# LABORATORY MADE DIFFERENTIAL CALORIMETER TO STUDY CEMENT HYDRATION

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**ABSTRACT:**
This contribution describes a laboratory made differential calorimeter, designed to enable scientific research into the process of cement hydration. The calorimeter was calibrated electrically by means of dissipated Joule’s heat and further validated by inputting a known heat by means of warm water. Transient heat transfer processes in the calorimeter was modeled by employing lumped system analysis. The estimation of calorimeter parameters: heat loss constant, cooling constant, heat capacity and voltage to temperature conversion constant for the thermopile, is described. Heat of hydration of calcium aluminate cement paste was investigated.

***Key words:*** *differential calorimeter, heat of hydration, calcium aluminate cement, heat loss constant, cooling constant, heat capacity, thermopile, lumped system analysis.*

## 1. INTRODUCTION

Heat evolution in a cement based material is a consequence of the exothermic chemical reactions that take place during the hydration of cement **[1-3]**. The heat of hydration evolution curve is a valuable piece of data used for controlling the technological processes of cement production as well as cement application in placement/production of cement based materials. Numerous laboratory techniques have been developed for determination of the heat of hydration of cement based materials, ranging from sophisticated heat-flux micro-calorimeters **[4-8]** to (semi-)adiabatic temperature measurements **[9, 10]** of a larger insulated block of a representative sample. Calorimetric methods of investigation are important for better cement application, quality control of cement and optimization of process parameters. In addition they contribute to a better understanding of the influence of cement admixture, development of microstructure and mechanical stress in materials as well as predicting the strength of a cement based material.

Micro-calorimeters are generally used for neat cement pastes. They enable the determination of the heat of hydration evolution with small changes of the sample temperature during hydration ($\Delta T_{\max} < 3$ °C). This makes them ideal for a systematic scientific research to give an insight into the complex process of the cement paste hydration **[1, 11]**.

### 1.1 Calcium aluminate cement

Calcium aluminate cement (CAC) is very versatile special cement advantageously used in numerous specific applications **[11]**. Studies in the field of calcium aluminate cement hydration are scarce and insufficient in comparison to Portland cement (PC) studies. Data on thermal properties of CAC are particularly interesting due to a high rate of heat generation during the reaction of hydration and resulting high temperature gradient in material. During the hydration of CAC a large quantity, typically 70 – 90% of total heat is liberated in a short period (first 24 h) that causes a considerable increase in the material's temperature, even above 100 °C. Moreover, as the hydration of CAC is highly temperature dependent, yielding structurally different hydration products that continuously alter material properties, a good knowledge of thermal properties at early stages of hydration is essential **[1-3]** to predict its properties.

## 2. THEORETICAL

### 2.1 Differential calorimeter

Differential calorimeters measure a temperature difference between the measuring cell and the reference cell. The reference cell is filled with the inert, i.e. fully hydrated sample. Such a differential mode of operation excludes background heat effects due to temperature changes of the experiment's surroundings **[4-8]**.

For an isoperibol calorimeter, the evolved heat in time $t$ equals:

$$Q(t) = Q_A(t) + Q_K(t) \tag{1}$$

where $Q_A$ is the accumulated heat in the calorimeter that results in the increase of the calorimeter temperature:

$$Q_A(t) = C_p\,\Delta T(t) \tag{2}$$

and $Q_K$ is the heat loss to the surroundings:

$$Q_K(t) = C_p\,\beta \int_0^t \Delta T(t) \tag{3}$$

Therefore, by substituting **eqs. (2)** and **(3)** in **eq. (1)** the final equation for calculating the evolved heat of hydration per gram of cement (J/g) states:

$$Q(t) = \frac{C_p}{m}\left(\Delta T(t) + \beta \int_0^t \Delta T(t)\right) \tag{4}$$

where: $C_\mathrm{p}$ – is the effective heat capacity of the calorimeter, J/$^\mathrm{o}$C
$\beta$ – cooling constant of the calorimeter, h$^{-1}$
$m$ – cement mass, g

**Fig. 1** depicts the example of the determination of the evolved heat (a cumulative amount) by separating the each of the heat terms in **eq. (1)**. The rate of the heat evolution can be obtained by differentiating the cumulative curve with respect to time. In experimental conditions with higher temperature changes ($\Delta T$ > 5K) and poor convection (mixing) of the thermostating fluid (approaching semi-adiabatic calorimeters), for better accuracy, the change of the cooling constant with time $\beta = f(\Delta T)$ should be determined **[9, 10]**.

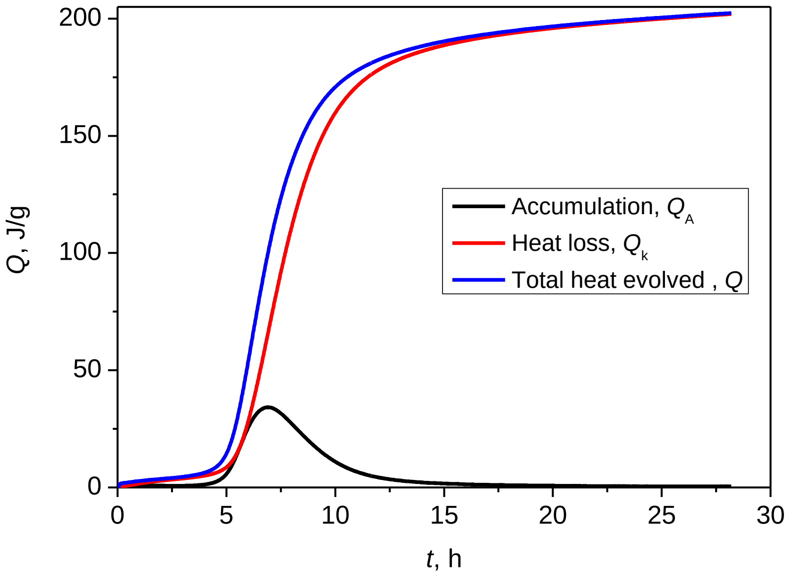


**Fig 1.** Example of the determination of the evolved heat in the isoperibolic calorimeter cell.

### 2.2 Lumped parameter model

**A** lumped parameter model reduces a thermal system (calorimeter) to a number of discrete “lumps” and assumes that the temperature difference inside each lump is negligible [**12**]. This approximation is useful to simplify complex differential heat equations to a simple first-order differential equation (i.e. Newton law of cooling, see below **eq. (8)**).

This common approximation in transient heat conduction may be used whenever heat conduction within an object is much faster than heat conduction across the boundary of the object.

Biot index **[12]** describes the ratio of the heat transfer resistances *inside of* and *at the surface of* an investigated system. This ratio defines whether or not the temperatures inside a body will vary significantly over space domain:

$$Bi = \frac{U_p \, l_k}{\lambda} \tag{5}$$

where $l_k$ [m] is a characteristic length of the system usually determined as a ratio of the volume and the external surface area of the system ($l = V / S$), $U_p$ is an overall heat transfer coefficient from the system to the surroundings [$\mathrm{Wm^{-2}K^{-1}}$], and $\lambda$ is the thermal conductivity of the system (i.e. cement paste sample). When calculating the heat transfer coefficient, $U_p$ one can neglect the convective heat transfer resistance ($1/\alpha_k \rightarrow 0$) between the surface of the insulation of the calorimeter and the thermostated bath due to an assured good mixing of the surrounding fluid.

$$U_p = \frac{1}{\left(\frac{d}{\lambda}\right)_{kond} + \left(\frac{1}{\alpha_k}\right)_{konv}} \tag{6}$$

where $d$ is the thickness of the insulating material [m], $\alpha_k$ is the convective heat transfer coefficient [$\mathrm{Wm^{-2}K^{-1}}$].

Values of the Biot number $\mathrm{Bi} < 0.1$ indicate that the heat conduction inside the system is much faster than the heat convection away from its surface, and temperature gradients are negligible inside of it. By assuring $\mathrm{Bi} < 0.1$ typically implies less than 5% error for assuming a lumped-parameter model of transient heat transfer.

Without internal heat generation the change in heat accumulation in the calorimetric system equals the amount of heat which is transferred to the surrounding:

$$C_p \frac{d\Delta T}{dt} = \alpha \, \Delta T \tag{7}$$

where $\alpha$ is a cooling constant of the calorimeter [J/(°C h)].
A lumped parameter model approximation resting on the assumption of the uniform temperature $T(t)$ brings the Newton law of cooling:

$$\frac{dT(t)}{dt} = \beta\left(T(t) - T_{okoline}\right) \tag{8}$$

where $\beta$ [$\mathrm{h^{-1}}$] is the reciprocal value of the time constant:

$$\beta = \frac{1}{\tau} = \frac{\alpha}{C_p} \tag{9}$$

Analytical solution of differential **eq. (8)** is:

$$T(t) = T_{surrounding} + (T_0 - T_{surrounding})\,e^{-\beta(t-t_0)} \tag{10}$$

where $T_0$ is the temperature of the system in time $t = t_0$ (start of the cooling), and $T_{\mathrm{surrounding}}$ is the temperature of the surrounding to which the system is relaxing.

## 3. EXPERIMENTAL

### 3.1 Differential calorimeter

The differential calorimeter consists of two cells: the sample cell and the reference cell. The two cells are thermally isolated by silicon rubber (or polyester resin) and connected by 30 thermocouples, **Fig 4**. The thermocouples are K-type (NiCr-AlCr) with a wire thicknes of 0.2 mm. The thermocouples are connected to form a thermopile (**Fig. 2**), whose voltage is proportional to the heat flux, is stored every 10 seconds by a data logger PICO Logger TC-08 (Pico Technology Ltd., UK: 20 bits, 8 channels, voltage resolution 1μV) connected to a personal computer with *PicoLog for Windows* software. The last thermocouple cold junction of the thermopile ended on the calorimeter cells from which the thermopile is connected to the input connectors of the *PICO Logger* by cooper wires with cooper connectors. The temperature change of the sample cell can be calculated by:

$$\Delta T = \Delta U / g \tag{11}$$

where $\Delta U$ is the voltage difference (referenced to the baseline) and $g$ is the voltage to temperature conversion constant for the thermopile. The heat evolution in the calorimetric cell is obtained according to **eq. (4)**.

Two materials were used to mold the calorimeter cells (with wall thickness of 19 mm): Köraform K31 silicon rubber (thermal conductivity $\lambda$ = 0,22 W/mK, **Fig. 3**) or a polyester resin in styrene (thermal conductivity $\lambda$ = 0,17 W/Mk, **Fig. 4**)). The calorimeter is then immersed in thermostated water bath. The glass ampoule (**Fig. 3 and 4**) is quantitatively filled with a cement sample (10g of cement). The glass ampoule which serves as a sample holder is put into the calorimetric cell ensuring a good thermal contact between the glass ampule and the calorimetric cell that are made from a thin layer of aluminum. Silicon rubber was shown to be a better choice of the molding (insulating) material, because of its low shrinkage (0.5 %) and very high elasticity.

To assure good wetting of the cement a hole through the cement sample in a sample holder was created by a glass stick (2 mm thick) and relatively high H/CAC ratios were used. The cement and an appropriate amount of water was left to reach thermal equilibrium (overnight) in an ultra thermostat before the thermostated water was injected (by a syringe) into the cement sample holder to start the hydration. The syringe filled with water was also in thermal equilibrium with the thermostated bath.

### 3.2 Calibration

The calibration constants (parameters) of the calorimeter were determined by applying a known voltage to a known electrical resistance (thin constantan wire) embedded in a block of hardened cement paste. The amount of the Joule heat (in J) that is introduced in the calorimeter is given by:

$$Q = U\,I\,t = I^2\,R\,t = \frac{U^2}{R}\,t \tag{12}$$

where $I$ – electrical current [A], $R$ – electrical resistance [Ω], $t$ – time of current flow [s].

**Heat loss constant**

In a steady state condition the heating power (W) in the calorimeter equals the heat loss to the surrounding (first part of the curve in Fig 2), therefore:

$$\alpha = \frac{U^2}{R\,\Delta T} \tag{13}$$

The applied voltage was 2 - 4 V, and the electrical resistance of the embedded thin constantan wire was 22 Ω. The voltage was applied until the steady state was achieved.

**Cooling constant**

The cooling constant of the calorimeter was obtained from the temperature response after switching off the Joule heat element in the calorimeter.

**Voltage to temperature conversion constant**

The voltage to temperature conversion constant for the thermopile of the differential calorimeter was determined by means of the two temperature sensors Pt-100 connected to the PICO Logger Pt-104 (Pico Technology Ltd). The reference cell was filled with the water and was left to reach the temperature of the surrounding water bath overnight with the Pt-100 sensor inserted into the calorimetric reference cells. After stabilization the sample cell was filled with the warm water and the second Pt-100 sensor placed in. During the slow cooling of the calorimeter the temperature difference was recorded with the two Pt-100 sensors simultaneously with the corresponding voltage output of the calorimeter.

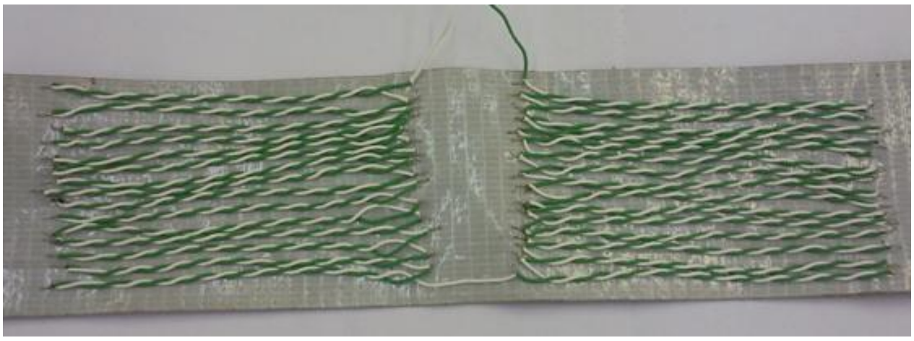


**Fig 2.** The thermopile assemblage for the incorporation into the laboratory made differential calorimeter.

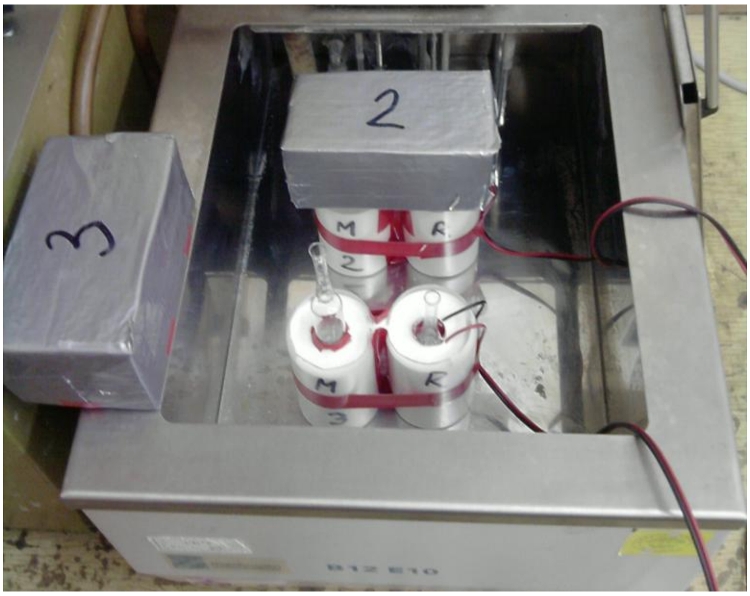


**Fig 3.** The two developed differential calorimeters molded with silicone rubber.

**Fig 4.** The developed differential calorimeter molded with polyester resin.

### 3.3 Validation

The developed calorimeters were further validated by applying a known heat by means of warm water. Firstly, the measuring cell ampule was filled with 2 g of water to mimic the same heat capacity as 10 g of cement powder. The ampule was inserted in the measuring cell of the calorimeter and left to reach thermal equilibrium in the thermostated bath ($T$ = 20 °C). The measurement started with the injection of 4 g of the warm water ($T$ ~ 35 °C) by means of a syringe. The exact temperature of warm water is measured with high precision Pt-100 sensors. The syringe with the warm water was left to reach thermal equilibrium in an ultra thermostat before warm water injection into the measuring cell.

## 4. RESULTS AND DISSCUSION

The developed calorimeters are capable of giving information on the heat evolution from the instant the water was injected in the sample holder. As hydration heat evolves the small temperature difference across a thermopile between the sample cell and reference cell produces a voltage that is logged at regular time intervals (10 s) by a micro voltmeter. The heat loss of the calorimeter was designed (with an appropriate thickness of the insolating molding material – silicone rubber and geometry of the cell) to avoid undesirable temperature rise in the cell, while ensuring sufficient quantity of a sample. 10 g of cement sample was used in this study.

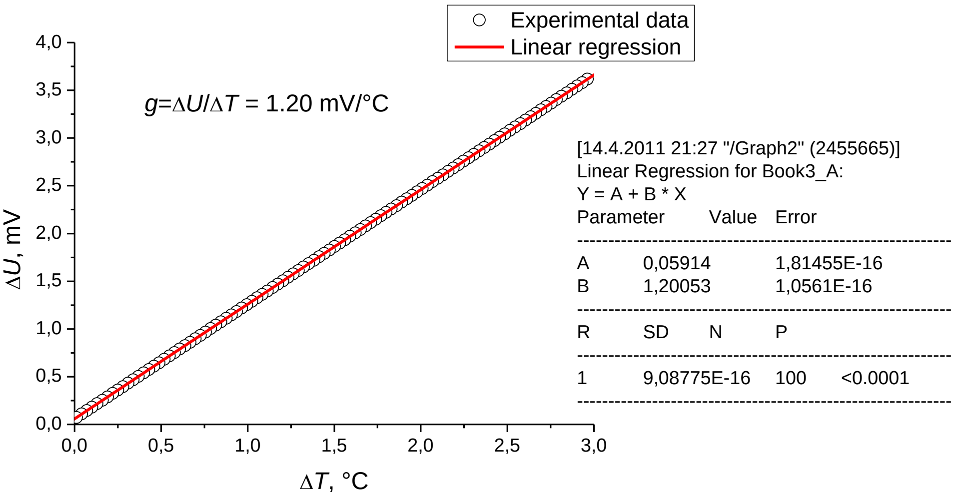
After the calorimeters were designed and developed (**Figs 2-4**), the next step was to calibrate them. The calibrated calorimeters were further validated by inputting a known heat by means of the warm water. Lastly, the heat evolution of the hydration of CAC (Istra 40, Istra Cement, CALUCEM) was investigated with a water to cement mass ratio of $w/c$ = 0.4 (10g of CAC and 4 g of deionised water).

### 4.1 Calorimeter parameters (calibration)

The following calorimeter parameters were estimated:
- the voltage to temperature conversion constant of the thermopile, $g$ (µV/°C),
- the heat loss constant ($\alpha$, J/(°C h)),
- the cooling constant ($\beta$, $h^{-1}$), and
- the effective heat capacity ($C_p$, J/$^o$C).

### 4.1.1 Voltage to temperature conversion

The calibration of the thermopile is described in section **3.2**. During the slow cooling of the calorimeter the temperature difference, simultaneously with the corresponding voltage output of the calorimeter, were both recorded. The results are then plotted as the thermopile voltage versus the temperature difference in the calorimetric cells. **Fig 5** shows an example set of results for this calibration. An excellent linear correlation is obtained (for a temperature range of 3K) with a correlation coefficient $R$ = 1. By linear regression the voltage to temperature conversion constant, $g$ (mV/°C) was estimated, **Fig 5**. The results of the estimated parameters for the four developed differential calorimeters are presented in **Table 1**.



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[14.4.2011 21:27 "/Graph2" (2455665)]
Linear Regression for Book3_A:
Y = A + B * X
Parameter       Value    Error
------------------------------------------------------------
A        0,05914           1,81455E-16
B        1,20053           1,0561E-16
------------------------------------------------------------
R        SD         N          P
------------------------------------------------------------
1        9,08775E-16    100      <0.0001
------------------------------------------------------------
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**Fig 5.** Calibration of the thermopile voltage to temperature conversion constant.

### 4.1.2 Heat loss constant

In a steady state condition the heating power in the calorimeter equals the heat loss to the surrounding and the heat loss constant was calculated by applying **eq. (13)**. Examples of the experimental results obtained by calibration (as described in 3.2) are shown in **Figs 6 and 7**. It can be seen that for the calorimeters in this study, the temperature dependence of the parameters can be neglected (for a temperature difference of up to ~ 3K).

The dependence of the heat loss constant on the temperature difference $\alpha = f(\Delta T)$ can be determined from an experimental series with varying heating power that yields a series of different stabilized temperature differences (**Fig 6**). For the calorimeters in this study, the temperature dependence of the parameters was neglected. The results of the estimated parameters for the four developed differential calorimeters are presented in **Table 1**.

### 4.1.3 Cooling constant

The cooling constant of the calorimeter was obtained from the temperature response after switching off the electrical current being passed through the electrical resistance embedded in the hardened cement paste sample in the calorimeter cell. The transient temperature response of the cooling can be described by the Newton law of cooling (**eq. (8 and 10)**). A cooling constant ($\beta$) was estimated by nonlinear regression (‘fitting’) of the analytical solution of differential **eq. (8 and 10)** to the transient experimental results of the calorimeter cooling, as shown in **Fig 7**. All other parameters in **eq. (10**) (the overall temperature change ($T_0 - T_{\text{surrounding}}$), the time of beginning of the cooling ($t_0$), and the end temperature of relaxation ($T_{\text{surrounding}}$)) were kept constant, as they have real physical meanings with precise values. In that way the interaction occurring between the parameters was excluded in order to avoid the falsely over-fit of the experimental curve. The results of the estimated parameters for the four developed differential calorimeters are presented in **Table 1**.

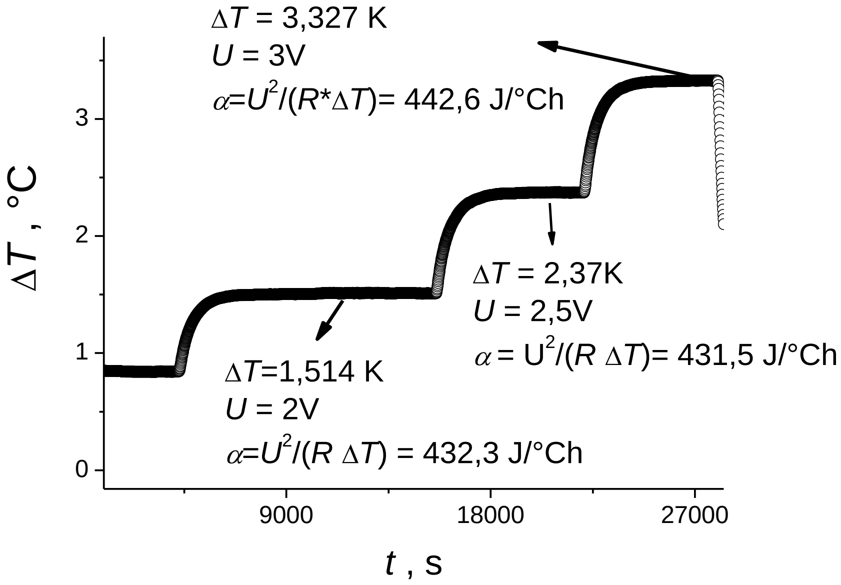

**Fig 6.** Calibration of the calorimeter with varying heating power that yields a series of different stabilized temperature difference. In a steady state conditions a heat loss constant ($\alpha$ W/K) was obtained (eq. 13).

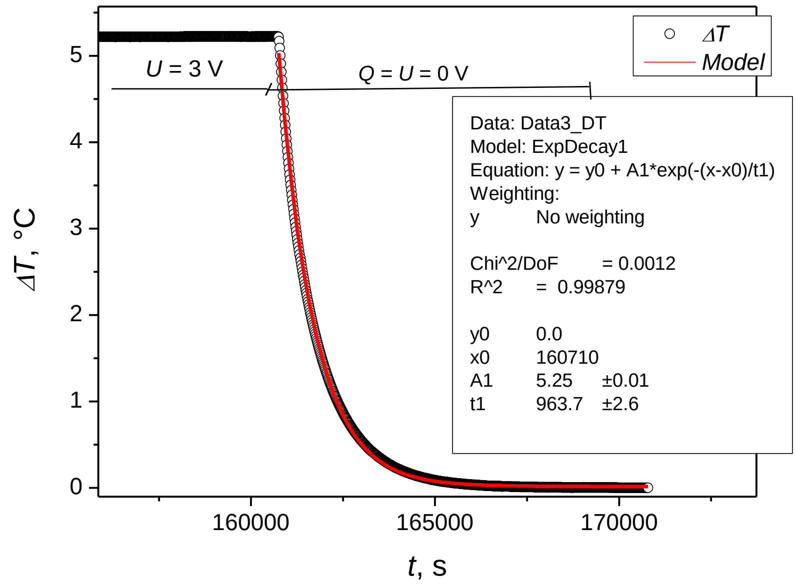

**Fig 7.** Nonlinear regression for estimating the cooling parameter of the calorimeter $\beta$, h$^{-1}$.

### 4.1.4 Effective heat capacity

Effective heat capacity of the calorimeter was obtained from the **eq. (9)** by using the experimentally determined values of the heat loss constant, $\alpha$ (determined in steady state condition, **eq. (13)**) and the cooling constant, $\beta$ (determined from transient cooling of the calorimeter, **Fig 2**). The results of the estimated parameters for the four developed differential calorimeters are presented in **Table 1**.

**Table 1.** Results of the estimated parameters of the four developed differential calorimeters.

| *Calorimeter* | Polyester 0 | Polyester 1 | Silicone 2 | Silicone 3 |
|---|---|---|---|---|
| $Bi^*$ | 0.033 | 0.033 | 0.042 | 0.042 |
| $\beta$, h$^{-1}$ | 3,74 | 3,40 | 5.96 | 5.33 |
| $g$, µV/°C | 1210 | 1205 | 1195 | 1202 |
| $\alpha$, J/°Ch | 277.9 | 290.0 | 430.0 | 385.0 |
| $C_p$, J/°C | 75.05 | 74.37 | 72.15 | 72.23 |

*for calculation details see Appendix

### 4.1.5 Biot number

Values of the Biot number for the developed calorimeters are calculated according to the **eqs. (5 and 6)** and the characteristics of the calorimeters (see Appendix and experimental part). From the calculated values, which are given in **Table 1**, it can be concluded that the Bi << 0.1. This indicates that the heat conduction inside the system is much faster than the heat convection away from its surface, and temperature gradients are negligible inside of it. This implies a negligible error for assuming a lumped-parameter model of transient heat transfer.

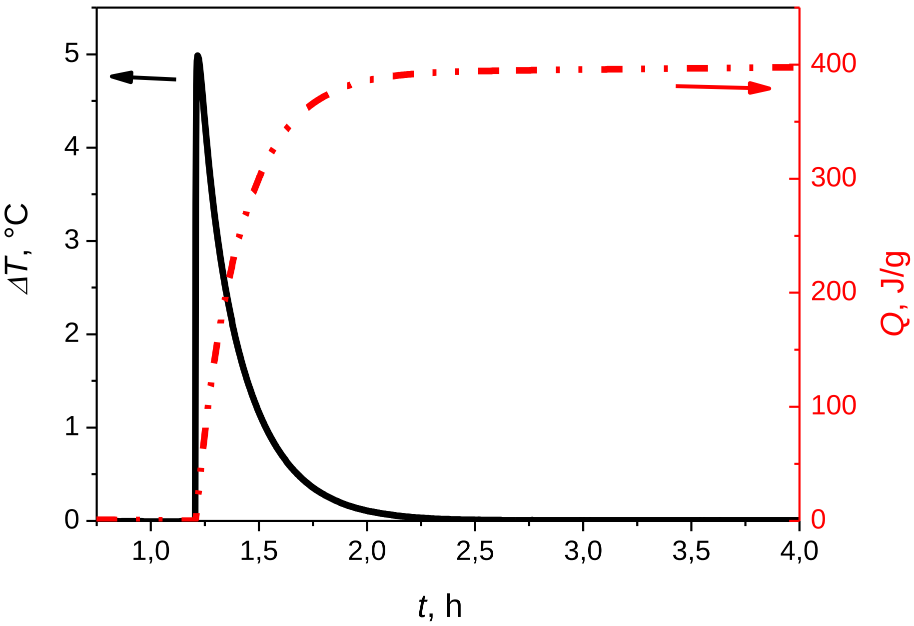

**Fig 8.** A validation of the calorimeters by injection of warm water.

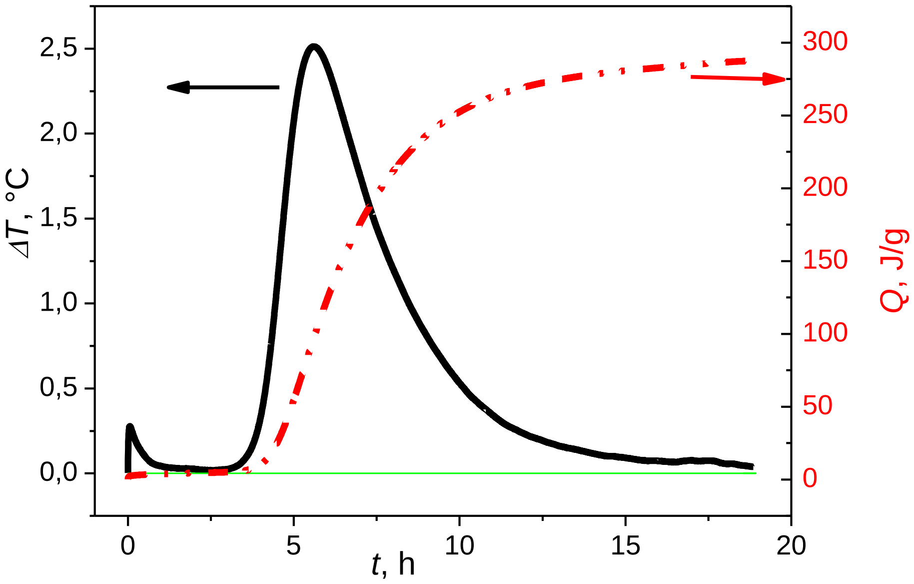

**Fig 9.** The heat of hydration evolution of CAC determined from the beginning of mixing with water.

### 4.2 Validation

After calibration, by means of electrical current (i.e. dissipation of the Joule heat), the calorimeters were further validated by another independent method, by means of an enthalpy change test. This was done by introducing the warm water into the calorimeter measuring cell, as described in **3.2**. The employment of different (non-electrical) method for the validation is needed in order to exclude possible systematic errors in the electrical calibration (such as the dissipation of energy through the thin electrical leads which were nevertheless kept at minimum). An example of the calorimeter validation experiment by the injection of warm water is shown in **Fig 8**. The temperature response and the corresponding calculated heat evolved is shown.

Very good agreement with an accuracy of within 2 % was found between the results of the experimental validation and theoretical data. The theoretical values were calculated as the enthalpy change for cooling down the 4 g of water by the exactly defined temperature difference (**eq. (2)**). This result validates the accuracy of the calculation method as well as the measurement apparatus.

The heat evolution of the hydration of CAC (type Istra 40) was investigated with a water to cement mass ratio of $w/c = 0.4$ (10g of CAC and 4 g of deionised water). The results of the temperature response and the corresponding calculated heat of hydration evolved is shown in **Fig 9**.

A repeatability analysis was also conducted on both the cement (CAC) samples (**Fig 9**) and warm water validation analysis (**Fig 8**) by repeating each of the sample measurements 10 times. A statistical analysis of the evolved heat (after 19h and 4h, for the cement and water sample, respectively) was performed. It was concluded that the results of the calorimeter evaluation yielded an accuracy of 2 % and a precision of 2 % (for 95% confidence).

The influence of the possible temperature change during the injection of the stabilized water due to manipulation with the syringe was investigated. This was examined by injection of the 4g of thermostated water into the measuring cell ampule filed with 2g of water (with the nominal temperature difference equal to zero K).

It was found that the measured maximal temperature difference after the injection of the water was as low as 0.010 K, indicating the suitability of the experimental measuring method with negligible effect of the thermal disturbance during manipulation with the syringe.

## 5. CONCLUSION

The developed calorimeters are capable of giving information on heat evolution of cement pastes from the instant the water is injected in sample holder. The calculated Biot numbers indicated a negligible error for assuming a lumped-parameter model of the investigated transient heat transfer.

The calorimeter was calibrated electrically by means of dissipated Joule’s heat and further validated by inputting a known heat by means of warm water. Very good agreement with an accuracy of within 2 % was found between the results of the experimental validation and theoretical data. A repeatability analysis of the measurements showed a precision of 2 % (for a 95 % confidence level).

## 6. ACKNOWLEDGEMENT

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## 8. APPENDIX

### Calculation of the Biot number

$\lambda$(cement paste) = 1 W/(mK)
$\lambda$(silicon rubber) = 0,22 W/(mK)
$\lambda$(polyester resin) = 0,17 W/(mK)
thicknes of the isolation: $d$ = 19 mm
Dimensions of the cement paste sample in the glass ampule sample holder: $2r$ = 17,75 mm; $h$ = 40 mm