SLOVENSKI STANDARD
SIST-TP CEN/TR 16632:2014

01-september-2014

Določanje toplote hidratacije cementa z izotermno kondukcijsko kalorimetrijo (ICC): stanje tehnike in priporočila

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

Ta slovenski standard je istoveten z: CEN/TR 16632:2014

ICS:

91.100.10	Cement. Mavec. Apno. Malta	Cement. Gypsum. Lime. Mortar

SIST-TP CEN/TR 16632:2014 **en,fr,de**

TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

CEN/TR 16632

June 2014

ICS 91.100.10

English Version

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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EUROPEAN COMMITTEE FOR STANDARDIZATION
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EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. CEN/TR 16632:2014 E

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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.

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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

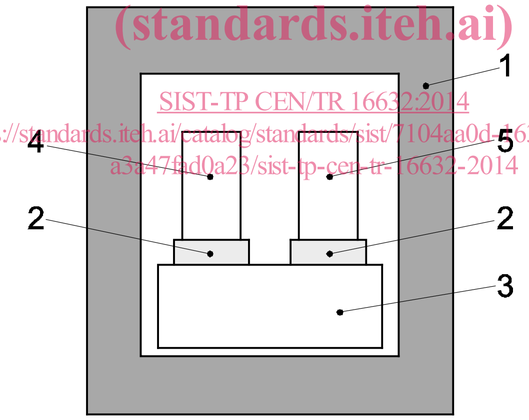
1 Basic principle and key points of ICC

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);

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:

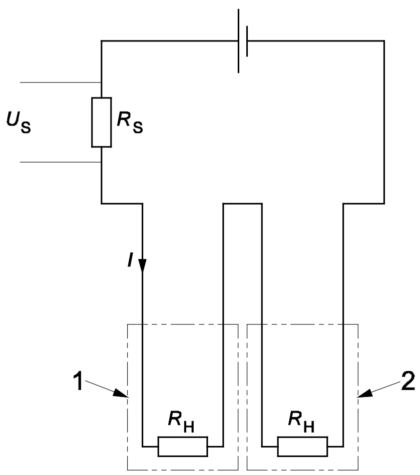
1) design and construction of the calorimeter;

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