Cement and Concrete Research 40 (2010) 58–65

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Unified modeling of setting and strength development

R.C.A. Pinto [a,*], A.K. Schindler [b]

[a] Department of Civil Engineering, Federal University of Santa Catarina, Florianópolis, SC 88040-910, Brazil
[b] Department of Civil Engineering, Auburn University, Harbert Engineering Center, Auburn, AL 36849, USA

ARTICLE INFO

Article history:
Received 19 December 2008
Accepted 13 August 2009

Keywords:
Maturity method
Aging (C)
Compressive strength (C)
Temperature (A)

ABSTRACT

The effect of temperature on the development of concrete compressive strength can be modeled by the maturity approach once the temperature sensitivity of the mixture, quantified by the activation energy (E_a) of its chemical reactions, is known. It is common in maturity applications to use a unique value of E_a obtained for the hardening period, even though the effect of temperature is different on the rate of setting and hardening. E_a-values presented in the literature suggest that the temperature sensitivity is lower before hardening. This paper proposes a new approach to the traditional maturity method unifying the distinctly different temperature sensitivities before final setting and during hardening. Results of setting and compressive strength of mixtures with different cementitious materials were analyzed with activation energy values calculated for the periods before final setting and during hardening. For the investigated mixtures, the new approach led to improved strength predictions, suggesting that it is useful to take into account setting behavior in the development of the strength–maturity relationship.
© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The maturity approach has been used to model temperature effects on the development of concrete compressive strength since around 1950 when steam curing treatments were initially applied to accelerate compressive strength gain [1]. Maturity accounts for the combined effects of temperature and time on the development of compressive strength (and other properties such as setting, degree of hydration, etc.), being evaluated from the temperature history of the concrete investigated.

In maturity applications, a strength–maturity relationship is established for a given mixture cured at known temperature conditions. Several mathematical relationships for the strength–maturity relationship have been proposed since Saul [2] defined the term maturity, in 1951. An appropriate strength–maturity relationship should take into account the dormant period of a concrete mixture, in which the material is still in a plastic state. This is essential, as strength development starts at final set, and inaccuracies in the estimated final set time may affect the early-age predicted strength. The extent of this period is related to the setting behavior of the concrete mixture which depends on the curing history of the concrete [3].

The precise definition of the time when setting starts and ends is somewhat subjective, since setting is caused by a gradual stiffening process. Nevertheless, this transition period starts when concrete loses its plasticity, and ends when measurable mechanical properties start to develop [4]. The hardening period follows in which concrete continuously gains strength with time.

The setting and hardening processes are physical consequences of the chemical activity in a mixture, and thus, are greatly affected by temperature. Arrhenius-based maturity functions have been proposed to the setting and to the hardening periods [3,5]. The temperature sensitivity of a given mixture can be quantified by the apparent activation energy (E_a) of its chemical reactions [6].

Traditionally, when the maturity approach is used to estimate strength, a single value of E_a is used [7] for the periods preceding final set and during hardening, even though the temperature sensitivity of the cement hydration reactions decreases as they turn from chemically controlled to diffusion controlled [8]. Researchers have attempted to include variable E_a-values during the hardening period [9,10]; however, it is common practice to use a single E_a-value to estimate setting and strength development. Some values of activation energy reported in the literature [11–21] for mixtures with Type I cement and replacements of various supplementary cementitious materials, obtained for the setting and hardening periods are summarized in Table 1. While there is a wide range of values due to the composition of the mixtures, the reported activation energies up to final set are generally less than those reported for the hardening period, suggesting that there may be differences in temperature sensitivity during the setting and hardening periods. Thus, the utilization of a fixed E_a-value obtained for the hardening period may lead to poor estimates of strengths at very early ages since the temperature sensitivity of the mixture up to final set has not properly been taken into account.

* Corresponding author. Tel.: +55 48 3721 7768; fax: +55 48 3721 5191.
E-mail address: rpinto@ecv.ufsc.br (R.C.A. Pinto).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.08.010

Table 1
Some activation energy values reported in the literature (kJ/mol).

	Reference	Activation energy from setting experiments — E_s	Activation energy for hardening period — E_a
Type I cement mixtures	Lachemi et al. [11]	30.2[a]	
	Lei and Strubble [12]	22.0[a]	
	Turcry et al. [13]	29.0[a]	
	Pinto and Hover [14]	37.9[a]	
	Garcia et al. [15]	29.6[b]	
	Wade et al. [16]	27.1 to 33.4[b,c]	
	Barnett et al. [17]		32.9 to 35.1[c]
	Carino and Tank [18]		43.6 to 63.6[c]
	Schindler and Folliard [19]		46.0
	Voigt et al. [20]		38.0
	Wirkin et al. [21]		35.6
Mixtures with fly ash	Wade et al. [16]	23.3 to 25.7[c,d]	
		27.0 to 29.0[c,e]	
	Carino and Tank [18]		30.0 to 36.6[c]
	Schindler and Folliard [19]		30.1 to 40.7[c,d]
			37.5 to 43.1[c,e]
Mixtures with GGBF slag	Wade et al. [16]	26.7 to 35.2[c]	
	Barnett et al. [17]		35.2 to 62.1[c]
	Carino and Tank [18]		42.7 to 56.0[c]
	Schindler and Folliard [19]		51.5 to 55.2[c]

[a] Up to initial set.
[b] Up to final set.
[c] Various w/cm ratio.
[d] Class F fly ash.
[e] Class C fly ash.

This paper proposes a new approach to the traditional maturity method to unify the distinctly different temperature sensitivities before setting and during the hardening period to improve the overall strength prediction of concrete at all ages. The effect of using different activation energies on the development of a strength–maturity relationship is assessed. Setting and compressive strength results of mortar and concrete mixtures incorporating different cementitious materials under various curing temperatures were analyzed with an activation energy value calculated for the period up to final set and another for the hardening period. For the somewhat limited mixtures investigated here, the proposed new approach led to improved strength predictions than the traditional maturity method. This result suggests that that strength predictions could be improved when the setting behavior is taken into account in the development of the strength–maturity relationship.

2. Review of the maturity approach to estimate compressive strength

According to the maturity rule proposed by Saul [2], a concrete mixture at a certain level of maturity attains the same strength regardless of the combination of time and temperature history to arrive at such maturity. The equivalent age maturity approach modifies the time-axis of the strength–age relationship by calculating a maturity index according to Eq. (1).

$$M(T_c, t) = \int_0^t f(T_c)dt \tag{1}$$

where,

$M(T_c,t)$ = maturity index,
$f(T_c)$ = a function of temperature,
T_c = concrete temperature, and
t = concrete age.

However, for most concrete mixtures, the level of ultimate strength development is affected by the early concrete temperatures [1]. Lower early curing temperatures often lead to higher ultimate strength, and vice versa. This effect is called the crossover effect and has been reported by various investigators [9,22]. It should be noted that the crossover effect does not occur in all types of mixtures [23]. If a concrete mixture is subjected to the crossover effect, the maturity rule as stated above will not be able to correctly estimate later-age strength, as a unique strength–maturity relationship does not exist. On the other hand, it can be shown that for a particular concrete mixture, there is a unique relationship between degree of hydration and maturity [24]. Considering that the degree of hydration can be assessed by the degree of strength development, i.e., the ratio between the strength at any time and the long-term strength, also called ultimate strength (which produces a relative strength), the maturity rule could thus be modified, and a unique relative strength–maturity relationship established. Carino [1] showed that a unique relationship between the relative strength ratio and maturity exists, even for mixtures that exhibit the crossover effect.

In 1956, Benhardt [25] proposed that the rate of strength gain at any age should be a function of the current strength and the temperature, as mathematically expressed in Eq. (2). According to the data analyzed in his paper, Benhardt believed that the value of the constant m in Eq. (2) is likely to be 2.

$$\frac{dS}{dt} = S_u\left(1 - \frac{S}{S_u}\right)^m k(T_c) \tag{2}$$

where,

S_u = ultimate strength,
S = compressive strength at age t,
$k(T_c)$ = rate constant, which is temperature dependent, and
m = constant.

Integration of Eq. (2), with the constant m being 2, can be performed assuming as the boundary condition that concrete strength starts to develop as soon as concrete is produced, resulting in the following expression:

$$\frac{S}{S_u} = \frac{kt}{1 + kt} \tag{3}$$

where,

kt = the result of the internal $\int_0^t k(T_c)dt$ (unitless).

One can notice that this integral corresponds to the maturity index as presented in Eq. (1). However, the assumption of the lower boundary condition is not strictly correct, since up to final setting the concrete is still a plastic material, and it is thus not able to develop any mechanical properties. The utilization of an offset time (t_o) as a lower boundary condition is then more appropriate, and Eq. (3) can thus be modified to Eq. (4). This function is commonly referred to as the "hyperbolic function" and is the preferred strength–age function in North American practice [7].

$$\frac{S}{S_u} = \frac{k(t - t_o)}{1 + k(t - t_o)}. \tag{4}$$

Maturity is often expressed in terms of equivalent age (t_e), which represents the curing age at a fixed reference temperature necessary to achieve the same level of maturity when cured at a different temperature history [5]. In this case, the chronological curing age of a concrete cured at any temperature is converted to an equivalent curing age for a specimen cured at a reference temperature (T_r). Eq. (5) expresses such a conversion.

$$t_e k_r = \int_0^t k(T_c)dt \tag{5}$$

where,

t_e = equivalent age at a reference temperature T_r and
k_r = rate constant at the reference temperature.

Since hardening of concrete is a consequence of the extent of cement hydration, Freiesleben Hansen and Pedersen [5] suggested the equivalent age maturity function presented in Eq. (6) based on the Arrhenius theory for the temperature influence on the rate of chemical reactions.

$$t_e = \sum_0^t exp\left[\frac{-E_a}{R}\left(\frac{1}{(T_c+273)} - \frac{1}{(T_r+273)}\right)\right]\Delta t \tag{6}$$

where,

E_a = activation energy (J/mol),
R = universal gas constant (8.314 J/mol/K), and
T_r = reference temperature (°C).

After substituting Eq. (6) into Eq. (4), the following relative strength-equivalent age expression is obtained in terms of equivalent age.

$$\frac{S}{S_u} = \frac{k_r(t_e - t_{or})}{1 + k_r(t_e - t_{or})} \tag{7}$$

where,

t_{or} = offset time at the reference temperature, T_r.

2.1. The offset time and its influence on the strength–maturity relationship

The offset time, t_o, defines the starting age for the maturity–strength relationship. The exact t_o time for a particular mixture is hard to determine experimentally. Several experimental methods, ranging from mechanical, electrical, calorimetrical and others can be used to determine t_o. However, as discussed by Weiss [26], research is still needed to relate these experimental methods to each other, and to determine how the properties measured by each test relate to the concrete's ability to transfer stresses.

Carino [27] recommended that the offset time should lie between the initial and final set as given by the penetration resistance method [28]. Mindess et al. [4] state that the final set given by ASTM C 403 [28] corresponds to a concrete strength of around 0.7 MPa. As a result, t_o is related to the setting behavior of the concrete mixture, and thus is temperature dependent.

There is no reason to assume that the period up to the offset time, t_o would have the same temperature sensitivity as the hardening phase. This means that a single activation energy value should not be used in maturity applications. The chemical activity during this early stage is not the same as the one during hardening. Moreover, it is common to incorporate chemical admixtures and also supplementary cementitious materials in the concrete mixture which may cause variations in setting times. Chemical admixtures were specifically developed to modify the early behavior of a concrete mixture.

One should thus explore the option of having different activation energies before and after the offset time, t_o, and how that difference would affect the development of a strength–maturity expression, as given by Eq. (7). Initially, it is necessary to make an assumption regarding the offset time. In the following discussion and throughout this study t_o was assumed to be given by the final set time. While a different assumption could also be made, it would not result in any significant modification in the equations nor in the discussion and conclusions presented in this paper.

In the development of the relative strength–maturity relationship, given by Eq. (7), the dependence of t_{or} with temperature is given by:

$$t_{or} = t_o exp\left[\frac{-E_a}{R}\left(\frac{1}{(T_c+273)} - \frac{1}{(T_r+273)}\right)\right] \tag{8}$$

A similar expression, Eq. (9), gives the dependence of the final set time with temperature, but with the activation energy determined from setting experiments, E_s, instead of E_a.

$$t_{sr} = t_s exp\left[\frac{-E_s}{R}\left(\frac{1}{(T_c+273)} - \frac{1}{(T_r+273)}\right)\right] \tag{9}$$

where,

t_s = final set time at temperature T_c,
t_{sr} = final set time at reference temperature T_r, and
E_s = activation energy to define the temperature sensitivity until final set.

Assuming that t_s is equal to t_o, and substituting Eq. (9) in Eq. (8), the following equation is obtained.

$$t_{or} = t_{sr} exp\left[\frac{(E_s - E_a)}{R}\left(\frac{1}{(T_c+273)} - \frac{1}{(T_r+273)}\right)\right]. \tag{10}$$

Therefore, only when the activation energies until final set (E_s) and during hardening (E_a) are the same, the assumption of final set as the offset time for the strength–maturity relationship will hold true, and as a consequence, there will be a unique relative strength–maturity relationship regardless of the curing temperature.

For instance, according to Eq. (10), when E_s is smaller than E_a, for a concrete cured at a curing temperature (T_c) greater than the reference temperature (T_r), the offset time (in equivalent ages, t_{or}) will be greater than the final set at the reference temperature (t_{sr}). If the concrete is cured at temperatures below the reference temperature, the opposite occurs, i.e. t_{or} is smaller than t_{sr}. The consequence of such a difference between E_s and E_a is schematically presented in Fig. 1 which shows that the relative strength–maturity relationship depends on the curing temperature.

3. Unified model to account for different temperature sensitivities before and after final set

In order to obtain a unique strength–maturity relationship when E_s is different from E_a, the equivalent age maturity, presented in Eq. (6), should be calculated considering different activation energy values before and after the final set. Fig. 2 schematically shows this

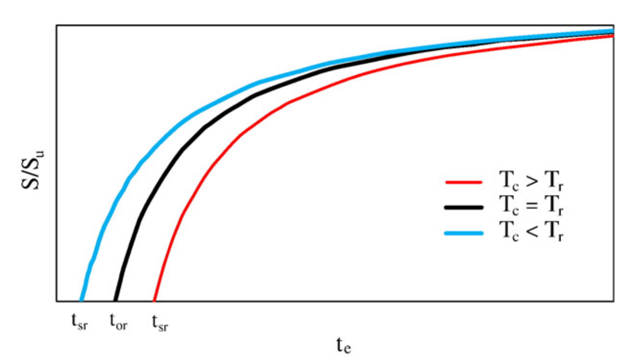

Fig. 1. Strength–maturity relationship — $E_s < E_a$.

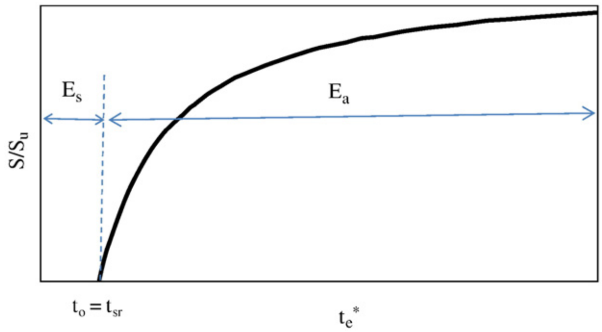

Fig. 2. Proposed method to calculate equivalent ages.

approach, which requires E_s and E_a-values to be known. The new proposed equivalent age maturity function to account for this behavior is presented in Eq. (11).

$$t_e^* = \sum_0^{t_{sr}} exp\left[\frac{-E_s}{R}\left(\frac{1}{(T_c + 273)} - \frac{1}{(T_r + 273)}\right)\right]\Delta t + \sum_{t_{sr}}^{t} exp\left[\frac{-E_a}{R}\left(\frac{1}{(T_c + 273)} - \frac{1}{(T_r + 273)}\right)\right]\Delta t \quad (11)$$

where, t_e^* = modified equivalent age at a reference temperature T_r.

The offset time included in the strength–maturity relationship should represent the final set of the concrete mixture at the reference temperature, according to Eq. (12). This method will account for the effect of temperature on each mixture's specific setting and strength behavior when cured at various temperatures.

$$\frac{S}{S_u} = \frac{k_r(t_e^* - t_{sr})}{1 + k_r(t_e^* - t_{sr})}. \quad (12)$$

4. Experimental verification

In order to verify the influence of using the proposed unified model to estimate compressive strength, setting and strength development data collected at different curing temperatures for various concrete mixtures are required. Data from the following two studies are analyzed in this paper: 1) mortar results from a NBSIR study reported by Carino [27], and 2) concrete results from an Auburn University study [16,29] that evaluated the behavior of Portland cement with several supplementary cementitious materials.

4.1. NBSIR study

Carino [27] studied a mortar mixture with a water–cement ratio (w/c) of 0.43, and Type I cement cured at different isothermal temperatures. The setting behavior was evaluated by the penetration resistance method [28] with specimens cured at 5 and 32 °C. Final set times were 21.4 and 5.3 h for these temperatures, respectively. Compressive strength development was monitored using 50-mm cubes cured at 5, 12, 23, 32, and 45 °C tested in accordance with ASTM C 109 [30]. The compressive strength results determined at each curing condition are presented in Table 2.

4.2. Auburn University study

Wade [29] studied the application of the maturity approach to estimate the compressive strength of nine different concrete mixtures. Additionally the setting behavior of these mixtures was also determined and are reported by Wade et al. [16]. Concrete mixture proportions for this study are as presented in Table 3. A reference mixture with Type I cement and a w/c of 0.41 was used. Two other mixtures were studied with w/c of 0.44 and 0.48. Six more mixtures were produced by replacing part of the cement mass present in the reference mixture by different levels of Class F fly ash (20% and 30%), Class C fly ash (20% and 30%), and ground-granulated blast-furnace (GGBF) slag (30% and 50%). Crushed limestone was used as fine and coarse aggregates.

All nine concrete mixtures were cured under three different temperature histories. One batch of each mixture was cured at a constant "control" temperature (between 20 °C to 23 °C); another batch was cured under a representative "hot" temperature history to simulate summer conditions; while the last batch was cured under a representative "cold" temperature history to simulate winter conditions. Both the "hot" and "cold" batches were cured under fluctuating temperatures. The curing temperature cycle for the "hot" mixtures was 32 °C to 41 °C and back to 32 °C in 24 h. The curing temperature cycle for the "cold" mixtures was from 4 °C to 13 °C and back to 4 °C in 24 h. In order to produce concrete with different fresh temperatures, the raw materials for the hot and cold mixtures were placed in an environmental chamber set at 46 °C and 4 °C, respectively, for at least 2 days prior to batching. This yielded fresh concrete temperatures of approximately 40 °C and 14 °C for hot and cold batches, respectively. The fresh concrete temperature of the control batch was between 20 and 24 °C.

The setting behavior was evaluated by the penetration resistance method in mortar samples sieved from the concrete mixture [28]. Initial and final set times are reported in [16] for all mixtures in the three curing regimes. The compressive strength development of the concrete was monitored by testing 150×300-mm cylinders tested at various ages in accordance with ASTM C 192 [31]. The compressive strength data obtained from this study are presented in Table 4.

5. Analysis

For each mixture described above, actual times for each compressive strength test were transformed into equivalent ages, and then the

Table 2
Compressive strength results [13].

Curing temperatures									
5 °C		12 °C		23 °C		32 °C		43 °C	
Age (days)	f_c (MPa)	Age (days)	f_c (MPa)	Age (days)	f_c (MPa)	Age (days)	f_c (MPa)	Age (days)	f_c (MPa)
1.3	2.2	1.0	4.5	0.5	3.0	0.4	4.3	0.2	3.1
3.4	15.6	2.0	14.5	1.1	13.6	0.8	13.8	0.6	17.6
6.9	29.2	4.5	27.8	2.4	25.5	1.8	27.0	1.4	31.5
13.3	44.6	9.0	43.5	5.0	40.3	4.1	40.3	3.1	41.3
27.0	56.3	19.0	54.4	10.0	49.5	8.9	48.2	6.0	44.0
47.0	62.1	31.9	54.4	21.0	57.1	16.0	52.6	12.9	51.2
67.1	64.6	45.9	62.6	33.9	59.1	25.8	53.1	20.0	54.7

Table 3
Concrete mixture proportions (kg/m^3) [16].

Constituent	Type I cement			Class F fly ash		Class C fly ash		GGBF slag	
	I-0.41	I-0.44	I-0.48	20%	30%	20%	30%	30%	50%
Water	158	162	177	158	158	158	158	158	158
Cement	390	368	368	312	274	312	274	274	195
Class F ash	–	–	–	78	117	–	–	–	–
Class C ash	–	–	–	–	–	78	117	–	–
GGBF slag	–	–	–	–	–	–	–	117	195
Coarse aggregate	1082	1165	1140	1082	1082	1082	1082	1082	1082
Fine aggregate	718	675	662	705	698	693	680	710	704
Water-reducer (mL/m^3)	762	360	–	762	762	762	762	762	762
Air-entraining (mL/m^3)	116	77	58	116	116	116	116	116	116

Table 4
Compressive strength results versus age [17].

Cold		Room		Hot		Cold		Room		Hot		Cold		Room		Hot	
Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)	Age (Day)	f_c (MPa)
I-0.41						I-0.44						I-0.48					
0.8	3.8	0.5	7.1	0.4	14.8	0.9	2.9	0.5	5.7	0.3	8.8	0.9	2.9	0.5	4.4	0.3	5.9
1.8	19.6	1.0	18.7	0.8	25.3	1.9	14.2	1.0	13.7	0.9	17.8	1.9	11.1	1.0	11.8	0.8	15.1
3.4	27.9	2.0	28.0	1.4	27.7	3.5	21.3	2.0	19.6	1.5	23.4	3.6	21.0	2.0	17.7	1.4	19.2
12.1	37.8	7.1	33.8	5.0	34.5	12.4	31.6	7.3	29.1	5.0	30.2	12.0	31.8	7.4	28.5	5.1	27.7
24.8	41.2	14.0	39.2	10.2	37.3	25.0	39.1	14.2	34.3	12.1	35.1	25.1	42.0	14.3	32.4	9.8	32.3
49.0	45.7	28.1	42.6	20.1	39.6	49.2	44.2	28.0	39.8	20.1	37.2	49.1	49.8	28.3	39.4	19.8	35.0
20% Fly ash F						30% Fly ash F						20% Fly ash C					
0.9	5.0	0.6	10.5	0.4	13.7	0.9	4.7	0.6	8.2	0.4	9.4	1.2	7.2	0.6	8.4	0.5	13.3
1.8	17.4	1.0	18.4	0.8	22.7	1.9	13.7	1.1	15.2	0.8	19.7	1.8	12.2	1.0	15.3	0.8	24.9
3.4	23.1	2.0	23.4	1.4	28.4	3.5	21.4	2.0	19.8	1.5	25.0	3.4	21.7	2.0	25.8	1.4	26.9
12.2	37.7	7.0	35.4	4.9	37.3	12.2	34.4	7.0	31.0	5.0	34.2	12.0	37.4	7.0	36.8	5.0	37.0
24.9	42.1	14.1	40.9	10.0	42.7	25.0	37.8	14.1	37.4	10.1	42.7	25.9	40.5	14.1	40.7	10.3	40.4
49.0	45.3	28.2	48.0	19.8	48.7	49.0	43.8	28.2	44.7	20.0	48.0	49.0	44.6	28.0	45.7	20.0	44.4
30% Fly ash C						30% GGBF slag						50% GGBF slag					
1.3	4.0	0.6	4.7	0.4	7.3	0.9	4.2	0.6	9.9	0.4	10.4	0.9	2.3	0.5	5.2	0.3	4.2
1.9	11.6	1.0	13.4	0.8	18.7	1.9	14.2	1.0	18.8	0.8	21.6	1.9	9.3	1.0	11.6	0.8	16.1
3.5	18.1	2.0	21.1	1.4	26.9	3.6	23.5	2.0	25.2	2.9	34.5	3.4	16.9	2.1	21.2	1.4	22.4
12.1	32.1	7.2	36.2	5.0	40.5	12.2	35.1	7.1	39.9	4.9	36.1	12.3	34.3	7.2	39.8	5.0	41.8
25.0	43.9	14.1	40.2	9.9	41.9	25.1	45.8	14.1	44.5	10.8	41.1	24.9	46.5	14.2	49.0	10.1	44.8
49.2	45.6	28.1	48.1	19.9	51.8	49.4	53.5	28.0	49.6	19.8	41.9	49.0	59.1	28.1	54.1	19.8	45.2

hyperbolic strength–maturity relationship was used to estimate the measured strength [as defined in Eq. (7) or Eq. (12)], according to three following approaches:

- Approach 1: A single value of activation energy obtained from setting experiments (E_s) was used. Equivalent ages were calculated according to Eq. (6), and used in Eq. (7);
- Approach 2: A single value of activation energy obtained from compressive strength experiments (E_a) was used. Equivalent ages were calculated according to Eq. (6), and used in Eq. (7);
- Approach 3: The activation energy values, E_s and E_a, as determined from Approach 1 and 2 were used. Equivalent ages were calculated according to Eq. (11), and used in Eq. (12). The offset time (t_{or}) was assumed as the final set time at the reference temperature (t_{sr}).

The activation energy up to final set, E_s, for the mortar mixture was calculated from the data presented in [27] according to the method proposed by Pinto and Hover [3]. For the concrete mixtures, the E_s-values presented in [16] were used. The final set times for the mortar mixture were obtained following the procedure in ASTM C 403 [28], while for the concrete mixtures, these values had been already calculated and presented in [16].

As far as E_a-values are concerned, the ASTM C 1074 [7] procedure was followed for the mortar mixture. However, since the concrete mixtures were not cured isothermally, a different method had to be applied to obtain E_a-values from compressive strength results. Thus, an iterative method was used to search for the best-fit E_a-value that yielded the least sum of the square errors between the relative strength (S/S_u) at the reference temperature and at the cold and hot temperatures. The activation energies for each mixture, as well as the final set times at the reference temperature used in this analysis are presented in Table 5. The reference temperature was set to 23 °C.

The three approaches previously outlined were evaluated for all ten mixtures. Using the apparent activation energies given in Table 5, equivalent ages at each testing time were calculated following one of the three approaches outlined earlier. Initially, the best-fit hyperbolic strength–maturity relationship, as presented in Eq. (4) was obtained from the strength data cured at the reference temperature. For the other curing regimes, an estimate of the ultimate strength (S_u) was also obtained, allowing the calculation of the relative strength at each equivalent age. The ultimate strengths obtained for each mixture are summarized in Table 6. As an example, the best-fit hyperbolic strength–maturity relationship at the reference temperature, and the data from the other two curing regimes for Mixture I-0.48 are shown in Figs. 3–5.

In order to compare the accuracy provided by these three approaches, the absolute error of the predicted strength to the measured strength was calculated for each strength testing age. The calculated errors for all mixtures at the various equivalent ages for all three approaches are shown in Fig. 6. It can be seen that the use of Approach 3 produced smaller absolute errors of the predicted strength than the other two approaches at early ages.

A statistical evaluation of the absolute error was performed. For a given mixture, the unbiased estimate of the standard deviation of the absolute error [32] for each approach was calculated by Eq. (13). The results are presented in Table 7.

$$S_j = \sqrt{\frac{1}{n-1}\sum_i^n \Delta_i^2} \tag{13}$$

where,

S_j = unbiased estimate of the standard deviation (MPa),
n = number of data points (unitless), and
Δ_i = absolute error (MPa).

An evaluation of the unbiased estimate of the standard deviation results reveals that when using an apparent activation energy given

Table 5
Activation energy values and final set times for the mixtures investigated.

Mixture	E_s (kJ/mol)	E_a (kJ/mol)	$t_o = t_s$ (hours at 23 °C)
Mortar	36.3	41.3	8.3
I-0.41	27.1	37.7	6.1
I-0.44	31.6	39.2	5.7
I-0.48	33.4	44.7	6.1
20% Fly ash F	25.7	32.7	6.9
30% Fly ash F	23.3	27.2	7.2
20% Fly ash C	27.0	39.3	8.5
30% Fly ash C	29.3	38.2	10.4
30% GGBF slag	26.7	54.6	5.7
50% GGBF slag	35.2	52.6	5.8

Table 6
Ultimate strength obtained from each approach (MPa).

Mixture	Approach	Curing temperatures				
		5 °C	12 °C	23 °C	32 °C	43 °C
Mortar	1	73.5	67.6	64.8	57.5	54.9
	2	73.5	67.6	64.8	57.5	54.9
	3	74.2	67.7	64.8	57.8	55.1
			Cold	Room		Hot
I-0.41	1		45.4	42.4		39.7
	2		45.6	42.6		39.8
	3		47.4	43.0		39.2
I-0.44	1		46.2	46.4		47.6
	2		41.6	41.8		41.1
	3		38.8	38.9		38.0
I-0.48	1		55.0	55.3		55.8
	2		41.8	42.0		40.6
	3		36.7	37.0		36.2
20% Fly ash F	1		47.7	47.8		48.4
	2		51.6	51.6		47.5
	3		49.6	49.7		47.4
30% Fly ash F	1		45.1	45.1		45.7
	2		50.1	50.1		44.7
	3		50.7	50.8		47.7
20% Fly ash C	1		47.2	47.3		47.9
	2		47.3	47.5		46.7
	3		44.4	44.5		43.8
30% Fly ash C	1		51.1	50.8		50.4
	2		50.3	50.4		49.7
	3		51.2	51.3		50.8
30% GGBF slag	1		58.6	59.4		59.2
	2		52.6	53.3		52.5
	3		43.2	43.5		43.8
50% GGBF slag	1		71.7	70.5		70.0
	2		62.1	62.7		62.9
	3		50.6	50.7		51.3

by the setting experiments, as in Approach 1, the standard deviation of the absolute errors were always greater than the other approaches. However, when comparing Approaches 2 and 3 the results contained in Table 7 are not conclusive, as Approaches 2 and 3 yielded smaller, larger, or similar S_j-values for various mixtures.

Due to the time-dependant behavior of the strength data, the normalized error as given by Eq. (14) is a more appropriate parameter to compare approaches, as suggested by Bazant and Panula [33]. This approach equally weights the effect of differing strengths at early ages versus those at later ages.

$$\overline{\Delta_i} = \frac{(S_i/S_u)_{pred} - (S_i/S_u)_{obs}}{(S_i/S_u)_{obs}} \quad (14)$$

where, $\overline{\Delta_i}$ = normalized error at test age i (unitless),
$(S_i/S_u)_{pred}$ = value of the predicted relative strength at test age i (unitless),
$(S_i/S_u)_{obs}$ = observed value of relative strength at test age i.

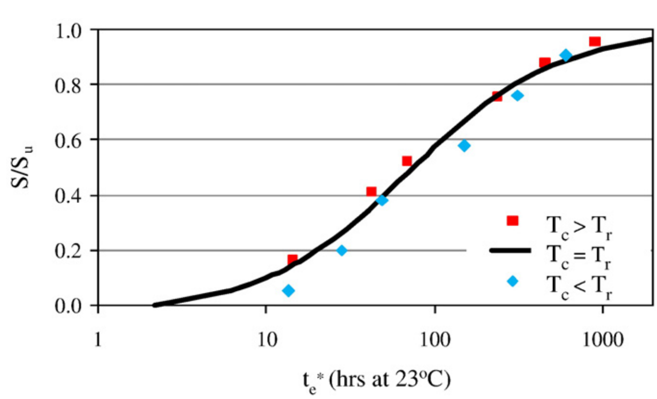

Fig. 3. Strength–maturity relationship for Mixture I-0.48 — Approach 1.

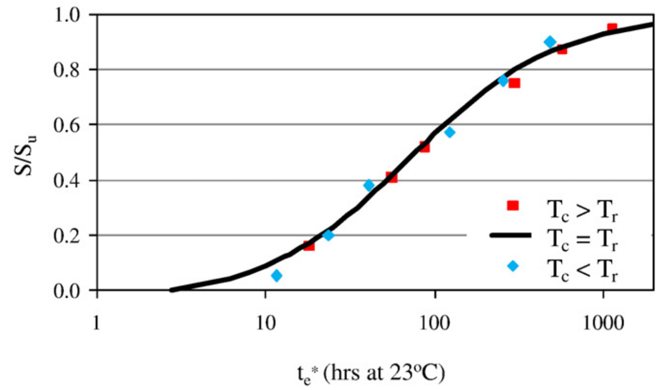

Fig. 4. Strength–maturity relationship for Mixture I-0.48 — Approach 2.

In order to compare approaches using the normalized errors, it is necessary to verify the homoscedasticity assumption, i.e., that the variance of errors remain constant with time [32]. Therefore, the normalized errors versus equivalent age for all mixtures are presented in Fig. 7. It can be seen that the normalized errors seem to be heteroscedastic, since the scatter band diminishes over equivalent age. However, at early ages, up to 36 equivalent hours, the plot seems much less heteroscedastic. Thus, standard deviation of the normalized error for each approach for all mixtures was calculated for the early-age data, as presented in Table 8. It can be seen that for the mixtures investigated here, the standard deviation of the normalized error given by Approach 3 is less than those obtained for the other two approaches. This indicates that the utilization of Approach 3, in which the setting behavior of the mixture is taken into account in the development of the strength–maturity relationship will yield improved early-age strength estimates when concrete is cured under various temperatures.

6. Discussion of results

The fundamental idea suggested earlier in this paper was that the periods up to final set and during hardening of concrete mixtures have different temperature sensitivities, and thus may affect the estimation of early compressive strength by the maturity approach. This was supported by the reported activation energy values in the literature for the periods up to final set and hardening, as presented in Table 1, which consistently shows greater values of activation energy for the hardening period.

This behavior was confirmed by the results presented in this paper. Activation energies from setting and compressive strength were both calculated from the same mortar or concrete mixtures made with various cementitious materials, as presented in Table 5. The activation

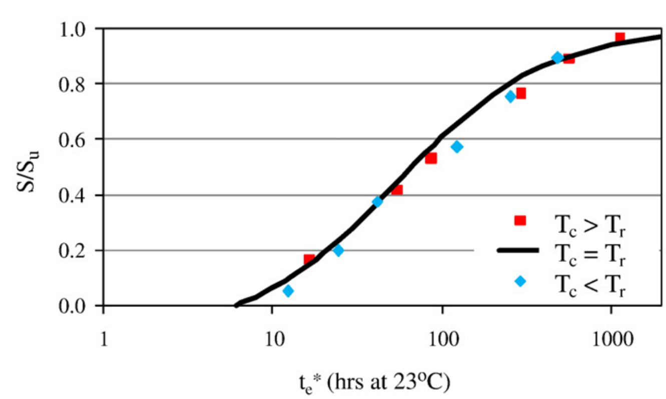

Fig. 5. Strength–maturity relationship for Mixture I-0.48 — Approach 3.

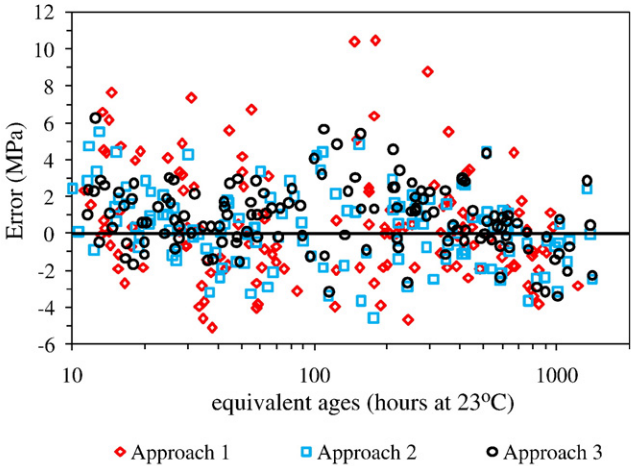

Fig. 6. Absolute errors for all mixtures.

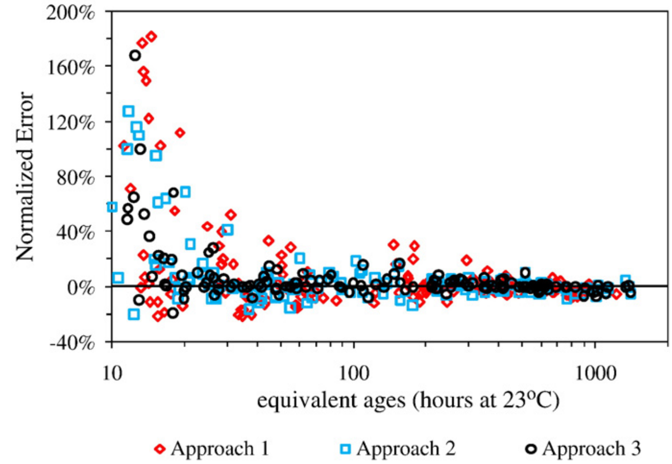

Fig. 7. Normalized error with equivalent ages for all mixtures.

energies obtained from the setting experiments were always lower than those obtained from compressive strength results for all these mixtures.

In fact, since the hydration of Portland cement is a heterogeneous process with more than one phase involved, the E_a-values calculated here can be seen as "average" values for the various hydration reactions occurring simultaneously. The lower E_a-values calculated for the period up to final set suggest that as an "average", the rate-limiting process may be diffusion controlled during this period. Lei and Scrivener [12] found a lower E_a-value of 22 kJ/mol for their mixture during the induction period, a value often encountered in diffusion controlled reactions [8].

Nonetheless, the difference in activation energies presented in Table 5 indicates that curing temperatures have a somewhat greater effect on the compressive strength development than on final set times. This difference was much more pronounced in the mixtures with GGBF slag. Moreover, the addition of supplementary cementitious materials modified the temperature sensitivity of the reference concrete mixture, as can be seen from the values presented in Table 5. The calculated activation energy from setting experiments, E_s, for Mixture I-0.41 was 27.1 kJ/mol, while in general greater values were observed when Class C fly ash and GGBF slag were added to the mixture. On the other hand, smaller activation energies were observed when Class F fly ash was incorporated. The same trend can be observed for the activation energies from compressive strength experiments. While the addition of GGBF slag and Class C fly ash increased the activation energy of the reference mixture, the addition of Class F fly ash decreased E_a-values.

This observed difference between E_s and E_a also explains the greater variability of the absolute errors of predicted strength obtained from Approach 1 when compared to Approaches 2 and 3, as depicted in Table 7. The utilization of activation energy from setting experiments in maturity calculations to predict compressive strength will under-estimate the temperature sensitivity, which will cause a loss of accuracy compared to when the activation energy is determined from compressive strength results.

The proposed model (Approach 3) produced improved early-age strength estimates for all mixtures, as can be graphically seen in Fig. 7. The standard deviations of the normalized errors when Approach 3 is used are smaller when compared to the ones given by traditional maturity calculations (Approach 2), as displayed in Table 8.

The proposed model takes into account the effect of temperature on the setting behavior of the concrete mixture in the equivalent age maturity calculation by considering a different temperature sensitivity up to final set versus the period of strength development. Before setting, the proposed method adjusts the t_o-value in the hyperbolic maturity–strength relationship to account for effect of temperature on the t_o-value.

It is suggested that the fundamental idea of applying different activation energy values for the periods up to final set and during hardening should be explored to other maturity functions.

Table 7
Estimate of standard deviation of the absolute error (MPa).

Mixture	Approach 1		Approach 2		Approach 3	
	E_s (kJ/mol)	S_Δ	E_a (kJ/mol)	S_Δ	E (kJ/mol)	S_Δ
Mortar	36.3	1.8	41.3	1.6	36.3/41.3	1.4
I-0.41	27.1	2.8	37.7	2.1	27.1/37.7	2.4
I-0.44	31.6	1.9	39.2	1.5	31.6/39.2	1.5
I-0.48	33.4	2.6	44.7	1.6	33.4/44.7	2.1
20% F	25.7	2.9	32.7	2.6	25.7/32.7	2.1
30% F	23.3	3.0	27.2	3.0	23.3/27.2	2.3
20% C	27.0	2.9	39.3	1.5	27.0/39.3	1.7
30% C	29.3	3.3	38.2	2.7	29.3/38.2	2.8
30% slag	26.7	5.6	54.6	2.3	26.7/54.6	2.5
50% slag	35.2	5.1	52.6	2.5	35.2/52.6	2.3

7. Conclusions

Based on the work documented in this paper, the following conclusions are offered:

- The activation energy values given by compressive strength measurements were always greater than the ones given by setting experiments, the difference was on the order of 10 kJ/mol for most mixtures, whereas the difference was approximately 28 kJ/mol for those that contained GGBF slag. Concrete mixtures with GGBF slag experienced a much greater increase in activation energy from setting to hardening phases.
- The proposed model takes into account the effect of temperature on the setting behavior of the concrete mixture in the equivalent age maturity calculation by considering a different temperature sensitivity factor up to final setting versus the period of strength development. For the limited number of mixtures investigated here,

Table 8
Estimate of standard deviation of the normalized error up to 36 equivalent hours.

Approach	$S_{\bar{\Delta}}$
1	0.60
2	0.41
3	0.37

the prediction of compressive strength was improved when the setting behavior was considered in the formulation of equivalent age. Before setting, the proposed method adjusted the t_o-value in the hyperbolic maturity–strength relationship to account for the effect of temperature on the t_o-value.
- The proposed model, as defined in Eq. (11), to calculate equivalent ages considering the setting behavior of the concrete mixture yielded improved strength estimates at early ages as compared to the traditional equivalent age formulation as defined in Eq. (6).

Acknowledgments

The authors would like to express their gratitude to CAPES — a Federal Brazilian Agency for giving support for this work. Additionally, the authors would like to thank the Alabama Department of Transportation (ALDOT) for funding part of the experimental work used for this paper.

References

[1] N.J. Carino, The maturity method, in: M.V. Malhotra, N.J. Carino (Eds.), Handbook of Nondestructive Testing of Concrete, CRC Press, 2004.
[2] A.G.A. Saul, Principles underlying the steam curing of concrete at atmospheric pressure, Magazine of Concrete Research 2 (6) (1951) 127–140.
[3] R.C.A. Pinto, K.C. Hover, Application of the maturity method to setting times, ACI Materials Journal 96 (6) (1999) 686–691.
[4] S. Mindess, J.F. Young, and D. Darwin, Concrete,Prentice Hall, 2003, 644 pp.
[5] P. Freiesleben Hansen, E.J. Pedersen, Maturity computer for controlled curing and hardening of concrete, Nordisk Betong 1 (1977) 21–25.
[6] A.K. Schindler, Effect of temperature on hydration of cementitious materials, ACI Materials Journal 101 (1) (2004).
[7] ASTM C 1074, Standard Practice for Estimating Concrete Strength by the Maturity Method, Annual Book of ASTM Standards, Vol. 04.02, 2004.
[8] E.M. Gardner, J.F. Young, D.A. Damidot, I. Jawed, Hydration of Portland cement, in: J. Bensted, P. Barnes (Eds.), Structure and performance of cements, 2nd ed., Spon Press, 2002.
[9] K.O. Kjellsen, R.J. Detwiller, Later-age strength prediction by a modified maturity model, ACI Materials Journal 90 (3) (1993) 220–227.
[10] J.K. Kim, S.H. Han, K.M. Lee, Estimation of compressive strength by a new apparent activation energy function, Cement and Concrete Research 31 (2001) 217–225.
[11] M. Lachemi, K.M.A. Hossain, C. Anagnostopoulos, A.R. Sabouni, Application of maturity method to slipforming operations: performance validation, Cement and Concrete Composites 29 (2007) 290–299.
[12] W.-G. Lei, L.J. Struble, Microstructure and flow behavior of fresh cement paste, Journal of the American Ceramic Society 80 (8) (1997) 2021–2028.
[13] P. Turcry, A. Loukili, L. Barcelo, J.M. Casabonne, Can the maturity concept be used to separate the autogenous shrinkage and thermal deformation of a cement paste at early age? Cement and Concrete Research 32 (2002) 1443–1450.
[14] R.C.A. Pinto, K.C. Hover, Combined effects of silica fume, superplasticizer and temperature on setting behavior, Magazine of Concrete Research 52 (5) (2002) 345–352.
[15] A. Garcia, D. Castro-Fresno, J.A. Polanco, Maturity approach applied to concrete by means of Vicat tests, ACI Materials Journal 105 (5) (2008) 445–450.
[16] S.A. Wade, J.M. Nixon, A.K. Schindler, R.W. Barnes, Setting behavior of concrete cured at fluctuating temperatures, Proceedings of the Transportation Research Board, Washington, D.C., January, 2005.
[17] S.J. Barnett, M.N. Soutsos, S.G. Millard, J.H. Bungey, Strength development of mortars containing ground granulated blast-furnace slag: effect of curing temperature and determination of apparent activation energies, Cement and Concrete Research 36 (2006) 434–440.
[18] N.J. Carino, R.C. Tank, Maturity functions for concrete made with various cements and admixtures, ACI Materials Journal 89 (2) (1992) 188–196.
[19] A.K. Schindler, K.J. Folliard, Heat of hydration models for cementitious materials, ACI Materials Journal 102 (1) (2005) 24–33.
[20] T. Voigt, Z. Sun, S.P. Shah, Comparison of ultrasonic wave reflection method and maturity method in evaluating early-age compressive strength of mortar, Cement and Concrete Composites 28 (2006) 307–316.
[21] E. Wirkin, M. Broda, B. Duthoit, Determination of the apparent activation energy of one concrete by calorimetric and mechanical means: influence of a super-plasticizer, Cement and Concrete Research 32 (2002) 1207–1213.
[22] G.J. Verbeck, R.H. Helmuth, Structural and physical properties of cement paste, Proceedings of the 5th International Symposium on the Chemistry of Cement, vol. III, 1968, pp. 1–32.
[23] A.G. Brooks, A.K. Schindler, R.W. Barnes, Maturity method evaluated for various cementitious materials, ASCE Journal of Materials in Civil Engineering 19 (12) (2007) 1017–1025.
[24] J. Byfors, Plain Concrete at Early Ages, CBI Research Report, No. 3:80, Swedish Cement and Concrete Research Institute, 1980.
[25] C.J. Bernhardt, Hardening of concrete at different temperatures, Proceedings RILEM Symposium on Winter Concreting Theory and Practice, Session B_{II}, Copenhagen, The Danish National Institute of Building Research, Copenhagen, 1956.
[26] J. Weiss, Experimental determination of the 'time zero', t_o ('maturity-zero', M_o), in: A. Bentur (Ed.), Early Age Cracking in Cementitious System, RILEM Report 25, 2003.
[27] N.J. Carino, Temperature Effects on the Strength–Maturity Relation of Mortar, Report No. NBSIR 81-2244, National Bureau of Standards, Washington, D.C., 1981 90 pp.
[28] ASTM C 403, Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance, Annual Book of ASTM Standards, Vol. 04.02, 2005.
[29] S.A. Wade, Evaluation of the Maturity Method to Estimate Compressive Strength, M.Sc. Theses, Auburn University, 2005, 340 pp.
[30] ASTM C 109, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens), Annual Book of ASTM Standards, Vol. 04.01, 2005.
[31] ASTM C 192, Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory, Annual Book of ASTM Standards, Vol. 04.02, 2006.
[32] R.H. McCuen, Statistical Methods for Engineers, Prentice-Hall, 1985 439 pp.
[33] Z.P. Bazant, L. Panula, Practical prediction of time-dependent deformations of concrete — Part VI: cyclic creep, nonlinearity and statistical scatter, Materials and Structures 12 (3) (1979) 175–183.