Measurements and Predictions of Heat of Hydration of Portland Cement Using Isothermal Conduction Calorimetry

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Abstract

Two industrial ASTM Portland cements were carefully tested for heat of hydration (HOH) continuously up to 7 days at 23° C using isothermal conduction calorimetry in accordance to ASTM C1702. Internal and external mixing procedures were implemented. The results for HOH measurements at 7 days using isothermal calorimetry were compared to those obtained through heat of solution method (ASTM C186). The results indicate that for a given Portland cement, the shape of the HOH curve can be predicted with sufficient accuracy by measuring the heat of hydration to an age corresponding to an approximately ten times the age at maximum heat flow or main hydration peak. The heat of hydration at ages up to 7 days can be predicted by fitting an analytical function similar to functions used in Maturity calculations. The suggested approach would eliminate the need for measuring data at ages when the heat flow has decreased substantially well past its maximum where the signal to noise ratio is low. This approach effectively proposes a method for predicting accurately the total heat generated at 7 days by Portland cement based on 3 days heat flow measurements.

Keywords: Cement heat of hydration, isothermal calorimetry, S-shaped function, signal to noise ratio, internal and external mixing

1. Introduction

Heat of hydration measurements is important in assessing temperature rise that accompanies the hydration process of Portland cement. Temperature rise that occurs on mixing cement with water is due to the exothermic nature of the interaction of anhydrous cement with water. Experimental measurements and calculations for the heat of hydration of different types of Portland cement had been published in the literature extensively. For several decades, Portland cement specifications adopted ASTM C186 for heat of hydration measurements, which is a heat of solution method. Recently, a new standard method for HOH determination was adopted by ASTM under specification C1702-09(2009). The method, isothermal calorimetry, indicates two possible mixing routines; namely, internal and external mixing. However, the use of this method has not been incorporated in cement specification ASTM C150.

For Type II (MH) and Type IV a maximum heat of hydration is indicated for 7 and 28 days per optional physical requirements of ASTM C150/C150M-09. The specification identifies ASTM C186 for HOH measurements in spite of the availability of ASTM C1702-09. Isothermal conduction calorimetry shows improved precision if compared with heat of solution method as shown in Table 1. Additionally, isothermal calorimetry offers simplicity in procedures and availability of commercial equipment to conduct the test.

Table 1: Comparison of precisions between isothermal calorimetry and solution calorimetry (per ASTM C1702-09)

Standard Deviation	ASTM C186	ASTMC1702 (Wadso's Data)	ASTM C1702 (VDZ 2006)
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)*

HOH measurements of Portland cements serve as an important indicator of the temperature rise that concrete elements, specifically, mass structures would experience. In an extensive study conducted by Wang et al (2009), it was concluded that isothermal calorimetry is well suited for heat of hydration measurements. It was further indicated that the 3-day experimental data displayed lower variation than 7-day experimental data. The reason for the observed increased variation at the later age was not identified. However, the authors of this paper believe that background noise, in many commercially available conduction calorimeters, interferes with the signal at longer ages where the signal to noise ratio is low. An alternative method is described in this paper, where an empirical relationship is proposed by which the HOH measurements up to 3 days can be used to predict accurately the 7 day HOH. The proposed S-shaped function is given in Equation (1).

$$H_t = C \cdot e^{-\left(\frac{\tau}{t}\right)^{\beta}}$$ Equation (1)

Where H_t = Total heat at given age, J/g
             C= Constant, J/g
             τ and $\boldsymbol{\beta}$= Constants defined by the curve shape

2. Experimental

Table 2 depicts the oxide chemical composition of the as received cements used in this study as determined by x-ray fluorescence spectrometry.   The two cements are typical Type II Portland cements that can also be classified as Moderate Heat (MH) Type II Portland cement. MH Type II Portland cements have physical requirements of a limited Blaine fineness of 4300 cm²/g. This limit would not apply if the heat index is less than or equal to 90. This implies that for Cement 1 with a heat index of 91, Blaine fineness criterion has to be satisfied for it to qualify as MH Portland cement. Additional optional physical requirements for MH Portland cements include maximum HOH (per ASTM C186) at 7 days of 290 KJ/Kg or 70 Cal/g. Both of the cements studied here would not satisfy this optional physical requirement for MH Type II Portland cement. However, if the optional physical requirement is not specified, then both cements can be classified as MH cements.

Each cement sample was tested in duplicate for heat of hydration up to 7 days according to ASTM C1702 Method A (internal mixing), using a TAM Air isothermal conduction calorimeter manufactured by TA instruments. Cement 1 was also tested according to ASTM C1702 Method B (external mixing) using the same instrument. The experimental matrix is summarized in Table 3. To minimize noise due to cross talk, only two out of the 8 channels were used simaltaneously, with the two active cells positioned diagonally opposite to each other and all other sample cells charged with Ottawa sand. The w/c ratio was fixed at 0.5 for all samples. The sand reference mass had a heat capacity matching the cement paste. The isothermal temperature used was 23 °C. Performance calibration was conducted in accordance with the manufacturer specifications. The highest overall heat flow measured from the cells charged with sand was used as a measure of the noise level during the heat of hydration test in order to access the noise to signal ratio at different measurement times.

Table 2: Chemical oxide composition of as-received cements

Analyte	Cement1 (w/o)	Cement3 (w/o)
% (SiO_2)	20.01	20.51
% (Al_2O_3)	5.15	4.91
% (Fe_2O_3)	3.86	3.70
% (CaO)	63.52	63.54
% (MgO)	0.92	0.63
% (SO_3)	3.18	3.03
%(Na_2O)	0.12	0.09
%(K_2O)	0.42	0.45
%(TIO_2)	0.26	0.31
%(P_2O_5)	0.13	0.12
%(Mn_2O_3)	0.01	0.04
%(SRO)	0.06	0.06
%(CR_2O_3)	0.01	0.01
%(ZnO)	0.01	0.05
% LOI	2.40	2.70

Potential Phase Compositions		
%(C_3S)	57	56
%(C_2S)	14	17
%(C_3A)	7	7
%(C_4AF)	12	11
$C_3S + 4.75*C_3A$	91	88
C_4A+2*C_3A	26	25
Fineness (Blaine)		
Fineness, m²/kg	417	393
Time of Setting (Vicat)		
Initial set, Minutes	90	80
Final Set, Minutes	175	178
Heat of hydration, ASTM C 186 Heat of Solution		
7-days heat of hydration, J/g (cal/g)	340(81)	335(80)

Table 3: Experimental matrix, isothermal calorimetry tests at 23 °C

Cement ID	Cement 1		Cement 3	
ASTM C 1702 internal mixing	*Sample 1*	*Sample 2*	*Sample 1*	*Sample 2*
Cement, g	*3.30*	*3.30*	*3.30*	*3.30*
Water, g	*1.65*	*1.65*	*1.65*	*1.65*
Sand reference, g	*12.33*	*12.33*	*12.33*	*12.33*
Test duration, h	*168*	*168*	*168*	*168*
ASTM C 1702 external mixing	*Sample 1*	*Sample 2*	*Not tested*	
Cement, g	*9.81*	*3.38*		
Water, g	*4.90*	*1.69*		
Sand reference, g	*37.37*	*12.61*		
Test duration, h	*168*	*168*		

3. Results and Discussion

3.1 Signal to noise

Figure 1 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 noise for the purpose of this study. Figure 1 (right) also compares the signal from a 3.3 g cement sample relative to the signal from the sand sample (noise), plotted from 4 days (96 h) and onwards.
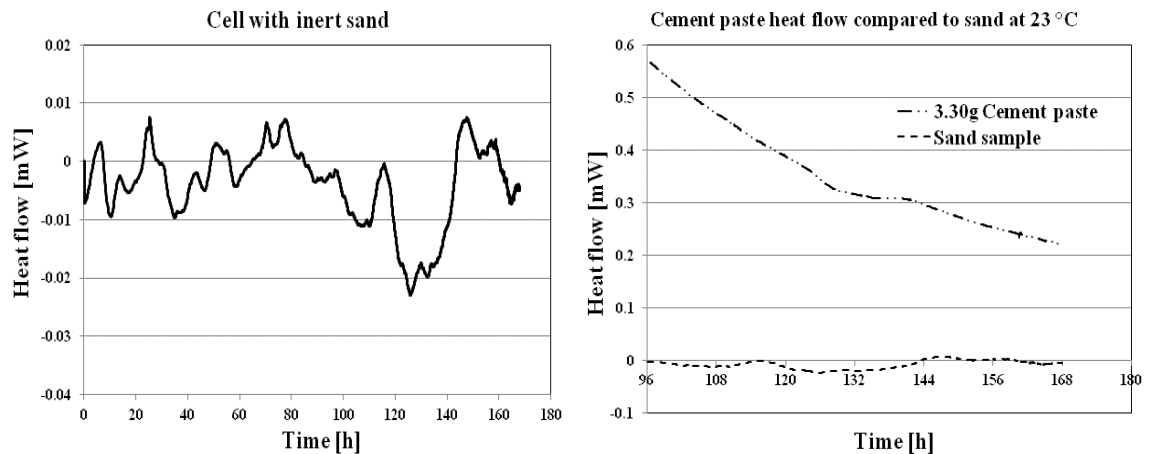

Figure 1: Left: Heat flow from sand sample, 0-7 days. Right: Heat flow from sand sample compared to the heat flow from a 3.30 g Portland cement sample towards the end of the 7 days test period.

The data displayed in Figure 1 indicate that up to a measurement age of 7 days, the noise signal was approximately at 0.008 mW while the heat signal from the cement paste was an order of magnitude higher. This is indicative that for the current system, the signal strength is significantly higher than the noise signal even at 7 days of hydration. However, for longer hydration times such as 28 days, that might not necessarily be the case. It is thus plausible that rather than specifying an absolute minimum signal and a maximum baseline error, it would be intuitive and practical to define a minimum signal to noise ratio to define the limits for valid HOH measurement for a given system or instrument. A convenient way to define the noise signal would be to measure the signal from an inert reference sample such as sand. It is further suggested that a 10:1 minimum signal to noise ratio would be adequate, which for the samples tested in this study would indicate that the test should not be carried out beyond a signal of 0.08mW from the active sample, to avoid possible interference between the collected signal and the inherent system noise. However, the suggested ratio needs to be verified with a larger sample matrix and compared with measurements from heat of solution method.

3.2 Heat flow and heat of hydration data from cement samples

Figures 2 and 3 present the heat of hydration (total energy) or the cumulative heat over a period of 7 days for the cement specimens studied here. The results indicate that the method of mixing (internal versus external) has an effect on the amount of heat measured by isothermal calorimetry; however, differences might not be that significant as seen from Figure 2 and 3. Internal mixing methods register the cement-water interaction instantly while external mixing, depending on the time of mixing, might result in missing the dissolution stage and most of the dormant stage of hydration. Internal mixing is expected to yield a more accurate measurement of the heat evolution initially (Figure 4), since some heat is either lost or gained from the environment during external mixing procedures. Furthermore, non-isothermal disturbances are expected to occur during external mixing, which in turn would result in a longer time to reach isothermal conditions in the sample and calorimeter. However, external mixing procedures generated a higher maximum heat flow rate compared to internal mixing, supporting a concern that internal mixing may not result in as efficient mixing as is easily achieved with external mixing. The higher heat values captured for the external mixing methods might also reflect differences in the mixing methodology.
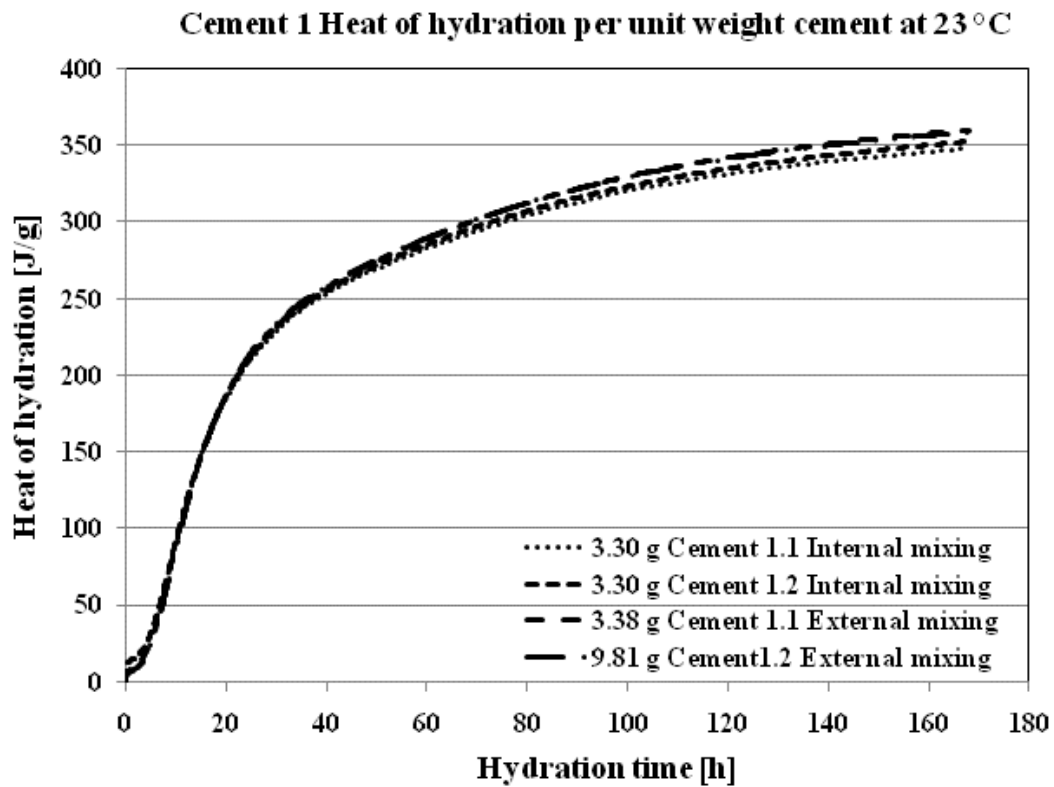
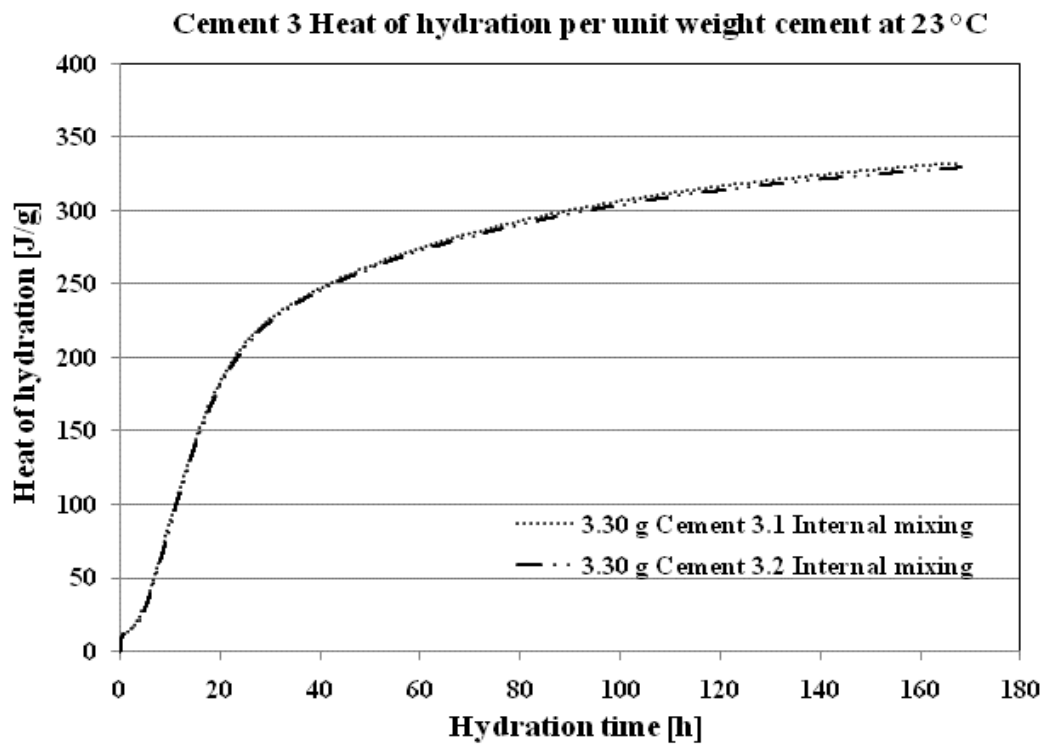**Figure 2: Heat of hydration Cement 1(internal and external mixing)**
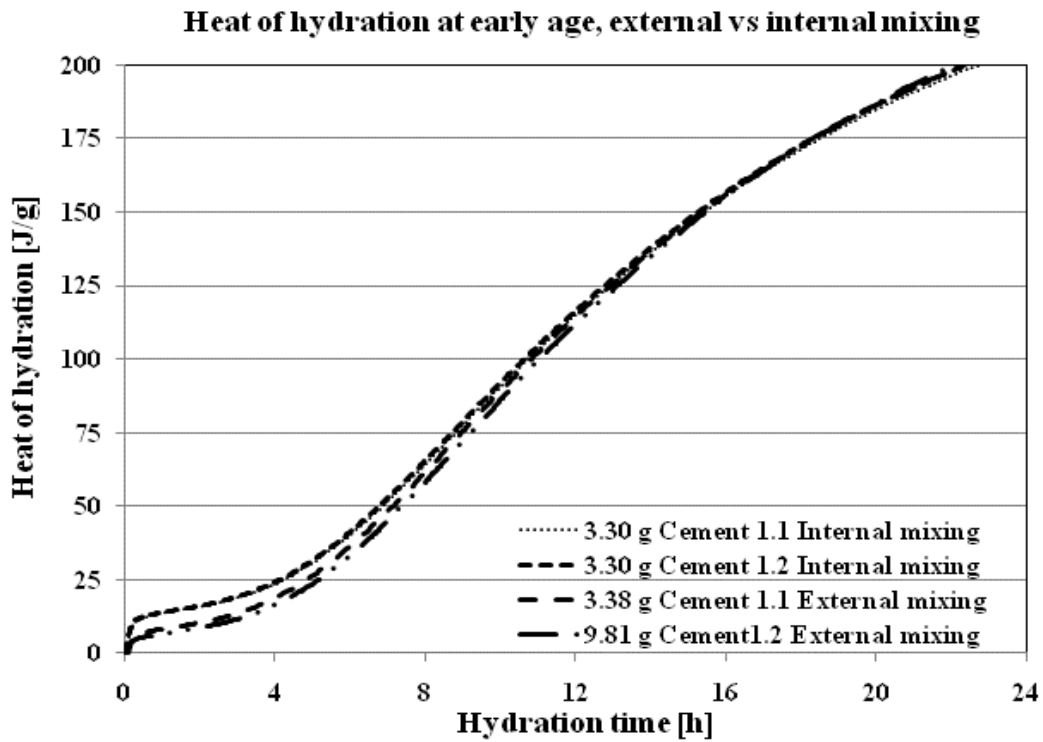

Figure 3: Heat of hydration for Cement 3

Heat of hydration at early age, external vs internal mixing

Figure 4a: Heat of hydration for cement 1, external vs. internal mixing

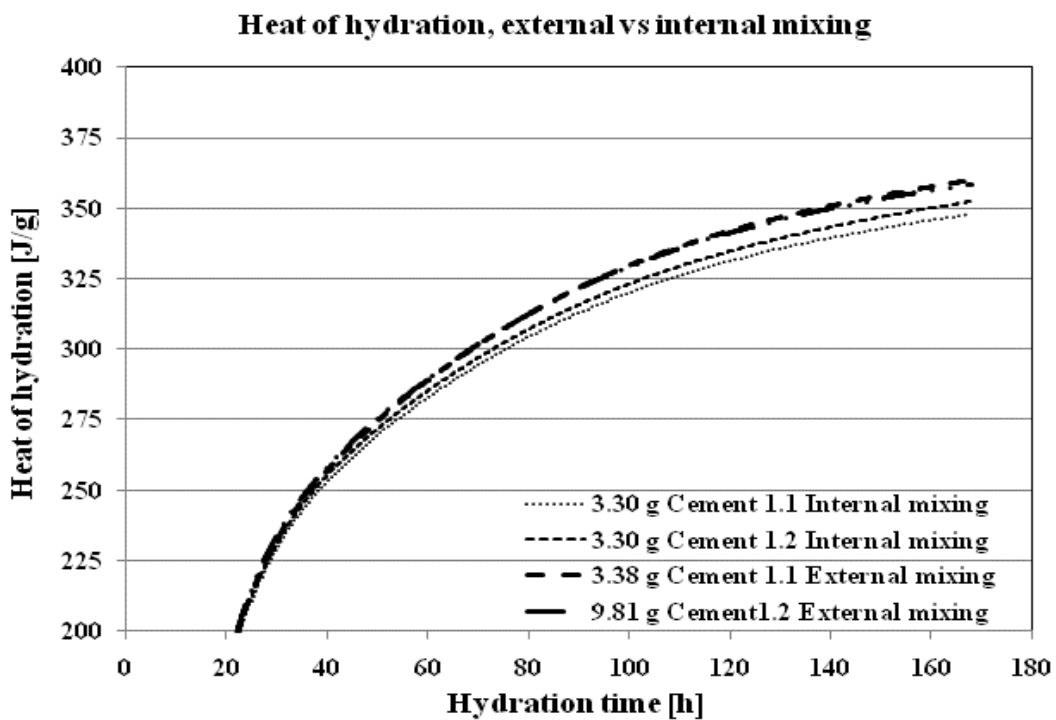**Heat of hydration, external vs internal mixing**

Figure 4b: Heat of hydration for cement 1, external vs. internal mixing

3.3 Extrapolation of total heat after 1-3 days of hydration

The S-shaped analytical function presented in Equation (1) was fitted to all experimental data measurements from 24 hours up to 48, 72, and 84 hours of hydration. The total heat was then extrapolated to 7 days and compared to the experimentally measured heat of hydration at 7 days as shown in Figure 5. The measured and extrapolated results are summarized in Table 4.
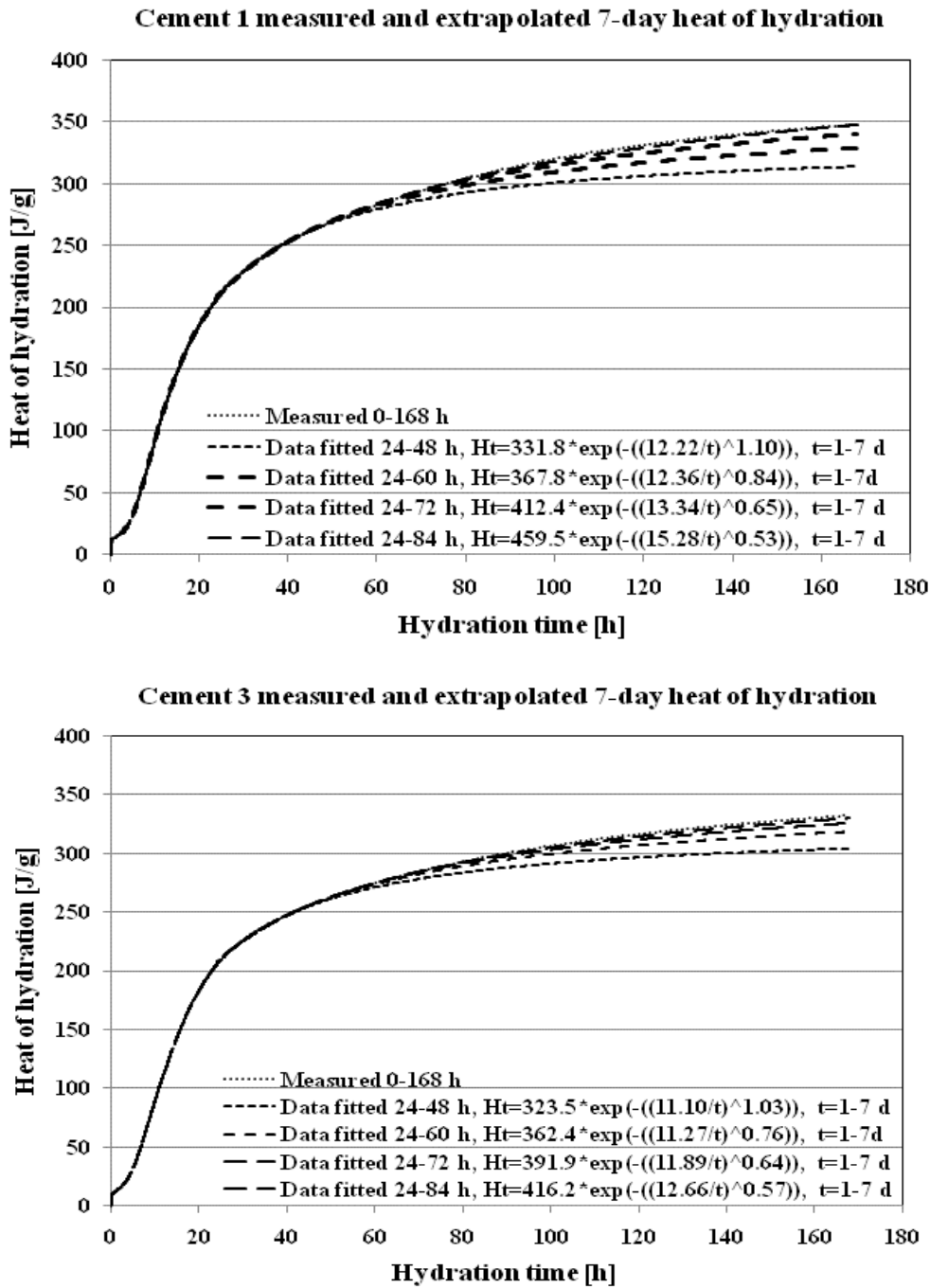

Figure 5: Measured and extrapolated heat of hydration.

Table 4: Measured and extrapolated 7-days heat of hydration by isothermal calorimetry.

Cement ID	Cement 1 internal mixing	Cement 1 external mixing	Cement 3 internal mixing
Time at maximum heat flow, h	8.8	8.8	8.9
Measured heat after 7 days, J/g	348	360	332
Measured heat after 7 days, J/g	352	358	329
Average	350	359	331
Stdev	2.83	1.41	2.12
COV, %	0.81	0.39	0.64
Extrapolated from 48 h to 7 days	314	323	304
Error, J/g	-36	-36	-27
Error, %	-10	-10	-8
Extrapolated from 60 h to 7 days	329	342	319
Error, J/g	-21	-17	-12
Error, %	-6	-5	-3
Extrapolated from 72 h to 7days	340	355	326
Error, J/g	-10	-4	-5
Error, %	-2.9	-1.1	-1.4
Extrapolated from 84 h to 7 days	348	362	330
Error, J/g	-2	3	-0.5
Error, %	-0.6	0.8	-0.2

As shown in Figure 5, fitting of a simple S-curve function to the heat of hydration data measured for at least 72 hours (3 days) gave a reasonable estimate of the 7-day heat of hydration. Since the calculated error (Table 4) was consistently less than the error associated with ASTM C186 heat of solution method, it appears that such an extrapolation method may be acceptable for the purpose of generating heat of hydration data for Portland cements conforming to ASTM C150.

While many commercially available isothermal conduction calorimeters are capable of accurately measuring the heat of hydration of Portland cement during the induction, acceleration and most of the deceleration stages of cement hydration, many instruments struggle with a low signal to noise ratio when measurements are extended to longer hydration times.

4. Conclusions

A careful study of the heat of hydration of Portland cement, using isothermal calorimetry, indicates that the total heat generated can be extrapolated from 3 days to 7 days using an S-curve function with acceptable accuracy when compared to the heat of solution method, ASTM C186. The authors suggest that a wider sample matrix be examined to validate the proposed function as an alternative method of predicting the heat of hydration of Portland cement at an age of 7 days. It is also suggested that the proposed function be examined for its suitability in predicting the 28 days HOH of Portland cement.

References

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