

INFLUENCE OF SUPPLEMENTARY CEMENTING MATERIALS ON THE HEAT OF HYDRATION OF CONCRETE

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ABSTRACT

This paper discusses the influence of different dosage levels of Class C fly ash, Class F fly ash, and GGBF Slag on the heat of hydration of concrete. Based on semi-adiabatic calorimeter tests, a heat of hydration model is presented to quantify the hydration of cementitious materials made from different mixture proportions and supplementary cementing materials.

INTRODUCTION

Mechanistic models to characterize the behavior of concrete exposed to in-place conditions are becoming common. 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.

Currently, limited guidance is available to the engineer to quantify the heat of hydration for cementitious systems that include supplementary cementing materials (SCMs). The objective of this paper is to describe and quantify the influence that the addition of different dosages of Class C fly ash, Class F fly ash, and GGBF Slag has on the heat of hydration of concrete. A model is presented that can be used to predict the heat of hydration of concrete when different mixture proportions, cement types, and SCMs are used.

HYDRATION MODEL DEVELOPMENT AND BACKGROUND

The hydration reaction of cement is an exothermic process. The total heat released during hydration is a function of the composition of cementitious materials, amount of cementitious materials, and the water-cementitious 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.

Quantifying the Total Heat of Hydration of the Cementitious Materials

Each of the cement constituents has been found to have a unique heat of hydration and the total heat of hydration of cement (H_{cem}) at complete hydration can be quantified as shown below (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 total cement content.

Limited data were found in literature to characterize the total heat contribution of fly ash or GGBF slag. Based on SCMs found in Japan, Kishi and Maekawa (2) recommended a heat of hydration of 209 J/g for fly ash (CaO = 8.8%), and 461 J/g for GGBF Slag. Bensted (3) reported total heat of hydration values between 355 and 440 J/g for GGBF slag. The total heat of hydration for GGBF slag recommended by Kishi and Maekawa (2) was selected for the initial model presented in this paper, and the use of this value will be re-evaluated based on laboratory tests performed on 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 100% hydration can be modeled as shown in Equations 2 and 3.

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

where, H_T = total ultimate heat of hydration of the concrete (J/m³),
 C_c = cementitious materials content (g/m³), 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 total cementitious content,
 p_{SLAG} = slag weight ratio in terms of total cementitious content,
 p_{FA} = fly ash weight ratio in terms of total cementitious content, and
 h_{FA} = heat of hydration of fly ash (J/g).

Quantifying the 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, with α varying 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 (4). The degree of hydration curve is used to characterize the hydration behavior of a specific concrete mixture at the reference temperature (T_r).

In this study, the indirect method of estimating the degree of hydration based on the heat development that occurs during hydration is used. It has been shown that the heat released divided by the total heat available provides a good measure of the degree of hydration (5), and this is mathematically express 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/m³).

Once test data of 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 Equation 5 has been shown to accurately represent the s-shape of the hydration development (6). The applicability of using this mathematical form to quantify the degree of hydration development will be shown with test data later in 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 (hours),
 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 (4) stated that in, "... most, if not all, cement pastes hydration stops before the cement is totally consumed." In Equation 5, a parameter (α_u) has been introduced to characterize the ultimate extent of the hydration reaction. This variable is strongly affected by the water-cement ratio (4, 7). Mills (4) performed numerous tests to determine the ultimate degree of hydration by measuring the amount of chemically bound water after hydration is completed. Mills (4) recommended that the ultimate degree of hydration for saturated portland cement concrete be determined as shown in Equation 6. It should be noted that the ultimate degree of hydration is unaffected by the curing temperature (8).

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

Temperature Sensitivity of Cementitious Materials

In the equivalent age maturity method, the activation energy defines the temperature sensitivity of a concrete mixture. By using the equivalent age maturity approach, the rate of hydration at any specific temperature can be determined from a known rate of hydration at the reference temperature. Freiesleben Hansen and Pedersen (9) proposed an activation energy formulation, which is a function of the concrete temperature. However, this formulation has been shown to be more suitable for use in early-age compressive strength prediction applications (10). Schindler (10) evaluated the temperature sensitivity of the hydration process over a temperature range of 4.4°C to 40.6°C. Schindler (10) developed the activation energy (E) model shown in Equation 7, which was found to be independent of curing temperature, which is in agreement with the Arrhenius theory for rate processes of chemical reactions.

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

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 the Heat Generation and Temperature Associated with Hydration

The temperature development in a concrete specimen curing under adiabatic conditions (where there is no heat transfer to the environment) can be determined with Equation 9 (11).

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

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

The rate of heat generation heat, Q_H , is dependent on the degree of hydration. The degree of hydration is a function of the time and temperature history, which can be characterized by the equivalent age maturity function. With this approach, the adiabatic temperature rise of the 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 (Equation 5), the rate of heat generation, at time t , can be determined as shown in Equation 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

Semi-adiabatic calorimetry was used during this study to quantify the hydration development of various cementitious systems. Tests were performed on 11 different mixture proportions and each test was performed over approximately a seven day period. A standard cement source was chosen, and the type and dosage level of the SCMs used with the cement were changed. The following combinations of SCMs and the Type I cement were tested: 15%, 25%, 35%, and 45% Class C Fly Ash; 15%, 25%, 35%, and 45% Class F Fly Ash; 30% and 50% GGBF Slag. The level of replacement of the SCMs was done on a volume basis, which is the practice in the state of Texas. The Class C fly ash had a CaO = 24.3% and the Class F fly ash a CaO = 10.8%. 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 can not be drawn solely from the present paper. However, a more comprehensive study is in

progress assessing a wider range of SCMs, and these results will allow for a more accurate delineation of general fly ash behavior. A Grade 120 GGBF slag was used. Complete properties of the cement, fly ash, GGBF slag are presented in the dissertation of the first author (12).

With semi-adiabatic calorimetry, a small amount of heat loss is allowed to occur over time. The temperature development is, therefore, not as high as it would be under fully adiabatic conditions. Due to the elevated 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 the test data is 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 result can thus be affected by inaccurate assumptions of activation energy (temperature sensitivity) and material properties such as thermal conductivity, specific heat, and density.

Test Data and Discussion of Results

Table 1 provides a summary of the best-fit hydration parameters that were obtained from the semi-adiabatic test data. The activation energy values listed in Table 1 were determined through the use of the activation energy model shown in Equation 7. A reference temperature of 21.1°C (70°F) was used during the back-calculation of the degree of hydration.

Table 1 - Hydration parameters obtained from semi-adiabatic testing ($T_r = 21.1^\circ\text{C}$)

Mix No.	Description	E (J/mol)	Hydration Parameters			H_u J/g
			β	τ	α_u	
1	Type I Cement	45,991	0.905	13.69	0.689	477
2	Type I + 15% Class C Fly Ash	43,148	0.874	13.81	0.713	471
3	Type I + 25% Class C Fly Ash	41,252	0.772	23.28	0.793	468
4	Type I + 35% Class C Fly Ash	39,357	0.716	29.43	0.893	464
5	Type I + 45% Class C Fly Ash	37,461	0.724	36.66	0.849	460
6	Type I + 15% Class F Fly Ash	40,703	0.825	15.97	0.797	444
7	Type I + 25% Class F Fly Ash	37,178	0.786	18.30	0.831	421
8	Type I + 35% Class F Fly Ash	33,653	0.809	19.08	0.838	396
9	Type I + 45% Class F Fly Ash	30,127	0.774	21.73	0.894	370
10	Type I + 30% GGBF Slag	51,510	0.625	25.22	0.822	472
11	Type I + 50% GGBF Slag	55,189	0.554	38.22	0.854	469

The test results from the semi-adiabatic calorimeter are summarized in Figures 1 to 3. From Figure 1, the following trends may be noted with an increase in Class C fly ash replacement level: the heat of hydration of the total cementitious system is minimally affected, and the start of the acceleration stage is retarded. From Figure 2, 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 3 indicates that the use of GGBF Slag significantly reduces the rate of hydration during the acceleration stage and GGBF also retards the hydration of the

total cementitious system. However, the total heat of hydration of Grade 120 GGBF slag appears to be similar to that of cement.

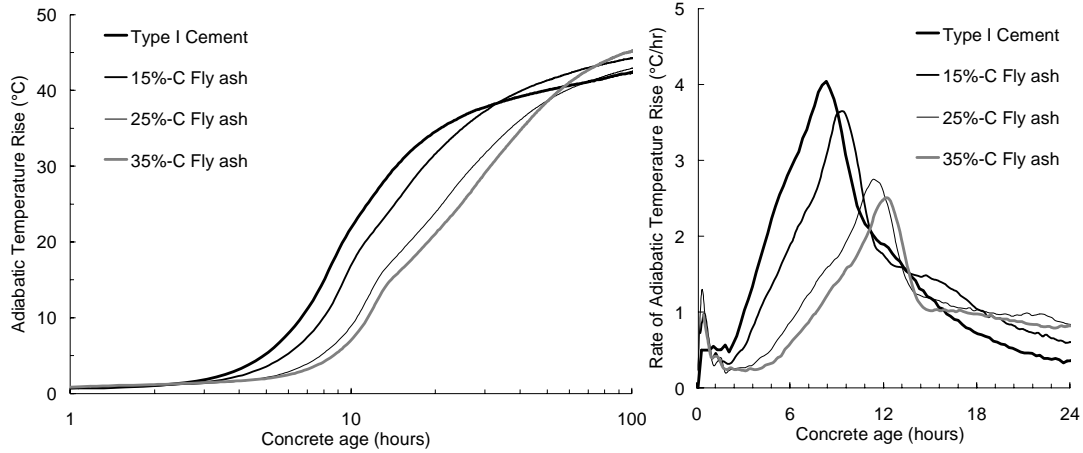


Figure 1 - Measured semi-adiabatic test results for Class C fly ash mixtures

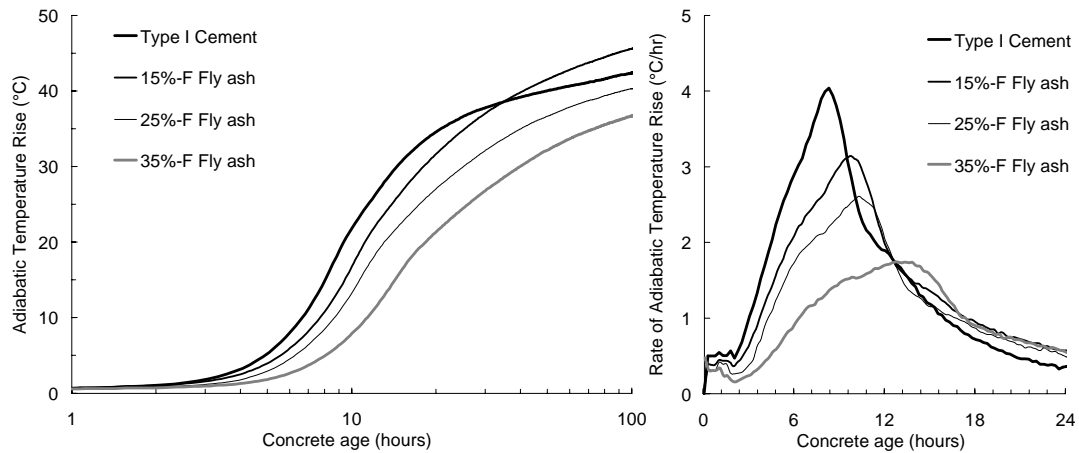


Figure 2 - Measured semi-adiabatic test results for Class F fly ash mixtures

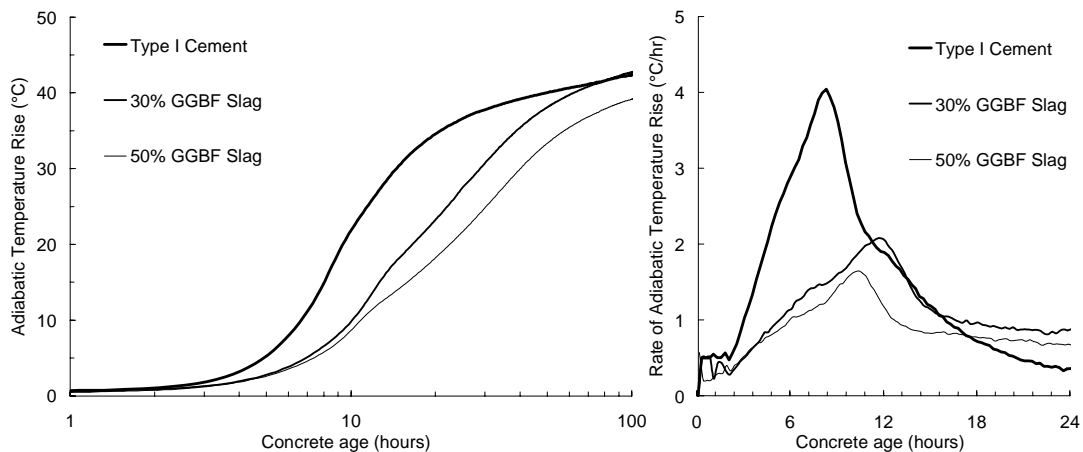


Figure 3 - Measured semi-adiabatic test results for GGBF Slag mixtures

CALIBRATION OF THE HYDRATION MODEL

A model that quantifies the hydration of various cements based on their chemical composition and fineness have been previously published ([12](#)). The effect of adding

the SCMs tested in this study to these different cements will be quantified in this section.

Heat of Hydration Contribution of Fly Ash and GGBF Slag

It is recommended to account for the difference in heat of hydration of different fly ash sources based on their CaO content. This approach is taken, since the CaO content is an indicator of the cementitious nature of the fly ash. 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 Equation 3 and by using a heat of hydration of the fly ash defined by $1800 \cdot p_{FA-CaO}$ (J/g), where p_{FA-CaO} is the fly ash CaO weight ratio in terms of the total fly ash content. The Class C fly ash used had a CaO = 24.3%, which according to the proposed formulation will provide a heat contribution of $24.3 \times 18 = 437$ J/g. Similarly, for the Class F fly ash used, it had a CaO = 10.8%, which will provide a heat contribution of $10.8 \times 18 = 194$ J/g.

Multivariate Regression Analysis

In this section, a general hydration model will be developed based on a multivariate regression analysis. The ultimate degree of hydration model presented in Equation 6 was used, and the additional increase in ultimate degree of hydration ($\Delta\alpha_u$) due to the presence of SCMs was incorporated. The increase in ultimate degree of hydration was found to be a function of the fly ash and GGBF slag dosage.

The response variables of the data set comprised of the degree of hydration values versus concrete equivalent age for each mixture. After including the effect of the SCMs to that previously determined for cements, the best-fit multivariate regression model shown in Equations 11 to 13 was obtained. An overall r^2 value of 0.988 was achieved for this model.

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

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

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

where, w/cm = the water-cementitious materials ratio.

Model Results

Since the ultimate degree of hydration (α_u) is influenced by the use of SCMs, the model in Equation 6 was modified as shown in Equation 13. Figure 4 presents the effect of the proposed ultimate degree of hydration model. When only cement is used, the model is as recommended by Mills (4). As the amount of SCMs and the w/cm is increased, the ultimate degree of hydration increases. Figure 5 presents the predicted degree of hydration for different Class C fly ash replacement levels. It may be seen that it is predicted that with an increase in the amount of Class C fly ash, 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 6 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, since it contributes little to the heat development. However, at later-ages the ultimate degree of hydration is increased. It is worth noting from Figures 5 and 6, that the fly ash CaO content appears to provide an effective means to characterize the hydration behavior of different fly ashes.

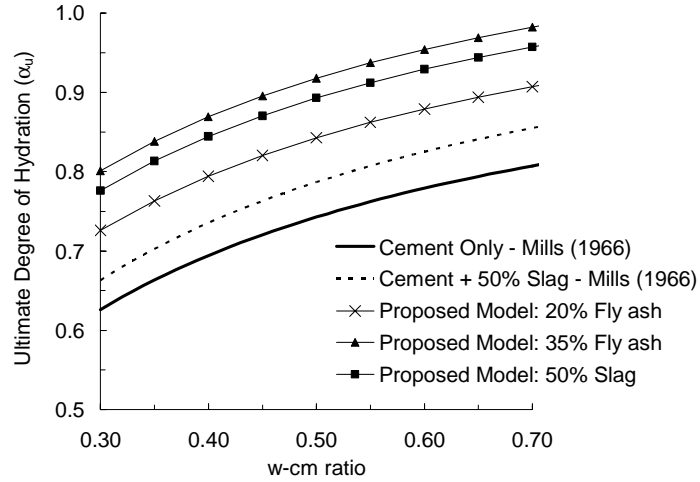


Figure 4 - The effect of water-cementitious ratio on the ultimate degree of hydration

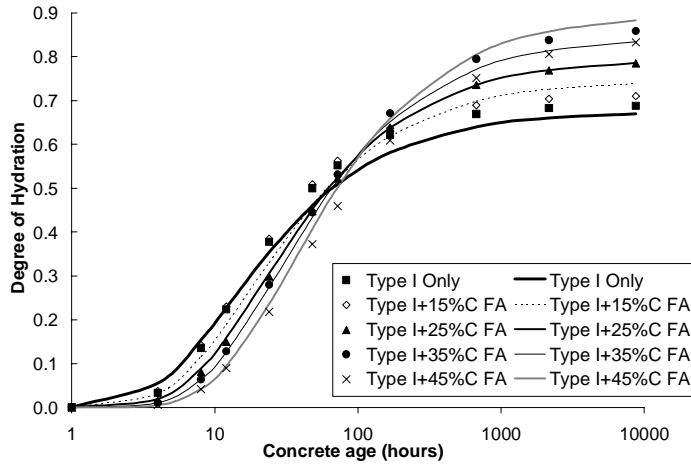


Figure 5 - Predicted and measured degree of hydration for **Class C** fly ash mixtures

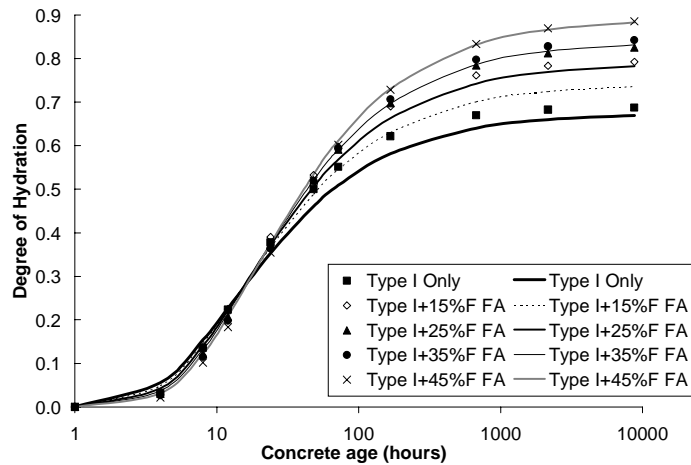


Figure 6 - Predicted and measured degree of hydration for **Class F** fly ash mixtures

Figure 7 presents the predicted degree of hydration when GGBF slag is used to replace Type I cement. The use of slag significantly retards the hydration of the cementitious material, and it 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 for the SCMs tested is in agreement with that measured by the semi-adiabatic calorimeter.

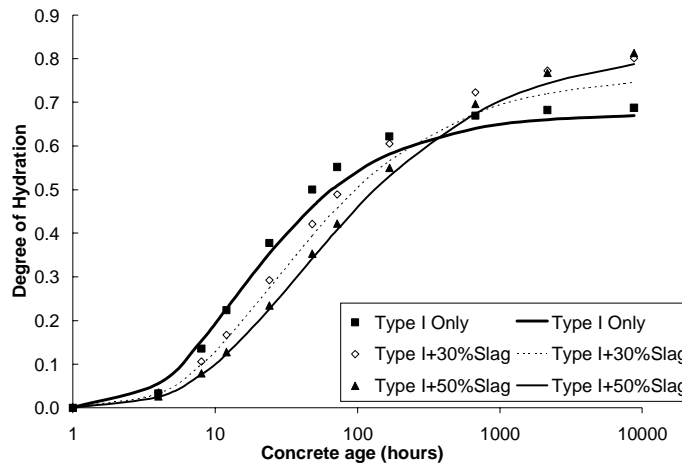


Figure 7 - Predicted and measured degree of hydration for GGBF Slag mixtures

SUMMARY AND CONCLUSIONS

The objective of this paper was to present the influence that the addition of different dosages of Class C fly ash, Class F fly ash, and GGBF Slag has on the heat of hydration of concrete. Semi-adiabatic calorimeter tests were performed as a means to indirectly characterize the formation of hydration products by measuring the heat released during hydration. Tests were performed by using a Type I cement with the following combinations of SCMs: 15%, 25%, 35%, and 45% Class C Fly Ash; 15%, 25%, 35%, and 45% Class F Fly Ash; 30%, and 50% Grade 120 GGBF Slag.

The degree of hydration of each mixture was determined to characterize the hydration behavior of a specific concrete mixture at the reference curing temperature. The results of the Class C fly ash tests indicate that with an increase in dosage, the hydration of the total cementitious system is retarded, the ultimate degree of hydration is increased, and the rate of the hydration reaction is unaffected. The results indicate that different replacement levels of Class F fly ash have little impact on the initial hydration process and this fly ash acts as an inert filler at early-ages. The use of Class F fly ash reduces the amount of heat generated. The use of GGBF slag significantly retards the hydration process and it 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. The heat of hydration model presented can be used to quantify the hydration of cementitious materials made from different mixture proportions and supplementary cementing materials.

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NOTATION

E	=	activation energy, J/mol
SCM	=	supplementary cementing materials
t_e	=	equivalent age, hours
α	=	the degree of hydration
α_u	=	ultimate degree of hydration
β	=	hydration shape parameter
τ	=	hydration time parameter, hours

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