Assessment of fast heat evolving processes using inverse analysis of calorimetric data

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ABSTRACT

A computational method for an enhanced assessment of experimental data produced by isothermal calorimeters is presented. Based on the inverse analysis of transient heat transport in the calorimeter, the proposed technique enables reconstruction of fast heat evolving processes. A practical utilization of the developed method is demonstrated for the heat evolution in lime hydrate-water- and Portland cement–water systems where the computational assessment makes it possible to find seven to twelve times higher initial-peak heat power values than the calorimetric measurements. The high level of agreement of original experimental data with its computational representation, $R^2 = 0.9984$ for the lime hydrate-water system and $R^2 = 0.9992$ for the Portland cement–water system, confirms an overall good accuracy of the model. The capability of the developed computational method to correct intrinsic distortions, which are characteristic for specific calorimetric techniques, such as the heat consumption by device components and signal delay, makes good prerequisites for its applications in physics, chemistry, and engineering.

1. Introduction

Manufacturing of building materials often requires wet processing which can lead to the evolution of heat. In particular, most binders based on cement, lime, or gypsum generate substantial heat amounts after mixing with water, which is mainly due to wetting, dissolution, or chemical reaction.

Heat of wetting, which is evolved when water wets a surface of solid matter, is generally very small. However, it can reach significant values in case of binders with high specific surface. Besides the surface area, the amount of released heat depends also on the surface tension of liquid (water) or lyophobic/lyophilic properties of the surface that determine the contact angle. Since the total interface energy is released during wetting, the amount of heat is equal to the change of enthalpy. It is also important to realize that heat of wetting concerns even the insoluble substances. The amount of released wetting heat is higher in cases of mixtures containing fine-grained fillers or microfillers [1], and their setting may thus be affected [2].

Heat of dissolution represents another source participating on the fast heat evolution after mixing of binders with water. While breaking of bonds within the solute and within the solvent is an endothermic process, the formation of solute–solvent attractions is much more exothermic, so the overall process of dissolution releases a certain amount of heat [3].

Heat of dissolution is usually merged in with heat of wetting as it is practically impossible to use experimental techniques that can distinguish these two sources of heat. Regarding the fact that dissolution processes last longer than processes of wetting, depending on the dissolution/dissociation rate, heat of dissolution may be evolved over a slightly longer period and usually reaches higher values [4]. However, in spot of global heat processes which occur in binders after mixing with water, these differences are usually not considered.

The major part of heat is released by binders due to their reaction with water, which is an essential condition for the formation of solid mass with high strength. During the hydration process new products, such as calcium silicate hydrates, calcium aluminate hydrates, or calcium hydroxide, are formed. Reaching up to 500 J/g [5], the hydration heat is released slower than heat of wetting or dissolution. Depending on the type of binder and its composition, nevertheless, the heat may be evolved very fast at the early stage of hydration. This is typical, e.g., for gypsum, high-alumina cements, or calcium cements with rapid strength increase [6,7].

In case of small-scale structures, such as beams, slabs or columns, the evolved heat dissipates rapidly. On the other hand, the dissipation is slow in massive constructions, which leads to

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increase of their internal temperature. This results in a substantial temperature gradient between the center and the surface of the mass, inducing thermal stress [8] that may even exceed the tensile strength of the material. Thermal cracks are formed subsequently in this case, being accompanied with other negative phenomena, such as reduction of integrity, penetration of various substances, or reduction of service life due to deterioration and corrosion [9]. Therefore, the heat evolving processes are supposed to be monitored before the particular building materials are used in a structure. Various experimental techniques and types of calorimeters, such as adiabatic, semi-adiabatic (isoperibolic), or isothermal, have been developed for this purpose so far.

The application of calorimetric methods is very extensive in the research practice, providing data not only about the heat development, but also data related to phase transition [10], thermal conductivity [11], heat capacity [12], adsorption heat [13], or enthalpy of combustion [14]. In connection with the heat evolving processes of binders, isothermal calorimetry was used, e.g., by Maheswaran et al. [15] for a description of hydration kinetics of two types of blended cement at early stage, or by Gu et al. [16] for investigations of the influence of modified SiO_2 nanoparticles on cement hydration at early age. Semi-adiabatic calorimeters were utilized, e.g., by Kong et al. [17] analyzing the influence of various types of superplasticizers on hydration properties of Portland cement, or Saeed et al. [18] who tried to quantify the amount of hydration heat of Portland cement with slag and find a link to cracking of concrete blocks. The extensive utilization of calorimetry in relation to cement products can be proven by a number of records in the Web of Science database which provides about two thousand publications based on that search pattern.

Probably the biggest challenge that most calorimetric techniques must face is the quantification of heat in early or very early stages of heat evolving processes when heat of wetting, heat of dissolution, or rapid hydration heat are involved. The first problem consists in the mixture preparation procedure that may cause the early heat to be released already before placing the mixture into a calorimeter. However, it can be eliminated by using a proper calorimeter construction that allows mixtures to be prepared inside. Meeting this requirement, such apparatuses have been described or used, e.g., by Evju [19], Tydlitát et al. [20], or Xu et al. [21]. The second problem is closely connected to the construction of calorimeters as well, since they may be responsible for a significant heat consumption due to their internal heat capacity. This possible inaccuracy can be neglected in case of major heat power peaks of binders that appear after sufficiently long periods of time. For example, many cements have the major peak approximately after 10 h [22], i.e., there is time enough to reach a thermal equilibrium. On the other hand, fast heat evolving processes are difficult to be detected precisely. The corresponding heat power peaks are usually higher than the major peaks but they are very narrow, thus the overall amount of heat is much smaller and easier to be consumed in the beginning of the measuring procedure. Calorimeters designed for large volume samples make this problem even more important, but small calorimeters must face this problem as well because of the proportionality of the device and the sample. Many researchers therefore plot their results with the initial phase being cut off [23–25].

The inaccuracy of calorimetric measurements of fast heat evolving processes can be reduced by common mathematical techniques, particularly by an application of Tian equation [26]. However, this solution is limited by its purely mathematical nature and is not able to deal with complex shapes of heat power vs. time functions or with thermal barriers that can occur inside calorimeters [27].

In this paper, a computational method for the assessment of fast heat evolving processes, which is based on the inverse analysis of transient heat transport phenomena in the calorimeter, is presented. The designed procedure utilizes the computational model of heat transport and storage processes in large-volume isothermal heat flow calorimeter developed in [28] which makes possible to calculate temperature fields in the calorimeter-sample system using a three dimensional computational representation of the real device. The proposed computational solution of the inverse problem of heat transport inside the calorimeter can reconstruct any heat evolving process, no matter how fast or intensive, based on experimental outputs which include imperfections of the known origin. In other words, using the computational modeling it is possible to find such a source heat power vs. time function that generates the same output as the real apparatus. It can be then considered as more precise than the experimental result because it is not distorted by imperfections related to the measurement techniques, such as the heat consumption by device components and signal delay.

2. Computational model of heat transport and storage processes in the isothermal calorimeter

The isothermal calorimeter used in the investigation of heat evolution processes in this paper is shown in Fig. 1. While operating in isothermal or near-isothermal mode, the construction of the calorimeter ($700 \times 400 \times 250$ mm) allows investigation of large volume samples in the temperature range of 5–60 °C. It consists of two vessels, reference and measuring, having a volume of 1370 cm^3. Each of the vessels 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 outer and inner boxes, there is a ventilated air gap with controlled temperature of 25 °C. A detailed specification of the calorimeter can be found in Tydlitát et al. [20]. A temperature difference between the vessels may occur only when a heat generation takes place inside the measuring vessel. After an experimental calibration of the calorimeter, any temperature difference can be recalculated to the heat power of the ongoing process.

The heat transport and storage processes occurring in the calorimeter were modeled using the computational simulation tool developed in [28]. Being an exact replica of the real device, the three-dimensional computational representation of the calorimeter consisted of 70,883 nodes and 366,544 finite elements. High performance parallel computing [29] was therefore required for an analysis of heat evolving processes that occurred inside. Physical properties of materials in the calorimeter-sample system are presented in Table 1.

The main outputs of the computational model were temperatures on the interfaces between the thermopiles and the vessels (the same positions as in the temperature measurements in the real apparatus), which were calculated for a chosen characteristic time period after the application of the heat source inside the measuring vessel. The temperature data were subsequently converged into the heat power, using the model calibration procedure described in [28].

3. Method of inverse analysis

The main objective of the inverse analysis was to find the heat power vs. time function, $P(t)$, that (after application in the compu-