Designation: C 1679 – 08

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

This standard is issued under the fixed designation C 1679; 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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.* (**Warning—**Fresh hydraulic cementitious mixtures are caustic and may cause chemical burns to skin and tissue upon prolonged exposure.[2])

2. Referenced Documents

2.1 *ASTM Standards:* [3]

C 125 Terminology Relating to Concrete and Concrete Aggregates
C 172 Practice for Sampling Freshly Mixed Concrete
C 219 Terminology Relating to Hydraulic Cement
C 305 Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency
C 403/C 403M Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance
C 511 Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes
C 778 Specification for Standard Sand
C 1005 Specification for Reference Masses and Devices for Determining Mass and Volume for Use in the Physical Testing of Hydraulic Cements
C 1602/C 1602M Specification for Mixing Water Used in the Production of Hydraulic Cement Concrete

2.2 *Other Standard:*

API Specification RP 10B-2/ ISO 10426-2 Recommended Practice for Testing Well Cements[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology C 125 and Terminology C 219.

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

3.2.2.1 *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.

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[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.

[4] Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, http://api-ec.api.org.

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

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

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

3.2.5 *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.

3.2.5.1 *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.

3.2.6 *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.

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

3.2.8 *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.

3.2.9 *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).

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

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

3.2.12 *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.

3.2.13 *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.

3.2.14 *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.

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

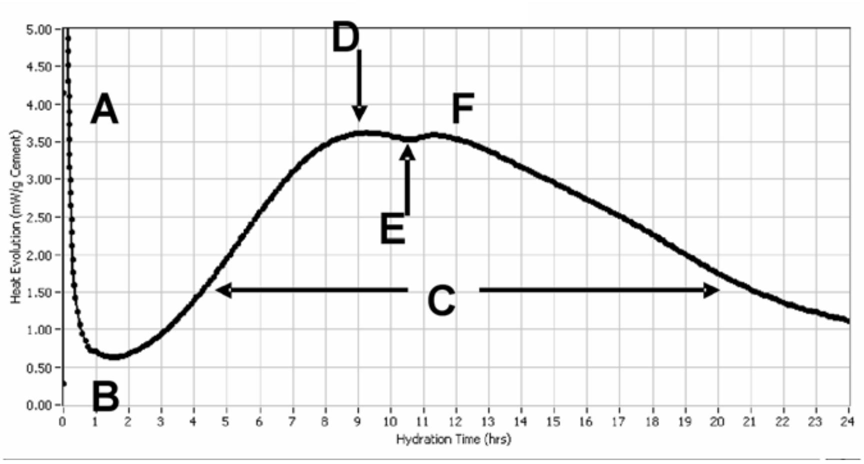
3.2.15.1 *Discussion*—The sulfate depletion point may become impossible to detect without further addition of gypsum or plaster for certain cements and more often in combined mixtures with admixtures or SCMs, or both. In some cases other sources of sulfate might be used to mimic potential conditions 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 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.

3.2.16 *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.

3.2.17 *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.

3.2.18 *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.

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



NOTE—(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,[6] followed by (F) accelerated aluminate activity.

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

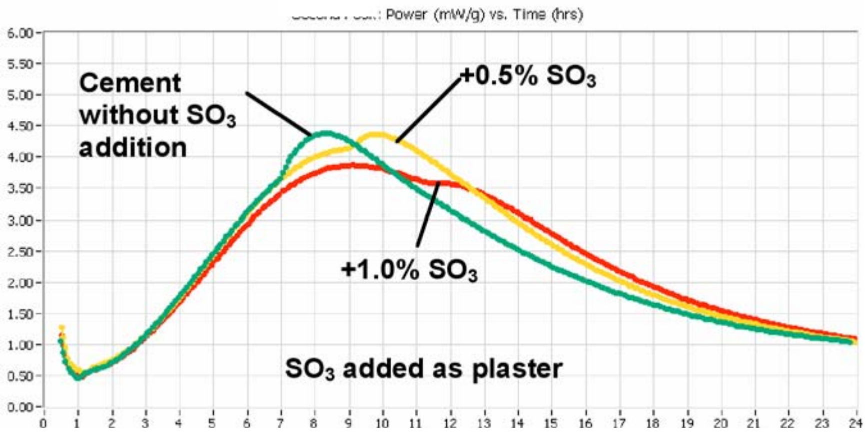


FIG. 2 Example of the Effect of Soluble Calcium Sulfate Addition on the Timing of the Sulfate Depletion Point for a Type I Portland Cement Mixed with Water Only at w/c = 0.45

3.2.19 *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. 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 C 172.

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 C 1005.

6.1.2 *Graduated Cylinders* shall conform to the requirements of Specification C 1005. 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 C 305.

6.1.4.2 *Paste Preparation*—A high shear blender,[5] or similar variable speed blender capable of maintaining a no-load speed of at least 15 000 r/min, with optional cooling device. 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 ± 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 properties (mainly heat capacity) as the test specimen shall exhibit a low random noise level and be stable against drift. The baseline measured at 23 ± 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 C 778 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 C 1602/C 1602M.

7.2.2 When specified, use job-specific water when performing a specific test series that is related to field application. Follow Specification C 1602/C 1602M 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 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.

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 C 511.

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 ± 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

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[5] Mixing devices described in API Specification RP 10B-2/ ISO 10426-2 have been found suitable for this purpose.

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 the Appendix 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 to 10 g and 50 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 opening cut to size to match the stiffness of the paste, or a spoon is used for mortar. Make sure that masses of all specimens that will be compared with each other do not differ by more than 20 %. Clean and dry the outside of the vials as needed.

12.2.5 Weigh and record the specimen mass to the nearest 0.1 g and seal the vial in order to be vapor tight.

12.2.6 Immediately place the vial into the calorimeter ensuring consistency between the specimens ages at the time specimens are placed in the calorimeter. Typical loading times are 1 to 2 min after the end of the mixing cycle, which for a 4-min cycle yields 5 to 6 min after the cementitious material is added to the water. Record the time the vial was introduced into the calorimeter.

12.3 *Measurement of Thermal Power*:

12.3.1 Start thermal power measurement immediately after specimen has been placed in calorimeter. In the case of internal mixing, start thermal power measurement before initial contact between the cementitious materials and the mixing water.

12.3.2 Measure the thermal power approximately every 60 s until at least two hours after the maximum of the main hydration peak (See Fig. 1). The testing duration and data sampling frequency are permitted to be modified according to the nature of the test program and the rate of change in thermal power.

NOTE 7—Paste studies are generally more repeatable than mortar, because less paste is needed to ensure known and uniform binder content in the specimen. However, certain mixtures may be sensitive to the mixing action. Paste mixtures with water reducing or retarding admixtures generally have longer retardation than the corresponding mortar mixtures. Especially when testing for the effect of admixtures with a retarding component, it is recommended to verify any results obtained in paste by testing in mortar. The larger the specimen, the longer it takes for heat transfer from specimen to calorimeter sensor. Also, the larger the specimen, the larger will be the temperature rise within the specimen, and the longer will be the time required to reach thermal equilibrium. Mortar studies are, on the other hand, more concrete-like and allow for parallel testing of other properties such as flow, stiffening, strength, and air content.

12.4 *Determination of Thermal Equilibrium Time*:

12.4.1 The thermal equilibrium time shall be determined for a given instrument and type of specimens (defined by specimen mass, initial temperature and type (paste or mortar) by preparing and testing a at least six replicate batches and measuring the elapsed hydration time when the range of the thermal power of replicate specimens falls to 0.2 mW/g of dry material (See Fig. 3).

12.5 *Determination of Repeatability of Results*:

12.5.1 The repeatability of the results of any mixing method must be determined by preparing and testing at least six replicate batches of a paste mixture that has a thermal indicator of setting time that is equal to or exceeds that of the most retarded mixture in the planned test program. The repeatability shall be recorded as the standard deviation of the time to reach the maximum of the main hydration peak (See Fig. 4). The repeatability must be measured annually or when the operator or mixing method has changed.

NOTE 8—It is convenient to develop a chart of repeatability versus time to reach the maximum of the main hydration peak for a particular mixing method used. This allows for estimation of repeatability for any given level of retardation in a particular experiment.

13. Calculation of Results

13.1 *Post-Processing of Data*—The aim of the evaluation is to monitor differences in the evolution of thermal power for different mixtures during the test period, typically 24 or 48 h. The data evaluation method consists of the following steps:

13.1.1 Remove the baseline:

$$V(t) = V_{raw}(t) - V_{bl} \qquad (1)$$

where:

V_{raw} = signal from the calorimeter, and
V_{bl} = measured baseline signal of the calorimeter.

13.1.2 Apply the calibration coefficient (ε) and divide by the mass of cementitious materials (m_c) in the specimen to obtain the normalized thermal power P per unit mass of cementitious material (W/g) as a function of time:

$$P(t) = \frac{\varepsilon \cdot V(t)}{m_c} \qquad (2)$$

13.1.3 Plot the normalized thermal power as a function of time. For example, see Fig. 1.

NOTE 9—The accumulated energy for a given mixture may serve as an indicator of potential strength development as a function of time. The accumulated energy, normalized to a unit mass of total cementitious materials (J/g), is obtained by integrating the area under the power curve.

14. Evaluation of Test Results

14.1 Calorimetry results are typically evaluated graphically by comparing differences in response from tests of different mixtures.

NOTE 10—The evaluation of calorimetry results depends on the nature of the test program. See examples in the Appendix.

14.2 If presenting results that include the initial, non-isothermal test period, present the data as two separate plots:

14.2.1 The first plot displays the initial thermal power, typically from 0 to 30 min or 0 to 60 min and, if external mixing was used, includes a statement that results were obtained while not at thermal equilibrium. Care must be taken in interpretation of these initial results.

14.2.2 The second plot displays the thermal power starting at the time of thermal equilibrium until the completion of the test.

15. Report

15.1 Report the following information:

15.1.1 Type of instrument used.

15.1.2 Date of last calibration.

15.1.3 Source and identity of all materials tested, method of conditioning them to test temperature, and temperature prior to mixing.

15.1.3.1 The specific type of sulfate source shall be included as part of the description of a sulfate addition, as well as its precise method and timing of addition. If plaster is used, evidence shall be supplied of its hydration state prior to testing.

15.1.4 Mixture proportions.

15.1.5 Temperature, date, starting time, and duration of test.

15.1.6 Mixing method and duration, including sequences and timing of mixing and scraping down, volume of container and speed of mixer.

15.1.7 Thermal equilibrium time determined for the type of mixture tested as determined in 12.4.

15.1.8 Standard deviation of time to reach maximum on the main hydration peak as determined in 12.5.

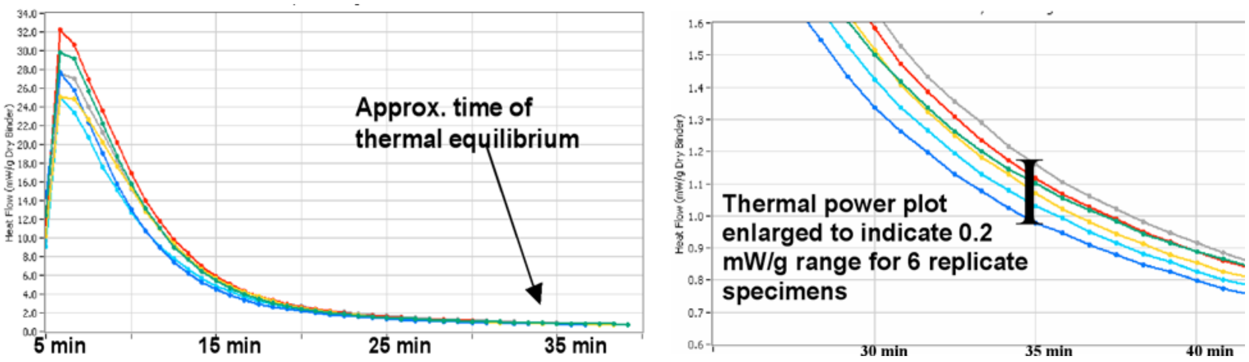
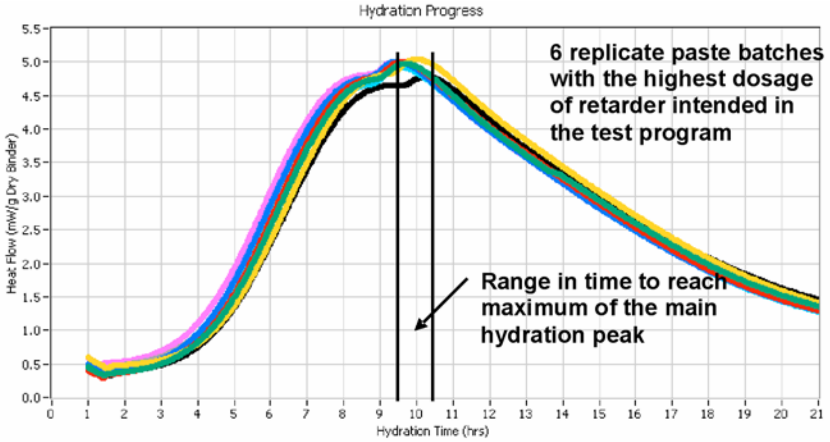


FIG. 3 Illustration of Estimated Time to Reach Thermal Equilibrium Using Six Replicate Specimens



NOTE—The range of results from which the standard deviation is calculated is shown.

FIG. 4 Procedure for Measuring Repeatability of a Mixing Procedure Using Replicate Batches of a Paste Mixture with Longest Setting Time in the Test Program

15.1.9 Admixture addition sequence, if applicable, and method of addition of admixture including description of any stock solutions used.

15.1.10 Any unusual observations, such as early stiffening during sample preparation.

15.1.11 If thermal indicators of relative setting time are used, method of calculating relative setting time if different from default method.

15.1.12 Plots of thermal power per unit mass of cementitious materials. See Appendix for examples. It is important to adapt the graphs to address each technical point on separate graphs. Plotting many together may cause confusion even among the experienced users of this technique.

15.1.13 Statement that the test was carried out in accordance with this practice and notes of all deviations from the described procedure.

16. Keywords

16.1 cement-admixture interactions; hydration kinetics; hydration performance; isothermal calorimetry; sulfate depletion

APPENDIXES

(Nonmandatory Information)

X1. DEFINITIONS OF TERMS USED IN APPENDIX

X1.1 *delay time, n*—period between initial contact of mix water and cementitious materials and when an admixture is added to the mixture.

X1.2 *delayed addition of admixture, n*—addition of admixture to the mixture when the delay time exceeds 10 s after the initial contact between mix water and cementitious materials.

X1.3 *heat of hydration, n*—total energy released at a given hydration time measured in joules per unit mass of cementitious material (J/g); the time integral of normalized thermal power.

X1.4 *tail end addition of admixture, n*—addition of admixture to the mixture within 2 to 10 s after the initial contact between mix water and cementitious materials.

Discussion—The exact addition time should be defined as needed in the test program; see examples.

X1.5 *upfront addition of admixture, n*—addition of admixture to mix water prior to mixing with cementitious materials.

X2. TYPICAL USES, EXPERIMENTAL DESIGNS AND EVALUATION

X2.1 *General*:

X2.1.1 Experimental designs are typically devised to study the effect of supplementary cementitious materials or admixture type, dosage and addition mode on the hydration kinetics of cementitious systems. Other parameters such as source of water, fine particles, mixing method, or curing temperature can be studied as well. The water content should be sufficient to produce a homogeneous mixture without excess bleeding. Tests of separate mixtures with additional source of soluble sulfate, corresponding to 0.5 % SO_3 by mass of portland cement or other amounts, added before testing, are typically performed to evaluate if additional sulfate would improve the hydration performance of mixtures with high SCM or admixture dosage. Several example experimental designs are shown in this appendix. It should be noted that each example represents a specific set of materials for the purpose of showing experimental designs. The example results cannot be extrapolated to other sets of materials.

Use of different SCMs or admixtures, or both, may result in mixtures with different workability. This can affect the amount of shear imparted to the cementitious particle by the mixing action, which may affect hydration kinetics. In cases where problems are found, it may be useful to alter the water-cementitious materials (*w/cm*) ratio in order to investigate its effect on the results.

X2.1.2 Admixture type, dosages, and addition modes can be selected based on local market conditions, experience, dosing equipment, or recommendations from the supplier. The dosage of admixtures may vary with weather conditions.

X2.1.3 It is strongly recommended to test for the effect of an admixture overdose. Mixtures that are sensitive to minor overdoses are likely to show abnormal performance in the field, given the inherent variability of typical concrete materials and production operations.

X2.1.4 It is also recommended to test for the effects of temperature change. Hot weather typically causes faster loss of workability and therefore higher dosages of water-reducing or set-retarding admixtures are often used. The combination of higher admixture dosage and higher temperature can cause abnormal performance in the field. Similarly, cold temperatures, especially with lower C_3A cements may result in extended setting time, especially when higher admixture dosages appropriate for warm weather are maintained during cold conditions.

X3. SULFATE BALANCE

X3.1 See Fig. 1 of this practice for an example of the portion of the thermal power output associated with aluminate reaction after sulfate depletion, point E, which is the small peak labeled F. This point is of concern as there is a correlation between this peak occurring before the completion of the main hydration peak, and problems with premature or severely delayed setting and slump loss of combined mixtures. In many cases, cements that have enough sulfate for proper control of their own hydration cannot supply enough sulfate when combined with various amounts of other materials, so it becomes of importance to understand the effect of the added materials on the location of the sulfate depletion point.

X3.2 The sulfate depletion point is indicated as the onset of either a sharp or shallow hump on the main hydration peak of the thermal power curve. The sulfate depletion point will move later in time relative to the maximum of the main hydration peak (point D in Fig. 1) and diminish in size when additional source of soluble sulfate is added to the system. This peak seen after the sulfate depletion point may be shallow and difficult to distinguish from the rest of the main hydration peak for some portland cements and in many combined mixtures containing SCM or admixture, or both. The peak typically is more visible with very active aluminate cement such as a high C_3A Type I, and decreases in sharpness as the C_3A content decreases, making it difficult to identify on many Type V cements. In such cases, performing additional tests with various sulfate addition levels may clarify the timing of the sulfate depletion point, (See Fig. 2 of this practice), but there are cases where no depletion point and subsequent peak can be resolved.

X3.3 The nature and position of the sulfate depletion point in most combined mixtures can be verified by monitoring the effect of incremental addition(s) of reagent grade calcium sulfate dihydrate (gypsum), Terra Alba gypsum or calcium sulfate hemihydrate (plaster) to the mixture, as shown in Fig. X3.1. Because few cements have enough sulfate to avoid any signs of sulfate depletion until after 24 h, a point of depletion is typically observed in the hydration profile. However, if the depletion occurs near the maximum of the main hydration peak it may not be discernible, and it is frequently found as merely a slight asymmetry of the peak and shown in curve #3 of Fig. X3.1. Addition of one or sometimes two levels of additional sulfate will cause the depletion point to move to later times, and therefore show up clearly as seen in curve #4 of Fig. X3.1.

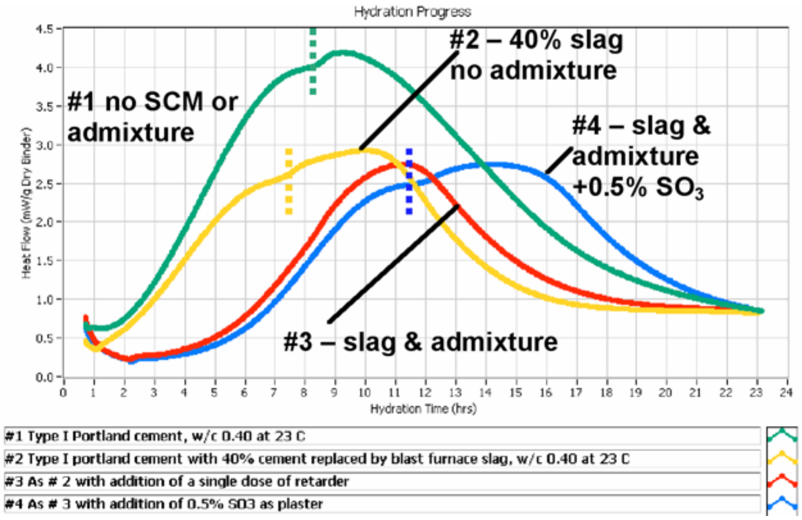


FIG. X3.1 Effect of SCM, Admixture and Sulfate Addition on the Sulfate Depletion Points, as Indicated by Vertical Dotted Lines

X4. MIXING METHODS

X4.1 Mixing intensity may significantly affect the results of isothermal calorimetry. Consistency in mixing method is vital for results to be compared, but as numerous techniques have proven useful, no one method is specified in this practice. Mixing may be either internal in the specimen vial, either by simple absorption of water or by mechanical means.

X4.2 Internal mixing has the advantage of allowing capture of the whole thermal power diagram, but the disadvantage of not being able to achieve shear rates approaching that in concrete. Delayed addition of admixture can be difficult or impossible depending on calorimeter design. Care must be taken that the full sample of paste is wetted equally; a means to verify this is to remove the hardened sample from the sample vial and crush it to see equal color. If significant variation in paste color is seen it should be so noted in the report.

X4.3 External mixing may be used for paste, mortar, or concrete. Depending on calorimeter design, concrete samples may be tested as concrete or as mortar separated according to the method in Practice C 172. Several methods that have been used successfully are outlined below.

X4.4 *Preparation of Paste Using a Hand-Held Kitchen Mixer or Similar Mixer*:

X4.4.1 Add cementitious materials into the mixing container. Add water including any dissolved admixtures, and immediately start the timer. Increase the speed of rotation of the mixing blades to 200 ± 100 r/min while avoiding splashing. Record the time of initial contact between cementitious materials and water.

X4.4.2 Mix at 200 ± 100 r/min to the 1 min 30 s mark.

X4.4.3 Stop mixing and for 30 s scrape corners of container to ensure all dry materials are mixed in, and scrape down any paste that may have collected on the sides of the container.

X4.4.4 Start the mixer at 500 ± 100 r/min and continue to mix at this speed for 2 min to the 4 min mark.

X4.4.5 Add admixtures at any time appropriate to the test program. Typical delay times are 10 s for tail end addition or 45 s for delayed addition. Unless specified otherwise, mix at 500 ± 100 r/min for at least 60 s after all admixtures have been added.

X4.5 *Preparation of Paste Using a High Speed Blender*:

X4.5.1 Add water and any admixture to be added upfront into the mixing jar. Increase the mixing speed over 10 s to 2000 ± 200 r/min while minimizing splashing. Add dry materials, and immediately start the timer. Record the time of initial contact between cementitious materials and water.

X4.5.2 Add admixtures at any time appropriate to the test program.

X4.5.3 Mix at 4000 ± 400 r/min for 10 s.

X4.5.4 Increase mixer speed to 13 000 ± 1000 r/min within 10 s and continue to mix at this speed to the 40 s mark.

X4.5.5 At the 40 s mark, decrease mixer speed to 2000 ± 200 r/min and continue to mix at this speed for 50 s (to the 1 min 30 s mark).

X4.5.6 Stop mixing and let the mixture rest for 60 s (to the 2 min 30 s mark).

X4.5.7 Start the mixer at 2000 ± 200 r/min and increase the mixer speed to 13 000 ± 1000 r/min within 10 s and continue to mix at this speed to the 4 min mark.

X4.5.8 Mix at 13 000 ± 200 r/min for at least 30 s after all admixtures have been added.

X4.6 *Preparation of Mortar (modified Practice C 305 procedure)*:

X4.6.1 Place the water and any admixtures to be added upfront into the mixing container.

X4.6.2 Add cementitious materials; then start the mixer and mix at the slow speed (140 ± 5 r/min), and immediately start the timer. Record the time of initial contact between cementitious materials and water. Mix for 30 s.

X4.6.3 Add the entire quantity of sand slowly over a 30-s period, while mixing at slow speed.

X4.6.4 Stop the mixer, change to medium speed (285 ± 10 r/min) and mix for 30 s.

X4.6.5 Stop the mixer and let the mortar stand for 1½ min. During the first 15 s of this interval, quickly scrape down into the batch any mortar that may have collected on the side of the bowl; then for the remainder of this interval, cover the bowl with the lid.

X4.6.6 Mix for 1 min at medium speed (285 ± 10 r/min).

X4.6.7 In any case requiring a remixing interval, any mortar adhering to the side of the bowl shall be quickly scraped down into the batch before remixing.

X4.6.8 Add admixtures at the appropriate time according to the test program.

X4.6.9 Mix for at least 30 s at medium speed (285 ± 10 r/min) after all admixtures have been added.

X4.7 *Obtaining Sample of Mortar from Concrete*:

X4.7.1 Mortar test samples may be obtained from concrete following the wet-sieving procedure in Practice C 172.

X5. GRAPHICAL EVALUATION OF RESULTS

X5.1 Prepare comparative graphs including a reference mixture and other mixtures of significance, in order to evaluate hydration characteristics such as:

X5.1.1 Retardation of the main hydration as a function of admixture type and dosage. Thermal indicators of setting time may be taken as the time to reach 50 % of the average maximum power of the main hydration peaks (See example in Fig. X5.1).

X5.1.2 Relation between the time of maximum of the main hydration peak and the time of sulfate depletion. This relationship may be used as an indicator for the overall sulfate balance of each combined mixture according to Lerch.[6] Note if there is any effect of adding extra SO_3 to the combined mixture before testing.

X5.1.3 Acceleration of early aluminate hydration as a function of admixture type and dosage.

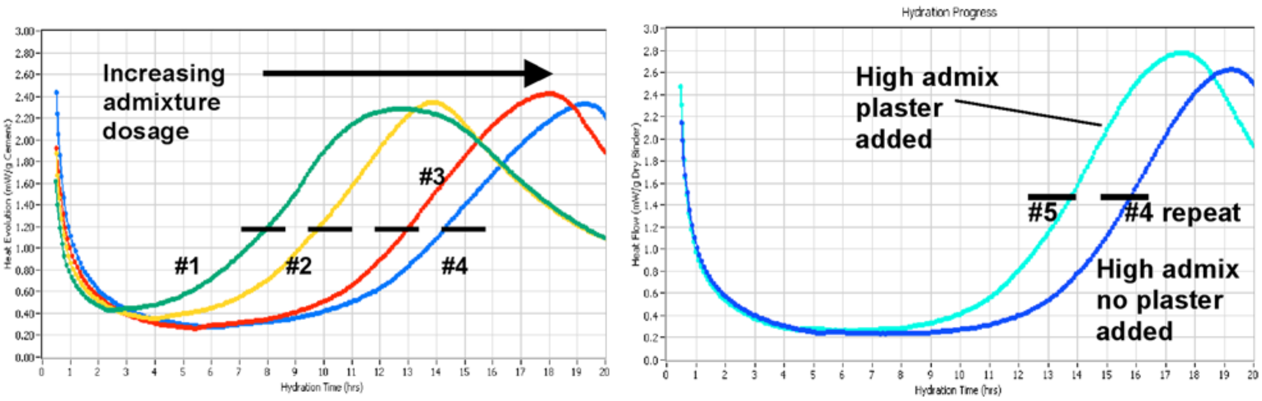


FIG. X5.1 (a) Effect of Admixture Dosage on the Thermal Indicator of Setting Time for This Given Set of Materials; (b) Effect of SO_3 Addition (as Plaster) for This Given Set of Materials

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[6] Lerch, W., "The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes," *Proceedings, Vol 46, of the American Society for Testing and Materials* , 1946, pp. 1252-1292.

X6. EXAMPLES

X6.1 *Study of Effect of Admixture Dosage and SCM Content on Thermal Indicator of Setting Time at Constant Temperature*:

X6.1.1 Different admixtures and SCM can have a strong effect on the setting time of a cementitious mixture. The relative effect of such changes on thermal indicators of setting time can be investigated by testing a series of mixtures. Table X6.1 shows an example of an experimental design for paste mixtures with a *w/c* of 0.40, Class C fly ash (CFA), and a water-reducing admixture. The sulfate addition test (Mixtures #5 and #8) is important for evaluation of whether a selected set of materials and dosages appears to be in sulfate balance.

X6.1.2 *Evaluation of Setting Time Study*—The thermal indicator of setting time is typically taken as the time to reach one-half the average maximum power of the main hydration peaks. Fig. X5.1(a) shows the response for mixtures 1 through 4 tested at room temperature. Fig. X5.1(b) shows the effect of SO_3 addition (as plaster) for mixture #5 with high admixture dosage. The thermal indicator of setting time is a relative value and can be correlated with a physical setting time method such as Test Method C 403/C 403M for a given mixture.

X6.1.3 *Indications*:

X6.1.3.1 The aluminate reaction peak after the sulfate depletion point appears to overlap the main hydration peak, indicating a mixture that is potentially sensitive to high admixture dosages.

X6.1.3.2 Increased admixture dosages retard the onset of the main hydration peak used to evaluate thermal indicators of setting time.

X6.1.3.3 The plaster addition (mixture #5) accelerated the onset of the hydration peak and also enlarged the height of the peak, indicating that the mixture with the high admixture dose is close to being out of sulfate balance. Note that the addition of sulfate showing in Fig. X5.1(b) did not result in a clear sulfate depletion point.

X6.1.4 Fig. X6.1(a) shows the effect of varying CFA dosage at typical dosage of admixture. Fig. X6.1(b) shows the effect of SO_3 addition (as plaster) to the mixture with high fly ash dosage.

X6.1.5 *Indications*:

X6.1.5.1 The CFA content had a strong effect on the hydration kinetics.

X6.1.5.2 Mixture # 7 with high amount of CFA displayed abnormal hydration with a strong premature exotherm indicated by the abnormally steep rise in thermal power at 6 to 7 h and no main hydration within 23 h. The abnormal peak may not be used for estimation of the thermal indicator of setting time. Mixture # 7 could stiffen and possibly flash set because of the abnormal exotherm at 6 to 7 h, but would not develop normal strength within 23 h.

X6.1.5.3 The plaster addition test confirmed that the premature exotherm at high dosage of CFA was caused by insufficient amount of available sulfate to control the aluminate hydration (probably as a result of aluminate in the CFA consuming some of the soluble sulfate from the cement).

TABLE X6.1 Example of 8-Mixture Calorimetry Test Design

Mixture #	Dosages		Remarks
	SCM-FA	Admixture	
1	20 % CFA	None	Reference
2	20 % CFA	Low	Admixture dosage window of interest,
3	20 % CFA	Typical	(water reducing admixture WRA)
4	20 % C	High	
5	20 % C	High	0.5 % SO_3 added to cement before test
6	10 % C	Typical	Fly ash dosage window of interest
7	30 % C	Typical	
8	30 % C	Typical	0.5 % SO_3 added to cement before test

X6.2 *Study of Effect of Curing Temperature on Hydration Kinetics*:

X6.2.1 Calorimetry is well suited for monitoring the effect of temperature on hydration kinetics. An example is shown in Fig. X6.2 for a portland cement mixture, with *w/c* = 0.45, with and without a water-reducing admixture, and tested at three different temperatures. One mortar mixture was prepared and tested in parallel at three different temperatures. Table X6.2 shows the experiment design.

X6.2.2 *Evaluation of Curing Temperature Study*—Fig. X6.2(a) shows the hydration kinetics for all mixtures in Table X6.2. Fig. X6.2(b) shows the effect of curing temperature on the increase in the thermal indicator of setting time caused by the admixture.

X6.2.3 *Indications*:

X6.2.3.1 The retarding effect of temperature on cement hydration was readily visible by isothermal calorimetry.

X6.2.3.2 The location of the sulfate depletion point, in relation to the main hydration peak, is affected by temperature with or without the admixture present.

X6.2.3.3 The retardation time caused by an admixture is often temperature dependent, as illustrated in this example.

X6.3 *Study of Effect of Admixture Dosage and Sequence of Addition on Setting Time*:

X6.3.1 The sequence of admixture addition can have a strong effect on setting times and early strength. The relative effect of changing the addition sequence can be investigated by a series of mixtures, preferably including a reference mixture with known setting times. Table X6.3 shows an example of an experimental design for mixtures with two different admixtures tested at two fly ash contents. The plaster addition test is important to evaluate whether a mixture appears to be in sulfate balance. In addition, temperature sensitivity can be assessed by testing each mixture at more than one temperature.

X6.3.2 *Evaluation of Admixture Addition Sequence Sensitivity Study*—Fig. X6.3(a) shows the response for mixtures with typical (20 %) CFA dosage and two admixtures at typical

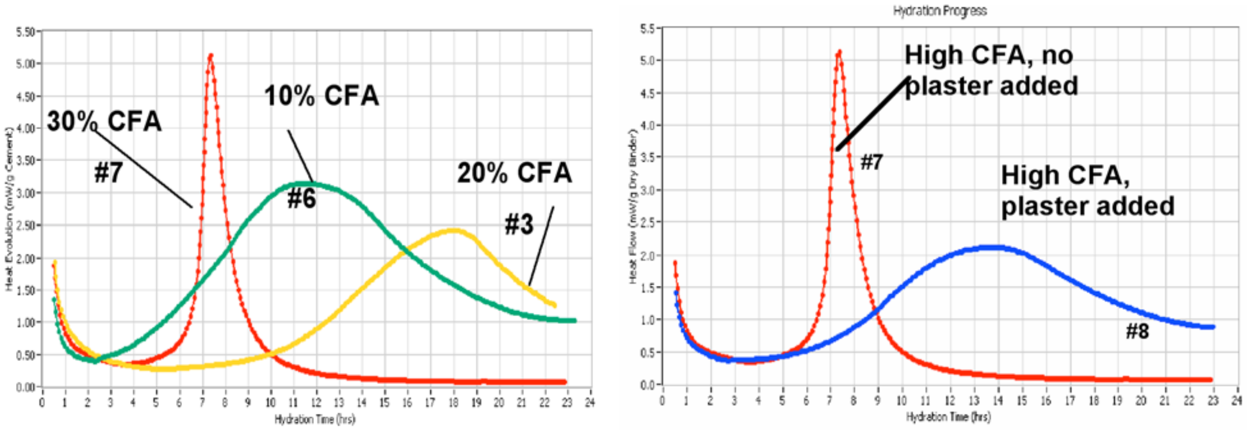

FIG. X6.1 (a) Effect of Fly Ash Dosage on Hydration Kinetics; (b) Effect of SO_3 Addition (as Plaster)

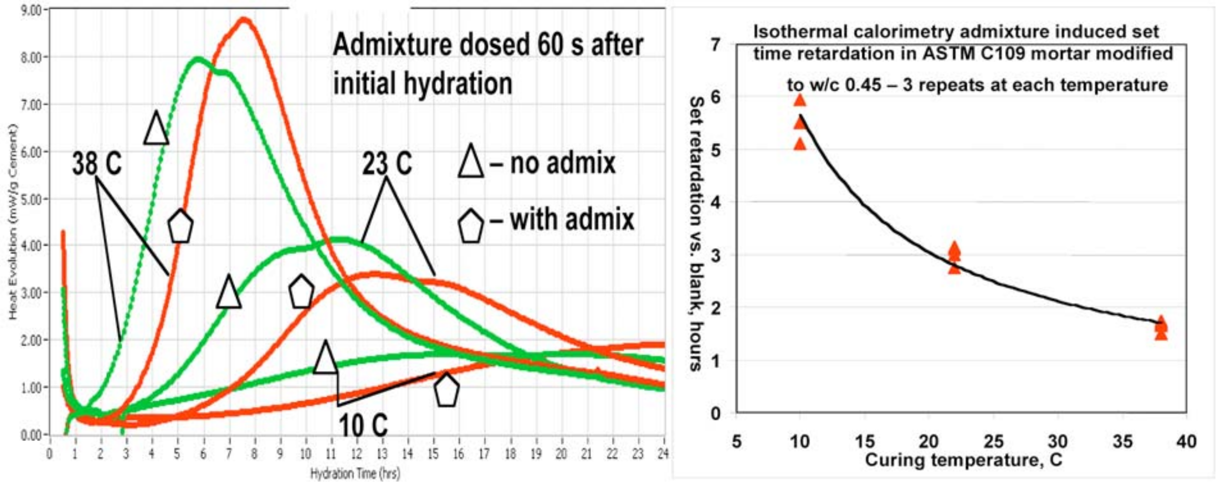

FIG. X6.2 (a) Effect of Temperature on the Hydration Kinetics;
(b) Effect of Temperature on Retardation of Setting Time

TABLE X6.2 Example of Calorimetry Test Design

Mixture	Admixture	Temperature
1	No	38 °C (100 °F)
2	Yes	38 °C (100 °F)
3	No	23 °C (73 °F)
4	Yes	23 °C (73 °F)
5	No	10 °C (50 °F)
6	Yes	10 °C (50 °F)

dosages but different dosing sequence, tested at room temperature. Fig. X6.3(b) shows the effect of SO_3 addition (as plaster) to the mixture with both admixtures dosed "tail end" (10 s delayed addition).

X6.3.3 *Indications*:

X6.3.3.1 Tail end addition of both admixtures extended the thermal indicator of setting time approximately 90 min compared with mixtures with same admixture dosages but either admixture or both added upfront.

X6.3.3.2 The plaster addition (mixture #6) accelerated the onset of the hydration peak and also enlarged the height and width of the peak, indicating that the mixture with the tail addition of both admixtures is not in sulfate balance.

X6.3.4 Fig. X6.4(a) shows the effect of overdosing admixture A or B, both added upfront. Fig. X6.4(b) shows the effect of plaster addition (0.5 % SO_3) to the cement prior to testing (#13 and #14).

X6.3.5 *Indications*:

X6.3.5.1 An overdose of admixture A caused abnormal exotherms indicated by the abnormally steep rise in thermal power at 50 % and 100 % overdose (#9 and #10), with no subsequent silicate hydration. Note flatline out to 22 hours.

X6.3.5.2 No abnormal hydration was seen when overdosing admixture B (#11 and #12).

X6.3.5.3 The plaster addition test (#13 and #14) confirmed that the premature exotherms at high dosages of admixture A were caused by uncontrolled aluminate hydration. Note that silicate hydration, although still severely delayed, is seen to start within the 22 hour test period.

TABLE X6.3 Example of Experimental Design for Screening Sensitivity to Admixture Dosage and Addition Sequence

Mixture No.	CFA Dosage	Admixture Dosages and Addition Sequence		Remarks
		A-WR	B-HRWR	
1	20 %	None	None	Reference
2	20 %	Typical upfront	Typical upfront	Actual mixture design
3	20 %	Typical tail end	Typical upfront	Effect of admixture addition sequence. Admixture typical dosages as in typical field application.
4	20 %	Typical upfront	Typical tail end	
5	20 %	Typical tail end	Typical tail end	
6	20 %	Typical upfront	Typical upfront	0.5 % SO_3 added to cement before test
7	10 %	Typical upfront	Typical upfront	Effect of fly ash dose
8	None	Typical upfront	Typical upfront	Effect of fly ash dose
9	20 %	150 % upfront	Typical upfront	Effect of admixture overdose
10	20 %	200 % upfront	Typical upfront	
11	20 %	Typical upfront	150 % upfront	
12	20 %	Typical upfront	200 % upfront	
13	20 %	150 % upfront	Typical upfront	Further tests with plaster addition are recommended for any mixture that displays signs of abnormal hydration kinetics. In this case mixtures 9 and 10 were retested with plaster addition (0.5 % SO_3).
14	20 %	200 % upfront	Typical upfront	

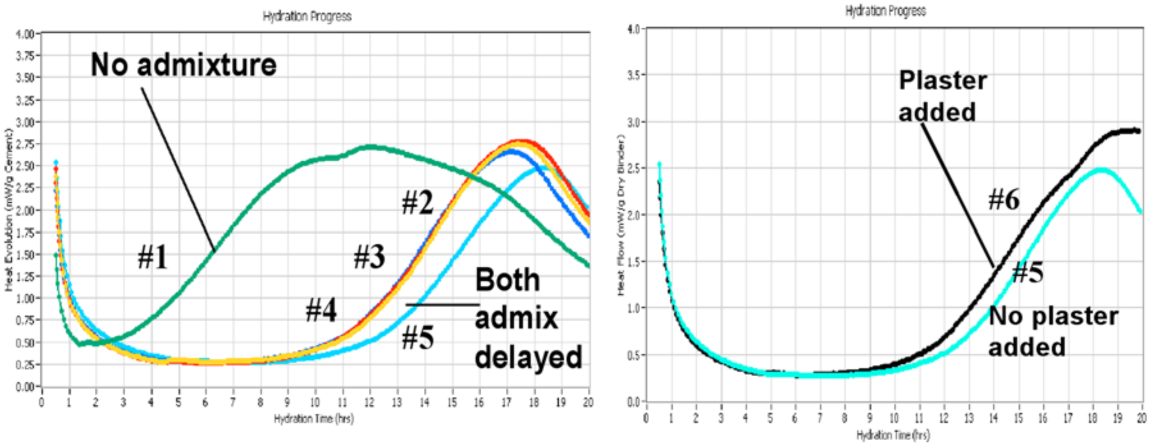

FIG. X6.3 (a) Effect of Admixture Addition Sequence on Cement Hydration Kinetics; (b) Effect of Plaster Addition with Delayed Addition of Both Admixtures

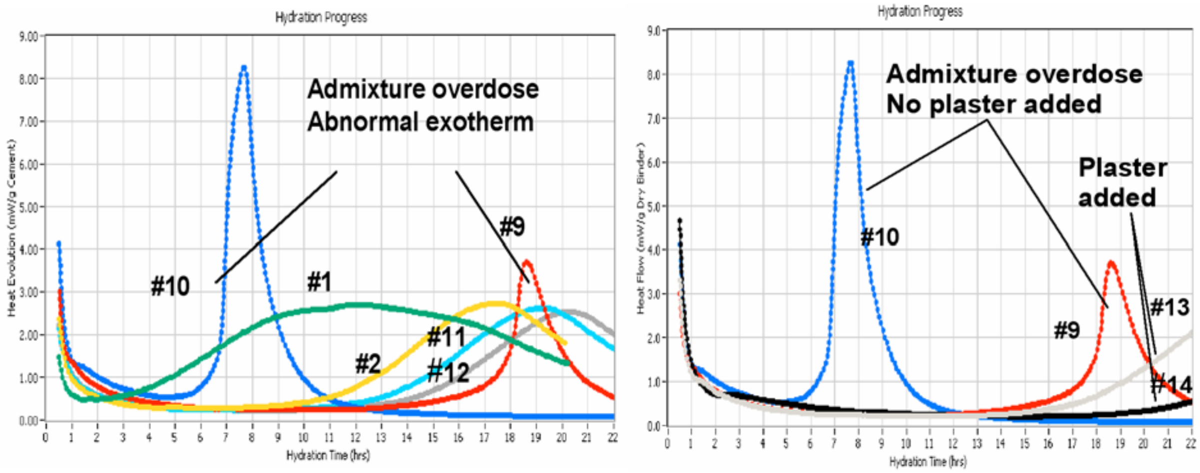

FIG. X6.4 (a) Effect of Different Admixture Dosages on Mixtures with High Fly Ash Dosage; (b) Effect of Plaster Addition to Mixtures with Overdose of Admixture A

SUMMARY OF CHANGES

Committee C09 has identified the location of selected changes to this practice since the last issue, C 1679 – 07, that may impact the use of this practice. (Approved June 1, 2008)

(*1*) Revised Note 2 to clarify how to avoid condensation inside the calorimeter.
(*2*) Made the making of diluted solutions of the admixtures optional in 6.1.3.
(*3*) Removed explanatory test in 12.1.1and placed it in new Note 5; renumbered subsequent notes

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