High temperature thermal properties of alkali activated aluminosilicate materials

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Abstract
High-temperature values of specific heat capacity, thermal diffusivity and thermal conductivity of an alkali activated aluminosilicate material on slag basis are measured in the temperature range up to 1200°C. The material is supposed to replace classical Portland or blended cement as traditional binder in concrete in the situation where high temperature resistance of the material is required. The irregularities observed on the measured dependences of specific heat capacity and thermal diffusivity on temperature are discussed using the results of DTA and X-ray diffraction analyses. The crystallization of akermanite is identified as the most important factor affecting the properties of the studied material in high-temperature range.

Key words: aluminosilicates, specific heat capacity, thermal diffusivity, thermal conductivity, high temperatures

1. Introduction
In the determination of fire resistance of building structures, the time period when the structure is capable of performing its heat-insulating function and protecting the other parts of the building from a fast temperature increase is one of the most important parameters. Duration of this period depends primarily on the external conditions such as the temperature of the fire. On the other hand, the influence of thermal material parameters of the fire-protecting structures is also very significant. Among these parameters, the thermal conductivity and the specific heat capacity are of greatest importance. Generally, most material parameters are commonly measured at room temperature only. The high-temperature range is usually not very interesting for engineers and designers. This may sometimes lead to serious mistakes in the evaluation of the structure’s response to a fire because for instance thermal conductivity of many materials can increase with temperature in the high temperature region.

Alkali-activated aluminosilicates belong to perspective materials in the field of fire protection because they exhibit remarkable high-temperature resistance (see e.g. Rovnaníková and Bayer, 2001) and very favorable mechanical properties (e.g. Byfors et al., 1989, Robins et al., 1992, Douglas et al., 1992 or the survey in Wang et al., 1995). 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.

Although the potential for high-temperature applications of aluminosilicate materials is obvious for years (see e.g. Davidovits, 1999), the measurements of their properties in high-
temperature range are very sparse in the scientific literature. The work by Shoaib et al. (2001) who studied the effect of heating to 600°C on the compressive strength of mortars on the basis of alkali-activated slag and by Rovnaníková and Bayer (2001) who studied the behavior of alkali-activated slag at high temperatures up to 1200°C belong to the few exceptions. Thermal parameters such as thermal conductivity and specific heat capacity were not yet seriously measured even in normal conditions. The dependence of thermal properties on high temperatures was not studied at all.

In this paper, high temperature values of thermal conductivity, thermal diffusivity and specific heat capacity of an alkali activated aluminosilicate material are measured in the temperature range up to 1200°C.

2. Materials and samples
Fine-ground slag of Czech origin (Kotouč Štramberk, Ltd.) was used for sample preparation. Its chemical composition is shown in Table 1, its granulometry in Table 2. 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 3.

Table 1 Chemical composition of applied slag

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>MnO</th>
<th>Cl⁻</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>38.6</td>
<td>0.52</td>
<td>7.22</td>
<td>38.77</td>
<td>12.90</td>
<td>0.50</td>
<td>0.06</td>
<td>0.21</td>
<td>0.38</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 2 Slag granulometry

<table>
<thead>
<tr>
<th>Sieve residue</th>
<th>Specific surface [cm²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.045 mm [%]</td>
<td>12.4</td>
</tr>
<tr>
<td>0.09 mm [%]</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>3920</td>
</tr>
</tbody>
</table>

Table 3 Composition of mixture for sample preparation

<table>
<thead>
<tr>
<th>Sand [g]</th>
<th>Slag [g]</th>
<th>Alkali-activation silicate admixture [g]</th>
<th>Water [ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG1</td>
<td>PG2</td>
<td>PG3</td>
<td>1350</td>
</tr>
<tr>
<td>1350</td>
<td>1350</td>
<td>1350</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td></td>
<td>190</td>
</tr>
</tbody>
</table>

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.
3. Experimental methods for determination of thermal parameters in high-temperature range

3.1. Specific heat capacity

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 (1993) was employed 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 liters. The volume of the measuring fluid (water in this case) is about 1 liter. The maximum volume of the measured samples 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, $T_w(t)$, is measured.

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 $\Delta T(t_j)$ obtained from the calibration curve $T_c(t)$,

$$T_r(t) = T_w(t) + \Delta T(t)$$

where

$$\Delta T(t) = \sum_{j=1}^{i} \Delta T(t_j)$$

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

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

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

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

$$mc(T_s - T_e) = (K + m_w c_w)(T_e - T_{w0}) + \Delta m \cdot L - Q_r$$

where $m$ is the mass of the sample, $c$ is the specific heat capacity of the sample in the temperature interval $[T_s, T_e]$, $K$ is the heat capacity of the calorimeter, $m_w$ is the mass of the water, $c_w$ is the specific heat capacity of water, $T_{w0}$ is the initial water temperature, $L$ is the latent heat of evaporation of water, $Q_r$ is the reaction heat, $\Delta m$ is the mass of evaporated water,
\[ \Delta m = m + m_{cw} - m_s - \Delta m_N - \Delta m_{sc} \]  

(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, \( \Delta m_N \) is the mass of water, naturally evaporated during the measurement (this heat loss is already included in the heat loss calibration curve), \( \Delta m_{sc} \) 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

\[ c_0 = \frac{(K + m_n c_n)(T_e - T_{wo}) + \Delta m \cdot L - Q_e}{m(T_s - T_e)} \]  

(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,

\[ c(T_i) = \frac{\partial h}{\partial T}(T_i) \]  

(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, \( T_k = 0^\circ \text{C} \). Upon adding

\[ Q = m \cdot c_e \cdot (T_e - T_k) \]  

(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

\[ h(T_i) = \frac{(K + m_n c_n)(T_e - T_{wo}) + \Delta m \cdot L - Q_e}{m} + c_e(T_e - T_k). \]  

(10)

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

\[ T_s - T_e \gg T_e - T_k \]  

(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 $T$.

### 3.2. Thermal diffusivity

For the determination of high-temperature thermal diffusivity the double integration method by Drchalová and Černý (1998) was used. The method was developed originally for moisture transport as a dynamic method based on an inverse analysis of moisture field. For heat conduction equation and temperature field it can be applied with minor changes only which are described in what follows.

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

$$
\int_{t_o}^{t_o x_o(\tau,t)} \int_0^{x_o(\tau,t)} \frac{\partial T}{\partial t} \, dx \, dt = \frac{a(\tau)}{\int_{t_o}^{t_o x_o(\tau,t)} \int_0^{x_o(\tau,t)} \frac{\partial T}{\partial x} (x_o(\tau,t),t) \, dx \, dt} - \int_{t_o}^{t_o} \frac{j_q(0,t)}{\rho(\tau) c(\tau)} \, dt
$$

where $j_q(0,t)$ 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:

$$
LS = \int_{t_o}^{t_o x_o(\tau,t)} \int_0^{x_o(\tau,t)} \frac{\partial T}{\partial t} \, dx \, dt = \int_0^{x_o(\tau,t)} \frac{\partial T}{\partial x} (x_o(\tau,t),t) \, dx + \int_0^{x_o(\tau,t)} \frac{\partial T}{\partial t} \, dx \int_{t_o}^{t_o x_o(\tau,t)} \int_0^{x_o(\tau,t)} \frac{\partial T}{\partial t} \, dt (13)
$$

Denoting

$$
\int \frac{\partial T}{\partial t} \, dt = \int dT = I_T(T)
$$

we obtain

$$
LS = \int_0^{x_o(\tau,t)} \left[ I_T(T(x,t)) \right] dx + \int_{x_o(\tau,t)}^{x_o(\tau,t)} \left[ I_T(T(x,t)) - I_T(T(x, t_o)) \right] dx = \left[ I_T(T(x,t)) \right] dx - \left[ I_T(T(x,t)) \right] dx - I_T(\tau) [x_o(\tau,t) - x_o(\tau,t_o)]
$$

Substituting (15) into (12) we arrive at
\[
\int_{x_0(t_0,t_i)}^{x_0(t_i,t_j)} I_T(T(x,t))\,dx - \int_{x_0(t_0,t_i)}^{x_0(t_i,t_j)} I_T(T(x,t))\,dx - I_T(\tau)[x_0(\tau,t_a) - x_0(\tau,t_i)] - \int_{t_i}^{t_j} \frac{\partial T}{\partial x}(x_0(\tau,t),t)\,dt
\]

\[
a(\tau) = \frac{\int_{t_i}^{t_j} j_\mathcal{Q}(0,t)\,dt}{\rho(\tau)c(\tau)}
\]

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

\[
j_\mathcal{Q}\left(0, \frac{t_j + t_i}{2}\right) = \frac{1}{t_j - t_i} \int_0^D \left[ \rho(T)c(T)T(x,t_j) - \rho(T)c(T)T(x,t_i) \right]\,dx
\]

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 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 \( T(x,t_j) \) curves, a set of 8-10 curves is chosen, and these curves are used in the computational treatment. First, the measured \( T(x,t_j) \) curves are subject of a regression analysis. Then, we choose a temperature value \( \tau \), determine the integration area for this value and calculate the corresponding value of thermal diffusivity \( a(\tau) \) by Eq. (16). This procedure is repeated for a sufficient number of \( \tau \) values so that we finally obtain a point-wise given function \( [\tau, a(\tau)] \).

### 3.3. Thermal conductivity

Thermal conductivity was calculated using the values of thermal diffusivity, specific heat capacity and density according to the common formula

\[
\lambda(T) = a(T)\rho(T)c(T)
\]

### 4. Experimental results and discussion

Bulk density and open porosity of the studied aluminosilicate material in dependence on temperature are presented in Table 4. The data were obtained using the common water vacuum saturation method (see e.g. Roels et al., 2004). We can see that the porosity begins to increase significantly after heating to 600\(^\circ\)C, achieves its maximum at 800\(^\circ\)C, and at 1000\(^\circ\)C and 1200\(^\circ\)C it is not changed significantly.

Table 4 Porosity and bulk density of the studied aluminosilicate material as functions of temperature

<table>
<thead>
<tr>
<th>Thermal load [(^\circ)C]</th>
<th>Porosity [(\text{m}^3/\text{m}^3)]</th>
<th>Bulk density [(\text{kg/m}^3)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.18</td>
<td>2170</td>
</tr>
<tr>
<td>200</td>
<td>0.22</td>
<td>2100</td>
</tr>
<tr>
<td>400</td>
<td>0.17</td>
<td>2170</td>
</tr>
<tr>
<td>600</td>
<td>0.22</td>
<td>2070</td>
</tr>
<tr>
<td>800</td>
<td>0.24</td>
<td>2030</td>
</tr>
<tr>
<td>1000</td>
<td>0.24</td>
<td>2050</td>
</tr>
<tr>
<td>1200</td>
<td>0.23</td>
<td>2050</td>
</tr>
</tbody>
</table>
Fig. 1 Specific heat capacity of the studied aluminosilicate material as function of temperature

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 (see Černý et al., 1996, for a more detailed analysis). In our case it means that a highly exothermal reaction could take place in the temperature range of approximately 800-1100°C.

The thermal diffusivity 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 diffusivity may be related to the increase in porosity in the temperature range of 25-600°C (see Table 4). The later decrease may be caused by the structural changes in the material resulting in variations of the porous structure.

![Graph](image)

**Fig. 3** Thermal conductivity of the studied aluminosilicate material as function of temperature

The thermal conductivity in Fig. 3 calculated from the values of thermal diffusivity, specific heat capacity and bulk density clearly follows the course of the $a(T)$ function. This is a common feature as the changes in thermal diffusivity with temperature are usually more significant then the changes in specific heat capacity or bulk density.

For a possible explanation of the irregularities observed on the measured $c(T)$ and $a(T)$ curves, additional material characterization experiments were performed. Fig. 4 shows the results of thermal analysis. The exothermal peak at the DTA curve at about 800°C corresponds with the beginning of the sharp increase in effective specific heat capacity observed in Fig. 1. The fast loss of mass on the TG curve in the temperature range of 100-300°C corresponds then with the increase of thermal diffusivity presented in Fig. 2. Therefore, it can be concluded that the results of thermal diffusivity and specific heat capacity measurements seem to agree with the DTA results in a qualitative way.
The loss of mass in the temperature range of 100-300°C was due to decomposition of CSH gels. It corresponds to water removal from reaction products. From the temperature 300 °C up to 800°C the mass subsequently decreased due to evolution of water from hydrated aluminosilicates and the residual water from CSH gels.
In order to explain the exothermal peak at about 800°C, X-ray diffraction analysis was done on the same material without aggregates for better identification of main features. Fig. 5 shows the reference material. The relatively high X-ray-amorphous background can be attributed to the CSH gels, i.e. to the main reaction product. The highest peak in Fig. 5 corresponds to the mineral akermanite, Ca$_2$MgSi$_2$O$_7$. Fig. 6 shows the results of the X-ray diffraction analysis of the sample subjected to heating to 1000°C which is well above the exothermal peak at about 800°C in the DTA analysis. Here, the X-ray-amorphous background practically disappeared so that it could be concluded that the CSH gels were decomposed. However, the amount of akermanite in Fig. 6 dramatically increased compared to the laboratory temperature which probably indicated its crystallization. Therefore, it can be assumed that the release of the latent heat of crystallization of akermanite was responsible for both the 800°C peak at the DTA curve and for the dramatic increase of the effective specific heat capacity in the temperature range of 800-1100°C.

5. Conclusions

The measurements of specific heat capacity, thermal diffusivity and thermal conductivity of the alkali activated slag based material in the temperature range up to 1200°C in this paper have shown that the material has a good potential for its future high-temperature applications in civil engineering. Both thermal diffusivity and thermal conductivity of the material 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.

The material characterization experiments using DTA and X-ray diffraction revealed a very good high-temperature resistance of the studied material. The mass loss was very low for temperatures higher than 300°C and almost negligible for temperatures higher than 800°C. The crystallization of akermanite beginning at approximately 800°C indicates a substantial change in the porous structure of the binder which should lead to an improvement in mechanical properties of the material. This is another sound argument for its further, more detailed investigation aimed to its industrial application.
Acknowledgements
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References


