



Estimation of compressive strength by a new apparent activation energy function

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Abstract

After reviews of the validity of models for estimating the compressive strength development of concrete subjected to various temperature histories, the shortcomings of present temperature functions are discussed. Based on the discussion, a model for compressive strength development that includes the new apparent activation energy function is proposed to correct the shortcomings of previous models that overestimate the effect of temperature on later-age strength development. The new model, with the apparent activation energy as a nonlinear function of temperature and age, provides good estimates of strength development obtained from the previous experimental studies. Finally, general equations based on regression analysis are proposed to estimate apparent activation energy and compressive strength development. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The influence of heat of hydration on strength in mass concrete structures has emphasized the importance of estimating the strength development of concrete as a function of temperature and age. Especially in mass concrete members, the temperature gradient between the inner and outer surfaces is large and changes with age. Tensile strength, which is the criterion of thermal cracking, is mainly estimated on the basis of compressive strength in most projects. Thus, accurate evaluation of compressive strength with age and temperature is of practical importance in mass concrete structures, as well as for concrete in cold-weather and hot-weather conditions.

Saul [1] developed the well-known maturity concept summarizing the findings about the effect of steam curing on the strength development of concrete. He hypothesized that age and temperature above a datum temperature had the equal effects on the strength devel-

opment of concrete and expressed the maturity as the following equation:

$$M = \sum_0^t (T^c - T_0^c) \Delta t \quad (1)$$

where M is the maturity at age t , T^c is the average temperature of concrete during time interval Δt (°C), and T_0^c is the datum temperature (°C). The datum temperature is the lowest temperature at which the strength gain is observed, and Saul proposed a datum temperature of -10.5°C . Saul stated the principle of the maturity concept as, “Concrete of the same mix at the same maturity has approximately the same strength whatever combination of temperature and age goes to make up that maturity.”

Bergstrom [2] found that the maturity method could be applied to concretes cured at normal curing temperatures. He used the maturity method, in which the datum temperature was taken as -10°C , in analyzing the experimental data of other researchers and demonstrated that the maturity method was valid for normal curing temperatures.

McIntosh [3] stated that concrete subjected to lower early-age temperature attained lower early-age strength and higher later-age strength than the concrete subjected

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to higher early-age temperature. So, he concluded that the maturity function of Eq. (1) could not accurately estimate the effect of temperature on the strength development of concrete.

Alexander and Taplin [4] reported the same conclusion as McIntosh. Based on the experimental results of concrete and cement paste cured at 5°C, 21°C, and 42°C, they concluded that the maturity rule (maturity was calculated with a datum temperature of –10°C) greatly underestimated the influence of temperature on the strength of concrete at early maturity and overestimated it at later maturity.

To correct this shortcoming of Saul's maturity function assuming that temperature has a linear effect on strength development, Freiesleben Hansen and Pedersen [5] proposed the following expression for equivalent age [6] based upon the Arrhenius equation:

$$t_e = \sum_0^t e^{-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_r})} \Delta t \quad (2)$$

where t_e is the equivalent age at the reference curing temperature, T is the average temperature (Kelvin, temperature will be in Kelvin unless stated otherwise) of concrete during time interval Δt , T_r is the reference temperature, E is the apparent activation energy (J/mol), and R is the gas constant and equal to 8.3144 J/K mol. Freiesleben Hansen and Pedersen proposed the apparent activation energy according to the following equations (Eq. (3)):

$$\begin{aligned} E(T^c) &= 33,500 + 1470(20 - T^c) \text{ J/mol, for } T^c < 20^\circ\text{C}, \\ E(T^c) &= 33,500 \text{ J/mol, for } T^c \geq 20^\circ\text{C} \end{aligned} \quad (3)$$

where T^c is the temperature (°C).

Jonasson [7] reported that the maturity method using Arrhenius function properly estimated the effect of temperature on the strength up to half of the 28-day strength. At a higher strength ratio, the maturity method overestimated the effect of temperature, particularly at higher curing temperatures. He tested concretes cured at temperatures of 20–50°C and with water–cement ratios (w/c) of 0.77 and 0.56.

Kjellsen and Detwiler [8] stated that the maturity method used along with Eq. (2) and the appropriate apparent activation energy could estimate the early-age strength accurately. However, at maturities above that corresponding to approximately 40% of the normal 28-day strength, the estimation might be erroneous. To improve the accuracy of strength estimation at later ages, they proposed the new expression of apparent activation energy as (Eq. (4))

$$E(T, \alpha) = \frac{\ln[(d\alpha/dt)_T / (d\alpha/dt)_{T_r}]}{T_r^{-1} - T^{-1}} R \quad (4)$$

where α is the degree of hydration, T is the temperature of concrete, T_r is the reference temperature, E is the apparent activation energy (J/mol), and R is the gas constant.

Chanvillard and D'Aloia [9] reported that the apparent activation energy could not be considered as a constant independent of time except during the beginning of hydration, and the extent of hydration with a constant apparent activation energy was lower than 40%. Kada-Benameur et al. [10] stated that the apparent activation energy remained more or less constant at a degree of hydration α ranging between 0.05 and 0.5, but it varied considerably outside this range.

The objective of this study is to propose a new function for estimating the apparent activation energy based on the characteristic properties of apparent activation energy stated in previously published papers and to formulate a new compressive strength equation using this function for the apparent activation energy.

2. Development of a new compressive strength model

Bernhardt [11] assumed that the rate of strength gain at any age was a function of the current strength and the temperature and proposed the mathematical expression as:

$$\frac{dS}{dt} = f(S)k(T) \quad (5)$$

where S is the compressive strength, $f(S)$ is a function of strength and $k(T)$ is a function of temperature. If Eq. (5) is integrated, the following equation can be obtained:

$$\int_0^S \frac{1}{f(S)} dS = \int_{t_0}^t k(T) dt \quad (6)$$

where t_0 is the age when the strength development is assumed to begin. The right side of Eq. (6) is the product of temperature and time and this represents the maturity function. As mentioned in previous paragraphs, Saul [1] proposed $(T^c - T_0^c)$ as a function for $k(T)$, and Freiesleben Hansen and Pedersen [5] proposed the Arrhenius function. Some investigators [3,4] reported that Saul's function underestimated the influence of temperature on the strength of concrete at early maturity and overestimated it at later maturity. Also, it has been reported [7–9] that the Arrhenius function overestimated the effect of temperature at later age. To correct the shortcomings of previous temperature functions, it is necessary to propose a new function. Because previous temperature functions either underesti-

Table 1
Variation of ratio of Arrhenius function with apparent activation energy

Apparent activation energy (J/mol)	40,000	30,000	20,000	10,000	5000	0
$\frac{(e^{-\frac{E}{R(50+273)}})}{(e^{-\frac{E}{R(23+273)}})}$	3.89	2.77	1.97	1.40	1.19	1.00

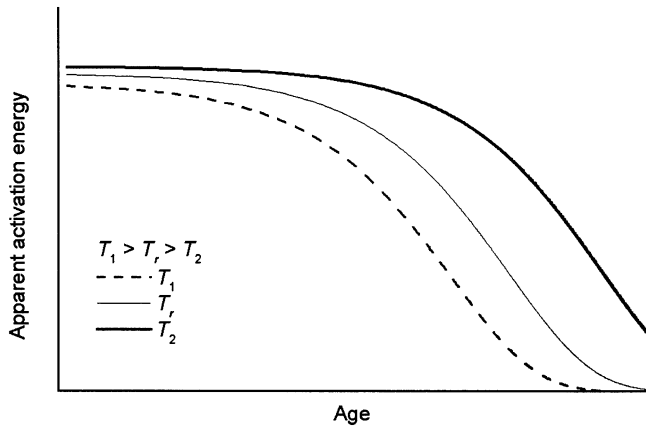


Fig. 1. Hypothetical apparent activation energy vs. age.

mate or overestimate the effect of temperature on the strength development at early ages or later ages, the accuracy can be improved if the function is expressed with age and temperature. So, Eq. (5) may be modified as the following equation:

$$\frac{dS}{dt} = f(S)k(T, t). \quad (7)$$

Because the Arrhenius function estimates the effect of temperature more accurately at early ages than Saul's temperature function [5,8], it is suggested that the function $k(T, t)$ is based on the Arrhenius equation as shown in Eq. (8).

$$\text{Arrhenius equation} = Ae^{-\frac{E}{RT}} \quad (8)$$

where A is a constant. The function $k(T, t)$ can be obtained from Eq. (8) if the Arrhenius equation becomes a function of age or an age function is added to Eq. (8). Because A and R of Eq. (8) are constants and T is the temperature, only the apparent activation energy E can be a function of age. If the apparent activation energy is a function of age, it is not necessary to add an age function to Eq. (8). Kjellsen and Detwiler [8] proposed the apparent activation energy as a function of degree of hydration considering the effect of "retardation" on degree of hydration at later ages. Chanvillard and D'Aloia [9] stated that the apparent activation energy could not be considered as a constant independent of time except during the beginning of hydration. Based on previous published papers, the apparent activation energy can be considered as a function of age. If the apparent activation energy is a function of age and Eq. (8) is substituted into Eq. (7), Eq. (7) is integrated as:

$$\int_0^S \frac{1}{f(S)} dS = \int_{t_0}^t k(T, t) dt = \int_{t_0}^t Ae^{-\frac{E(t)}{RT}} dt. \quad (9)$$

Previous investigators [8,9] stated that the apparent activation energy changes slightly at early ages and decreases greatly at later ages. Table 1 shows the variation of the ratio of Eq. (8) at temperatures of 23°C and 50°C with apparent activation energy. As shown in Table 1, a decrease in apparent activation energy can reduce the overestimation of the effect of temperature on the strength development at later ages [8]. At an infinite age, the apparent activation energy will converge to 0 as the temperature does not affect strength development. Because Jonasson [7] reported that

Table 2
Regression results

	Curing temperature (°C)	Ages of experimental data (days)	E_0 (J/mol)	α	R_u	t_0 (days)
Brooks and Al-Kaisi [16] concrete, w/c=0.42	20	0.5, 1, 3, 7, 14, 28, <u>365</u>	43,789	0.0037	1.24	0.26
	40		42,629	0.0054	1.09	0.26
	47		41,120	0.0064	1.05	0.30
	60		41,869	0.0129	1.02	0.21
Tank and Carino [17] concrete, w/c=0.45	10	1, 2, 5, 15, 28, 57, <u>365</u>	41,295	0.0013	1.28	0.90
	21.5	0.5, 1, 2, 4, 7, 14, 28, <u>365</u>	41,352	0.0039	1.11	0.00
	41	0.5, 1, 2, 4, 7, 15, 28, <u>365</u>	38,512	0.0100	1.03	0.00
Klieger [14] concrete, w/c=0.77	4.4	1, 3, 7, 28, 90, 365	43,684	0.0026	1.48	0.99
	13		42,702	0.0023	1.29	0.55
	23		42,192	0.0033	1.15	0.23
Kim et al. [15] concrete, w/c=0.35	5	1, 2, 3, 7, 14, 28, <u>365</u>	42,233	0.0019	1.40	0.42
	20		39,837	0.0036	1.10	0.60
	40		38,467	0.0057	1.03	0.00
Kim et al. [15] concrete, w/c=0.55	5	1, 2, 3, 7, 14, 28, <u>365</u>	43,518	0.0001	1.88	0.56
	20		42,344	0.0031	1.20	0.31
	40		42,048	0.0048	1.07	0.00
Kjellsen and Detwiler [8] mortar, w/c=0.50	5	1.9, 3, 7, 14, 28, 91, <u>365</u>	40,216	0.0001	1.35	1.12
	13	1, 2, 3, 7, 28, 91, <u>365</u>	39,566	0.0018	1.15	0.66
	20	0.5, 1, 2, 7, 28, 91, <u>365</u>	39,221	0.0020	1.11	0.37
	35	0.5, 1, 3, 28, <u>365</u>	38,023	0.0056	1.03	0.22

All experimental data are the compressive strength of Type I cement concrete.

All experimental data are fitted on the basis of $A=10^7$.

Relative strength at the underlined age is an estimated value.

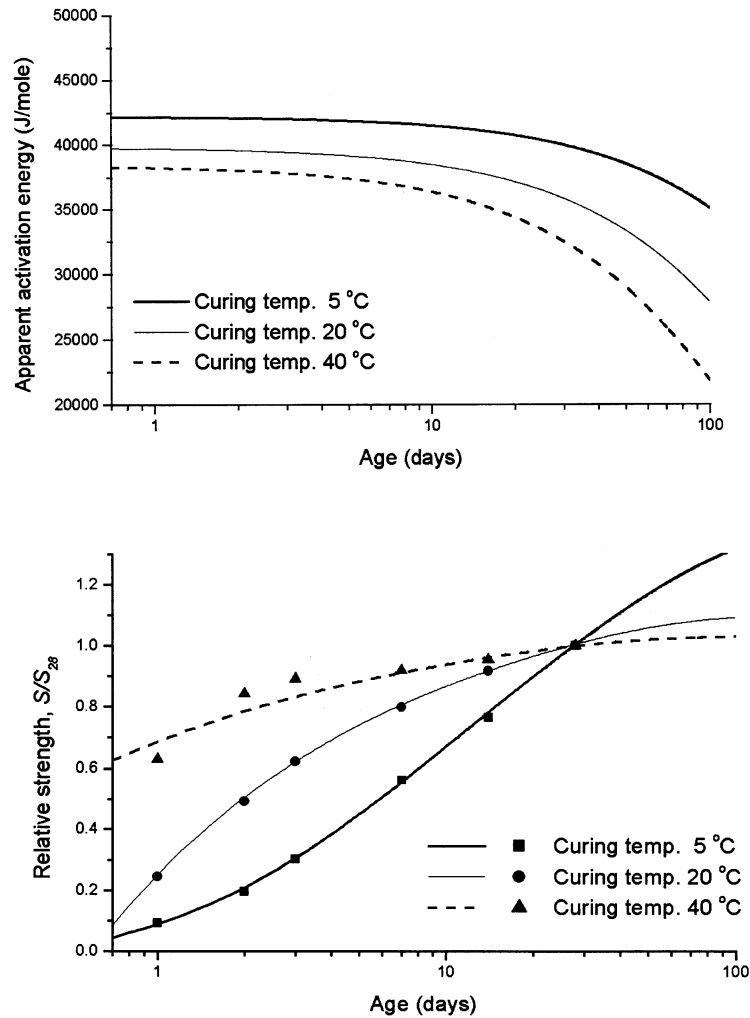


Fig. 2. Apparent activation energy and relative strength vs. age for new compressive strength model (Kim et al. [15] concrete, w/c=0.35).

the overestimation of the influence of temperature on the strength development is greater at high temperature, the apparent activation energy of concrete cured at high temperature will decrease more quickly than that cured at normal temperature. If the variation of apparent activation energy with age is considered on the basis of these findings, it can be represented as shown in Fig. 1. In order to represent the variation of apparent activation energy shown in Fig. 1, the following exponential function is proposed:

$$E = E_0 e^{-\alpha t} \quad t \geq t_0 \quad (10)$$

where E_0 is the initial apparent activation energy (J/mol) and α is a constant.

If the curing temperature is constant, the following equation can be obtained by substituting Eq. (10) into Eq. (9) and integrating the right-hand side of Eq. (9) as:

$$\begin{aligned} \int_{t_0}^t k(T, t) dt &= \int_{t_0}^t A e^{-\frac{E_0}{RT} e^{-\alpha t}} dt \\ &\cong \frac{1}{2} A \left[e^{-\frac{E_0}{RT} e^{-\alpha t}} + e^{-\frac{E_0}{RT} e^{-\alpha t_0}} \right] (t - t_0). \end{aligned} \quad (11)$$

The difference between relative compressive strength by the integral function and that by the approximate function is less than 1.5%.

If a hyperbolic equation is used for the strength function [11,18], Eq. (9) can be expressed as:

$$\int_0^S \frac{1}{S_u \left[1 - \frac{S}{S_u} \right]^r} dS = \int_{t_0}^t k(T, t) dt \quad (12)$$

where S_u is the strength at infinite time and r is a reaction coefficient. Eq. (12) is integrated as:

$$S = S_u \left\{ 1 - \frac{1}{\left[1 + (r-1) \int_{t_0}^t k(T, t) dt \right]^{\frac{1}{r-1}}} \right\}. \quad (13)$$

Moon [12] suggested that a reaction coefficient r equal to 3 estimates the later-age strength development more accurately than that equal to 2. Thus, it is assumed that r is equal to 3. Substituting Eq. (11) into Eq. (13) and expressing

the relative strength in terms of 28-day strength, the following strength equation can be obtained:

$$\frac{S}{S_{28}} = R_u \left\{ 1 - \frac{1}{\sqrt{1 + A \left[e^{-\frac{E_0}{RT}} e^{-\alpha t} + e^{-\frac{E_0}{RT}} e^{-\alpha t_0} \right] (t - t_0)}} \right\} \quad (14)$$

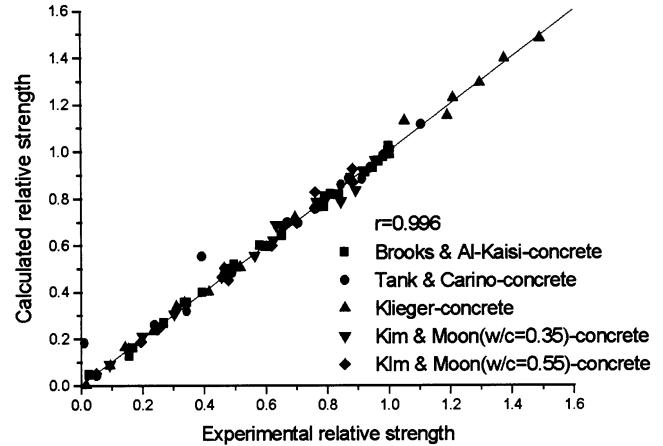
where R_u is the limiting relative strength with $R_u = S_u/S_{28}$.

3. Results and discussions

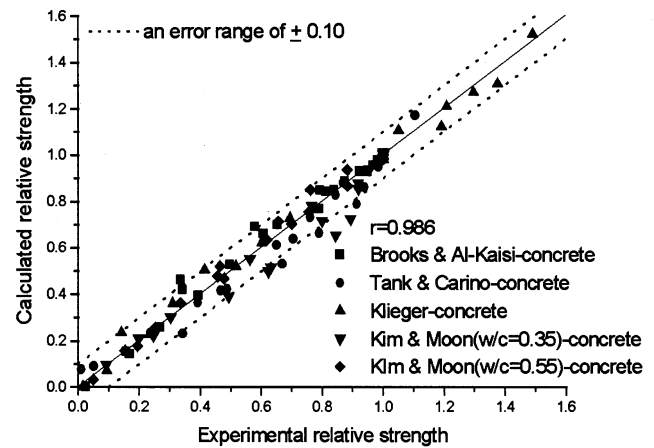
3.1. Regression results of experimental data

Eq. (14) represents relative strength development under constant curing temperature as functions of five unknown parameters (R_u , A , E_0 , α , and t_0). Table 2 tabulates the regression results from fitting the new compressive strength model of Eq. (14) to published data by using a commercial data analysis program. Because A is not a function of age and temperature and preliminary regression results showed that A changed slightly with mixture proportions, it is safe to assume that A is constant. The parameter α represents the decrease in apparent activation energy with age. Because the decrease in apparent activation energy reduces the influence of temperature on later-age strength development [7,8], α is related to later-age strength development. As most experimental data are obtained from tests within 28 days, the regression based on these data may have some error in estimating α and the limiting relative strength R_u . In order to improve the accuracy of the estimation of α and R_u , the relative strength at the age of 1 year, approximated on the basis of the experimental results of other researchers [13,14], was included with experimental data. All strength–age curves with experimental data up to 1 year were represented in terms of S/S_{28} , and the 1-year relative strengths of concrete without 1-year experimental data were estimated by extrapolating the strength–age curves.

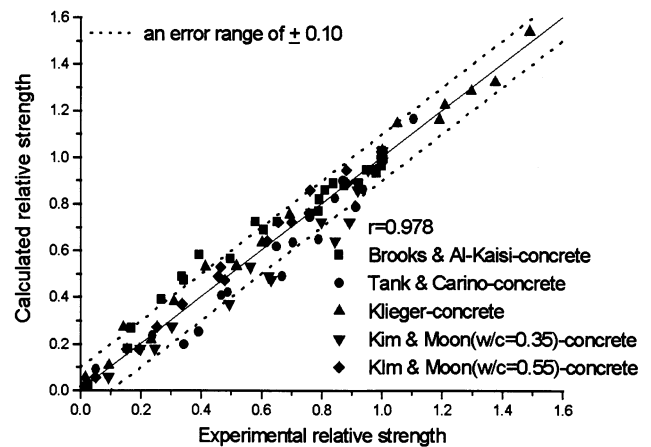
Fig. 2 shows the regression results for the experimental data of Kim et al. [15] ($w/c=0.35$). As shown in Fig. 2, the new compressive strength model of Eq. (14) provides good estimates of the development of relative strength with temperature and age. The curves of apparent activation energy vs. age are similar to the hypothetical curves of Fig. 1. Also, the apparent activation energy of concrete cured at high temperature decreases at a faster rate than that of concrete cured at low temperature [7,8]. The calculated relative strengths are compared with the experimental values in Fig. 3(a). As shown in Fig. 3(a), the new compressive strength model provides a good representation of relative strength development for all the analyzed data.



(a) Variable E_0 , α , R_u and t_0

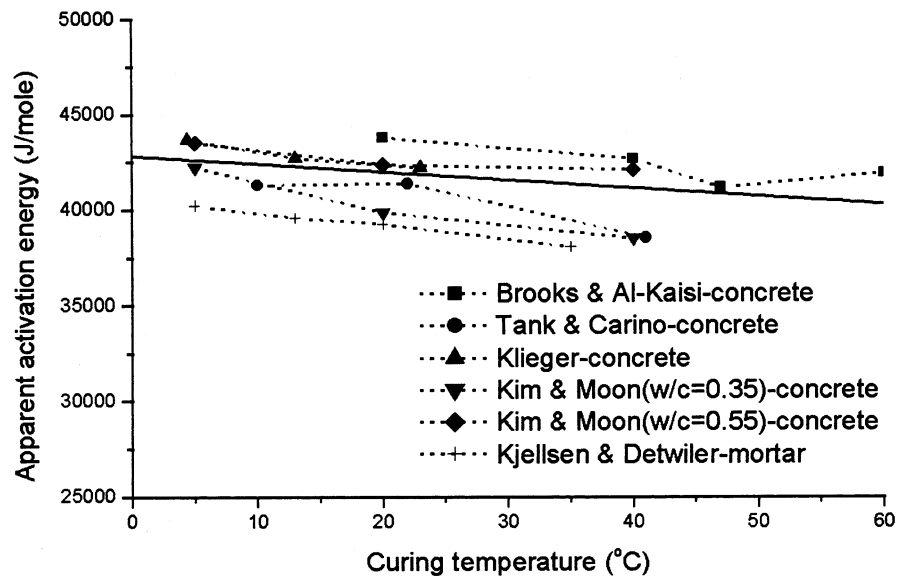
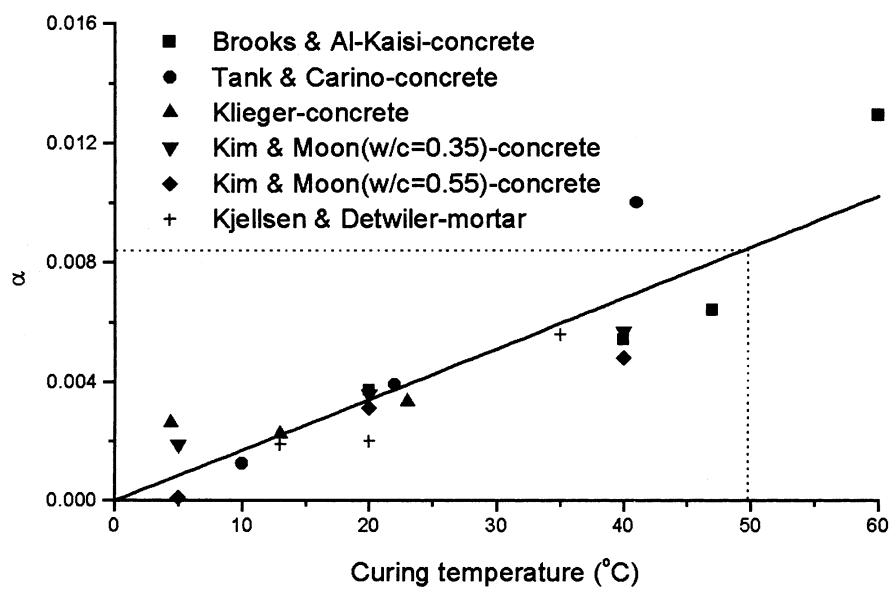


(b) Variable R_u and t_0



(c) General E_0 , α , R_u and t_0

Fig. 3. Experimental and calculated relative strength.

(a) E_o (b) α Fig. 4. Regression results of E_o and α .

3.2. Calculation of apparent activation energy and compressive strength

Concrete with same mixture proportions will have the same apparent activation energy at the initial age after mixing. But concrete cured at different temperatures during setting will have different material properties and relative strength gains at time t_0 when rapid strength development begins. So, the initial apparent activation energy that represents the influence of temperature on the initial rate of relative strength gain will be a function of temperature [8,9]. As shown in Fig. 4(a), the initial apparent activation energy of each researcher decreases slightly with increasing temperature. The decrease in the initial apparent activation energy with temperature is smaller than in other studies [5,7,8]. Based on the regression results, the variation of initial apparent activation energy with curing temperature can be presented as:

$$E_0 = 42,830 - 43T^{\circ}\text{C} \quad (15)$$

As stated in previous paragraphs, the apparent activation energy of concrete cured at high temperature will decrease with age more quickly than that cured at normal temperature. Because the apparent activation energy decreases at a faster rate as α increases, α will increase with temperature. As shown in Fig. 4(b) for the analyzed data, α increases with curing temperature. Based on these calculated α values, the following α –temperature relationship can be obtained:

$$\alpha = 0.00017T^{\circ}\text{C} \quad (16)$$

where $T^{\circ}\text{C}$ is the curing temperature ($^{\circ}\text{C}$).

Using Eqs. (10), (15), and (16) to represent the variation of apparent activation energy with temperature and age, the strength–age data of various researchers were reanalyzed to obtain the best-fit values of R_u and t_0 , which

are tabulated in Table 3. In Fig. 3(b), the relative strengths estimated by the new compressive strength model including the equations of apparent activation energy, i.e., Eqs. (15) and (16), are compared with the experimental relative strengths. As shown in Fig. 3(b), the new compressive strength model based on the general equations of apparent activation energy slightly overestimates or underestimates the experimental relative strength. But the deviation between calculated and experimental values is generally within 0.10, as shown in Fig. 3(b). Thus, Eqs. (15) and (16) provide reasonable estimates of the variation of apparent activation energy for the new compressive strength model.

If there are equations that estimate t_0 and R_u as a function of temperature, a general model for estimating the compressive strength of concrete under isothermal curing can be obtained. The regression data of Table 3 were fitted to obtain the following equations to represent t_0 and R_u as a function of curing temperature:

$$t_0 = 0.66 - 0.011T^{\circ}\text{C} \geq 0 \quad (17)$$

$$R_u = 2.04T^{\circ\text{C}-0.18} \geq 1. \quad (18)$$

Fig. 3(c) shows the relative strength estimated on the basis of the new compressive strength model using Eqs. (15)–(18) compared with the experimental relative strength. In most cases, the new model estimates the relative strength within ± 0.10 of the experimental value. Thus, it is concluded that the new compressive strength model developed in this study can estimate the compressive strength development with age and temperature for isothermal curing condition. Fig. 5 shows the apparent activation energy and the relative strength based on Eqs. (15)–(18).

Even if concrete is subjected to different curing temperature with age, the maturity function of the right-hand side of Eq. (9) can be calculated with Eqs. (15)–(17) estimating α ,

Table 3
Regression results based on the equations of E_0 and α

	Curing temperature ($^{\circ}\text{C}$)	Ages of experimental data (days)	E_0^a (J/mol)	α^a	R_u	t_0 (days)
Brooks and Al-Kaisi [16] concrete, w/c=0.42	20	0.5, 1, 3, 7, 14, 28	41,970	0.0034	1.14	0.49
	40		41,110	0.0068	1.03	0.38
	47		40,809	0.0080	1.03	0.33
	60		40,250	0.0102	1.02	0.34
Tank and Carino [17] concrete, w/c=0.45	10	1, 2, 5, 15, 28, 57	42,400	0.0017	1.36	0.56
	21.5		41,905	0.0037	1.14	0.26
	41		41,067	0.0070	1.04	0.00
Klieger [14] concrete, w/c=0.77	4.4	1, 3, 7, 28, 90, 365	42,641	0.0009	1.54	0.99
	13		42,271	0.0022	1.27	0.69
	23		41,841	0.0039	1.12	0.34
Kim et al. [15] concrete, w/c=0.35	5	1, 2, 3, 7, 14, 28	42,615	0.0009	1.50	0.34
	20		41,970	0.0034	1.17	0.24
	40		41,110	0.0068	1.04	0.00
Kim et al. [15] concrete, w/c=0.55	5	1, 2, 3, 7, 14, 28	42,615	0.0009	1.52	0.78
	20		41,970	0.0034	1.16	0.42
	40		41,110	0.0068	1.04	0.22

^a Based on Eqs. (15) and (16).

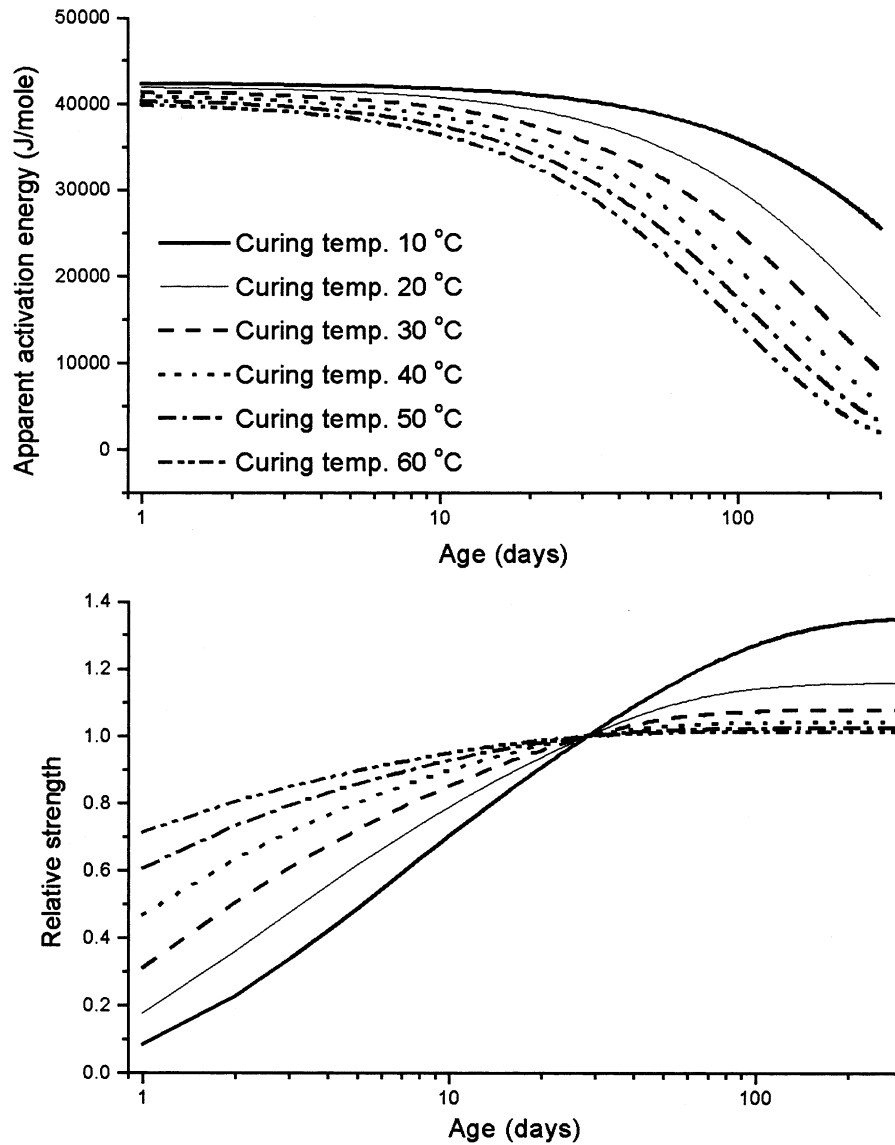


Fig. 5. Apparent activation energy and relative strength under isothermal curing by Eqs. (15)–(18).

E_0 , and t_0 . But, in this case, Eq. (18) cannot estimate R_u , because R_u of concrete subjected to different curing temperature with age varies with age, as well as curing temperature. In order to solve the problem, Eq. (14) must be converted to the following relative strength–maturity relationship, which does not include R_u .

$$\frac{S}{S_u} = \left\{ 1 - \frac{1}{\sqrt{1 + 2 \int_{t_0}^t k(T, t) dt}} \right\}$$

$$= \left\{ 1 - \frac{1}{\sqrt{1 + \sum_{i=1}^n A \left[e^{-\frac{E_0}{RT} e^{-\alpha t_i}} + e^{-\frac{E_0}{RT} e^{-\alpha t_{i-1}}} \right] (t_i - t_{i-1})}} \right\} \quad (19)$$

where t_i is the final age of time step i and t_{i-1} is the initial age of time step i . If S/S_u values at 28 days and other ages are calculated using Eq. (19) and the values at all ages are divided by S_{28}/S_u , S/S_{28} at all ages can be obtained. Therefore, the development of concrete strength subjected to different curing temperature with age can be estimated on the basis of Eq. (19).

4. Conclusions

Previous temperature functions such as Saul and Arrhenius functions underestimated or overestimated the effect of temperature on strength development at early and later ages. In order to correct these shortcomings, a new function in which the apparent activation energy is a nonlinear function of temperature and age is proposed. A compressive

strength equation including this function was formulated. The suitability of this new model was investigated by comparing the strengths estimated by the model with experimental data. Based on the results, the following conclusions have been made.

(1) The compressive strength model that includes the new apparent activation energy function for estimating the influence of temperature on the strength development provides a good representation of relative strength development by other researchers.

(2) The decrease in apparent activation energy with age and temperature can correct the overestimation of the effect of temperature on strength development at later ages. The apparent activation energy of concrete cured at high temperature decreases at a faster rate than that cured at normal temperature, reducing the overestimation at higher temperature.

(3) The compressive strength model based on the equations of E_0 and α estimates the experimental relative strength within an error range of ± 0.10 . General equations for R_u and t_0 are suggested on the basis of the regression results.

Acknowledgments

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