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# Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry<sup>1</sup>

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 ( $\epsilon$ ) 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:*<sup>2</sup>

C186 [Test Method for Heat of Hydration of Hydraulic Cement](#)

C670 [Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials](#)

C1679 [Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry](#)

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

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

3.1.6.1 *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

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

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

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 power level. The integral of the thermal power over the time of the test is the heat of hydration.

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 outside of the calorimeter 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. Methods of correction are offered for these potential errors.

## 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 (Poole (2007) (4)).

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.

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  $0.010 \pm 0.0002$  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 100-300 ohms is a convenient value when using voltages of 0.1-10 volts 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.

6.1.8 *Insulated Container*—Used in the Method B described in 8.3.5.1. This device can be fabricated using a 500 mL (approximate volume) container insulated with at least 30 mm of polystyrene on the sides and top.

6.1.9 *Temperature Measuring Device*—Used in Method B described in 8.3.5.1. The device shall be capable of measuring temperature changes to the nearest 0.1 °C and of a physical configuration that allows it to operate in the confines of the insulated container described in 6.1.8.

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, 6.2.2, and 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

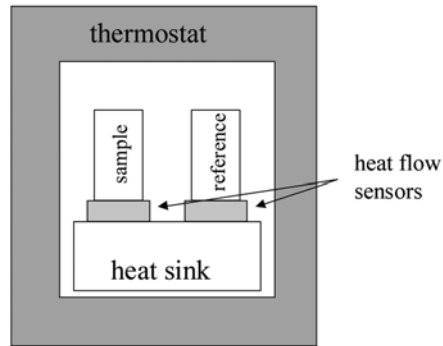


FIG. 1 Schematic Drawing of a Heat Conduction Calorimeter

during a time period of 3 days shall be  $\leq 20 \mu\text{J/s}$  per gram sample per hour of the test and a baseline random noise level of  $\leq 10 \mu\text{J/s}$  per gram sample (see Note 3). In practice the baseline is measured for 3 days and a straight line is fitted to the power ( $\text{J/g/s}$ ) versus time (h) data using a linear regression procedure. The long term drift is then the slope in the line  $\text{J/g/s/h}$  and the baseline noise level is the standard deviation ( $\text{J/g/s}$ ) around this regression line.

NOTE 3—The rationale for these limits is found in Poole (2007) (4).

6.2.2 *Instrument Sensitivity*—The minimum sensitivity for measuring power output shall be  $100 \mu\text{J/s}$ .

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.

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  $\leq 20 \mu\text{J/s}$  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.

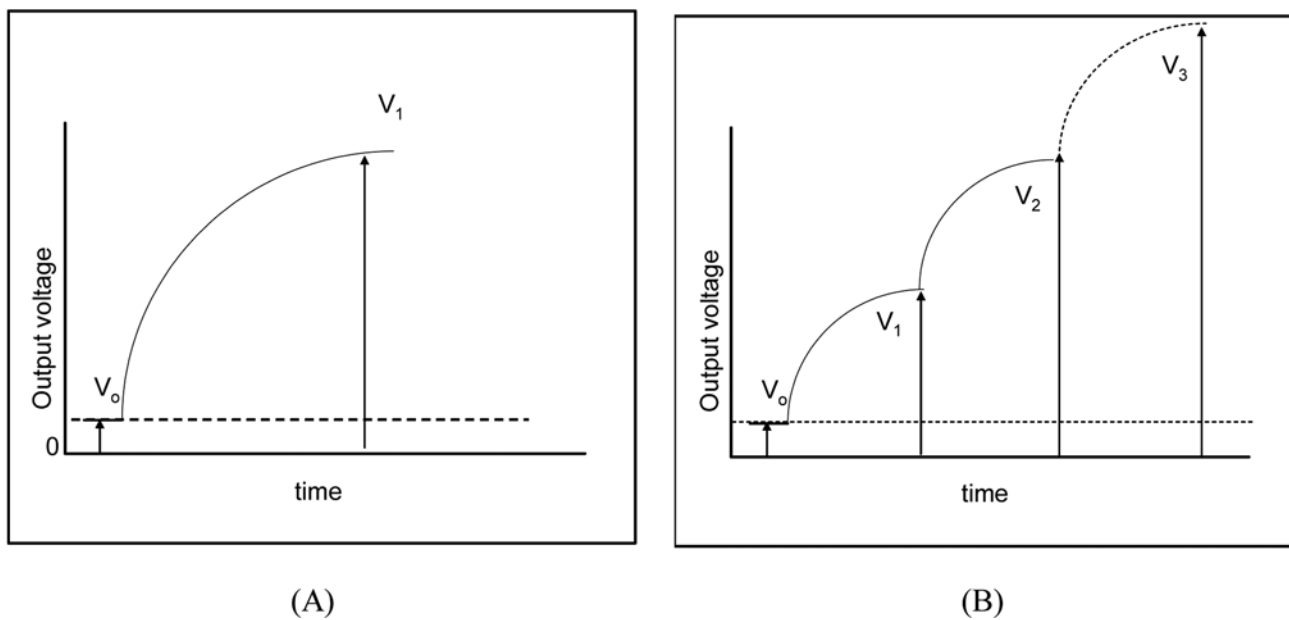


FIG. 2 (A) Schematic Steady-State Calibration Using A 2-Point Calibration Process And (B) Multi-Point Calibration Process

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

(1)  $P = I^2R$

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  $\leq 0.1$  % over 60 min or  $\leq 0.05$  % 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/s/g. The alite phase typically evolves heat at a maximum power of about 0.002 J/s/g during the first 24 h of hydration. A 5 g sample then generates power peaks in the range of 0.10 J/s/g in the first few minutes after adding water, and in the range of 0.010 J/s/g in the first 24 h.

7.1.3 *Calibration Coefficients*—Calculate calibration coefficients by fitting the power versus voltage output data 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/s/mV, 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 Turn on the calorimeter equipment and data acquisition unit. Determine that the calorimeter is at temperature equilibrium by verifying that the baseline is stable over a period of a few minutes. The temperature of the heat sink during the test shall be  $23.0 \pm 1.0$  °C, unless a different temperature is required by the analysis.

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.