

An isothermal heat flow calorimeter for large-volume applications

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Abstract Design, construction, calibration, and testing of a new isothermal heat flow calorimeter suitable for investigation of large-volume specimens are presented. The measuring vessel has the volume of 1370 cm³, and the calorimeter allows for the measurement at surrounding air temperatures of 5–60 °C. A practical application of the device is demonstrated at the determination of specific hydration heat of cement paste and concrete with silica-aggregate size of up to 16 mm, having the same water/cement ratio. The differences over the whole measuring time period of about 100 h are lower than 2% which indicates a good potential of the calorimeter for the measurement of total hydration heat of composite materials. A reference measurement of hydration heat of cement paste using common isothermal heat flow calorimeter with the measuring vessel of 1 cm³ shows an agreement within ±7%, which seems acceptable, taking into account the heat transport processes in the far larger specimens. The designed calorimeter may find use in future also in other applications where larger specimens are required, such as the measurement of adsorption heat, solution heat, various reaction heats, and enthalpy of liquid–solid transition in heterogeneous systems with large representative elementary volumes.

Keywords Isothermal heat flow calorimeter · Large-volume specimens · Design · Construction

Introduction

Calorimeters were originally constructed for the measurement of specific heat capacity, and this application remained the most frequent hitherto [1, 2]. Their current usage is, however, much wider. The enthalpy of phase transition [3], enthalpy of combustion [4], adsorption heat [5], enthalpy of formation [6], heat of salt hydration [7], solution enthalpy [8], and thermal conductivity [9] present only a few characteristic examples of parameters which are measured in physical and chemical laboratories using calorimetric techniques. In engineering laboratories, hydration heat of cementitious systems belongs to the class of most extensively studied parameters. Isothermal [10], isoperibolic [11], and adiabatic calorimeters [12] present the commonly used devices. The effects of silica fume [13], finely ground limestone [14], fly ash [15], blast furnace slag [16], or wastes from fluidized bed combustion [17] on cement hydration are typical examples of problems that are being studied.

Most commercial calorimeters use rather small measurement vessels, typically in the range of 1–10 cm³, which suits well their major purpose for many materials and applications. If the investigated specimens can be considered homogeneous over this volume, which is often the case in scientific laboratories, then a smaller volume is an advantage because higher measurement accuracy can be achieved.

Heterogeneous materials or their systems with large representative elementary volumes have been subject of calorimetric studies much less often than homogeneous systems. The measurements of specific heat capacity of composite materials using a mixing calorimeter reported in [18–20] belong to the few exceptions in that respect. However, the calorimetric measurements over larger volumes can provide useful information on systems with

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large-scale inhomogeneities, which are currently not available. To give only a couple of examples, in composite materials with coarse aggregates the possible role of aggregates in the hydration process can be assessed, in porous materials with large pores the heat of adsorption of water on the porous matrix or the amount of ice frozen in the pore system (based on the known enthalpy of water/ice transition) can be determined.

In this article, we present a new isothermal heat flow calorimeter suitable for investigation of large-volume specimens typical for highly inhomogeneous systems.

Design, construction, and calibration of the calorimeter

The main design criteria were formulated as follows:

- The calorimeter should operate in isothermal or near-isothermal mode to be able to assign the heat evolved in the measurement vessel to a specific temperature;
- The measurement vessel should be large enough to allow investigation of materials with inhomogeneities up to 25 mm in diameter;
- The inner surface of the calorimeter box should be maintained at a constant temperature in the range of 5–60 °C for a sufficiently long time period, typically several days.

The isothermal heat flow calorimeter constructed according to the above criteria (it will be denoted as KB 01 in what follows) is shown in Fig. 1. Figures 2 and 3 present the vertical and horizontal cross sections, respectively. The outer box (1, 2, and 3 in Figs. 2 and 3) is made of 6-mm



Fig. 1 The isothermal heat flow calorimeter for large-volume applications

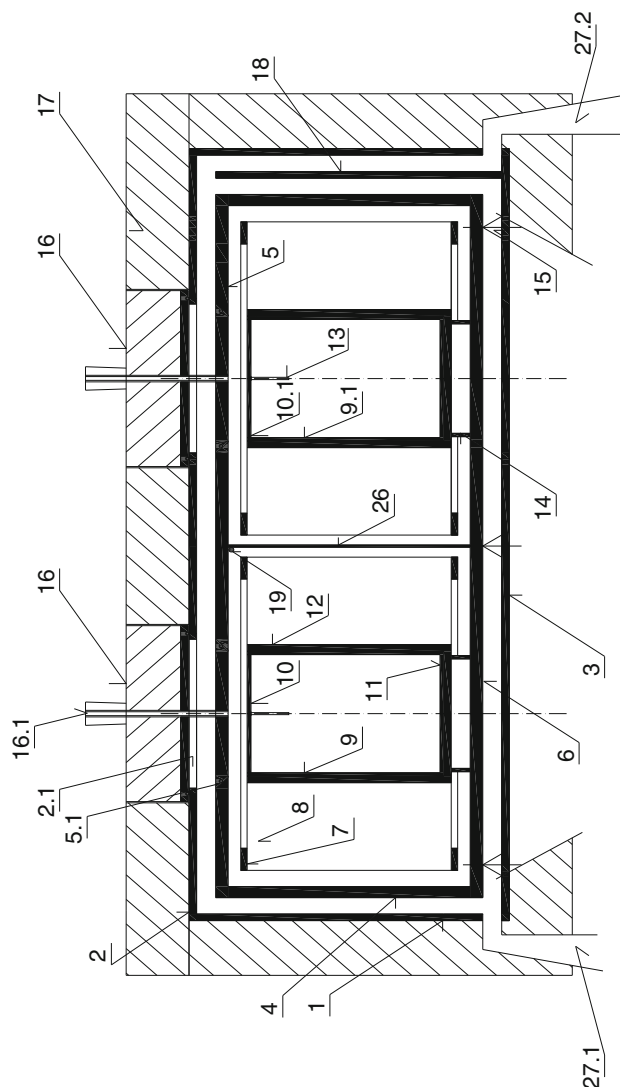


Fig. 2 Vertical cross section of the isothermal heat flow calorimeter. 1 Vertical walls of the outer metallic coat, 2 outer cup, 2.1 cover hole, 3 outer bottom, 4 internal wall, 5.1 hole in the internal wall, 6 internal bottom, 7 plastic connecting ring, 8 the plate with thermopile (thermal flow sensor), 9 wall of the measuring vessel, 9.1 wall of the reference vessel, 10 lid of the measuring vessel, 11 bottom of measuring vessel, 12 thermal flow sensor, 13 hole for the resistance thermometer, 14 supporting plastic ring, 15 supporting plastic pyramid, 16 lid, 16.1 central hole, 17 thermal insulation, 18 front wall, 19 plastic tube outlet for cables, 26 reflective partition, 27.1 inlet of controlled-temperature air, 27.2 outlet of air

aluminum sheet, the inner box (4, 5, and 6) of 10-mm aluminum sheet. The air temperature in the space between the boxes is measured and regulated by an electronic controller with a Pt–Pt10%Rh thermocouple. The thermocouple is placed between the upper walls (between 2 and 5) of the inner and outer boxes. The air temperature regulator (not shown) consists of a compressor cooling unit, an electric heater, and a radial fan. The temperature is kept within a ± 0.15 °C range.

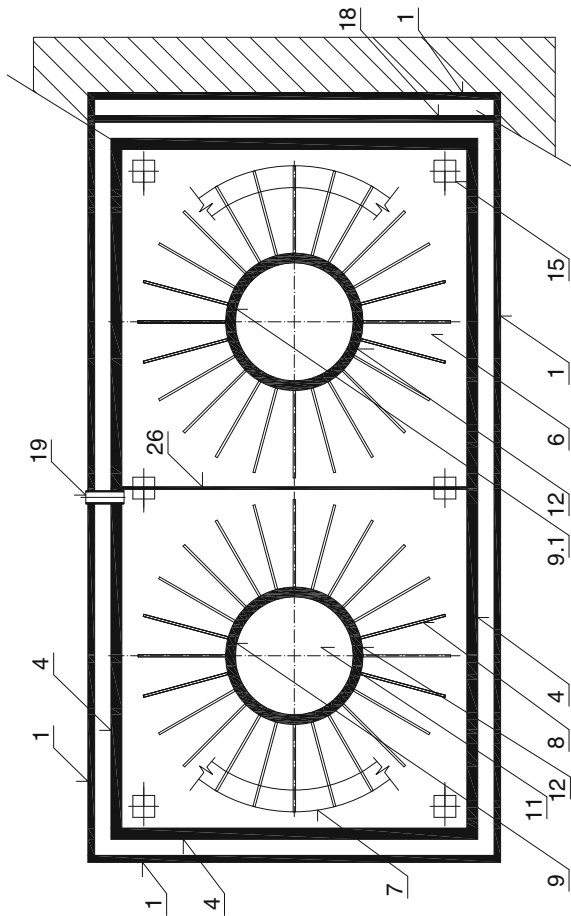


Fig. 3 Horizontal cross section of the isothermal heat flow calorimeter—labeling is the same as in Fig. 2

The measurement itself is based on monitoring the time resolved production of heat by a material specimen, which is placed in the measurement vessel (9, 11) having volume of 1370 cm³ and wall thickness of 3 mm. The measurement vessel is inserted inside a thermal flow sensor (12) which has a 6-mm-thick wall. There are 24 hard plastic ribs (8) glued to its surface. A constantan/copper thermopile is wound on each rib. Thermocouple junctions are partly on the sensor surface (electrically insulated), and partly on the far end of the rib, near to the surface of the inner box. The heat is transported from the ribs by thermopiles to the black isothermal inner surface of the inner box (4, 5, and 6) through the air by radiation, convection, and conduction. The heat flow through the ribs of the sensor vessel generates a temperature gradient and produces thermoelectric voltage on the thermopile. The 24 thermopiles of each sensor are connected in series. The thermoelectric voltage is proportional to the heat flow. The signal from a reference set of thermopiles is subtracted from the sensor signal electrically, being connected in reverse series. This arrangement eliminates an external

influence on the stability of the heat flow measurement. The difference signal (in mV) is recorded by a data logger (Fig. 4).

The calibration is carried out using an aluminum insert shaped as the measuring vessel (9, 11). It uses Joule heat produced by constantan wire with a resistance of 72.1 Ω, wound on the insert. The results of calibration are presented in Fig. 5. The interpolated parabolic calibration curve at 20 °C was only slightly different from a straight line; its temperature dependence in the range of 5–30 °C was found negligible.

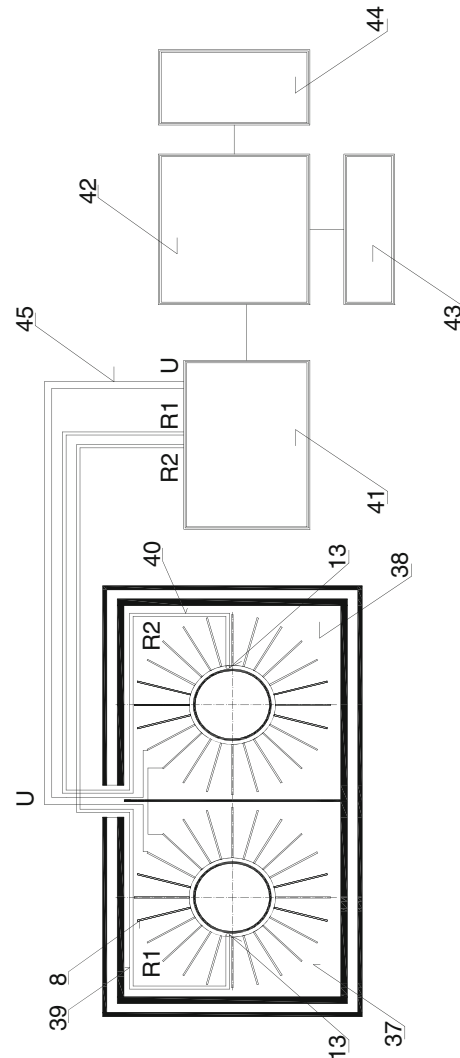


Fig. 4 Signal paths in the circuit of the isothermal heat flow calorimeter. 8 Thermopile, 37 measuring part of the calorimeter, 38 reference part of the calorimeter, 39 signal from the resistance thermometer R2 in the measuring part, 40 signal from the resistance thermometer R1 in the reference part, 41 COMET MS5 data logger, 42 personal computer, 43 keyboard, 44 display, 45 differential signal in mV from the heat flow sensors 13

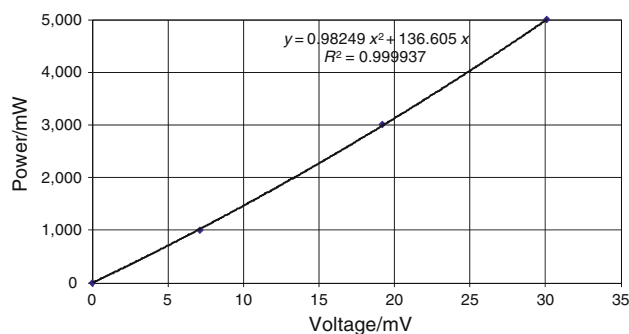


Fig. 5 The calibration curve of isothermal heat flow calorimeter

Measuring procedure

In the first calorimetric period, the particular components of an analyzed specimen are put separately into the calorimeter. The solid components are placed in polyethylene (PE) bags, and closed tightly by a rubber band. Liquid components are stored in a tight PE flask. The equilibration of temperature field in the calorimeter containing specimen's components takes about 24 h, depending on thermal diffusivity of the specimen. Afterward, the components are taken out of the calorimeter and mixed together for about 3 min in a PE bag, which is then sealed, weighed, and put in the measuring vessel of the calorimeter. The output signal is recorded during the whole process of removing the parts of the sample, mixing, reinserting it, and closing the apparatus. The duration of the initial phase of the procedure can be read from the record.

The second, main calorimetric period is the measurement itself. It begins about three and a half minutes after mixing the components, which is necessary for the specimen's fixing in the calorimeter, and is finished after the heat power generated in the system decreases below a certain limit. The third, final calorimetric period is the homogenization of temperature field in the calorimeter after specimen's removal. It may overlap with the first period of the next measurement.

The output voltage (in mV) from the differential systems of measuring and reference thermopile heat flow sensors is recorded with a 15-s period. COMET 5+ data logger is used in the current experimental setup. The commercial software of the data logger is utilized for the measurement control and data acquisition. The output signal is recorded

by an input channel working in -2 to $+100$ mV range. The temperatures of measurement and reference vessels are recorded simultaneously by platinum resistance thermometers of 3-mm diameter. The data from data logger are loaded by a PC, transformed to a MS Excel sheet, and recalculated to heat power values using the calibration curve. Typically, there are about 30,000 voltage values per measurement and as many values of the temperatures of the measurement- and reference vessels, recorded concurrently. For validation, the air temperatures, both preferred and actual, are recorded in a protocol of the air temperature control device.

The time dependence of heat power (in mW) obtained as the measurement output can then easily be recalculated to specific heat power (in mW g^{-1}) and integrated to obtain the production of total heat (in J) or specific heat (in J g^{-1}) as a function of time.

Example of application and discussion

The designed isothermal heat flow calorimeter was tested at the measurement of hydration heat of concrete with aggregate size up to 16 mm and cement paste. Silica aggregates, which were not supposed to participate in the heat development during the hydration reaction, were used, and the water/cement ratio was the same in both cases (Table 1). In this way, a direct comparison of the course of hydration reactions in concrete and cement paste could be done.

In the specimen preparation phase (the first calorimetric period), for cement paste, the solid component was only cement, and for concrete, it was cement and a separate mixture of sand and two different gravel aggregates (Table 1). After equilibration of temperature field, water was added to the bag containing solid components, and the bag was sealed. The mixing was then performed in the closed bag to avoid any loss of fine components or water. The measurement was then carried out in the same way as described in the previous section.

The development of specific hydration heat power (in mW per gram of cement) in Fig. 6 shows that, for cement paste, both the maxima and minima were more distinguished than for concrete. It was caused by absorption of a part of the heat generated by cement hydration in the

Table 1 Composition of cement paste and concrete/g

| Material | Cement CEM I 42.5R | Water | Sand/mm | Gravel/mm | | Mass of the specimen |
|--------------|--------------------|-------|---------|-----------|------|----------------------|
| | | | | 4–8 | 8–16 | |
| Cement paste | 600 | 300 | 0–4 | | | 900 |
| Concrete | 360 | 180 | 564 | 120 | 276 | 1,500 |

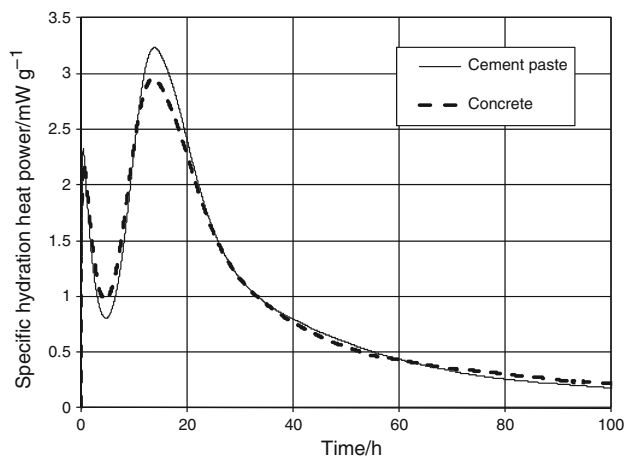


Fig. 6 Specific hydration heat power of cement paste and concrete

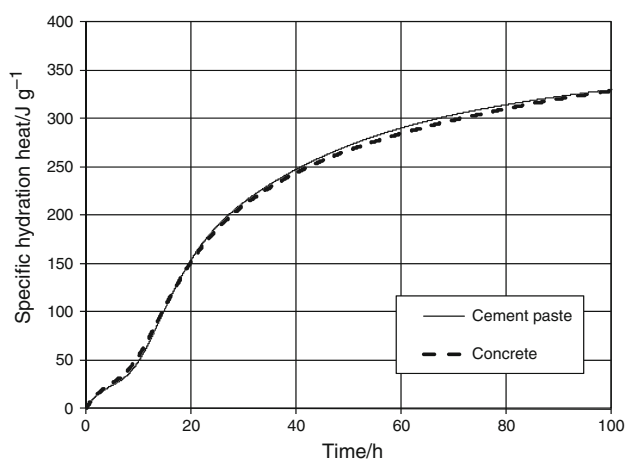


Fig. 7 Specific hydration heat of cement paste and concrete

aggregates, which was later transported back to the cement matrix. The total specific hydration heat registered by the calorimeter as a function of time (in J per gram of cement) differed for cement paste and concrete only within 2% in the whole time period of 100 h (Fig. 7). The highest differences were observed between 40 and 80 h when the heat generated in the second phase of alite hydration (the second peak) and absorbed at first in the aggregates was released back to the matrix. After 100 h, the difference in specific hydration heat of concrete and cement paste was lower than 0.5%.

Sources of uncertainty in the determination of specific hydration heat power derive from uncertainty associated with measurement of specimen's mass, measurement of voltage and time, and determination of calibration constants. In calculating the combined uncertainty of specific hydration heat power, we assumed the relative standard uncertainty of mass measurement to be 0.003%, voltage measurement 0.1%, and time measurement 0.003%; for the calculation of calibration constants, A and B, it was 1%.

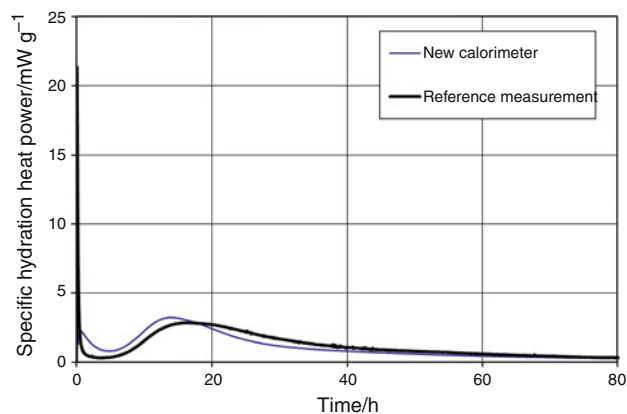


Fig. 8 Comparison of the specific hydration heat power of cement paste with reference measurement

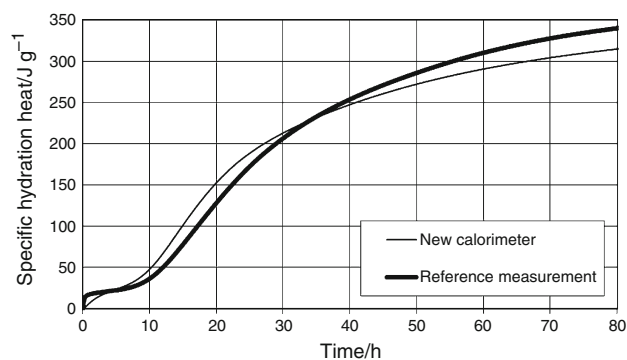


Fig. 9 Comparison of the specific hydration heat of cement paste with reference measurement

The combined relative standard uncertainty (square root of the sum of squares of all uncertainties) was then 1.4%, the combined expanded uncertainty 2.8%.

The time resolution of the designed calorimeter was tested at the comparison of the measured course of hydration reaction in cement paste with the analogous measurements performed using the isothermal heat flow calorimeter KC 01 described in [21, 22] which has the measuring vessel of about 1 cm³. Figure 8 shows that the first peak (corresponding to the heat generated at the hydration of tricalcium aluminate and during the first phase of alite hydration) found by KC 01 at the time of about 4 min after beginning the hydration reaction was not adequately recorded by the new calorimeter KB 01; the first maximum was observed at 30 min. This finding, being a logical consequence of the large sample dimensions used in the new calorimeter, sets some basic limitations to the use of KB 01 in the presented arrangement. The course of fast heat generation processes up to several minutes cannot be monitored using the current data-acquisition method. Perhaps, the determination of time constant and subsequent application of Tian equation [23, 24] might help us to deal with this limitation. On the other hand, the total specific

hydration heat measured by KC 01 and KB 01 during the whole analyzed time period of 100 h (except for the initial time period of about 4 h) differed within the range of $\pm 7\%$ (Fig. 9), which can be considered a reasonable agreement taking into account the large differences in sample size.

Conclusions

A new isothermal heat flow calorimeter suitable for investigation of large-volume specimens was designed and tested. The dimension of inhomogeneities in analyzed specimens can be up to 25 mm. The measuring vessel has the volume of 1370 cm³. The calorimeter allows the measurement at air temperatures of 5–60 °C. The basic accuracy expressed in terms of combined expanded uncertainty is 2.8%.

An example of comparative measurement of hydration heat of cement in cement paste and concrete with coarse aggregate was presented. It was found that silica aggregates did not influence the hydration heat per gram of cement in a significant way when the water/cement ratio and temperature were the same. In a time resolution test, reference measurement of the course of hydration reaction in cement paste with the same water/cement ratio was done, using an isothermal heat flow calorimeter with the measuring vessel of about 1 cm³. It revealed while the new calorimeter was not able to monitor adequately the time course of fast heat generation processes taking up to several minutes, the total specific hydration heat measured by both calorimeters differed within the range of $\pm 7\%$ which can be considered an acceptable agreement.

The robustness of construction of the new calorimeter makes possible its utilization for systems with large-scale inhomogeneities such as composite materials with coarse aggregates or porous materials with large pores. The simplicity of construction indicating a reasonable price of the calorimeter at production series on mass scale, together with its relatively good accuracy, makes good prerequisites for its potential applications in future in science and engineering.

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