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Characterization and Performance Prediction of Cement-Based Materials Using a Simple Isothermal Calorimeter

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Abstract

In the present study, early-age heat evolution of over 120 mortar mixes was monitored for 24 hours after mixing using a simple isothermal calorimetry device. This paper describes the processes of calorimetric characterization and performance prediction of these mortar materials. The features of the heat evaluation curves obtained from the calorimetry tests and the effects of the mortar materials, mix proportions, and curing conditions on the heat evaluation curves were studied. A derivative method was employed for exemplifying the physical changes in the tested materials from the heat evolution curves, and the results were compared with set times from ASTM C403 tests. The study indicates that the simple calorimetry technique can be used to flag changes in cementitious materials, pre-screen concrete materials and/or mix design, identify incompatibility of cementitious materials, and forecast setting time and early-age strength.

1. Introduction

Early-age concrete properties, such as workability, setting time, strength gain, and thermal shrinkage behavior, are predominantly influenced by the hydration kinetics of the cementitious materials. Hydration of cementitious materials consists of a number of chemical reactions that liberate heat. The heat evolution process is closely associated with the rate of chemical reaction of the cementitious materials and influenced by chemical admixtures, concrete mix proportions, construction procedures, and curing conditions. As a result, the deviations in characteristics of concrete materials and the effects of construction conditions on concrete performance can be detected or predicted by monitoring the heat of hydration of cementitious materials (Mindess *et al*. 2003; PCA 1997).

Modern concrete mixtures have a much more complex chemical system than before. The complexity of the mixtures results from the increasing number of ingredients used (such as supplementary cementitious materials (SCMs) and chemical admixtures) and the various types and sources of the ingredients supplied to any given project. The compatibility issue related to the adequate use of concrete materials is gaining increasing attention. Abnormal early hydration resulting from incompatible combinations of certain concrete materials have resulted in flash setting behavior and excessive retardation, which can affect concrete placement, strength development, early-age cracking, and durability (Taylor *et al*. 2006). The influences of construction and environmental conditions often aggravate these problems. However, the existing construction guidelines lack information on the proper test methods for identifying these problems.

Lately, the advances in using thermal measurements in laboratories have demonstrated that calorimetry tests have a high potential for detecting concrete incompatibility problems, predicting concrete set time, and assessing concrete strength gain and thermal cracking under various climatic conditions (Cost and Knight 2007; Ruiz *et al*. 2007). Various calorimetry test methods are available; but most of them require expensive equipment, complex testing procedures, and extensive test time. Also, most isothermal calorimeters only test small amount of paste samples instead of mortar or concrete samples. A simple unthermostated calorimeter has been introduced, but it is limited to the qualitative study of cement hydration (Wadsö 2004).

In the present study, a relative inexpensive isothermal calorimeter was employed to test various mortar samples. The equipment was calibrated and evaluated before being used for characterization of cementitious materials. Based on the test results, performance of the tested materials was then assessed. The detailed information on the equipment evaluation, material characterization and performance prediction is presented in the section below.

2. Experimental work

The equipment evaluation included examining varia-

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tions of test results from (1) the eight different units, or channels, of the calorimeter used in a given test, (2) tests repeated by a given operator at different times for a given mortar mixture, and (3) tests repeated by three different operators for a given mortar mixture.

The cementitious material characterization was performed using the simple isothermal calorimeter on mortar samples. The major factors that affect the heat evolution of cement-based materials, such as cement type and source, fly ash (Class C) source and replacement level, water-to-cementitious materials ratio (w/cm), and curing condition, were studied. The original and derivatives of the calorimetry curves of the tested materials were analyzed. In addition, the set time and strength development of the mortars were also measured according to ASTM C 403 and C 109, respectively.

To assess and predict mortar performance based on calorimetry test results, the relationship between the calorimetry test results and the corresponding ASTM test results were established. These relationships include (1) the relationship between the time when the first derivative of a calorimetry curve reaches the highest or zero values and the mortar set time measured according to ASTM C403, and (2) the relationship between the heat obtained from the calorimetry tests and the compressive strength of the mortar measured according to ASTM C109 at one day. Based on these relationships, performance of cementitious materials, such as set time and early-age strength can be predicted. In addition, through examining the features of a calorimetry test curve, such as locations and durations of major heat peaks, material incompatibility of the tested mortar can be assessed.

2.1 Materials

Nine cements (one Type I, one Type III, two Type ISM, and five Type I/II cements from different sources), six Class C fly ashes (from different sources), four fly ash replacement levels (10%, 20%, 30%, and 40%) were studied under four different temperatures (10ºC, 20ºC, 30ºC, and 40ºC). Among these, one mortar mix was selected to study the effect of w/cm on heat evolution, where w/cm of 0.5, 0.42, and 0.35 were used. Another mortar mix, with and without water-reducing agent (WRA), was selected to evaluate whether or not an incompatibility problem could be identified using the simple isothermal calorimeter.

The chemical properties of these cements and fly ashes are shown in **Table 1** and **Table 2**, respectively. Type ISM cement contains 80% Type I cement and 20% Ground Granulated Blast Furnace (GGBF) slag. The cement and GGBF slag were blended by the cement manufacture. The sand used for mortars was natural river sand, with a specific gravity of 2.6 and absorption level of 1.37%. The water reducing admixtures used were Mira 70 and WRDA 82 from Grace Construction Products. The air-entraining agent used was MB-AE 90 from Master Builder Inc.

2.2 Specimens and test methods

Mortar samples were prepared according to ASTM C 305 and used for calorimetry, set time, and strength tests. All mortar mixes, except those used for studying the effect of w/cm and incompatibility, had w/cm of 0.43 and sand-to-cementitious material ratio (s/cm) of 2.22. The mortar set time tests were conducted based on ASTM C 403. Strength tests were conducted following ASTM C 109. The mortar cubes (50 mm x 50 mm x 50 mm) were cured under water at designed temperatures. The mortar strength was tested at 1, 3, 7, and 28 days.

The simple isothermal calorimeter, manufactured by Thermometric Inc., was used for calorimetry tests. In order to control the test condition, the calorimeter was placed in a temperature control chamber as shown in **Fig. 1**. The calorimeter has eight separate units, or channels, which allows testing eight samples at the same

Table 1 Chemical composition of cement.

Chemical Composition, %	Type I	Type III	Type I/II				
			1	2	3	4	5
CaO	64.61	64.42	64.62	63.7	61.8	61.8	63.1
SiO_2	20.58	21.26	20.6	20.0	20.3	21.5	20.6
Al_2O_3	5.38	5.30	4.50	4.29	4.62	4.76	4.82
Fe_2O_3	2.14	2.09	2.50	2.96	3.05	3.11	3.06
MgO	2.08	1.95	2.50	2.82	3.82	3.30	1.80
K_2O	0.46	0.44	N/A	0.70	0.47	0.67	0.43
Na_2O	0.26	0.3	N/A	0.30	0.17	0.12	0.26
$(Na_2O)eq$	0.56	0.58	0.22	0.76	0.47	0.56	0.54
SO_3	3.01	3.08	2.70	2.77	2.66	2.84	3.50
C_3S	58.83	53.30	65.00	66.00	54.20	43.50	54.10
C_2S	14.62	20.74	10.00	7.70	17.40	28.80	18.00
C_3A	10.64	10.51	8.00	6.40	7.10	7.40	7.60
C_4AF	6.51	6.36	7.60	9.00	9.30	9.50	9.30
Free Lime	1	0.77	1.50	N/A	N/A	N/A	1.50
Fineness (m^2/kg)	368	551	372	N/A	N/A	N/A	363

Table 2 Chemical composition of fly ash.

Chemical Composition, %	Fly Ash Source					
	P	C	L	K	O	B
SiO_2	34.12	35.74	34.58	35.99	33.53	32.15
Al_2O_3	17.75	20.66	18.80	15.74	17.23	16.87
Fe_2O_3	6.65	5.80	6.25	6.89	5.72	6.26
SiO_2 +Al_2O_3 +Fe_2O_3	58.52	62.2	59.63	58.62	56.48	55.28
SO_3	2.69	2.39	2.25	2.48	3.66	2.64
CaO	27.34	24.32	26.38	26.76	25.75	28.56
MgO	5.13	4.24	4.78	6.12	5.99	7.20
Na_2O	1.38	1.60	1.93	1.95	3.80	2.31
K_2O	0.38	0.44	0.33	0.43	0.61	0.34
(Na_2O) eq	1.63	1.89	2.15	2.23	4.20	2.50
LOI (%)	0.33	0.47	0.16	0.27	0.32	0.40

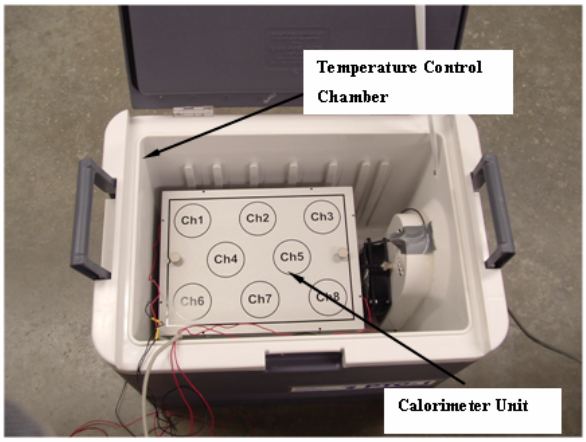


Fig. 1 Calorimetric unit placed in the environmental chamber.

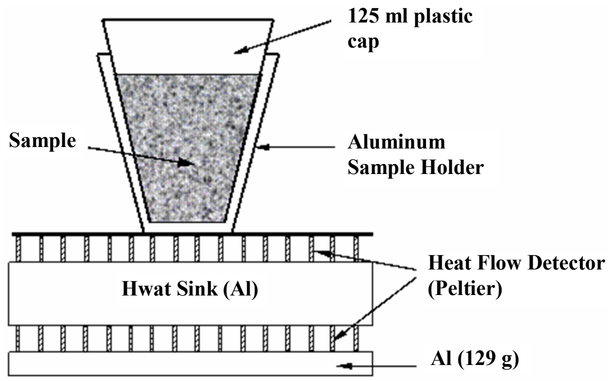


Fig. 2 Configuration of the calorimeter module.

time. As illustrated in **Fig. 2**, each unit of the isothermal calorimeter has an aluminum sample holder. The sample holder is placed on a heat flow sensor (Peltier thermocouple plate) that is attached on a common heat sink, which is a large block of aluminum. On the other side of the heat sink is another heat flow sensor and a piece of 129-gram aluminum block. This aluminum block is used as a reference to reduce the noise signal in this conduction calorimeter.

When a sample is placed in the calorimeter unit, the heat produced by hydration will flow rapidly to its surroundings. The main route for heat exchange between the sample and the surroundings is through the heat flow detector. The heat flow, caused by the temperature difference across the sensor, creates a voltage signal proportional to the heat flow. This voltage signal is corrected by the reference and converted to the rate of heat evolution by applying the calibration factor.

To conduct a calorimetry test, a mortar sample was mixed according to ASTM C 305. Right after mixing, approximately 100 grams of the fresh mortar was poured into 125 ml (4.2 fl oz) plastic cups. The cups were then placed into the sample holders of the calorimeter. The readings of the voltage were recorded every 30 second and converted to the rate of heat evolution. A total testing time was 24 hours for most samples, except for the samples cured at 10ºC, for which the total testing time of 48 hours was used due to the slow hydration of cementitious materials at that temperature.

A total of 128 calorimetry tests, 118 ASTM set time tests, and 117 mortar strength tests were performed in the present study.

3. Test results and discussions

3.1 Calorimeter equipment evaluation

Before used for formal tests, the calorimeter equipment was calibrated by a set of 50 Ω resistors under a certain voltage. The variations in the test results measured from different units of the calorimeter and the results from single and different operators were examined. The results showed that the variations caused by the equipment and operators were less than 5%. The simple isothermal calorimeter and its test procedure used were repeatable. Detailed information on the calorimeter calibration process and results can be found in a separate publication (Wang *et al*. 2006).

3.2 Calorimetric characterization of cement-based materials

In the material characterization study (as described below), four samples of each mortar mix were tested in four channels of the isothermal calorimeter. The calorimetry tests were conducted under 10, 20, 30, and 40 °C. The selected results are presented in **Figs. 3-8.**

3.2.1 Effects of cements types and sources

Figure 3 shows the rate of heat generation of mortars made with three different types of cement (Types I, III, and ISM). There were clear differences in the heat evolution curves among the mortars made with different cements. As seen in **Table 1**, Type III cement had a similar chemical composition to Type I cement but much higher fineness. Since the finer cement had a larger specific area to contact and react with water, the Type III cement displayed a higher rate of heat evolution during hydration. The blended cement, Type ISM cement, contained 80% Type I cement and 20% slag. Since the slag hydration was relatively slow and generated less heat than portland cement, the mortar made with Type ISM cement showed a reduced rate of hydration at early age and delayed peak in its heat evolution curve (Kishi and Maekawa 1994).

Figure 4 shows the hydration curves for five Type I/II cements collected from different cement manufacturers. Although all classified as Type I/II cement, these cements had different chemical compositions (see **Table 1**) and therefore displayed different heat evolution curves. The figure demonstrates that the calorimeter tests used in the present study can clearly show the difference among the same type of cements coming from different sources.

3.2.2 Effect of water-to-cementitious materials ratio (w/cm)

Figure 5 shows that as w/cm ratio decreased, the peak of heat evolution of the tested mortar was shifted slightly to the left. This is consistent with previous studies (Danielson 1962; Taplin 1959). One of the possible mechanisms for this phenomenon is that the initial ion concentration for mixes with different w/cm was different. For the mortar with a low w/cm, more cement particles were dispersed in a given volume of water when compared with the mortar having a high w/cm. Due to the relatively higher chemical ion concentration in the low w/cm mortar system, a more rapid hydration occurred and a slightly higher rate of heat evolution was therefore measured at the early age. After a certain time of cement hydration, the mortar with a low w/cm started to set earlier than the mortar with a high w/cm due to the hydration products coated the surfaces of the unhydrated cement particles and filled the limited spaces among the cement particles. As a result, the cement hydration slowed down. Consequently, the main peak of the hydration curve was only shifted rather than significantly changed.

3.2.3 Effect of fly ash type and replacement level

Figures. 6 and **7** show the influence of fly ash type and replacement level on the rate of heat generation. As the fly ash replacement level increased (**Fig. 6**), the region between the end of the first peak and the beginning the second peak, also called "dormant period", of the mortar

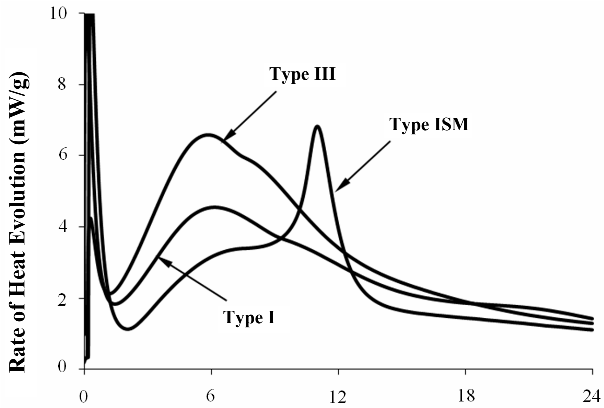


Fig. 3 The rate of heat generation for different cements under 20 °C (w/cm=0.43, s/cm=2.2).

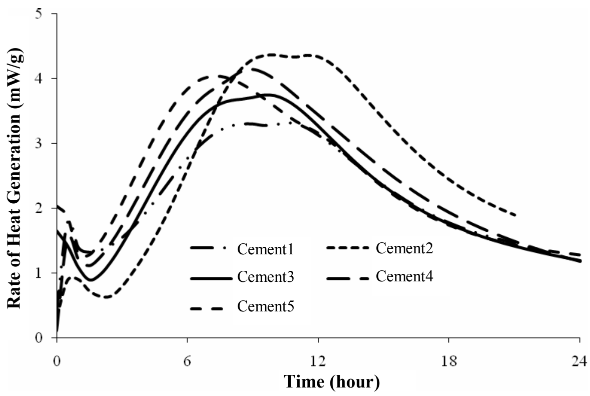


Fig. 4 Effect of cement sources on heat of hydration (w/cm=0.43, s/cm=2.2, cured at 20 °C).

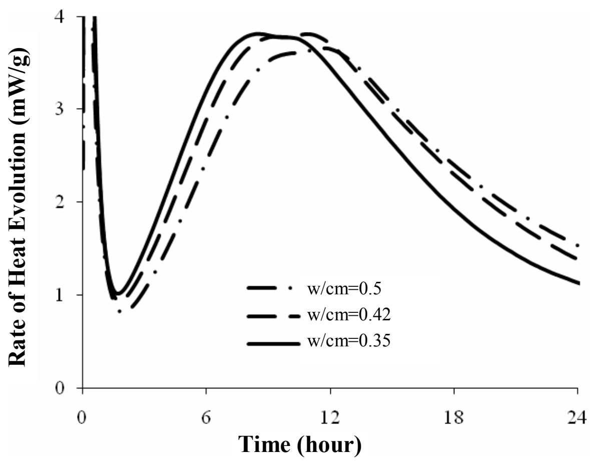


Fig. 5 Rate of heat generation for mortars with different water-to-cementitious ratio (Type I/II cement, s/cm=2.2, cured at 20 °C).

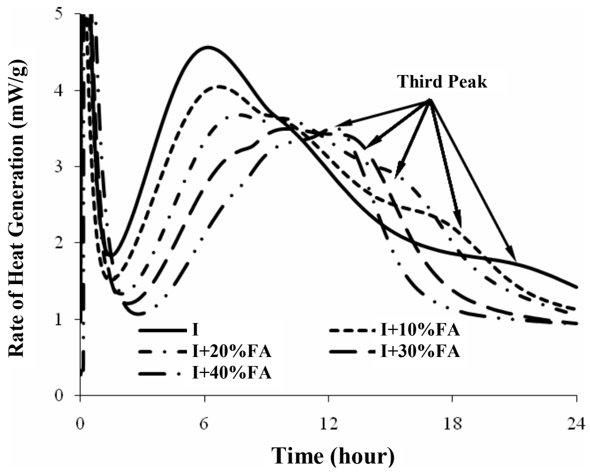


Fig. 6 Effect of fly ash replacement level on heat of hydration (source B, w/cm=0.43, s/cm=2.2, cured at 20ºC).

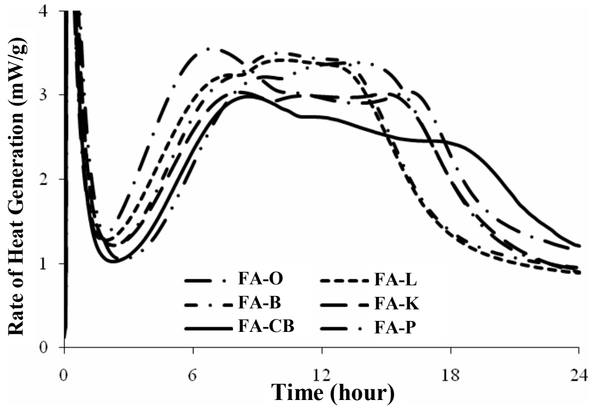


Fig. 7 Effect of fly ash sources on heat of hydration (30% replacement, w/cm=0.43, s/cm=2.2, cured at 20ºC).

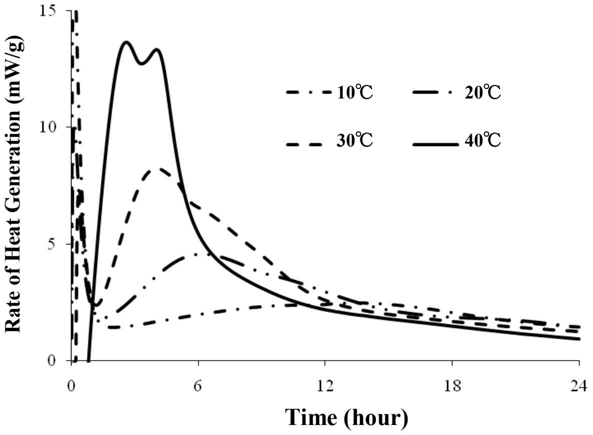


Fig. 8 Effect of curing temperature on heat of hydration (Type I cement, w/cm=0.43, s/cm=2.2)

and the time to reach the second heat evolution peak were increased. The value of the second peak was decreased due to less heat generation from the pozzolanic reaction. The third peak became more apparent with the increased fly ash replacement level.

Figure 7 shows the heat evolution curves of mortar samples made with fly ashes from different sources at the same replacement level (30%). The heat evolution curves of the mortar samples were similar but not the same, which reflected the differences in the chemical properties of the Class C fly ashes used (see **Table 1**).

3.2.4 Effect of curing temperature

Figure 8 shows the typical effect of environmental or testing temperature on the cement hydration process. The cement hydration was generally accelerated at early ages with increased curing temperature. However, at the end of the measurement period, the rate of hydration decreased as the temperature increased. The main peak, which was primarily attributed to C_3S hydration, appeared earlier and the peak value increases significantly as the curing temperature increased. The main peak was also much narrower than that of mortar cured at a lower temperature. These observations are again consistent with previous research (Escalante-Barcia and Sharp 2000) and related to the microstructure development of the cement-based materials (Kjellsen and Detwiler 1992).

3.3 ASTM test results

3.3.1 Mortar set time from ASTM C430 tests

Table 3(a) summarizes the set times of all mortar samples. For all curing conditions, mortars made with Type III cement had the lowest initial and final set times due to higher rate of hydration. Unlike Type III cement, ISM cement had longer set times compared with Type I cement due to slag replacement. At 20ºC, there were 36 and 48 minutes of delay for the initial and final set times, respectively. This is consistent with the research results from Hogan and Meusel (1981), which indicated 10- to 20-minute delay for each 10% addition of slag. The curing temperature had the same effect on the set times for all different mortars. The set times increased when the curing temperature decreased. The effect of temperature was more apparent for high fly ash replacement levels.

Fly ash replacement increased both initial and final set times of a mortar regardless of curing temperature, which was in agreement with previous research (Brooks 2002; Brooks *et al.* 2000; Eren *et al* 1995) and results from the retardation and water reduction effects of fly ash in mortar or concrete. Set times were also different for cements with fly ash from different sources. The cement with fly ash from source O had shorter set times compared with cements with other fly ashes. This may again be caused by the different chemical composition and physical properties of each fly ash.

3.3.2 Mortar strength development measured from ASTM C 109 tests

Figure 9 shows the strength test results of selected mortars. More strength results can be found in another publication (Wang *et al.* 2006). The results, as described

Table 3a Setting times determined from ASTM method at 10, 20, 30, and 40 °C.

Cement		Fly Ash		Initial Setting Time (hour)				Final Setting Time (hour)			
Type	%	Source	%	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C
I	100	-	0	4.9	3.1	1.8	1.5	7.6	4.5	2.6	2.1
III	100	-	0	-	2.3	1.6	1.2	-	3.4	2.3	1.7
ISM	100	-	0	6.2	3.7	2.5	-	10.3	5.3	3.7	-
I	90	O	10	5.7	3.6	2.5	1.6	8.6	5.2	3.5	2.3
I	80	O	20	6.7	4.1	2.7	1.9	10.1	5.8	3.7	2.6
I	70	O	30	7.7	4.4	3.2	2.1	11.6	6.3	4.4	2.9
I	60	O	40	8.7	4.8	3.5	2.4	12.6	6.6	4.7	3.3
I	90	K	10	6.3	3.8	2.4	1.6	10.2	5.5	3.4	2.3
I	80	K	20	7.3	4.5	2.9	2.0	11.1	6.4	4.3	2.7
I	70	K	30	9.5	5.5	4.1	2.2	13.7	7.6	5.9	3.0
I	60	K	40	10.1	5.9	4.7	2.5	14.5	8.3	6.5	3.4
I	90	L	10	5.9	4.1	2.2	1.7	9.1	5.9	3.1	2.3
I	80	L	20	6.7	4.9	2.6	2.0	10.0	7.0	3.5	2.8
I	70	L	30	8.4	4.8	3.0	2.4	12.5	7.0	4.1	3.2
I	60	L	40	9.8	5.2	3.5	2.6	14.0	7.2	4.8	3.6
I	90	B	10	6.4	3.8	2.4	1.7	9.6	5.4	3.4	2.4
I	80	B	20	7.6	4.8	2.9	1.9	11.3	6.8	3.8	2.6
I	70	B	30	8.7	4.7	3.3	2.3	13.0	6.5	4.6	3.3
I	60	B	40	10.5	5.4	3.8	2.8	14.7	7.4	5.2	3.7
I	90	P	10	8.2	3.7	2.3	1.7	12.6	5.3	3.2	2.3
I	80	P	20	9.8	4.4	2.9	2.2	13.7	6.1	4.0	2.9
I	70	P	30	11.5	5.5	3.4	2.3	16.2	7.3	4.7	3.1
I	60	P	40	13.1	6.1	4.1	2.8	17.8	8.0	5.4	3.8
I	90	C	10	8.0	4.4	2.4	1.7	12.9	6.4	3.2	2.3
I	80	C	20	8.9	5.2	2.8	2.1	13.3	7.2	4.0	2.8
I	70	C	30	11.1	5.8	3.3	2.4	16.2	8.0	4.3	3.3
I	60	C	40	11.6	6.3	3.9	2.9	16.8	8.7	5.2	3.9
I/II	100	-	0	-	4.9	-	-	-	6.8	-	-
I/II	100	-	0	-	5.1	-	-	-	7.1	-	-
I/II	100	-	0	-	4.0	-	-	-	6.1	-	-
I/II	100	-	0	-	5.2	-	-	-	7.4	-	-
I/II	100	-	0	-	5.6	-	-	-	7.5	-	-
Max	100	-	0	-	4.8	-	-	-	6.7	-	-

below, are typical and consistent with previous research findings (Mindess *et al*. 2003; Neville 1996):

(1) Mortars made with different types of cement had different rates of strength development. The mortar made with Type III cement displayed clearly higher strength at a given age than those made with Types I and IS, especially at a relative low curing temperature;

(2) High temperature curing facilitated mortar strength development. The facilitation was more effective for mortars containing slag or fly ash;

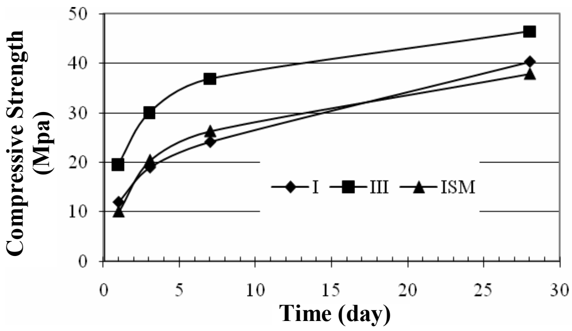
(3) For a given fly ash, mortar strength decreased with the level of the fly ash replacement at an early age. The effect of the fly ash replacement level on mortar strength reduced as the curing temperature increases;

(4) At a given replacement level, mortars made with different types of fly ashes exhibited different strength values.

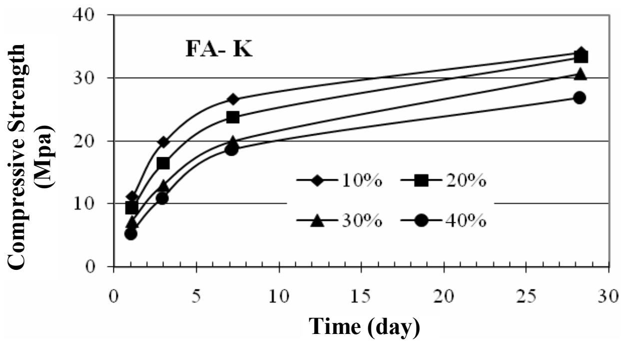
(5) As described in the following section, the ASTM test results were correlated with the results obtained from calorimetry tests, and the relationships were used for predicting mortar performance.

4. Performance prediction of cementitious materials based on the calorimetric test results

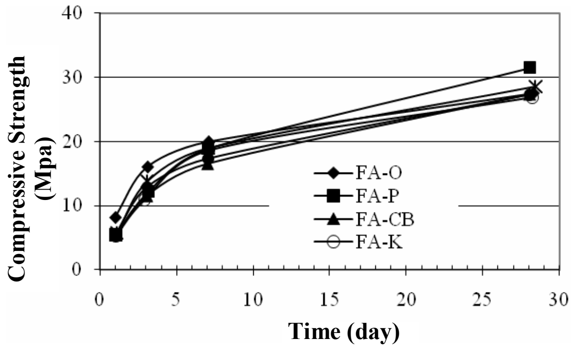
Research has demonstrated that concrete performance can be predicted from calorimetry test results, and the calorimetry test results can be used for concrete quality control (Taylor *et al*. 2006; Cost and Knigth 2007; Ballim 2004). As discussed in the previous section, the present study had illustrated the clear differences in the heat evolution curves of the mortars made with different types of cements (**Fig. 3**), a given type of cement from



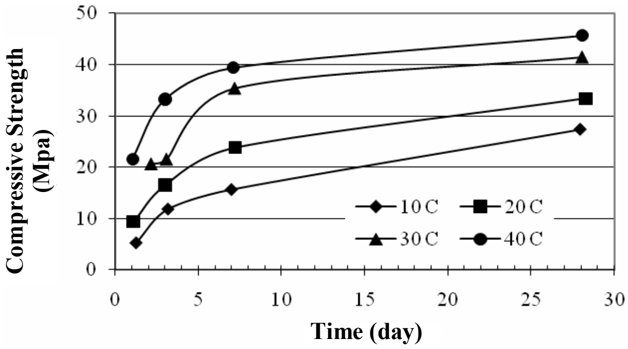
(a) Effect of cement type on strength development



(b) Effect of Fly ash replacement level on strength development



(c) Effect of Fly ash sources on strength development (40% fly ash replacement)



(d) Effect of curing temperature on strength development type K fly ash, 20% replacement)

Fig. 9 Strength development of mortars made with different cementitious materials and cured under different temperatures (w/cm=0.43, s/cm=2.22).

different sources (**Fig. 4**), different w/cm (**Fig. 5**), different fly ash replacement levels (**Fig. 6**), a given replacement level with different fly ash sources (**Fig. 7**), and different curing temperatures (**Fig. 8**). These results imply that concrete heat evolution test results can also be used for pre-screening cement-based materials, flagging the changes in cementitious materials, and verifying mix proportions (such as w/cm). In addition to these applications, as discussed later, the area under a heat evolution curve was closely related to the strength of the tested material. Therefore, changes in the heat evolution curves also provide engineers with the insight onto the changes in strength of the materials at the early age. Furthermore, as described below, the two points (peak and zero values) on the heat derivative curve (**Fig. 10**) could be used to predict initial and final set times of the tested materials.

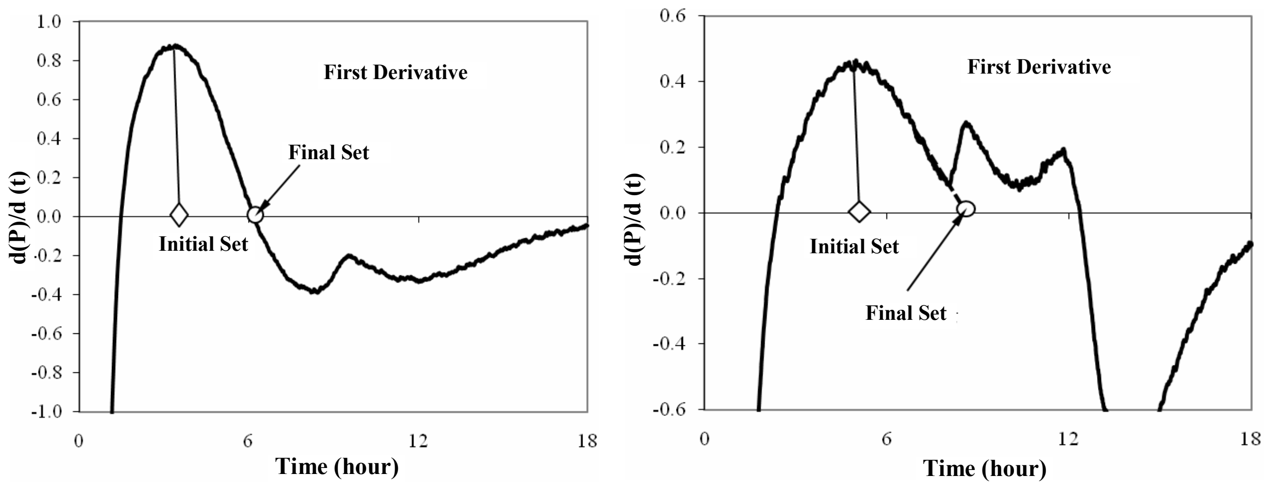
4.1 Prediction of concrete set time from heat evolution curve

Concrete set times are normally determined from the mortar sieved from the fresh concrete and tested according to ASTM C 403. This method is time and labor consuming, especially, for the concrete having a long set time. The accuracy of the ASTM method is also affected by the skill of the operator. In addition to the ASTM method, recent research has studied the use of concrete temperature to determine thermal set times. ASTM is proposing a new method to determine set times based on the first and second derivatives of concrete temperature history. Sandberg and Liberman (2007) determined the set times using both derivatives and fraction methods based on concrete temperature development under a semi-adiabatic condition. The set times were correlated to ASTM set times. However, for the semi-adiabatic method, the effect of curing temperature is measured implicitly and could not illustrate the setting behavior of concrete under isothermal conditions. The proposed method, as introduced below, is able to study the effect of curing temperature, requires little labor compared to ASTM C 403, and is less operator dependent.

Setting of concrete is a transition period between the fluidity and rigidity stages (Mindess *et al*. 2003; Mehta and Monteiro 1986). Concrete setting behavior is controlled by its three-dimensional microstructure development that involves new phase growth, nucleation, percolation, and networking of cement hydration products (Nonat 2006). These processes are greatly related to the cement hydration process, which can be simply characterized by its heat evolution (Neville, 1996). Therefore, it is rational to determine concrete set time from the heat evolution curve of the mortar sieved from the concrete.

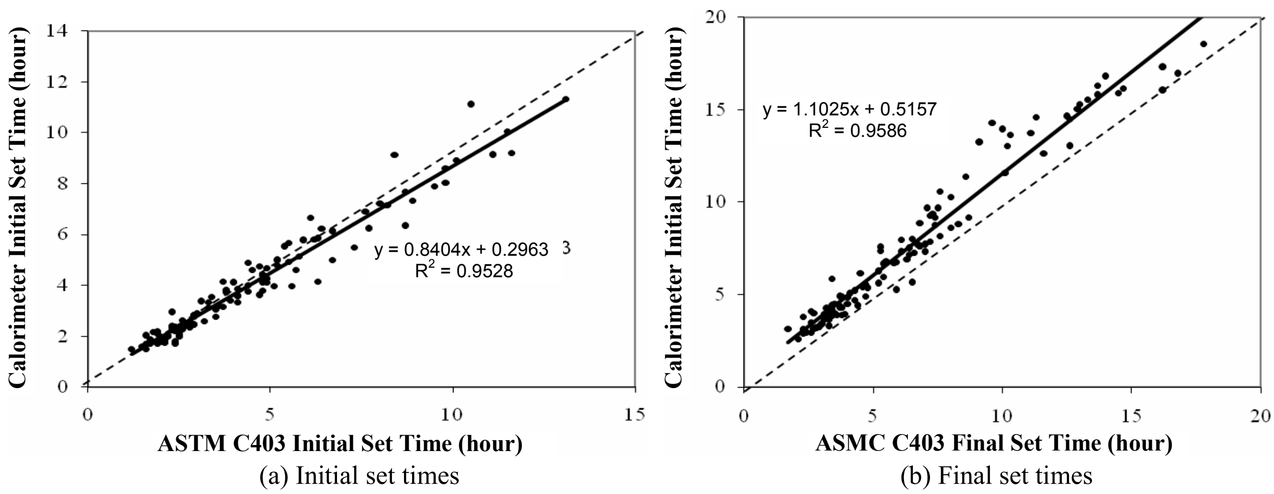
Figure 10 demonstrates the method for determining set time of a mortar from a calorimetry test result, which is similar to the method used for the AdiaCal calorimeter data analysis (Sandberg and Liberman 2007). In this method, the first derivative of the rate of heat evolution (P) curve with respect to time (t), $d(P)/d(t)$, is derived from the original heat evolution test data. At the point when the first derivative curve reaches its highest value, the increase in the rate of heat generation is the fastest. This point is around the starting time of the 2nd hydration peak and should be related to the initial set time. Therefore, in this paper, this point is defined as the initial set of the tested materials. After this point, the first derivative value starts to decrease. When the value of the first derivative drops to zero, it indicates that the rate of heat generation of the material starts to slow down. The time of this point is defined as the final set of the tested materials.

As mentioned before, for the mortar or concrete containing supplementary cementitious materials, either slag or fly ash, a third peak is generally seen clearly in the heat evolution curve. **Figure 10(b)** shows the determination of the set time of the sample with 40% fly ash replacement. As seen in the figure, there were three peaks in the positive sides of the heat evolution curve. The initial thermal set of the tested mortar is still defined as the time at which the first derivative of the heat evolution curve reaches its highest value. In contrast to the mortar made with 100% Portland cement, the first derivative of the rate of heat evolution of the mortar with fly ash started increasing again before descending to zero. In order to determine the final set under this situation, the line A in **Fig. 10(b)** was extended to cross



(a) Cement sample (b) Cement with 40% fly ash.

Fig. 10. Determination of set times from heat evolution curve.



(a) Initial set times (b) Final set times

Fig. 11 Relationship between the set times from ASTM C 403 and calorimetry tests.

with the time-axis, and the intersecting point is defined as the final set time of the mortar containing fly ash.

Table 3(b) presents the set times determined from the heat evolution curves of all mortar mixes tested in the present study. **Fig. 11** illustrates that the thermal set times determined from the calorimeter method had good relationships with the set times determined from the ASTM C403 method. For the initial set, the calorimetry test results were slightly shorter than the ASTM results, especially for the materials that had a long set time. However, there was a significant linear relationship with an R^2 value of 0.95. In contrast to initial set time, **Fig. 11** shows that the final set times determined by the calorimetry method was a little longer than those determined by the ASTM method. Again, the linear relationship between these two test results was strong with an R^2 value of 0.96.

The differences between the two test results may result from the following facts:

(1) The two methods have very different definitions for concrete set time. The ASTM C 403 method is based on the penetration force, while the calorimetry method is based on the rate of chemical reaction; and
(2) The two test methods provide test samples with different environmental/temperature conditions. During the ASTM C 403 tests, mortar samples are tested in a 150 mm (diameter) x 178 mm (height) container and under a room-temperature condition. Due to the semi-adiabatic effect, the temperature of the tested samples increased with time. However, during the calorimetry tests, the samples were in a controlled-environment condition. The temperature of the samples was kept constant.

Despite of the small difference between the two test results, the heat evolution curves from the simple isothermal calorimeter test could be used for forecasting concrete set time.

Table 3b Set times determined from calorimetry method at 10, 20, 30, and 40 °C.

Cement		Fly Ash		Initial Setting Time (hour)				Final Setting Time (hour)			
Type	%	Source	%	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C
I	100	-	0	4.7	3.4	2.1	1.6	10.6	6.2	4.1	2.6
III	100	-	0	-	3.0	2.0	1.5	-	5.9	3.8	3.1
ISM	100	-	0	5.8	3.2	2.2	-	13.6	7.6	4.3	-
I	90	O	10	4.6	3.2	2.0	1.5	11.4	6.3	4.0	2.9
I	80	O	20	5.0	3.9	2.4	1.7	11.6	6.7	4.3	2.9
I	70	O	30	6.3	3.8	2.6	1.7	12.6	6.9	4.4	3.2
I	60	O	40	6.4	4.1	2.8	1.8	13.1	7.3	4.9	3.3
I	90	K	10	4.2	3.7	2.3	1.7	13.0	6.8	4.2	3.0
I	80	K	20	5.5	4.6	2.8	1.8	13.7	7.5	4.7	3.2
I	70	K	30	7.9	4.9	3.3	2.0	16.3	8.2	5.3	3.4
I	60	K	40	8.9	5.8	3.6	2.3	15.9	8.8	5.7	3.9
I	90	L	10	5.8	3.6	2.0	1.9	13.3	6.8	4.0	3.1
I	80	L	20	6.1	4.1	2.6	2.0	14.0	7.3	4.5	3.2
I	70	L	30	9.1	4.4	2.9	2.2	14.7	7.7	5.1	3.7
I	60	L	40	8.6	5.0	3.0	2.3	16.8	9.3	5.4	3.9
I	90	B	10	6.2	3.8	2.4	1.8	14.3	6.7	4.4	3.0
I	80	B	20	6.9	4.4	2.8	2.2	14.6	7.6	4.9	3.5
I	70	B	30	7.7	4.7	3.3	2.4	15.3	8.0	5.4	4.1
I	60	B	40	11.1	5.5	3.8	2.6	16.2	9.2	6.3	4.9
I	90	P	10	7.1	4.1	2.3	1.7	14.5	7.4	4.3	3.0
I	80	P	20	8.0	4.9	2.8	2.0	15.8	8.0	4.8	3.3
I	70	P	30	10.1	5.7	3.5	2.2	17.3	9.4	5.5	3.6
I	60	P	40	11.3	6.7	3.6	2.4	18.6	10.3	6.0	3.9
I	90	C	10	7.2	4.0	1.7	1.7	15.0	7.1	3.8	3.0
I	80	C	20	7.3	4.8	2.5	1.9	15.6	7.9	4.5	3.2
I	70	C	30	9.2	5.1	3.1	2.3	16.1	8.6	5.2	3.6
I	60	C	40	9.2	5.9	3.4	2.5	17.0	9.2	5.6	3.9
I/II	100	-	0	-	4.3	-	-	-	8.9	-	-
I/II	100	-	0	-	4.0	-	-	-	9.7	-	-
I/II	100	-	0	-	4.1	-	-	-	7.3	-	-
I/II	100	-	0	-	5.0	-	-	-	8.8	-	-
I/II	100	-	0	-	4.0	-	-	-	9.7	-	-
Max	100	-	0	-	3.8	-	-	-	7.7	-	-

4.2 Identifying materials incompatibility

Materials compatibility is an important issue for concrete construction. Incompatible materials can cause unexpected or unacceptable performance features such as flash set and delayed early strength development. Research has indicated that use of fly ash containing high reactive aluminate together with Type A water reducer in concrete has a potential to cause incompatibility problem and high temperature curing often increases the risk of incompatibility (FHWA 2006). The major cause of incompatibility is a shortage of soluble sulfate with significant amounts of SCMs and admixtures (Sandberg and Roberts 2005; Wang *et al.* 2006) . The Class C fly ash normally contains Reactive calcium aluminate, which will consume the soluble sulfate in the cement system and cause a potential deficiency of sulfate in the mixture.

In the present study, a known incompatible mix (IS+FA+WR), made with Type IS cement, 25% Class C fly ash, and water reducer (WR), was obtained and tested at 30ºC. **Fig. 12** shows the heat evolution curve of the mix and its reference mixes (IS and IS+FA). As shown in the figure, when 25% fly ash was used to replace IS cement, the value of the main (second) peak of the heat evolution curve was reduced and the time for the mortar sample to reach the peak was postponed. However, the broad area under the main heat evolution curve of the IS+FA sample indicated that significant cement hydration was processed, and the IS+FA mix performance was normal. However, when the WR was added to the IS+FA system, the time for the mortar sample to reach the peak rate of heat evolution was significantly reduced. A sharp exothermal heat evolution started at early age, which is commonly caused by uncontrolled aluminate hydration, and there was little cement hydration from 6 to 12 hours, which suggested most C_3S hydration of the mortar might be delayed, not showing during the testing time period. The severely delayed C_3S reaction can cause the slow strength development.

In addition to material compatibility, the curing temperate could also cause incompatible problems, especially for concrete mixture with fly ash. **Figure 13** shows the results for a mix with 20% Type C fly ash under different curing temperature. At the test temperature of 20°C and above, all calorimetry curves displayed a regular shape and possessed a certain peak height and width, indicating no incompatibility problem. However, when the temperature dropped to 5°C, the rate of heat generation was significantly reduced. There was no major hydration peak during the first 72 hours. Therefore, the mixture would have prolonged set times and slow strength gain and cause potential construction problems.

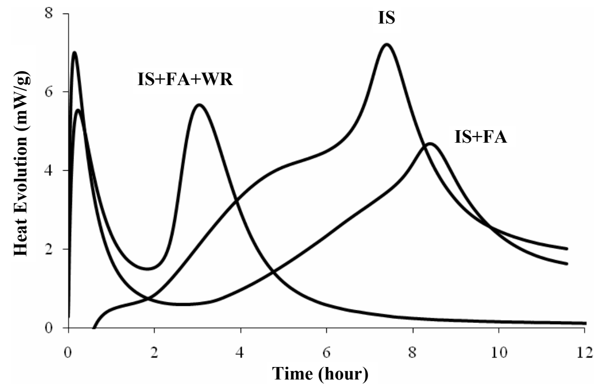


Fig. 12. The influence of fly ash and water reduce on material compatibility (w/cm=0.45, s/cm=1.68).

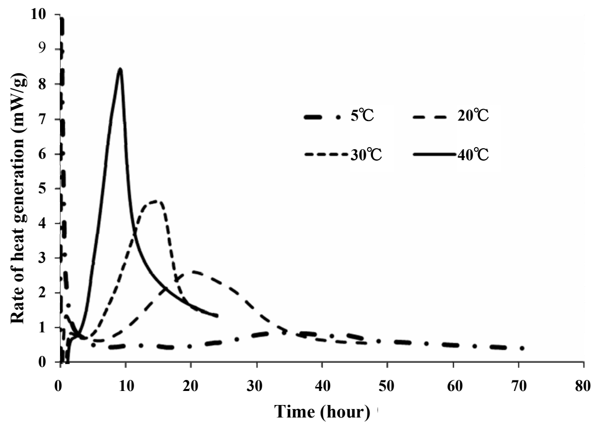


Fig. 13. The influence of temperature on material compatibility (Type I cement, w/c=0.45, s/cm=2.45).

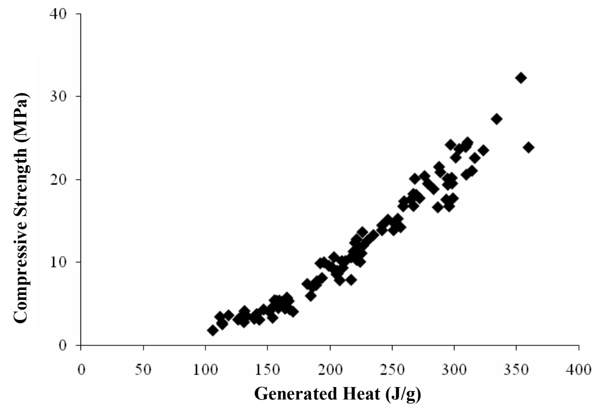


Fig. 14. Relationship between strength and measured heat for all mortar samples.

4.3 Prediction of early-age strength

Figure 14 correlates strength of mortars with the measured heat in the corresponding mortar. The measured heat was calculated as the area under the rate of heat generation curve from the beginning of the calorimetry test to the time when the corresponding mortar strength was tested. A very good relationship is seen in the figure for all mortar samples tested, regardless the mortar materials and mix proportions. Based on this figure, the early strength of concrete can be predicted, and the information can be used for concrete formwork removal and pavement saw cutting.

5. Conclusions

The following findings and conclusions can be drawn from the present study:

(1) The selected isothermal calorimeter device is reliable, capable, and sensitive enough to differentiate the characteristics of the mortars made with different materials and subjected to different curing conditions.

(2) The calorimeter test results can be used to (1) flag changes in cementitious materials (such as material types and sources), (2) pre-screen concrete materials and/or mix design (such as replacement level of supplementary cementitious materials), (3) identify incompatibility of cementitious materials, and (4) forecast setting time and early-age strength. Since the heat evolution curve illustrates the amount and rate of heat generation, the calorimeter results can also be used to predict the risk of concrete thermal cracking while coupled with other computations.

(3) The set time of cement-based materials can be well predicted from the first derivative of the heat evolution curve measured by the isothermal calorimeter used. The predicted results have a very good relationship with those from the ASTM C403 tests.

(4) Consistent with the previous research, the area under the calorimeter curve, or the total heat generated from a tested material, is closely related to the strength of the tested materials.

It is noted that conclusions 2-4 above are not directly related to the equipment used, and they could also result from other isothermal calorimeter measurements.

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