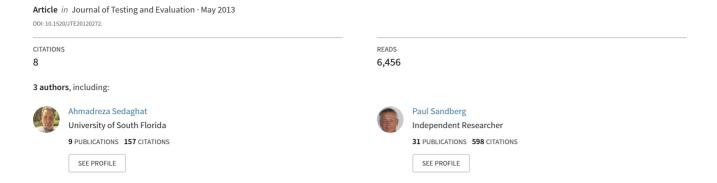
## Measurement and Prediction of Heat of Hydration of Portland Cement Using Isothermal Conduction Calorimetry



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# Measurement and Prediction of Heat of Hydration of Portland Cement Using Isothermal Conduction Calorimetry

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**ABSTRACT:** Ten industrial Portland cements were carefully tested continuously for up to seven days for their heat of hydration at 23°C, using isothermal conduction calorimetry in accordance with ASTM C1702. The internal mixing procedure was implemented for all the mixes, and external mixing was conducted on one of the cements. The results indicate that for a given Portland cement, the shape of the heat of hydration curve from three days to seven days can be modeled using an exponential function similar to that used in maturity concepts. The findings also indicate that such a function can be used in predicting the seven-day heat of hydration of Portland cement based on data collected for up to 84 h. The suggested approach could eliminate the need for measuring heat of hydration data at ages when the heat flow has decreased substantially to levels at which the signal-to-noise ratio is low. This work effectively proposes a method for accurately predicting the total heat generated by Portland cements at seven days based on heat flow measurements for up to 84 h.

**KEYWORDS:** cement heat of hydration, isothermal conduction calorimetry, S-shaped function, signal-to-maximum baseline deviation ratio, internal and external mixing

#### Introduction

Heat of hydration measurements are important for assessing cement hydration rates, as well as for assessing the potential temperature rise/fall in concrete elements. Temperature increases that occur when cement is mixed with water are caused by the exothermic nature of the interaction of anhydrous cement with water [1]. There is interest in the cement heat of hydration primarily because of its contribution to cracking in massive concrete elements [2]. It is well established that a large temperature increase occurs within a few days of concrete placement, typically within the first 24 to 72 h. In structural elements, this temperature increase and the subsequent cooling result in shrinkage strains that have been implicated in concrete cracking. The resulting tensile stress is partly a function of the temperature elevation experienced by the concrete element [2]. The latter is a strong function of the heat of hydration of Portland cement, which is primarily affected by the mineralogy and fineness of the cement.

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Experimental measurements and calculations for the heat of hydration (HOH) of different types of Portland cement have been extensively published in the literature. For several decades, Portland cement specifications adopted ASTM C186 [3] for HOH measurements, which is the heat of solution method. Although the ASTM C186 method has been reported to cause difficulties during implementation [3–5], it has the advantage of not requiring the instrument to be occupied for the whole period of the experiment. In fact, several tests can be run on overlapping schedules using only one instrument. The test can be used for long test ages, as it measures the HOH indirectly instead of adding up the heat for a long period of time [5].

Recently, a new standard method for HOH determination was adopted by ASTM International under ASTM C1702-09 [6]. The method, isothermal conduction calorimetry, indicates two possible mixing routines, namely, internal and external mixing. However, the use of this method has not been incorporated into the cement specification ASTM C150 [7]. For Type II (MH) and Type IV, a maximum HOH is indicated for seven days, and for Type IV an additional maximum is given for 28 days in accordance with the optional physical requirements of ASTM C150/C150M-09. Also, ASTM C595 [8] and ASTM C1157 [9] have set limits for HOH in accordance with physical requirements, and ASTM C1600 [10] has set limits per optional physical requirements. The ASTM specification identifies ASTM C186 for HOH measurements in spite of the availability of ASTM C1702-09.

Isothermal conduction calorimetry has the advantage of measuring the HOH instantly from the time when water is mixed with

TABLE 1—Comparison of precisions for isothermal conduction calorimetry and solution calorimetry (per ASTM C1702-09) [6].

Standard Deviation	ASTM C186	ASTM C1702 (Wadso and Colleagues' Data) [22,23]	ASTM C1702 (VDZ 2006) [24]
Within lab	14.8 kJ/kg (7 days)	Not available	4.6 kJ/kg (7 days)
Between lab	16.9 kJ/kg (7 days)	10.5 kJ/kg (3 days)	13.6 kJ/kg (7 days)

cement. It is therefore a useful instrument in analyzing the effects of admixtures on cement hydration. This method can be executed with low labor input and with better precision than the heat of solution method [11]. Isothermal conduction calorimetries typically operate at a range of temperatures and with different waterto-cement ratios. The major advantage of isothermal conduction calorimetry is that it not only measures the total heat but also records the thermal power "heat flow" at different times. This instrument can perform well with blended cements, whereas solution calorimetry is less suited for such materials [12]. Isothermal conduction calorimetry shows improved precision relative to the heat of solution method, as shown in Table 1 [6]. Additionally, isothermal conduction calorimetry offers a simple procedure and the availability of commercial equipment with which to conduct the test. Long-term studies by Wadso [13] indicate that the calibration coefficients are remarkably stable over time as long as there is no hardware or bath temperature change. It is noteworthy that the ASTM C1702 method is not dependent on knowledge of the compound composition, which makes it much more useful for the analysis of non-Portland cement.

The prediction of Portland cement HOH had been proposed earlier using several relationships. Poole [4] has summarized the different approaches that were proposed in the literature. Primarily, the relationships rely on other standard test properties of Portland cement known to relate to HOH. Seven relationships were analyzed for Portland cement, with five of them incorporating cement potential phase composition; two of the five

expressions incorporated fineness. The other two expressions analyzed in this work were based on the mortar cube strength at three and seven days, with the former showing better random error and no apparent bias, a finding that has been confirmed by others [11]. Based on this work [4], ASTM C150 has adopted a heat index expression that would ensure a seven-day HOH for Type II MH of 80 cal/g or less. Ferraro and Ishee's [14] analysis indicates that the expression needs to be modified in order to ensure an appropriate prediction of the HOH using the heat index concept. A concern about the heat index is the fact that it relies on the potential phase composition of Portland cement, namely, tricalcium silicate and tricalcium aluminate. Previous research has indicated that the potential compound composition for those two phases can be considerably different from direct quantification techniques such as petrography or x-ray diffraction [15].

An alternative method, as described in this paper, proposes an empirical relationship by which the 84 h HOH can be used to predict accurately the seven-day value. The proposed empirical S-shaped function is given in Eq 1. The general exponential function has been used previously by Schindler and Folliard [16] to quantify the degree of hydration development based on the equivalent age concept. It has also been used by others to model strength development [17]. Initially, an effort was made to model HOH data from the time when cement was mixed with water to up to seven days later; however, using a single exponential function to fit all different stages of hydration did not seem to work very well. It is well established in the literature that the hydration

TABLE 2(a)—Chemical oxide composition of as-received cements.

Analyte	A	В	С	D	Е	F	G	Н	I	J
SiO <sub>2</sub> , %	20.01	20.02	20.51	20.85	20.83	20.74	20.86	18.67	19.01	19.67
Al <sub>2</sub> O <sub>3</sub> , %	5.15	5.32	4.91	4.9	4.61	4.45	4.42	5.7	5.66	4.17
Fe <sub>2</sub> O <sub>3</sub> , %	3.86	3.88	3.70	3.62	4.2	4.07	3.86	2.63	2.55	2.89
CaO, %	63.52	63.43	63.54	63.5	64.33	64.83	64.02	60.15	60.89	62.94
MgO, %	0.92	0.93	0.63	0.64	0.83	0.92	1.12	2.92	2.76	2.58
SO <sub>3</sub> , %	3.18	3.99	3.03	3.33	2.06	2.58	2.82	4.83	4.6	3.23
Na <sub>2</sub> O, %	0.12	0.12	0.09	0.09	0.07	0.07	0.11	0.41	0.37	0.25
$K_2O$ , %	0.42	0.43	0.45	0.45	0.29	0.28	0.28	1.1	1.02	1.07
TIO <sub>2</sub> , %	0.26	0.27	0.31	0.29	0.29	0.28	0.26	0.25	0.26	0.22
P <sub>2</sub> O <sub>5</sub> , %	0.13	0.13	0.12	0.11	0.11	0.1	0.1	0.26	0.25	0.05
$Mn_2O_3$ , %	0.01	0.01	0.04	0.03	0.08	0.08	0.08	0.07	0.08	0.05
SRO, %	0.06	0.06	0.06	0.06	0.04	0.04	0.04	0.28	0.28	0.04
CR <sub>2</sub> O <sub>3</sub> , %	0.01	0.01	0.01	0.01	0.01	0.01	0.01	< 0.01	< 0.01	0.01
ZnO, %	0.01	< 0.01	0.05	0.05	0.05	0.05	0.05	0.06	0.07	0.03
LOI, %	2.4	1.68	2.7	2.3	1.36	1.22	1.44	2.58	2.54	2.77

Note: LOI = Loss on ignition.

TABLE 2(b)—Potential phase composition, Blaine fineness, and measured and predicted seven-day heat of hydration of as-received cements.

Potential Phase Compositions	A	В	С	D	Е	F	G	Н	I	J
C <sub>3</sub> S, %	57	53	56	52	61	63	59	47	49	65
C <sub>2</sub> S, %	14	17	17	20	14	12	15	18	18	7
C <sub>3</sub> A, %	7	8	7	7	5	5	5	11	11	6
C <sub>4</sub> AF, %	12	12	11	11	13	12	12	8	8	9
$C_3S + 4.75*C_3A$	91	89	88	85	85	87	83	99	101	94
$C_4AF + 2*C_3A$	26	28	25	25	23	22	22	30	30	21
Fineness (Blaine), m <sup>2</sup> /kg	417	612	402	590	325	414	575	405	530	426
Measured seven-day HOH, J/g (cal/g), ASTM C1702 isothermal conduction calorimetry (internal mixing)	348 (83)	387 (93)	332 (79)	356 (85)	296 (71)	322 (77)	371 (89)	386 (92)	406 (97)	344 (82)
Predicted seven-day HOH, J/g (cal/g), based on Eq 1 and 24 to 72 h data fitting	340 (81)	390 (93)	326 (78)	354 (85)	283 (68)	307 (73)	384 (92)	401 (96)	408 (98)	347 (83)
Predicted seven-day HOH, J/g (cal/g), based on Eq 1 and 24 to 84 h data fitting	347 (83)	389 (93)	330 (79)	356 (85)	291 (70)	314 (75)	382 (91)	394 (94)	406 (97)	344 (82)
Measured seven-day HOH, J/g (cal/g), ASTM C186 heat of solution	349 (83)	370 (88)	337 (80)	367 (88)	312 (75)	340 (81)	366 (87)	361 (86)	391 (93)	362 (86)

process is primarily diffusion controlled once the hydration process is well into the steady state stage [18]. Implementing the proposed S-function for the HOH data from between 24 and 84 h was therefore considered, as the HOH profile can be used successfully to predict HOH at seven days.

$$H_t = C_1 e^{[(\tau_1/t_1)^{\beta_1}]}$$
 (24 <  $t_1$  (h) \le 72 or 84)

where:

 $H_t$  = total heat at given age, J/g,

 $C_1 = \text{constant}$ , J/g,

 $t_1$  = time from mixing of cement and water, h, and

 $\tau_1$  and  $\beta_1$  = constants defined by the curve shape.

#### **Experimental**

Tables 2(a) and 2(b) depict the oxide chemical composition and potential phase composition of as-received cements (labeled A-J) used in this study as determined via x-ray fluorescence spectrometry. The ten cements studied were typical industrial Portland cements with Blaine fineness values in the range of  $325-612 \text{ m}^2/\text{kg}$ ; C<sub>3</sub>S and C<sub>3</sub>A were in the range of 52 % to 65 % and 5 % to 11 %, respectively. Each cement sample was tested in duplicate runs for HOH for up to seven days in accordance with ASTM C1702 (Method A, internal mixing) [6] using a TAMAIR isothermal conduction calorimetry manufactured by TA Instruments. Cement A was also tested in accordance with ASTM C1702 (Method B, external mixing) using the same instrument. The experimental matrix is summarized in Table 3.

An admixer and 20 ml glass vial, as shown in Fig. 1, were used for the internal mixing procedure. Internal mixing was conducted by preconditioning the cement and distilled water at  $23^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ . The specified mass of cement was weighed in the glass vial and later was attached to the bottom of the admixer. The admixer syringe was filled with the required mass of water, and a small amount of vacuum grease was placed at the tip of the needle to prevent the evaporation of water and reaction with cement in the vial. It is noteworthy that a small amount of air between the tip of the needle and the water in the syringe can successfully prevent the evaporation of water and undesired reaction with the cement. The prepared admixer was left in the calorimeter cell for 90 min to achieve a baseline stabilization of  $\pm 2 \mu W$ . Afterward, the TAMAIR Assistant software was set to record the heat flow at 10 s intervals, and the water was injected into the vial over a period of 10 s before 60 s of manual internal mixing.

The external mixing procedure was conducted by preconditioning cement and distilled water at 23°C ± 0.2°C. The specified masses of cement and distilled water were weighed in two separate glass vials. At the time of mixing, the distilled water was added to the cement and manually mixed over a period of 45 s with a toothpick inside the vial. Afterward, the toothpick was left in the vial, and the vial was immediately sealed and placed into

TABLE 3—Experimental matrix, isothermal conduction calorimetry tests at 23 °C.

Cement ID	Cement A, B, C, D, E, F, G, H, I, J	H, I, J Cement A			
ASTM C1702	Internal mixing	External mixing 1	External mixing 2		
Cement, g	3.30	9.81	3.38		
Water, g	1.65	4.90	1.69		
Sand reference, g	12.33	37.37	12.61		
Test duration, h	168	168	168		

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FIG. 1—Admixer and vial for internal mixing (isothermal conduction calorimetry).

the calorimetry cell. The data logging was initiated one minute before placing the vial into the calorimeter. The baseline stabilized at  $\pm 2 \,\mu W$  before logging. This method of external mixing has the advantage of taking less than one minute, and there are minimal thermal effects due to mixing and handling. It appears that external mixing corrections, as outlined in ASTM C1702, can be avoided for both mixing and handling and lost HOH data at early

The isothermal conduction calorimetry used in this study has eight twin channels that partially share the same heat-sink; therefore, there is a possibility that thermal power in one channel might affect the power in neighboring channels (crosstalk). This might occur when two adjacent channels have a significant difference in thermal power or if a sample with a significantly different temperature than the calorimetry is inserted into the calorimeter [13]. To minimize noise due to crosstalk, only two out of the eight channels were used simultaneously, with the two active cells positioned diagonally to each other and all other sample cells charged with Ottawa sand. The water-to-cement ratio was fixed at 0.5 for all samples. The sand reference mass had a heat capacity matching that of the cement paste. The isothermal temperature used was 23°C. Performance calibration was conducted in accordance with the manufacturer's specifications [19]. The highest overall heat flow measured from the cells charged with sand over a period of seven days was used as a measure of the baseline level during the HOH test. The baseline level was used to assess the signal-to-baseline ratio at different measurement times. The baseline noise level was examined for conformance to the instrument stability criteria, as specified in ASTM C1702, for all the cells used for HOH measurements [6].

#### **Results and Discussion**

#### Ratio of Signal to Maximum Baseline Deviation

Figure 2(a) shows the heat flow measured from the sample cell charged with sand that displayed the highest overall heat flow. This was taken as a measure of the baseline deviation for the purposes of this study. Figure 2(b) also compares the signal from a 3.30 g cement sample to the signal from the sand sample (baseline deviation), plotted from four days (96 h) onward. The data displayed in Fig. 2(a) indicate that for a measurement age of up to seven days, the maximum baseline deviation was 0.023 mW while the heat flow signal from the cement paste was an order of magnitude higher. This indicates that for the current system, the signal strength is significantly higher than the maximum baseline deviation even at seven days of hydration. However, for longer hydration times, such as 28 days, that might not necessarily be the case. It is plausible that, rather than specifying the baseline noise level and drift as defined in ASTM C1702, it would be intuitive and practical to define a minimum signal to maximum baseline deviation ratio of five in addition to specifying the baseline deviation limit of  $\pm 20 \,\mu\text{W}$  to define the criteria for valid HOH measurement for a given system or instrument. A convenient way to define the baseline deviation would be to measure the signal for a period of seven days from an inert reference sample such as sand, with the mass matching the heat capacity of the targeted sample, and then establish the maximum baseline deviation.

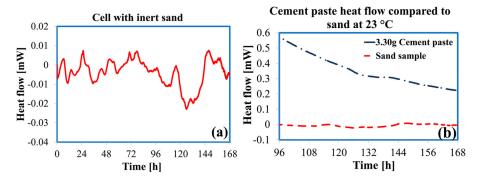


FIG. 2—(a) Heat flow from sand sample, 0–7 days. (b) Heat flow from sand sample compared to the heat flow from a 3.30 g Portland cement sample toward the end of the seven-day test period.

#### Heat Flow and Heat of Hydration Data from Cement Samples

Figures 3 and 4 present the HOH or the cumulative heat and heat flow over a period of seven days for cement A using internal and external mixing methods. The results indicate that the method of mixing (internal versus external) has an effect on the amount of heat measured via isothermal conduction calorimetry; however, the differences might not be that significant, as seen in Figs. 3 and 4. The internal mixing method registers the cement and water interaction instantly, whereas external mixing, depending on the time of mixing, might result in missing the dissolution stage and

Cement A heat of hydration at 23 °C 400 Heat of hydration [J/g] (a) 350 300 250 200 150 3.30 g Cement A.1 Internal mixing 100 - 3.30 g Cement A.2 Internal mixing 3.38 g Cement A.1 External mixing 50 9.81 g Cement A.2 External mixing 0 0 24 48 96 120 144 168 Time [h]

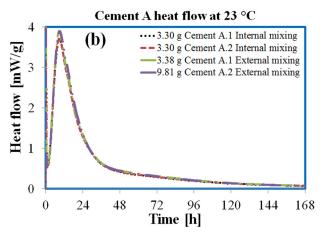
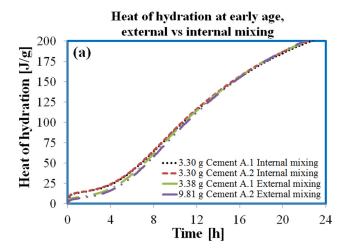


FIG. 3—(a) Heat of hydration of cement A (internal and external mixing). (b) Heat flow of cement A (internal and external mixing).

most of the dormant stage of hydration. Internal mixing is expected to yield a more accurate measurement of the heat evolution initially [Fig. 4(a)], as some heat is either lost or gained from the environment during the external mixing procedure. Furthermore, non-isothermal disturbances are expected to occur during external mixing, which in turn would result in more time being needed in order to reach isothermal conditions in the sample and the calorimeter. However, the external mixing procedure generates more total heat than internal mixing, supporting a concern



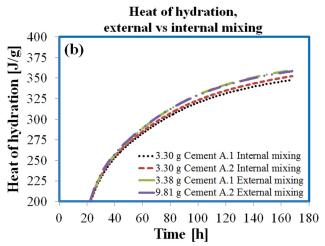


FIG. 4—Heat of hydration for cement A, external versus internal mixing.

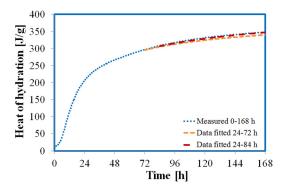


FIG. 5—Measured and extrapolated seven-day heat of hydration of cement A (typical figure).

that internal mixing might result in less efficient mixing than is easily achieved with external mixing. The higher heat values captured for external mixing methods might also reflect differences in the mixing methodology and might not necessarily duplicate the actual concrete mixing methodology.

### Extrapolation of Total Heat after 24 to 84 h of Hydration

All experimental HOH data measurements (isothermal conduction calorimetry) from 24 h up to 72 or 84 h of hydration were fitted to the S-shaped analytical function presented in Eq 1. Fitting parameters for Eq 1 were obtained using the Solver command, executable in Excel (2010) software. The Microsoft Office Excel Solver tool uses the Generalized Reduced Gradient (GRG2) nonlinear optimization code [20]. The total heat was then extrapolated for up to seven days and was compared to the seven-day HOH, experimentally measured via isothermal conduction calorimetry as shown in Fig. 5, for cement A. Table 4 shows the measured and predicted seven-day HOH values of cements A and C based on the internal mixing method (isothermal conduction calorimetry) in addition to HOH prediction results based on the external mixing method (isothermal conduction calorimetry) for cement A. The results indicate that the proposed equation could predict the seven-day HOH of cement accurately for both internal and external mixing methods. It is further indicated that fitting the 24 to 84 h experimental HOH data to the proposed equation can lead to more accurate predictions of the seven-day HOH than 24 to 72 h data fitting.

To evaluate the hypothesis, eight industrial Portland cements (labeled B and D–K) were selected, and their HOH was measured using the internal mixing method (isothermal conduction calorimetry) as tabulated in Table 2(b). The measured and predicted (using Eq 1) seven-day HOH values were compared to each other to determine the suitability of Eq 1 for predicting the seven-day HOH. Fitting parameters for Eq 1 (based on isothermal conduction calorimetry method measurements) for all the cements (A–J) are tabulated in Table 5.

Figure 6 shows the difference between the measured HOH (internal mixing, isothermal conduction calorimetry) and the predicted HOH (Eq 1) at seven days. The mean and standard deviation of error were calculated as -0.8 and  $10 \, \text{J/g}$  (24 to 72 h data fitted) and 0.5 and 5.6 J/g (24 to 84 h data fitted), respectively.

The results indicate that fitting 24 to 84 h of experimental data measurements generates less difference between the predicted and actual HOH measurements for seven days. The difference between the predicted and measured seven-day HOH ranged from -8 J/g to about 11 J/g resulting from the 24 to 84 h experimental data fitting. To better analyze the data, the measured seven-day HOH was plotted versus the predicted at seven days as shown in Fig. 7.

The results indicate that the relationship is linear with a high coefficient of determination (R<sup>2</sup>), exceeding 0.97 for both 24 to 72 h and 24 to 84 h experimental data fitting. Comparing this value to values reported earlier in the literature, it appears that the proposed equation shows less random error than Bogue dependent relationships for the seven-day HOH predictions. The line of equivalency indicates minimal bias, especially for the predicted seven-day HOH resulting from fitting the 24 to 84 h experimental data.

The confidence intervals based on two sample t-test hypotheses also were calculated and are shown in Fig. 7. In general, the 95 % confidence interval is dependent on the sample size incorporated into the calculation of means and standard deviations [21]. It is recognized that two data sets with the same means and standard

TABLE 4—Measured and	nredicted seven-da	y heat of hydration via isothermal	calorimetry

Cement ID	Cement A Internal Mixing	Cement A External Mixing	Cement C Internal Mixing
Time at maximum heat flow, h	8.8	8.8	8.9
Measured heat after seven days, J/g	348	360	332
Measured heat after seven days, J/g	352	358	329
Average	350	359	331
Standard deviation (measured duplicate runs)	2.83	1.41	2.12
Extrapolated from 24 h to 72 h	340	355	326
Error, J/g	-10	-4	-5
Error, %	-2.8	-1.1	-1.5
Extrapolated from 24 h to 84 h	347	362	330
Error, J/g	-3	3	-1
Error, %	-0.8	0.8	-0.1

TABLE 5—S-shaped analytical function consta	ants.
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Cement ID	Constar	nts for Data Fitting, 24	to 72 h	Constants for Data Fitting, 24 to 84 h		
	$C_1$	$ au_1$	$\beta_1$	$C_1$	$ au_1$	$\beta_1$
Cement A (internal mixing)	409.0	13.3	0.66	454.1	15.0	0.54
Cement A (external mixing)	457.2	15.3	0.57	519.4	19.0	0.47
Cement B (internal mixing)	485.1	11.4	0.56	478.9	11.2	0.58
Cement C (internal mixing)	390.7	11.9	0.64	414.9	12.6	0.57
Cement D (internal mixing)	457.1	10.3	0.49	470.1	10.8	0.47
Cement E (internal mixing)	452.9	21.9	0.37	732.3	117.8	0.23
Cement F (internal mixing)	377.1	9.8	0.55	441.1	12.4	0.41
Cement G (internal mixing)	625.5	17.5	0.32	594.4	15.1	0.34
Cement H (internal mixing)	440.4	17.9	1.06	423.1	17.7	1.17
Cement I (internal mixing)	421.1	11.7	1.30	416.7	11.9	1.37
Cement J (internal mixing)	376.5	12.5	0.96	369.1	12.6	1.02

deviations but different sample sizes shall create different confidence intervals. As a simple example, a data set with ten pairs of determined sample sizes (measured and predicted seven-day HOH) has a confidence interval about three times larger than a data set with 30 pairs of determinations, even if both data sets have similar means and standard deviations [21]. In this study, the confidence intervals for seven-day HOH were calculated as  $\pm 36 \text{ J/g}$  (24 to 72 h experimental data fitting) and  $\pm 34 \text{ J/g}$  (24 to 84 h experimental data fitting). It is believed that the confidence intervals (Fig. 7) are large as a result of the small sample size (ten pairs of determinations for each data set).

Statistically, a smaller sample size shall result in a larger confidence interval. This measure cannot accurately evaluate the proposed equation because of the small sample size, but it can be used as a suitable means in future works in which data sets with larger sample sizes are implemented in order to validate the

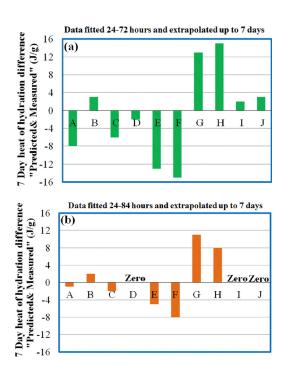
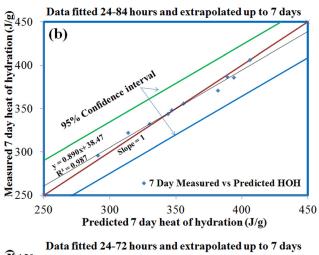


FIG. 6—Seven-day heat of hydration difference: predicted and measured.

model. It is understood that different models can be compared if one determines the confidence interval for each model with the same sample size as used for all the models; then, the model with the smallest confidence interval is the most suitable for prediction purposes.

Considering the mean and standard deviation of error for the predicted seven-day HOH resulting from fitting the 24 to 72 and



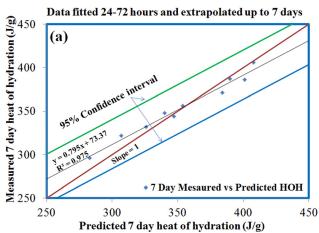


FIG. 7—Measured versus predicted seven-day heat of hydration of cements (internal mixing)

24 to 84 h measured HOH data and the smaller confidence interval of  $\pm 34 \text{ J/g}$  (24 to 84 h data fitted) as compared to  $\pm 36 \text{ J/g}$  (24 to 72 h data fitting), the seven-day HOH can be predicted with better accuracy if 24 to 84 h of experimental data are fitted to Eq 1.

Because of the low systematic bias and random error observed when working with ten cements, it is proposed that a larger matrix of cements be examined in order to further verify the usefulness of the proposed method for specification consideration. It is expected that if the sample size is increased to 30 cements, with the same means and standard deviations as for the sample size of 10 cements, the confidence limits of approximately  $\pm 12$  J/g resulting from 24 to 72 h fitted data and  $\pm 11$  for 24 to 84 h fitted data can be observed for seven-day HOH.

#### **Conclusions**

A careful study on the HOH of Portland cement using isothermal conduction calorimetry indicates that the total heat generated at seven days can be predicted with acceptable accuracy, relative to the heat measured using isothermal conduction calorimetry (ASTM C1702), based on heat measurements for only 84 h and using an S-curve function. The authors suggest that a wider sample matrix (larger sample size) be examined in order to validate the proposed function as an alternative method of predicting the HOH of Portland cement at seven days. It is also suggested that the proposed function be examined for its suitability for predicting the 28 day HOH of Portland cement.

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