

Methods of testing cement

Part 9: Heat of hydration — Semi-adiabatic method

ICS 91.100.10

EUROPEAN STANDARD

EN 196-9

NORME EUROPÉENNE

EUROPÄISCHE NORM

March 2010

ICS 91.100.10

Supersedes EN 196-9:2003

English Version

Methods of testing cement - Part 9: Heat of hydration - Semi-adiabatic method

Prüfverfahren für Zement - Teil 9: Hydratationswärme -
Teiladiabatisches Verfahren

This European Standard was approved by CEN on 21 February 2010.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG**Management Centre: Avenue Marnix 17, B-1000 Brussels**

Contents

	Page
Foreword.....	3
1 Scope	4
2 Normative references	4
3 Principle	4
4 Apparatus	4
5 Determination of the heat of hydration	7
5.1 Laboratory	7
5.2 Procedure	8
5.2.1 Mortar composition	8
5.2.2 Mixing.....	8
5.2.3 Positioning of the test sample.....	8
5.3 Measurement of heating	8
6 Calculation of the heat of hydration	9
6.1 Principles of calculations	9
6.2 Calculation of the heat accumulated in the calorimeter	9
6.3 Calculation of heat lost into ambient atmosphere	10
6.4 Calculation of heat of hydration.....	11
7 Expression of results	11
7.1 Reporting of results.....	11
7.2 Precision.....	11
7.2.1 Repeatability.....	11
7.2.2 Reproducibility.....	11
Annex A (normative) Calibration of the calorimeter.....	12
A.1 Principle.....	12
A.2 Apparatus and power supply	12
A.3 Calibration procedure	13
A.3.1 Determination of the coefficient of total heat loss, α	13
A.3.2 Determination of the thermal capacity	15
Annex B (informative) Worked example of determination of heat of hydration	17
B.1 General test conditions	17
B.2 Basic calculations.....	17
B.3 Determination of test results	17
Bibliography	20

Foreword

This document (EN 196-9:2010) has been prepared by Technical Committee CEN/TC 51, "Cement and building limes", the secretariat of which is held by NBN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2010, and conflicting national standards shall be withdrawn at the latest by September 2010.

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.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

This document supersedes EN 196-9:2003.

EN 196, *Methods of testing cement*, consists of the following parts:

- *Part 1: Determination of strength*
- *Part 2: Chemical analysis of cement*
- *Part 3: Determination of setting times and soundness*
- *Part 5: Pozzolanicity test for pozzolanic cement*
- *Part 6: Determination of fineness*
- *Part 7: Methods of taking and preparing samples of cement*
- *Part 8: Heat of hydration — Solution method*
- *Part 9: Heat of hydration — Semi-adiabatic method*
- *Part 10: Determination of the water-soluble chromium (VI) content of cement*
- CEN/TR 196-4, *Methods of testing cement — Part 4: Quantitative determination of constituents*

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard describes a method of measuring the heat of hydration of cements by means of semi-adiabatic calorimetry, also known as the Langavant method. The aim of the test is the continuous measurement of the heat of hydration of cement during the first few days. The heat of hydration is expressed in joules per gram of cement.

This standard is applicable to all cements and hydraulic binders, whatever their chemical composition, with the exception of quick-setting cements.

NOTE 1 An alternative procedure, called the solution method, is described in EN 196-8. Either procedure can be used independently.

NOTE 2 It has been demonstrated that the best correlation between the two methods is obtained at 41 h for the semi-adiabatic method (EN 196-9) compared with seven days for the heat of solution method (EN 196-8).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 196-1, *Methods of testing cement — Part 1: Determination of strength*

EN 573-3:2009, *Aluminium and aluminium alloys — Chemical composition and form of wrought products — Part 3: Chemical composition and form of products*

3 Principle

The semi-adiabatic method consists of introducing a sample of freshly made mortar into a calorimeter in order to determine the quantity of heat emitted in accordance with the development of the temperature. At a given point in time the heat of hydration of the cement contained in the sample is equal to the sum of the heat accumulated in the calorimeter and the heat lost into the ambient atmosphere throughout the period of the test.

The temperature rise of the mortar is compared with the temperature of an inert sample in a reference calorimeter. The temperature rise depends mainly on the characteristics of the cement and is normally between 10 K and 50 K.

4 Apparatus

4.1 Calorimeter, consisting of an insulated flask sealed with an insulated stopper and encased in a rigid casing which acts as its support (see Figure 1). Both the calorimeter used for the test and that for the reference (see 4.2) shall have the following construction and characteristics:

- a) **Insulated flask** (e.g. Dewar flask), made of silver plated borosilicate glass; cylindrical in shape with a hemispherical bottom. The internal dimensions shall be approximately 95 mm in diameter and 280 mm in depth; and external diameter of approximately 120 mm. A rubber disc of approximately 85 mm diameter and 20 mm thickness shall be placed at the bottom of the flask to act as support for the sample container and evenly distribute the load on the glass wall.
- b) **Very rigid casing**, having a sufficiently wide base to ensure good stability of the whole unit (e.g. made of duralumin, 3 mm thick). The flask shall be separated from the lateral walls of the casing by approximately 5 mm air space and rest on a support 40 mm to 50 mm thick made of a material having low thermal

conductivity (e.g. expanded polystyrene). The upper edge of the flask shall be protected by a rubber gasket above, and in contact with, which shall be a ring, not less than 5 mm thick, made of low thermal conductivity material, fixed to the calorimeter casing. The ring shall serve to locate the flask in position and provide a bearing surface for the stopper so as to ensure the tightness of the locking device.

c) **Insulating stopper**, made of three parts:

- 1) the lower part, which is inserted into the flask and which serves to provide a maximum prevention of heat loss into the external atmosphere. It shall be cylindrical in shape, of diameter equal to the internal diameter of the flask, and in thickness approximately 50 mm. It shall be made of expanded polystyrene (class 20 kg/m³ approximately) or of another material of similar thermal characteristics. Its base can be protected by a layer of plastic (e.g. polymethyl methacrylate), approximately 2 mm thick;
- 2) the central part, which serves to ensure the tightness of the calorimeter whilst contributing to the reduction of losses, shall consist of a foam rubber disc 120 mm in diameter;
- 3) the upper part, which is intended to ensure the correct and consistent positioning of the stopper unit against the Dewar flask, shall consist of a rigid casing incorporating a snap locking device in such a way as to compress the foam rubber central part ensuring the tight fitting of the stopper.

d) **Performance characteristics.** The coefficient of total heat loss of the calorimeter shall not exceed 100 J·h⁻¹·K⁻¹ for a temperature rise of 20 K. This value, together with the thermal capacity, shall be determined in accordance with the calibration procedure given in Annex A (see A.3.1).

Recalibration is necessary:

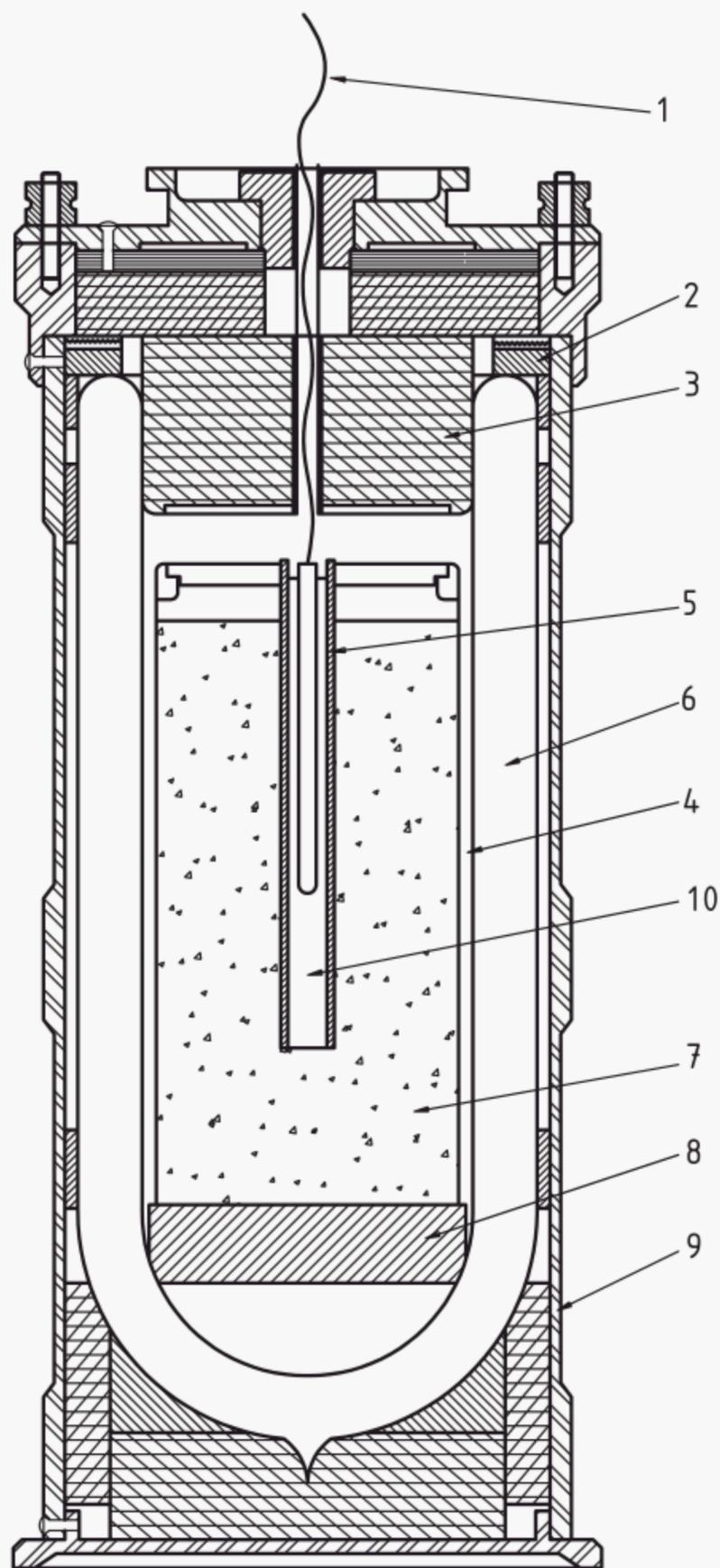
- at least every four years or after 200 tests;
- whenever deterioration occurs in the calorimeter or an insulating component.

In order not to impair the insulation of the calorimeter, the temperature of the mortar under test shall not exceed 75 °C.

4.2 Reference calorimeter, having the same construction and characteristics as the test calorimeter (see 4.1).

It shall contain a mortar box in which is a sample of mortar mixed at least 12 months previously (and is considered to be inert).

NOTE Where an inert sample is not available an aluminium cylinder of the same thermal capacity as the mortar box and mortar sample may be used.



Key

- | | | |
|-----------------------------------|----------------------|----------------|
| 1 platinum resistance thermometer | 5 thermometer pocket | 9 rigid casing |
| 2 gasket | 6 dewar flask | 10 oil |
| 3 insulating stopper | 7 mortar sample | |
| 4 mortar box | 8 rubber disc | |

Figure 1 — Typical calorimeter

4.3 Platinum resistance thermometers, for the reference calorimeter and each test calorimeter, having a minimum range 19 °C to 75 °C.

If the conductors of the electrical resistor are made of copper they shall have a sectional area not greater than 0,25 mm² in the part which passes through the stopper. If they are made of another metal the total thermal resistance per centimetre of conductor shall be greater than 0,10 K·mW⁻¹ (thermal resistance equivalent to that of a copper conductor with a sectional area of 0,25 mm² and 1 cm in length).

The thermal output of the thermometer shall not exceed 3 mW. Direct current supply, which constitutes a power input, shall be avoided if the thermal output exceeds 0,2 mW. It is advisable to ensure the accuracy of the overall temperature measuring and recording equipment.

The temperature of the test sample shall be measured to an accuracy of ± 0,3 °C.

Where the calorimeter is calibrated in situ with the conductors used for the tests of heat of hydration, the total sectional area of the conductors will be a maximum of 0,80 mm² (four wires 0,5 mm in diameter), but shall be such that the coefficient of heat loss of the calorimeter is less than 100 J·h⁻¹·K⁻¹ for a temperature rise of 20 K (see A.3.1.1).

The protective sheath of these conductors shall be made of a material having a low thermal conductivity.

4.4 Mortar box, consisting of a cylindrical container fitted with a cover, having a volume of approximately 800 cm³, designed to contain the sample of mortar under test.

The mortar box, discarded after each test, shall be impermeable to water vapour. This shall be checked in use by weighing the mortar box after each test (see 5.2.3). It shall be made of electrically counter welded tin plate of nominal thickness 0,3 mm; have a diameter of approximately 80 mm and a height of approximately 165 mm. Its height shall be designed to provide an air space of approximately 10 mm between the top of the mortar box and the stopper.

The lid of the mortar box shall be fitted with a central thermometer pocket in the form of a cylindrical pipe, closed at its base. The internal diameter of the pocket shall be slightly greater than that of the thermometer. Its length shall be approximately 100 mm to 120 mm and enable it to extend to the centre of the test sample.

4.5 Temperature recording apparatus, capable of recording the measurements taken by each thermometer.

4.6 Mortar mixing apparatus, conforming to EN 196-1.

5 Determination of the heat of hydration

5.1 Laboratory

The laboratory where the mortar is mixed shall be maintained at a temperature of (20 ± 2) °C.

The room where the test is carried out shall be maintained at a temperature of (20,0 ± 1,0) °C. The measured temperature of the reference calorimeter shall be considered to be the ambient temperature and shall be maintained during the test within ± 0,5 °C. The distance between each of the calorimeters shall be approximately 120 mm. The velocity of the ventilation air around the calorimeters shall be less than 0,5 m·s⁻¹.

When several tests are being carried out simultaneously, at least one reference calorimeter shall be provided for every six test calorimeters; where several test calorimeters are used with one reference calorimeter, a hexagonal arrangement shall be used with the reference calorimeter in the centre.

5.2 Procedure

5.2.1 Mortar composition

The composition of the mortar shall be in accordance with EN 196-1 and the test sample shall have a total mass of $(1\,575 \pm 1)$ g. Each batch of mortar to be mixed shall consist of $(360,0 \pm 0,5)$ g cement; $(1\,080 \pm 1)$ g sand from a sample of CEN standard sand complying with the requirements in EN 196-1; and $(180,0 \pm 0,5)$ g distilled or deionised water.

NOTE Since it is not possible to recover all the material added to the mixer bowl the mortar batch to be mixed should be slightly more than 1 575 g, the proportions by mass of the various constituents being maintained.

5.2.2 Mixing

The cement, the water, the sand, the mortar box, the mixer bowl and the other instruments coming into contact with the mortar shall be stored in the test room.

With the mixer in the operating position, pour the sand and then the cement into the mixer bowl; homogenise the mixture of sand and cement for 30 s at low speed; pour in the water, record the time, and mix immediately at low speed for 60 s; set the mixer to high speed and mix for a further 60 s.

NOTE In order to avoid thermal losses, it is recommended to carry out the mixing in a relatively short time. It is for this reason that the mixing time prescribed in EN 196-1 has been shortened.

5.2.3 Positioning of the test sample

Immediately after mixing weigh $(1\,575 \pm 1)$ g of mortar into the box (see 4.4) which has previously been weighed, with its lid, to an accuracy of $\pm 0,5$ g. Place the lid in position making sure that it seals tightly. Fill the thermometer pocket with $(2,5 \pm 0,5)$ cm³ of oil (e.g. thin mineral oil) in order to improve the thermal contact between the test sample and the thermometer.

Weigh the filled mortar box, to an accuracy of $\pm 0,5$ g in order to be able to check at the end of the test for any leakage of water vapour. Immediately after weighing place the mortar box in the test calorimeter (see 4.1) and close with the stopper. Immediately place the thermometer (see 4.3) in position in the thermometer pocket, so that it is approximately in the centre of the test sample. Seal the opening across the stopper by means of the locking device.

NOTE The stopper can also be sealed by means of a flexible sealant or mastic.

Not more than 6 min shall be taken for the mixing and the positioning of the test sample.

At the end of the test the mortar box with its contents shall be weighed again, to an accuracy of $\pm 0,5$ g. If a reduction in mass of more than 2 g is found the test is not valid and shall be repeated.

5.3 Measurement of heating

The time of addition of water shall be taken as the start of timing. The measurement of heating consists of reading, at specific moments in time, the temperature of the test sample and that of the inert sample located in the reference calorimeter (see 4.2).

At least one reading shall be taken in the first 30 min followed by readings at least every: 1 h for the first 24 h; 4 h during the second day; and 6 h until the expiry of the selected test period. The frequency of these measurements may be increased according to the characteristics of the cement being tested. The time of each temperature reading shall be recorded in hours and minutes.

At each temperature reading the temperature rise of the test sample, θ_t , shall be determined as the difference between the temperature of the test sample, T_s , and that of the inert sample, T_r , in the reference calorimeter.

6 Calculation of the heat of hydration

NOTE A worked example is given in Annex B.

6.1 Principles of calculations

The heat of hydration, Q , in joules per gram of cement, at elapsed time, t , is calculated from Equation (1):

$$Q = \frac{c}{m_c} \theta_t + \frac{1}{m_c} \int_0^t \alpha \times \theta \times dt \quad (1)$$

where

m_c is the mass of cement contained in the test sample, in grams;

t is the hydration time, in hours;

c is the total thermal capacity of the calorimeter (see 6.2), in joules per Kelvin;

α is the coefficient of heat loss of the calorimeter (see 6.3), in joules per hour per Kelvin;

θ_t is the difference in the temperature of the test calorimeter compared with that of the reference calorimeter (see 5.3) at time t , in Kelvins.

The first term in Equation (1) represents the heat accumulated in the calorimeter A , and the second term represents the heat lost into the ambient atmosphere B (each in joules per gram of cement).

Equation (1) can be simplified to Equation (2):

$$Q = \frac{c}{m_c} \theta_t + \frac{1}{m_c} \sum_{i=1}^{i=n} \bar{\alpha}_i \times \bar{\theta}_i \times \Delta t_i \quad (2)$$

where

$\bar{\alpha}_i$ and $\bar{\theta}_i$ are the mean values of the coefficient of heat loss and of the difference in the temperature of the test calorimeter compared with that of the reference calorimeter during period of time, Δt_i .

6.2 Calculation of the heat accumulated in the calorimeter

Heat accumulated in the calorimeter, A , in joules per gram of cement, shall be calculated from the total thermal capacity, c , of the calorimeter, the mass of cement, m_c , and the difference in the temperature of the test calorimeter compared with that of the reference calorimeter, θ_t , at point in time, t by Equation (3):

$$A = \frac{c}{m_c} \theta_t \quad (3)$$

where the total thermal capacity of the calorimeter, c , including the mortar box and mortar sample under test is expressed by Equation (4):

$$c = 0,8(m_c + m_s) + 3,8m_w + 0,50m_b + \mu \quad (4)$$

where

0,8 is the thermal capacity per unit of mass of cement plus sand, in joules per Kelvin per gram;

3,8 is the average thermal capacity per unit of mass of water, in joules per Kelvin per gram;

0,50 is the thermal capacity per unit of mass of the mortar box, in joules per Kelvin per gram;

μ is the thermal capacity of the empty calorimeter, in joules per Kelvin;

m_c is the mass of cement, in grams;

m_s is the mass of sand, in grams;

m_w is the mass of water, in grams;

m_b is the mass of empty mortar box plus lid, in grams.

NOTE Bound water has a thermal capacity per unit of mass lower than $4,18 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$.

6.3 Calculation of heat lost into ambient atmosphere

Heat lost shall be calculated for known periods of hydration represented by the time elapsed between successive measurements of the temperature of the test sample (see 5.3).

The coefficient of heat loss of the calorimeter, α , in joules per hour per Kelvin, is given by Equation (5):

$$\alpha = a + b \times \theta \quad (5)$$

where

a and b are the calorimeter calibration constants (see A.3.1.1);

θ is the difference in the temperature of the test calorimeter compared with that of the reference calorimeter in Kelvins.

The heat lost into the ambient atmosphere, B , in joules per gram of cement, during the period of hydration, t_n , is given by Equation (6):

$$B = \frac{1}{m_c} \sum_{i=1}^n \bar{\alpha}_i \times \bar{\theta}_i \times \Delta t_i \quad (6)$$

where

Δt_i is the elapsed time between the measurement of temperature at point in time, $t_{(i-1)}$, and the next measurement at point in time, $t_{(i)}$, in hours;

$\bar{\theta}_i$ is the difference in the temperature of the test calorimeter compared with that of the reference calorimeter, between times t_i and $t_{(i-1)}$, in Kelvins, given by Equation (7):

$$\bar{\theta}_i = \frac{\theta_i + \theta_{(i-1)}}{2}; \quad (7)$$

$\bar{\alpha}_i$ is the average coefficient of total heat loss of the calorimeter (see Equation (5)) in the period of time, Δt_i , in joules per hour per Kelvin, given by Equation (8):

$$\bar{\alpha}_i = a + b \times \bar{\theta} \quad (8)$$

6.4 Calculation of heat of hydration

The heat of hydration, Q , expressed in joules per gram of cement, shall be calculated as the sum of the heat accumulated in the calorimeter and the heat lost into the ambient atmosphere as follows:

$$Q = A + B \quad (9)$$

7 Expression of results

7.1 Reporting of results

The results of the measurements shall be set out in a test report, normally in the form of a table, indicating: the heat of hydration, in joules per gram of cement, at the specified hydration age and including intermediate results (e.g. at: 12 h, one day, two days, three days, five days and seven days), as applicable.

The results reported for the heat of hydration shall be expressed, in joules per gram of cement, to the nearest whole number.

7.2 Precision

7.2.1 Repeatability

The standard deviation of repeatability, σ_r , of the heat of hydration determination is $5 \text{ J}\cdot\text{g}^{-1}$.

Therefore, if two results of properly conducted tests from the same laboratory on samples of the same cement are compared, they should not differ from each other by more than $14 \text{ J}\cdot\text{g}^{-1}$.

7.2.2 Reproducibility

The standard deviation of reproducibility, σ_R , is $15 \text{ J}\cdot\text{g}^{-1}$.

Therefore, if the results of two properly conducted tests from two different laboratories on samples of the same cement are compared, they should not differ from each other by more than $42 \text{ J}\cdot\text{g}^{-1}$.

Annex A (normative)

Calibration of the calorimeter

A.1 Principle

The calibration method consists of replacing the mortar box and test sample in the calorimeter to be calibrated with a calibration cylinder (see A.2.4) of equivalent dimensions. A known electrical supply is applied to the calibration cylinder causing it to increase in temperature. The amount of electrical energy applied is equal to the increased heat in the calorimeter and the heat lost to atmosphere. The determination of heat lost is made from the electrical energy required to maintain a constant temperature. The determination of the thermal capacity is made by disconnecting the electrical supply and measuring the rate of fall in calorimeter temperature.

NOTE The time required for a calorimeter to reach thermal equilibrium (steady state) is at least eight days. When moving from one calibration temperature to the next, by applying the new input voltage at the resistor terminals, the time required to reach a new steady state condition is approximately six days.

A.2 Apparatus and power supply

A.2.1 Reference calorimeter, (see 4.2) shall be placed approximately 120 mm from the calorimeter being calibrated.

A.2.2 D.C. voltmeter, shall have an accuracy of $\pm 0,1$ % and be operable between 0 V and 100 V.

A.2.3 Resistor measuring bridge or an ohmmeter, shall have an accuracy of $\pm 0,2$ %.

A.2.4 Calibration cylinder, (see Figure A.1) shall be composed of an aluminium core on which is wound a resistor of known value of at least 2 000 Ω , using a material with a high resistivity (e.g. constantan wire of 0,2 mm diameter). The characteristics of the aluminium used for the core shall be designated: EN AW 1080 A according to EN 573-3:2009 (corresponding to 99,8 % aluminium of specific heat 900 J·kg⁻¹·K⁻¹).

The core shall be screwed into a jacket having the same dimensions as the mortar box (see Figure 1 and 4.4); the connecting wires of the resistor shall have a small sectional area (0,05 mm² maximum) in order to avoid thermal losses.

A.2.5 Platinum resistance thermometers, shall be fitted with conductors complying with the requirements for maximum sectional area set out in 4.3 for the part which passes through the stopper of the calorimeter and be accurate to $\pm 0,15$ °C over the temperature range 20 °C to 60 °C.

A.2.6 Stabilized power supply, with voltage adjustable between 2 V and 60 V minimum; stability as a function of load: $\Delta V/V \leq 2 \times 10^{-4}$; and stability as a function of the mains voltage: $\Delta V/V \leq 1 \times 10^{-4}$.

A.2.7 Test room, the test room conditions shall be maintained in accordance with 5.1.

A.3 Calibration procedure

A.3.1 Determination of the coefficient of total heat loss, α

A.3.1.1 Procedure

The coefficient, α , shall be obtained by measuring, in steady state conditions:

- the heat output emitted by Joule effect in the calibration cylinder (see A.2.4) previously placed in the calorimeter to be calibrated;
- the temperature of this cylinder in relation to the temperature of the inert test sample placed in the reference calorimeter located close by (see A.2.1).

When steady state conditions are achieved the heat supplied is equal to that lost into the ambient atmosphere and the losses are expressed by Equation (A.1):

$$p = V^2 \times R^{-1} = \alpha \times \theta_c \quad (\text{A.1})$$

from which the coefficient of total heat loss, in watts per Kelvin, is expressed by Equation (A.2):

$$\alpha = V^2 \times R^{-1} \times \theta_c^{-1} \quad (\text{A.2})$$

or, in joules per hour per Kelvin, by Equation (A.3):

$$\alpha = 3\,600 V^2 \times R^{-1} \times \theta_c^{-1} \quad (\text{A.3})$$

where

V is the input voltage at resistor terminals, in volts;

R is the resistance of the heating coil, in ohms;

p is the rate of loss of heat, in watts;

θ_c is the temperature difference between the calibration cylinder and the inert reference sample, in Kelvins;

α is the coefficient of total heat loss of the calorimeter at temperature difference, θ_c , in joules per hour per Kelvin.

The measurement of rate of loss of heat shall be made with an accuracy of $\pm 0,5\%$. Since the coefficient, α , approximates to a linear function of θ , it can be determined with the required accuracy by calculation at five points within the temperature range anticipated during tests (see Table A.1).

NOTE For example, measurements may be made for temperature rises of 10 K, 17 K, 24 K, 31 K and 38 K, approximately.

Having determined the five values of α , the equation for the calibration line can be written as Equation (A.4):

$$\alpha = a + b \times \theta \quad (\text{A.4})$$

and the constant terms a and b shall be calculated by the method of least squares. The calibration points shall approximate to a straight line (if the coefficient of linear correlation is less than 0,97 the calibration shall be repeated). The coefficient, α , shall not exceed $100 \text{ J}\cdot\text{h}^{-1}\cdot\text{K}^{-1}$ for a temperature rise of 20 K.

A.3.1.2 Example calculation

The following worked example (see Table A.1 and Equation A.3) sets out the calculation stages:

Table A.1 — Measurement of coefficient of total heat loss, α

Temperature of calibration cylinder	°C	31,60	37,10	41,70	48,40	58,70
Reference temperature	°C	19,97	19,83	19,77	19,80	19,88
difference in the temperature of the test calorimeter compared with that of the reference calorimeter, θ_c	K	11,63	17,27	21,93	28,60	38,82
Voltage V	V	20,78	25,52	28,95	33,48	39,60
Resistance R	Ω	2 036	2 036	2 036	2 036	2 036
Output P	W	0,212 1	0,319 9	0,411 6	0,550 5	0,770 2
Coefficient α	$\text{J}\cdot\text{h}^{-1}\cdot\text{K}^{-1}$	65,65	66,68	67,57	69,30	71,43

Analysis of the straight line equation, $\alpha = a + b \times \theta_c$ results in the values of 63,0 for a and 0,216 for b with a coefficient of linear correlation of 0,99.

The value of the coefficient of total heat loss for the calorimeter, α , for a temperature rise of 20 K, is calculated as $(63 + 0,216 \times 20) = 67,3 \text{ J}\cdot\text{h}^{-1}\cdot\text{K}^{-1}$ and, as the coefficient of linear correlation is 0,99, the calibration is therefore valid and the calorimeter meets the performance requirements.

A.3.2 Determination of the thermal capacity

A.3.2.1 Procedure

The measurement of the thermal capacity, μ , of the empty calorimeter shall be carried out by the method of spontaneous cooling. For this purpose the calibration cylinder shall be disconnected from its electrical power supply after reaching the steady state condition for the last point of calibration to determine α (see A.3.1). Determine the total thermal capacity, c_T , of the calorimeter containing the calibration cylinder (see A.2.4) of known thermal capacity, c_c , from which that of the empty calorimeter itself, μ , shall be calculated.

The thermal capacity of the calibration cylinder shall be calculated by weighting by mass the specific heats of the different elements which constitute the cylinder.

During cooling, the heat exchange is given by Equation (A.5):

$$-c_T \times d\theta = \alpha \times \theta \times dt = (a + b \times \theta) \times \theta \times dt \quad (\text{A.5})$$

from which the total thermal capacity, c_T , of the calorimeter containing the calibration cylinder, in joules per Kelvin is expressed by Equation (A.6):

$$c_T = \frac{a \times t_d}{\ln((\theta_0 \times \alpha) / (\theta \times \alpha_0))} \quad (\text{A.6})$$

where

t_d is the elapsed time since disconnecting the power supply, in hours;

θ_0 is the temperature difference between the calorimeter being calibrated and the reference calorimeter at the time of disconnecting power, in Kelvins;

α_0 is the coefficient of total heat loss, in joules per hour per Kelvin, for the temperature difference, θ_0 ;

θ_t is the temperature difference at point in time, t_d , in Kelvins;

α_t is the coefficient of total heat loss, in joules per hour per Kelvin, for the temperature difference, θ_t .

The initial temperature difference, θ_0 , shall be between 35 K and 40 K. The value of the thermal capacity of the empty calorimeter, μ , in joules per Kelvin, shall be calculated from the equation:

$$\mu = c_T - c_c \quad (\text{A.7})$$

The cooling period shall be between 22 h and 30 h.

A.3.2.2 Example calculation

The following worked example (see Table A.2) sets out the calculation stages:

Table A.2 — Measurement of thermal capacity of empty calorimeter, μ

Time	h	0	22	24	26	28
Temperature of calibration cylinder	°C	58,70	39,50	38,32	37,23	36,20
Reference temperature	°C	19,88	19,81	19,79	19,79	19,77
Temperature difference, θ	K	38,82	19,69	18,53	17,44	16,43
Coefficient of total thermal loss, α	J·h ⁻¹ ·K ⁻¹	71,39	67,25	67,00	66,77	66,55
Total thermal capacity, c_T	J·K ⁻¹	-	2 238	2 236	2 234	2 234
Thermal capacity of cylinder, c_c	J·K ⁻¹	-	1 852	1 852	1 852	1 852
Thermal capacity of empty calorimeter, μ	J·K ⁻¹	-	386	384	382	382

The thermal capacity of the cylinder was calculated to be 1 852 joules per Kelvin (see A.3.2.1). From the above the average thermal capacity of the calorimeter is 384 joules per Kelvin.

The initial temperature rise was 38,82 K and the test period was 28 h therefore the determination meets the requirements for a valid calibration.

Annex B (informative)

Worked example of determination of heat of hydration

B.1 General test conditions

The cement, on which these tests were carried out, was a CEM III/B class 32,5 cement according to EN 197-1:2000.

The temperature in the test room was 20,0 °C.

The characteristics of the test calorimeter were:

- coefficient of total thermal loss, α , = $63,0 + 0,216 \times \theta \text{ J}\cdot\text{h}^{-1}\cdot\text{K}^{-1}$;
- thermal capacity of empty calorimeter, μ , = $384 \text{ J}\cdot\text{K}^{-1}$.

B.2 Basic calculations

The total thermal capacity, c , of the calorimeter, mortar box and mortar, in joules per Kelvin, (see Equation (4)), was calculated by the equation:

$$c = 0,8 (350 + 1\,050) + (3,8 \times 175) + (0,50 \times 138) + 384 = 2\,238 \quad (\text{B.1})$$

and the total thermal capacity per gram of cement, in joules per Kelvin per gram, is calculated by Equation (B.2):

$$\frac{c}{m_c} = \frac{2\,238}{350} = 6,39 \quad (\text{B.2})$$

B.3 Determination of test results

Table B.1 sets out a summary of results for:

- times at which measurements of test and reference sample temperatures were taken;
- temperature rise, being the difference in the temperature of the test calorimeter compared with that of the reference calorimeter;
- heat losses from the calorimeter;
- calculated heat of hydration over the first 24 h.

Table B.1 — Calculation of heat of hydration

Time h	Temperature rise K	Heat losses J·g ⁻¹	Heat of hydration J·g ⁻¹
0,33	1,92	0,06	12,3
1	1,99	0,29	13,0
2	2,15	0,67	14,4
3	2,40	1,08	16,4
4	2,85	1,56	19,8
5	3,56	2,14	24,9
6	4,47	2,87	31,4
7	5,50	3,79	38,9
8	6,54	4,89	46,7
9	7,54	6,19	54,4
10	8,47	7,67	61,8
11	9,39	9,33	69,4
12	10,24	11,15	76,6
13	11,04	13,14	83,7
14	11,77	15,27	90,5
15	12,47	17,55	97,3
16	13,15	19,95	104,0
17	13,85	22,49	111,0
18	14,55	25,18	118,2
19	15,22	27,99	125,3
20	15,77	30,93	131,8
21	16,16	33,96	137,3
22	16,39	37,05	141,8
23	16,48	40,18	145,5
24	16,40	43,30	148,2

Table B.2 sets out the stages by which the calculation of heat of hydration is made.

It records (row 1) the hydration age and (row 2) the determined temperature rise of the test sample above that of the reference sample (see 5.3).

Calculations are made for: (row 3) the heat accumulated in the calorimeter, per gram of cement, (see Equation (3)); (row 4) the average temperature rise during each period (see Equation (7)); (row 5) the average coefficient of total heat loss during the calculation period (see Equation (8)); and (row 6) the duration of each period.

From the above the total heat lost to atmosphere (row 7), and the heat lost per gram of cement (row 8), to the end of each period are determined (see Equation (6)), The cumulative heat of hydration to the end of each

period (row 9) is determined as the sum of the heat accumulated in the calorimeter (row 3) and the total heat lost (row 8) (see Equation (9)).

Table B.2 — Details of calculations for first four time intervals

(Row 1) Age h	0,33	1,00	2,00	3,00
(Row 2) $\theta_i = T_s - T_R$ K	1,92	1,99	2,15	2,40
(Row 3) $A = \frac{c}{m_c} \times \theta_i = 6,39 \times \theta_i$ J·g ⁻¹	12,28	12,72	13,75	15,35
(Row 4) $\bar{\theta}_i = \frac{\theta_i + \theta_{(i-1)}}{2}$ K	$(1,92 + 0)/2 = 0,96$	$(1,92 + 1,99)/2 = 1,95$	$(2,15 + 1,99)/2 = 2,07$	$(2,40 + 2,15)/2 = 2,27$
(Row 5) $\bar{\alpha}_i = a + b \times \bar{\theta}_i$ J·h ⁻¹ ·K ⁻¹	$63 + (0,216 \times 0,96) = 63,2$	$63 + (0,216 \times 1,95) = 63,4$	$63 + (0,216 \times 2,07) = 63,4$	$63 + (0,216 \times 2,27) = 63,5$
(Row 6) $\Delta t_i = t_i - t_{(i-1)}$ h	$0,33 - 0 = 0,33$	$1 - 0,33 = 0,67$	$2 - 1 = 1$	$3 - 2 = 1$
(Row 7) $\sum \bar{\alpha}_i \times \bar{\theta}_i \times \Delta t_i$ J	$63,2 \times 0,96 \times 0,33 = 20,02$	$20,02 + (63,4 \times 1,95 \times 0,67) = 103,1$	$103,1 + (63,4 \times 2,07 \times 1) = 234,4$	$234,4 + (63,5 \times 2,27 \times 1) = 378,9$
(Row 8) $B = \frac{I}{m_c} \sum \bar{\alpha}_i \times \bar{\theta}_i \times \Delta t_i$ J·g ⁻¹	$(1/350) \times 20,02 = 0,06$	$(1/350) \times 103,1 = 0,29$	$(1/350) \times 234,4 = 0,67$	$(1/350) \times 378,9 = 1,08$
(Row 9) $Q = A + B$ J·g ⁻¹	$12,28 + 0,06 = 12,3$	$12,72 + 0,29 = 13,0$	$13,75 + 0,67 = 14,4$	$15,35 + 1,08 = 16,4$

Bibliography

- [1] EN 196-8, *Methods of testing cement — Part 8: Heat of hydration — Solution method*
- [2] EN 197-1:2000, *Cement — Part 1: Composition, specifications and conformity criteria for common cements*

BSI - British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover. Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001. Fax: +44 (0)20 8996 7001 Email: orders@bsigroup.com You may also buy directly using a debit/credit card from the BSI Shop on the Website <http://www.bsigroup.com/shop>

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact Information Centre. Tel: +44 (0)20 8996 7111 Fax: +44 (0)20 8996 7048 Email: info@bsigroup.com

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration. Tel: +44 (0)20 8996 7002 Fax: +44 (0)20 8996 7001 Email: membership@bsigroup.com

Information regarding online access to British Standards via British Standards Online can be found at <http://www.bsigroup.com/BSOL>

Further information about BSI is available on the BSI website at <http://www.bsigroup.com>.

Copyright

Copyright subsists in all BSI publications. BSI also holds the copyright, in the UK, of the publications of the international standardization bodies. Except as permitted under the Copyright, Designs and Patents Act 1988 no extract may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, photocopying, recording or otherwise – without prior written permission from BSI.

This does not preclude the free use, in the course of implementing the standard, of necessary details such as symbols, and size, type or grade designations. If these details are to be used for any other purpose than implementation then the prior written permission of BSI must be obtained.

Details and advice can be obtained from the Copyright and Licensing Manager. Tel: +44 (0)20 8996 7070 Email: copyright@bsigroup.com