Developing a Simple and Rapid Test for Monitoring the Heat Evolution of Concrete Mixtures for Both Laboratory and Field Applications

National Concrete Pavement
Technology Center

Phase II Report
January 2007

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16. Abstract

Recently, activities and interest in monitoring the heat evolution of cement hydration in concrete have increased. This is because the development of early-age concrete properties (such as workability, setting time, strength gain, and thermal cracking resistance) is predominantly influenced by the kinetics of cement hydration. Various test methods are currently available for measuring heat of cement hydration; however, most existing methods require expensive equipment, complex testing procedures, and/or extensive time, thus making them unsuitable for field application. Although ASTM C 186 is used for determining the heat of hydration of cement, there is no standard test method for concrete.

The overall object of this three-phase study is to identify, develop, and evaluate a standard test procedure for monitoring pavement concrete using a calorimetry technique. It is envisioned that the newly developed calorimetry test method will be able to verify appropriate concrete proportions, to identify potentially incompatible materials and conditions, and to predict concrete performance. The primary objective of Phase II (presented in this report) is to establish a standard test procedure as well as the methods for interpreting the calorimeter test results.

The newly developed calorimeter test is completed more quickly than ASTM C 186, in approximately 24 hours. Among a number of uses, the test can be utilized as a quality control measure for prescreening concrete materials and a prediction tool for early-age cracking. The Phase II results demonstrate that the new calorimetry test method has a high potential for detecting concrete incompatibility problems, predicting fresh concrete properties (such as set time), and assessing hardened concrete performance characteristics (such as strength gain and thermal cracking).

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DEVELOPING A SIMPLE AND RAPID TEST FOR MONITORING THE HEAT EVOLUTION OF CONCRETE MIXTURES FOR BOTH LABORATORY AND FIELD APPLICATIONS

Phase II Report
January 2007

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EXECUTIVE SUMMARY

This project was designed to identify, develop, and evaluate a standard test procedure for monitoring performance of pavement concrete materials using a relatively simple, economical, and reliable calorimetry device.

The project includes three phases. Phase I, completed in December 2005, aimed to identify the user needs for a calorimeter test and potential applications of calorimeter test results. The goals of Phase II were to establish a standard test procedure as well as the methods for interpreting the calorimeter test results. Phase III, a future project, will verify the major applications of the calorimeter test method and develop the specification for calorimeter testing of field concrete.

Phase II included the following work items:

- Performed a series of lab tests for approximately 120 mortar mixes using a Thermometric isothermal calorimeter
- Tested the set time and strength development for these mortar mixes
- Developed the heat index method for interpretation of the calorimetry test results
- Studied the relationships between the mortar set times obtained from the calorimetry and ASTM tests
- Identified the potential applications of the calorimeter test results
- Performed two field tests using AdiaCal semi-adiabatic calorimeter
- Estimated pavement performance using HIPERPAV and field calorimetry data

The Phase II results demonstrate that the calorimetry test method has a high potential for detecting concrete incompatibility problems, predicting fresh concrete properties (such as set time), and assessing hardened concrete performance (such as strength gain and thermal cracking). Some specific findings of the Phase II study include the following:

- The test method developed for the selected isothermal calorimeter device is easy and repeatable.
- The calorimeter test can be used to differentiate the heat evolution of mortars made with different materials and subjected to different curing conditions.
- The calorimeter test can be used to identify material incompatibility and to flag cementitious changes.
- The heat indexes, related to the first derivative of the calorimeter curve and the area under the curve, are able to characterize the features of mortar. They can also be used to predict the mortar set time and early-age strength (up to two days).
- Incorporated with the HIPERPAV computer program, calorimeter test results are able to provide insight into the risk of thermal cracking in field concrete.
- The selected semi-adiabatic calorimeter test device (AdiaCal) is also easy to use. The test result provides a very good prediction on the set time of field concrete.

INTRODUCTION

Background and Problem Statement

Recently, activities and interest in monitoring the heat evolution of cement hydration in concrete have increased. This is because the development of early-age concrete properties (such as workability, setting time, strength gain, and thermal cracking resistance) is predominantly influenced by the kinetics of cement hydration. Hydration of cementitious materials in a concrete mixture results in a number of exothermic chemical reactions that liberate heat. The heat evolution process is strongly influenced by the chemical and physical properties of Portland cement, supplementary cementitious materials (SCMs), chemical admixtures, concrete mix proportions, construction procedures, and curing conditions of concrete. As a result, deviations in the quantities and characteristics of the concrete constituents can be detected, as well as the effects of construction conditions, and concrete performance can be predicted by monitoring the heat of cement hydration (*1*, *2*).

Modern concrete mixtures have a very complex chemical system. The complexity of the mixtures results from the number of ingredients used (such as various 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 quickly gaining attention. Abnormal early hydration resulting from “incompatibility” of concrete materials has resulted in erratic set and strength-gain behavior and the associated finishing, curing, and early-age cracking behaviors. The influences of construction and environmental conditions, such as cold and hot weather, often aggravate these problems. However, the existing guidance lacks information on the proper test methods for identifying these problems.

Lately, the advances in using thermal measurements of the early heat development of concrete mixtures in the laboratory have demonstrated that calorimetry tests have a high potential for detecting concrete incompatibility problems, predicting fresh concrete properties (such as set time), and assessing hardened concrete performance (such as strength gain and thermal cracking) under various climatic conditions (*3*, *4*).

Various test methods are currently available for measuring heat of cement hydration; however, most existing methods require expensive equipment, complex testing procedures, and/or extensive time, thus making them unsuitable for field application. Although ASTM C 186 is used for the determination of the heat of hydration of cement, there is no standard test method for concrete. The urgent need for standardization of concrete calorimeters has been addressed in Task 15 of the project report “Concrete Pavement Technology Long Term Research and Technology Plan” (*5*).

The overall object of the proposed study is to identify, develop, and evaluate a standard test procedure for monitoring pavement concrete using a calorimetry technique. It is envisioned that the newly developed calorimetry test method will be able to verify appropriate concrete proportions, identify potentially incompatible materials and conditions, and predict concrete performance.

The focuses of this study are (1) developing performance-based specifications for calorimetry equipment selection, which will be similar to the FHWA coefficient of thermal expansion (CTE) test equipment specification, (2) establishing standard test procedures, including methods for interpreting the calorimetry test results, and (3) verifying the major applications of the calorimetry technique with less expensive devices. The new calorimeter test is generally completed quicker than ASTM C 186, in approximately 24 hours. Among a number of uses, the test can be utilized as a quality control measure for prescreening concrete materials and a prediction tool for material incompatibility and early-age cracking.

Research Approach and Scope

The project was originally designed to consist of two phases. Phase I was to conduct a literature and experts survey, identifying the user needs for a calorimeter test and synthesizing existing test methods for measuring the heat of hydration. It started in October 2004 and was completed in August 2005. Phase II was to develop a prototype system, including the test equipment and procedure, associated models and software, and criteria for accepting the test results.

While working toward the objectives of this project in Phase I, the research team members developed a much clearer vision of the pavement industry’s specific needs for the calorimeter tests and identified practical future applications of the calorimeter tests. In Phase II, a more focused systematical study was carried out to bring test equipment, procedure development, heat evolution curve characterization, pavement performance prediction, and test/equipment specifications all together.

In Phase II, two available calorimeter devices, an isothermal calorimeter manufactured by Thermometric Inc. (approximately $8,000) and a semi-adiabatic calorimeter device made by AdiaCal (approximately $3,000), were studied. These devices were selected because they were likely to be purchased at a fair cost and produce results that could differentiate the heat signatures of various concrete materials in a short time span.

The specific research activities included the following items:

- Conducting a series of lab tests using the Thermometric isothermal calorimeter. A wide range of paste and mortar mixtures were tested to evaluate the effects of the concrete materials (i.e., ingredients, sources, and proportions), equipment, and environmental conditions on the calorimetry test results. Some mixes known to be incompatible were specially selected and tested (~120 total mortar mixes).
- Developing a method for interpretation of the calorimetry test results (heat indexes)
- Studying the relationships between the results from the calorimetry and ASTM tests (set time and strength)
- Identifying the potential applications of the calorimeter test results
- Performing two field tests using AdiaCal semi-adiabatic calorimeter
- Estimating pavement performance using HIPERPAV and field calorimetry data

Summary of Phase I Study

In Phase I, a collaborative research team consisting of members from the PCC Center, Iowa State University (ISU), and the Transtec Group worked on the following two major tasks:

- Task 1: Identify the user needs for a calorimeter test, including performance requirements and precision and bias limits.
- Task 2: Identify and synthesize existing test procedures for measuring the heat of hydration of concrete using calorimetry and other methods, including efforts both in the U.S. and abroad.

These tasks have been accomplished through three major activities: (1) collecting inputs and advice from the project technical working group (TWG), (2) conducting a literature survey, and (3) performing some trial tests at the PCC Center's research lab.

The project started with a kickoff meeting on October 1, 2004. All TWG and research team members attended the meeting. The TWG members included Mr. Gary Knight (Holcim), Dr. Paul Sandberg (WR Grace), Mr. Wes Woytowich (Lafarge), Dr. Peter Taylor (CTL), Dr. Anton Schindler (Auburn University), Mr. Todd Hanson (Iowa DOT), Mr. Gary Crawford (FHWA), and Mr. Leif Wathne (FHWA). Valuable inputs on the needs, importance, and current practices of various calorimeter tests were provided by the TWG members at the meeting. Broad discussions were held that addressed specific issues on the product development (e.g., product configuration, cost, test procedure, result interpretation, and application). These inputs and discussions have been summarized and thoroughly considered by the research team members in their recommendations for the new device development of the Phase II study.

A literature review on heat evolution tests was conducted, and the results were synthesized to provide the following information:

- Factors affecting the concrete heat evolution
- Existing devices and test methods for heat evolution measurement (type of calorimeter, configurations, procedures, measurements, advantages, disadvantages, applications, and accuracy)
- Existing temperature sensors and dataloggers (temperature range and sensitivity)
- Existing models for predicting heat of hydration and interpreting raw data
- Potential applications of the test results (such as predicting concrete set time, determining sawing/finishing time, identifying incompatibility problems, and checking cement characteristics for various sulfate phases)

A series of mini-tests was performed at the PCC Center using different Dewar devices to investigate the effects of device insulation, sample size, curing temperature, and mineral admixtures on heat evolution curves.

The results from the Phase I study indicate the following:

1. The factors affecting concrete heat evolution include cementitious material properties (such as chemical composition, sulfate content, and fineness), concrete mix design (water-to-cement ratio (w/c), replacement level of SCMs, and type and amount of chemical admixtures), and construction conditions (such as placement and curing temperatures). Limited research has been reported regarding the effects that dimensions of concrete pours or sample sizes have on heat measurements.
2. Existing calorimetry tests can be divided into three major categories: adiabatic, semi-adiabatic/isothermal, and isothermal calorimetry tests.
    - Adiabatic calorimeters (temperature loss < 0.02 k/h) are most commonly used for concrete tests. The materials used for heat insulation of the devices can be water, air, and heated containers, of which water insulation is the most popular choice. A major drawback of adiabatic calorimeters is that the test method does not account for the effect of curing temperature on concrete heat evolution.
    - Isothermal calorimetry tests, often used for studying the reaction of kinetics of cement pastes, are conducted at a constant temperature. The heat of cement hydration is directly measured by monitoring the heat flow from the specimen. The total heat evolution can be readily determined from the sum of the measured heat over time. However, isothermal tests do not take into account the cement reactivity change due to the change of temperature. It is hard to predict the temperature increase of concrete from these results. Thus, the conditions in the real structure where the temperature continually changes are not reflected. Both adiabatic and isothermal calorimeter tests generally take as long as a week to complete. Semi-adiabatic calorimeters allow some heat loss to the environment (maximum heat loss < 100 J/ (h·K)).
    - The semi-adiabatic curve of a tested material is generally lower than the curve from an adiabatic test. This heat loss is measured and accounted for in the calculation of heat flow under adiabatic conditions. Semi-adiabatic calorimetry test methods are suitable for pastes, mortars and concrete samples.
    - RILEM has conducted a “Round Robin” test program to compare the performances of different types of calorimeters. Fourteen different organizations participated in the program, using different calorimeters with the same materials and mixing proportions. They found that for all adiabatic tests, 50% of the adiabatic temperature rise variations were in a narrow range spanning only 2 K, and the specimen size and the temperature did not significantly affect the temperature rise. For the semi-adiabatic tests, the mean temperature rises were 2–3% below the results from the adiabatic tests, and the semi-adiabatic calorimeters were able to predict the adiabatic temperature rise.
3. Many simple and inexpensive calorimetry tests have been practically used by the cement and concrete industry. Most of these tests are semi-adiabatic calorimetry tests, and some (such as the unthermostated heat conduction test) are semi-isothermal calorimetry tests. The simple, inexpensive devices identified for heat evolution tests include Dewar, coffee cup, and sprayed-foam basket. These test methods generally provide critical feedback within 12–48 hours. They have been used for investigating the effects of SCMs or chemical admixtures on hydration and identifying the compatibility of these materials. However, the accuracy and sensitivity of such simple

tests are rarely reported.

4. There also are many different types of temperature sensors and dataloggers available for monitoring cement and concrete heat evolution. With different temperature ranges and accuracies, their costs range from $20 to $1,000. Models and computer programs for test data analyses are often developed for specific sophisticated heat evolution devices and sensors, rather than simple and inexpensive ones.
5. In addition to the maturity/strength prediction, concrete heat evolution test results can also be used for
    - flagging changes in cementitious materials,
    - prescreening materials and/or mix design,
    - identifying incompatibility of cementitious materials,
    - verifying mix proportions,
    - forecasting setting time,
    - estimating sawing and finishing time, and
    - predicting risk of thermal cracking.

After reviewing the initial results from the Phase I study, the research team members discussed and identified the major gaps between the existing calorimeter tests and the needs of the pavement industry regarding calorimeter tests. The research team found that, although various calorimeter tests have been conducted for assorted purposes and the potential uses of calorimeter tests are clear, there is no consensus on how to utilize the heat evolution curves to characterize concrete materials or how to effectively relate the characteristics of heat evolution curves to concrete pavement performance. The research team determined that the goal of the Phase II study should be to close these gaps.

EXPERIMENTAL WORK

Materials

Nine cements (one Type I, one Type III, two Type ISM, and five Type I/II from different sources) and six Class C fly ashes (from different sources) were used in this research project. Type I and III cements were from the Holcim plant at Mason City, Iowa. Type I/II cements were from the Lafarge plants at Davenport, Iowa; Grand Chain, Illinois; Sugar Creek, Missouri; Fredonia, Kansas; and Tulsa, Oklahoma. Type ISM cements were from the Lafarge plant at Davenport, Iowa, and the Holcim plant at Mason City, Iowa. The chemical properties of the cements are shown in Table 1. The Type III cement had a much higher Blaine value (551 m^2/kg) than the Type I cement (368 m^2/kg). The Type I cement had higher C_3S content and lower C_2S content (58.83% and 10.64%, respectively) than the Type III cement (53.3% and 20.74%, respectively). Both cements had about 10% C_3A. The five Type I/II cements from different sources had different chemical compositions. The C_3S in these cements ranged from 43.5% to 66.0%. C_2S content was 7.7%–28.8%. The C_3A content was similar for all five cements (6.4–8%). The SO_3 contents ranged from 2.66% to 3.5%.

Table 1. Chemical composition of cement

Chemical Composition	**Type I**	**Type III**	**Type I/II-1**	**Type I/II-2**	**Type I/II-3**	**Type I/II-4**	**Type I/II-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	5.3	4.5	4.29	4.62	4.76	4.82
Fe_2O_3	2.14	2.09	2.5	2.96	3.05	3.11	3.06
MgO	2.08	1.95	2.5	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	2.7	2.77	2.66	2.84	3.50
C_3S	58.83	53.3	65	66.0	54.2	43.5	54.1
C_2S	14.62	20.74	10	7.7	17.4	28.8	18
C_3A	10.64	10.51	8	6.4	7.1	7.4	7.6
C_4AF	6.51	6.36	7.6	9.0	9.3	9.5	9.3
Free Lime	1	0.77	1.5	N/A*	N/A*	N/A*	1.5
Fineness (m^2/Kg)	368	551	372	N/A*	N/A*	N/A*	363

*Values not received from the cement company or measured in the lab

The six Class C fly ashes were all from Iowa. Their chemical properties are listed in Table 2. These fly ashes had CaO content ranging from 24.32% to 28.56% and SO_3 content from 2.25% to 3.66%, which was less than the maximum content defined by ASTM C 618, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*. The equivalent alkaline of these ashes ranges from 1.64% to 4.20%, and the loss on ignition (LOS) is less than 0.5% for fly ashes from all distributors. Due to the test time and equipment availability, the fineness of the fly ashes was not measured.

The sand used for the mortar mixes was natural river sand from Ames, Iowa, and it had a specific gravity of 2.6 and absorption of 1.37%.

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	4.2	2.5
LOI (%)	0.33	0.47	0.16	0.27	0.32	0.40

*Fly ash P was from Port Neal; C from Council Bluffs; L from Lousia; K from Kapp; O from Ottumwa; and B from Burlington, Iowa.

Specimens

Mortar samples were used both for tests of calorimetry and ASTM C 403, S*tandard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance*. The samples were mixed according to ASTM C 305, *Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*.

All mortar mixes, except those used for studying the effect of water-to-cement ratio (w/c), had the same sand-to-cementitious material ratio (s/cm) of 2.22 and water-to-cementitious materials ratio (w/cm) of 0.43. These two ratios are similar to those in a typical pavement concrete mix used in Iowa. The air entraining agent MB-AE 90 from Master Builder Inc. was used in this project.

Experimental Design

The experimental work conducted in the Phase II study included (1) calorimeter equipment evaluation, (2) cementitious material characterization, and (3) field trial of simple calorimeter device.

As mentioned before, two available calorimeter devices, an isothermal calorimeter manufactured by Thermometric Inc. and a semi-adiabatic calorimeter device manufactured by AdiaCal were studied in the Phase II study. The equipment evaluation has been completed for the isothermal calorimeter and the evaluation for the AdiaCal is still in progress. In addition to the equipment calibration, experiments were also conducted to study (1) variation of the test results from the eight channels of the isothermal calorimeter used, (2) repeatability of the test results obtained by a given operator for a given mix performed at different times, and (3) repeatability of tests performed by three different operators for a given mix.

Using the selected isothermal calorimeter, cementitious material characterization was performed on mortar samples in the consideration of six major factors that affect cement hydration: cement type and source, Class C fly ash source and replacement level, w/cm ratios, and curing condition. In addition to heat evolution, the set time and strength development of the mortar were also evaluated. Besides the use of nine cements and six Class C fly ashes, four fly ash replacement levels (10%, 20%, 30%, and 40%) were also studied under four different curing temperatures (10ºC, 20ºC, 30ºC, and 40ºC). In addition, one set of mortar materials was selected to study the effect of w/cm ratio on heat evolution, where ratios of 0.5, 0.43, and 0.35 were used. Another set of mortar mixes, with and without water-reducing agents (WRA), were selected to evaluate whether or not an incompatibility problem could be identified by the selected isothermal calorimeter. In total, 124 calorimetry tests, 118 ASTM set time tests, and 117 mortar strength tests were performed in Phase II.

Two field calorimeter tests were conducted, one in New York state and the other in South Dakota. In addition to the tests performed regularly in the Portland cement concrete mobile lab, the AdiaCal calorimetry test and set time test were also performed in the field.

Experimental Methods

ASTM Standard Tests

Two ASTM standards tests, ASTM C 403 and C 109, were performed to determine the set time and strength. To conduct an ASTM C 403 test, a mortar sample was placed in a 6 x 7 in. (15.2 x 17.8 cm) steel container, and its surface was leveled using a spatula after mixing and casting. The sample was cured under the designed condition and covered with wet burlap. After a certain elapsed time, penetration needles of different sizes were forced to penetrate 1 in. (25 mm) over a 10-second period. The penetration resistance and time were recorded for each measurement. The size of needle was progressively decreased as concrete stiffened. The initial set and final set times are determined based on the measured penetration resistance.

The strength tests were conducted following ASTM C 109. The 2 x 2 in. cubes were cast and cured under the designed the environment. The samples were demolded after one day and put in water for further curing until the testing time. The strength was tested at 1, 3, 7, 28 and 56 days.

Isothermal Calorimetry Test

In order to control the test condition, the isothermal calorimeter manufactured by Thermometric Inc. was placed in a temperature control chamber as shown in Figure 1. The isothermal calorimeter contains eight separate channels, or units, that will hold eight samples during a test. As illustrated in Figure 2, each unit has an aluminum sample holder. The sample holder rests on a heat flow sensor (peltier) that is placed 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.

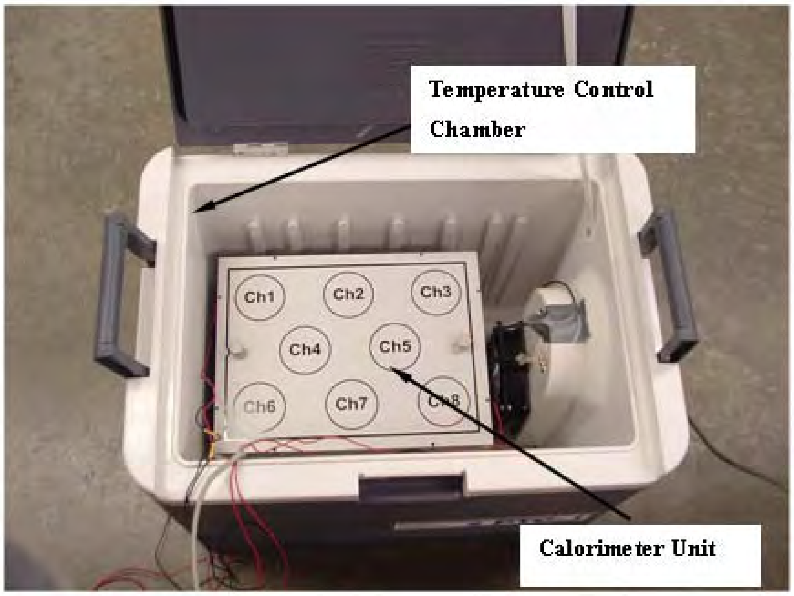


Figure 1. Calorimeter unit

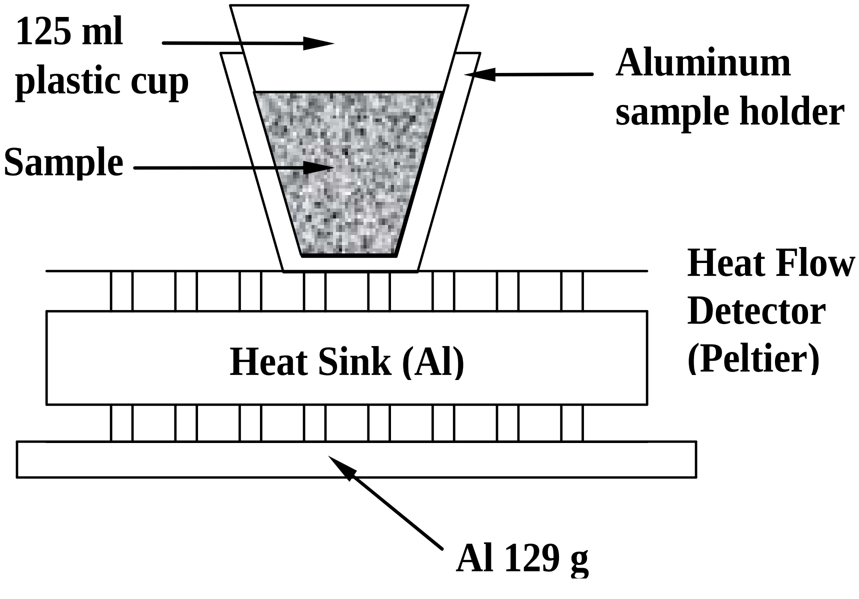


Figure 2. Configuration of the calorimeter module

When a sample is placed in the 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. The system was calibrated by a set of 50 Ω resistors under a certain voltage. The calibration units are shown in Figure 3. For each cup, there is a 50 Ω resistor at the bottom. Each cup is filled with 192-gram epoxy. Eight cups were connected as shown in Figure 4.

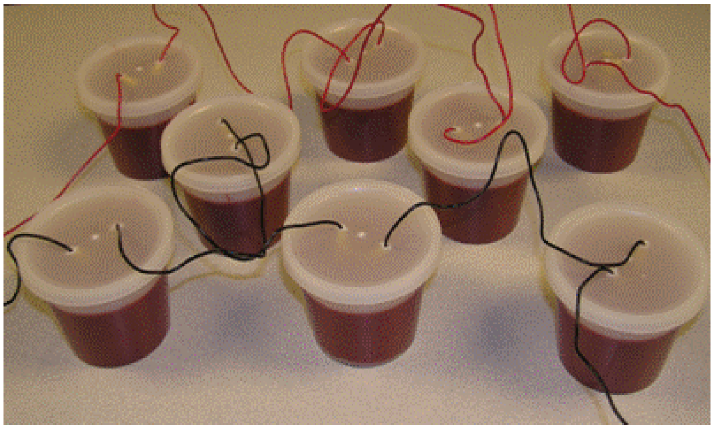


Figure 3. Calibration units

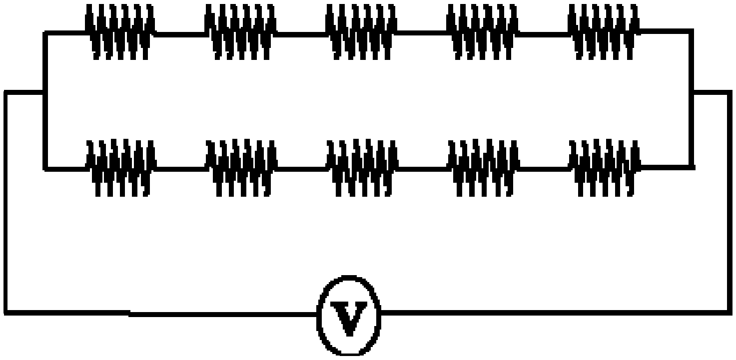


Figure 4. Connection of the calibration units

To initiate the calibration test, the environmental chamber was first set at the desired temperature. The calibration units were then placed into the calorimeter when the environmental temperature was stable. The reading of the calorimeter was recorded every 30 seconds. When the reading (baseline) was stable, the voltage generator was turned on and kept constant until the steady-state reading (U_{steady}) was achieved. The voltage generator was then shut down. The test was ended when the reading was stable again. The calibration factor was calculated based on the output. The determination of the calibration factor is shown in Figure 5.

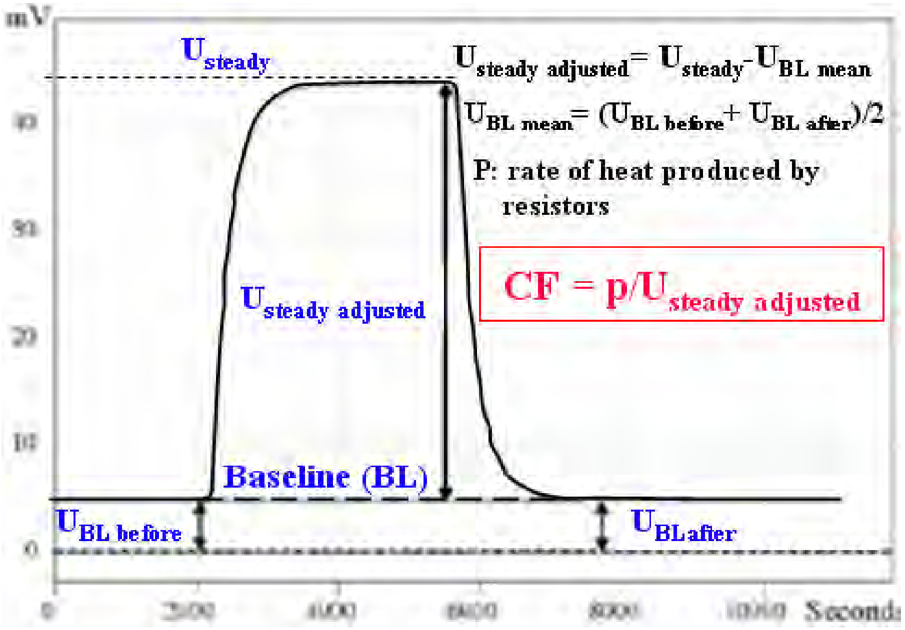


Figure 5. Output of the calibration process

The mortar samples were prepared according to ASTM C 305, *Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*. Right after mixing, approximately 100 grams of mortar was poured in each of the 125 ml (4.2 fl oz) plastic cups. The cups were then placed onto the sample holders of the calorimeter. The reading was recorded every 30 seconds for a total period of 24 hours. For each mix, four samples were tested. The samples were cured at 10ºC and were tested for about 48 hours due to the low rate of hydration.

AdiaCal Test

The AdiaCal calorimeter is manufactured by Solidus Integration, Massachusetts (see Figure 6). This eight-channel semi-adiabatic calorimeter is used for monitoring the hydration process of cement, mortar, or concrete samples. The thermocouples are mounted at the bottom of the insulation block. Since the calorimeter allows you to sample the concrete or mortar directly from the mixer, this calorimeter was used in the field.

Figure 6. AdiaCal calorimeter unit

The thermal setting times can be determined from the measured sample temperature history by two methods—the ASTM-proposed "derivatives" and "fractions" methods. The two methods are defined as the following:

> The 'derivatives' method defines the initial set time as the time corresponding to the peak of the second derivative of temperature versus time function (see Figure 7). It defines the final set time as the time corresponding to the peak of the first derivative of temperature versus time function (see Figure 8). This method works well for very clean sets of data (no noise or crosstalk), but it is sensitive to any extraneous peaks in the data and to changes in the environment. The 'fractions' method defines the initial and final set times as the times corresponding to the temperature reaching the corresponding fractional value of the peak-baseline range (see Figure 9). E.g. if the baseline temperature is 15°C and the temperature peaks at 25°C, and the initial set time fraction is defined as 0.25 and the final fraction is 0.50, then the initial and final set times will be times corresponding to the temperature reaching 17.5°C and 20°C respectively. This method is more robust than the 'derivatives' method with respect to environmental changes, crosstalk, and noise, but it is more sensitive to determination of the baseline temperature. (*6*)

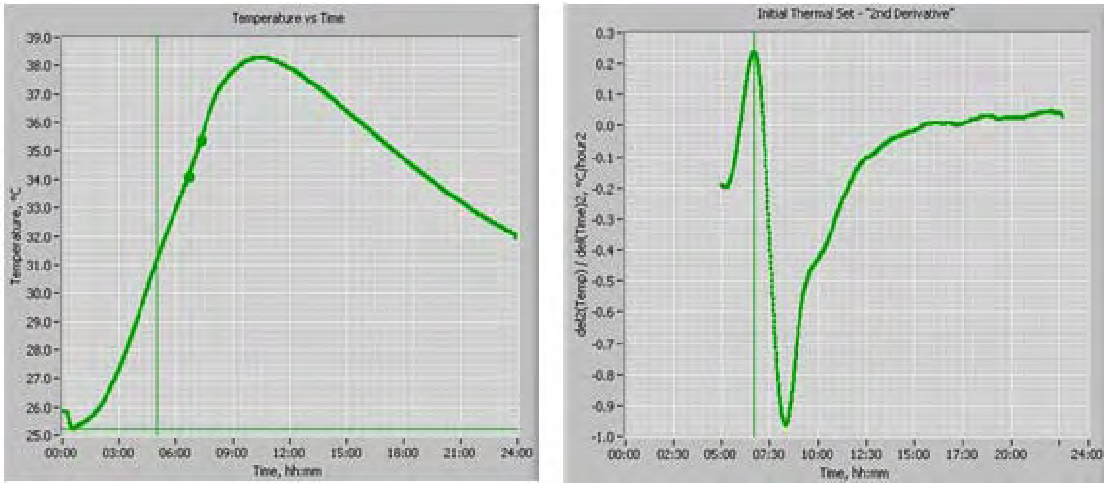


Figure 7. Determining initial set time from the derivatives method

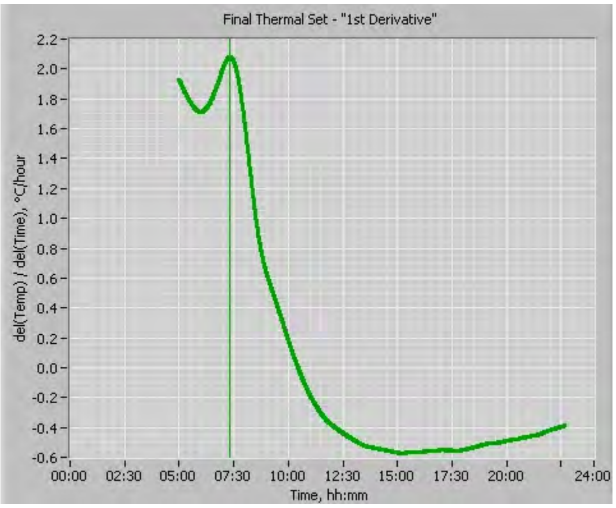


Figure 8. Determining final set time from the derivatives method

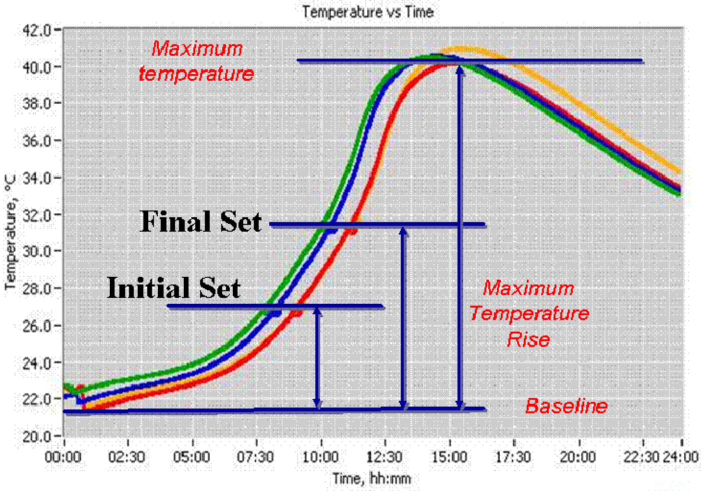


Figure 9. Determining set times from the fractions method

For the field test, the 3 x 6 in. concrete samples were collected at two places, the mixing station and the right before the paver. The tests were performed in a controlled environment (inside the ISU mobile lab) and also in the field environment. The temperature was monitored for around 24 hours and then analyzed by the software to determine the set times.

LAB TEST RESULTS

The following section shows the results of the calorimetry, set time, and strength tests. The isothermal calorimeter tests include two parts. One is the evaluation of the calorimeter performance; another is material characterization. The calorimetry results will be used for the heat index development and concrete performance prediction. In this section, only several typical results are presented.

Isothermal Calorimeter Test: Equipment Evaluation

Figure 10 shows the variation of the test results obtained from the eight channels of the isothermal calorimeter. As the figure indicates, the variation between results is very small. In terms of the peak value, all results are within 5% variation from the mean value.

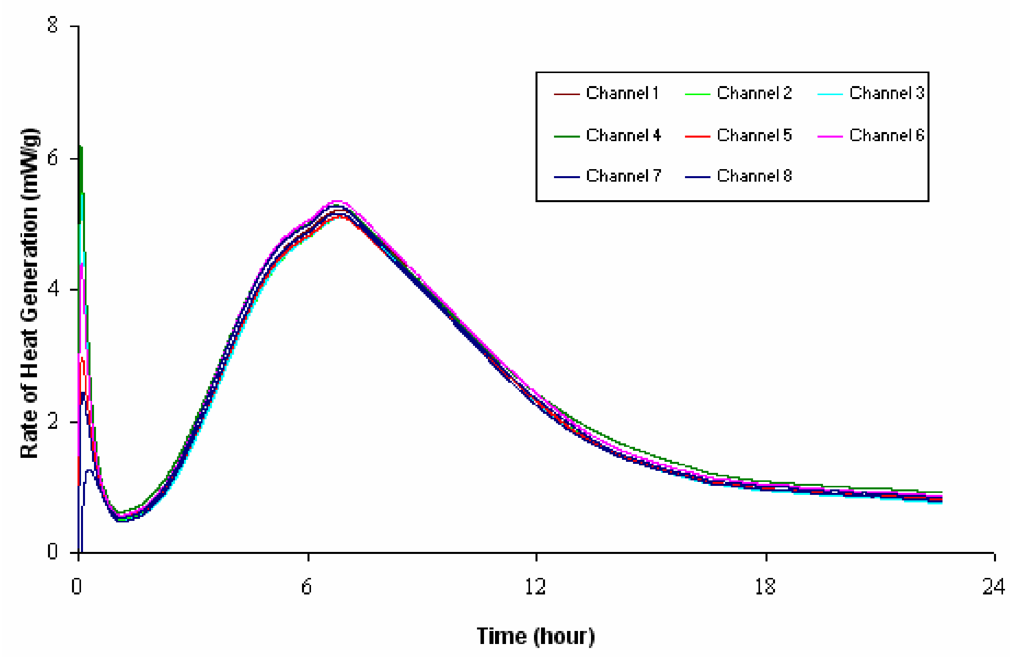


Figure 10. Variation for different channels

Figure 11 indicates that there is a slight difference in the average results of eight channels before the peak. However, after the peak, the two tests results are almost the same. Figure 12 shows the variation caused by different operators using the same mix. The average results of eight channels from different operators are very close. These results indicate that the new calorimeter test is repeatable and suitable for testing the process of the heat evolution.

Since the test results are repeatable, only four channels were used per test for most tests performed in this project. The test repeatability was also tested by performing two tests at different times using the same mixture.

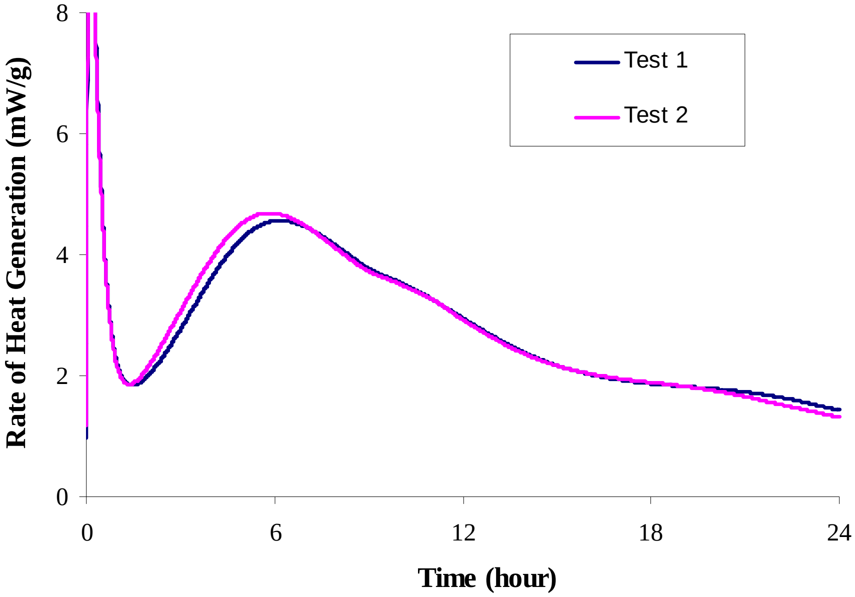


Figure 11. Repeatability of calorimeter tests performed by a given operator at different times

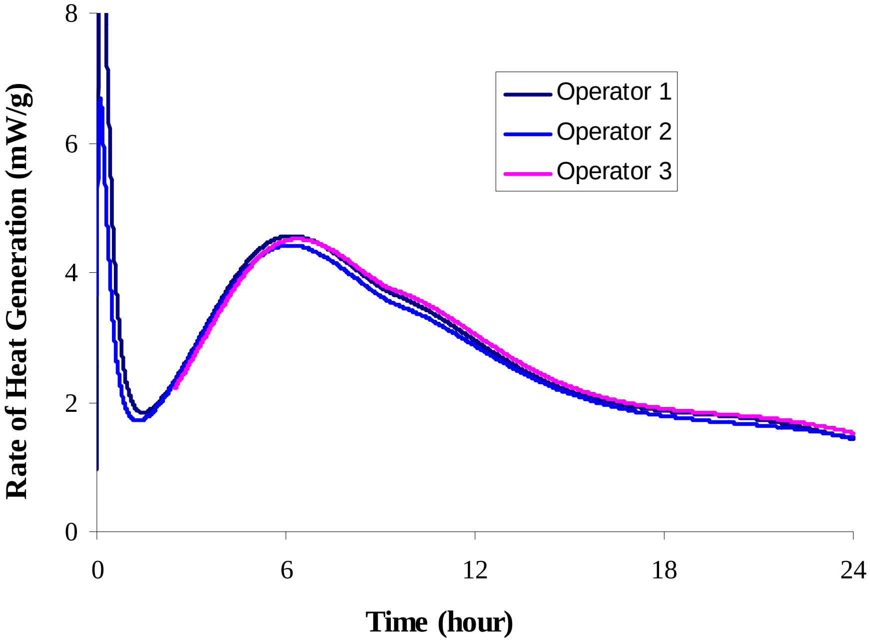


Figure 12. Repeatability of the calorimeter test with three different operators

Isothermal Calorimeter Test: Material Characterization

Effect of the Cement Type and Sources

Figure 13 shows the rate of heat generation for different types of cement. The first peak corresponds to the initial hydration of cement, mainly caused by wetting and by the C_3A reaction with gypsum. The second peak corresponds to the primary hydration of cement, mainly caused by the C_3S and C_2S reactions. The differences among these cements are primarily due to variations in chemical composition and physical properties, which are listed in Table 1. Type I and III cements have similar chemical composition, but Type III cement has much higher fineness. Since hydration occurs at the surface of cement particles and since higher specific area means there is more area in contact with water, finely ground cement will have a higher rate of hydration. Figure 13 shows that the Type III cement has a much higher rate of heat evolution than Type I cement. Type ISM cement is blended cement, which contains 85% Type I cement and 15% slag. The addition of the slag decreases the rate of hydration at early age. The second peak (at approximate 12 hours) is mainly caused by the reaction of slag (*7*).

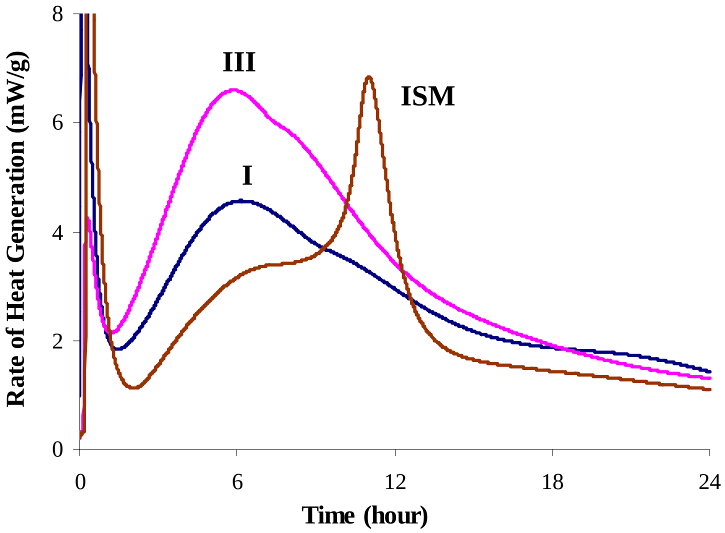


Figure 13. Effect of cement type on heat of hydration

Figure 14 shows the hydration curves for five Type I/II cements from different sources. Although all cements are Type I/II cement, their chemical compositions are different (as shown in Table 1), possible due to differences in the raw materials. All five cements have different heat evolution curves. Cement 2 has the lowest rate of hydration for the first few hours and the highest peak value, which may be caused by the low C_3A and high C_3S contents, respectively. Figure 14 indicates that the calorimeter is able to identify the cements from different sources.

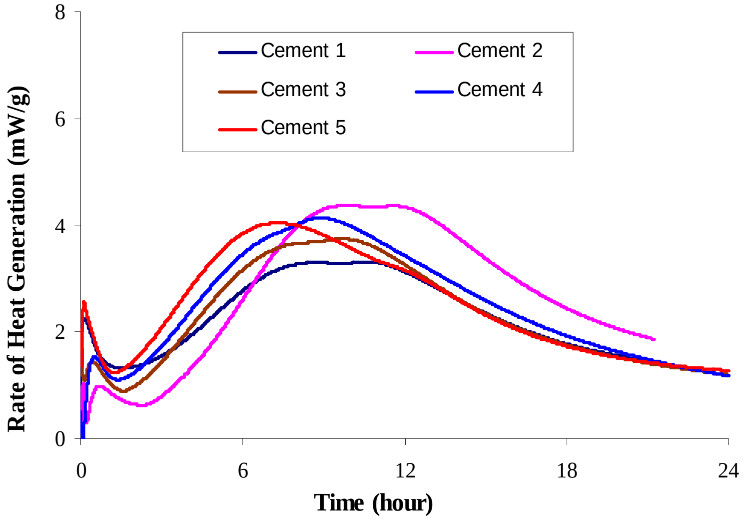


Figure 14. Effect of cement sources on heat of hydration

Effect of Water-to-Cement Ratio (w/c)

Figure 15 shows the early-age heat of hydration of mortar samples with different w/c ratios. The sample with lowest w/c ratio exhibits a higher rate of heat evolution before the peak value. After that, the two samples with the highest w/c ratio have the highest rate of heat evolution. This is consistent with previous studies (*8*, *9*). The peak of the hydration curve is postponed as the w/c ratio increase. The time of the peak value is pushed back about 3 hours when the w/c ratio changes from 0.35 to 0.5.

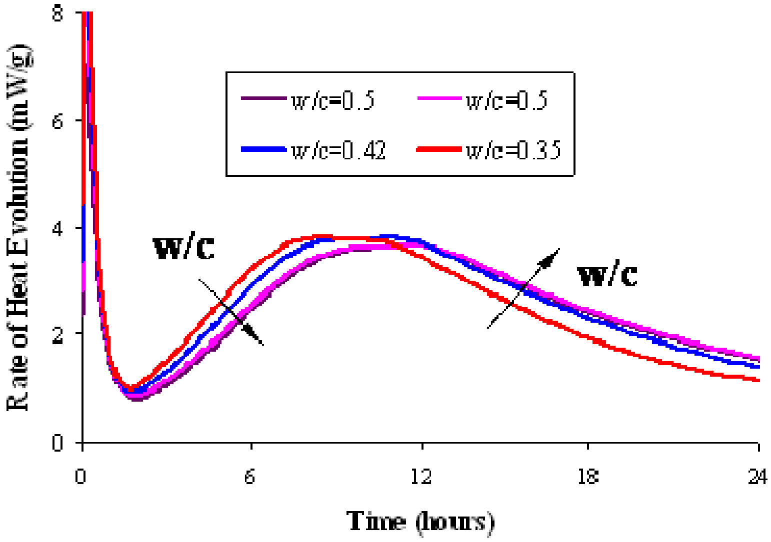


Figure 15. Effect of water-to-cement ratio on heat of hydration

Effects of Fly Ash Type and Replacement Level

Figures 16 and 17 show the influence of fly ash type and replacement level on the rate of heat generation. The addition of the fly ash increases the dormant period, reduces and postpones the peak value, and expands the span of the peak. The third peak for the sample with fly ash—which is attributed to the secondary C_3A reaction (*10*)—becomes more apparent as the fly ash replacement level increases. As the fly ash replacement level increases, the distance between the second peak and third peak is reduced. Figure 17 shows that samples with different fly ashes have different heat of hydration curve. At the same replacement level, different fly ashes have different hydration curves. Fly ash from source O has the highest rate of hydration for the first several hours. The second and third peaks collapse for fly ashes from sources B, L, and K.

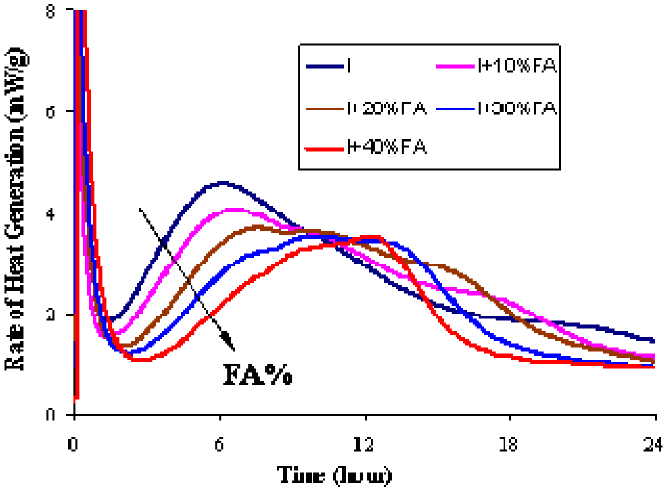


Figure 16. Effect of fly ash replacement level on heat of hydration (source B, cured at 20ºC)

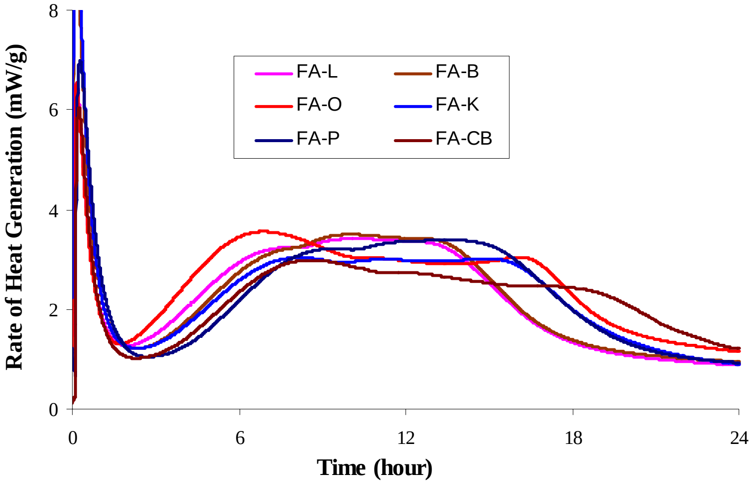


Figure 17. Effect of w/c ratio on heat of hydration (30% replacement, cured at 20ºC)

Curing Temperature

Figure 18 shows the typical effect of curing temperature on the hydration process. Cement hydration is accelerated at early ages under high environmental temperatures but is decelerated later on. The main peak, which is attributed to the hydration of C_3S, is shifted to an earlier time and the value is greatly increased as the temperature increases. The main peak is much broader and at a lower temperature. These trends are consistent with previous research (*11*). The position of the peak value changes from 2.6 hours to 9.8 hours as the constant temperature is lowered from 40ºC to 10ºC, and the peak value itself decreases from 13.6 to 2.5 mW/g.

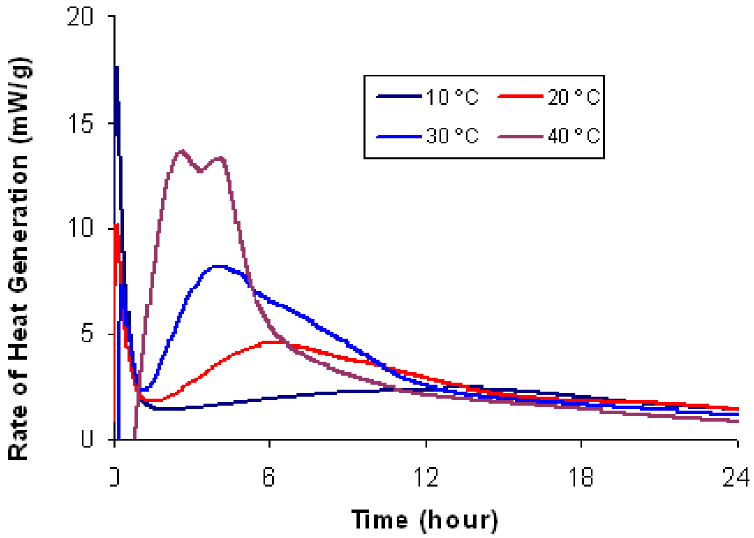


Figure 18. Effect of curing temperature on heat of hydration (Type I cement)

Set Time Tests

According to ASTM C 403, the initial set time of a cement-based material is defined as the time when the tested specimen has 500 psi (3.5 MPa) penetration resistance. The final setting time is defined as the time when the penetration resistance reaches 4000 psi (27.6 MPa). Figure 19 illustrates that the penetration resistance of a tested specimen is a function of time, and it can be well-fitted by a power function curve. The set times are determined from this solidification curve. The mortar samples made with different cements and fly ash replacements displayed different penetration resistance values at any given time.

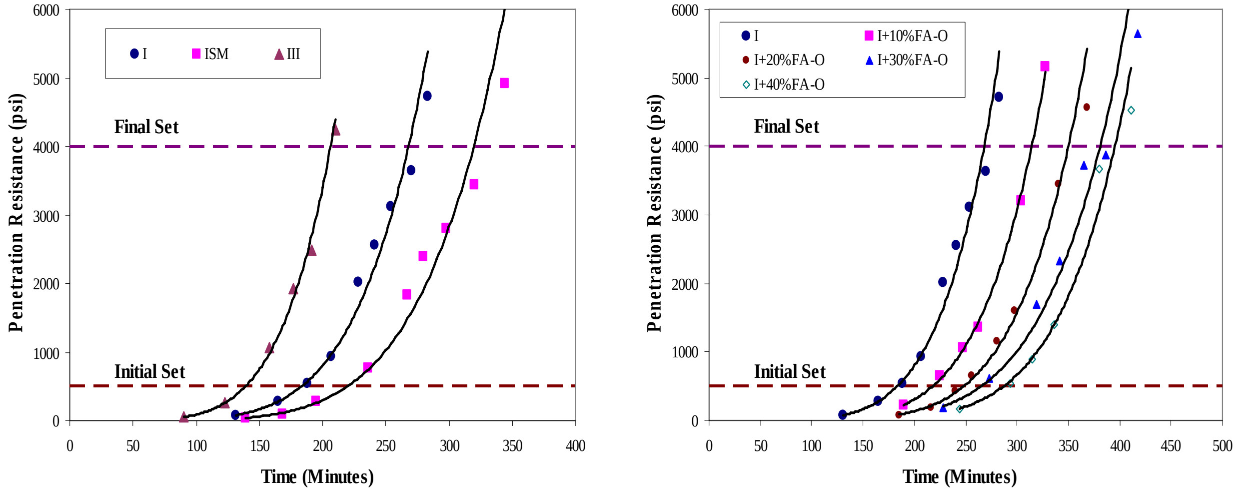


Figure 19. Determination of set times

Figure 20 show the set times of different types of cement under different curing conditions. For all curing conditions, mortars made with Type III cement have the lowest initial and final set times due to their higher surface area. Since hydration occurs at the surface of anhydrated cement particles, finely ground cement will have a higher rate of hydration which, in turn, results in shorter set times. Unlike Type III cement, ISM cement has longer set times compared with Type I cement due to slag replacement. At 20ºC, there are 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, which indicate a 10- to 20-minute delay for each 10% addition of slag (*12*). The curing temperature has the same effect on the set times for all different mortars. The set times decrease when the curing temperature increases. The set times of Type I cement increase about 3.4 and 5.5 hours for the initial and final set times, respectively. These increases were about 2.6 and 4.1 hours for the Type III cement.

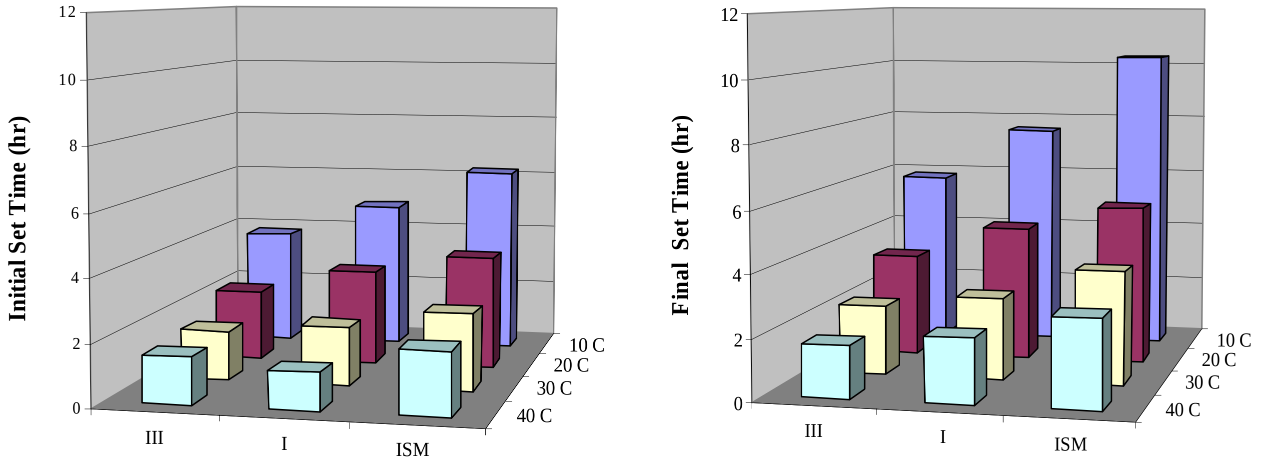


Figure 20. Effect of cement type and temperature on set times

Figure 21 and 22 show the typical effects of fly ash source, fly ash replacement levels, and temperature on concrete set time. The addition of fly ash increased both initial and final set times regardless of curing temperature, which is consistent with previous research results (*13*, *14*, *15*). The increased set times are due to the hydration retardation effect of fly ash. Set times increase as the temperature decrease. The effect of temperature is more apparent for high fly ash replacement levels. For 40% fly ash (source O), the set times increase 6.3 and 9.3 hours for initial and final set times, respectively, when the set curing temperature decreases from 40ºC to 10ºC. For 10% fly ash replacement level, the set times only increases 4.1 and 6.3 hours for initial and final set times, respectively.

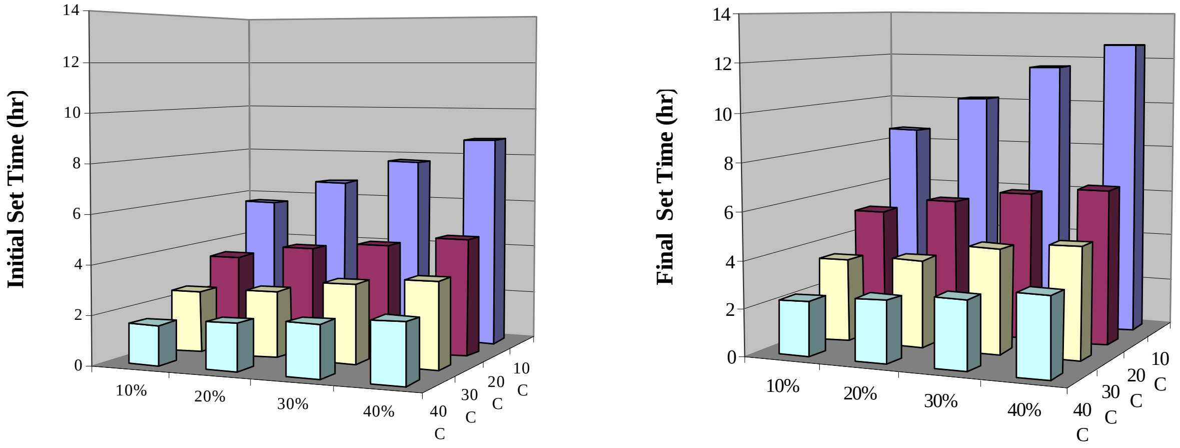


Figure 21. Effect of fly ash replacement and temperature on set times (source O)

Figure 22 shows that the set times are also different for cements with fly ash from different sources. The cement with fly ash from source O has shorter set times compared with cements with other fly ashes. This may be caused by the different chemical composition and physical properties of each fly ash.

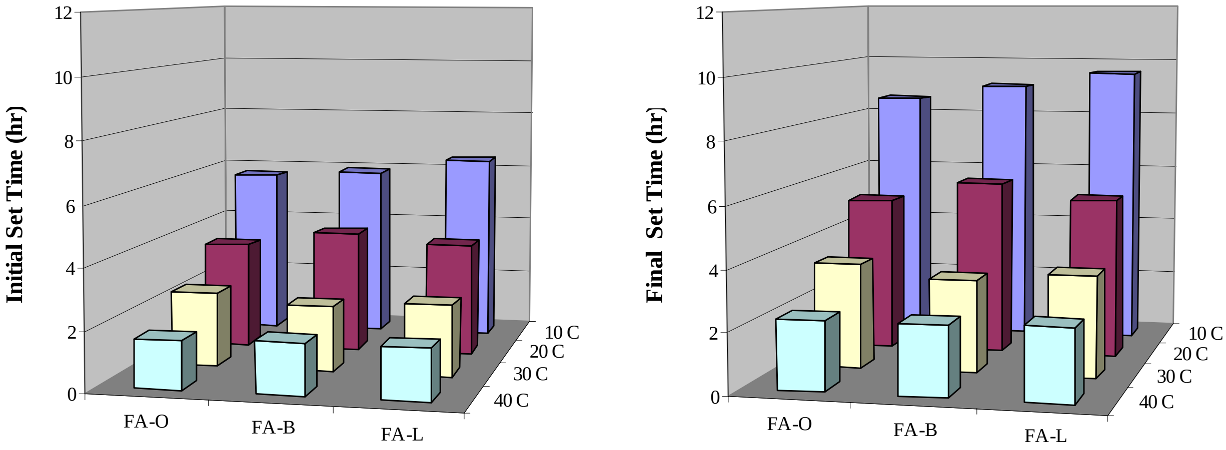


Figure 22. Effect of fly ash type and temperature on set times

Mortar Strength

Mortar was cured under different temperatures and tested at 1, 3, 7, 28, and 56 days. Figures 23 to 25 show the typical strength results. Different cement types have different strengths. Type III cement has the highest strength, especially at early age, due to the high early-age hydration. The strength difference decreases as the curing times increases. The Type ISM cement has similar strength to the Type I cement under the 20ºC curing condition.

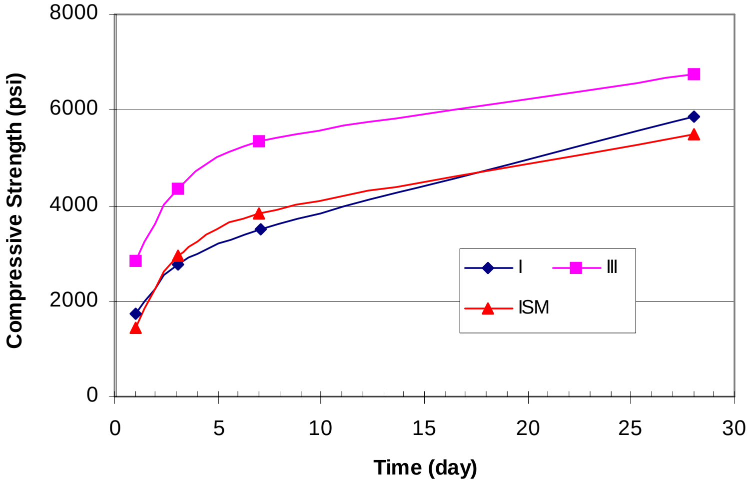


Figure 23. Effect of cement type on strength development (cured at 20ºC)

Fly ash replacement reduces the strength at early age. The more fly ash, the lower the strength is; however, the strengths for different fly ash replacement levels get closer to each other at later age (see Figure 24). At 28 days, the strength difference is less than 10%. At early age, however, mortar with 40% fly ash has much lower strength compared to mortar with Type I cement.

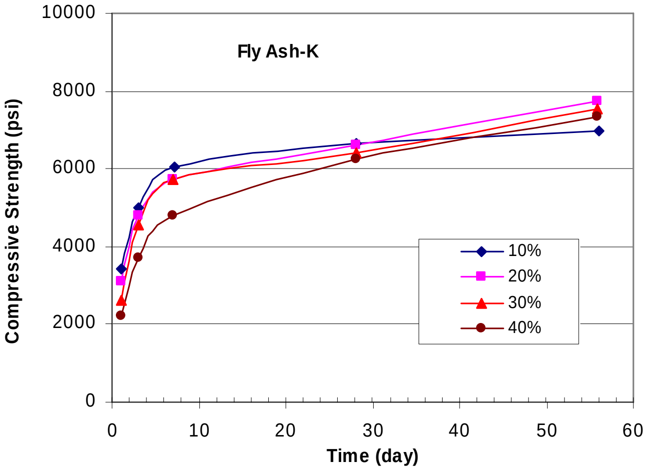


Figure 24. Effect of fly ash replacement level on strength development (cured at 40ºC)

Mortars made with different types of fly ash have different strengths (see Figure 25). The difference is small for the first 3 days but becomes more apparent at 28 and 56 days. The strength difference is caused by the properties of the different fly ashes.

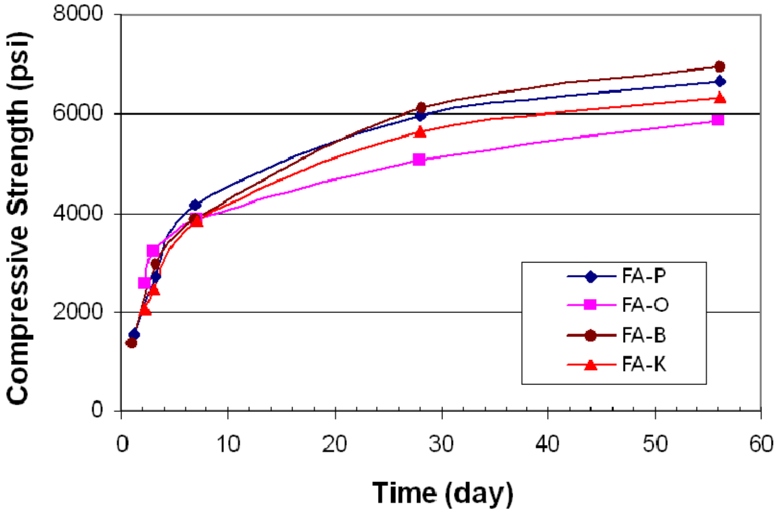


Figure 25. Effect of fly ash type on strength development (cured at 30ºC, 40% replacement)

INTERPRETATION AND APPLICATION OF THE TEST RESULTS

Potential Application of Calorimetry Results

During the second TWG meeting on April 11, 2006, there was a discussion on the importance of the calorimetry test for use in concrete paving projects. To incorporate the results of this project into an implementable and valuable product, it was important to identify the needs that it would fulfill and to assess its viability. This section will precisely identify the applications for a calorimetry test in concrete paving projects.

The TWG identified eight potential techniques, then ranked each one regarding feasibility of use, predictive capability, importance of the value, and competing procedures. The TWG also looked at other critical values that would impact future implementation: assessment steps to gage complexity and time toward implementation, level of difficulty or complexity in interpreting results, strengths and weaknesses of the technique, future steps, and competing procedures.

The use of calorimetry devices on concrete paving projects can have a number of applications, including the following:

- Forecasting time of set
- Predicting strength gain

- Evaluating risk of thermal cracking
- Estimating sawing time and finishing time
- Flagging cementitious changes
- Identifying materials incompatibility
- Verifying mix proportions
- Prescreening mix designs and materials

Each of the above applications is briefly described in the sections below.

Forecasting Time of Set

ASTM is currently in the process of developing an ASTM test procedure for determining setting time directly from the heat evolution curve. The derivative of the semi-adiabatic temperature curve is being used to determine setting. The maximum of the first derivative is correlated to final set, and the maximum of the second derivative is correlated to initial set. Although a good relationship has been found, this test is sensitive to the environment and any extraneous peaks in the data. Additional work is being conducted to modify this procedure.

In a different approach, a study by Byfors has shown a very reasonable correlation of setting time with the degree of hydration and the water-to-cementitious materials ratio (*16*). Schindler recently found a correlation of this type which is related to the ASTM C 403 initial and final set times (*17*). It is important to mention that a reliable prediction of set time in the field can only be accomplished with the use of maturity methods that take into account the concrete temperature in the field and adjust the set time prediction accordingly. The equivalent age concept can be used to predict time of set in the field based on time of set results in the laboratory under standard conditions of temperature via ASTM C 403 or as predicted via degree of hydration. This was demonstrated by Pinto and Hover (*18*).

Various competing test methods are currently available for measuring set time in the laboratory. Some of these include ASTM C 191 (AASHTO T 131) or ASTM C 266 (AASHTO T 153) for cement paste and the ASTM C 403 for mortar sieved of concrete mixtures. These methods can be similarly complemented with the equivalent age concept to predict set time in the field. However, variations may be expected on the time of set prediction for concrete with both fine and coarse aggregates, due to the structural and thermal properties of the aggregate materials.

Predicting Strength Gain

Similarly, correlations to the degree of hydration and 28-day strength values have been developed for strength gain. Although these models do not provide a true prediction of strength, they provide a good prediction of strength gain under given environmental conditions with the use of the maturity concept, provided that a strength benchmark value (e.g., strength at 28 days) is known. These relationships of degree of hydration to strength development are valid only for a given set of mix proportions and materials. In addition, sufficient curing must be provided to minimize moisture loss.

For the competing methods, prediction of strength gain can be currently obtained with the use of the ASTM C 1074 maturity test procedure. Strength predictions with the maturity method can also be complemented with match curing to get a more reliable prediction of concrete strength in the field.

Evaluating Risk of Thermal Cracking

Evaluating the risk of thermal cracking is an excellent application for the heat evolution test. The HIPERPAV software currently uses predictive models to determine the temperature development in the concrete slab. These models capture the heat of hydration, climatic conditions, pavement geometry, and construction procedures to assess the temperature development in the pavement. Typical values of chemical characteristics of ASTM C 150 and C 595 cementitious materials are used in HIPERPAV. However, it is well known that cement characteristics may vary from one cement plant to another and that there are even significant variations within the same cement kiln. Rather than predictive models that use typical values of cement characteristics, heat evolution tests are excellent for determining the heat of hydration characteristics of the materials used.

Aside from HIPERPAV and heat evolution characterization, only guidelines on maximum allowable thermal gradients or curing temperatures are available for minimizing the risk of thermal cracking.

Estimating Sawing Time and Finishing Time

The sawing and finishing times depend to a great extent on the concrete hardening process which, in turn, depends on the hydration and environmental conditions. For this application, a tool like HIPERPAV, complemented with heat evolution tests on the materials to be used, could be applied to get a good prediction of sawing and finishing windows.

Sawing has to be applied within a window of time that starts when the concrete hardens enough to support sawing equipment without raveling and ends when excessive stresses develop that could result in random cracking if saw cutting has not been completed by then. Experienced contractors typically rely on the scratch test to determine sawing windows.

Initial finishing time typically depends on the bleeding and workability characteristics of the concrete mix. Texture finishing, however, is more closely related to the hardening characteristics of the concrete mix. Texturing must be accomplished in a timely manner so that the specified texture depth is achieved.

Flagging Cementitious Changes

Changes in cement or cementitious materials characteristics may affect the performance of the concrete in terms of set times, strength development, and other properties. If these changes can be identified early on, necessary tests can be performed to ensure that such cement change will not compromise pavement performance. The heat evolution test can flag cementitious changes by allowing comparison of the heat development with that of a reference set of materials. If the heat development curve is significantly different, more detailed testing would be warranted to ensure that pavement performance is not compromised.

For the competing methods, calorimetry and time of set tests are currently used for flagging cement changes.

Identifying Materials Incompatibility

Similar to the above application, testing materials for incompatibility can be accomplished by performing a calorimetry test. By comparing the resulting heat curve with that of a typical mix, compatibility problems may be identified. Some incompatibility problems are accentuated under specific environmental conditions; therefore, for this application, it is necessary to perform the heat evolution test under a similar temperature regimen as that experienced on the project where the materials will be used.

Different tests have been identified, depending on whether incompatibility is related to stiffening, air void system, or cracking. Recommended tests include set time, heat evolution, mini-slump/concrete slump loss, rheology, stiffening (ASTM C 359), strength development, ring test, foam index, foam drainage, air void analyzer, hardened air, and clustering.

Verifying Mix Proportions

During normal concrete production, one is likely to encounter variations in concrete mix proportions due to the inherent variability of aggregate properties (e.g., moisture content and specific gravity). The calorimetry test may be able to capture significant variations in concrete proportions that can result from using varying amounts of cementitious materials in each batch of concrete. Such variations may result in undesirable changes in concrete properties later on in a construction project.

In addition to the calorimetry test, a unit weight test is used for verifying mix proportions. This method assumes that, given the different specific gravities of concrete constituents, any significant change in proportions will result in a change in the unit weight.

Prescreening Mix Designs and Materials

Although a given cement or cementitious material may be a good option under a given set of environmental conditions, it may not be ideal under different conditions. The calorimetry test may be helpful at the mix design level to characterize mixtures suitable for a specific application. In this way, materials can be prescreened for different seasons of the year or different environmental conditions. No alternate method to heat evolution testing was identified for prescreening of mix designs and materials.

During the last TWG meeting, the above applications of the heat evolution test were discussed, and several criteria were identified that need to be evaluated in order to determine how likely it is this test could be implemented into concrete paving practice (see Tables 3a and 3b). These criteria included the following:

- Feasibility of predictions (i.e., how capable the heat evolution test is of being successfully used for a given application in the concrete paving industry)
- Importance (i.e., how valuable or useful it would prove to paving contractors)
- Competing procedures (i.e., other tests or procedures that are currently being used or that could be used for such applications)
- Assessments steps (i.e., steps that need to be followed for any given application that would help in comparing this test to other currently available techniques in terms of complexity, practicality, etc.)
- Interpretation of results
- Weaknesses of technique
- Future steps

Table 3a. TWG member ranking on the potential applications of calorimetry tests

Application	Forecasting Time of Set	Predicting Strength Development	Evaluating Risk of Thermal Cracking w/HIPERPAV	Estimating Saw Time and Finishing Time w/HIPERPAV	Flagging Cementitious Changes	Identifying Incompatibility	Verifying Mix Proportions	Prescreening Mix Designs and Materials w/HIPERPAV
Feasibility	H-10***** M-0 L-0	Not ranked	H-4 M-6 L-0	H-6 M-4 L-0	H-8 M-2 L-0	H-7 M-3 L-0	H-0 M-2 L-8	H-10 M-0 L-0
Importance	H-10 M-0 L-0	Not ranked	H-5 M-5 L-0	H-7 M-2 L-1	H-6 M-2 L-2	H-8 M-2 L-0	H-1 M-5 L-4	H-7 M-3 L-0

*H = high, M = medium, and L = low

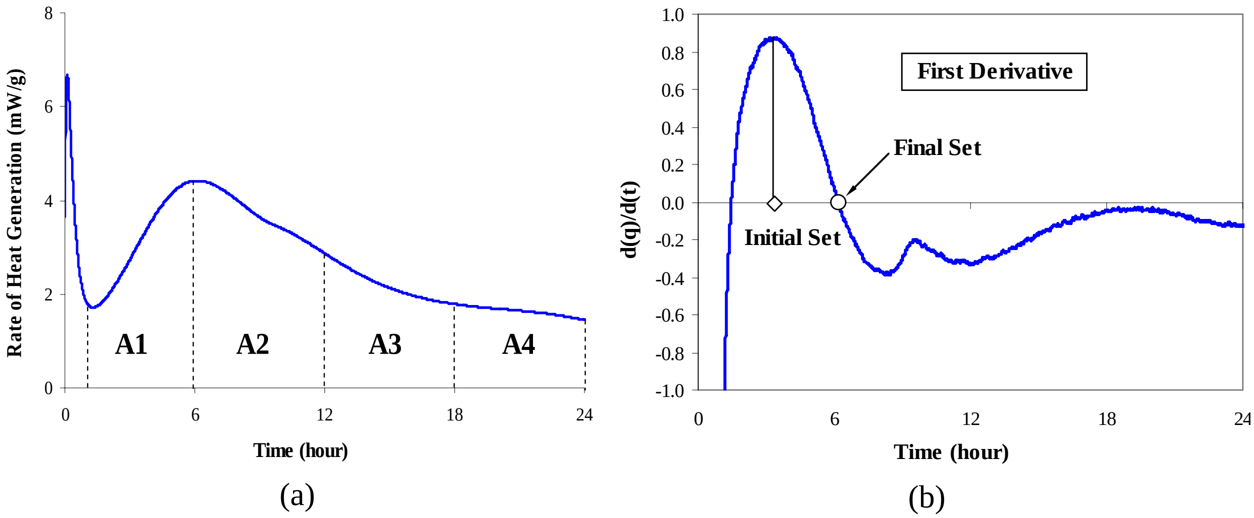
Table 3b. Comparison of calorimetry test with other available tests*

Application	**Forecasting Time of Set**	**Predicting Strength Development**	**Evaluating Risk of Thermal Cracking w/HIPERPAV**	**Estimating Saw Time and Finishing Time w/HIPERPAV**	**Flagging Cementitious Changes**	**Identifying Incompatibility**	**Verifying Mix Proportions**	**Prescreening Mix Designs and Materials w/HIPERPAV**
Competing Methods	Vicat, Gillmore, penetration resistance, P-wave	Maturity, match curing	Guidelines and rules of thumb	Scratch test	Vicat, Gillmore	Setting time, mini-slump/ slump loss, stiffening (ASTM C 359)	Unit weight (UW)	No other test identified
Assessment Steps	Develop HE curve. Manipulate curve results by derivation. Convert heat curve to DOH. Complement with maturity.	Convert heat curve to DOH. Estimate benchmark strength value. Complement with maturity.	Convert to DOH. Determine HE parameters. Input into HIPERPAV.	Convert to DOH. Determine HE parameters. Input into HIPERPAV.	Determine HE parameters. Compare to standard mix.	Determine HE parameters. Compare to standard mix.	Determine HE parameters. Compare to standard mix.	Convert to DOH. Determine HE parameters. Input into HIPERPAV,
Interpretation of Results	Requires software/ experienced staff	Requires software/ experienced staff	HIPERPAV interpretation of stress/strength	HIPERPAV interpretation requires additional output flags	Requires software/ experienced staff	Requires software/ experienced staff	Requires software/ experienced staff	HIPERPAV interpretation of stress/strength requires additional flags
Weakness of Technique	**HE:** Difficult to predict certain cement phases and SCMs **Other:** Only for cement paste or mortar; requires sieving; P-wave only measured in real time	**HE:** Susceptible to sampling error; needs maturity **Maturity and MC:** Not truly predictive or real-time results	**HE:** Temperature sensitive; needs aggregate thermal properties **Guidelines:** May not be always applicable	**HE:** Requires validation **Scratch test:** Requires constant monitoring	**HE:** Requires interpretation **Setting time:** Identify only changes affecting set time; exclude information on full hydration development	**HE:** Requires interpretation; cannot identify problems with air void system **Setting time, stiffening, AVA, air content, etc:** May need HE to fully understand incompatibility process	**HE:** Takes too long; complex **UW:** No major weakness identified	N/A

*HE = heat evolution; DOH = degree of hydration

Calorimeter Test Result Interpretation: Heat Index Development

After a calorimeter measurement, it is very important for engineers to interpret the meaning of the heat evolution curve correctly and effectively. In this project, heat indexes were established to help engineers interpret the calorimeter results. These heat indexes can also be used to predict concrete performance and can also be used for concrete quality control. The typical heat evolution curves have been presented above (see also Figure 26a). In order to describe the heat evolution curve, six parameters (heat indexes) were developed. These parameters include four areas (A1–A4) underneath the heat evolution curve (see Figure 26a) and two points on the heat derivative curves, which correspond to initial and final set times of the tested materials (see Figure 26b).



(a) (b)

Figure 26. Development of the heat indexes

The area under the heat evolution curve is the heat generated during the period. A1 represents the heat generated from hours 1 to 6. The data prior to 1 hour is not used, because the calorimeter system needs a certain time to reach equilibrium status after the sample is loaded. Area A2 is the heat generated between 6 and 12 hours, A3 is 12–18 hours, and A4 is 18–24 hours.

The heat indexes of initial set and final set times are determined from the first derivative of the heat evolution curve. Setting of concrete is a transition period between the fluidity and rigidity stages (*1*, *19*). Concrete setting behavior is controlled by its three-dimensional microstructure development that involves new phase growth, nucleation, percolation, and networking of cement hydration products (*20*). These processes are greatly related to the cement hydration process, which is often characterized by its heat evolution (*10*). Therefore, it is rational to determine concrete set time from a heat of cement hydration curve.

From a microscopic point of view, concrete initial set is the time when cement hydration products, which initially surround individual cement particles, start to form a network (*19*). This corresponds to the beginning of a rapid temperature rise in concrete that follows the dormant period (*1*). Concrete final set is the time when a primary network of hydration products has developed (*19*). It may relate to the time the concrete heat evolution reaches its maximum rate during the acceleration period, which corresponds to the approximate midpoint of the major peak hydration process (*1*).

Figure 26 demonstrates the proposed approach for determining the set time of the tested mortar from a calorimetry test. This method is similar to the derivatives method for the AdiaCal calorimeter. The first derivative of the calorimetry results, d(q)/dt, is derived from the original heat evolution data. In this study, the initial set time is defined as the time when the first derivative curve reaches its highest value. At this point, the increase in the rate of heat generation is the fastest. After the initial set time, the first derivative value starts to decrease. The time when the first derivative becomes zero is defined as the final set. This point corresponds to the time when the highest rate of hydration is achieved in the original heat evolution curve.

When fly ash is added, both the calorimetry result and its first derivative curve could change. Figure 27 shows the determination of the set time of the sample with 40% fly ash replacement. As seen in the figure, the initial set is still defined as the time when the first derivative curve reaches its highest value. It is noted that the first derivative also decreases after the initial set time. Differently from Figure 26, however, the first derivative of the rate of heat generation of the sample with fly ash starts to increase again before descending to zero. In order to determine the final set under this situation, the line A in Figure 27 is extended to cross with the x-axis. This intersecting point is defined as the final set time.

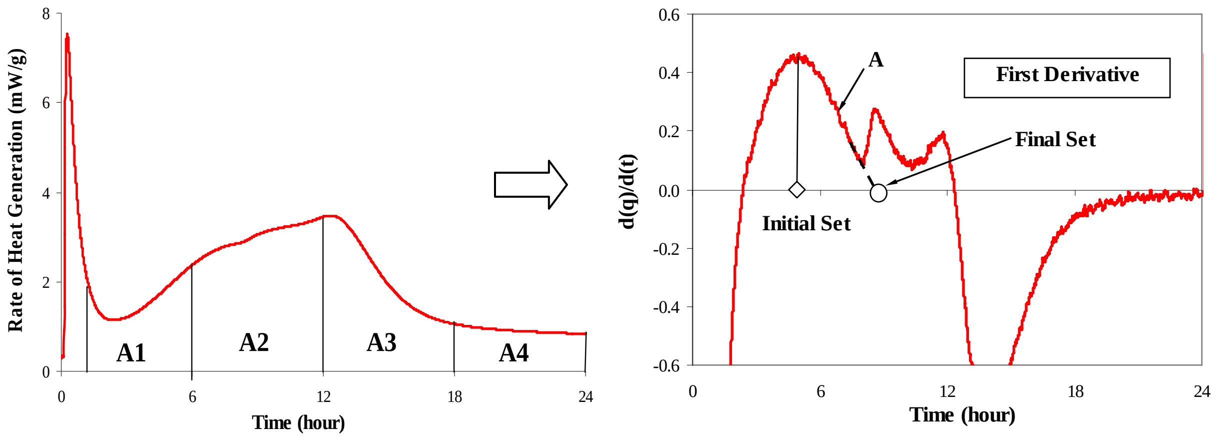


Figure 27. Development of heat indexes for mortar containing fly ash

Application of the Heat Indexes and Calorimeter Results

The above sections state the potential applications of the calorimeter test and the heat index development. This section will explain how to use the heat index to achieve these potential applications.

Prediction of Set Time

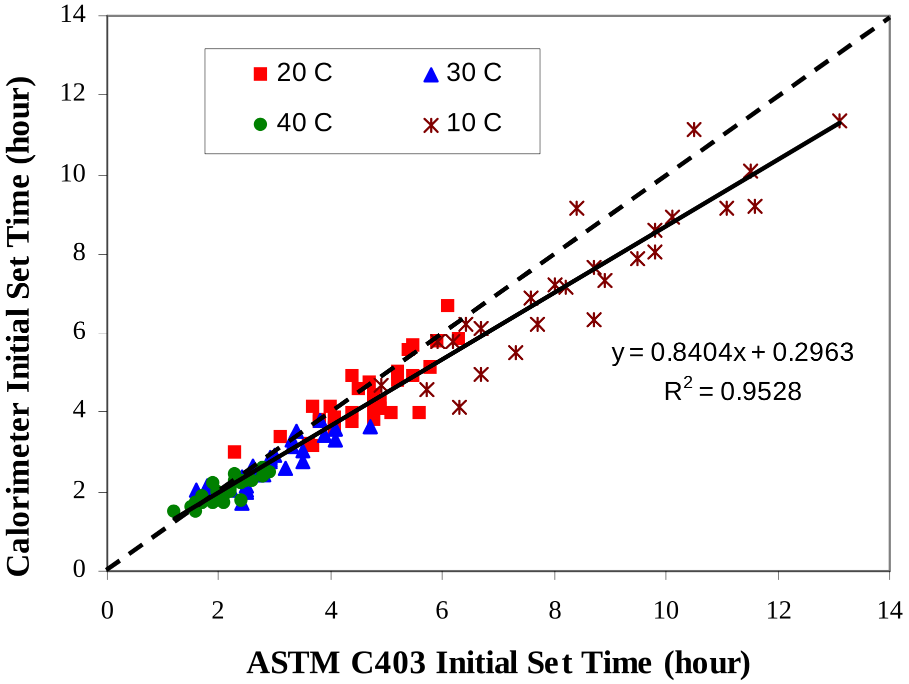
Prediction of set times was rated high in importance and feasibility by the TAC members at the meeting. The two parameters of the indexes (initial and final set times) are used to predict the set times. Since the set times are being tested by the ASTM standard, these results are used to validate the set times predicted from the calorimeters. The set times obtained from ASTM C 403 and calorimetry tests are plotted in Figure 28, demonstrating that the set times determined from the calorimeter method have good relationship with the times determined by ASTM methods.

For the initial set times, the calorimetry tests results are slightly lower than the ASTM results, especially for the materials that have a long set time. However, there is a clear linear relationship, with an R^2 value of 0.95. The set times determined at 20ºC, 30ºC, and 40ºC are closer to the ASTM times than are the results at 10ºC.

Conversely, Figure 28b shows that almost all points are above the equality line, indicating that the final setting determined by the calorimetry method is a little higher than that of the ASTM method. However, there is a good linear relationship (with an R^2 value of 0.96) between these two test results. The differences between the two test results may result from two primary facts:

- The two methods have very different definitions for concrete set time. The ASTM C 403 method is based on the penetration force, and the calorimetry method is based on the microstructure development.
- The two test methods provide test samples with different environmental/temperature conditions. During the ASTM C 403 tests, mortar samples in a 6 x 7 in. container were tested 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. Therefore, the final set from the calorimeter results could be longer than the ASTM results.

(a) Initial set times



(b) Final set times

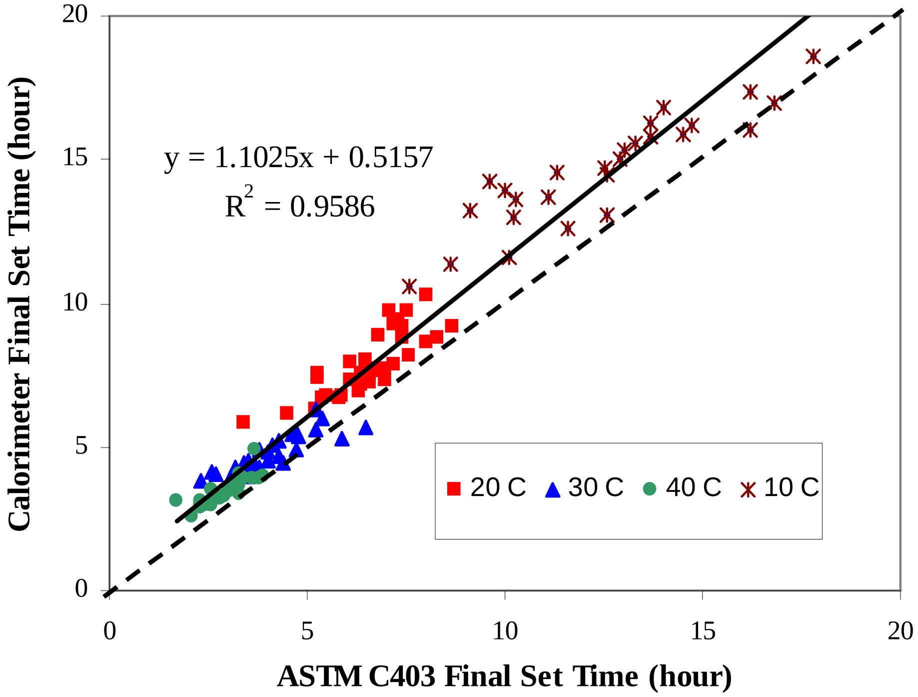


Figure 28. Comparison of the set times from ASTM C 403 and calorimetry tests

Identifying Materials Incompatibility

Materials compatibility is an important issue for concrete pavement. Incompatible materials can cause unexpected or unacceptable performance features such as flash set and delayed early strength development. The usage of fly ash containing C_3A and Type A water reducer may cause incompatibility problems. High temperature can also increase the risk of incompatibility (*21*). Researchers have found that the major cause of incompatibility is a shortage of soluble sulfate with significant amounts of SCMs and admixtures (*22*, *23*, *and 24*) . The Class C fly ash normally contains C_3A, which will consume the soluble sulfate in the cement system and cause a potential deficiency of sulfate in the mixture.

In order to test the isothermal calorimeter's ability to identify the incompatibility problem, an incompatible mixture was obtained from Construction Technology Laboratories (CTL). Figure 29 shows the heat evolution curve of the mixtures. The samples were tested at 30ºC. When 25% Class C fly ash and water reducer were added, the mixture demonstrates incompatibility problems. The heat indexes of these three curves are shown in Table 4. When the water reducer is added, the heat indexes clearly show that the initial set decreases (from 6.2 to 2.6 hours), as does final set (from 8.4 to 3.0 hours). As for the areas under the heat evolution curve, area A1 increases from 20.2 to 44.0, while area A2 drops from 59.9 to 4.8. All the heat indexes show that there is an early and sharp exothermal starting at early age and not much hydration from 6 to 12 hours. Therefore, the heat indexes are able to detect the incompatibility problems.

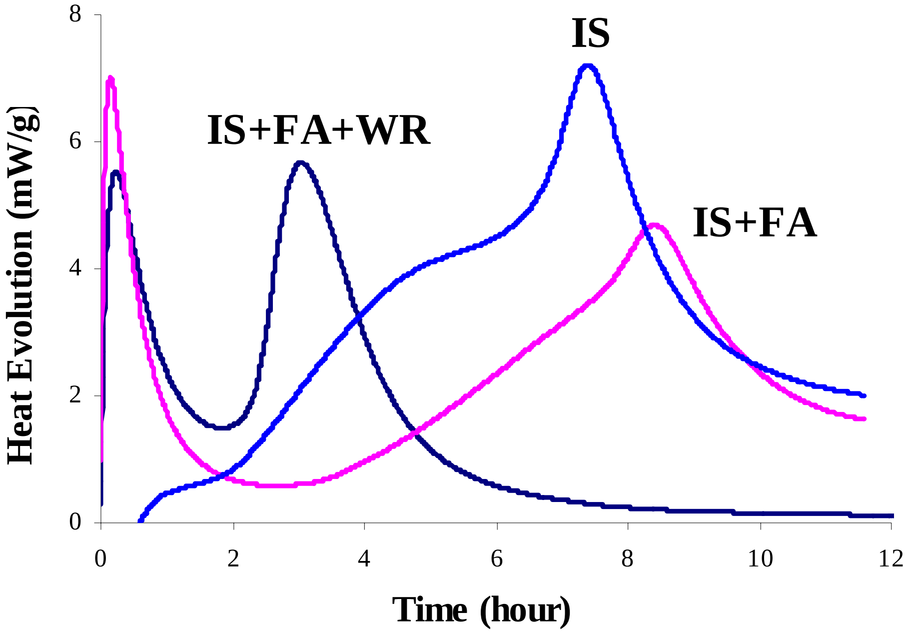


Figure 29. Calorimetry results for the incompatible materials

Table 4. Summary of heat indexes for the incompatible materials

	IS	IS+FA	IS+FA+WR*
Initial set (hr)	3.1	6.2	2.6
Final set (hr)	5.8	8.4	3.0
A1 (mwh/g)	46.2	20.2	44.0
A2 (mwh/g)	79.3	59.9	4.8

*IS = Type IS cement, FA = fly ash, WR = water reducer

Potential Use for Concrete Quality Control

As previously shown, a change in cementitious materials will change heat of hydration curves which, in turn, change the heat indexes of the samples. Figures 30–34 show the areas of different mixes; set times from the calorimeter tests are listed in Table 5. These figures indicate that the heat indexes are able to flag cementitious change, mix proportion, and curing environment changes. Figure 30 shows the indexes for different cements. As cement changes, the areas will change. The Type III cement has the highest values for A1 and A3 and also has the lowest set times. These data indicate that the Type III cement hydrates faster at early age than Type I and ISM cements. Compared with Type I cement, Type ISM cement has lower A1 but higher A2. This means that ISM cement will hydrate slower in the first six hours but faster at 6–12 hours.

In Figure 31, A1 and A2 values decrease as the fly ash replacement level increases. However, the A3 trend contrasts with that of A1 and A2; A3 increases with higher fly ash content. At 40% fly ash, A2 is similar to A3. Also, the set times are different for different levels of fly ash. Therefore, the indexes are able to flag a change in fly ash content. For example, if the design fly ash content is 10%, the A3 and A4 calculated from the hydration curve are similar. That means the dosage of concrete may not be correct. Same as for the fly ash replacement level, the indexes can also be used for flag the change of fly ash type, curing condition, and w/c ratio. However, for some fly ashes, the heat of hydration curves are similar (e.g., the fly ashes from sources B and L). In this situation, the heat indexes are unable to flag the change.

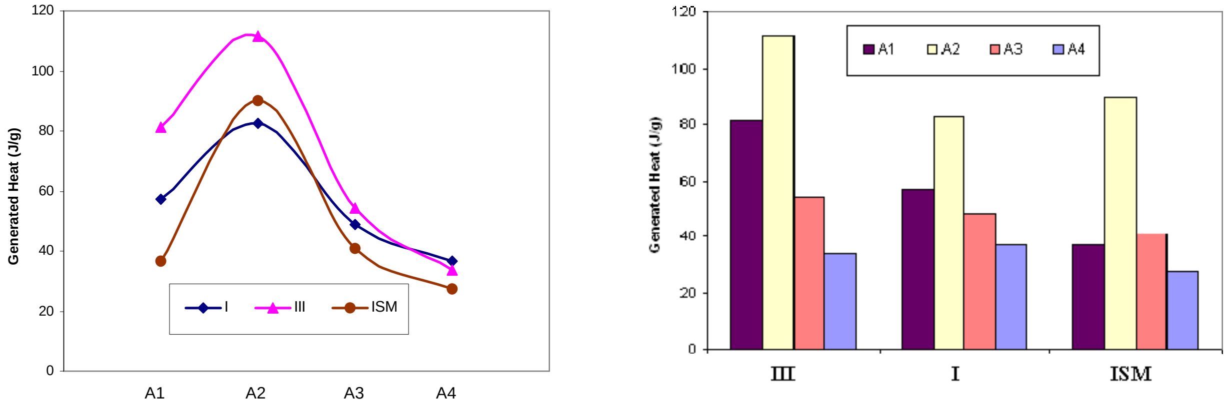


Figure 30. Heat indexes for different types of cement

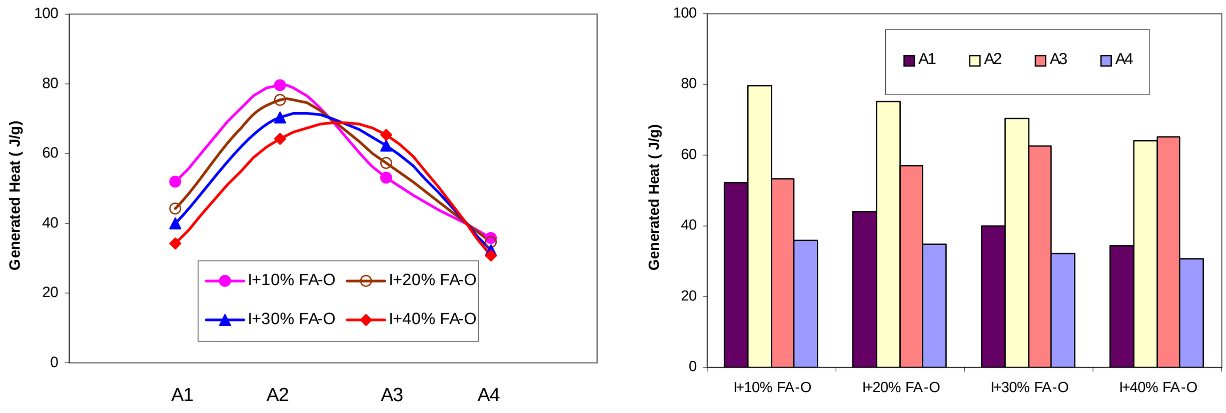


Figure 31. Heat indexes for samples with different fly ash replacement levels

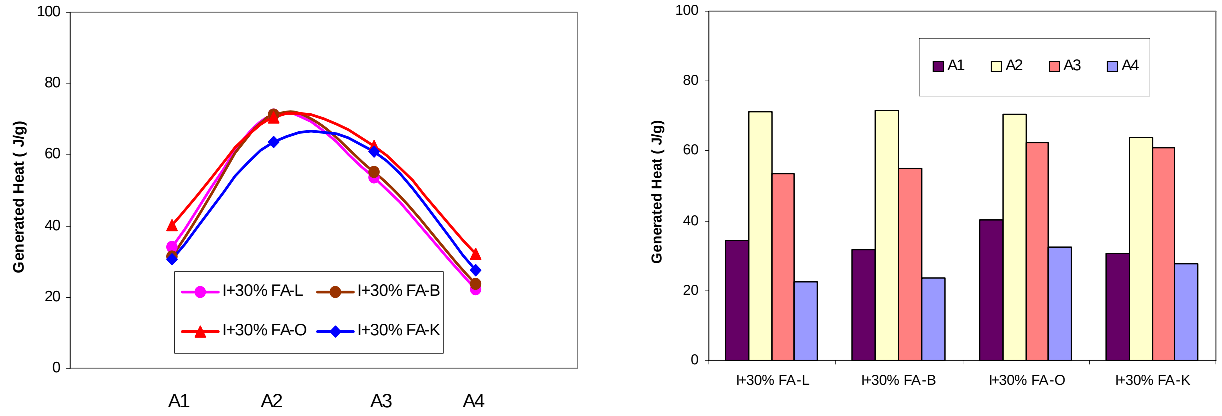


Figure 32. Heat indexes for samples with different fly ashes

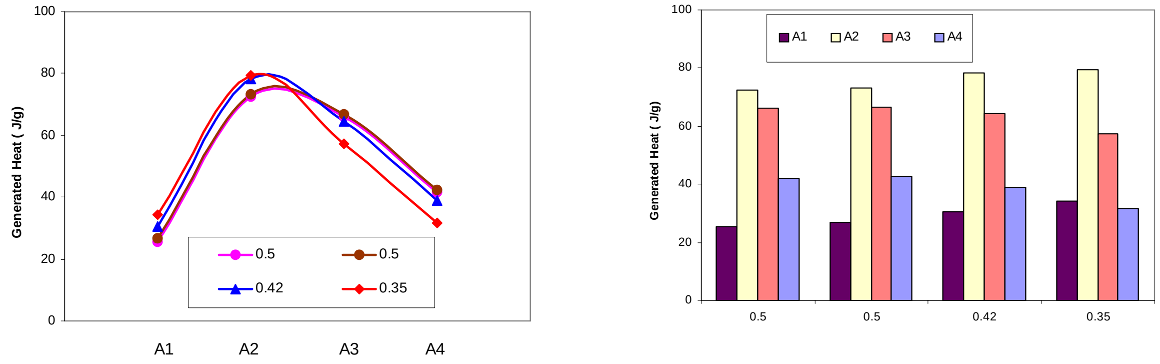


Figure 33. Heat indexes for samples with different w/c ratios

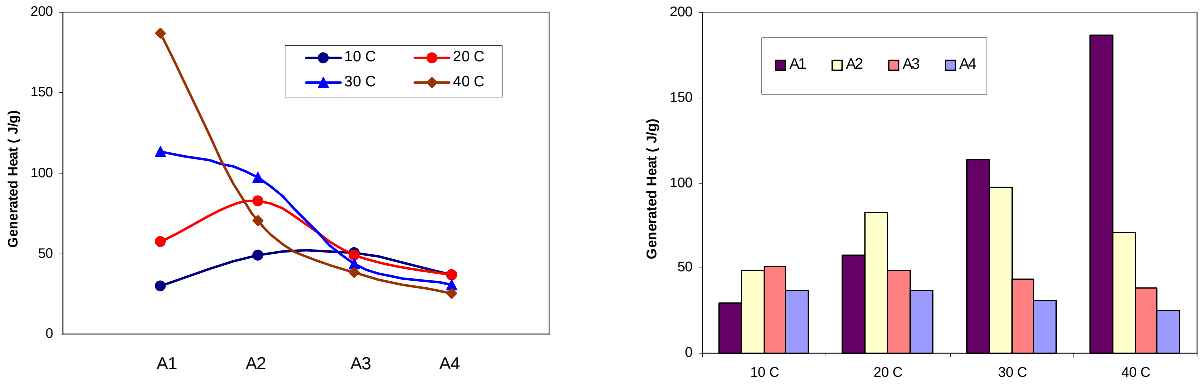


Figure 34. Heat indexes for samples under different curing conditions

Table 5. Summary of heat indexes (initial and final set) for different materials

Factor Being Evaluated	**Cement Type**			
	I	**III**	**ISM**	*****
Initial set (hr)	3.4	3.0	3.2	
Final set (hr)	6.2	5.9	7.6	
FA content	**10% FA**	**20% FA**	**30% FA**	**40% FA**
Initial set (hr)	3.2	3.9	3.8	4.1
Final set (hr)	6.3	6.7	6.9	7.3
FA type	**L**	**B**	**O**	**K**
Initial set (hr)	4.4	4.7	3.8	4.9
Final set (hr)	7.7	8.0	6.9	8.2
W/c	**0.5**	**0.5**	**0.42**	**0.35**
Initial set (hr)	5.2	5.2	4.8	4.6
Final set (hr)	11.6	11.6	9.3	8.5
Curing temp (°C)	**10**	**20**	**30**	**40**
Initial set (hr)	4.6	3.4	2.1	1.7
Final set (hr)	9.8	6.2	4.0	2.6

*The gap in the table is due to the fact that only three types of cement were studied.

Prediction of Early-Age Strength

Strength is related to the hydration of the cementitious materials. Correlations between the degree of hydration and 28-day strength have been developed. Since the degree of hydration could be estimated from the heat of hydration curve, it is possible to predict the strength from the generated heat. Figure 35 shows the strength and generated heat for mortar samples up to two days. It indicates there is a linear relationship between the generated heat and strength. Together with other software, which is able to calculate the heat generation under the field condition, the heat of hydration curve can be used to predict the strength and saw cutting time.

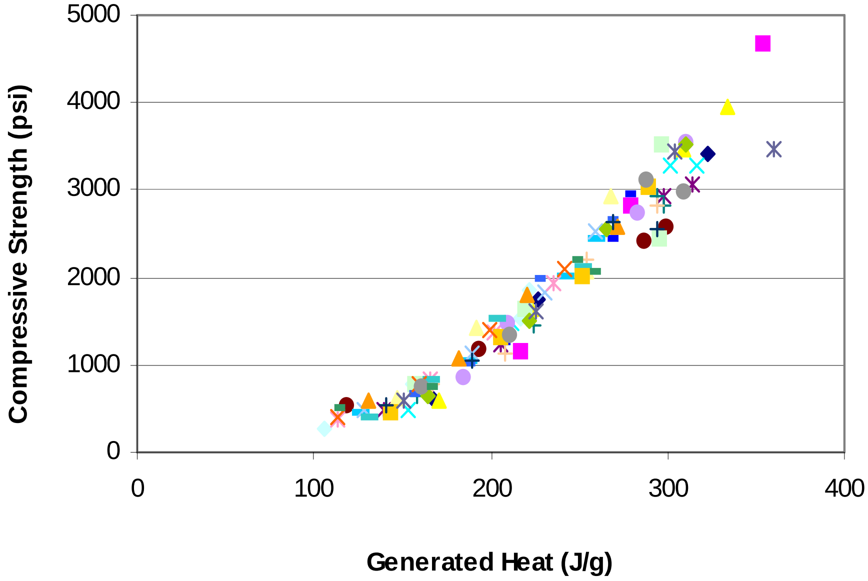


Figure 35. Relationship between strength and generated heat

USE OF CALORIMETRY RESULTS IN HIPERPAV

Currently, the HIPERPAV program uses predicted heat evolution based on concrete mix design and cement characteristics (from a database of the chemical compositions of cements and cementitious materials). This heat evolution information is a fundamental input to HIPERPAV for the prediction of pavement concrete set time, strength, and stress development during early age. In this project, instead of using predictions of heat evolution, calorimetry results are used as input data for the HIPERPAV program analysis, thus improving the reliability of the HIPERPAV analysis. (That is, in this project, the HIPERPAV program has been modified and will be further modified to include the inputs for characterization of the heat evolution of concrete mixtures. Thus, users will have the ability to directly enter heat evolution parameters obtained from a calorimetry test for the concrete strength and stress analysis.) The results from the HIPERPAV analysis are expected to be used for concrete quality control, optimization of pavement designs, prediction of pavement performance, and contractor assistance in managing the temperature of concrete based on concrete mix designs and specific climate and project conditions.

In Phase II of this research project, heat evolution from semi-adiabatic and isothermal calorimetry was used to determine the degree of hydration (DOH) for a concrete mix. In this exercise, heat evolution data for seven days of calorimetric testing with both semi-adiabatic and isothermal methods was used to determine the DOH and estimate the total heat of hydration for this mix. This information is used in the HIPERPAV software to predict the temperature development in the pavement slab as exposed to given environmental conditions and controlled with specific curing methods. In turn, concrete properties that depend on the maturity of the concrete mix (such as strength, stiffness, and setting time) are also predicted by HIPERPAV.

The objectives of this work were to

- evaluate DOH with semi-adiabatic versus isothermal test results,
- evaluate DOH with semi-adiabatic for seven-day testing versus 24-hour testing,
- look at HIPERPAV performance predictions for DOH computed with seven-day versus 24-hour testing, and
- provide recommendations for future testing.

Heat evolution data collected from a concrete mix used in a South Dakota paving project was evaluated for this purpose.

Evaluate DOH with Semi-Adiabatic versus Isothermal Test Results

Comparisons of the DOH with semi-adiabatic testing versus isothermal testing showed that there is a significant difference in the DOH predicted with these two methods. Potential reasons for this include the following:

- The estimation of the total heat of hydration may have been inaccurate. The total heat of hydration was predicted using available models as a function of the chemical composition of the cement. It is therefore recommended that total heat of hydration be determined with ASTM C 186.
- Although the thermal properties of the aggregates, such as thermal conductivity and specific heat, were accounted for in determining the degree of hydration of the concrete sample, it should be recognized that hydration of a concrete sample may be different from the hydration of a cement paste/mortar sample. This should be investigated further.
- The specific heat of the isothermal equipment was not accounted for in this exercise, and this may have introduced errors in determining the degree of hydration with this method.

Evaluate DOH with Semi-Adiabatic for Seven-Day versus 24-Hour Testing

One of the objectives in this project has been to evaluate the feasibility of using up to 24 hours' worth of calorimetric testing (as opposed to the typical three to seven days of required testing for a precise estimation of PCC heat evolution) to make rapid decisions in the field regarding the characteristics and suitability of the concrete mix for the given environment.

In this task, determination of the DOH was performed with both 24 hours and seven days of semi-adiabatic data for the same mix. The objective of this exercise was to evaluate the precision lost by using only 24 hours' worth of data. For this purpose, the determined DOH parameters with each data set were input into HIPERPAV to assess the difference in predicted performance. The results of this comparison are presented in the following section.

Examine HIPERPAV Performance Predictions for DOH Computed with Seven-Day versus 24-Hour Testing

The DOH parameters obtained with the 24-hour and seven-day data sets for the same mix were input into HIPERPAV to predict time of set, strength gain, and critical stress-to-strength ratio for the first 72 hours after construction.

Considerable differences were observed in set, strength gain, and stress-to-strength ratio predictions for the DOH computed with 24-hour heat evolution data when compared to the seven-day DOH data set used as a reference. In this exercise, the analysis reliability was set at 50% for the run with the seven-day DOH data set, and the reliability of the run with the 24-hour data set was adjusted to match the stress-to-strength ratio predictions with the seven-day DOH data set. A reliability of 60% was found to match the stress-to-strength ratio predictions of the seven-day DOH data set. This appears to indicate that by using a higher reliability for the heat evolution computed with a reduced testing time of 24 hours, one may be able to approximate the performance results obtained with standard testing of seven days.

Recommendations for Future Testing

Based on the above findings on heat of hydration characterization for prediction of pavement performance, the following recommendations are provided for future implementation in this project:

- A similar approach to the one described above should be performed to conduct a sensitivity analysis on the heat of hydration characterization for multiple mixes. This approach should include mixes with different SCMs and mixture proportions. HIPERPAV should be used to evaluate the sensitivity of reduced calorimetric testing time on pavement performance indicators such as set time, strength, and stress-to-strength ratio.
- During the field testing stage of this project, it is recommended that HIPERPAV predictions of pavement performance be verified with field pavement performance measurements.
- The semi-adiabatic testing has been proven in the past for the characterization of the DOH of concrete pavement mixtures. Additional evaluation of the isothermal calorimetry method is required before this method is further considered in the characterization of the DOH.
- The isothermal method is a proven test for evaluating the thermal sensitivity of concrete mixtures (i.e. activation energy). For thorough verification of the HIPERPAV predictions, the isothermal method should be used to determine the thermal sensitivity of the evaluated mixtures.
- In addition to the degree of hydration and the thermal sensitivity, the total heat of hydration of the evaluated mixtures should be tested in the laboratory to compare with the predicted total heat of hydration currently used in HIPERPAV.

FIELD TEST RESULTS

Two locations were selected for field testing. One is the intersection of I-86 and US-15 at Painted Post, New York. The other is the south-bound lane of I-29 in Beresford, South Dakota. For both field tests, two sets of tests were performed at each site: ASTM set time and AdiaCal calorimeter tests. For the ASTM set time, an iButton was inserted in the middle of the mortar sample to monitor the temperature history. Most tests were conducted inside the mobile lab, which has a controlled environment during the daytime. In order to study the effect of the curing condition, one set of tests was performed under the field condition outside the mobile lab to compare with the tests inside the mobile lab.

Besides set time and AdiaCal tests, the sawing time was also recorded for the New York field test. The pavement in South Dakota is continuous reinforced concrete pavement. Therefore, no sawing time was recorded. Field materials from the South Dakota work site were brought back to the lab to perform one set of tests using the same mix proportions as those used in the field.

Figure 36 shows the typical temperature profiles from the eight samples for the AdiaCal tests. All the samples are from the same concrete. It shows that, even with the same concrete, there is still variation among these temperature profiles. The set times determined from these temperature profiles are very similar. The results show that the largest variation among the eight testing channels is 10.5%, but most of the variations are under 6%–7%.

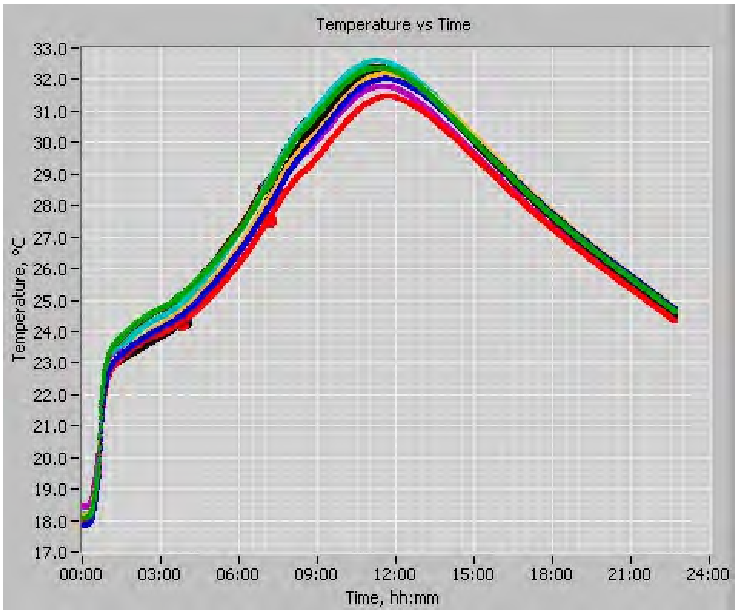


Figure 36. Typical sample temperature profiles from the AdiaCal tests

Figure 37 shows set times determined by the ASTM C 403 and AdiaCal method for both field sites. All points are along the equality line. The set times determined from the fraction method are closer to the ASTM set times. The set times from the derivatives methods have larger variation, because this method is sensitive to any extraneous peaks in the data and to changes in the environment.

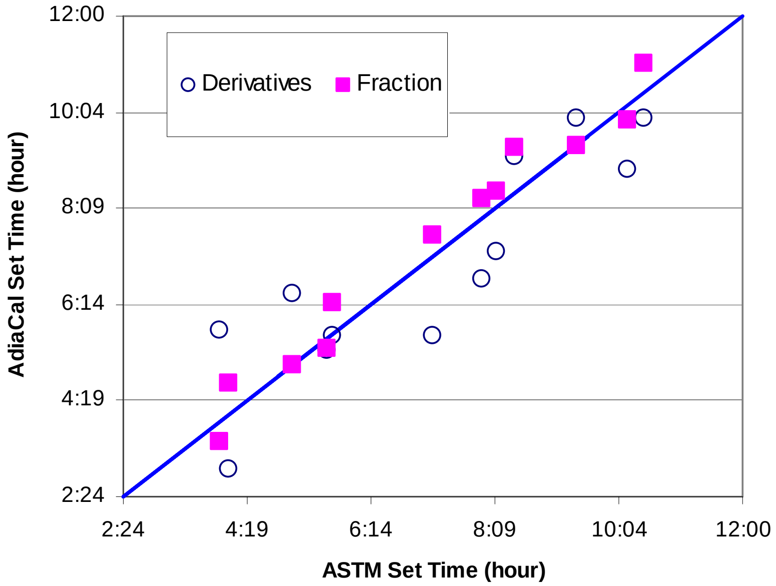


Figure 37. Set times for the New York and South Dakota field tests

Samples tested under lab and field conditions have different temperature histories (see Figure 38). The sample under the lab condition has much lower temperature due to the low temperature inside the mobile lab; the peak value is also postponed compared with the sample under the field conditions. The initial set times from ASTM test are 4.05 and 3.88 hours for the lab and field conditions, respectively. The final set times are 5.63 and 5.03 hours, respectively. For the AdiaCal test, initial set times vary by 1.16 hours and final set times by 1.27 hours.

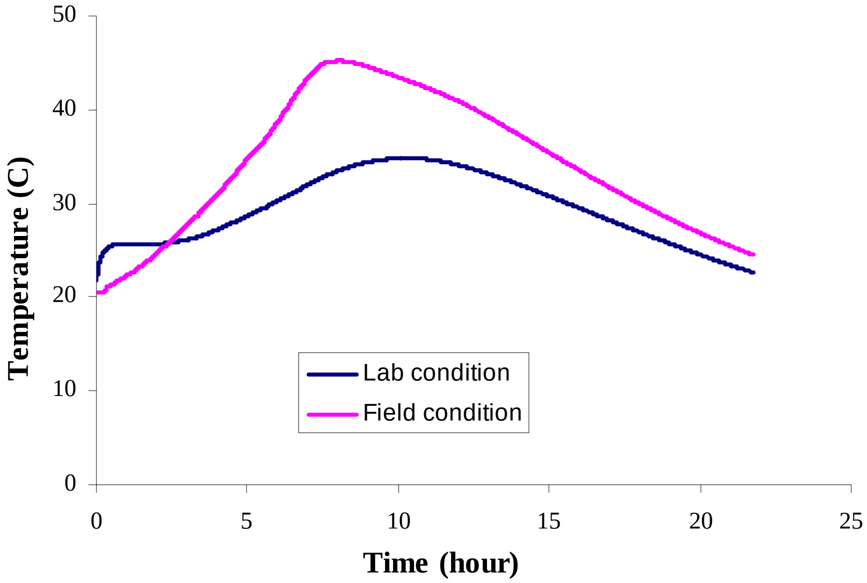


Figure 38. Average temperature history of samples cured in different environments

SUMMARY

The overall objective of this project is to identify, develop, and evaluate a standard test procedure for monitoring performance of pavement concrete materials using a relatively simple, economical, and reliable calorimetry device. The project contains three phases. Phase I, completed in December 2005, identified user needs for a calorimeter test and potential applications of calorimeter test results. Phase II, presented in this report, aimed to establish a standard test procedure as well as the methods for interpreting the calorimeter test results. Phase III will verify the major applications of the calorimeter test method and develop the specification for calorimeter testing of field concrete.

This report summarized the activities and major findings from the Phase II study. The following activities were conducted in Phase II:

- Performed a series of lab tests for approximately 120 mortar mixes using a Thermometric isothermal calorimeter
- Tested the set time and strength development for these mortar mixes
- Developed the heat index method for interpretation of the calorimetry test results
- Studied the relationships between the mortar set time obtained from the calorimetry and ASTM tests
- Identified the potential applications of the calorimeter test results
- Performed two field tests using AdiaCal semi-adiabatic calorimeter
- Estimated pavement performance using HIPERPAV and field calorimetry data

The major findings from the Phase II study are summarized below:

- The test method developed for the selected isothermal calorimeter device is easy to apply and repeatable.
- The calorimeter test can be used to differentiate the heat evolution of mortars made with different materials and subjected to different curing conditions.
- The calorimeter test can be used to identify material incompatibility and to flag cementitious changes.
- The heat indexes, related to the first derivative of the calorimeter curve and the area under the curve, are able to characterize the features of mortar. They can also be used to predict the mortar set time and early-age strength (up to two days).
- When incorporated with the HIPERPAV computer program, calorimeter test results are able to provide insight onto the risk of thermal cracking in field concrete.
- The selected semi-adiabatic calorimeter test device (AdiaCal) is also easy to use, and the test results provide a very good prediction of the set time of field concrete.
- The AdiaCal calorimeter or similar equipment can be modified to compute temperature losses and can inexpensively replicate the results of semi-adiabatic testing in the field.
- Used with HIPERPAV, semi-adiabatic testing of concrete in the field is the recommended procedure for prediction of pavement performance characteristics, including set times, strength gain, and thermal cracking risk.

Phase II has provided necessary preliminary results for potential applications of calorimetry. However, due to the limited time and funding, the previous research did not include sufficient field tests and HIPERPAV analyses that verify the validity of the Phase II results. The proposed Phase III is to focus on the field verification and implementation of the research results from Phase II. The following tasks will be performed in Phase III:

- Evaluate the applicability of AdiaCal calorimeter tests and compare the test results with those from Thermometric isothermal calorimeter.
- Conduct field tests and verify the heat indexes developed in Phase II.
- Modify the HIPERPAV computer program and compare the predicted and field results.
- Develop the performance-based specification for calorimeter equipment and test procedures based on the field test results.

REFERENCES

1. Mindess, S., J. F. Young, and D. Darwin, *Concrete*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2003.

2. Portland Cement Association, “Portland Cement, Concrete, and Heat of Hydration,” *Concrete Technology Today* 18, no. 2, 1997, 1–4.

3. Knight, G, “Comparative Calorimetry Testing.” Technical working group meeting for Heat Evolution Test Research, Des Moines, IA, Oct. 1, 2004.

4. Ruiz, J. M., R. O. Rasmussen, and T. R. Ferragut, “Characterization of Concrete Paving Mixtures with HIPERPAV.” Special publication of the technical session Concrete Heat Development: Monitoring, Prediction, and Management, at the ACI Convention, Atlanta, GA, April 22–26, 2007.

5. FHWA and Iowa State University, “Road Map for PCC Pavement Research: Concrete Pavement Technology Long Term Research and Technology Plan,” March 7, 2005. http://www.pcccenter.iastate.edu/publications/task15.cfm.

6. Solidus Integration, *AdiaCal Manual*, Version 1, 2006.

7. Kishi, T., and K. Maekawa, “Thermal and Mechanical Modeling of Young Concrete Based on Hydration Process of Multi-Component Cement Minerals,” In *Thermal Cracking in Concrete at Early Ages, Proceeding of RILEM*, ed. R. Springenschmid, 1994, 11–18.

8. Danielson, U., “Heat of Hydration of Cement as Affected by Water-Cement Ratio,” *Proceedings of the Fourth International Symposium on the Chemistry of Cement*, Paper IV-S7, 519–526. Fourth International Symposium on the Chemistry of Cement, Washington, 1962.

9. Taplin, J. H., “A Method for Following the Hydration Reaction in Portland Cement Paste,” *Australian Journal of Applied Science* 10, 1959, 329–345.

10. Neville, A. M., *Properties of Concrete*, 4th ed. New York: John Wiley and Sons, 1996.

11. Escalante-Garcia, J. I., and J. H. Sharp, “Effect of Temperature on the Early Hydration of Portland Cement and Blended Cements,” *Advances in Cement Research* 12, no. 3, July 2000, 121–130.

12. Hogan, F. J., and J. W. Meusel, “Evaluation for Durability and Strength Development of a Ground Granulated Blast Furnace Slag,” *Cement, Concrete, and Aggregates* 3, no. 1, 1981, 40–52.

13. Brooks, J. J., “Prediction of Setting Time of Fly Ash Concrete,” *ACI Materials Journal* 99, no. 6, 2002, 591–596.

14. Brooks, J. J., M. A. Megat Johari, and M. Mazloom, “Effect of Admixture on the Setting Times of High-Strength Concrete,” *Cement and Concrete Composites* 22, 2000, 293–301.

15. Eren, O., J. J. Brooks, and T. Celik, “Setting Times of Fly Ash and Slag-Cement Concretes as Affected by Curing Temperatures,” *Cement, Concrete, and Aggregates* 17, no. 1, 1995, 11–17.

16. Byfors, J., *Plain Concrete at Early Ages*, Research 3:80. Stockholm, Sweden: Swedish Cement and Concrete Research Institute, 1980.

17. Schindler, A. K., “Prediction of Concrete Setting.” International RILEM Symposium on Concrete Science and Engineering: A Tribute to Arnon Bentur, Evanston, IL, March 21–24, 2004.

18. Pinto, R. C. A., and K. C. Hover, “Application of Maturity Approach to Setting Times,” *ACI Materials Journal* 96, no. 6, 1999, 686–691.

19. Mehta, P. K., *Concrete: Structure, Properties, and Materials.* Englewood Cliffs, NJ: Prentice-Hall, 1986, 325–326.

20. Nonat, A., Preface, *Proceedings of the Second International RILEM Workshop*, vol. 1. Second International RILEM Workshop, Dijon, France, June 11–13, 1997.

21. FHWA, *Protocol to Identify Incompatible Combinations of Concrete Materials*, Report FHWA-HRT-06-082, 2006.

22. Sandberg, P., and L. Roberts, “Cement-Admixture Interactions Related to Aluminate Control,” *Journal of ASTM International* 2, no. 6, 2005.

23. Wang, H., C. Qi, H. Farzam, and J. Turici, “Interactions of Materials Used in Concrete,” *Concrete International* 28, no. 4, 2006, 47–52.

24. Cost, T., “Incompatibility of Common Concrete Materials: Influential Factors, Effects, and Prevention.” Proceedings of the 2006 Concrete Bridge Conference, Reno, NV, 2006.