This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: C1679 – 22

Standard Practice for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry[1]

This standard is issued under the fixed designation C1679; 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 practice describes the apparatus and procedure for measuring relative differences in hydration kinetics of hydraulic cementitious mixtures, either in paste or mortar (see Note 1), including those containing admixtures, various supplementary cementitious materials (SCM), and other fine materials by measuring the thermal power using an isothermal calorimeter.

NOTE 1—Paste specimens are often preferred for mechanistic research when details of individual reaction peaks are important or for particular calorimetry configurations. Mortar specimens may give results that have better correlation with concrete setting and early strength development and are often preferred to evaluate different mixture proportions for concrete. Both paste and mortar studies have been found to be effective in evaluating concrete field problems due to incompatibility of materials used in concrete mixtures.

1.2 This practice does not cover the measurement of heat of hydration. Heat of hydration can be determined according to Test Method C1702.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* (**Warning—**Fresh hydraulic cementitious mixtures are caustic and may cause chemical burns to skin and tissue upon prolonged exposure.[2])

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C125 Terminology Relating to Concrete and Concrete Aggregates

C172/C172M Practice for Sampling Freshly Mixed Concrete

C219 Terminology Relating to Hydraulic and Other Inorganic Cements

C305 Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency

C403/C403M Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance

C511 Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes

C778 Specification for Standard Sand

C1005 Specification for Reference Masses and Devices for Determining Mass and Volume for Use in Physical Testing of Hydraulic Cements

C1602/C1602M Specification for Mixing Water Used in the Production of Hydraulic Cement Concrete

C1702 Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry

C1738/C1738M Practice for High-Shear Mixing of Hydraulic Cement Pastes

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology C125 and Terminology C219.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *baseline, n*—the signal from the calorimeter when there is an inert specimen in the instrument.

3.2.2 *calcium aluminate, n*—various aluminate phases including but not limited to the tricalcium aluminate and ferrite phases in portland cement clinker, calcium aluminate phases occurring in some supplementary cementitious materials, and

[1] This practice is under the jurisdiction of ASTM Committee C09 on Concrete and Concrete Aggregates and is the direct responsibility of Subcommittee C09.48 on Performance of Cementitious Materials and Admixture Combinations.

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[2] Section on Safety Precautions, Manual of Aggregate and Concrete Testing, *Annual Book of ASTM Standards*, Vol 04.02.

[3] 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.

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

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calcium-alumino-silicate glasses also occurring in some supplementary cementitious materials, that are capable of consuming the sulfate phases present in hydrating cementitious systems.

3.2.3 *calibration coefficient, n*—a factor that relates the value recorded by the data acquisition system to the thermal power output.

3.2.3.1 *Discussion*—Normally recorded data are in volts and the calibration coefficient has units of watts per volt (W/V). Some calorimeters may have internal automatic calibration and will give the output in watts without the user having to specify the calibration coefficient.

3.2.4 *combined mixture, n*—combination of all the materials that are introduced into the calorimeter for measuring hydration kinetics.

3.2.5 *hydration time, n*—the elapsed time from initial contact between the cementitious materials and the mix water.

3.2.6 *inert specimen, n*—specimen placed within the isothermal calorimeter made of a non-reactive material of similar thermal properties (mainly heat capacity) as the reacting specimen made of the cementitious test mixture.

3.2.6.1 *Discussion*—The output from the calorimeter is the difference between the heat flow from the test specimen and the inert specimen. The use of an inert specimen substantially decreases the noise and drift of the measured heat flow.

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

3.2.8 *isothermal calorimetry, n*—an experimental technique to monitor the thermal power output from a specimen kept at near isothermal conditions.

3.2.9 *isothermal hydration profile, n*—the thermal power plotted as a function of hydration time, which provides an indication of the rate of hydration over time at a given temperature.

3.2.10 *main hydration peak, n*—the broadest peak in the isothermal hydration profile that starts at the end of the dormant period and for a well-balanced mixture lasts for several hours (see Fig. 1).

3.2.11 *near isothermal conditions, n*—a constant temperature with a permissible variation of ± 1.0 °C.

3.2.12 *specimen holder, n*—container within the isothermal calorimeter that conducts the heat from the specimen in the vial to the heat flow sensor.

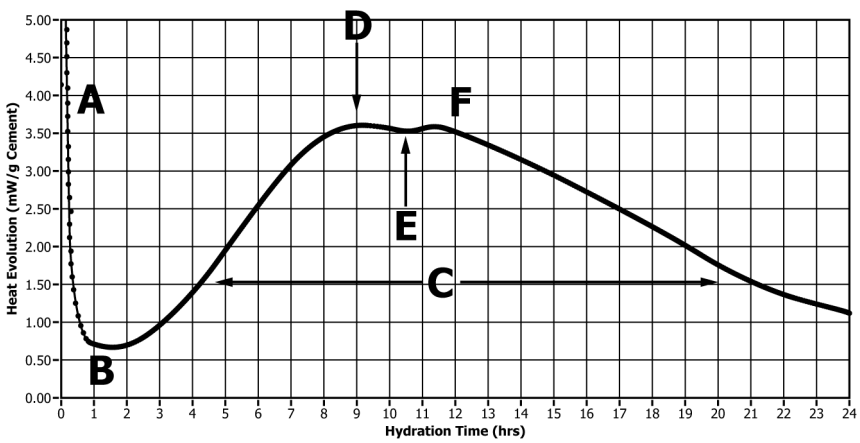
3.2.13 *stock solution, n*—a solution of admixture in water prepared to enable more precise volumetric addition of small quantities of admixture, typically made by pipetting known volumes of admixture into a volumetric flask and diluting it to the flask's fixed volume.

3.2.14 *sulfate addition, n*—the addition of a soluble sulfate source (such as gypsum, calcium sulfate hemihydrate, alkali sulfate) to a combined mixture to investigate whether a given combination of materials is in sulfate balance.

3.2.15 *sulfate balance of mixture, n*—the situation when the size of the main hydration peak is not increased by sulfate additions; in some cases where the main peak is increased in size by added sulfate, it will also be accelerated in time.

3.2.16 *sulfate depletion point, n*—the onset of accelerated calcium aluminate activity that for a portland cement in absence of supplementary cementitious material (SCM) and admixture may take place after the main hydration peak.

3.2.16.1 *Discussion*—The sulfate depletion point may become impossible to detect without further addition of soluble calcium sulfate for certain cements and more often in combined mixtures with admixtures or SCMs, or both. In some cases other sources of sulfate might be used to mimic potential conditions in the system. Among these are anhydrite, arcanite, calcium langbeinite, aphthitalite, syngenite, and others. Fig. 2 shows an example of the effect of added sulfate on the sulfate depletion point. Added sulfate may, in some combined mixtures with admixtures or SCMs, or both, accelerate the onset of



NOTE 1—(A) initial thermal power by dissolution of cement and initial cement hydration; (B) dormant period associated with very low thermal power indicating slow and well-controlled hydration: (C) main hydration peak associated mainly with hydration reactions contributing to setting and early strength development, with maximum at (D); and (E) sulfate depletion point,[4] followed by (F) accelerated calcium aluminate activity.

FIG. 1 Example of Thermal Power Curve for Isothermal Hydration of Portland Cement

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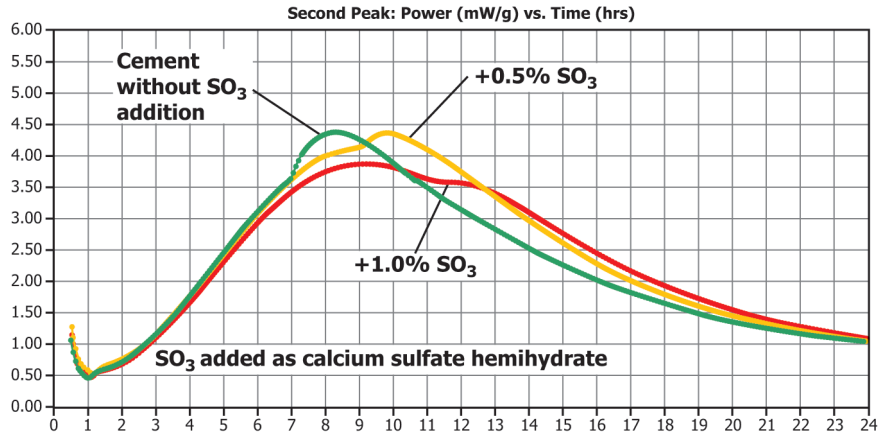

FIG. 2 Example of the Effect of Soluble Calcium Sulfate Addition on the Timing of the Sulfate Depletion Point for a Type I Portland Cement Mixed with Water Only at w/c = 0.45

the main hydration peak. When a combined mixture is at sulfate balance, further addition of soluble sulfate will not increase the size, or accelerate the onset, of the main hydration peak.

3.2.17 *thermal equilibrium time, n*—the elapsed hydration time when the thermal power of replicate mixtures do not differ by more than 0.2 mW/g of dry material.

3.2.18 *thermal indicator of setting time, n*— the hydration time to reach a thermal power of 50 % of the maximum value of the main hydration peak.

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

3.2.19.1 *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 × A + 4.18 × 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).

3.2.20 *thermal power, n*—heat production rate measured in watts (W) or joules per second (J/s), usually expressed in relation to the mass of cementitious material, as mW/g or J/s/g.

3.2.20.1 *Discussion*—The thermal power is an indicator of the rate of various chemical reactions between cementitious materials, other fine particles, mix water and admixtures.

3.2.21 *vial, n*—container into which the freshly mixed cementitious mixture is placed for a measurement.

4. Summary of Practice

4.1 An isothermal calorimeter consists of heat sink with a thermostat, two heat flow sensors and a specimen vial holder attached to each sensor. A vial containing a freshly prepared mixture is placed in contact with one of the vial holders and a thermally inert material is placed in contact with the other. The heat of hydration released by the reacting cementitious specimen is transferred and passes across a heat flow sensor. The calorimeter output is calculated from the difference between the outputs from the test specimen heat flow sensor and the inert specimen heat flow sensor. Because the heat is allowed to flow away from the specimen, the measurement will take place at essentially constant temperature (isothermal conditions).

4.2 Mixtures with cement, SCM, admixtures, water and optional fine aggregate are prepared and introduced into an isothermal calorimeter. Isothermal calorimetry tests are performed on a series of different mixtures for relative comparison of the hydration kinetics. The output of the calorimeter is evaluated by graphical and mathematical means to evaluate retarding and accelerating effects of different combinations of materials. Calcium sulfate may be added as a probe to determine if the addition of admixture, SCMs, or both have increased the mixture's demand for sulfate beyond that which is available in the cement.

5. Significance and Use

5.1 Thermal power curves are used to evaluate the isothermal hydration kinetics of the combined mixture of different materials during the early period after being mixed with water. These isothermal power curves, or hydration profiles, may provide indications relative to setting characteristics, compatibility of different materials, sulfate balance and early strength development. The isothermal hydration profiles can also be used to evaluate the effects of compositions, proportions, and time of addition of materials as well as curing temperature. Special care must be used in evaluating extended retardation with paste specimens, which have been shown to overestimate the retardation of some mixtures containing cement, SCM, and admixtures.

5.2 This procedure can be used to measure the effect of chemical admixtures on the cement hydration profile. In many cases, the addition of chemical admixture changes the kinetics of cement hydration.

5.3 Although this technique has been used historically to understand issues related to setting and slump loss, it must be emphasized that isothermal calorimetry results cannot predict concrete performance definitely, either positively or negatively.

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Extensive verification in concrete at planned dosages and temperatures, and at higher dosages, is needed. Isothermal calorimetry is an effective tool to identify sensitivities, so that concrete testing can be efficiently planned and performed.

5.4 This practice provides a means of assessing the relative hydration performance of various test mixtures compared with control mixtures that are prepared in a similar manner.

5.5 The procedure and apparatus can be used to monitor the thermal power from pastes and mortars alone or in combination with chemical admixtures.

5.6 The isothermal calorimeter described here can be used to measure the thermal power and heat of hydration of mortars prepared independently or obtained by wet sieving from concrete in accordance with Practice C172/C172M.

6. Apparatus

6.1 Devices for mixing to produce a homogeneous mixture of cement, SCM, admixtures, water and optional other fine materials or aggregate and devices for charging the mixture into the specimen vial.

6.1.1 *Weights and Weighing Devices* shall conform to the requirements of Specification C1005.

6.1.2 *Graduated Cylinders* shall conform to the requirements of Specification C1005. The permissible variation for graduated cylinders of less than 100-mL capacity shall be ±1.0 % of the rated capacity.

6.1.3 *Graduated Syringes* of suitable capacities to contain the desired volume of liquid admixture or stock solution at 20 °C. The permissible variation of the measured volume shall not exceed 3 % of the volume to be delivered. When admixture quantities required are less than 2 mL, or are viscous in nature, optionally prepare stock solutions at appropriate dilution, to avoid problems with small volumes measured volumetrically. Care shall be taken to inspect stock solutions for separation and any admixture that is prone to separation in stock solution must be added in an alternative fashion, such as by analytical syringes.

6.1.4 *Mixing Apparatus:*

6.1.4.1 *Mortar Preparation*—The mixer shall comply with Practice C305.

6.1.4.2 *Paste Preparation*—A high shear mixer as described in Practice C1738/C1738M. A handheld household mixer capable of mixing paste at not less than 400 r/min or other mixers for paste or mortar preparation are also permitted.

6.1.4.3 The repeatability of results for any mixing method must be measured and reported as described in 12.5.

6.1.5 *Vials* that can be sealed and fit into the specimen vial holders of the calorimeter.

6.1.6 *Pipette, Funnel or Syringe* to facilitate charging the sample to the vials. The neck of the device must be large enough to avoid sample segregation.

6.2 *Calorimeter and Data Acquisition System* of suitable capacity and calibrated to monitor the thermal power of mortar or paste in a repeatable fashion. The actual design of an individual instrument, whether commercial or custom-built, may vary, but it shall meet the following criteria, and shall be verified to do so on a yearly basis or at any time that equipment is modified.

6.2.1 The standard deviation in thermal power for six replicate specimens sampled from *one mixture* of a portland cement paste without chemical admixture at w/c 0.45 tested at 23 °C ± 4.0 °C shall be no greater than 0.5 mW/g of dry material measured at the maximum of the main hydration peak (see Fig. 1 for identification of the main hydration peak). For calorimeters which do not allow external mixing, prepare six replicate mixtures.

6.2.2 The baseline measured with an inert specimen of similar thermal mass as the test specimen shall exhibit a low random noise level and be stable against drift. The baseline measured at 23 °C ± 4 °C during a time period of 24 h shall have a long-term drift of less than 0.5 mW per day per gram of inert material used and a baseline random noise level of less than 0.2 mW per gram of inert material used. In practice, the baseline is measured for 24 h or longer and a straight line is fitted to the data using a linear least squares procedure. The long-term drift is the slope of the line and the baseline random noise level is the standard deviation of the data about the best-fit line.

6.2.3 The vials shall be vapor tight so that endothermic heat of evaporation does not significantly influence the measurements. This shall be verified with a 24 h measurement with water instead of the mortar or paste specimen. The difference between the measured thermal powers of an empty vial and one containing water shall be less than 0.2 mW per gram of water when calculated according to the procedure in 13.1.

6.2.4 The data acquisition equipment shall be capable of performing continuous logging of the calorimeter output with a time interval between the measurements that is no larger than 60 s.

7. Materials

7.1 *Sand:*

7.1.1 Unless specified otherwise, use standard graded sand as defined in Specification C778 for preparing mortar samples.

7.1.2 When specified, use job-specific sand when performing a specific mortar test series that is related to field application.

7.2 *Water:*

7.2.1 Unless specified, use potable water as defined in Specification C1602/C1602M.

7.2.2 When specified, use job-specific water when performing a specific test series that is related to field application. Follow Specification C1602/C1602M in reporting the type of water used.

7.3 *Sulfate Source:*

7.3.1 Unless specified otherwise, use reagent grade calcium sulfate dihydrate or hemihydrate prepared from reagent grade calcium sulfate dihydrate to verify whether a mixture is in sulfate balance. See Appendix X6 for examples.

7.3.2 When specified, use a source-specific calcium sulfate for performing a specific test series that is related to field application.

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8. Temperature and Humidity

8.1 *Sample Preparation Temperature*—Unless specified otherwise, maintain the temperature of the air in the vicinity of all equipment and materials used in accordance with the requirements for cement mixing rooms in Specification C511.

8.1.1 When specified, different temperature conditions are permitted for research purposes or to simulate field conditions.

8.1.2 To reduce the time to reach thermal equilibrium, it is permitted to cool the mixture during mixing. It is also permitted to adjust the temperature of the mix water or the starting materials, or both, in order to obtain a temperature of the prepared mixture close the temperature of the calorimeter. This is especially needed when using high shear mixing.

8.2 *Isothermal Calorimeter Test Temperature*—The temperature of the isothermal calorimeter shall be set at 23.0 °C ± 4.0 °C and allowed sufficient time to stabilize at that temperature.

8.2.1 When specified, a different calorimeter test temperature is permitted for research purposes or to simulate field conditions. Take precaution to prevent condensation of moisture inside the calorimeter if the calorimeter test temperature is set below the temperature of the laboratory.

NOTE 2—Condensation inside the calorimeter cells can be prevented by controlling the humidity inside the calorimeter, or by controlling the humidity or temperature of the testing environment that is in direct contact with the calorimeter. Condensation will not occur inside the calorimeter cells if the temperature of the testing environment is at or below the temperature of the thermostat.

9. Test Specimens

9.1 The number of specimens and number of test batches depend on the purpose of the test program. Replicate testing of specimens sampled from a single prepared batch shall be done initially to establish acceptable repeatability of the apparatus as defined in 6.2. Replicate testing of separately-prepared specimens is also required in 12.5 to establish the repeatability of results for each mixing method. The number of replicates for routine testing is addressed in 12.2.1.

NOTE 3—See Appendix X6 for examples of different test programs.

9.2 The specimen size placed in the calorimeter depends on the instrument used as well as the type of mixture (paste or mortar).

NOTE 4—Typical specimen sizes for paste and mortar are 5 g to 10 g and 50 g to 100 g, respectively. A smaller specimen will reduce the time to reach isothermal conditions if the initial specimen temperature differs from the calorimeter test temperature.

10. Composition of Paste or Mortar Mixtures

10.1 Mixture proportions depend on the purpose of the test program (see Note 4).

10.2 Record mixture proportions for each mixture that is tested, including complete description of mixing method, order and timing of admixture addition.

11. Preparation of Apparatus

11.1 *Determination of Baseline*—Baselines are determined during calibrations or before each measurement, preferably when the calorimeter contains inert specimens, as this reduces the noise. If baselines are stable over time as defined in 6.2.3, they need only be determined at calibrations. If they are not stable, they shall be determined before each measurement.

11.2 *Calibration*—Calibration shall be made according to manufacturer's recommendations at regular intervals of one year or less to determine the calibration coefficient. If the calibration coefficient differs more than 5 % from one calibration to the next, calibration intervals shall be reduced to 90 days. The length of the time intervals between calibrations depends on the instrument and the personnel. For the purpose of this practice, the calibration coefficient can be assumed to be constant independent of the level of the signal.

12. Procedure

12.1 *Mixing:*

12.1.1 Various mixing methods that have been found useful are described in the Appendix. Because mixing intensity is a variable that may influence the interaction of materials used to prepare cementitious mixtures, in many cases different mixing procedures (speeds or durations) may be needed, depending on the goal of the testing. Unless mixing intensity is a defined variable in a testing program, mixtures prepared under different mixing conditions shall not be compared. External mixing may result in a temperature increase in the sample that may lead to temporary non-isothermal conditions after loading the specimen into the calorimeter. The thermal equilibrium time shall be estimated in accordance with 12.4. The results obtained at hydration times shorter than the equilibrium time are less repeatable and shall only be used if the measured effects are larger than the variation found when estimating the thermal equilibrium time (see Note 5).

NOTE 5—The isothermal calorimeter will bring the temperatures of specimens into thermal equilibrium, but the time required to do so depends on the instrument parameters, specimen size, mixing method, and materials used. Differences in initial thermal power caused by differences in initial temperature can optionally be minimized by keeping all materials at equal temperature, including any water used in cleaning mixing equipment. If needed, the temperatures of the starting materials may be adjusted to compensate for temperature changes during mixing, so that the temperature after mixing is as close as possible to the calorimeter set point.

12.2 *Loading Specimen into Calorimeter:*

12.2.1 Two specimens shall be prepared from one batch, unless the standard deviation of the time to reach the maximum of the main hydration peak for six replicate *separately-prepared* specimens has previously been determined according to 12.5.1 to be less than 60 min, in which case one specimen is adequate (see Note 6).

NOTE 6—A sub-sample of the prepared mixture is used in this method, and it is necessary to obtain a representative sample. Normally, replicate measurements are made initially as specified in 12.5 in order to establish the error associated with variability in specimen composition, preparation, and sampling.

12.2.2 Wear insulating gloves or use tweezers to minimize warming of the vial and specimen by heat from hands.

12.2.3 Weigh and record the empty mass of the vial to be used, or tare the scale to zero with the empty vial on the scale.

12.2.4 Place a representative sample of fresh paste or mortar into the specimen vial resting on the scale. Typically a plastic disposable pipette is used for paste, with the operating temperature

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