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CALORIMETRY OF BUILDING MATERIALS

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Abstract

Classical adiabatic methods for measuring specific heat in a wide temperature range are very suitable for homogeneous, well defined materials. However, measurements on inhomogeneous materials require large samples, which makes using of adiabatic treatments extremely expensive. In this paper, a nonadiabatic method for determining the specific heat of inhomogeneous building materials within the wide temperature range of –30 to 1200°C is presented. The method is relatively simple, very cheap, and sufficiently accurate for use with building materials. Tests of the new developed method on two typical building materials, concrete and basalt fibreboards, demonstrate the method's applicability to practical measurements.

Keywords: building materials, calorimetry, specific heat

Introduction

Specific heat is one of the important thermophysical parameters in various theoretical analyses and calculations in civil engineering, such as energy balances and the determination of temperature fields in constructions with given initial and boundary conditions. Particularly in high-temperature applications, such as in fire protection of buildings, the temperature dependence of specific heat needs to be taken into account. In large temperature ranges, the values of specific heat can reach order-of-magnitude differences [1, 2].

Using the classical adiabatic-calorimetry methods in measuring the specific heat of building materials can lead to certain difficulties due to the following reasons:

a) The samples of building materials have to be relatively large because of their inhomogeneity

b) Due to the low thermal conductivity of most of building materials it can take a relatively long time to reach temperature equilibration over large dimensions, resulting in significant heat loss.

In this paper, a nonadiabatic method for determining the temperature-dependent specific heat of large samples at high temperatures, suitable for building materials is described.

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The nonadiabatic calorimeter

The new developed calorimeter has a mixing vessel with a volume of 2.5 liters. The volume of the measuring fluid (usually water) is about 1 liter. The maximum volume of the measured samples of building materials is 1 liter.

The amount of heat loss of the nonadiabatic system is determined using a calibration. The calorimeter is filled with water, whose temperature is different from the ambient air. Then, the relation of water temperature to time, $T_c(t)$, is measured. Three mercury thermometers with the relative accuracy of 0.02 K are used to measure the water temperature. The air temperature, T_m, measured by the same thermometers at two points must be kept constant (a maximum deviation of about 1 K during the measurement is permitted). Therefore, the experiments are performed in an isolated room where sudden changes of temperature can be eliminated. The mixing vessel is located on a laboratory stand ensuring direct contact of its bottom with the ambient air. A low-speed ventilator fan near the calorimeter bucket is used to reach steady-convection conditions.

Tests show that the calibration curve $T_c(t)$ is nearly exponential; small differences in measuring conditions cause only small changes in the calibration curve. The experiments have a reproducibility better than 1%.

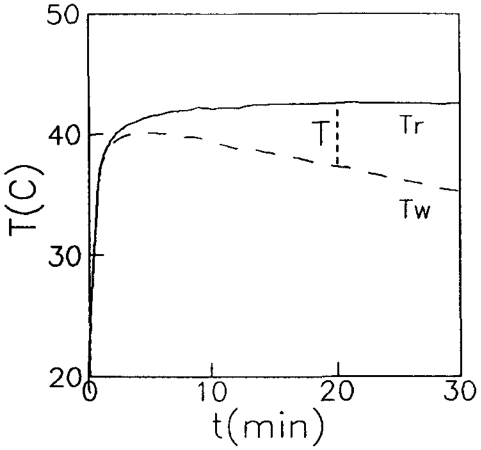

Fig. 1 Schematic of temperature corrections for the determination of the equilibrium temperature

The method of high-temperature measurement of specific heat

The measuring method is based on well-known principles. The sample is heated to a predetermined temperature T_s in a muffle furnace and then put into the calorimeter with water. Then, the relation of water temperature to time $T_w(t)$ is measured, water being slowly stirred all the time, until the temperatures of the measured sample and the calorimeter are equal. The duration of temperature equilibration ranges from 20 minutes to 1 h, depending on the thermal conductivity and size of the material being measured.

As mentioned above, the heat loss calibration curve is used to calculate the theoretical equilibrated temperature (in absence of heat loss), T_e, of the system sample-calorimeter. The principle of this approach is shown in Fig. 1. The corrected water temperature $T_r(t_i)$ taking heat loss into account can be calculated as follows:

$$T_r(t_i) = T_w(t_i) + \Delta T(t_i) \tag{1}$$

$$\Delta T(t_i) = \sum_{j=1}^{i} \Delta T(\Delta t_j) \tag{2}$$

$$t_i = \sum_{j=1}^{i} \Delta t_j \tag{3}$$

The symbols is Eqs (1)–(3) are defined in Fig. 1. The usual value of Δt_j is 1 minute. For the equilibrated temperature T_e we can write

$$T_e = \lim_{t \to \infty} T_r(t) \tag{4}$$

The heat balance of the system sample-calorimeter has the form:

$$mc(T_s - T_e) = (K + m_w c_w)(T_e - T_{wo}) + \Delta m \cdot L - Q_r, \tag{5}$$

where m is the mass of the sample, T_s is the temperature of the sample prior to being put into the calorimeter, c is the specific heat of the sample in the temperature interval $[T_e, T_s]$, K is the heat capacity of the calorimeter, m_w is the mass of the water, c_w is the specific heat of water, T_{wo} is the initial water temperature, L is the latent heat of evaporation of water, Δm is the mass of evaporated water,

$$\Delta m = m + m_{cw} - m_s - \Delta m_N - \Delta m_{sc}, \tag{6}$$

m_{cw} is the mass of the calorimeter with water before the measurement, m_s is the mass of the system calorimeter-water-sample after measurement, Δm_N is the mass of water, naturally evaporated during the measurement (this heat loss is already included in the heat loss calibration curve), Δm_{sc} is the change of mass due to the chemical reaction of the sample with water (e.g., hydrolysis). This value we can obtain as $\Delta m_{sc}=m-m_D$, where m_D is the mass of the dried sample after the measurement, and Q_r is the reaction heat.

Determining the specific heat c directly from the Eq. 5 we obtain a mean value of specific heat, c_o, in the interval $[T_e,T_s]$ by

$$c_o = \frac{(K + m_w c_w)(T_e - T_{wo}) + \Delta m \cdot L - Q_r}{m(T_s - T_e)} \tag{7}$$

However, from the physical point of view, it is more correct to determine the value of the specific heat 'pointwise', in accordance with the definition of specific heat,

$$c(T_i) = \left(\frac{\partial h}{\partial T}\right)_{T_i} \tag{8}$$

where h is the specific enthalpy.

Using relation (6) to determine specific heat, we have to specify the zero-point of the enthalpy scale, i.e., we have to ensure that all the enthalpy calculations are related to a certain constant temperature. This reference temperature can be, for example, $T_k=0°\mathrm{C}$. Upon adding

$$Q = m \cdot c_o \cdot (T_e - T_k) \tag{9}$$

where c_o is the mean specific heat of the sample in the temperature interval $[T_k,T_e]$, to both sides of Eq. (5), and dividing by m, we obtain the following

$$h(T_s) = \frac{(K + m_w c_w)(T_e - T_{wo}) + \Delta m \cdot L - Q_r}{m} + c_o(T_e - T_k). \tag{10}$$

The value of c_o is considered to be constant, taking into account the condition

$$T_s - T_e >> T_e - T_k, \tag{11}$$

and it can be measured, for example, using the classical adiabatic method.

Performing a set of measurements for various sample temperatures T_i, we obtain a set of points $[T_i,h(T_i)]$. A regression analysis of this pointwise given function results in a functional relationship for $h=h(T)$ and, using relation (8), also in the function $c=c(T)$ as the first derivative of h with respect to T.

Experimental results

The experimental measurements of specific heat in the dependence on temperature were performed on two typical building materials, concrete (the vol-

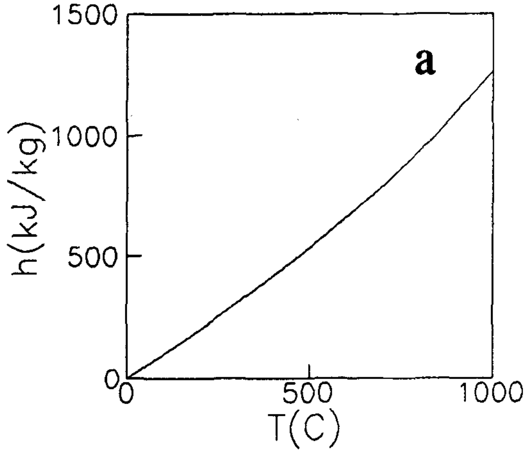

Fig. 2a Relation of the specific enthalpy of concrete to temperature

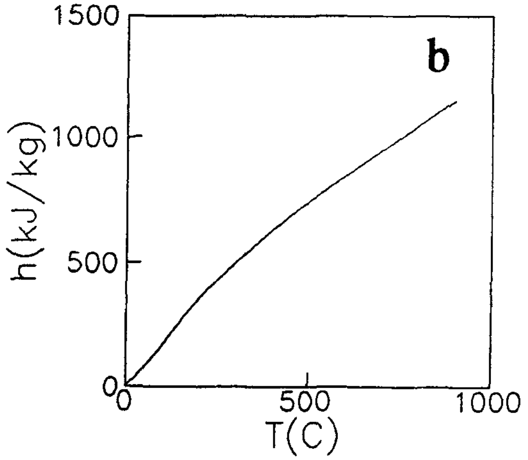

Fig. 2b Relation of the specific enthalpy of basalt fibreboards to temperature

ume mass $\rho=2250\ \mathrm{kgm}^{-3}$) and basalt fibreboards (the volume mass $\rho=150\ \mathrm{kgm}^{-3}$).

Figures 2a, b show the relations of the specific enthalpy h of concrete and basalt fibreboards to temperature, computed using relation (10).

Figures 3a, b show the corresponding specific heat relations to temperature for the mentioned materials. Solid lines in Figs 3a, b mean the computations using the pointwise definition (8), dashed lines the mean specific heat in the temperature interval $[T_e,T]$, computed by relation (7).

The results show (Fig. 3a) that for concrete, the $c(T)$ curve has an increasing character in the whole temperature range from 0°C to 1000°C, which is an expected character of the temperature dependence of specific heat [1]. However, the specific heat of basalt fibreboards (Fig. 3b) increases only in the temperature interval 0–200°C but sharply decreases in the range 200–500°C. The physical reason for these changes of specific heat lies in structural changes in the material due to burning-out or the dry distillation of certain components (e.g., organic bond). Above 500°C, the specific heat is almost independent of temperature; this is due to a certain stabilization of the material before its thermal degradation at approximately 900°C.

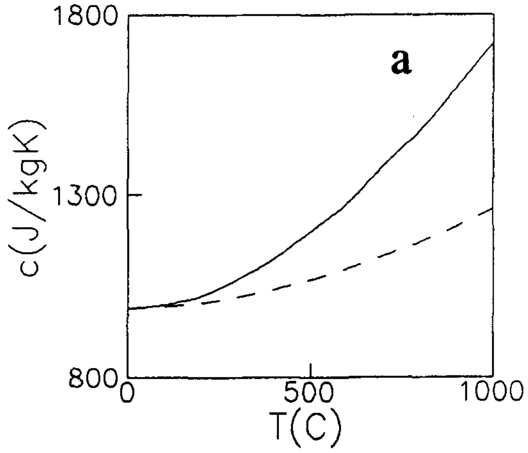

Fig. 3a Temperature dependence of the specific heat of concrete; the solid line is for the pointwise value, the dashed line for the mean value

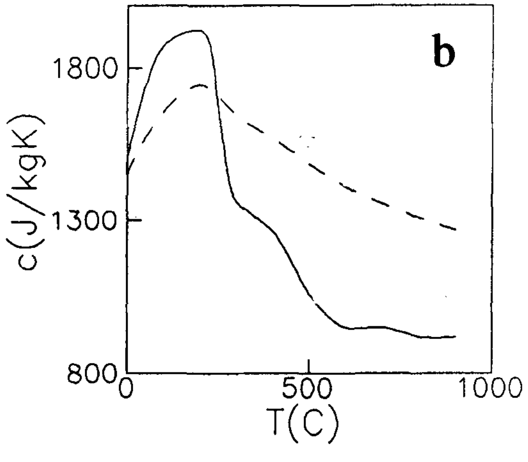

Fig. 3b Temperature dependence of the specific heat of basalt fibreboards; the solid line is for the pointwise value, the dashed line for the mean value

The determination of specific heat using the method presented above includes measurements of many quantities which are subject to further numerical analysis. Therefore, an estimate of experimental and numerical uncertainties is desirable. The estimates of experimental errors can be summarized as follows:

$$m = \pm 0.01 \text{ g}$$

$$(\Delta T)_1 = \pm 0.02 \text{ K (water temperature)}$$

$$(\Delta T)_2 = \pm 2 \text{ K (temperature in the furnace).}$$

Using these estimates in an error analysis of Eq. (10), and then Eq. (8) leads to a margin of error for the measurements of specific heat performed in this paper of $\delta_c < 8\%$. Inhomogeneity of most building materials results in local differences of density which typically reach 5–10%. Thus, the local differences in other thermophysical parameters due to the inhomogeneity should be of the same order. Considering this fact, the accuracy of the new developed method is quite satisfactory.

Conclusion

The nonadiabatic method for determining specific heat which was described in this paper is relatively simple and is suitable for measurements on large samples of inhomogeneous materials in a wide temperature range. The pointwise measurement of specific heat makes it possible to include the influence of structural changes during the heating process, and to determine the temperature range of chemical reactions in the heated material. This knowledge can be very useful, particularly in the solution of problems related to fire protection of buildings. Good heat insulating materials effective at lower temperatures are not necessarily good fire protecting materials. Once an exotherm reaction occurs at higher temperatures, due for example to the fact that the material contains organic compounds, the effective value of specific heat decreases rapidly and the material loses its heat insulating function because the temperature conductivity increases.

References

1 J. Toman, Influence of External Conditions on Building Materials and Constructions (in Czech) Thesis, CTU Prague 1986.
2 J. Toman and O. Kutman, Effect of External Influences on Thermophysical Parameters of Building Materials. CTU Prague, 1986.

Zusammenfassung — Klassische adiabatische Methoden zur Messung der spezifischen Wärme in einem breiten Temperaturbereich sind für homogene, gut definierte Substanzen sehr geeignet. Dagegen fordern Messungen an inhomogenen Stoffen umfangreiche Proben, was den Einsatz von adiabatischen Behandlungen äußerst teuer macht. Vorliegend wird eine nichtadiabatische Methode zur Ermittlung der spezifischen Wärme von inhomogenen Baustoffen in einem Temperaturbereich von –30 bis 1200°C vorgestellt. Diese Methode ist relativ einfach, sehr billig und ausreichend genau für den Einsatz bei Baustoffen. Die Erprobung der neu entwickelten Methode an zwei typischen Baustoffen wie Beton und Basaltfiberplatten zeigen die Einsetzbarkeit der Methode für praktische Messungen.