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Isothermal Conduction Calorimetry (ICC) for the determination of heat of hydration of cement: State of Art Report and Recommendations

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National foreword

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Isothermal Conduction Calorimetry (ICC) for the determination of heat of hydration of cement: State of Art Report and Recommendations

Bestimmung der Hydratationswärme von Zement durch isotherme Wärmeflusskalorimetrie: Stand der Technik und Empfehlungen

This Technical Report was approved by CEN on 26 November 2013. It has been drawn up by the Technical Committee CEN/TC 51.

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Contents

Page

Foreword

This document (CEN/TR 16632:2014) has been prepared by Technical Committee CEN/TC 51 “Cement and building limes”, the secretariat of which is held by NBN.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

It is divided into two sections. The first section is a State of Art Report of the test method based on the collection of the technical data sheets of the calorimeters adopted in the European cement laboratories and also on the collection of the results of several experimental activities. The second section is made of recommendations for the measurement of heat of hydration of cement by ICC. Based on the State of Art Report, this section provides some basic elements of the test procedure with the aim to become a first guide for the laboratories that are currently using ICC or for those laboratories that would start to adopt this method. By using the information and adopting the procedures given in the document it will be possible to compare in a more reliable way both the performances of the different calorimeters and the test results.

Annex A (informative) provides a Glossary.

Introduction

In 2007, CEN/TC 51, through resolution 495, agreed that WG 12/TG 3 investigates the suitability for standardization of the test method based on isothermal conduction calorimetry (ICC). The Task Group 3 has been reactivated and held its first meeting in 2008.

Since no national standard on ICC for the determination of heat of hydration of cement was available, TG 3 started its activity on the item by gathering the available information on recommendations or published scientific papers, inter-laboratory experimental exercises. The available information, collected into a State of Art report, has been analysed and discussed in order to identify those aspects of the test method that can be already considered consolidated as well as those elements that still need further development.

The second step of the activity was the redaction of a Recommendations document including a testing procedure for the measuring of heat of hydration of cement by ICC. The circulation of this document in the laboratory actually involved in ICC testing, would lead to the application of uniform general principles and, therefore, to a better data reproducibility.

In this CEN/TR, the State of Art document and the Recommendations document are reviewed into a single document divided into two parts:

a) State of art report on the application of ICC for the determination of heat of hydration of cement;

b) Recommendations for the measurement of Heat of Hydration of Cement by Isothermal Conduction Calorimetry.

PART A

State of art report on the application of ICC for the determination of heat of hydration of cement

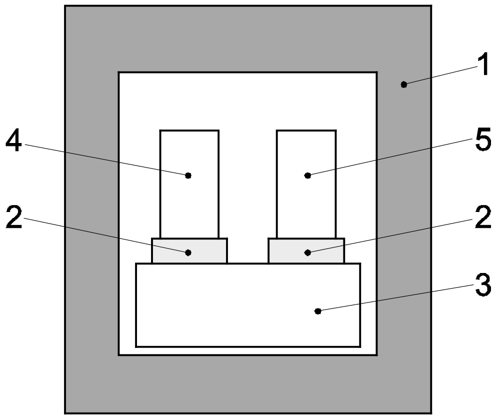
1 Basic principle and key points of ICC

1.1 Basic Principle

The test method is designed to measure the heat of hydration of cement when mixed with water. The measurement takes place at essentially constant temperature, if the instrument and the measurement are well designed, therefore it is assumed to be the "isothermal heat of hydration of cement".

An isothermal heat conduction calorimeter (here called calorimeter) consists of a thermostatic heat sink upon which two heat flow sensors are placed. The sample is placed in an ampoule that is placed in an ampoule holder that is in contact with one of the heat flow sensors, and an inert reference is placed in contact with the other. The sample ampoule and the reference ampoule are thermally connected by heat flow sensors to a thermostatic heat sink. The output from the calorimeter is the difference between the outputs from the sample heat flow sensor and the reference heat flow sensor. A general scheme of a heat conduction calorimeter is given in Figure 1.

However the actual design of an individual instrument, whether commercial or home-built, may vary.



Key

1 thermostat

2 heat flow sensors

3 heat sunk

4 sample

5 reference

Figure 1 — A schematic drawing of a heat conduction calorimeter

Most part of the calorimeters can measure the heat of hydration of samples mixed outside from the instrument, therefore the heat produced during the mixing is not measured. It is not easy to solve this problem designing a calorimeter provided with an internally mixing device having the proper efficacy.

1.2 Key points of ICC

When performing ICC measurements on cement samples some key points have to be considered and correctly managed:

- Constant value of the temperature of the thermostat;
- Stability of the temperature of the thermostat all over the test duration;
- Control of the maximum difference between sample temperature and thermostat temperature (isothermal conditions);
- The baseline of the instrument (measured with an inert sample of similar thermal properties of test sample) should be both repeatable and stable;
- Calibration of the calorimeter. The method currently used is based on the joule effect produced by a resistor feed with an electrical current; no standard material for the calibration is available for the time being;
- Check that the ampoule is vapour tight enough (so that endothermic thermal powers of evaporation do not influence the measurements).

2 Normative references

Not applicable.

3 Technical data sheets of available calorimeters

One of the expected results from this CEN/TR is a general and comprehensive overview of the technical data sheets of the currently existing conduction calorimeters because the quality of the test results of ICC is strongly influenced by the characteristics of the apparatus, where the word “characteristics” has to be intended in the sense of “fit for use” when measuring heat of hydration of cement.

A number of instruments that have been used for calorimetric measurements on cement have been considered and their technical specifications have been compared. The list of the instruments that have been considered is given in Table 1.

Table 1 — List of Instruments considered for the analysis of technical data sheets

Instrument	Manufacturer
Thermal Activity Monitor TAM AIR	Thermometric, Sweden
Thermal Activity Monitor TAM 2277	Thermometric, Sweden
Thermal Activity Monitor TAM III	TA instruments
ToniCAL 7338	Toni Technik
MS 80 Calorimeter	Setaram
C 80 Calorimeter	Setaram
Calorimeter Italcementi	Italcementi

Basically the relevant specifications of each instrument are useful to describe two main aspects:

- sensitivity and related uncertainty;

— stability (Baseline drift, Baseline noise).

The final result of this activity should be the identification and definition of performance requirements for ICC suitable for the determination of heat of hydration of cements, but with reference to this expected result, the collected data does not allow to reach this objective.

Unfortunately the data provided by the technical sheets are not expressed in a standardised way, so any comparison of the characteristics of the calorimeter has to be preceded by a unification of the definitions and expression of the main instrumental parameters.

TG 3 has already defined a program of the activity suitable to fill the gap related to:

— unified procedures for the determination of fundamental technical specifications;

— technical specifications for performances related to Sensitivity and Stability.

4 Experimental data

Several inter-laboratories round-robin exercises have been collected:

— International inter-laboratory trial 2003 by Lund University;

— Swiss inter-laboratory trials 2005/2006 (Cemsuisse);

— German inter-laboratory trials 2006/2007 (VDZ);

— NL reference test on cement;

— Experiences from US (PCA);

— Validation of conduction calorimetry (VDZ).

All these tests had two main objectives:

— determination of precision data of ICC method;

— comparison of ICC test results with the corresponding results of the reference methods: solution method (EN 196-8) and semi-adiabatic method (EN 196-9).

In practice, only few data are available for semi-adiabatic method, therefore no comparison can be made for semi-adiabatic method and ICC, while for the solution method there is a lacking of data for Type II, Type IV and Type V cements.

Focusing only on the comparison of ICC with solution method, the following considerations can be made:

1) repeatability (within-laboratory precision) is better than for solution calorimetry ((5 ÷ 6) J/g[1)] for ICC vs. 8 J/g for EN 196-8);

2) reproducibility (inter-laboratory precision) is somewhat better than for solution calorimetry (ranges from 10 to 20 J/g1 for ICC vs. 18 J/g for EN 196-8);

3) comparative testing data with solution method (EN 196-8) are quite limited and even more limited with semi-adiabatic method (EN 196-9);

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1) Determined for duration of test ranging from 3 d to 7 d.

4) solution method data at 7d and ICC data at 7d do not match very well;

5) some systematic deviation seems to exist between the data of two methods: values from ICC are higher than those from Solution Method;

6) for the time being no sound correlation has been found between ICC data and solution method data; characteristics of instruments seem to play a role;

7) some doubts still exist about the capability of the method to measure with the needed accuracy the heat of hydration in the time interval 3 d - 7 d when the heat flow developed by the cement paste is very low.

5 Calibration

5.1 Calibration of isothermal heat conduction calorimeters

Calibration is in general a fundamental activity of a test method. The ICC of cement does not represent an exception to this rule.

This test method is completely automated and, therefore, the precision intended as repeatability and reproducibility (or extended uncertainty) is determined by:

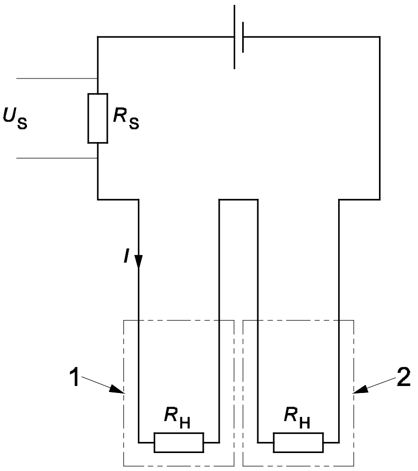
1) design and construction of the calorimeter;

2) proper use and maintenance;

3) calibration procedure.

Points 1) and 2) depend on manufacturer activity and training of users, while point 3) should be considered at a more general level.

Currently the calibration is made by producing a known electrical thermal power close to where the sample will be placed in the calorimeter and measuring the electrical signal by the data acquisition equipment. Heaters can be placed in sample ampoules with inert contents or fixed in the ampoule holders.



Key

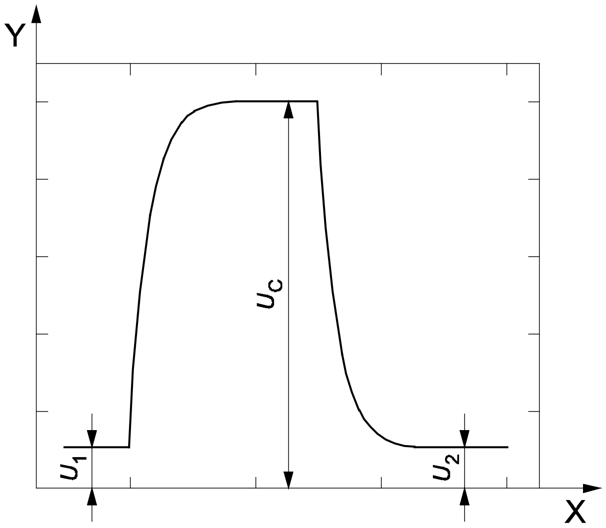
1 calibration heater 1

2 calibration heater 2

Figure 2 — A schematic drawing of the set-up for the simultaneous calibration of two calorimeters

There are two ways of calibration: steady-state calibration that is convenient for manual calibration and pulse calibration that is done on automated systems. These two ways of calibrating give the same result.

Steady-state calibration is made by first measuring the baseline U_1 before the calibration. The current to the heater is then turned on until a new stable output value is obtained. When the output is constant, its value is noted as U_C. The current is then switched off and the signal returns back to the baseline. The baseline U_2 after the calibration is then measured. Figure 3 shows such calibration schematically.



Key

X time [s]

Y output voltage [V]

Figure 3 — Schematic steady-state calibration

The calibration coefficient ε is calculated as the produced thermal power *(P*) divided by the resulting output:

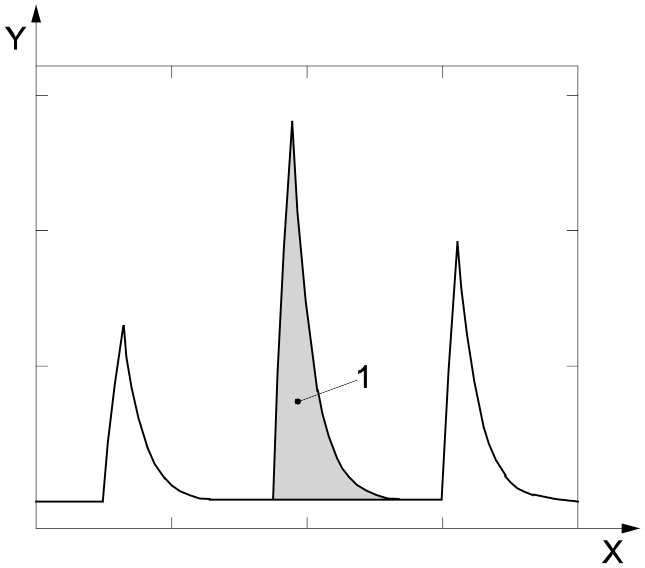
$$\varepsilon = \frac{P}{U_c - (U_1 + U_2)/2} \tag{1}$$

Pulse calibrations are made by producing a pulse of heat in the calorimeter, without attaining steady-state, and dividing the heat input by the integral of the output peak. This, in principle, will give the same value of the calibration coefficient as the steady-state method given above. Figure 4 shows such a non-steady state calibration schematically. As the calibration current is constant the heat is the product of the input thermal power and the duration of the calibration (Δt):

$$Q = I^2 R_H \Delta t \tag{2}$$

For the non-steady state calibration the calibration coefficient ε is calculated as the produced heat (Q) divided by the integral of the resulting output above the baseline:

$$\varepsilon = \frac{Q}{\int U dt} \tag{3}$$



Key

1 $\int U dt$ [V s]

X time [s]

Y output voltage [V]

Figure 4 — Schematic of pulse calibration

The calibration peaks can have different input thermal powers and different durations.

The described procedures are theoretically simple and also practically simple to apply, nevertheless some aspects still need to be understood and clarified.

For example it seems that the calibration coefficient is depending from the intensity of the thermal power. During the hydration process of the cement the thermal power varies in the range of mW to the tenths of mW but usually a unique coefficient of calibration is applied in the calculation of the heat produced (see 5.3).

5.2 Determination of the baseline

Baseline noise (BN) and baseline drift (BR) are determined with reference ampoules in both the sample and reference positions, and the suggested output recording should be at least 24 h long.

In any case there is no generally accepted procedure for the determination of the baseline and for the expression of the two parameters BN and BR (W or W/g).

5.3 Open question

Basic assumption of the calibration procedure is that the behaviour of the thermal sensor is linear. This means that the ratio between the thermal power and the voltage output is constant or slightly variable.

In practice this seems to be true only when considering a limited range of thermal power. On the other hand the heat of hydration of cement has a peculiar pattern that covers a large range of thermal power: high during the main hydration peak period and low in the following. Nevertheless this secondary hydration phase covers a long time period so its contribution to the total heat of hydration is relevant.

There is some experimental evidence[2] of the fact that the response of sensor is not linear below a limit threshold of thermal power. Therefore an accurate evaluation of the impact of this non-linearity of the calorimeter sensitivity on the ICC test results is needed.

6 Final remarks

The experimental results have pointed out mainly two items:

1) Repeatability (within-laboratory precision) is better than for solution calorimetry and reproducibility (inter-laboratory precision) is somewhat better than for solution calorimetry; better performances have been found in particular when are compared testing results obtained by testing apparatus with the same (or similar) design. These data are relevant to testing activities involving Type I and Type III cements.

2) Considering the limited availability of comparative data there are, for the time being, difficulties to establish a suitable correlation between ICC test results and reference methods test results (EN 196-8 or EN 196-9); it seems that there is a tendency for ICC to give results systematically higher with respect to EN 196-8 solution test results.

With respect to the systematic deviation of the comparative results there are two options of aligning the heats of hydration that can be considered:

— 7-day ICC values should be multiplied by a correction factor;

— heats of hydration should be read off at an earlier time.

When applied to the inter-laboratory trial data an “optimum” measuring time of about 120 h was obtained for ICC.

In the elaboration of the data of the VDZ validation round robin to minimise this bias a correction factor was determined.

Using the factor “k = 0,88” the average deviation decreased to only 11 J/g.

Adopting the second option, the best agreement between ICC and solution method was achieved by shortening the hydration time of ICC method up to 110 h. The average deviation was then again only 11 J/g.

In any case it has to be considered that the application of the correlation concept based on a “k” factor which differs from 1 or an offset of time duration of testing, could not be justified on theoretical basis because the solution method and ICC, are both isothermal methods at the same reference temperature of 20 °C, therefore they should give equivalent results.

---

[2] 12th International Workshop on THERMAL INVESTIGATIONS of ICs and SYSTEMS 27-29 September 2006, Nice, Côte d'Azur, France – Design issues of a variable thermal resistance (Székely V., Mezősi G.).

PART B
Recommendations for the measurement of Heat of Hydration of Cement by Isothermal Conduction Calorimetry

7 Scope and field of application

This test procedure specifies the apparatus and procedure for determining the heat of hydration of cements and other hydraulic binders at different test ages by isothermal conduction calorimetry.

The test procedure is intended for measuring the heat of hydration of cement up to 7 d in order to obtain data homogeneous with EN 196-8. Nevertheless this test duration may be critical for some apparatus, even if they can work properly at shorter test ages.

In contrast to EN 196-8 (solution method) this method gives the heat of hydration continuously over the time. Additionally, the heat flow versus time is given.

8 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

8.1
isothermal conduction calorimeter
apparatus able to measure the heat flow generated by a sample kept at constant temperature

Note 1 to entry: The constant temperature condition is achieved by maintaining the sample in thermal contact with a heat sink.

8.2
output of calorimeter
electric signal from the calorimeter expressed in V

8.3
thermal power
heat rate produced by the sample during the test and commonly expressed, with reference to the unit mass of cement, in W/g or J/(s*g)

8.4
heat
time integral of the thermal power and expressed in J/g

8.5
baseline
output of the calorimeter when there is an inert sample in the testing and reference cell, both with the same thermal capacity

Note 1 to entry: The recording of this signal is the Baseline output (*BO*).

8.6
baseline drift
BD
slope of the linear regression of the Baseline output vs time measured over a specified period and expressed in W/g per time period, with reference to the unit mass of cement

8.7
baseline noise
BN
variance of the baseline output of the regression of the Baseline output vs time measured over a specified period and expressed in W/g, with reference to the unit mass of cement

8.8
testing cell
testing ampoule
measuring cell specifically dedicated to the sample under test which is the sample that generates heat

8.9
reference cell
reference ampoule
measuring cell specifically dedicated to an inert sample which is a sample that does not generate heat, and used to reduce the *BD* and *BN*

8.10
time constant
τ
measure of the thermal inertia of the test cell, which is expressed in s

8.11
detection limit
DL
minimum value of thermal power that can be detected by an apparatus

Note 1 to entry: This value is an estimation of the quality of the measurement that is dependent on the whole measuring chain and not only on the design of the instrument.

9 Apparatus

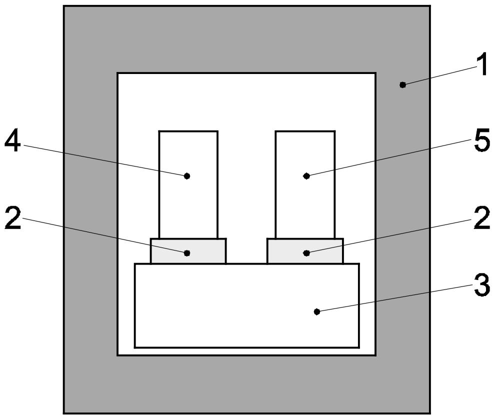
9.1 General

This part gives general requirements related to the relevant properties and design of a calorimeter. Although the design of individual calorimeters from different manufacturers may vary, it should meet the specifications as described below.

An isothermal heat conduction calorimeter has to consist of:

- a constant-temperature heat sink to which at least two heat-flow sensors and sample holders (calorimetric cells) are attached in a manner resulting in good thermal conductivity;
- one or more cells containing the sample of interest;
- one or more reference cells, containing a blank sample that does not convey heat. If the calorimeter contains more than two cells, at least one has to act as reference cell. The conduction calorimeters with more than two cells often have their own reference cells for each of the sample cells. The design and material of the heat sensors and the ampoule holders of both reference and sample should be identical.

The heat released by the hydrating cement sample flows across the sensor into the heat sink. The voltage output from a measurement is the difference between the voltages from the test cell and the reference cell. The heat-flow sensor senses the small temperature gradient that develops across the device. However, the heat is removed from the hydrating sample fast enough so that, for practical purposes, the sample remains at a constant temperature (isothermal).



Key

1	thermostat
2	heat flow sensors
3	heat sink
4	sample
5	reference

Figure 5 — A schematic drawing of a heat conduction calorimeter

9.2 Thermostat

Although the driving force of heat flow is a temperature gradient, the overall temperature in the calorimeter (heat sink) during the test should be essentially constant (isothermal). For this purpose the calorimeter should be equipped with a thermostat. The temperature instability of the thermostat should not exceed 0,2 °C. The working temperature of the apparatus should be at (20 ± 0,2) °C.

9.3 Calorimeter technical parameters

The technical parameters of the calorimeters that have to be specified to perform the heat of hydration determinations and to assure an acceptable robustness of the results are the following:

— Detection limit (*DL*)

— Baseline noise (*BN*)

— Baseline drift (*BD*)

The calorimeter has to meet the following specifications:

— *DL*: < 2,8 μW/g

— *BN*: < 10,5 μW/g

— *BD* : < 5,5 μW/g per week

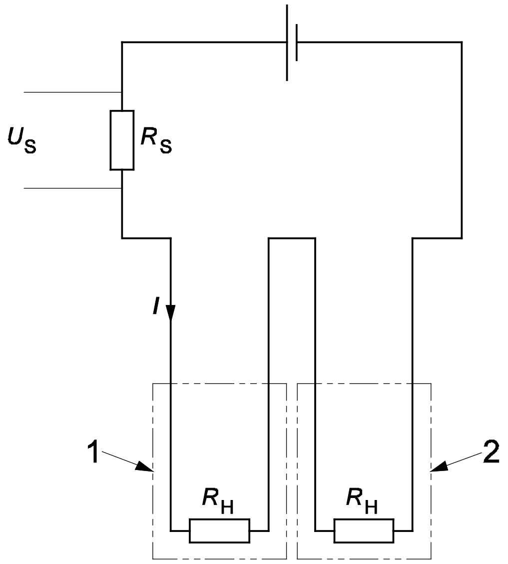
NOTE The above specifications have been defined on the basis of the technical specifications of the apparatus currently used for calorimetric measurements on hydraulic binders. For the time being there are not experimental data correlating these specifications with the trueness and precision (repeatability and reproducibility) of the heat of hydration results.

10 Calibration

10.1 General

In this clause, two calibration procedures are described. The described procedures are theoretically simple and also practically simple to apply, nevertheless some aspects related to the linearity of the calorimeter output in the range of the thermal power developed during the cement hydration still needs to be understood and clarified.

In general, the calibration is made by producing a known electrical thermal power close to where the sample will be placed in the calorimeter and measuring the response from the data acquisition equipment. Heaters can be placed in sample ampoules with inert contents or fixed in the ampoule holders. It is recommended to fill the sample ampoule with inert content selected in order to match the heat capacity of the samples to be tested (see 11.3).



Key

1 calibration heater 1

2 calibration heater 2

Figure 6 — A schematic drawing of the set-up for the simultaneous calibration of two calorimeters

The calibration heaters have the resistances R_H. The resistance R_S is used both to get a suitable current and to determine the current from the voltage (U_s) measured over it.

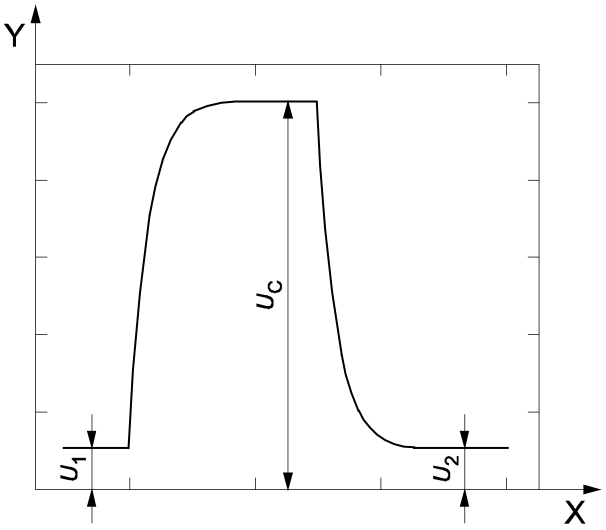
There are two alternative ways of calibration: steady-state calibration that is convenient for manual calibration and pulse calibration that is done on automated systems. These two ways of calibrating give the same calibration coefficient ε. For both these ways of calibration an electrical current is passed through the heater resistances in series. Figure 6 shows an example of how this can be arranged. It is important to calculate the thermal power in the heaters from the current and the heater resistances, as the current is the same in the whole circuit.

Both ways of calibrating can be used to calculate the time constants of the calorimeters that is needed to make corrections to the measurements when the heat flow is determined according to the test procedure based on external mixing (see 12.2).

10.2 Steady state calibration

10.2.1 General

Steady-state calibration is made by first measuring the baseline output U_1 before the calibration. The current to the heater is then turned on until a new stable output value is obtained. When the output is constant, its value is noted as U_C. The current is then switched off and the signal returns back to the baseline. The baseline U_2 after the calibration is then measured. Figure 7 schematically shows such calibration.



Key

X time [s]

Y output voltage [V]

Figure 7 — Schematic steady-state calibration

10.2.2 Calibration coefficient (ε)

The calibration coefficient ε, is calculated as the produced thermal power P divided by the resulting output:

$$\varepsilon = \frac{P}{U_c - \left(U_1 + U_2\right)/2} \tag{4}$$

If $U_{i\ (i=c,\ 1,\ 2)}$ is expressed as V and P is expressed as W, the resulting calibration coefficient ε will be expressed in W/V.

10.2.3 Time constant (τ)

As described in 10.2, at the end of the steady state period the current is switched off and the signal returns back to the baseline. The data acquired during this period (starting from the time instant in which the current is switched off and ending when the baseline is reached) are expressed in V. This data have to be converted into thermal power data by using the calibration coefficient *ε* and then the time constant (*τ*) can be calculated by looking for the best fitting to the following curve:

$$\ln P = A - \frac{t}{\tau} \tag{5}$$

If time t is expressed in s, the resulting time constant will be expressed in s.

A is a coefficient not relevant for the calibration of the calorimeter.

10.3 Pulse calibration

10.3.1 General

Pulse calibrations are made by producing a pulse of heat in the calorimeter, without attaining steady-state, and dividing the heat input by the integral of the output peak. Sketch in Figure 8 shows such a non-steady state calibration schematically. As the calibration current is constant, the heat is the product of the input thermal power and the duration of the calibration (Δt):

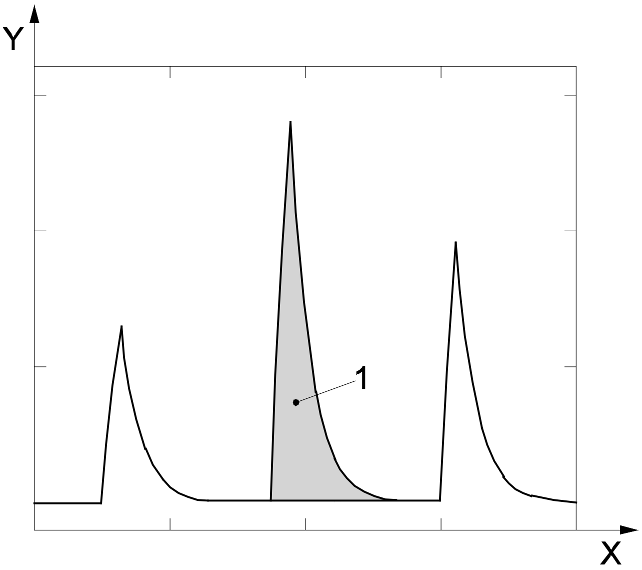
$$Q = I^2 R_H \Delta t \tag{6}$$

Here I is expressed as A, R_H is expressed as Ω and Δt is expressed as s. The resulting heat Q will be expressed as J.

For the non-steady state calibration the calibration coefficient ε is calculated as the produced heat Q divided by the integral of the resulting output above the baseline:

$$\varepsilon = \frac{Q}{\int U dt} \tag{7}$$

Here Q is expressed as J, U is expressed as V and dt is expressed as s. The resulting calibration coefficient ε will be expressed as W/V.



Key

1 $\int Udt$

X time

Y output voltage

Figure 8 — Schematic of pulse calibration

The calibration peaks can have different input thermal powers and different durations. Note that the integration is performed on voltages that have been corrected for the baseline output.

10.3.2 Time constant (τ)

Following the procedure described in 10.3, after the peak of the pulse the signal returns back to the baseline. The data acquired during this period (starting from the time instant in which the output voltage begins to decrease ending when the baseline is reached) are expressed in V. This data have to be converted into thermal power data by using the calibration coefficient ε and then the time constant (τ) can be calculated by looking for the best fitting to the following curve:

$$\ln P = A - \frac{t}{\tau} \tag{8}$$

If time t is expressed in s, the resulting time constant τ will be expressed in s.

A is a coefficient not relevant for the calibration of the calorimeter.

10.4 Determination of the calorimeter parameters

Baseline noise (*BN*) and baseline drift (*BD*) are determined with reference materials in both the sample and reference positions[3], and the suggested output recording should be at least 7 d long.

10.5 Improvement of common calibration procedure

A basic assumption of the calibration procedures is that the behaviour of the thermal sensor is linear, i.e. is the ratio between the thermal power and the voltage output is constant.

There is evidence of the fact that the response of sensors could be not linear below a limit threshold of thermal power (see Note 2).

It is recommended, to improve the calibration accuracy of the apparatus, to take care of this aspect by considering a range of current feed to the heater covering thermal power from 1×10^{-3} to 10×10^{-3} W/g. The calibration coefficients are correlated with the applied thermal power by a linear or no linear best fit regression calculation to obtain a correlation function $\varepsilon = f(W)$ that can be used in the calculation of the heat of hydration (see 12.5).

11 Sample

11.1 General

The test method requires the selection of two different samples: the test sample and the reference sample. The size of the test sample is mainly influenced by the apparatus in use, but, in any case, some rules can be adopted.

11.2 Test sample

In order to reduce possible errors such as non perfectly isothermal conditions or heat loss, it is recommended to use small samples with low thermal powers.

A sample size ranging between (3 and 10) g of cement is recommended, always taking into account the indications of the apparatus supplier.

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[3] The BN and BD values can be determined also with the testing ampoule kept empty. In this case a higher scattering of the output is expected.

11.3 Reference sample

The reference sample has to be selected in order to get a heat capacity that matches that of the test sample. “Reference sample” and “test sample” are everything that is on the reference and sample sides of the calorimeter, respectively; that is ampoule holder, ampoule and ampoule contents. However, as the ampoule holders are the same on both sides of the calorimeter their heat capacities are already matched. The same applies for the ampoules if ampoules of the same material and mass are used on both sides.

The only things that need to match are thus the contents of the ampoules.

Formula (9) gives the mass of the reference sample m_r made of a reference material with heat capacity c_r, when the test sample is cement paste.

$$m_r = \frac{m_c c_c + m_w c_w}{c_r} \tag{9}$$

The numerator is the heat capacity of the cement paste composed of cement and water.

Symbols *m* and *c* indicate respectively masses and specific heat capacities of cement (*c*) and water (*w*) under testing.

12 Testing procedure

12.1 General

Before starting the test, the calorimeter equipment has to be in temperature equilibrium. This means the temperature stability of the heat sink and the baseline noise has to comply with threshold limit specified in 9.2 and 9.3. The temperature stability has to be checked by using a reference external thermometer.

It is recommended to place the calorimeter in a room without large and fast temperature changes (e.g. no direct sun radiation) at (20,0 ± 0,5) °C. An air-conditioned room is favoured.

For the testing two procedures are possible:

- Method A with “External mixing”;
- Method B with “Internal mixing”.

12.2 Method A - “External mixing”

This method is used when cement paste is mixed outside of the calorimeter and then loaded into the calorimeter. In this procedure a small amount of the early heat-of-hydration data will be lost.

All materials shall be at the temperature of (20,0 ± 0,5) °C before mixing.

The cement paste should be mixed in such a way that the time between the addition of water and the time when the sample ampoule is put into the calorimeter is less than 4 min.

As only small amounts of cement paste (typically (3 to 15) g) are needed for each sample the mixing can be done manually or mechanically with a handheld mixer, e.g. with a stainless steel device in a stainless steel or glass beaker or with a test tube shaker. Mix vigorously for about 2 min. Typically each mix is made in the region of 50 g cement and 20 g water. The amount of cement should be at least 20 g. The water/cement-ratio has to be 0,40[4].

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[4] It is also possible to mix a sample directly in the measurement ampoule with a test tube mixer.

Use deionised or distilled water.

Determine the mass of the paste sample to the nearest 0,01 g, put it into the calorimeter sample holder, and cover the sample to prevent evaporation of mixing water.

It is essential that the sample and the ampoule are not warmed up due to handling, e.g. by heat of hands.

Wear insulating cotton gloves.

Normally two samples should be taken from two separate mixes. A third measurement will be necessary if the reproducibility is not high enough.

12.3 Method B - “Internal mixing”

This method is used when an instrument is configured so that cement and water can be temperature equilibrated and mixed while in place in the calorimeter.

Weigh an adequate amount of cement to the nearest 0,01 g and place it in the calorimeter cell. Weigh or determine volumetrically water to give a paste water/cement-ratio of 0,40. Use deionised or distilled water.

NOTE The amount of sample required varies among calorimeter designs. Since the exothermic reaction tends to slow down after the first 24 h, a sample that is too small will generate a signal late in the test period that is too weak to detect reliably. Typically, sample sizes between (3 and 10) g have been reported to be useful for maintaining an appreciable signal late in the test for (Portland) cements. Normally a signal at the end of the test at least twice the Baseline Noise (BN) of the apparatus is sufficient to give good results.

Start data collection, then mix immediately the water with the cement to form a uniform paste (typically for 60 s).

Normally two measurements have to be made. A third measurement will be necessary if the reproducibility is not high enough.

12.4 Measurement

If the measurement is performed to determine the heat of hydration of a cement, the hydration time has to be 7 d with a time tolerance of 2 h[5].

Some commercial calorimeters and data acquisition equipments are programmable to collect data at prescribed interval lengths or at intervals that vary with the rate of change of power levels. Data are collected more rapidly when power output is high than when it is low. If this flexibility is not a feature of the data acquisition component of the calorimeter, then collect readings every 30 s throughout the length of the test.

12.5 Calculations

The output of the calorimeter is transformed into thermal power by multiplying the coefficient ε (W/V) and applying the correction for the baseline drift and divide by the mass of cement m_c:

$$P(t) = [\varepsilon \cdot U(t) - BD]/m_c \tag{10}$$

Integrate the curve from t_i s to t_e s:

$$Q = \int_{t_i}^{t_e} P(t) \cdot dt \tag{11}$$

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[5] The described test procedure can be adopted also for the measuring of the heat of hydration at different testing ages.

Here, t_i is the time at which the measurement started and t_e is the time at which the measurement ended as calculated from the time of mixing cement and water. *Q* is the heat produced expressed in J/g.

NOTE In the case of Method A the calculation of the total heat of hydration requires the correction of the test result Q by the addition of two further quantities:

— Q_{mix}: heat evolved immediately after the mixing and before the sample is put into the calorimeter. To calculate this quantity, the temperature rise in the sample during the mixing needs to be known.

— Q_τ: heat flow due to the temperature differential between the sample and the calorimeter when the sample is put into the calorimeter. This heat contribution can be determined on the basis of the time constant using the following formula where symbols have already been defined.

$$Q_\tau = \tau \cdot \left[P(t_e) - P(t_i)\right] \qquad (12)$$

12.6 Result

Express the heat of hydration as the mean of two measurements, expressed to one decimal place.

The Test Report should give the following information:

a) reference to this document;

b) dates of start and completion of the test;

c) reference to the type of instrument used specifying:

  1) number of testing and reference cells;

  2) internal or external mixing;

d) sample composition;

e) mass of sample charged in each cell;

f) value of calibration coefficient;

g) plotting of the resulting thermal power curve;

h) calculated heat of hydration;

i) any factors which may have affected the results, such as any incidents or any operating details not specified in this document.

Data file should be available under request.

Annex A
(informative)

Glossary

A.1 Ampoule

The container into which the sample is placed for a measurement.

A.2 Ampoule holder

The holder into which the ampoule is placed for a measurement. The ampoule holder conducts the heat from the sample in the ampoule to the heat flow sensor.

A.3 Baseline

The signal from the calorimeter when there is no sample or an inert sample in the instrument.

A.4 Calibration coefficient

Thermal power per unit output from the data acquisition equipment. Normally the calibration coefficient has a unit of watts per volts (W/V).

A.5 Isothermal

The instruments used are called “isothermal” as the temperature changes in them (if the instrument and the method are well designed) are so low so that the results are – from a practical point of view – the same as if the measurement had been made at perfectly isothermal conditions. The term is convenient to use here as most other cement calorimeters are (semi-) adiabatic, but it does not imply that the measurements are made under perfectly isothermal conditions.

A.6 Reference

Each calorimeter is equipped with a reference. The output from the calorimeter (V) is the difference between the signal from the sample and the signal from the reference. If an inert sample with similar heat capacity as the sample is charged into the reference ampoule, noise and drift will be substantially decreased (balancing).

A.7 Thermal power

Heat production rate measured in watts (W) or joules per second (J/s).

Bibliography

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