Applied Thermal Engineering 121 (2017) 547–553

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

Computational analysis of heat transport and storage processes in large-volume isothermal heat flow calorimeter

Václav Kočí, Jiří Maděra, Miloš Jerman, Robert Černý *

Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Prague 6, Czech Republic

HIGHLIGHTS

- Large-volume isothermal heat flow calorimeter is analyzed.
- Three dimensional computational representation of the real device is constructed.
- Computational model is calibrated using four different constant heat power pulses.
- Model is verified in an independent heat power scheme.
- Experimental and computational outputs show a high level of agreement, $R^2 = 0.9998$.

ARTICLE INFO

Article history:
Received 6 October 2016
Revised 13 March 2017
Accepted 24 April 2017
Available online 25 April 2017

Keywords:
Isothermal heat flow calorimetry
Large-volume calorimeters
Heat transport
Heat inertia
Computational modeling

ABSTRACT

Isothermal heat flow calorimeters for large-volume applications are utilized for monitoring heat generation in highly inhomogeneous systems mostly. However, the time delay of measured data caused by internal heat inertia limits their effective use to slower processes. In this paper, a computational analysis of heat transport and storage processes in a large-volume isothermal heat flow calorimeter is presented. Using a three dimensional computational representation of the real device, thermal processes occurring in the calorimeter-sample system are simulated and the time delay between the generation of internal heat and its subsequent detection is identified. The computational model is calibrated at first, using four different constant heat power pulses, and then verified in an independent heat power scheme. The comparison of experimental and computational outputs shows a very high level of agreement, $R^2 = 0.9998$, which gives the applied modeling approach good prerequisites for successful practical applications. Apparently, the computational model introduced in this paper is able to provide higher accuracy than common mathematical corrections of experimental outputs that have been used so far.

1. Introduction

Isothermal heat flow calorimeters of various types are widely used in thermal science and engineering. Determination of waste heat produced by silver zinc batteries [1], hydration heat development in $MgSO_4$ hydrates [2], composite binders [3], and low-clinker cements [4], or specific heat capacity and thermal conductivity of lithium batteries [5] can be listed as just a few characteristic examples in that respect. Most commercial devices use small measurement vessels, typically up to 10 cm^3, which suits well for many materials and applications. In the case of heterogeneous materials or their systems, large-volume calorimeters making possible handling the specimens up to 1000–1500 cm^3 can be required to monitor properly the interactions of system components [6].

Despite the apparent advantages over some other calorimetric techniques, such as a straightforward calibration process and the measurement at an exactly specified temperature, making possible to obtain data well defined from the physical point of view [7], the use of isothermal heat flow calorimeters may be affected by their intrinsic drawbacks, which are to be taken into account in the experiments. Probably the most significant one is the lower accuracy at short measurement times. The heat power is not determined directly; it is calculated using the measured temperature difference between the calorimetric cell and the environment or between the calorimetric cell and the reference cell [8]. Since a certain amount of the heat released in the specimen is consumed by the inner parts of the calorimeter and heat transfer from the specimen to the temperature sensor takes some time, the measured heat power can be delayed in time. Practically it means that, for instance, the main heat power peak in Portland cement appearing approximately after 10 h [9] can be detected and quantified

---

* Corresponding author.
E-mail address: cernyr@fsv.cvut.cz (R. Černý).

http://dx.doi.org/10.1016/j.applthermaleng.2017.04.118
1359-4311/

reliably. On the other hand, monitoring the hydration heat development of calcium sulfate anhydrite III, which has its maximum after several minutes only [10], may exhibit much lower accuracy. The measuring uncertainties can be magnified particularly for voluminous samples that require utilization of large-volume calorimeters with appreciable internal heat capacity [6].

The time-delay problem of isothermal heat flow calorimeters can easily be demonstrated by a comparison of a constant calibration pulse of known heat power with the corresponding calorimetric output. Even though these quantities are supposed to be identical, in practical experiments they are not [8]. Probably the most frequently used correction represents the application of Tian equation [11]. Gao et al. [12] used it for the transformation of curves describing the hydration process of calcium phosphate cement. Another application of Tian equation was reported by Dumas et al. [13], who used it for the characterization of phase change materials. García-Cuello et al. [14] successfully exploited the Tian equation at the determination of the time response at the calibration of their calorimetric system.

However, at the study of initial hydration heat development in cementitious materials Evju [8] pointed out a disadvantage of the application of Tian equation, as it assumes uniform temperature within the cells. It is obvious that this assumption is unrealistic, e.g., for fast reactions or thermal transfer barriers that exist inside calorimeters [15]. Therefore, Evju [8] assumed two zones with uniform temperatures which led to a second-order differential equation with two time constants. As an alternative to Tian equations of any order, the deconvolution method was presented [16] which was based on reproducing the hydration curves using numerical algorithms based on fast Fourier transform. Nevertheless, Evju [8] was unable to reproduce the original rectangular calibration pulse using any of these methods. The reason can be seen in the mathematical nature of the solution which cannot handle the problem of unsmoothed curves that are typical for calibration pulses.

The application of computational modeling has been found an effective tool for solving specific problems of various calorimetric methods before. For instance, Haloua et al. [17] analyzed the processes in a reference calorimeter for natural gas, Choinski et al. [18] studied the thermal properties of a heat flow chip calorimeter, Sen et al. [19] presented a numerical model of a continuous flow microfluidic calorimeter.

In this paper, a three dimensional computational model of a large-volume isothermal heat flow calorimeter is introduced. The model is calibrated using rectangular heat pulses and verified for an independent heat power function. By solving the time-delay problem with a higher accuracy than common mathematical methods, the developed model makes possible to investigate also fast heat generation processes which is not feasible using standard calorimetric procedures.

2. Description of the analyzed large-volume isothermal heat flow calorimeter

Fig. 1. The investigated isothermal heat flow calorimeter.

Fig. 2. The aluminum calibration insert.

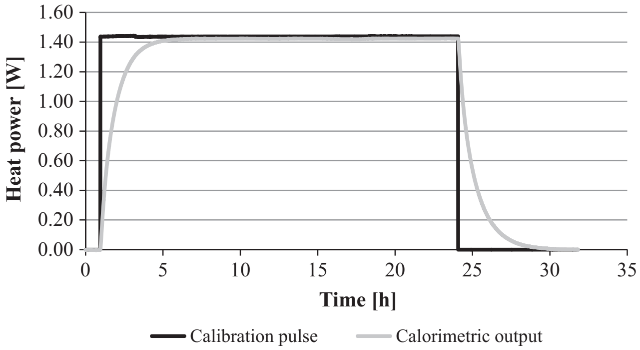

Fig. 3. Example of the response of the analyzed calorimeter to a rectangular heat pulse.

The investigated isothermal heat flow calorimeter, which was designed by Tydlitát et al. [6], is shown in Fig. 1. While operating in isothermal or near-isothermal mode, the construction of the calorimeter (700 × 400 × 250 mm) allows investigation of large volume samples in the temperature range of 5–60 °C. It consists of two vessels, measuring and reference, each of them is provided with 24 thermopiles. Each thermopile contains a set of constantan/copper thermocouples and has two functions: it transfers heat and generates a thermoelectric voltage. All the thermopiles are connected in series so the thermoelectric voltage is proportional to the heat flow. The thermopiles from the reference vessel are connected in reverse series allowing an elimination of an external influence on the stability of the heat flow measurement. The vessels with thermopiles are placed inside an inner aluminum box. Between the outer and inner boxes, there is a ventilated air gap with controlled temperature. A detailed description of the calorimeter can be found in [6]. The calibration of the calorimeter is performed using Joule heat produced by a constantan wire wound on an aluminum insert of known resistance which is