,100 \cdot p_{C_3A}^{0.30} \cdot p_{C_4AF}^{0.25} \cdot \text{Blaine}^{0.35} \quad (11)$$

where

p_{C_3A} = weight ratio of C_3A in terms of total cement content;

p_{C_4AF} = weight ratio of C_4AF in terms of total cement content; and

Blaine = Blaine value, specific surface area of cement (m^2/kg).

With the activation energy as modeled with Eq. (11), the scatter plot of the experimentally determined versus predicted degree of hydration values are shown in Fig. 7. This figure indicates that the proposed activation energy formulation accurately accounts for the change in degree of hydration due to curing at different temperatures. Based on the r^2 value of 0.981, it may be seen concluded that 98.1% of the experimental variation of the response variable variation is explained by the model. The mean square of the error s^2 provides an unbiased estimate of the standard deviation of the error as it is corrected for the degrees of freedom in the model. For this model, $s^2 = 0.00095$, which is a very small number (0.095%) as desired. Because a random distribution of the unexplained error is desired, residual plots were used to evaluate the homogeneity of variance. These figures were evaluated and indicate that the error appears to be random for all degrees of hydration (Schindler 2002). Based on the

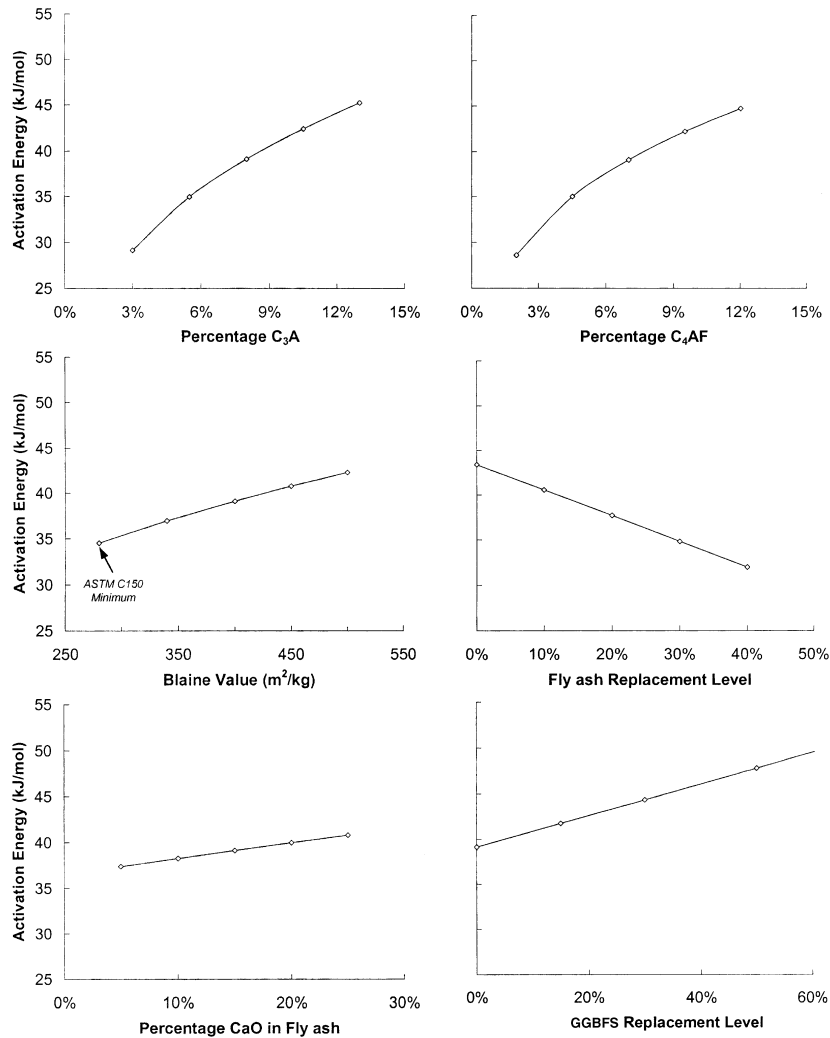


Fig. 8—Sensitivity analysis of proposed activation energy model. (Baseline parameters: $C_3A = 8\%$; $C_4AF = 7\%$; Blaine = $400 m^2/kg$; $p_{FA} = 15\%$; and $p_{FACaO} = 15\%$.)

cumulative distribution of the error, it was found that 95% of the error is within a degree of hydration of ± 0.055 and that 99% of the error is within a degree of hydration range of ± 0.085 . Therefore, it may be concluded that the model provides an accurate prediction of the measured degree of hydration at different curing temperatures.

Effect of mineral admixtures

Mineral admixtures have been shown to affect the rate of hydration at different temperatures, which would thus impact the activation energy value for a specific concrete mixture (Ma et al. 1994). Limited heat of hydration test data performed at various temperatures are available to use for the development of an appropriate model, however. Few references even consider the effect of mineral admixtures on the activation energy. RILEM Technical Committee 119-TCE recommends the use of the FHP activation energy model for all cements and that a constant activation energy value ($E = 48,804 J/mol$), irrespective of the amount of GGBFS, be used.

Ma et al. (1994) calculated the activation energy for different cementitious materials based on isothermal calorimeter test performed at curing temperatures of 10, 15, 20, 25, 30, 35, 40, 45, 50, and 55 °C. Ma et al. used the same cement type and then produced different blended cements by either

adding Class F fly ash or GGBFS. To determine the best-fit activation energy, the Arrhenius plot was constructed, which showed no temperature dependency for any of the cementitious systems tested. Ma et al. found that for Type I cement, $E = 39,000 J/mol$; for Type I cement with 17% Class F fly ash, $E = 26,700 J/mol$; and for Type I cement with 65% GGBFS, $E = 49,300 J/mol$.

Based on the experimental evidence produced by Ma et al. (1994), it is apparent that the use of mineral admixtures will affect the activation energy. It is thus necessary to account for this effect when such materials are used. Because no other data are currently available, the change in activation energy obtained by Ma et al. will be used together with engineering judgment to quantify the effect of fly ash and GGBFS on the activation energy. This model should be considered as preliminary and this area requires more experimental work.

The Class F fly ash used by Ma et al. had a CaO content of 3.6%, which is typical for East Coast Class F fly ashes. The CaO content of the fly ash will be used to differentiate between the different fly ash types. According to their results, the use of 17% fly ash reduces the activation energy by 32%, and when 65% GGBFS is used, the activation energy is increased by 26%. The following assumptions will be made to develop the model:

1) the change in activation energy value is directly proportional to the amount of mineral admixtures used; and 2) the change in activation energy is identical for all combinations of cements and mineral admixtures.

The activation energy for each cement will be determined based on the formulation provided in Eq. (11), and then the activation energy modification factor f_E as shown in Eq. (12) will be multiplied with the value calculated for the cement.

$$f_E = 1 - 1.05 \cdot p_{FA} \cdot \left(1 - \frac{p_{FACaO}}{0.40}\right) + 0.40 \cdot p_{SLAG} \quad (12)$$

where

f_E = activation energy modification factor;
 p_{FA} = mass ratio replacement of fly ash;
 p_{FACaO} = mass ratio of CaO content in fly ash; and
 p_{SLAG} = mass ratio replacement of GGBFS.

The influence of each variable in the activation energy model as defined by Eq. (11) and (12) was evaluated. This is performed by choosing a baseline condition and then only one of the parameters is varied at a time. This does not necessarily reflect what would happen for actual cements; however, to evaluate the effect of a change in each parameter, this is considered appropriate. The ranges of variables were determined based on what is typically found in the Southern parts of the United States. Figure 8 presents the results obtained from this analysis and provides insight to the contribution of each of the parameters to the value of the activation energy. An increase in C_3A , C_4AF , cement fineness, CaO content of the fly ash, and GGBFS replacement level will all result in an increase in the activation energy of the cementitious system. An increase in the amount of fly ash used will decrease the activation energy of the cementitious system. The range of activation energy values shown in Fig. 8 appear appropriate in comparison with the values reported in previous research efforts.

SUMMARY AND CONCLUSIONS

The activation energy defines the temperature sensitivity of a mixture. This document presents evidence from various sources that different activation energy values should be used when mechanical properties and the development of hydration (chemical effects) are considered. The cross-over effect develops only when mechanical properties are considered and not when the degree of hydration development is considered. The maximum degree of hydration is unaffected by the curing temperature. The use of an activation energy determined from strength testing is not recommended for the purpose of predicting the progress of hydration.

The temperature sensitivity of the hydration process was evaluated based on heat of solution and conduction calorimeter test data. The tests were performed over a temperature range of 4.4 to 40.6 °C. In all cases investigated, the data indicated that the heat of hydration results obey the Arrhenius principle because the activation energy was determined to be independent of the hydration temperature. This is in agreement with the Arrhenius theory for rate processes in chemical reactions. The results obtained from the analysis of the Lerch and Ford (1948) data set showed that the activation energy varied with the cement composition. The highest activation energy was obtained for Type III cements and the lowest values for Type IV

and V cements. The activation energy for different cements ranged from 36,132 to 54,467 J/mol.

An activation energy model is developed that accounts for differences in cement chemical composition, cement fineness, and the use of mineral admixtures. The final model is as defined in Eq. (11) and (12).

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NOTATION

Blaine	=	Blaine value, specific surface area of cement, m ² /kg
E	=	activation energy, J/mol
$f(T_c)$	=	age conversion factor determined at concrete temperature T_c
f_E	=	activation energy modification factor
k	=	specific rate of reaction
p_{C_3A}	=	weight ratio of C_3A in terms of total cement content
p_{C_4AF}	=	weight ratio of C_4AF in terms of total cement content
p_{FA}	=	mass ratio replacement of fly ash
p_{FACaO}	=	mass ratio of CaO content in fly ash
p_{SLAG}	=	mass ratio replacement of GGBFS
R	=	universal gas constant, 8.3144 J/mol/K
T	=	absolute reaction temperature, °K
T_c	=	average concrete temperature, °C
T_r	=	reference temperature, °C
t	=	chronological time, h
t_e	=	equivalent age, h
α	=	degree of hydration
α_u	=	ultimate degree of hydration
β	=	hydration shape parameter
Δt	=	chronological time interval, h
τ	=	hydration time parameter obtained for curing at reference temperature, h
τ_T	=	hydration time parameter obtained for curing at temperature T_c , h

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