

METHODS FOR DETERMINATION OF HIGH-TEMPERATURE PROPERTIES OF ALUMINOSILICATES

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Abstract:

Methods suitable for determination of high temperature values of specific heat capacity and thermal conductivity of alkali activated aluminosilicate materials are presented in the paper and their practical application is tested for a selected aluminosilicate composite in the temperature range up to 1200 °C.

Keywords:

Aluminosilicates, high temperatures, thermal conductivity, specific heat capacity

INTRODUCTION

Alkali-activated aluminosilicate materials are known to exhibit remarkable high-temperature resistance and very favorable mechanical properties. Therefore, this type of materials is capable of replacing classical Portland or blended cement as traditional binder in concrete in the situation where high temperature resistance of the material is required. The knowledge of their high-temperature properties is, however, indispensable for their proper application in fire resistance measures. In this paper, methods suitable for determination of high temperature values of specific heat capacity and thermal conductivity of alkali activated aluminosilicate materials are presented and their practical application is tested for a selected aluminosilicate in the temperature range up to 1200 °C.

METHODS FOR DETERMINATION OF HIGH-TEMPERATURE PROPERTIES

As the adiabatic methods are not very suitable for measuring high-temperature specific heat capacity of building materials, mainly because of the necessity to use relatively large samples, a nonadiabatic method by Toman and Černý [1] was chosen for the determination of temperature-dependent specific heat capacity. We will present the main idea of the method in what follows.

The nonadiabatic calorimeter has a mixing vessel with a volume of 2.5 L. The volume of the measuring fluid (water in this case) is about 1 L. The maximum volume of the measured samples is 1 L. 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. Six thermocouples are used to measure the water temperature. The air temperature measured by the same thermometers at two points must be kept constant (the 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.

The measuring method itself is based on well-known principles. The sample is heated to a predetermined temperature T_s in a 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 corrected (adiabatic) temperature $T_r(t)$ taking the heat loss into account is calculated using the corrections $\Delta T(t_i)$ obtained from the calibration curve $T_c(t)$,

$$T_r(t_i) = T_w(t_i) + \Delta T(t_i), \quad (1)$$

where

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

$$t_i = \sum_{j=1}^i \Delta t_j. \quad (3)$$

Practically it means that the correction of the temperature T_w at the time t_i from the beginning of the experiment due to heat loss to the surroundings during the time interval of Δt_i , $\Delta T(\Delta t_i)$, is determined using the calibration curve $T_c(t)$ at the point T_w . The total temperature correction for the time t_i is obtained by adding up the particular corrections $\Delta T(\Delta t_j)$ from the time equal to zero to the time t_i .

The theoretical equilibrated temperature of the sample-calorimeter system at the end of the test T_e is then calculated as

$$T_e = \lim_{t \rightarrow \infty} T_r(t). \quad (4)$$

The heat balance of the sample-calorimeter system can be written in the form:

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

where m is the mass of the sample, c is the specific heat capacity 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 capacity of water, T_{wo} is the initial water temperature, L is the latent heat of evaporation of water, Q_r is the reaction heat, Δm is the mass of evaporated water,

$$\Delta m = m + m_{cw} - m_s - \Delta m_N - \Delta m_{sc} \quad (6)$$

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 can be obtained as $\Delta m_{sc} = m - m_D$, where m_D is the mass of the dried sample after the measurement. The remaining symbols in Eq. (5) are the same as before.

Determining the specific heat capacity c directly from Eq. (5) we would obtain a mean value of the specific heat capacity, c_0 , in the interval $[T_e, T_s]$ by

$$c_0 = \frac{(K + m_w c_w)(T_e - T_{wo}) + \Delta m \cdot L - Q_r}{m(T_s - T_e)} \quad (7)$$

However, from the physical point of view, it is more correct to determine the value of the specific heat capacity "point-wise", in accordance with the definition of specific heat capacity,

$$c(T_i) = \frac{\partial h}{\partial T}(T_i) \quad (8)$$

where h is the specific enthalpy.

Using relation (8) to determine the specific heat capacity, 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, $T_k = 0$ °C. Upon adding

$$Q = m \cdot c_e \cdot (T_e - T_k) \quad (9)$$

where c_e is the mean specific heat capacity of the sample in the temperature interval $[0, T_e]$, to both sides of equation (5), and dividing by m , we obtain the following

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

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

$$T_s - T_e \gg T_e - T_k \quad (11)$$

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 point-wise 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 .

For the determination of high-temperature thermal conductivity we used the double integration method, a dynamic method based on an inverse analysis of the temperature field which was used previously for determination of moisture diffusivity in dependence on moisture content [2]. As the heat conduction equation is of the same type as the moisture conduction equation, the method of inverse analysis presented in [2] can be applied also for thermal conductivity determination with only slight modifications.

The basic principle of the method consists in measuring the temperature field $T(x, t)$ in the sample at one-sided heating and the subsequent solution of the inverse heat conduction problem. We suppose $T(t)$ and $T(x)$ to be monotonic functions and choose a constant value of temperature, $\tau = T(x, t)$. Then must exist one-to-one parametrizations $x = x_o(\tau, t)$, $t = t_o(\tau, x)$ where both x_o and t_o are monotonic functions. Considering this fact, an integration of heat conduction equation by x and t leads to

$$\int_{t_1}^{t_n} \int_0^{x_0(\tau,t)} \rho c \frac{\partial T}{\partial t} dx dt = \lambda(\tau) \int_{t_1}^{t_n} \frac{\partial T}{\partial x} (x_0(\tau,t), t) dt - \int_{t_1}^{t_n} \lambda [T(0,t)] \frac{\partial T}{\partial x} (0,t) dt \quad (12)$$

where

$$- \lambda [T(0,t)] \frac{\partial T}{\partial x} (0,t) = j_Q(0,t) \quad (13)$$

is the heat flux at $x=0$.

The left-hand side (LS) of Eq. (12) can be modified by accounting for the shape of the integration area:

$$LS = \int_{t_1}^{t_n} \int_0^{x_0(\tau,t)} \rho c \frac{\partial T}{\partial t} dx dt = \int_0^{x_0(\tau,t)} dx \int_{t_1}^{t_n} \rho c \frac{\partial T}{\partial t} dt + \int_{x_0(\tau,t_1)}^{x_0(\tau,t_n)} dx \int_{t_0(\tau,x)}^{t_n} \rho c \frac{\partial T}{\partial t} dt \quad (14)$$

Denoting

$$\int \rho c \frac{\partial T}{\partial t} dt = \int \rho(T)c(T)dT = I_T(T) \quad (15)$$

we obtain

$$\begin{aligned} LS &= \int_0^{x_0(\tau,t_n)} [I_T(T(x,t_n)) - I_T(T(x,t_1))] dx + \int_{x_0(\tau,t_1)}^{x_0(\tau,t_n)} [I_T(T(x,t_n)) - I_T(\tau)] dx = \\ &= \int_0^{x_0(\tau,t_n)} I_T(T(x,t_n)) dx - \int_0^{x_0(\tau,t_1)} I_T(T(x,t_1)) dx - I_T(\tau)[x_0(\tau,t_n) - x_0(\tau,t_1)] \end{aligned} \quad (16)$$

Substituting (16) into (12) we arrive at

$$\lambda(\tau) = \frac{\int_0^{x_0(\tau,t_n)} I_T(T(x,t_n)) dx - \int_0^{x_0(\tau,t_1)} I_T(T(x,t_1)) dx - I_T(\tau)[x_0(\tau,t_n) - x_0(\tau,t_1)] - \int_{t_1}^{t_n} j_Q(0,t) dt}{\int_{t_1}^{t_n} \frac{\partial T}{\partial x} (x_0(\tau,t), t) dt} \quad (17)$$

where for $t_j > t_i$ the heat flux at $x=0$ can be calculated as

$$j_Q\left(0, \frac{t_j + t_i}{2}\right) = \frac{1}{t_j - t_i} \int_0^D [\rho(T)c(T)T(x,t_j) - \rho(T)c(T)T(x,t_i)] dx \quad (18)$$

where D is the length of the one-dimensional domain under consideration.

The measuring procedure consists then in the following. One-side heating of a specimen (for cement based materials and similar composites typically 71x71x71 mm) with thermally insulated

lateral faces is realized using a furnace where a constant temperature is maintained. Along the longitudinal axis of the sample, a set of temperature sensors is positioned, which makes it possible to record the temperature field through a measuring unit by a PC. From the measured $T(x, t_i)$ curves, a set of 8-10 curves is chosen, and these curves are used in the computational treatment. First, the measured $T(x, t_i)$ curves are subject of a regression analysis. Then, we choose a temperature value τ , determine the integration area for this value and calculate the corresponding value of thermal conductivity $\lambda(\tau)$ by Eq. (17). This procedure is repeated for a sufficient number of τ values so that we finally obtain a point-wise given function $[\tau_i, \lambda(\tau_i)]$.

MATERIALS AND SAMPLES

Fine-ground slag of Czech origin (Kotouč Štramberk, Ltd.) was used for sample preparation. As alkali activator, water glass solution was used. It was prepared using Portil-A dried sodium silicate preparative (Cognis Iberia, s.l. Spain). The sand aggregates were normalized according to EN 196-1 with the granulometry PG1, PG2, PG3. The composition of the mixture for sample preparation is presented in Table 1.

The technology of sample preparation was as follows. First, the silicate preparative was mixed with water. The solution was then mixed into the homogenized slag-sand mixture. The final mixture was put into 71x71x71 mm molds and vibrated. The specimens were demolded after 24 hours and then stored for further 27 days in water bath at laboratory temperature. Three specimens were studied for every measurement.

Table 1 Composition of mixture for sample preparation

Sand [g]			Slag [g]	Alkali-activation silicate admixture [g]	Water [ml]
PG1	PG2	PG3			
450	450	450	450	90	190

EXPERIMENTAL RESULTS AND DISCUSSION

Bulk density and open porosity of the studied aluminosilicate material in dependence on temperature are presented in Table 2. The data were obtained using the common water vacuum saturation method. We can see that the porosity begins to increase significantly after heating to 600 °C, achieves its maximum at 800 °C, and at 1000 °C and 1200 °C it is not changed significantly.

Table 2 Porosity and bulk density of the studied aluminosilicate material as functions of temperature

Temperature [°C]	Porosity [m^3/m^3]	Bulk density [kg/m^3]
25	0.18	2170
200	0.22	2100
400	0.17	2170
600	0.22	2070
800	0.24	2030
1000	0.24	2050
1200	0.23	2050

Fig. 1 shows the dependence of specific heat capacity of the studied aluminosilicate material on temperature. The $c(T)$ function has a maximum between 400 °C and 500 °C and after decreasing a little at 700 °C it begins to increase very sharply, with a maximum at about 1100 °C. This last maximum is too high for any pure specific heat capacity considerations (it exceeds two times the value of specific heat capacity of water). However, it should be noted that the result of the applied method is in fact a value of “effective specific heat capacity” which may also reflect some other changes in enthalpy as for instance the enthalpy of chemical reactions taking place in a particular temperature range or enthalpy of phase change. In our case it means that a highly exothermal reaction could take place in the temperature range of approximately 800-1100 °C.

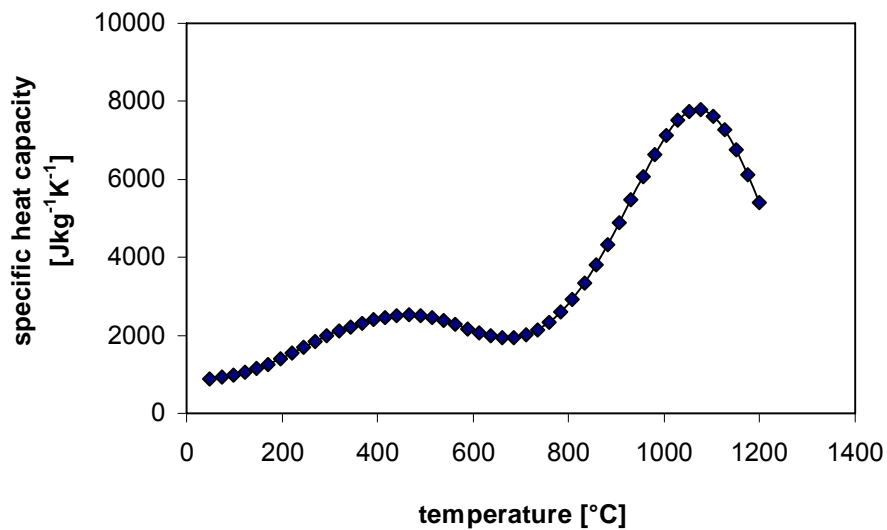


Figure 1 Specific heat capacity of the studied aluminosilicate material as function of temperature

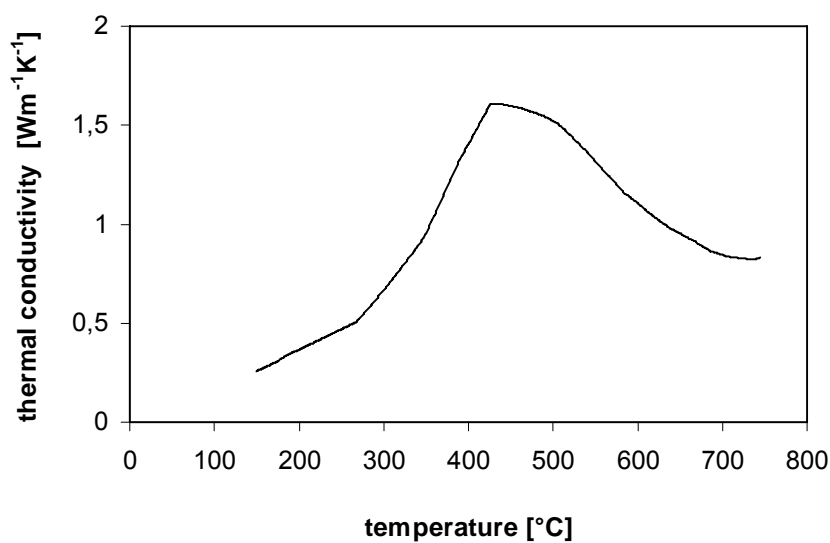


Figure 2 Thermal conductivity of the studied aluminosilicate material as function of temperature

The thermal conductivity vs. temperature function determined by the double integration method in Fig. 2 increased about three times between 150 °C and 400 °C and then it began to decrease. The observed increase in thermal conductivity may be related to the increase in porosity in the temperature range of 25-600 °C (see Table 2). The later decrease may be caused by the structural changes in the material resulting in variations of the porous structure.

CONCLUSIONS

The methods for measurement of specific heat capacity and thermal conductivity in high temperature range up to 1200 °C in this paper were shown to be well applicable for the studied alkali activated aluminosilicate. The material itself was found to be very stable up to 1200 °C and its thermal conductivity decreased with the increasing temperature for the temperatures higher than 400 °C which is a very positive feature for a material potentially applicable as fire protecting layer in building structures.

ACKNOWLEDGEMENT

This research has been supported by the Ministry of Education, Youth and Sports of Czech Republic, under grant No MSM: 6840770031.

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