METHOD PERFORMANCE STUDY ON HEAT OF HYDRATION DETERMINATION OF CEMENT BY HEAT CONDUCTION CALORIMETRY

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Abstract

In collaboration with HeidelbergCement and Dyckerhoff, the Research Institute of the German Cement Industry initiated a method performance study on heat of hydration determination of cement. 24 laboratories from 6 different countries participated in this collaborative trial. Each participant tested five different cement samples by conducting four individual measurements per sample. In addition to heat conduction calorimetry (21 participants), based on the Nordtest Method NT BUILD 505, the already standardized heat of solution method (EN 196-8, 9 participants) and semi-adiabatic method (EN 196-9, only 3 participants) were applied. Both repeatability (4.6 vs. 8 J/g) and reproducibility (13.6 vs. 17.6 J/g) of heat conduction calorimetry were better than the respective precision parameters of the traditionally used heat of solution method – if only instruments complying with the requirements of Nordtest Method NT BUILD 505 were considered. It was observed that the heat of hydration determined by heat conduction calorimetry was consistently higher than the value obtained via heat of solution method. With regard to the state-of-the-art TAM calorimeters this average difference amounted to about 22 J/g. This systematic deviation is nonsatisfying and must be addressed within the scope of the intended standardization of heat conduction calorimetry as an additional reference method for heat of hydration determination of cement.

Key words

Cement, heat of hydration, heat conduction calorimetry, solution calorimetry, semi-adiabatic calorimetry, validation of testing methods
1 INTRODUCTION

Heat of hydration is the heat generated when cement and water react. The quantity of heat generated mainly depends on the chemical composition of the cement, with C$_3$A and C$_3$S being the phases primarily responsible for high heat evolution. The water/cement ratio, fineness of the cement, and temperature of curing also are relevant factors. An increase in the fineness, cement content, and curing temperature increases the heat of hydration. Although Portland cement can evolve heat for many years, the rate of heat generation is greatest at early ages. A large amount of heat evolves within the first three days with the greatest rate of heat liberation usually occurring within the first 24 hours. For most concrete elements, such as slabs, heat generation is not a concern because the heat is quickly dissipated into the environment. However, in massive structures (greater than a meter thick), the rate and amount of heat generated are important. If this heat is not rapidly dissipated, a significant rise in concrete temperature can occur. This may be undesirable since, after hardening at an elevated temperature, nonuniform cooling of the concrete mass to ambient temperature may create undesirable internal stresses.

EN 197-1 + A1 [1] defines standard cement with low heat of hydration (LH), whereas EN 14216 [2] describes special cements with very low heat of hydration (VLH). The heat of hydration of LH cements is limited to a maximum of 270 J/g, for VLH cements the maximum is 220 J/g. ASTM C 150 [3] requires a maximum of 290 J/g for type II cements with moderate heat of hydration and a maximum of 250 J/g for type IV cements with low heat of hydration. The heat of solution method for measuring the isothermal heat of hydration of Portland cements was developed by Woods et al. [4] and has become the traditional method specified in National Standards (EN 196-8 [5] and ASTM C 186 [6], respectively). The heat of solution method consists of measuring, at a particular age of hydration – in general seven days, the difference between the heats of dissolution of partly hydrated and of unhydrated cement in a mixture of nitric and hydrofluoric acid. The difference is equivalent to the heat of hydration at that particular age. The semi-adiabatic method (EN 196-9 [7]) 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.

EN 197-1 + A1 also describes properties, test procedures and minimum test frequencies for the internal monitoring of the producer as well as statistical evaluation procedures. Here, it is clearly stated that, if it is acceptable according to the respective part of EN 196, alternative procedures may be applied, provided that the results of these procedures correlate with those of the reference procedure and are comparable to them. In the case of heat of hydration determination of cement heat conduction calorimetry is a promising alternative method. Isothermal calorimeters, occasionally referred to as heat conduction or as heat flow calorimeters, maintain a reaction system close to constant temperature. Necessary for the measurement of heat conduction, a temperature gradient is propagated from the reaction ampoule to or from a surrounding heat sink. Correction is made for this small imbalance of temperature. Peltier units are located within the temperature gradient of a reacting system, between the reaction ampoule and surrounding heat sink, so that the transmission of energy can be measured. Various designs of heat sinks in
heat conduction calorimeters have been used [8]. Modern instruments like the TAM calorimeters produced by TA Instruments have a twin ampoule configuration incorporating a reaction ampoule linked to a reference ampoule. The observed calorimetric signal is the differential of the two signals eliminating a considerable amount of external noise. Such calorimeters are highly sensitive and have exceptional long-term base-line stability. Calibration of isothermal calorimeters is made using an electrical heater. A known amount of power is supplied over a given time period to which the calorimetric signal is set.

2 PURPOSE AND SCOPE OF THE STUDY AND METHOD

Based on the experiences gained from previously conducted collaborative studies [9] the precision characteristics (repeatability and reproducibility) [10, 11] of the heat of hydration determination of cement by heat conduction calorimetry should be determined. Furthermore, heat conduction calorimetry should be compared with the reference procedures heat of solution and semi-adiabatic method. Long-term objective is to establish heat conduction calorimetry as a standardized reference procedure for the monitoring of cements with moderate, low or very low heat of hydration.

3 DESIGN OF THE COLLABORATIVE STUDY

The measurement of the heat of hydration by heat conduction calorimetry was mainly based on the Nordtest Method NT BUILD 505 [12]. Calorimeters should be operated in an air-conditioned laboratory at a temperature of (20 ± 2) °C. Before starting the measurements the calorimeters had to be calibrated. For this purpose the ampoules were filled with inert material, e.g. sand or water. Then the base-line was measured over a period of 24 hours, followed by the actual calibration using heat resistors and by an additional measurement of the base-line over 24 hours. The measured base-line should have a long-term drift less than 2 μW per week per gram of sample used and mean base-line fluctuations less than 5 μW per gram of sample.

In the case of external sample preparation water and cement were mixed outside the calorimeter. For each independent determination (50 ± 0.01) g of cement and (20 ± 0.01) g of water (w/c ratio of 0.40) were mixed by intensive stirring over a period of 30 seconds. Within 240 seconds after starting the mixing process 5 to 10 g – depending on the calorimeter type – of the cement paste were weighed out into an ampoule, the ampoule was transferred into the calorimeter, and the measurement process was started. The mass of the individual components and the mass of the sample were noted.

In the case of internal sample preparation (5 ± 0.01) g of dry cement were filled in an admix ampoule, and the admix ampoule was transferred into the calorimeter. (2 ± 0.01) g of water were added via a syringe inside the calorimeter. Immediately after water addition, cement and water were mixed for 60 seconds using the built-in stirrer of the admix ampoule. Then the measurement process was started. The measurements were performed over a period of seven days. A measurement interval of 60 seconds was recommended. The heat of solution method was exactly carried out according to EN 196-8 (w/c ratio of 0.40), and the semi-adiabatic method followed the instructions given in EN 196-9 (w/c ratio of 0.50).
3.1 General Principles

The purpose of this collaborative study was to provide a realistic estimate of the attributes of heat conduction calorimetry, particularly the systematic and random deviations, to be expected when the method was used in actual practice. The collaborative study provided information on the best performance to be expected. The Research Institute of the German Cement Industry organized this method performance study and obtained the necessary administrative and operational approvals. Experienced specialists from HeidelbergCement and Dyckerhoff reviewed both the design of the study and the statistical analysis of the data.

3.2 Participating Laboratories

In accordance with the international orientation of this method performance study 24 laboratories from 6 different countries participated. Figure 1 shows the geographical distribution of the participants and gives an overview of the applied measurement procedures. All laboratories involved were familiar with the analytical problem and using the methods in practice.

Figure 1 – Provenance of the participants and number of participants per method.

For the heat of solution method and in particular for heat conduction calorimetry the number of laboratories was sufficient for statistical analysis and in line with relevant standards [13]. For semi-adiabatic calorimetry the number of participants was definitely too low.

3.3 Test Materials

The materials used were representative of commodities usually analyzed, with customary and extreme values for the analyte. Homogeneity was established by testing a representative number of laboratory samples taken at random before shipment. Laboratory samples were coded at random so that there was no preselection from order of presentation. Analyte levels covered the heat range of interest up to the most important limit value of 270 J/g. Five different slag-containing cements from five different German cement plants were chosen:

- Cement C1: CEM III/A 32.5 N-LH/LA
- Cement C2: CEM III/B 32.5 N-LH/HS
- Cement C3: CEM III/B 32.5 N-LH/HS
• Cement C4: CEM III/A 32.5 N-LH
• Cement C5: CEM III/A 32.5 N-LH/LA

3.4 Replication
Differing from the applied Nordtest Method, for each cement four independent measurements were conducted. While ISO [14] does not specify the number of replicates, the German standard [13] prescribes to perform at least two “parallel determinations”, but recommends a larger number. Moreover, this norm requires that the product of the number of laboratories and the number of replicates has to be equal to or larger than 24. This requirement was met for heat conduction and solution calorimetry.

4 PREPARATION OF MATERIALS
The cement samples were homogenized to a degree that residual differences between the compositions of the distributed samples contributed virtually nothing to the variability of the participants’ results. This basic prerequisite was proven by a formal homogeneity test, documented in the International Harmonized Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories [15]: Three selected sample bags per cement were separately homogenized and from each two test portions were taken. The six test portions per cement were analyzed by heat conduction calorimetry in a random order under repeatability conditions, i.e. in a single run. The above-mentioned protocol required a minimum of 10 sample bags for homogeneity testing, but due to the long measurement time – seven days – and limited measurement capacity the number of samples had to be reduced.

Sampling variance, $s^2$, and analytical repeatability variance, $s_a^2$, were estimated by one-way analysis of variance, without exclusion of outliers. The target standard deviation for reproducibility, $\sigma_R = 18 \text{ J/g}$ was taken from EN 196-8. The results are summarized in the following table.

<table>
<thead>
<tr>
<th></th>
<th>Cement C1</th>
<th>Cement C2</th>
<th>Cement C3</th>
<th>Cement C4</th>
<th>Cement C5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$ (F-test)</td>
<td>10.33</td>
<td>4.30</td>
<td>3.48</td>
<td>1.65</td>
<td>6.20</td>
</tr>
<tr>
<td>$s_a$ [J/g]</td>
<td>1.22</td>
<td>1.29</td>
<td>1.87</td>
<td>9.07</td>
<td>0.91</td>
</tr>
<tr>
<td>$s_s$ [J/g]</td>
<td>2.65</td>
<td>1.66</td>
<td>2.08</td>
<td>5.16</td>
<td>1.47</td>
</tr>
<tr>
<td>$s_s / \sigma_R$</td>
<td>0.15</td>
<td>0.09</td>
<td>0.12</td>
<td>0.29</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Except for cement C1 the calculated $F$ values were lower than the critical $F$ value of 9.55, proving that there were no significant differences between the samples. The ratio of $s_s / \sigma_R$ was less than 0.3 in all five cases, indicating sufficient homogeneity.

5 STATISTICAL ANALYSIS
Beyond an initial graphical review of the collaborative data material the Grubbs test was applied to identify and remove outliers. Repeatability ($s_t$) and reproducibility ($s_R$) were determined according to ISO 5725-1 [16] and 5725-2 [14].
6 RESULTS AND DISCUSSION

The following table shows the mean values and standard deviations of the heat of hydration calculated for the five different cement samples after removing outliers.

Table 2 – Heat of hydration of five different cement samples determined by three different measurement methods

<table>
<thead>
<tr>
<th>Heat [J/g]</th>
<th>Cement C1</th>
<th>Cement C2</th>
<th>Cement C3</th>
<th>Cement C4</th>
<th>Cement C5</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN 196-8 [a]</td>
<td>261 ± 20</td>
<td>191 ± 18</td>
<td>207 ± 19</td>
<td>248 ± 8</td>
<td>229 ± 18</td>
</tr>
<tr>
<td>EN 196-9 [b]</td>
<td>272 ± 24</td>
<td>188 ± 39</td>
<td>205 ± 24</td>
<td>243 ± 5</td>
<td>222 ± 1</td>
</tr>
<tr>
<td>HCC – Al [c]</td>
<td>278 ± 13</td>
<td>198 ± 24</td>
<td>228 ± 17</td>
<td>263 ± 18</td>
<td>248 ± 21</td>
</tr>
<tr>
<td>HCC – TAM [d]</td>
<td>280 ± 10</td>
<td>208 ± 13</td>
<td>234 ± 14</td>
<td>268 ± 13</td>
<td>254 ± 15</td>
</tr>
<tr>
<td>HCC – OI [e]</td>
<td>248 ± 31</td>
<td>174 ± 29</td>
<td>202 ± 29</td>
<td>217 ± 31</td>
<td>226 ± 22</td>
</tr>
</tbody>
</table>


Of course, the statistical basis for the semi-adiabatic method was poor. Therefore, the calculated numbers for EN 196-9 are not representative. For the same reason precision data were only determined for heat conduction calorimetry (all, TAM and other instruments) as well as heat of solution method. Table 3 summarizes the outcome of the statistical calculations according to ISO 5725-2.

Table 3 – Repeatability ($s_r$) and reproducibility ($s_R$) of heat of hydration determination of cement by heat conduction calorimetry and heat of solution method

<table>
<thead>
<tr>
<th>$s$ [J/g]</th>
<th>HCC – Al [a]</th>
<th>HCC – TAM [b]</th>
<th>HCC – OI [c]</th>
<th>EN 196-8 [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s_R$</td>
<td>$s_r$</td>
<td>$s_R$</td>
<td>$s_r$</td>
</tr>
<tr>
<td>C1</td>
<td>19.5</td>
<td>5.6</td>
<td>11.0</td>
<td>5.5</td>
</tr>
<tr>
<td>C2</td>
<td>23.2</td>
<td>5.5</td>
<td>13.3</td>
<td>3.9</td>
</tr>
<tr>
<td>C3</td>
<td>19.9</td>
<td>6.5</td>
<td>14.6</td>
<td>5.4</td>
</tr>
<tr>
<td>C4</td>
<td>16.1</td>
<td>5.2</td>
<td>14.0</td>
<td>4.1</td>
</tr>
<tr>
<td>C5</td>
<td>20.8</td>
<td>4.9</td>
<td>15.2</td>
<td>4.2</td>
</tr>
<tr>
<td>MV [e]</td>
<td>19.9</td>
<td>5.5</td>
<td>13.6</td>
<td>4.6</td>
</tr>
</tbody>
</table>


The average repeatability calculated for the heat of solution method is exactly in accordance with the value reported in EN 196-8 (8 J/g). The reproducibility of 17.6 J/g is also close to the value given in EN 196-8 (18 J/g). Those observations underscore that the design of this collaborative study was realistic and practice-oriented.

Evaluating heat conduction calorimetry – including all instrument types – results in a repeatability of 5.5 J/g and a reproducibility of 20 J/g. It becomes apparent that these values are strongly dependent on the performance of the used instruments. If the evaluation is limited to the state-of-the-art TAM instruments the repeatability de-
creases to 4.6 J/g and the reproducibility to 13.6 J/g. Both values are significantly lower than the standard deviations of the heat of solution method and highlight the precision and quality of heat conduction calorimetry – if only instruments complying with the strict requirements of Nordtest Method NT BUILD 505 are considered.

A comparison of the characteristics of both procedures [17,18] clearly reveals the superiority of heat conduction calorimetry to the heat of solution method: It is advantageous that the solution method can be used for long-term measurements, i.e. ages in excess of 28 days, and that the required apparatus is relatively inexpensive. On the other hand the solution method is labor- and cost-intensive. Only an experienced operator can obtain repeatable results, and systematic errors caused by partial insolubility of particular cement constituents, e.g. blast furnace slag or pulverized fuel ash, can occur. ASTM C 186 clearly states that the results of this test method may be inaccurate if some of the components of the hydraulic cement are insoluble in the nitric acid/hydrofluoric acid solution. Furthermore, the solution method is an indirect procedure, the heat of hydration being the difference between two large numbers. Handling hydrofluoric acid causes a severe health hazard for the operators.

In contrast, heat conduction calorimetry causes low expenditure of human labor and time, resulting in low analysis costs. It is less demanding of operator skills and as a direct method independent of solubility differences and of the type of cement. Since it is a continuous measurement, data other than the fixed values given by the heat of solution method may be obtained, e.g. rate data or early-age data. Standard deviations are lower than with the heat of solution method, and no hazardous chemicals are needed, complying with the German substitution precept. Of course, the apparatus is relatively expensive and the length of the test is limited by the ability of the equipment to measure very low heat output rates, but these disadvantages are more than compensated by the benefits.

As already observed in previous method performance studies [9] the heat of hydration determined by heat conduction calorimetry is consistently higher than the value obtained via the heat of solution method. With regard to the TAM instruments this average difference amounts to 21.6 J/g. This deviation would still meet the demands of EN 196-8 that, 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 22 J/g. Nevertheless, this systematic deviation is nonsatisfying and must be addressed in the future: Either the superior and more precise method (heat conduction calorimetry) will be adjusted to the currently accepted but error-prone standard procedure (heat of solution method), e.g. by introducing a correlation function or by shortening the measurement time as it had been done for EN 196-9 (41 hours vs. seven days). Or heat conduction calorimetry will be adopted as an independent and very precise reference method, and the relevant limit values for LH cements will be revised.

7 CONCLUSIONS AND OUTLOOK

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. The systematic difference between the values resulting from the two methods demands a pragmatic and unambiguous solution. Within the scope of CEN TC51/WG
12 an initiative has been started to standardize heat conduction calorimetry as an additional reference method for heat of hydration determination of cement.

REFERENCES

[13] DIN 38402-41:1984 German standard methods for the examination of water, waste water and sludge; general information (group A); interlaboratory trials in water analysis; planning and organization (A 41).