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Operational issues in isothermal calorimetry

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ABSTRACT

Isothermal (heat conduction) calorimetry is a general technique to study processes through the thermal power they produce. This paper deals with operational issues concerning isothermal calorimeters. In this paper it is shown that steady-state and pulse calibrations give the same result; that the use of mobile heaters (placed in the reaction ampoule) give more accurate results than fixed heaters (placed in the ampoule holder); and that at least the tested calorimeter had calibration coefficients that were independent of the thermal power level. It is shown that well balanced references are necessary to get low noise and low drifts. It is discussed how baselines should be measured. The influence of temperature and sample size is also discussed and it is shown that large cement paste samples with high thermal powers will show an accelerated reaction. Finally, the thermal dynamics of a heat conduction calorimeter is discussed.

1. Introduction

Isothermal (heat conduction) calorimetry is a laboratory method to measure thermal power (heat production rate, heat rate) as a function of time on small samples at constant temperature. It has found uses in many areas of science and technology, for example in pharmaceutics [1], microbiology [2] and cement science [3]. In an isothermal (heat conduction) calorimeter the sample (typically of 1-10 g) is in an ampoule that is inserted into an ampoule holder in contact with a heat flow sensor on a thermostated heat sink. As heat – endothermal or exothermal – is produced in the sample, the sample temperature will change, and this gives rise to a heat flow that is measured by the heat flow sensor as a voltage. The heat flow sensor work by the Seebeck principle in which a temperature difference over the sensor produces a voltage.

All heat conduction calorimeters are twin calorimeters, i.e., there is also a reference system in which an inert sample is placed, and it is the difference between the output of the sample and the reference sensors that is recorded. This output can be converted to thermal power as a function of time and integrated to get heat. The thermal power is related to the rate of the studied process, while the produced heat is a function of the extent of the reaction [4,5].

There are in practice three properties of a calorimeter that should be considered during evaluations of calorimetric results: the calibration coefficient ε (W V^{-1}), the baseline U_0 (V) and the time constant τ (s). The use of these can be explained with reference to the following two equations for the calculation of thermal power P (W) from the voltage signal U (V):

$$P = \varepsilon(U - U_0) \quad (1)$$

$$P_c = P + \tau\frac{dP}{dt} \quad (2)$$

Eq. (1) is the standard equation to use to calculate thermal power from voltage; Eq. (2) is the Tian equation (named after a French scientist who developed isothermal calorimeters in the 1920s) to correct rapid processes for the time lag of an instrument (P_c is the corrected thermal power). Throughout this paper the term “thermal power” will be used when referring to the rate of heat production in the sample. It is also common to see the terms “heat flow” and “heat flow rate”, but these terms are best reserved for discussions on heat flows within calorimeters.

Note that not all the above mentioned three properties are needed for all types of measurements. For the measurement of the heat produced during 7 days of cement paste hydration both the calibration coefficient and the baseline are important; for the study of the rapid initial reactions that take place when cement is mixed with water the Tian correction – and thus also the time constant – is needed in order to separate different events; and for studies of the retardation of the cement hydrations by an admixture (additive), none of these three parameters are actually needed as it is only, e.g., the time of the peak of the main hydration that is of interest.

Although isothermal calorimeters are used in many cement laboratories, there is an uncertainty on how accurate these instruments are. This has delayed the standardization of isothermal calorimetry in the cement field, where many companies make extensive use of isothermal calorimetry within their organizations, while still relying on traditional and standardized calorimetric techniques in communicating

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with their customers. This paper reports experimental studies of operational issues for isothermal (heat conduction) calorimeters. The aim of the work was to provide guidance for users of these instruments on for example how to calibrate. Note that – as heat is a ubiquitous phenomenon - there are many sources of error in calorimetric measurements not covered here; see for example reference [6].

The experimental work has been made on TAM Air calorimeters (Thermometric AB, Järfälla, Sweden; now manufactured by TA Instruments, New Castle DE, USA), which today appears to be the most common isothermal calorimeter in the cement field. It is similar in basic construction to most other isothermal calorimeters in that it is a twin heat conduction instrument, but it has eight twin calorimeters with partially shared heat sinks in one thermostat [3]. The experimental examples presented are from the author's laboratory except where noted.

Although the general design of most heat conduction calorimeters is similar, caution should be exercised when applying the present results on other types of isothermal calorimeters which have other thermostats, heat flow sensors, amplifiers etc. Note that also even seemingly identical instruments of the same brand may behave differently, for example concerning baseline stability, as they are placed in different environments or have been differently treated.

2. The reference

This paper starts with a discussion on reference samples, as a suitable reference is crucial for successful isothermal calorimetry. The reference is a second ‘sample’ that should not produce any heat, but otherwise have similar thermal properties as the sample. In a calorimeter, the sample and the reference occupy two measurement positions and the heat flow sensors in these two measurement positions are connected so that the difference between the two is measured. If a calorimeter is thermally balanced this will result in a measurement with low noise and low drift. This is further discussed below in connection to Fig. 9.

The reference should be chosen so that it has the same thermal properties as the sample, except that it shall not produce any heat. The most important of these properties is the heat capacity of the reference, which should be the same as that of the sample. Typical materials used are quartz sand and water. Never use more complex materials like hydrated cement mortar as reference materials, as such samples can produce heat, for example from water movements inside the sample induced by temperature changes.

One way to balance a calorimeter is to calculate the heat capacity of the sample and then the mass of a reference material that has the same heat capacity. For composite materials one has to add the heat capacities of the different component. For example, for a cement mortar sample that is made from cement (C), water (W) and sand (S) the following equation is used to calculate the mass of the reference (R):

$$m_R = \frac{c_C m_C + c_W m_W + c_S m_S}{c_R} \tag{3}$$

Here, m (g) is the mass and c (J g^{-1} K^{-1}) is the specific heat capacity Note that one does not have to take the ampoule or the ampoule holder into account here as long as they are the same on the sample and reference sides. Some values of specific heat capacities are found in Table 1.

A problem with the above simple method is that the heat capacity of a cement paste will decrease during hydration as the water is bound in the hydration products. These changes may be quite significant for cement paste samples. For example does a $w/c = 0.4$ paste have a specific heat capacity at 1.73 J g^{-1} K^{-1} when mixed, but only 1.35 J g^{-1} K^{-1} at a degree of hydration of 0.7 [7]. However, compared to the total heat capacity of the ampoule holder and the ampoule (typically 30 J/K for a TAM Air) this heat capacity change is quite small for normal samples.

Table 1
Specific heat capacities of some materials. Value for cement is taken from reference [15].

Material	Specific heat capacity / J g^{-1} K^{-1}
Sand (quartz), glass	0.8
Cement	0.75
Water	4.18
Aluminum	0.8

3. Calibration coefficients

The calibration coefficient is the proportionality constant between the calorimeter output (a voltage) and the thermal power. The most common method of calibrating heat conduction calorimeters is electrical calibration. A current I (A) is passed through a calibration heater (resistor) and the response is measured. The thermal power P (W) produced in a calibration heater with resistance R (Ω) is obtained from:

$$P = I^2 R \tag{4}$$

Preferably one should measure the current in the calibration circuit as the current is the same throughout the circuit. Measurements of the voltage over the calibration heater will include the voltage drops over the leads and may produce erroneous results. If one does not have a current meter one can measure the voltage over an external resistor and calculate the current.

On the following a number of studies on calibration issues are discussed. Note that many TAM Air calorimeters do not measure true volts from the heat flow sensors. The values of the calibration coefficients given in this paper do therefore not give any information on how sensitive the heat flow sensors are, and should only be seen as proportionality constants between the measured signal and the thermal power.

3.1. Steady-state vs. pulse calibration

One can make two basic types of electrical calibrations. Either one will keep the current on until a steady-state is reached or one can make shorter thermal pulses. These two types of calibrations are illustrated in Fig. 1. The calibration coefficient ε is calculated by one of these equations:

$$\text{Steady-state calibration}: \quad \varepsilon = \frac{P}{U} \tag{5}$$

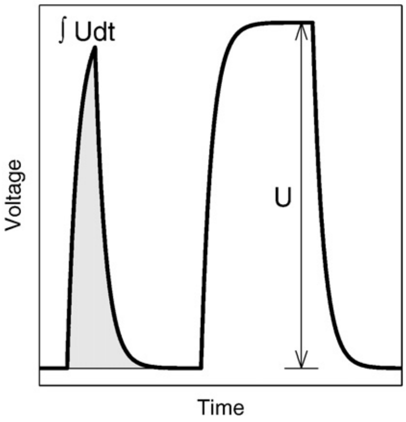


Fig. 1. The two types of electrical calibration: to the left a pulse calibration in which one integrates the result from a calibration pulse caused by a certain calibration heat; to the right a steady-state calibration in which one waits for steady-state to evaluate the voltage change caused by the calibration thermal power.

$$\text{Pulse calibration}: \ \varepsilon = \frac{P \cdot \Delta t}{\int U\, dt} \tag{6}$$

Here, P (W) is the thermal power produced in the heater, U (V) is the output voltage, and Δt (s) is the duration of the pulse.

Steady-state and pulse calibrations were made simultaneously in the eight calorimeters of a TAM Air instrument. The steady-state calibrations were made by keeping the calibration thermal power on until a steady-state was reached, while the pulse calibrations were made with repeated 100 or 500 s pulses with 5000 s between the pulses. In both cases, a mean of the baselines determined before and after each pulse were used. The results show that these two types of calibrations are equivalent. The largest difference between calibration coefficients from these two calibration methods for any one of the calorimeters was 0.12%. However, the eight calorimeters in the instrument had slightly different values of their calibration coefficients (the standard deviation was about 2% of the mean).

3.2. Fixed vs. mobile heaters

Calibration heaters can either be mounted in the ampoule holder of a calorimeter (fixed heaters) or be placed in an ampoule (mobile heaters), i.e., inserted into the calorimeter for a calibration. Fixed heaters are more convenient and are used in calorimeters that have automatic calibration or calorimeters that have a built-in calibration voltage source. However, with a mobile heater the calibration heat is in most cases produced closer to where the heat in a measurement is produced. Published studies [8–11] all indicate that heaters placed in the reaction zone are more accurate that heaters placed in other positions, for example in the ampoule holders.

In an isothermal heat conduction calorimeter, not all the heat produced in the sample passes through the heat flow sensor. There will always be other heat flow paths, for example heat conduction through the air surrounding the ampoule holder. It is therefore important to arrange so that the same fraction of heat flows through the sensor during calibration as during a measurement.

In this study, calibrations with mobile and fixed heaters were made in a TAM Air. All eight calorimeters were calibrated simultaneously with heaters connected in series. The small fixed heaters (100.0 ± 0.1 Ω) are placed in a cavity in the bottom of the ampoule holders. Mobile heaters were made from precision resistors (100.0 ± 0.1 Ω) placed in glass ampoules. To increase the heat transfer rate these resistors was placed in about 1 mL of paraffin oil. The fixed heaters showed an average of 2.6% (standard deviation ± 0.3%) lower calibration coefficients than the mobile heaters. This is natural as the fixed heaters are closer to the heat flow sensors; there are slightly higher heat losses with a mobile heater as this is placed higher up in the calorimeter. As the optimal calibration is one in which the heat losses are the same as during a measurement, this makes mobile heaters a better choice as they have a comparable heat flow pattern as a reacting sample.

Mobile heaters have two potential problems: heat is generated not only in the heater, but also in the connecting wires, and there are heat losses through the wires. The first of these problems is shared by fixed heaters, but the second problem is unique to mobile heaters because their wires are normally not in the calorimeter during a measurement. The effect of these two potential error sources depends on what wires that are used. In the present study 100.0 Ω heaters and rather thin wires were used (7 x 0.08 mm copper wires with an electrical resistance of 0.55 Ω/m in a 0.74 mm outer diam. Teflon coating). The wires to the calibration heater were in contact with the heat sink of the calorimeter and then went about 5 cm through air before entering through the lid of the ampoule and then approximately a further 5 cm down to the heater. An approximate thermal power produced in the wires and measured in the calorimeter can be calculated by assuming that all the heat that is produced in the wires inside the ampoule is measured, but only half the heat produced in the wires between the ampoule and the heat sink. The total length of heat producing wire relevant for this study is then 15 cm which has a resistance of about 0.08 Ω. This gives an additional 0.08% heat produced in the wires for a 100 Ω heater. The error from this is about -0.1% (negative as the calibration coefficient will be slightly too low if 100.0 Ω is used instead of 100.08 Ω). This error is thus rather small, and can be made even smaller by using a calibration heater with higher resistance.

The error from heat conduction through the wires to the calibration heater was investigated by a series of experiment in which different numbers (2 to 9) of identical electrical wires were connected between the ampoule and the heat sink. Only two were used for the electrical calibration, the rest only increased the heat losses through the wires. A series of pulse calibrations were made on all channels in a TAM Air calorimeter so that all channels were calibrated with all different numbers of wires. The calculated calibration coefficients are shown in Fig. 2 as a function of the number of wires used. It is clear that the heat losses increase as the number of wires increase. The relatively large spread in the results is probably caused by variations in how the wires made contact with the heat sink. The error from heat conduction through the wires is the difference between the value at two wires and the extrapolated value at zero number of wires in Fig. 2. This error is about + 0.25% (the heat loss gives a lowered output from the heat flow sensors, which gives an increased calibration coefficient).

The use of mobile heaters can thus give rise to two types of errors that, however, partly compensate each other. In the present case the calculated overall error from the use of mobile heaters was about + 0.15%.

3.3. Heat capacity calibrations

Bunyan [8] has described an absolute calibration method for isothermal calorimeters in which the calibration coefficient is calculated from the peak that is the result of a small change in the temperature of the calorimeter thermostat with a known mass of a material with known specific heat capacity as sample. The temperature step has to be made twice – with and without the standard material – as a calorimeter is not perfectly balanced with empty ampoules.

Heat capacity calibrations were made on a TAM Air instrument according to Bunyan's method, but as the TAM Air thermostat is slow in changing the temperature of the calorimeters, only temperature increases were made and 16 extra heaters giving a total of 16 W were placed in the heat sink. Temperature steps of 5 K (from 20 to 25 °C)

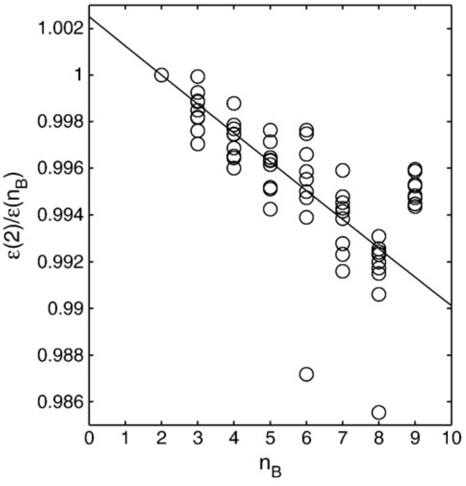


Fig. 2. Results of pulse calibrations with mobile heaters in eight calorimeters using different numbers of electrical wires (n_B) between the ampoule and the heat sink. The calibration coefficients are given relative to those coefficients (for each calorimeter) determined with only two wires.

could then be made in less than 10 h. About 10 g of sapphire (aluminum oxide, heat capacity reference material 720 from former National Bureau of Standards (now: NIST), USA) was used as heat capacity reference material. The temperature of the calorimeter was measured by a calibrated resistance thermometer (ASL F250, Automatic Systems Laboratories, Croydon, UK) using a Pt100 sensor.

The heat capacity calibrations gave calibration coefficients that were closer to the coefficients for mobile heaters, than to the coefficients for fixed heaters. Taking the calibration coefficients from heat capacity calibrations as reference values, the mean relative errors for the mobile and fixed heaters for a total of nine measurements were -0.4 and -2.4%, respectively (in both cases the standard deviations were 0.8%). It thus seems that mobile heaters are preferable to fixed heaters placed in the ampoule holder. These results agree with Bunyan's [8], who found that mobile heaters and absolute heat capacity calibration were “broadly in agreement” for his calorimeter, but that the fixed heaters gave approx. 2% too high calibration coefficients.

3.4. Calibration at different thermal powers

The physical principles of a heat conduction calorimeter (heat conduction, radiation, and the Seebeck effect, all at very low temperature differences) are such that one would expect the voltage from the heat flow sensor to be proportional to the thermal power at steady-state. The calibration coefficient should then be independent of the thermal power level. To investigate this, calibrations were made at nine different thermal power levels from 0.090 to 24 mW. The calibrations were made with the pulse method and each result is the mean of at least two pulses. The result in Fig. 3 shows that the calibration coefficients determined at between 3 and 24 mW are the same, but that at lower thermal powers the coefficients deviates significantly. If we believe that the physics of the heat conduction calorimeter itself is linear, there are two possible reasons for a non-constant calibration coefficient: higher calibration uncertainties at lower thermal powers or non-linear electronics.

An error analysis of an electrical calibration can be used to find the uncertainties associated with an electrical calibration. For simplicity, this calculation is made for a steady-state calibration, but the result would be similar for a pulse calibration. In practice the calibration coefficient ε is calculated as (cf. Eqs. (3) and (4)):

$$\varepsilon = \frac{(U_{ex}/R_{ex})^2 R}{U - U_0} \tag{7}$$

Here, U_{ex} (V) is the voltage measured over the external resistance R_{ex} (Ω) to calculate the current, R (Ω) is the heater resistance, U (V) is the measured voltage when the heat production is on, and U_0 (V) is the measured baseline value. Both resistances are assumed to be precision resistances of 100.0 ± 0.1 Ω. Each of these parameters is associated with an uncertainty given in Table 2. Using these uncertainties Monte Carlo simulations (10000 calculations of Eq. (7) made at thermal powers between 0.1 and 100 mW) were made and the result is given in Fig. 3. It is seen that the error starts to increase when calibrations are made at thermal powers lower than about 2 mW. Above that value the uncertainty is determined by uncertainties in factors that are not dependent on the thermal power level, e.g., the heater resistance. These results compare well with the experimental results.

Although a heat conduction calorimeter itself will behave linearly, it is possible that the electronic equipment (amplifiers and A/D-converters) are non-linear. The calibrations discussed above were made with an ADC-24 amplifier and A/D-converter (Pico Technology, St Neots, UK), which is the same electronic equipment that is used in recent TAM Air calorimeters. The used ADC-24 was checked against a calibrated multimeter (34401A, Agilent Technologies, Santa Clara CA, USA). At the higher end of the used measurement range (4 mV corresponding to about 25 mW) the maximal deviation was about 0.05%, and at lower voltages (down to 0.050 mV) the deviation was never more than 0.001 mV. So the deviating results at low thermal powers shown in Fig. 3 cannot be explained by non-linear electronics, but are instead fully explained by uncertainties in the calibration parameters. Therefore one only needs to calibrate at one – not too low – thermal power level.

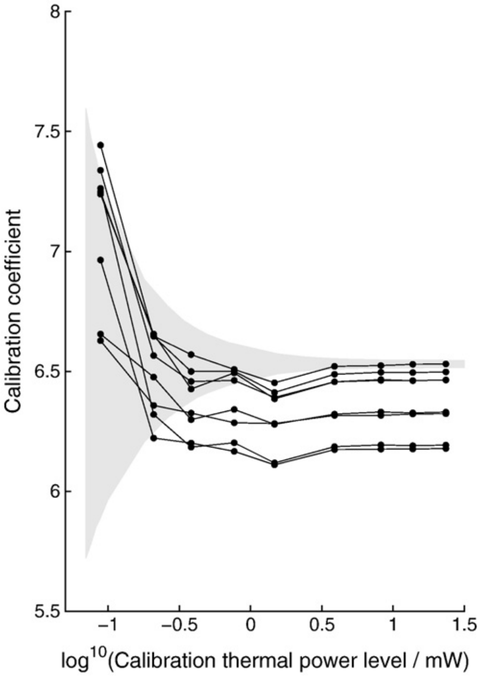


Fig. 3. Results of 500 s pulse calibrations in eight calorimeters as a function of the thermal power generated in the heaters. The gray area shows the result of a Monte Carlo simulation of electrical calibrations made at different thermal powers using the uncertainty data in Table 2. In the absence of errors, the simulated calibration coefficient was 6.531, equal to the highest measured coefficient in the figure, and the points within the gray area are within ± one standard deviation of 6.531.

3.5. Calibration at different temperatures

The properties of the heat flow sensor materials are temperature dependent, so the calibration coefficients will change when the temperature is changed. To test this, calibrations were made at several temperatures. The results in Fig. 4 shows the same temperature dependence for all eight calorimeters, and this temperature dependence is similar to what is expected from data on the physical properties of the heat flow sensor materials. The temperature dependence of the calibration coefficients is thus predictable, and this type of results can be used to at least approximately recalculate the calibration coefficients of one calorimeter at one temperature to another temperature.

3.6. Long-term stability

Data were collected from industrial laboratories that had made steady-state calibrations with internal heaters over a period of several years. As is seen in Fig. 5 the calibration coefficients are quite constant. The highest

Table 2
Uncertainties used in Monte Carlo simulation of electrical calibrations.

U_{ex}	Relative standard deviation 0.001
R_{ex}	Standard deviation 0.05 Ω
R	Standard deviation 0.05 Ω
U	Standard deviation 1 μV
U_0	Standard deviation 1 μV

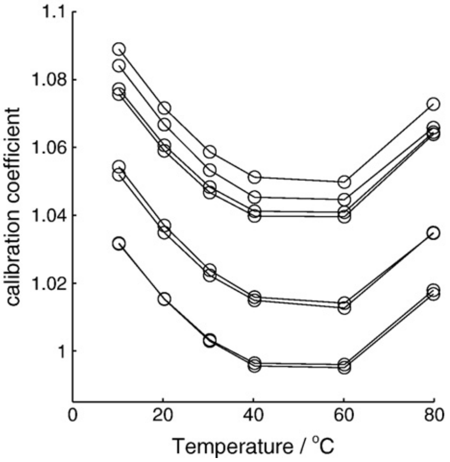


Fig. 4. Calibration coefficients of eight calorimeters measured as a function of temperature.

change seen in any of the studied calorimeters (three TAM Air instruments with 24 calorimeters) during a four year period was 0.7%. The conclusion is that the studied calorimeters were stable instruments.

4. Baselines

The baseline U_0 (Eq. (1)) is the output signal from a calorimeter when there is no heat produced. Baselines should be measured when there is a good balance between the sample and the reference sides, but with no heat production anywhere. Typically, one will charge identical "reference ampoules" (empty or with for example water) on both the sample and reference sides. In the following, a number of issues concerning baselines are discussed. Note that in all cases below the balance between samples and references were good and the calorimeters were not disturbed more than necessary (cf. discussion in section on the calorimeter as a dynamic system).

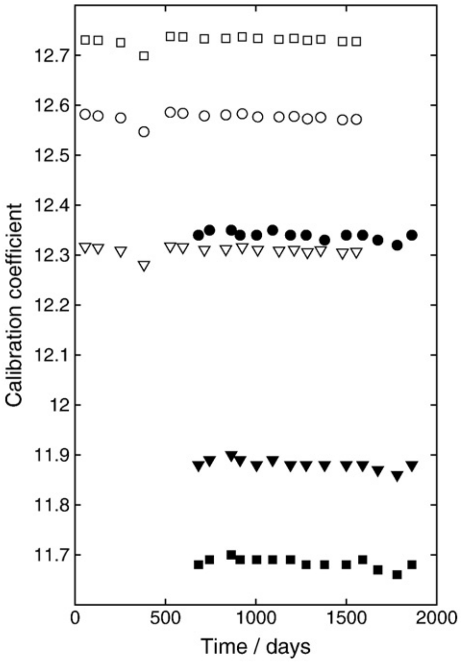


Fig. 5. Calibration coefficients as a function of time. Typical data from two laboratories that made regular calibrations using the same method over several years. The dip in the calibration coefficients for one of the labs (open symbols) was correlated with a measured lower calibration voltage. Data from EMPA, Switzerland, and Heidelberg Technology Center, Germany.

4.1. Material in reference ampoule

Different ampoule types (glass, polyethylene) and different reference materials (water, sand, sand + water) were tested in determining baselines (using identical ampoules and materials on both sides). No systematic differences in baselines were found between the different ampoules or the different materials. Different masses of materials were also tested and also here no visible differences in the baselines were observed. It thus seems that one can chose the type of ampoule, the type of inert reference material, and the mass of that material that one finds most convenient.

4.2. Long-term stability

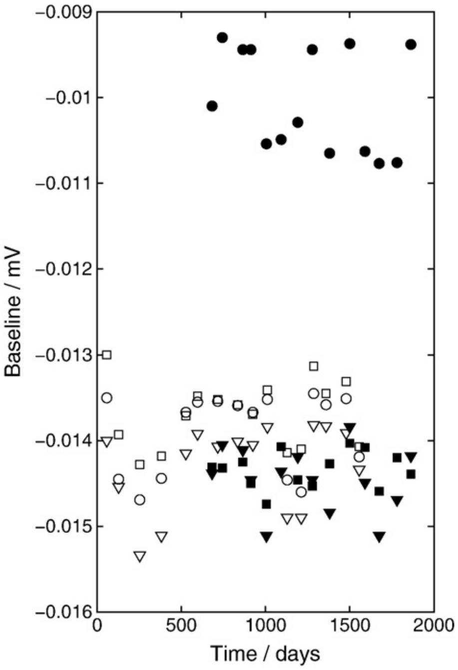
Fig. 6 shows measurements of baselines over several years on a number of calorimeters (their calibration coefficients are shown in Fig. 5). It is seen that the baselines are stable – the changes correspond to less than 5 μW per year.

4.3. Repeated charging

Repeated charging of a "reference ampoule" on the sample side was made while having an identical reference ampoule on the reference side. Identical repeated chargings resulted in a similar baseline values every time. It thus seems that this type of calorimeter does not show variations in baseline values; something that is often seen in more sensitive microcalorimeters [6].

5. Time constants

In the Tian equation (Eq. (2)), the time constant τ describes the thermal inertia of the sample. This time constant can either be measured or calculated. To measure it one needs a decaying signal from the calorimeter when there is no heat production in the sample. If one has an ampoule with an inert material with the same heat capacity as the sample, one can charge this into the calorimeter and calculate the time



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constant from the exponential decay of the signal, for example as the time it takes for the signal to decrease from any value to 36.8% of that value, i.e., exp(-1). It is also possible to thermally disturb a sample during a part of a measurement when the thermal power is constant or low, for example at the end of a long cement hydration measurement. This can be made by turning on the calibration heater for a short time or by quickly lifting and again placing the ampoule in the calorimeter. In either case one will get an exponentially decaying peak from which one can calculate the time constant for the sample one is using (do not use the very first part of a decay curve as the thermal gradients in the calorimeter may not have developed by then).

To calculate the time constant for a calorimeter one can also use the following equation:

$$\tau = \frac{\Sigma C}{k} \qquad (8)$$

Here, ΣC (J K^{-1}) is the heat capacity of everything on the sample side of the heat flow sensor (sample, ampoule, ampoule holder) and k (W K^{-1}) is the apparent thermal conductance of the heat flow sensor (the conductance of the sensor with a correction for that not all heat flows through the heat flow sensors). To use Eq. (8) one needs to know the heat capacity of ampoule holders (15 J K^{-1}) and ampoules (15 J K^{-1}) and the apparent thermal conductance of the heat flow sensor (0.17 W K^{-1}). A manufacturer of calorimeters should be able to give these values (the values above are approximate values for one TAM Air calorimeter).

Note that ΣC in Eq. (8) is a combined property of the sample and the instrument, while k is an instrument property. As the time constant is a function of the sample heat capacity one cannot use the same time constant for different samples (as one can do with calibration coefficients and baselines).

The Tian equation (Eq. (2)) is not needed in the study of slow processes, like the main hydration of cement, but is very useful in the study of, e.g., early hydration and other rapid processes. In most cases the Tian equation with one time constant is enough to correct for the thermal inertia of the calorimeter, but one can also use more complex models; see for example Evju [12] who compared the Tian correction with other more complex models.

6. Temperature

In an isothermal measurement the temperature should be constant, but in practice isothermal heat conduction calorimeters are not perfectly isothermal, but instead "essentially isothermal". This can be defined as "with such low temperature deviations in the sample that the result of a measurement looks the same to a user as if the conditions would have been perfectly isothermal". It is important to arrange a measurement so that this definition is fulfilled. Note that “isothermal” is not an inherent property of a calorimetric instrument as it depends – following the definition above – on the thermal power of the sample and how sensitive to temperature changes that a measurement is.

There are three aspects of the temperature in isothermal heat conduction calorimeters. Firstly, the set temperature of the thermostat should be checked regularly. When delivered, a new calorimeter thermostat will be calibrated and the actual temperature will be within, e.g., ± 0.2 K of the set temperature. However, after a few years of use a thermostat may have changed, so regular calibration/validation of the temperature is essential. Secondly, a heat producing sample will increase the temperature of itself. The approximate temperature change ΔT (K) can be calculated as [13]:

$$\Delta T = \frac{P}{k} \qquad (9)$$

Here, P (W) is the thermal power and k (W K^{-1}) is the same thermal conductance of the heat flow sensor as in Eq. (8). This type of temperature increases can lead to problems for kinetic measurements (cf. section on sample size). Thirdly, if large amounts of heat are produced in the calorimeters (or if the heat-sink is thermally disturbed, for example if the lid is removed) the heat sink temperature will change. The extent to which such a disturbance will show up in the results depends on the sample-reference balance. This is further discussed in the section on the calorimeter as a dynamic system.

7. Sample size

In several tests in the present study, sample size was shown to influence the results of cement hydration measurements. In most cases slightly higher specific thermal powers were measured from larger samples, but the opposite behavior was also seen. An example of the former is shown in Fig. 7. There are several reasons why sample size can influence the result of a calorimetric measurement:

1. The temperature will be slightly higher in a larger sample (cf. discussion on temperature above). In the two samples in Fig. 7 the maximal thermal powers are 4 mW for the smaller sample and 54 mW for the larger sample. The resulting maximal temperature rises will be approximately 0.02 and 0.3 K, respectively (Eq. (9)). As the activation energy of the main cement hydration peak is approx. 35 kJ mol^{-1} [14] the heat production rate will be approx. 1.4% faster when the temperature increases 0.3 K (the ratio of the peak thermal powers in Fig. 7 is 1.8%).
2. Large samples may possibly lose slightly more heat than small samples (cf. discussion on fixed vs. mobile heaters). This would tend to give lower specific values for larger samples.
3. If one makes a baseline error for all samples, for example by not correcting for the baseline at all, this will influence smaller samples more. This error can be either way, depending on which side one errs.

To reduce these errors one should use samples with low thermal powers, small samples and make baseline corrections. With the TAM Air it is for example in most cases sufficient with 3 g of cement paste or 10 g of mortar. The main problem with the measurement shown in Fig. 7 is that the larger sample is so large so that that measurement cannot be considered to be isothermal.

8. The calorimeter as a dynamic system

In many cases calorimetric measurements are easy to conduct, but one can be fooled by this apparent simplicity. A calorimeter often needs to be seen as a dynamic system, where one can get a signal not

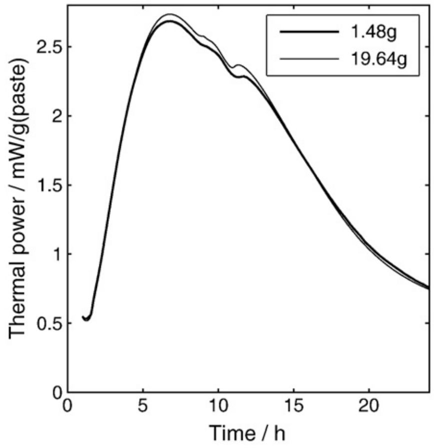

Fig. 7. One example of the influence of sample size on measured thermal power. The samples are cement pastes from the same mix.

only from heat production in the sample, but also from heat moving around in calorimeter.

A simple thermal model of a heat conduction calorimeter (Fig. 8) helps in understanding the thermal processes that takes place in a calorimeter. If heat is produced in the sample (A), the temperature of A will increase. Because of this, heat will diffuse from A to the heat sink (H) and this will cause the temperature of H to also increase. However, as H has a much higher heat capacity than A, the resulting temperature changes in the H are much lower than those in A. The heat that flows into H from A will be conducted out into the thermostat (0), but also “backwards” into the reference (B). There will thus also be small temperature changes in B when heat is produced in A.

According to Eq. (8) the time constant τ of a thermal decay process is the ratio of the heat capacity *C* and the thermal conductance *k*. We can thus calculate time constants for the thermal connection of the sample (and the reference) to the heat sink, but also for the thermal connection of the heat sink to the thermostat. These time constants are about 400 s and 4 h, using the data given in Fig. 8. The time constant for the sample (this is the time constant used in the Tian correction) is much lower than the time constant of the heat sink. Let us take 5τ as the time it takes for a disturbance to die out (this time corresponds to that less than 1% of a disturbance is left). If the sample temperature differs from that of the heat sink, the equilibration time will be 35 min, but if the heat sink temperature is disturbed and differs from the temperature of the thermostat it will take almost a day before this disturbance has died out.

Users of heat conduction calorimeters will observe the effect of the sample time constant every time a sample is charged as this is the factor that governs the decay of the initial disturbance. It is more difficult to see the effect of the time constant of the heat sink, but this can be the cause of problems, for example with baseline drift. If the heat sink temperature is disturbed when an inert sample of very different temperature than the calorimeter is charged for a baseline determination, the baseline may take up to a day to stabilize, because this is the time it takes for the thermostat to set the heat sink temperature correct again. One should therefore disturb the temperature of the heat sink as little as possible. Do not remove parts of the thermostat insulation; do not turn the thermostat off between measurements; and pre-thermostat sample ampoules in a heating block if the sample temperature is significantly different from the thermostat temperature.

In the differential (twin) arrangement, the measured output voltage is the difference between the voltages from the sample and reference sensors. The Seebeck-voltage from a “heat flow sensor” is not caused by the heat flow itself. It is caused by the temperature difference over the sensor and is – for small temperature differences – proportional to the temperature difference. However, as heat flow is also proportional to the temperature difference (Fourier's law of heat conduction), the voltage will also be proportional to the heat flow. The result of the twin arrangement is that one measures not the temperature difference between the sample and the heat sink (A-H), but between the sample and the reference (A-B), i.e, the difference between the heat flow from the sample to the heat sink and the heat flow from the reference to the heat sink is measured.

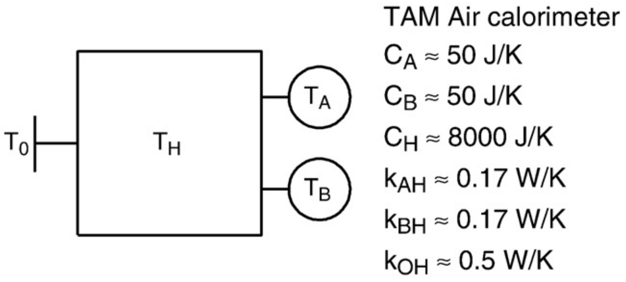

Fig. 8. A schematic thermal model of one TAM Air heat conduction calorimeter. The calorimeter is modeled by three heat capacities, each with uniform temperature. "A" is the sample, "B" is the reference, "H" is the heat sink, and "0" is the thermostat. The lines are thermal conductances between the heat capacities. The thermostat has a constant temperature. The values of heat capacity *C* (J K^{-1}) and thermal conductance *k* (W K^{-1}) given are typical for a TAM Air calorimeter with a 10 g mortar sample. The value for C_H is for all eight channels in a TAM Air calorimeter as the calorimeters have a partially shared heat sink.

A balanced twin arrangement significantly reduces three types of errors. First of all, thermal disturbances tend to reach the sample and the reference at the same time as they are placed closely together, and they will then be disturbed in the same way. As the difference between the signals is measured, a major part of most disturbances will be removed. An example of this is given in Fig. 9A where the balanced calorimeter has significantly less noise than the other calorimeters, and the noise level also increases as the unbalance increases (the ratios of total heat capacities between the sample sides and the reference sides are here about 1.0, 0.7, 0.4 and 0.2). Note also that the lowest curve is in anti-phase compared to the three other curves. This calorimeter is well balanced, but the unbalance that still exists is opposite compared to the other three calorimeters, i.e., the sample side has slightly lower heat capacity than the reference side.

Secondly, and related to the discussion above, when a sample produces heat, this heat will flow out into the heat sink and the heat sink temperature will be slightly increased. As the heat sink temperature is the reference temperature for the sample heat flow sensor, this sensor will show slightly lower voltage than it would have shown if the heat sink had been an ideal heat sink with constant temperature. However, some heat will also flow from the heat sink to the reference and give a negative signal from the reference heat flow sensor. When this is subtracted from the sample signal, the effect of the temperature drift of the heat sink is compensated for. Note that although the temperature drift of the heat sink needs to be compensated for by a reference to give stable baselines, the absolute temperature changes are small. Typically the sample temperature is increased by less than 0.1 K and the heat sink temperature by less than 1 mK during a well-designed cement hydration measurement.

Thirdly, when the heat sink temperature is disturbed this disturbance will cause heat flows through both the sample and reference sensors. Also in this case, a balanced twin arrangement will result in significantly lowered error in the output signal. Disturbances can have many sources. For example, a short removal of part of the thermostat insulation (Fig. 1B) or charging of ampoules with very different temperatures than the thermostat (Fig. 1C).

The result in Fig. 1C illustrates the thermal dynamics of the system shown in Fig. 8. The instrument was disturbed by the charging of eight ampoules with 17.5 mL water that was 10 K colder than the calorimeter. This corresponds to a total of about 7000 J which will cool the heat sink about 0.6 K before the thermostat restores the set temperature.

Note that in both Fig. 1B and C, the effect of the disturbances is first to increase the signals of the three unbalanced calorimeters, but after some time the signals crosses over on the other side. The reason for this is that in both cases the temperature of the heat sink is lowered by the disturbances. When the temperature of the heat sink is lower than the temperature of the sample and the reference, heat will flow out from the sample and the reference. In the present case the unbalanced calorimeters have higher heat capacity on their sample sides, so more heat will flow out of the sample heat flow sensor, than of the corresponding reference sensor. As heat flowing out of the sample side is counted positive (as it is normally caused by heat production in the sample), the first peak will be positive. During this initial phase the heat sink is cooler than the samples and references, but as the thermostat holds a constant temperature the heat sink will return back to its original temperature, and after some time a point will be reached when the heat sink temperature equals the sample temperature. At this time the heat sink is still not at the thermostat

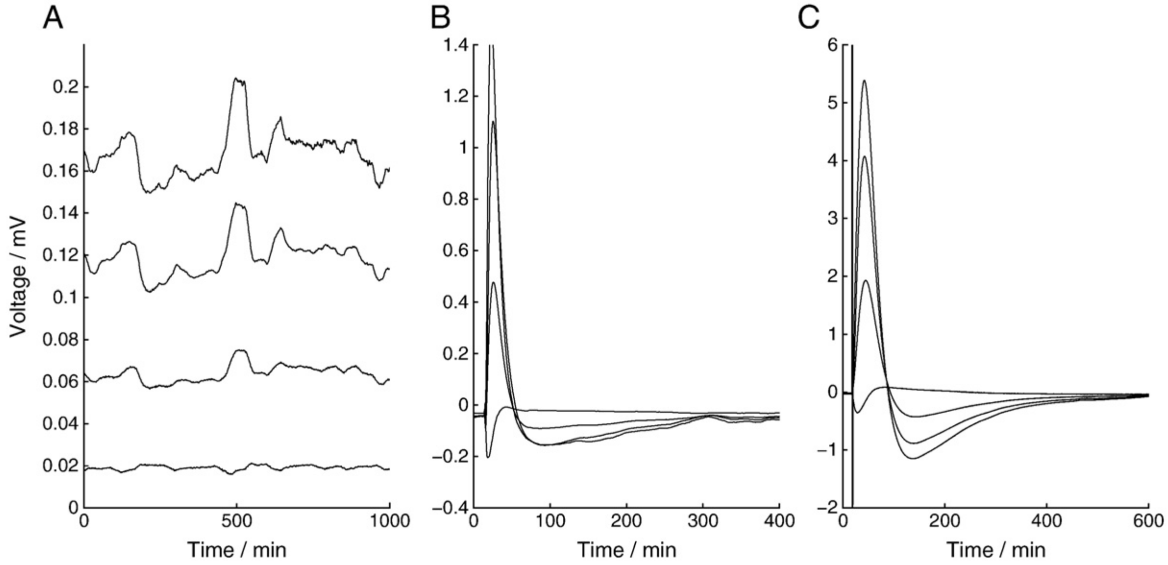

Fig. 9. Results from measurements at 30 °C on four calorimeters with ampoules with 10 mL water on the sample side, but different references (ampoules with 10, 5 and 0 mL of water or no ampoule at all) in one thermostat. In all figures, the amount of noise or disturbance increases as the unbalance of a calorimeter increases. A. Baselines (the curves have been shifted in the y-direction). B. Result of a disturbance caused by removing the insulated lid of calorimeter for about 20 s. C. Result of inserting eight 20 °C ampoules with 17.5 mL water into the sample and reference positions of the four calorimeters whose results are not shown.

temperature, so there will be a second phase during which the heat sink temperature increases back to the thermostat temperature. Then the sample and references lag behind and the situation is the reverse of what it was right after the disturbance and the signals will then be negative. So the complex appearance of the signals is the result of internal heat transfer in an instrument with unbalanced calorimeters.

It is in practice impossible to perfectly balance a calorimeter, but by making a good balance – for example within 5% heat capacity – one will get significantly lower noise and less influence of disturbances, and will be able to make good measurements. It should also be noted that the major parts of the disturbance seen in Fig. 1B and C could have been avoided if one had not lifted the thermostat lid (Fig. 1B) and if the samples had been pre-thermostated in a heating block prior to charging them into the calorimeter (Fig. 1C).

In conclusion, the calorimeter is a dynamic system in which the reference is an important part as it hides the major part of the dynamics of the system, so that the user only sees the thermal power of the sample. However, how well the reference works depends on how well the thermal properties of the reference are adjusted to those of the sample.

9. Cross-talk

The TAM Air calorimeter is different from most other calorimeters in that it has eight twin calorimeters that partially share the same heat-sink. There is thus a possibility that heat produced in one calorimeter also affects the neighboring calorimeters (cross-talk). In practice this is seldom a problem if the calorimeters are well balanced, as a thermal disturbance entering a well-balanced calorimeter will be significantly reduced. However, even if proper references are used, cross-talk can be a problem in extreme cases, for example if charged samples have significantly different temperatures from the calorimeter, or the sample in one calorimeter produces a high thermal power while the other calorimeters are measuring low thermal powers. This is seen in Fig. 1C where even the well-balanced calorimeter did show a small cross-talk disturbance. Under conditions when cross-talk can be expected to be a problem, some care must be taken in designing methods; for example, one may pre-thermostat samples or refrain from using all eight channels at the same time.

10. Discussion

An isothermal heat conduction calorimeter can make precise and accurate quantitative measurements if one follows appropriate protocols. A central issue in all protocols for isothermal calorimetry is the balancing of the calorimeter, i.e., the choice of a proper reference. It is also important that baselines are determined under undisturbed conditions and that measurements are made in such a way as to minimize the thermal disturbance of the heat sink.

In many cases, method development is a question of finding the balance between conflicting demands. For example, too high thermal powers will give significant temperature changes in the sample, but too low thermal powers will give unacceptably low resolution (cf. discussions on electrical calibration and sample size). Also the designer of isothermal calorimeters needs to balance conflicting demands. For example is there a conflict between low noise and the rate at which the thermostat temperature can be changed. The factor that controls both these properties is the thermal conductance between the thermostat and the heat sink (k_{0H} in Fig. 8). If k_{0H} is low, thermal disturbances from the thermostat will be dampened and the temperature stability of the calorimeters will be high, but at the same time it will be take a long time to change the calorimeter temperature.

The simple model presented in Fig. 8 is a useful conceptual model of an isothermal heat conduction calorimeter. All the dynamical phenomena discussed in his paper can be modeled, simulated and understood from reasoning based on this model. One can for example make a simulation model of the situation in Fig. 1C and arrive at similar results as are shown in the figure.

In many cases a good baseline value is essential for a successful result. An illustrative example is the determination of the total heat of hydration of a cement paste sample during 7 days. As the measurement time is long and the integral of the measured thermal power is the result of interest, small errors in the baseline value will result in relatively large errors in the final result. Typically, 300 J/g is produced during 7 days hydration. The influence of an error in the baseline value on these values is dependent on the sample mass. Let us assume that the mass of cement in a sample is 1 g and that the error in the baseline is 10 μW. A thermal power of 10 μW during 7 days is equivalent to 6 J of heat. For the sample with 1 g cement the resulting relative errors in the determined heats are then about 2% for 7 days heat of hydration.

The results in Figs. 5 and 6 show that isothermal calorimeters can be robust instruments that will run for a long time without any major changes in the calibration coefficients or the baseline values. However, a calorimeter will of course not last forever. Either it will change its properties in a way that the operator will notice (for example if the thermostat breaks down) or there will be a gradual change in instrument properties which is difficult to see (for example if a crack develops in a heat flow sensor) unless one makes frequent calibrations.

Even if isothermal calorimeters can be stable instruments, it is necessary to calibrate them regularly if one is doing quantitative measurements. The choice of calibration interval is dependent on the type of work being done and how much data that one is prepared to lose if the calorimeter does change its properties or break down, as one cannot then judge the quality of the data measured since the last calibration.

11. Conclusions

Here are the main findings from this study on isothermal calorimeters of the TAM Air type:

- Steady-state and pulse calibrations give similar results.
- Mobile heaters (in the ampoules) are preferable to fixed heaters as the latter gave an error in the order of 2%.
- The studied calorimeter was linear in its response.
- Calibration coefficients should not be determined at too low thermal powers as errors in input parameters than makes the result uncertain.
- The temperature dependence of calibration coefficients is predictable and can in some cases be used to calculate calibration coefficients at one temperature from data at another temperature.
- The calibration coefficients of the studied calorimeters had been extremely stable over a four year period and a decision on calibration interval should not be based on drift etc., but rather on how much data one is prepared to lose if a calorimeter does change its properties or break down.
- It is important to use balanced references as this will reduce noise, drift and the result of disturbances.
- Baselines can be determined with any type of balanced ampoules, but baseline measurements should have a duration of least 10 h so that one can make sure that one is actually measuring the baselines and not long-term drifts.
- In the studied calorimeters the baselines were stable over several years.
- The size of samples of cement-based materials should not be made too large as this will cause acceleration of the hydration.

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References

[1] G. Buckton, Applications of isothermal microcalorimetry in the pharmaceutical sciences, Thermochim. Acta 248 (1995) 117–129.
[2] L. Gustafsson, Microbiological calorimetry, Thermochim. Acta 193 (1991) 145–171.
[3] L. Wadsö, Applications of an eight-channel isothermal conduction calorimeter for cement hydration studies, Cement Int. 5 (2005) 94–101.
[4] L.D. Hansen, Calorimetric measurements of the kinetics of slow reactions, Ind. Eng. Chem. Res. 39 (2000) 3541–3549.
[5] R.J. Willson, et al., Determination of thermodynamic and kinetic parameters from isothermal heat conduction microcalorimetry: applications to long-term-reaction studies, J. Phys. Chem. 99 (1995) 7108–7113.
[6] I. Wadsö, L. Wadsö, Systematic errors in isothermal micro- and nanocalorimetry, J. Thermal Anal. Calorim. 82 (3) (2005) 553–558.
[7] D.P. Bentz, Transient plane source measurements of the thermal properties of hydrating cement pastes, Mater. Struct. 40 (2007) 1073–1080.
[8] P.F. Bunyan, An absolute calibration method for microcalorimeters, Thermochim. Acta 327 (1999) 109–116.
[9] S.J. Gill, I. Wadsö, Flow-microcalorimetric techniques for solution of slightly soluble gases. Enthalpy of solution of oxygen in water at 298.15 K, J. Chem. Thermodynamics 14 (1982) 905–919.
[10] S.O. Nilsson, I. Wadsö, A flow-microcalorimetric vessel for solution of small quantities of easily of slightly soluble liquids. Solution of benzene in water at 298.15 K, J. Chem. Thermodynamics 16 (1984) 317–330.
[11] M. Görman Nordmark, et al., Design and testing of a new microcalorimeric vessel for use with living cellular systems and in titration experiments, J. Biochem. Biophys. Methods 10 (1984) 187–202.
[12] C. Evju, Initial hydration of cementitious systems using a simple isothermal calorimeter and dynamic correction, J. Thermal Anal. Calorim. 71 (2003) 829–840.
[13] L. Wadsö, Temperature changes within samples in heat conduction calorimeters, Thermochim. Acta 366 (2000) 121–127.
[14] H. Kada-Benameur, E. Wirquin, B. Duthoit, Determination of apparent activation energy of concrete by isothermal calorimetry, Cement Concrete Res. 30 (2000) 301–305.
[15] G. De Shutter, L. Taerwe, Specific heat and thermal diffusivity of hardening concrete, Mag. Concrete Res. 47 (172) (1995) 203–208.