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An international round robin test on isothermal (conduction) calorimetry for measurement of three-day heat of hydration of cement

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ABSTRACT

The results of a round robin test on isothermal (heat conduction) calorimetry are presented. A total of 18 participants using three types of instruments conducted 3-day measurements of the hydration of one rapidly hardening Portland cement and one slag-containing cement. The results confirm that isothermal calorimetry is a suitable method for the determination of heat of hydration. As a part of the study, two laboratories also conducted measurements with the standardized heat of solution method. For the Portland cement, these results were in good agreement with the isothermal measurements, but for the slag-containing cement the results differed, both between the two laboratories and between their results and the result of isothermal calorimetry. However, this method performance study clearly shows that the heat of hydration determination of cement by heat conduction calorimetry is more precise than the traditional heat of solution method described in EN 196-8, if state-of-the-art calorimeters are used.

1. Introduction

The release of heat is an important property of the cement hydration reaction that in different ways has been used since the early 20th century to characterize and study cements. Today, there are four types of calorimeters in use for measurements of heat of hydration: solution calorimetry, semi-adiabatic calorimetry, adiabatic calorimetry, and isothermal (heat conduction) calorimetry.

In solution calorimetry, the energy content of hydrated and unhydrated cements is measured, and the total heat produced during the hydration is calculated as the difference between these two values. The measurements are made by dissolving samples in a mixture of nitric and hydrofluoric acids in a Teflon-coated Dewar flask and measuring the heat production through the temperature increase (note that the method measures isothermal heat production, as the sample is stored isothermally during the hydration period). This method is standardized as EN 196-8 [1] and ASTM C186-13 [2], and is used to classify cements into different types according to their heat production by measurement of 3- or 7-day heat of hydration. Solution calorimetry is a difficult method to use because of the hazardous acid solution, and there are indications that it does not work well for blended cements [3].

Semi-adiabatic calorimetry is the measurement of the temperature increase in a more or less well-insulated sample of cement paste, mortar or concrete. Results are often recalculated to isothermal conditions by using activation energy and heat capacity. The method is standardized both for smaller mortar samples as the Langavant calorimeter [4] and for larger (10–30 kg) samples of concrete [5].

In adiabatic calorimeters, no heat is allowed to escape from the sample, and such instruments are mainly used to assess the properties at high temperatures, typically at 60 °C, reached in the center of massive concrete constructions [6].

Isothermal (conduction) calorimetry is the measurement of heat production rate (thermal power) in small cement paste or mortar samples. This technique is used, both in cement science and industry, and in other fields of science and technology, for example in the areas of pharmaceutics [7], food science [8], animal science [9] and microbiology [10]. There are many reports on the usefulness of this method in cement science [11–16], but it has not been standardized for the measurement of heat of hydration until 2009 when ASTM C1702 [17] was introduced and it is still not standardized in Europe [18]. However, CEMBUREAU issued a recommendation already in 1977 [19] on how to use it.

All the above-mentioned methods can be used to measure heat of hydration, and their results can be compared if the semi-adiabatic and adiabatic methods are recalculated to isothermal conditions. It has been found that results from solution calorimetry and isothermal calorimetry agree well for Portland cements, but less well for blended cements [2]. This has been attributed to difficulties with dissolving the slag components in solution calorimetry [3].

The present study was conducted in 2003 to lay the basis for standardization of isothermal calorimetry for the determination of heat of hydration of cement. It was left unpublished, but as a draft of this paper is referenced in the North American standard ASTM C1702 [17] and has been discussed in the European work towards a CEN-

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standard, we felt that this study should be properly published. It also complements other round robin studies [20] in that it focuses on methods of evaluating heat of hydration from measurements by isothermal calorimetry.

In the present study we wanted to assess the state of the technique, taking into account that there are different types of such instruments in use today, relying on slightly different procedures. The main objectives of this collaborative study were to:

- determine the repeatability (within-laboratory precision) and reproducibility (among-laboratories precision) of isothermal calorimetry for the measurement of 3-day heat of hydration;
- assess different methods of evaluating the results;
- compare the isothermal calorimetry results with the results from solution calorimetry.

This study was initiated and coordinated by the first author. The calorimetric evaluation was prepared by the first author and the statistical evaluation by the second author.

2. Method of isothermal calorimetry

2.1. General

Isothermal calorimeters measure thermal power (heat flow rate) [14]. A small sample—typically 1–10 ml—is placed in contact with a heat flow sensor, which is in contact with a heat sink. The heat leaves the sample by heat conduction and a well-designed experiment will be essentially isothermal (typically having temperature changes less than 0.1 K at the main hydration peak). Three types of isothermal calorimeters were used in the study: a calorimeter designed at Erlangen University [21], TAM 2277 (Thermometric, Sweden) [22] ; and TAM Air (Thermometric, Sweden, now TA Instruments, USA) [14].

2.2. Instruments

The results from three different types of isothermal calorimeters (here called 1–3) are presented. All calorimeters are heat conduction calorimeters.

Type 1: This instrument has four measurement positions, one of them is used as a reference [22]. The samples are transferred into sealed plastic cups that are placed in contact with the heat flow sensors with the help of a heat conducting paste.

Type 2: This instrument is a modular microcalorimeter with up to four calorimeters placed in a water bath [21]. Each calorimeter has its own reference. The samples are charged into 3 ml disposable glass ampoules sealed with Teflon-coated rubber septa and aluminum caps that are placed in aluminum sample holders in contact with the heat flow sensors.

Type 3: This instrument has eight calorimeters placed in one air thermostat [14]. Each calorimeter has its own reference. The samples are charged into 20 ml disposable glass ampoules sealed with Teflon-coated rubber septa and aluminum caps, and placed in aluminum sample holders in contact with the heat flow sensors.

2.3. Participants

A total of 19 participants in Europe and USA, both industrial and academic laboratories, delivered isothermal calorimetric measurements. One set of measurements was clearly made with a non-functioning calorimeter, and was excluded. Of the remaining 18 participants, 1 used calorimeter type 1, 4 used calorimeter type 2, and 13 used calorimeter type 3. In the following sections, these participants have randomly been assigned letters A–R (Table 1).

2.4. Experimental procedure

The round robin participants were provided with a recommended procedure (presented below), but allowed to make deviations from this procedure if necessary, e.g. the participants using calorimeter type 2 had to decrease the sample mass, as their microcalorimeters are too sensitive for 5 g of sample. Deviations were noted in deviation reports (the most important deviations are given in Table 1).

The following general advice was given to the participants:

1. Each measurement should cover at least 3 days (counting from the time of mixing).
2. Participants should make at least 12 measurements, six on each of the two cement types. For both cements, at least two mixes should be prepared (minimum requirements).
3. Both sample handling (mixing, etc.) and measurement should take place at 20 °C.
4. For calorimeters with different sensitivity ranges, choose a range, at which the measurements will not go out of range at the start of the measurement.
5. Avoid handling ampoules with bare hands, as this approach heats up the samples (use cotton gloves).

The procedure to start a measurement was given as follows:

1. Store cement, water and mixing utensils in a room at 20 °C for at least 10 h before a measurement.
2. Weigh (50 ± 0.01) g of cement into a beaker of glass, plastics or stainless steel. Note the actual cement mass.
3. Add (22.5 ± 0.01) g of distilled or deionized water and note the time when this was done. Note the actual water mass.
4. Hand-mix the paste with a stainless steel utensil until there is no more dry cement (all cement is wetted).
5. Mix vigorously for a further 30 s.
6. Tare an ampoule on the balance.
7. Charge a sample of 5–15 g into the glass ampoule. Note the actual sample mass.
8. Seal the ampoule.
9. Charge the ampoule into the calorimeter within 240 s (4 min) after water was added to the cement.
10. Return to point 6 if you are going to charge more than one sample from the same mix.

Table 1
Used calorimeters and deviations from the recommended procedure.

Participant	Calorimeter type	Comments
A	3	Measurements were only run over a period of 70 h and have been linearly extrapolated to 72 h.
B	2	0.725 g of cement paste was mixed inside the ampoules on a test tube mixer.
C	3	Measurements completed 6 months after the other participants.
D	3	–
E	2	0.4–1.1 g of sample.
F	3	–
G	3	–
H	1	–
I	2	40 mg of sample mixed by tapping the ampoule with cement and water on the bench.
J	3	–
K	3	–
L	2	0.7–2.5 g of sample.
M	3	–
N	3	Used two different amplifier ranges of the calorimeter.
O	3	–
P	3	–
Q	3	–
R	3	Used two different amplifier ranges and two operators.