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Standard Test Method for
Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry[1]

This standard is issued under the fixed designation C1702; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method specifies the apparatus and procedure for determining total heat of hydration of hydraulic cementitious materials at test ages up to 7 days by isothermal conduction calorimetry.

1.2 This test method also outputs data on rate of heat of hydration versus time that is useful for other analytical purposes, as covered in Practice C1679.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C186 Test Method for Heat of Hydration of Hydraulic Cement
C1679 Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *baseline, n*—the time-series signal from the calorimeter when measuring output from a sample of approximately the same mass and thermal properties as a cement sample, but which is not generating or consuming heat.

3.1.2 *heat, n*—the time integral of thermal power measured in joules (J).

3.1.3 *isothermal conduction calorimeter, n*—a calorimeter that measures heat flow from a sample maintained at a constant temperature by intimate thermal contact with a constant temperature heat sink.

3.1.4 *reference cell, n*—a heat-flow measuring cell that is dedicated to measuring power from a sample that is generating no heat.

3.1.4.1 *Discussion—*

The purpose of the reference cell is to correct for baseline drift and other systematic errors that can occur in heat-flow measuring equipment.

3.1.5 *sensitivity, n*—the minimum change in thermal power reliably detectable by an isothermal calorimeter.

3.1.5.1 *Discussion—*

***A Summary of Changes section appears at the end of this standard**

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[1] This test method is under the jurisdiction of ASTM Committee C01 on Cement and is the direct responsibility of Subcommittee C01.26 on Heat of Hydration.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

For this application, sensitivity is taken as ten times the random noise (standard deviation) in the baseline signal.

3.1.6 *thermal mass, n*—the amount of thermal energy that can be stored by a material (J/K).

3.1.6.1 *Discussion*—

The thermal mass of a given material is calculated by multiplying the mass by the specific heat capacity of the material. For the purpose of calculating the thermal mass used in this standard, the following specific heat capacities can be used: The specific heat capacity of a typical unhydrated portland cement and water is 0.75 and 4.18 J/(g·K), respectively. Thus a mixture of A g of cement and B g of water has a thermal mass of $(0.75 \times A + 4.18 \times B)$ J/K. The specific heat capacity of typical quartz and limestone is 0.75 and 0.84 J/(g·K), respectively. The specific heat capacity of most amorphous supplementary cementitious material, such as fly ash or slag, is approximately 0.8 J/(g·K).

3.1.7 *thermal power, n*—the heat production rate measured in joules per second (J/s).

3.1.7.1 *Discussion*—

This is the property measured by the calorimeter. The thermal power unit of measure is J/s, which is equivalent to the watt. The watt is also a common unit of measure used to represent thermal power.

4. Summary of Test Method

4.1 *Principle*—An isothermal heat conduction calorimeter consists of a constant-temperature heat sink to which two heat-flow sensors and sample holders are attached in a manner resulting in good thermal conductivity. One heat-flow sensor and sample holder contains the sample of interest. The other heat-flow sensor is a reference cell containing a blank sample that evolves no heat. The heat of hydration released by the reacting cementitious sample flows across the sensor and into the heat sink. The output from the calorimeter is the difference in heat flow (thermal power) between the sample cell and the reference cell. The heat-flow sensor actually senses a small temperature gradient that develops across the device, however the heat is removed from the hydrating sample fast enough that, for practical purposes, the sample remains at a constant temperature (isothermal).

4.2 The output from the heat-flow sensor is an electrical voltage signal that is proportional to the thermal power from the sample. This output must be calibrated to a known thermal power. In this method this is accomplished by measurements on a heat source that emits a constant and known thermal power. The integral of the thermal power over the time of the test is the heat of hydration. Alternatively, a cementitious material with a known heat of hydration can be used for calibration as described in Appendix X1.

4.3 Two methods are described. In Method A the sample and water are both temperature equilibrated and mixed inside the calorimeter. This method is the most direct way to determine heat of hydration. In Method B the sample is mixed in the sample vial outside of the calorimeter using temperature equilibrated materials then put into the calorimeter. This method offers certain practicality, but depending on the materials being analyzed and procedures used for mixing and handling, this method may suffer from small errors due to periods of hydration being missed or spurious heat being introduced or taken away from the calorimeter during setup or combinations thereof.

5. Significance and Use

5.1 This method is suitable for determining the total heat of hydration of hydraulic cement at constant temperature at ages up to 7 days to confirm specification compliance. It gives test results equivalent to Test Method C186 up to 7 days of age (**1**).[3]

5.2 This method compliments Practice C1679 by providing details of calorimeter equipment, calibration, and operation. Practice C1679 emphasizes interpretation significant events in cement hydration by analysis of time dependent patterns of heat flow, but does not provide the level of detail necessary to give precision test results at specific test ages required for specification compliance.

6. Apparatus

6.1 *Miscellaneous Equipment:*

6.1.1 *Balance*—Accurate to 0.01 g.

6.1.2 *Volumetric Dispenser*—A device for measuring volume or mass of water, accurate to 0.1 mL. This could be a syringe, pipette, or weighing device.

6.1.3 *Sample Holder*—A device that holds the cement paste and provides intimate contact with the calorimeter heat sensing device and prevents evaporation of mixing water. If using commercially manufactured equipment, consult the recommendations of the manufacturer in choosing sample holders.

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[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

6.1.4 *Resistance Heater*—An electrical device fabricated from material with similar heat capacity and shape as the test sample, but containing a resistor connected to a constant-voltage power supply such that a stable output of 0.010 ± 0.0002 J/s can be generated (see Note 1).

NOTE 1—A simple procedure for fabricating heaters and blanks having the same approximate shape and heat capacity as a sample is to make specimen similar to one used in a determination out of plaster of Paris embedded with a small resistor. Plaster of Paris has only a transient heat of hydration and is not aggressive to electronic components. A resistance of 100 to 300 Ω is a convenient value when using voltages of 0.1 to 10 V to drive heat production.

6.1.5 *Reference Specimen*—A sample fabricated from an inert material with similar heat capacity and shape as the test sample. This is used in the reference cell.

6.1.6 *Multimeter*—An instrument for measuring DC voltage and resistance values for the resistance heater described in 6.1.4 to an accuracy of 1 %. This instrument is only required if the calorimeter does not contain built-in calibration capability.

6.1.7 *Power Supply*—A constant voltage DC power supply with a power output range sufficient to simulate the maximum output of a hydrating cement sample (see Note 2). This equipment is only required if an instrument does not contain built-in calibration capability.

NOTE 2—A power output of at least 0.33 J/s is needed for most applications.

6.2 *Calorimeter*—The schematic design of a calorimeter is given in Fig. 1. It shall consist of a sample holder for the test and reference specimens, each thermally connected to heat-flow sensors, which are thermally connected to a constant-temperature heat sink. The actual design of an individual instrument, whether commercial or homemade, may vary, but it should follow the criteria given below. Any other suitable arrangement that satisfies sections 6.2.1 – 6.2.3 is acceptable.

6.2.1 *Instrument Stability*—The baseline shall exhibit a low random noise level and be stable against drift. This property shall be verified on a new instrument and whenever there are questions about performance. The rate of change of the baseline measured during a time period of 3 days shall be ≤20 µJ/s per gram sample per hour of the test and a baseline random noise level of ≤10 µJ/s per gram sample (see Note 3). In practice the baseline is measured for 3 days and a straight line is fitted to the power (J/(g·s)) versus time (h) data using a linear regression procedure. The long term drift is then the slope in the line (J/(g·s·h)) and the baseline noise level is the standard deviation (J/(g·s)) around this regression line.

NOTE 3—The rationale for these limits is found in Poole (2007) (1).

6.2.2 *Instrument Sensitivity*—The minimum sensitivity for measuring power output shall be 100 µJ/s.

6.2.3 *Isothermal Conditions*—The instrument shall maintain the temperature of the sample to within 1 K of the thermostated temperature.

6.3 *Data Acquisition Equipment*—Data acquisition equipment may be built into the calorimeter instrument package, or it may be an off-the-shelf, stand-alone, item. The data acquisition equipment shall be capable of performing continuous logging of the calorimeter output measurement at a minimum time interval of 10 s. It is useful, for purposes of reducing amount of data, to have the flexibility to adjust the reading interval to longer times when power output from the sample is low. Some data acquisition equipment is designed to automatically adjust reading intervals in response to power output. The equipment shall have at least 4.5-digit-measuring capability, with an accuracy of 1 %, or comparable capabilities to condition the power output into the same quality as integrated signal amplifiers.

7. Instrument Calibration

7.1 *Instrument Calibration*—Commercially manufactured instruments designed for measuring heat of hydration of cementitious materials may have instrument specific calibration procedures. Conform to these procedures if they exist. In addition, the instrument shall be capable of providing data described in 7.1.1.1, 7.1.2.1, and 7.1.2.2, and calculations in 7.1.4. If there are no instrument calibration procedures, calibrate the instrument according to the following procedure. Calibration shall be at least a two-point process. This is illustrated schematically in Fig. 2 Alternatively use a generic calibration procedure for a cementitious

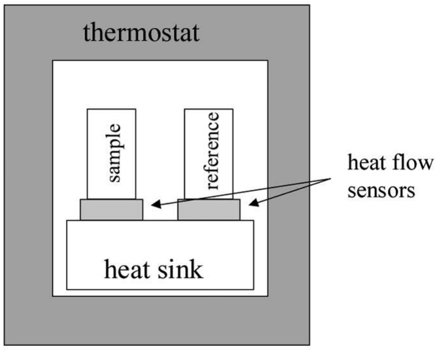
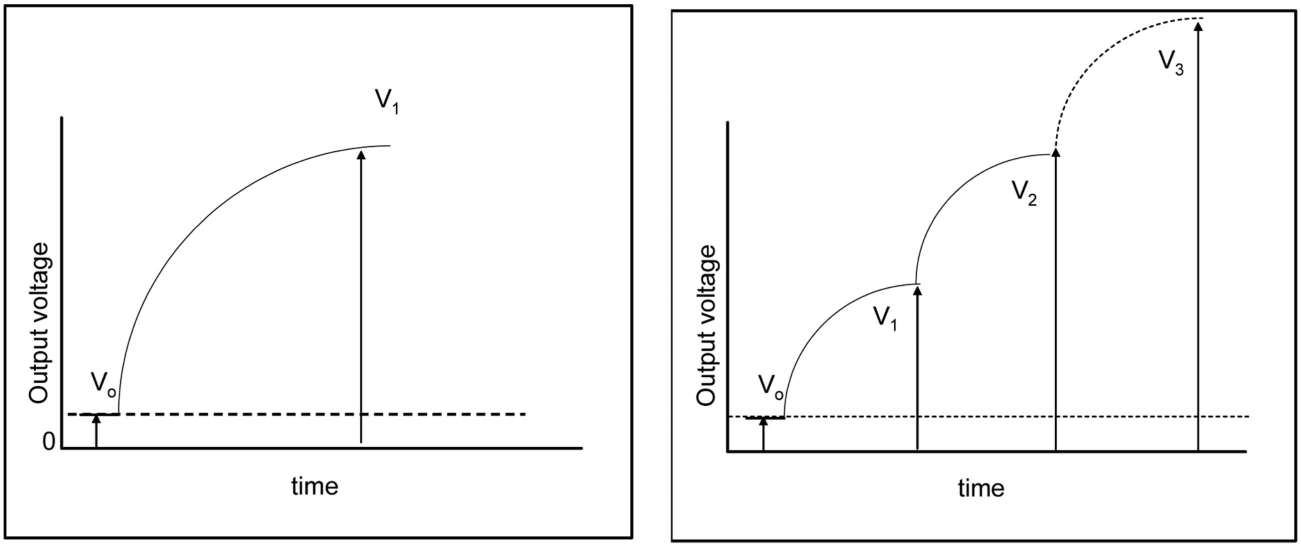


FIG. 1 Schematic Drawing of Heat Conduction Calorimeter



(A) (B)

FIG. 2 (A) Schematic Steady-State Calibration Using 2-Point Calibration Process, and (B) Multi-Point Calibration Process

material with known heat of hydration as described in Appendix X1. Alternatively, use a generic calibration procedure for a cementitious material with known heat of hydration as described in Appendix X1.

7.1.1 Mount the resistance heater and the blank specimen in their respective measuring cells and start data collection. This step measures the baseline calorimeter output (in units of V or mV) when no heat is being generated.

7.1.1.1 Measure this baseline when it reaches a constant value (drift ≤ 20 µJ/s per gram sample per hour).

7.1.1.2 Record this output as V_0 for $P_0 = 0$ (see Note 4).

NOTE 4—V_0 may not be zero voltage, but may be a positive or negative number. The practice of using a test cell and a reference cell usually results in the V_0 being a relatively small number but, depending on the variability in properties of some hardware, it may not be zero.

7.1.2 Power in the heater circuit is related to voltage and resistance by the following equation:

$$P = I^2R \tag{1}$$

where:

P = power, J/s,
I = applied current, amperes, and
R = resistance, ohms.

Apply sufficient voltage to the heater circuit to generate a heat output of approximately 0.1 J/s, measured to an accuracy of 5 %.

7.1.2.1 Allow the output to stabilize signal at a drift of ≤0.1 % over 60 min or ≤0.05 % over 30 min.

7.1.2.2 Record this output as V_1 for a power P_1 (see Note 5). This is the minimum requirement for a calibration sequence. At the users discretion any number of voltage levels may be used to characterize the operating range of the calorimeter.

NOTE 5—The early C_3A reaction of a typical portland cement evolves a maximum power of about 0.02 J/(g·s). The alite phase typically evolves heat at a maximum power of about 0.002 J/(g·s) during the first 24 h of hydration. A 5-g sample then generates power peaks in the range of 0.10 J/s in the first few minutes after adding water, and in the range of 0.010 J/s in the first 24 h.

7.1.3 *Calibration Coefficients*—Calculate calibration coefficients by fitting the power versus voltage output data to a to a mathematical relationship using standard curve fitting techniques. Power (P), in units of J/s (or watts), is the dependent variable (y) in the calibration equation, and output voltage (V), in units of mV, is the independent variable (x). This equation is then used to translate mV output to power units meaningful for calculating heat flow (see Note 6).

NOTE 6—A linear calibration equation is found to be suitable in many instruments over the operating range necessary to analyze portland cements, as in the following equation: $P = A + BV$. In this case, the fitted coefficients A (y-axis intercept) and B (slope) are in units of J/s and J/(mV·s), respectively.

7.1.4 In a multi-channel instrument containing several calorimeters, all channels shall be calibrated individually. However, it is possible to calibrate all calorimeters simultaneously using multiple resistance heaters and having the same current passing through the heaters in all calorimeter cells.

7.1.5 Calibration shall be executed at regular intervals to determine the calibration coefficient. The length of the time intervals between calibrations is dependent on the instrument and the personnel, and must be determined empirically. If the calibration coefficient differs more than 2 % from one calibration to the next, then calibrations intervals must be reduced until this stability limit is reached.

8. Procedure

8.1 The thermal mass of the inert reference specimen should always be similar to the thermal mass of the target cement paste. Verify that the calorimeter equipment temperature is within 0.2°C of target temperature with the proper mass of inert material charged in the reference cells no later than one day before performing a test. Determine that the calorimeter is at temperature equilibrium by verifying that the baseline is stable over a period of 30 min or longer. The temperature of the heat sink during the test shall be 23.0 ± 1.0°C, unless a different temperature is required by the analysis.

NOTE 7—The time required to reach thermal equilibrium depends on the instrument. Generally, it is recommended to set the temperature control unit of the calorimeter at target temperature at least 18 h before testing.

8.1.1 *Baseline Verification Test*—This test is recommended prior to testing and required whenever there is a change in the operating temperature of the calorimeter or in ambient operating conditions. For each active calorimeter cell, prepare a sample of water without any cement and without any mixing, but with the same thermal mass as the inert reference specimen. Alternatively, use another inert material with equal thermal mass as the inert reference specimen. Seal each vial with a vapor-tight lid (see Note 8). For each active calorimeter cell, load the sample container with water or other inert material of equal thermal mass into the calorimeter and start logging. Log the signal for a minimum of 24 h. Calculate the heat as a function of time per gram cement normally used in the calculation section, although no cement is used for this baseline verification test. A re-calibration is required if the absolute value of the calculated heat per hour obtained 6 h from start of logging to the end of the test is higher than 0.10 J/(gh), where the mass (g) refers to the mass of cement intended to be used.

NOTE 8—The effectiveness of this sealing in preventing any evaporation (and its accompanying evaporative cooling) is variable depending on the materials and techniques employed. Determining the mass of the sealed vial to the nearest 0.001 g for a small (up to 10.000 g) sample or 0.01 g for a larger sample at the beginning and end of the test is a convenient method to assess the adequacy of the sealing operation for a sample with hydrating cementitious material. As a rule of thumb, for a w/c = 0.5 cement paste, 0.3 % loss of water due to evaporation over 7 days, may, if not corrected for, result in a heat loss of approximately 3.7 J/g cement. If the measured mass loss is assumed to be due to water evaporation, it can be converted to an equivalent heat release (loss) using the known heat of vaporization of water of 43.99 kJ/mol or 2440 J/g at 25°C. A convenient method to approximate and compensate for the heat loss due to evaporation during calibration is to measure the voltage signal and mass loss with water in the sample vials as part of the baseline calibration.

NOTE 9—The results from the baseline verification test can be used to recalculate the baseline value P_0 in 7.1.

NOTE 10—When performing the baseline verification test, use the same thermal mass of water as in target cement paste.

NOTE 11—Representative values of specific heat capacity for selected materials tested by this method are listed in Appendix X3.

NOTE 12—Calculation of thermal mass. The heat capacity of a typical portland cement and water is 0.75 and 4.18 J/g/K, respectively. If, for example, a cement paste is prepared using 3.00 g cement and 1.5 g water, the resulting cement paste has an approximate thermal mass of (3.00 × 0.75 + 1.5 × 4.18) = 8.52 J/K, which is also the target thermal mass of the inert reference specimen. If using water for the baseline verification test, the corresponding mass of water used is (8.52 4.18) = 2.04 g. After completion of the baseline verification test, a fraction of this water (1.5 g in this example) can be used for the heat of hydration tests in the procedure section.

8.2 *Method A*—This method is used when an instrument is configured so that cementitious materials and water can be temperature equilibrated and mixed while in place in the calorimeter cell.

8.2.1 Weigh at least 3 g of cementitious material (see Note ~~12~~13), the mass recorded to the nearest 0.01 g, and place in the calorimeter cell. Weigh or determine volumetrically sufficient water to give a paste water-cementitious materials ratio of at least 0.40, but in any case sufficient water to completely wet the sample, and place the water holder in the cell. Higher water-cementitious materials ratios may be required to get thorough mixing of cement and water (see Note ~~13~~14). Allow any change in the calorimeter output caused by this process to return to the baseline level.

NOTE 13—Amount of sample required varies among calorimeter designs. Since the exothermic reaction tends to slow down after the first 24 h, a sample that is too small will generate a signal late in the test period that is too weak to detect reliably. If inconsistent results are obtained, then a larger sample size may be required. Sample sizes between about 3 and 15 g have been reported to be useful for maintaining a strong signal late in the test for portland-cement based cements. Normally a signal of at least 10 μJ/(g·s) at the end of the test is sufficient to give good results. Tests designed to run for 1 to 3 days can use a sample mass at the smaller end of this range, while longer tests, such as 7 days, require a sample mass at the larger end of this range.

NOTE 14—The w/c required for good mixing will probably have to be determined empirically by examining specimens after completion of testing for evidence of poor mixing.

8.2.2 Start data collection, then mix the water with the cementitious materials to form a uniform paste. Some commercial calorimeters and data acquisition equipment are programmable to collect data at prescribed interval lengths or at intervals that vary with the rate of change of power levels. Data are collected more rapidly when power output is high than when it is low. If this flexibility is not a feature of the data acquisition component of the calorimeter, then collect readings every 30 s throughout the length of the test (see Note ~~14~~15).

NOTE 15—It is only necessary to collect data every 10 s through the period of an early and short-lived heat evolution peaks. In portland cements this is over within approximately 30 min. Data collection every 10 min is adequate after this point. Adopting this practice will reduce the size of data files.

8.3 *Method B*—This method is used when cement paste is mixed in the sample vial outside of the calorimeter using temperature equilibrated materials and then loaded into the calorimeter cell. In this procedure, a small amount of the early heat-of hydration data may be lost. For some rapidly hardening cements, the error could be more significant. Also, the baseline may also be disturbed during the early period of the test due to spurious heat gains to the sample or losses from the sample while outside of the calorimeter, for example, during mixing and handling.

8.3.1 *Conditioning Materials*—The mix water shall be conditioned to the same temperature as the calorimeter within 0.2°C before mixing. All cementitious materials shall be conditioned to the same temperature as the calorimeter within 1.0°C before mixing.

NOTE 16—It may be convenient to condition vials with mix water in the active calorimeter cells several hours prior to mixing and charging of cement paste. This will ensure that the mix water is at the same temperature as the calorimeter prior to mixing. Start logging the signal after charging vials with water into the active calorimeter cells and continue logging until the signal remains stable for several hours.

8.3.2 Start data collection, then mix the water with the cementitious materials to form a uniform paste, and collect data as described in 8.2.2.

8.3.2.1 *Mixing and Charging of Cement Paste*—The mixing of the cement paste shall be made in the sample vial in such a way that the time between the addition of water and the time when the sample is put into the calorimeter is less than 2 min. Determine the mass of the cement sample to the nearest 0.01 g and the mass of mixing water to the nearest 0.1 g. Mix sufficient cement paste at a water-cementitious materials ratio of 0.40 or higher to give a sample containing a mass of dry cement in the range described in Method A or as recommended by the instrument manufacturer.

NOTE 17—Use of a vortex-type mixing device (as commonly used for mixing materials in test tubes) has been found to generate adequate mixing of cement paste typically in less than 60 s, for samples vials smaller than 50 mL. Hand mixing using disposable spatulas left inside the vial after mixing has been found to generate adequate mixing of cement paste typically in less than 60 s, for samples vials larger than 50 mL. If needed, after mixing tap the sample vial ten times against a flat surface to consolidate the paste sample against the bottom of the sample vial.

8.3.2.2 Care should be taken that the incidental warming or cooling of the sample and the sample holder due to handling are minimal.

NOTE 18—Use of insulating cotton gloves may be helpful in minimizing heating of the sample from handling.

8.3.3 Load the sample vial with cement paste into the calorimeter.

9. Calculation

9.1 The total heat of hydration, Q_t, is the integrated value of the power versus time data, collected as described in 8.2 (Method A) or 8.3 (Method B).

9.1.1 *Remove Leading Edge Data*—For both Methods A and B, there may be data collected during instrument setup and thermal equilibration that is not pertinent to the final determination. These data shall be removed.

9.1.2 Many data acquisition units and commercial calorimeters incorporate the calibration equation into the software and present the raw output data in units of J/g of cement. If this is not the case, then the output data will be in units of mV, and must be transformed into thermal power using the calibration coefficients determined from Eq 2.

$$P_n = A + BV_n \tag{2}$$

where:

P_n = power input level used in the instrument calibration, and
V_n = voltage output level used in the instrument calibration.

9.1.3 *Calculation of Q_t*—The total heat of hydration of the sample, Q_t, is calculated by integrating the power/g versus time data over the time interval of the test (t_0 to t_e, in units of seconds) as in Eq 3:

$$Q_t = \int_{t=t_0}^{t_e} P dt \tag{3}$$

where:

t_0 = the time the cement and water are mixed, taken as zero, and
t_e = the end of the test.

9.1.4 Operationally, the integration is executed by averaging the power output from two consecutive readings and multiplying by the time interval of the reading, giving an output for each time increment in units of J/g. The heat so calculated in each time increment is then summed over the duration of the test, as in Eq 4.

$$Q_t = \sum_{t=t_0}^{t_e} \left(\frac{P(t_i) + P(t_{i+1})}{2} \right) \times (t_{i+1} - t_i) \tag{4}$$

where:

$P(t_i)$ = the power output at the time t_i, and
$P(t_{i+1})$ = the power output at the next time interval (t_{i+1}).

In Method A, t_0 is taken as zero when water is added to the cement.