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Heat of Hydration Models for Cementitious Materials

by Anton K. Schindler and Kevin J. Folliard

The objective of this paper is to present the formulation of a general hydration model for cementitious materials. The degree of hydration characterizes the formation of hydration products as hydration progresses over time, and each concrete mixture has a unique degree of hydration development. Semi-adiabatic calorimeter tests were performed during this study, providing a convenient, indirect means of characterizing the formation of hydration products by measuring the heat released during hydration. The heat of hydration of concrete under different curing temperatures can be characterized with knowledge of the temperature sensitivity (activation energy), the degree of hydration development at the reference temperature, and the total heat of hydration of the mixture. The proposed hydration model incorporates the effect of following variables: cement chemical composition, cement fineness, supplementary cementing materials (Class F fly ash, Class C fly ash, and ground-granulated blast-furnace (GGBF) slag cement), mixture proportions, and concrete properties (density, thermal conductivity, and specific heat).

Keywords: adiabatic; fly ash; heat of hydration; slag.

INTRODUCTION

Mechanistic models to characterize the behavior of concrete exposed to in-place conditions are becoming common. Methods to quantify the heat of hydration of cementitious materials form an essential component of such models. Without an accurate estimate of the early-age in-place concrete temperature, the in-place concrete behavior cannot be accurately modeled. Currently, few models are available to quantify the heat of hydration, and those contained in ACI 207.2R[1] do not provide the user with guidelines should supplementary cementing materials (SCMs) be used. To reduce in-place concrete temperatures and to improve the durability of structures, the use of SCMs is becoming more and more common. Therefore, models that quantify the heat of hydration when SCMs are used in concrete are needed.

During the hydration of cementitious materials, numerous factors and interaction are involved, some of which are currently not fully understood. As part of this paper, a general hydration model is developed to characterize the heat of hydration of concrete for different cementitious materials and mixture proportions. The model was developed from 33 different mixtures made from 23 different cements. The model considers the effect of cement chemical composition, cement fineness, SCMs (Class F fly ash, Class C fly ash, and ground-granulated blast-furnace (GGBF) slag cement), mixture proportions, and concrete properties.

The curing temperature has a significant impact on the rate of hydration.[2] The higher the concrete temperature, the faster the rate of hydration, and the more rapidly heat is generated in the concrete member. The higher the cement content, the greater the potential temperature rise in the concrete. The cement influences the hydration process through its chemical composition and fineness. The effect of chemical composition can be identified by evaluating the rate of hydration of the different Bogue compounds, and their individual contribution to the total heat of hydration of the cement.[3] The amount of C_3A and C_3S compounds affect both the early-age rate of hydration and the total heat of hydration. Mindess and Young[4] comment that because "C_3S and C_3A are responsible for most of the early liberation of heat, reduction in the amounts of these compounds substantially reduces the amount of heat produced."

The more finely ground the cement, the more surface area is exposed to react with water, and the more rapid the heat development. This is confirmed by the following statement from the U.S. Bureau of Reclamation:[5] "higher fineness increases the rate at which cement hydrates, causing greater early strength and more rapid generation of heat." It is important to note that the total heat released during hydration is unaffected by the cement fineness.[6]

The use of SCMs has been found to reduce the rate of hydration, which in turn reduces the in-place concrete temperature, the rate of setting, and even the rate of slump loss.[7] In this paper, the effects of all the parameters discussed previously will be evaluated and their influence on the heat of hydration quantified.

RESEARCH SIGNIFICANCE

Currently, limited guidance is available to the engineer to quantify the heat of hydration for cementitious systems that include fly ash and GGBF slag. This paper presents a general hydration model that can be used to predict the development of in-place temperatures when different cement types and SCMs are used. An accurate estimate of the heat of hydration development under various curing temperatures forms an essential component of any mechanistic model that predicts the in-place early-age and long-term performance of concrete members.

HYDRATION MODEL DEVELOPMENT AND BACKGROUND

The hydration reaction of portland cement is an exothermic process, and the total amount of heat generated may affect the in-place performance of some structures. The total heat released during hydration is a function of the composition of cementitious materials, amount of cementitious materials, and the water-cementitious material ratio of the mixture. In the remainder of this section, models to quantify the total heat of hydration, degree of hydration, ultimate degree of hydration, temperature sensitivity, and the temperature associated with the hydration of concrete are presented. It should be noted that the degree of hydration

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

ACI member **Kevin J. Folliard** *is an assistant professor in the Department of Civil Engineering at The University of Texas at Austin. He received his PhD in civil engineering from the University of California at Berkeley, Berkeley, Calif., in 1995. He is a member of ACI Committees 201, Durability; 229, Controlled Low-Strength Material; 236, Material Science of Concrete; and 544, Fiber-Reinforced Concrete. He received the ACI Young Member Award for Professional Achievement in 2002.*

development plays a key role in the overall temperature prediction scheme. The degree of hydration is used to characterize the hydration behavior of a specific concrete mixture at the reference temperature T_r. The activation energy defines the temperature sensitivity of the hydration process, and with the equivalent age maturity method, the degree of hydration development can be estimated at any curing temperature.

Quantifying total heat of hydration of cementitious materials

The total heat of hydration (at 100% hydration) per unit weight of portland cement in the system can be estimated directly from the cement chemistry.[3] Each of the cement constituents have been found to have a unique heat of hydration, and the total heat of hydration of the cement at complete hydration H_{cem} can be quantified as shown in Eq. (1)

$$H_{cem} = 500p_{C_3S} + 260p_{C_2S} + 866p_{C_3A} + 420p_{C_4AF} + 624p_{SO_3} + 1186p_{FreeCaO} + 850p_{MgO} \quad (1)$$

where H_{cem} = total heat of hydration of the cement (J/g), and p_i = weight ratio of i-th compound in terms of the total cement content.

In this study, the effects of using SCMs such as fly ash and GGBF slag will be evaluated. Only limited data were found in literature to characterize the total heat contribution of these SCMs. Based on SCMs found in Japan, Kishi and Maekawa[8] recommended a heat of hydration of 209 J/g for fly ash (CaO = 8.8% and SiO_2 = 48.1%), and 461 J/g for GGBF slag (CaO = 43.3% and SiO_2 = 31.3%). Bensted[9] reported total heat of hydration values between 355 and 440 J/g for GGBF slag. The total heat of hydration for GGBF slag as recommended by Kishi and Maekawa[8] was selected for the initial model presented in this paper, and the use of this value will be reevaluated based on the results of laboratory tests performed with GGBF slag.

With knowledge of the total cementitious materials content C_c, and the heat of hydration H_u per unit weight of all the cementitious materials, the ultimate heat of hydration H_T for cements and SCMs at complete hydration can be quantified as shown in Eq. (2) and (3). The applicability of this model will be evaluated with test data collected from cements and SCMs.

$$H_T = H_u \cdot C_c \quad (2)$$

where H_T = ultimate heat of hydration of the concrete (J/m^3), C_c = cementitious materials content (g/m^3), and H_u = total heat of hydration of cementitious materials at 100% hydration (J/g), defined as follows

$$H_u = H_{cem} \cdot p_{cem} + 461 \cdot p_{SLAG} + h_{FA} \cdot p_{FA} \quad (3)$$

where p_{cem} = cement weight ratio in terms of the total cementitious content, p_{SLAG} = slag weight ratio in terms of the total cementitious content, p_{FA} = fly ash weight ratio in terms of the total cementitious content, and h_{FA} = heat of hydration of fly ash (J/g).

Quantifying degree of hydration development

The degree of hydration α is a measure of the extent of the reactions between the cementitious materials and the water and is defined as the ratio between the quantity of hydrated cementitious material and the original quantity of cementitious material. The degree of hydration is a function of time, and it varies between 0% at the start of hydration, and 100% when hydration is fully completed. In reality, not all of the cementitious material always hydrates, and a degree of hydration of 100% may never be reached.[10]

The degree of hydration for a concrete mixture can experimentally be determined by a number of techniques, some direct and others indirect. With direct methods, the quantity of hydration products that has formed is determined, but as stated by RILEM Commission 42-CEA,[11] it is "almost impossible to make a direct determination of the quantity of cement gel formed or the quantity of hydrated cement." Note that the use of strength to estimate the degree of hydration is not recommended because the relationship between the degree of hydration and mechanical properties is affected by the curing temperature.[2]

In this study, the indirect method that is based on the heat development that occurs during hydration is used to estimate the degree of hydration. It has been shown that the heat released, divided by the total heat available, provides a good measure of the degree of hydration;[12,13] this is mathematically expressed as follows

$$\alpha(t) = \frac{H(t)}{H_T} \quad (4)$$

where $\alpha(t)$ = degree of hydration at time t, and $H(t)$ = cumulative heat of hydration released at time t, (J/m^3).

Once test data on the degree of hydration development have experimentally been determined, the data can be represented by a best-fit mathematical model. The exponential formulation shown in Eq. (5) has been shown to accurately represent the s-shape of the hydration development.[14,15] The applicability of using this mathematical form to quantify the degree of hydration development will be shown with test data in a following section of this paper

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

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

Ultimate degree of hydration

After investigating the hydration of a range of different cementitious materials, Mills[10] stated that in "most, if not all, cement pastes hydration stops before the cement is totally consumed." In Eq. (5), a parameter α_u has been introduced to characterize the ultimate extent of the hydration reaction. The ultimate degree of hydration is strongly affected by the water-cement ratio (w/c).[16,17] Mills[10] performed numerous tests to determine the ultimate degree of hydration by measuring the amount of chemically bound water after hydration is completed. Mills[10] recommended that the ultimate degree of hydration for saturated portland cement concrete be determined as shown in Eq. (6). It should be noted that the ultimate degree of hydration is unaffected by the curing temperature.[18]

$$\alpha_u = \frac{1.031 \cdot w/c}{0.194 + w/c} \quad (6)$$

Temperature sensitivity of cementitious materials

By using the equivalent age maturity approach, the rate of hydration at any temperature can be determined from a known rate of hydration at a reference temperature. The activation energy defines the temperature sensitivity of a concrete mixture in the equivalent age maturity method. Freiesleben Hansen and Pedersen[19] proposed an activation energy formulation that is a function of the concrete temperature. This formulation, however, has been shown to be more suitable for use in early-age compressive strength prediction applications.[2]

Schindler[2] evaluated the temperature sensitivity of the hydration process over a temperature range of 4.4 to 40.6 °C. Schindler[2] developed the activation energy E model shown in Eq. (7), which was found to be independent of curing temperature and which is in agreement with the Arrhenius theory for rate processes of chemical reactions. This activation energy formulation provides an accurate prediction of the degree of hydration development for different cementitious materials at different curing temperatures.

$$E = 22{,}100 \cdot f_E \cdot p_{C_3A}{}^{0.30} \cdot p_{C_4AF}{}^{0.25} \cdot Blaine^{0.35} \quad (7)$$

where p_{C_3A} = weight ratio of C_3A in terms of the total cement content; p_{C_4AF} = weight ratio of C_4AF in terms of the total cement content; $Blaine$ = Blaine value, specific surface area of cement (m^2/kg); and f_E = activation energy modification factor for SCMs, defined as

$$f_E = 1 - 1.05 \cdot p_{FA} \cdot \left(1 - \frac{p_{FACaO}}{0.40}\right) + 0.40 \cdot p_{SLAG} \quad (8)$$

where p_{FACaO} = weight ratio of the CaO content of the fly ash.

Modeling heat generation and associated concrete temperature

The temperature development in a concrete specimen curing under adiabatic conditions (where there is no heat transfer to the environment) can be determined with Eq. (9).[20]

$$\frac{dT}{dt} = \frac{Q_H}{\rho \cdot c_p} = \frac{dH}{dt}\left(\frac{1}{\rho \cdot c_p}\right) \quad (9)$$

where T = temperature of the concrete (°C), ρ = concrete density (kg/m^3), c_p = concrete specific heat capacity (J/kg/°C), Q_H = rate of heat generation (W/m^3), and H = heat of hydration of the concrete (J/m^3) equal to $H_u \cdot C_c \cdot \alpha$.

The specific heat capacity c_p of hardening concrete changes over time and is influenced by the unbound water in the concrete. The model for the specific heat and thermal conductivity for hardening concrete as presented by Schindler[21] is used. The rate of heat generation Q_H is dependent on the degree of hydration. The degree of hydration is a function of the time and temperature history that can be characterized by the equivalent age maturity method.[2] With this approach, the adiabatic temperature rise of a concrete specimen can be evaluated at discrete times after batching. By using the equivalent age maturity method and the exponential formulation to quantify the degree of hydration (Eq. (5)), the rate of heat generation at time t can be determined as shown in Eq. (10)

$$Q_H(t) = H_u \cdot C_c \cdot \left(\frac{\tau}{t_e}\right)^{\beta} \cdot \left(\frac{\beta}{t_e}\right) \cdot \alpha(t_e) \cdot \frac{E}{R}\left(\frac{1}{273 + T_r} - \frac{1}{273 + T_c}\right) \quad (10)$$

EXPERIMENTAL WORK

Under adiabatic conditions, a concrete specimen is sealed to prevent heat exchange with its surroundings. With semi-adiabatic calorimetry, a small amount of heat loss is allowed to occur over time. Under semi-adiabatic conditions, the temperature development is not as high as it would be under fully adiabatic conditions. In some instances, this might be an advantage because hydration occurs at lower temperatures, and less temperature correction is required for the conversion to an isothermal reference curing temperature. Due to the high temperatures reached during hydration, most of the hydration is completed in a short period of time (7 days). A disadvantage of the semi-adiabatic test method is that the true adiabatic heat development has to be calculated from the test results, and losses associated with the test have to be accounted for. Once test data are collected, the degree of hydration can be computed based on heat transfer principles and with the heat of hydration model developed in this paper. The back-calculated semi-adiabatic test result can thus be affected by inaccurate assumptions of activation energy (temperature sensitivity) and material properties such as thermal conductivity, specific heat, and density. Currently, no standardized ASTM test method exists for this procedure, but a draft RILEM test procedure has been proposed.[12]

Test data collected

Semi-adiabatic calorimetry was used during this study to quantify the hydration development of various cementitious systems. The calorimeter consisted of an insulated 55 gal. steel drum that uses a 6 x12 in. cylindrical concrete sample. Probes are used to record the concrete temperature, heat loss through the calorimeter wall, and air temperature surrounding the test setup. The heat loss through the calorimeter was determined by a calibration test performed by using heated water. Once the concrete was batched, a 6 x 12 in. cylinder was made and placed in the calorimeter. Each test was performed over a period of approximately 7 days.

Semi-adiabatic calorimetry tests were performed on 13 different concrete mixtures. Table 1 provides a summary of the concrete mixtures tested. A standard ASTM Type I cement from Texas was chosen, and the type and dosage level of the

Table 1—Summary of concrete mixtures tested by semi-adiabatic calorimetry

No.	Description	Cement, kg/m^3	Fly ash, kg/m^3	GGBF slag, kg/m^3	Coarse aggregate, kg/m^3	Fine aggregate, kg/m^3	*w/cm*
1	Type I cement: Source A	341	0	0	1104	756	0.37
2	85% Type I cement + 15% Class C fly ash	290	45	0	1104	756	0.37
3	75% Type I cement + 25% Class C fly ash	256	74	0	1104	756	0.38
4	65% Type I cement + 35% Class C fly ash	222	104	0	1104	756	0.38
5	55% Type I cement + 45% Class C fly ash	188	134	0	1104	756	0.39
6	85% Type I cement + 15% Class F fly ash	290	38	0	1104	756	0.38
7	75% Type I cement + 25% Class F fly ash	256	63	0	1104	756	0.39
8	65% Type I cement + 35% Class F fly ash	222	88	0	1104	756	0.40
9	55% Type I cement + 45% Class F fly ash	188	114	0	1104	756	0.41
10	70% Type I cement + 30% GGBF slag	239	0	95	1104	756	0.38
11	50% Type I cement + 50% GGBF slag	171	0	158	1104	756	0.38
12	Type I cement: Source B	307	0	0	1073	742	0.50
13	Type I cement: Source C	307	0	0	1073	742	0.50

Table 2—Chemical and physical characteristics of cementitious materials

Parameter	Type I portland cement			Fly ash		GGBF slag
	No. 1	No. 12	No. 13	Class C	Class F	
Silicon dioxide SiO_2, %	19.9	20.9	20.1	35.6	54.1	—
Aluminum oxide Al_2O_3, %	5.7	5	5.3	21.4	26.2	—
Iron oxide Fe_2O_3, %	2.9	1.8	3.2	5.6	3	—
Calcium oxide CaO, %	63.6	65.4	65.5	24.3	10.8	—
Free CaO, %	2.9	1	0.8	—	—	—
Magnesium oxide MgO, %	1.3	1.4	0.6	4.8	2.4	—
Alkalies $Na_2O + 0.658K_2O$, %	0.69	0.52	0.67	1.4	0.3	—
Sulfur trioxide SO_3, %	3.5	2.9	3.3	1.2	0.3	1.6
Sulfide sulfur S, %	—	—	—	—	—	1.0
Loss on ignition LOI, %	1.9	1.44	1.2	0.3	0.1	—
Tricalcium silicate C_3S, %	57	63	64	—	—	—
Dicalcium silicate C_2S, %	14	12	9	—	—	—
Tricalcium aluminate C_3A, %	10	10	8	—	—	—
Tetracalcium aluminoferrite C_4AF, %	8	6	10	—	—	—
Specific surface area, m^2/kg	358	354	367	—	—	506
Specific gravity	—	—	—	2.75	2.33	2.91

SCMs used with the cement were varied. Two additional cement sources from Texas were tested. The Class C and F fly ashes had CaO contents of 24.3 and 10.8%, respectively, and both are commonly used in Texas. A single source of Grade 120 GGBF slag was also incorporated into the study. The chemical composition and some physical properties of the cementitious materials are presented in Table 2. The level of replacement of the SCMs was done on a volume basis, which is the practice in the state of Texas. The analysis method used to determine the degree of hydration from the semi-adiabatic test results is presented elsewhere.[21] Table 3 provides a summary of the best-fit hydration parameters obtained from the semi-adiabatic test data.

Test results obtained from the semi-adiabatic calorimeter are summarized in Fig. 1. From Fig. 1(a), the following trends may be noted with an increase in Class C fly ash replacement level: the total heat of hydration of the cementitious system is minimally affected, and the start of the acceleration stage is retarded. From Fig. 1(b), it may be seen the total heat of hydration and the rate of hydration of the cementitious system are significantly reduced with an increase in Class F fly ash replacement level. It appears that Class F fly ash has little contribution to the early-age heat development. Figure 1(c)

Table 3—Best-fit hydration parameters obtained from semi-adiabatic testing

No.	Description	E, J/mol*	Hydration parameters			H_u, J/g
			β	τ	α_u	
1	Type I cement: Source A	45,991	0.905	13.69	0.689	477
2	Type I cement + 15% Class C fly ash	43,148	0.874	13.81	0.713	471
3	Type I cement + 25% Class C fly ash	41,252	0.772	23.28	0.793	468
4	Type I cement + 35% Class C fly ash	39,357	0.716	29.43	0.893	464
5	Type I cement + 45% Class C fly ash	37,461	0.724	36.66	0.849	460
6	Type I cement + 15% Class F fly ash	40,703	0.825	15.97	0.797	444
7	Type I cement + 25% Class F fly ash	37,178	0.786	18.30	0.831	421
8	Type I cement + 35% Class F fly ash	33,653	0.809	19.08	0.838	396
9	Type I cement + 45% Class F fly ash	30,127	0.774	21.73	0.894	370
10	Type I cement + 30% GGBF slag	51,510	0.625	25.22	0.822	472
11	Type I cement + 50% GGBF slag	55,189	0.554	38.22	0.854	469
12	Type I cement: Source B	41,977	0.719	16.88	0.887	513
13	Type I cement: Source C	46,269	0.727	16.32	0.882	492

*Determined by formulation shown in Eq. (7).

indicates that the use of GGBF slag significantly reduces the rate of hydration during the acceleration stage; however, the total heat of hydration of Grade 120 GGBF slag appears to be similar to that of cement.

Data obtained from past research projects

Lerch and Ford[22] tested the heat of hydration of 20 different cements, and these results were incorporated to expand the calibration database of the model described in this paper. The Lerch and Ford[22] data set is one of the largest available on the development of heat of hydration for different U.S. cements. Although the chemical composition and fineness of cement in the U.S. has changed since the 1950s, the effect of each different cement component on the degree of hydration development should still be applicable today. The results for the non-air-entraining cement test by Lerch and Ford[22] were used, which include eight Type I cements, five 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 an isothermal temperature of 23.9 °C. With the heat of solution method, pastes were cured for 1 yr at 21.1 °C. The heat of solution and the condition calorimetry tests have been shown to produce comparable results.[3,13] A reference temperature of 21.1 °C (70 °F) was used to back-calculate the degree of hydration development for this data.

CALIBRATION OF GENERAL HYDRATION MODEL

To calibrate the general hydration model, a database of test results and all known variables was developed for the 13 mixtures tested in this project and the 20 cements tested by Lerch and Ford. In this section, the models developed and introduced in the previous sections will be calibrated through the use of this database.

Heat of hydration contribution of fly ash and GGBF slag

The difference in heat of hydration of different fly ash sources will be accounted for based on their CaO content. This approach is taken because the CaO content is an indicator of the cementitious nature of the fly ash. Class F ashes are generally produced from coals, which rarely contain more than 15% calcium oxide, and Class C fly ashes generally contain more than 20% of CaO.[23] During the analysis of the results obtained from the semi-adiabatic tests, it was determined that the total heat of hydration can best be modeled by the formulation shown in Eq. (3) and by using a heat of hydration of the fly ash defined by 1800 · p_{FACaO} (J/g), where p_{FACaO} is the fly ash CaO weight ratio in terms of the total fly ash content.

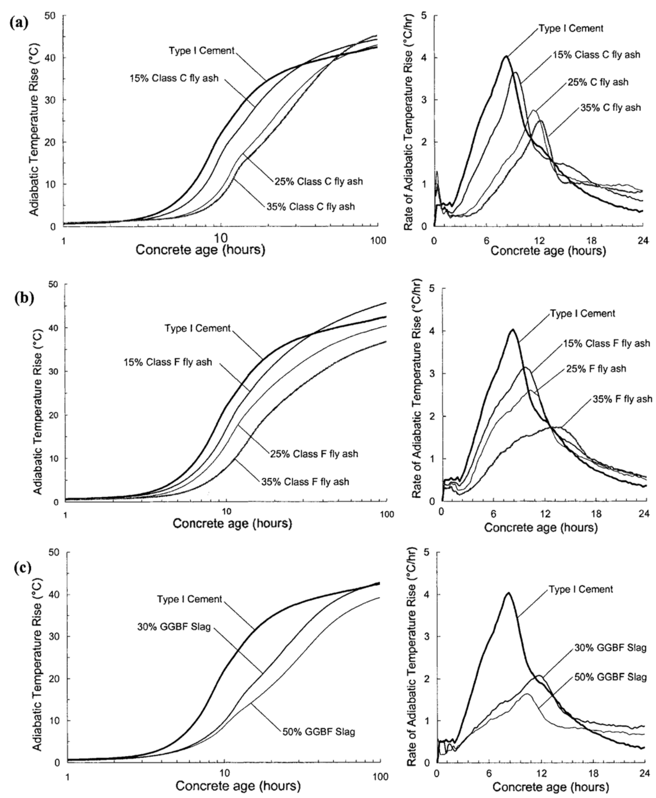

Fig. 1—Measured semi-adiabatic test results for: (a) Class C fly ash; (b) Class F fly ash; and (c) GGBF slag mixtures.

The Class C fly ash used had a CaO content of 24.3%, which, according to the proposed formulation, will provide a heat contribution of 24.3 × 18 = 437 J/g. Similarly, the Class F fly ash had a CaO content of 10.8%, which thus provides a heat contribution of 10.8 × 18 = 194 J/g. The value obtained

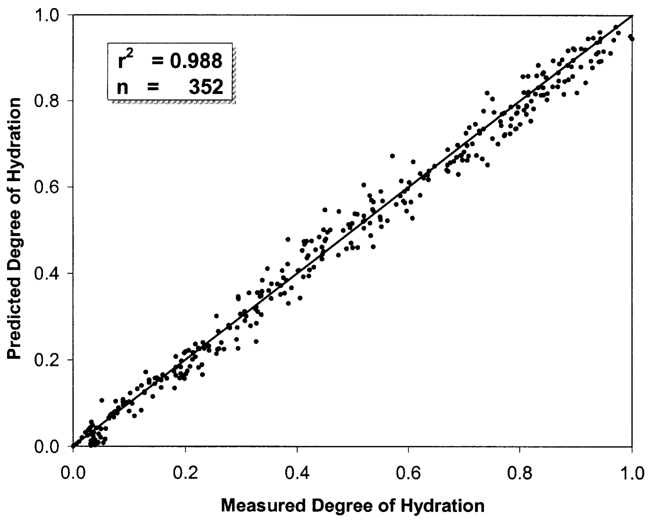

Fig. 2—Plot of measured versus predicted degree of hydration.

for the Class F fly ash is in the order of magnitude used by Kishi and Maekawa,[8] which recommended 209 J/g for a fly ash with a CaO content of 8.8%.

Multivariate regression analysis

In this section, a general hydration model will be developed based on a multivariate regression analysis. The data obtained from the semi-adiabatic tests were discretized to correspond to the test intervals used by Lerch and Ford.[22] This is necessary to ensure that all test data contribute equally to the statistical analysis.

The independent variables of the nonlinear analysis were selected by developing linear regression models to predict each of the three degree of hydration parameters (Eq. (5)) for all 33 mixtures. The following variables were found to provide the best statistical fit:

- Hydration time parameter: $\tau = f(p_{C_3A}, p_{C_3S}, Blaine, p_{SO_3}, p_{SLAG}, p_{FA}, p_{FA\text{CaO}})$; and
- Hydration slope parameter: $\beta = f(p_{C_3A}, p_{C_3S}, Blaine, p_{SO_3}, p_{SLAG})$

where p_{SO_3} = sulfate weight ratio in terms of total cement content, and p_{C_3S} = weight ratio of tricalcium silicate in terms of the total cement content.

The ultimate degree of hydration model developed by Mills[10] was used as a basis to incorporate the fact that complete hydration will not be achieved. In addition to this formulation (Eq. (6)), the increase in ultimate degree of hydration when SCMs are used was incorporated. The increase in ultimate degree of hydration was found to be a function of the fly ash p_{FA} and GGBF slag p_{SLAG} contents.

Based on engineering judgment, it may be reasoned that the use of the independent variables identified previously are intuitively appropriate. Both high C_3A and Blaine values are associated with cements with high early-age strength gains such as Type III cements. Cements consist of 50 to 70% of C_3S, and since "C_3S and C_3A are responsible for most of the early liberation of heat, reduction in the amounts of these compounds substantially reduces the amount of heat produced."[4] Therefore, the inclusion of the C_3S parameter to quantify the hydration parameters is in accordance with engineering judgment. The presence of sulfates (gypsum) slows the early hydration of C_3A, and this prevents flash setting. Gypsum is added to the clinker during the grinding process and is used to regulate the hydration rate of the cement.[24] Therefore, the presence of sulfates as a variable that predicts both the hydration time and slope parameter is not unexpected.

With the independent variables selected for the three hydration parameters, initial values for the regression model were determined with a multivariate linear regression analysis. From the analysis of variance (ANOVA) table, small p-values (0.001) were obtained that indicate that there is a statistically significant relationship between all of the independent variables and the degree of hydration. Furthermore, the F-statistic indicated that the prediction accuracy is incrementally improved as each independent variable is added.

Next, all of the degree of hydration data were used to develop the final model. The response variables of the data set comprised of the degree of hydration values versus concrete equivalent age for each mixture. Since the degree of hydration development is a nonlinear function, a nonlinear regression analysis was performed. Based on 352 response variables, the best-fit model shown in Eq. (11) to (13) was obtained. An overall r^2 value of 0.988 was achieved for this model.

$$\tau = 66.78 \cdot p_{C_3A}{}^{-0.154} \cdot p_{C_3S}{}^{-0.401} \cdot Blaine^{-0.804} \cdot p_{SO_3}{}^{-0.758} \cdot \exp(2.187 \cdot p_{SLAG} + 9.50 \cdot p_{FA} \cdot p_{FA-\text{CaO}}) \quad (11)$$

$$\beta = 181.4 \cdot p_{C_3A}{}^{0.146} \cdot p_{C_3S}{}^{0.227} \cdot Blaine^{-0.535} \cdot p_{SO_3}{}^{0.558} \cdot \exp(-0.647 \cdot p_{SLAG}) \quad (12)$$

$$\alpha_u = \frac{1.031 \cdot w/cm}{0.194 + w/cm} + 0.50 \cdot p_{FA} + 0.30 \cdot p_{SLAG} \le 1.0 \quad (13)$$

where w/cm = the water-cementitious material ratio.

With the degree of hydration as modeled in Eq. (11) to (13), the scatter plot of the experimentally determined versus predicted degree of hydration values are shown in Fig. 2. This figure indicates that the proposed model accurately predicts the measured results. The manner in which the predicted degree of hydration characterizes the measured data is shown for some mixtures in Fig. A1 through A5 in the Appendix.*

Based on the r^2 value of 0.988, it may be concluded that 98.8% of the experimental variation of the response variable 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 = 0.01%, which is very small, 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.[21] Based on the cumulative distribution of the error, it was found that 95% of the error is within a degree of hydration of ±0.0490. Therefore, it may be concluded that the model provides a statistically significant prediction of the measured degree of hydration.

*The Appendix is available in xerographic or similar form from ACI headquarters, where it will be kept permanently on file, at a charge equal to the cost of reproduction plus handling at time of request.

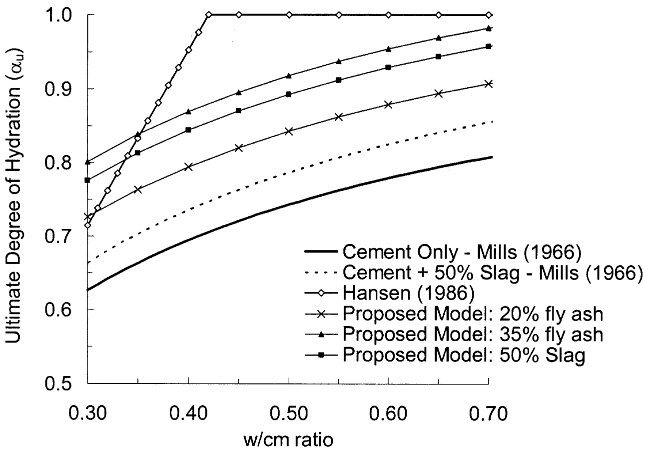

Fig. 3—Effect of water-cementitious material ratio on ultimate degree of hydration.

Figure 3 presents the effect of the proposed ultimate degree of hydration model α_u. When only cement is used, the model is as recommended by Mills.[10] Figure 3 shows the results of the proposed model as compared with some other previously published models. As the amount of SCMs and *w/cm* is increased, the ultimate degree of hydration is predicted to increase. From Fig. 3, it may be concluded that the proposed model yields results within the ranges found by other research studies.

Comments on model assumptions and limitations

The proposed model assumes that the interaction between the SCMs and the base cement source applies to all combinations of cements and SCMs. Due to the vast amount of interactions between different cementitious materials, it is anticipated that this model will provide limited accuracy for different combinations of cementitious materials. Because only a single Class F fly ash and a single Class C fly ash were used in this study, general trends regarding these classes of fly ash cannot be drawn solely from the present paper. A more comprehensive study is in progress (Texas Department of Transportation Project 4563), that is assessing a wider range of portland cements, SCMs, chemical admixtures, and mixture proportions. The effects of chemical admixtures are currently not considered in the proposed hydration model. For projects where higher confidence levels for temperature prediction is deemed necessary, it is recommended to subject the proposed concrete to semi-adiabatic calorimeter testing to accurately characterize its heat of hydration development.

SENSITIVITY ANALYSIS OF PROPOSED HYDRATION MODEL

In this section, the sensitivity analysis of the general hydration model developed in this paper will be presented. This is performed by choosing a baseline condition, and then one of the independent parameters is varied. This does not necessarily reflect what would happen for actual cements; to evaluate the effect of each parameter, this approach is considered appropriate. The range of each variable was determined based on what is typically encountered in the southern regions of the U.S. The effect of each parameter is summarized in Table 4. Figure 4 through 7 present the results obtained from the sensitivity analysis. These results provide insight to the contribution of each of the parameters to the overall hydration process.

Table 4—Effect of different parameters on proposed hydration model

Parameter	Change	Refer to Fig.	Effect on degree of hydration		
			Start of acceleration phase	Rate (slope)	Ultimate value
Cement fineness (Blaine value)	↑	4(a) and (b)	Large	Large	—
C_3S content	↑	5(a)	—	Medium	—
C_3A content	↑	5(b)	—	Large	—
SO_3 content	↑	6(a)	—	Very Large	—
GGBF slag dosage	↑	6(b)	—	Large	Large
Class C fly ash dosage	↑	7(a)	Small	—	Large
Class F fly ash dosage	↑	7(b)	—	—	Large
w/cm	↑	—	—	Small	Large

Since a change in fineness is generally accompanied by a change in gypsum to control the rate of setting, the amount of sulfates was adjusted according to the formulation presented by Frigione.[24] The optimum gypsum content p_{SO_3} can be determined from[24]

$$p_{SO_3} = 0.556 \cdot p_{Alkalies} + 0.00177 \cdot Blaine - 0.1072 \cdot P_{Fe_2O_3} - 0.00360 \quad (14)$$

where $p_{Alkalies}$ = weight ratio of equivalent alkalies, and $p_{Fe_2O_3}$ = weight ratio of ferric oxide.

Equation (14) was used to incorporate the inherent effect a change in fineness will have on the sulfate content. Figure 4 presents what effect a change in cement fineness has on the degree of hydration development and the rate of hydration. The higher the cement fineness, the earlier the acceleration phase of the cement will start. This is due to the larger surface area of cement grains that are exposed to water. This is in accordance with past research findings.[5,6]

Figure 5(a) presents the predicted effect of changes in C_3S content. The change in C_3S does not seem to have a significant impact on the degree of hydration development. The analysis

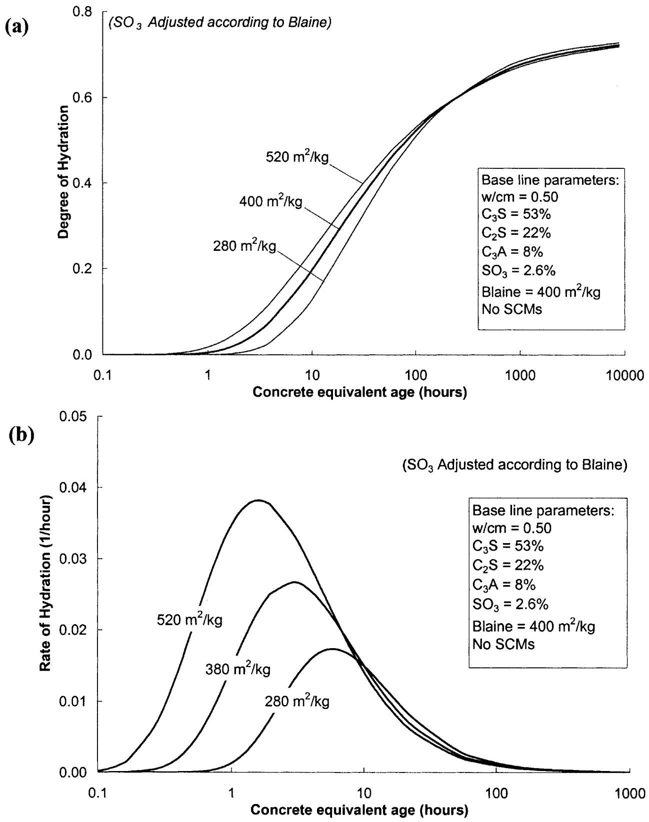

Fig. 4—Sensitivity analysis of proposed model: effect of Blaine value on: (a) degree of hydration; and (b) rate of hydration.

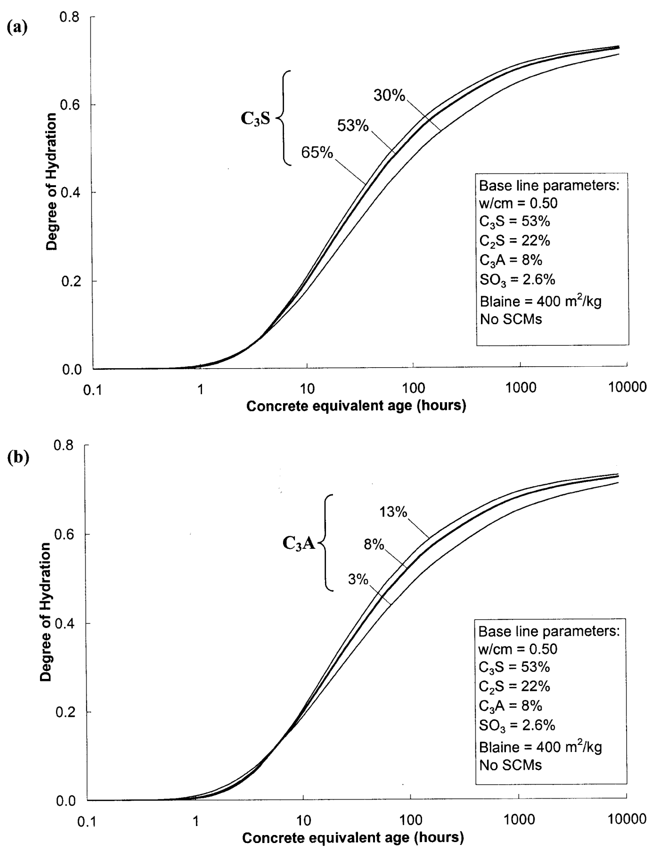

Fig. 5—Sensitivity analysis of degree of hydration model: effect of: (a) C_3S; and (b) C_3A.

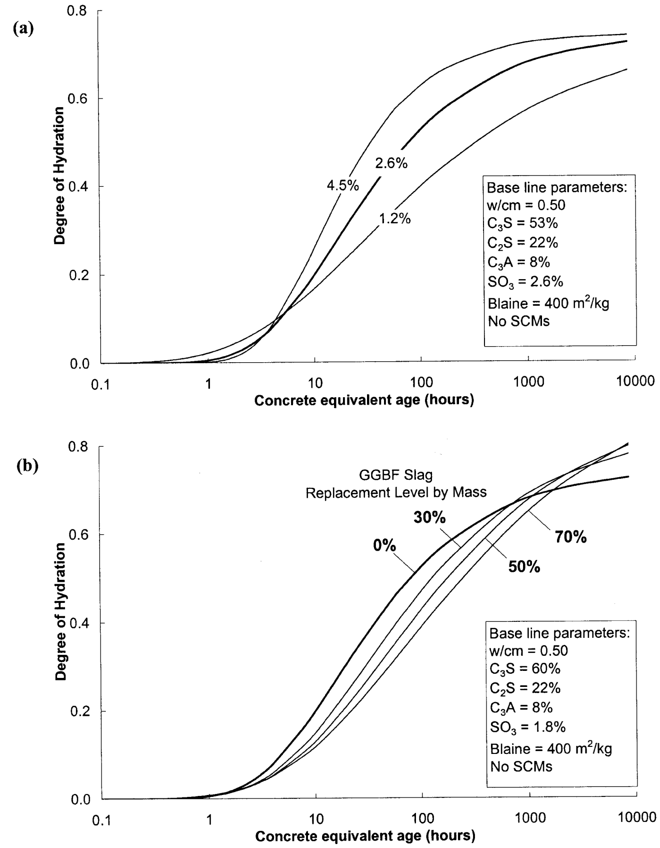

Fig. 6—Sensitivity analysis of degree of hydration model: effect of: (a) SO_3; and (b) GGBF slag.

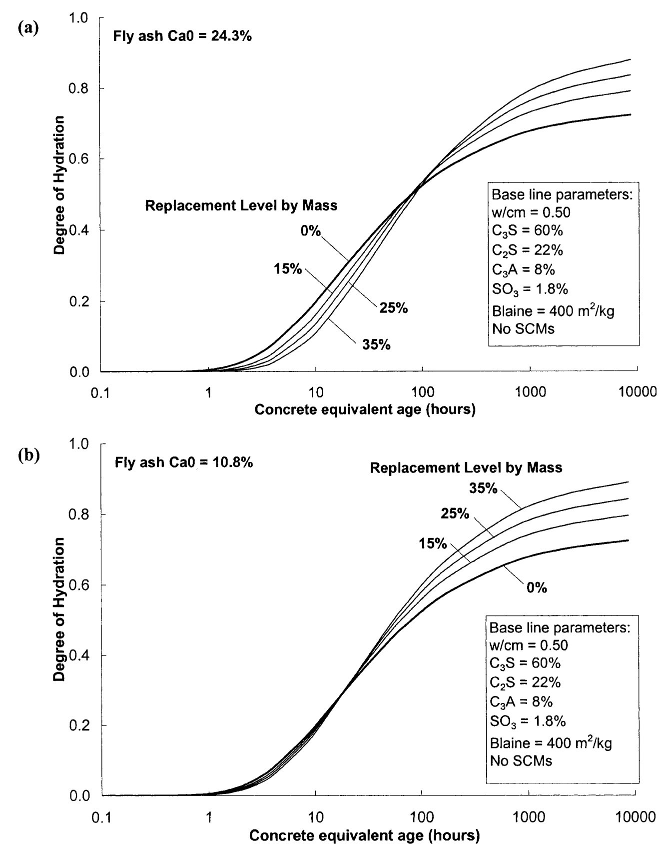

Fig. 7—Sensitivity analysis of degree of hydration model: effect of: (a) Class C fly ash; and (b) Class F fly ash.

results indicate that the higher the C_3S content, the steeper the slope of the degree of hydration curve, which was also found by previous researchers.[25]

Figure 5(b) presents the predicted effect of change in C_3A content. The higher the C_3A content, the higher the slope of the degree of hydration curve. This effect is in accordance with past published results.[25] Type II cements typically have lower C_3A contents, which is one reason why they exhibit slow early-age strength gains.

Figure 6(a) presents the significant effect a change in SO_3 content has on the degree of hydration development. The higher the sulfate content, the faster the early-age rate of hydration. These findings are in accordance with published results.[24] The effect of sulfate on hydration can be explained by keeping the production of cement in the context of Eq. (14) in mind. During the manufacture of cement, most of its chemical composition is balanced to provide cement with the required rate of setting and appropriate rheology. Equation (14) indicates that when a higher fineness is desired (longer grinding) more sulfates are required to help with the grindability during production.[24] Sulfates are used to retard the hydration of C_3A to avoid flash set, and a high amount of sulfate indicates that a higher reactive amount of C_3A is present that needs to be controlled.

Figure 6(b) presents the predicted degree of hydration when GGBF slag is used to replace Type I cement. The use of slag significantly reduces the rate of hydration of the cementitious system. It may further be seen that the ultimate degree of hydration is increased with higher GGBF slag dosage levels. The predicted degree of hydration behavior is in accordance with that measured from the test results.

Figure 7(a) presents the predicted degree of hydration for different Class C fly ash replacement levels. The following trends are predicted with an increase in the amount of Class C fly ash used: the hydration of the total cementitious system is retarded, the ultimate degree of hydration is increased, and the rate (slope) of the hydration reaction is unaffected.

Figure 7(b) presents the predicted degree of hydration for different Class F fly ash replacement levels. It appears that Class F fly ash has little impact on the initial hydration process. It may be concluded that it acts as inert filler at early ages because it contributes little to the heat development. At later ages, however, the ultimate degree of hydration is increased. It is worth noting from Fig. 7(a) and (b) that the fly ash CaO content appears to provide an effective means to characterize the hydration behavior of different fly ashes.

SUMMARY AND CONCLUSIONS

The degree of hydration characterizes the formation of hydration products as hydration progresses, and each concrete mixture has a unique degree of hydration development. Numerous semi-adiabatic calorimeter tests were performed during this study, which provides a convenient indirect means of characterizing the formation of hydration products by measuring the heat released during hydration. Based on the temperature sensitivity (activation energy), the degree of hydration development at the reference temperature, and the total heat of hydration, the heat of hydration of a concrete mixture under different curing temperatures can be characterized.

A general hydration model was calibrated by using semi-adiabatic test data performed on 13 different concrete mixtures and with heat of hydration data from 20 different cement types. The final model is defined in Eq. (11) through (13). The model provides a reasonable and accurate representation of the heat of hydration development under different curing temperatures. The heat of hydration is influenced by the cement chemical composition, cement fineness, use of SCMs, and the concrete mixture proportions. The effect of each parameter is summarized in Table 4. The model considers the effect of:

- Cement chemical composition: C_3A, C_3S, C_4AF, and SO_3;
- Cement fineness: specific surface area (Blaine index);
- Supplementary cementing materials: Class F fly ash, Class C fly ash, and GGBF slag;
- Mixture proportions: cement content, water-cementitious material ratio, and SCM replacement levels; and
- Concrete properties: density and specific heat.

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NOTATION

Blaine	=	Blaine value, specific surface area of cement, m^2/kg
E	=	activation energy, J/mol
f_E	=	activation energy modification factor
h_{FA}	=	heat of hydration of fly ash, J/g
h_{SLAG}	=	heat of hydration of GGBF slag, J/g
t	=	chronological time, h
t_e	=	equivalent age, h
α	=	degree of hydration
α_u	=	ultimate degree of hydration
β	=	hydration shape parameter
τ	=	hydration time parameter, h

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