Water Transport Properties of Alkali Activated Alumino-silicate Composite Determined by Two Different Methods

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Abstract: Moisture diffusivity of alkali activated alumino-silicate composite with electrical porcelain aggregates is determined as function of thermal loading up to 1200°C using two different methods. The first method is based on the sorptivity concept and provides a single moisture diffusivity value which can be considered as apparent moisture diffusivity. The second method consists in inverse analysis of moisture profiles measured for characteristic times in a 1-D experiment with simple initial and boundary conditions. It makes possible to determine moisture diffusivity as function of moisture content. Experimental results show that the moisture diffusivity depends on previous thermal load in a very significant way. One-order-of-magnitude increase in moisture diffusivity is observed after heating to 1200°C compared to reference specimens.

Key words: Alumino-silicate materials, moisture diffusivity, sorptivity, moisture profiles

INTRODUCTION

Alkali-activated alumino-silicates belong to perspective materials in the field of fire protection because they exhibit remarkable high-temperature resistance and very favorable mechanical properties (Zuda et al., 2006). Therefore, this type of materials is potentially 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. However, a successful application of alkali-activated alumino-silicates in building structures is not as straightforward as with common cement based materials and requires a more detailed knowledge of their properties and behavior in various external environments. Unfortunately, properties of alkali activated alumino-silicate materials were studied only relatively seldom to date. In most cases, just mechanical properties at normal temperatures were investigated (Palacios and Puertas, 2005, 2007; Puertas et al., 2006).

Water transport properties are of particular importance for alkali activated alumino-silicates. Fast water removal from a material which is supposed to be subjected to high temperatures is critical to avoid damage of the porous structure. Nevertheless, the current state of knowledge of these parameters is far from ideal. The first problem is already in the definition of water transport parameters because transport processes of water in composite materials can be described basically by two different treatments. The first one utilizes the analogy to water transport in soils and employs the hydraulic conductivity K (m sec⁻¹) defined by the Darcy’s law (Bear, 1988).
\[ v = -K \text{ grad } h \] (1)

Where:
- \( v \) = The average velocity of water in porous medium,
- \( v = Q/A, \ Q = \) The rate of flow of water (m\(^3\) sec\(^{-1}\)),
- \( A \) = The cross-sectional area of the porous medium,
- \( h = \) The hydraulic head (m).

This description is employed by the most of researchers specialized in the testing of concrete (Neville, 1995; Bazant and Kaplan, 1996; Christensen et al., 1996; El-Dieb and Hooton, 1995; Halamickova et al., 1995). The coefficient of hydraulic conductivity is denoted here water permeability which is probably a matter of tradition.

An alternative treatment which is preferred by the researchers working in the field of building physics (Kiesel, 1983; Kuenzel, 1995; Pleinert et al., 1998) uses the moisture diffusivity \( \kappa \) (m\(^2\) sec\(^{-1}\)) as the main phenomenological coefficient:

\[ j = -\kappa \text{ grad } \rho_m \] (2)

Where:
- \( j \) = The water flux (kg m\(^{-2}\) sec\(^{-1}\)),
- \( \rho_m \) = The partial density of water in a porous material which can be expressed using either moisture content by mass \( u \),
- \( \rho_m = \rho_u, \ \rho_u \) = The partial density of the porous matrix, or moisture content by volume \( w \),
- \( \rho_m = \rho_w, \ \rho_w \) = The density of water.

As for the quality of description of water transport in porous media, the two aforementioned treatments are practically equivalent, although both soil physicists and building physicists restrict themselves for one of them in most cases. However, it looks again more or less like a matter of tradition. In any case, the phenomenological coefficients are convertible between each other as it has been shown already by Philip and de Vries (1957).

In isothermal conditions, a simple relation between \( K \) and \( \kappa \) can be derived taking into account that

\[ j = \rho_w v \] (3)

Commonly used assumptions \( \rho_u = \text{const.}, \ \rho_w = \text{const.} \) lead to the following conversion formulas

\[ \kappa = K \frac{\rho_w}{\rho_u} \frac{\partial h}{\partial u} \] (4)

\[ \kappa = K \frac{\partial h}{\partial w} \] (5)

Where, \( \frac{\partial h}{\partial u}, \ \frac{\partial h}{\partial w} \) can be obtained from the water retention curves \( h = h(u) \) or \( h = h(w) \), respectively.

The second, possibly even more important problem with the water transport parameters of alkali activated aluminosilicates is that they were not measured very frequently until now. The papers by
Shi (1996) who measured water permeability of concrete based on the alkali-activated slag and Černý et al. (2006) who determined moisture diffusivity of alkali activated slag mortar with quartz sand aggregates belong to the very few exceptions.

In this study, water transport parameters of alkali activated aluminosilicate material with electrical porcelain aggregates which is subjected to various thermal pre-treatment conditions are studied which should add to the currently very limited knowledge of this type of parameters. As for the type of analyzed water transport properties, the second of the treatments mentioned above is followed and moisture diffusivity as the main water transport parameter is determined using two independent methods, namely using the sorptivity concept and the inverse analysis of moisture profiles.

**MATERIALS AND METHODS**

**Basic Properties**

The bulk density, matrix density and open porosity were the properties analyzed for getting the basic characteristics of the studied material. The water vacuum saturation method (Roels et al., 2004) was used in the measurements. Each sample was dried in a drier to remove majority of the physically bound water. After that the samples were placed into the desiccator with deaired water. During three hours air was evacuated with vacuum pump from the desiccator. The specimen was then kept under water not less than 24 h.

From the mass of water saturated sample \( m_w \) and the mass of the immersed water saturated sample \( m_{ws} \), the volume \( V \) of the sample was determined from the equation

\[
V = \frac{m_{ws} - m_w}{\rho_i}
\]

Where, \( \rho_i \) is the density of water. The open porosity \( \psi_o \), the bulk density \( \rho \) and the matrix density \( \rho_{mat} \) were calculated according to the equations:

\[
\psi_o = \frac{m_w - m_d}{V\rho_i}
\]

\[
\rho = \frac{m_d}{V}
\]

\[
\rho_{mat} = \frac{m_d}{V(1 - \psi_o)}
\]

Where:

- \( m_d \) = The mass of the dry sample.

**Water Sorptivity**

Water sorptivity was analyzed using a standard experimental setup. The specimen was water and vapor-proof insulated on four lateral sides and the face side was immersed 1-2 mm in the water, constant water level in tank was achieved by a Mariotte bottle with two capillary tubes. One of them, inside diameter 2 mm, was duded under the water level, the second one, inside diameter 5 mm, was above water level. The automatic balance allowed for recording the increase of mass. The water absorption coefficient \( A \) (kg m\(^{-3}\) sec\(^{-1/2}\)) was then calculated using the formula:
\[ i = A \sqrt{t} \]

Where:
\( i \) = The cumulative water absorption (kg \( \text{m}^{-3} \)),
\( t \) = The time from the beginning of the suction experiment.

The water absorption coefficient was then employed for the calculation of the apparent moisture diffusivity in the form (Corny et al., 2002)

\[ \kappa_{eq} \approx \left( \frac{A}{w_s - w_e} \right)^2 \]

Where:
\( w_s \) = The saturated moisture content (kg \( \text{m}^{-3} \)),
\( w_e \) = The initial moisture content (kg \( \text{m}^{-3} \)).

**Moisture Profiles**

In the experimental determination of moisture profiles (Fig. 1) the specimen is fixed in horizontal position in order to eliminate the effect of gravity on moisture transport. The lateral sides of the specimen are water and vapor-proof insulated in order to simulate 1-D water transport. A viscous sponge arranged for a good contact of the specimen surface with water is put into a Perspex water-filling chamber and applied to one face side of the specimen. The sponge sucks water from a free surface being about 10 mm below the lower side of the specimen. Water in the chamber is maintained on constant level using a float. If water level in the filling chamber decreases due to water suction by the specimen, water level in the float chamber decreases in the same way. The needle of the float opens the hole in the cover of the float chamber and water from a burette flows through the hole into the float chamber until the needle closes the hole again due to water level increase. In this way, a continuous

![Experimental setup for determination of moisture profiles](image-url)
water supply to the measured specimen is achieved. After specified time of water uptake, the experiment is interrupted, the specimen cut into 1 cm thick pieces and the moisture profile determined by the gravimetric method.

Inverse Analysis

The experimental moisture profiles were approximated by the linear filtration method with Gaussian weights (Hamming, 1962) and the moisture diffusivity calculated in dependence on moisture content using the Matano method (Matano, 1933).

For determination of moisture diffusivity coefficient by the Matano method, it is necessary to know one moisture profile and the time from the start of experiment corresponding to this curve. The Matano method consists in application of Boltzmann transformation, which is possible to be used for short times, when the boundary condition on the dry end of the specimen is not yet effective (Drchalová and Černý, 1998).

The moisture balance equation is formulated in the non-linear diffusion form:

\[
\frac{\partial \tilde{u}}{\partial t} = \frac{\partial}{\partial x} \left( \kappa(\tilde{u}) \frac{\partial \tilde{u}}{\partial x} \right),
\]  

(12)

Where:
\( \tilde{u} \) = The moisture content by mass (kg kg\(^{-1}\)),
\( \kappa \) = The moisture diffusivity (m\(^2\) sec\(^{-1}\)).

with the boundary conditions

\[ u(0, t) = u_1 \] \hspace{1cm} (13)

\[ u(l, t) = u_2 \] \hspace{1cm} (14)

and the initial condition

\[ u(x, 0) = u_3 \] \hspace{1cm} (15)

Where:
\( l \) = The length of the specimen,
\( u_1 \) = The moisture content on the wet end of the specimen,
\( u_2 \) = The moisture content on the dry end of the specimen.

The Boltzmann transformation

\[ \eta = \frac{\kappa}{2\sqrt{t}} \] \hspace{1cm} (16)

gives

\[
\frac{d}{d\eta} \left( \kappa(\eta) \frac{d\tilde{u}}{d\eta} \right) + 2\eta \frac{d\tilde{u}}{d\eta} = 0
\] \hspace{1cm} (17)

with
\[ u(x, t) = \alpha(\eta) \]  

(18)

The boundary conditions are now expressed as:

\[ \alpha(0) = u_0 \]  

(19)

\[ \alpha(\infty) = u_i \]  

(20)

Equation 17 can be integrated with the result (Drchalová and Černý, 1998)

\[ \kappa(\omega_c) = \frac{2}{\frac{d\omega}{dx}(\eta_0)} \int_{\eta_0}^{\infty} \eta \frac{d\omega}{dx} d\eta \]  

(21)

Where: \( \omega_c = \omega(\eta_0) \).

If only the moisture distribution \( u(x) \) in time \( t = t_0 \) is known, the second transformation

\[ \eta = \frac{x}{2\sqrt{t_0}} \]  

(22)

\[ u(x, t_0) = \alpha(\eta) \]  

(23)

can be performed and Eq. 21 is transformed in the form (with \( u_z = u(x, t_0) \))

\[ \kappa(u_z) = \frac{1}{2t_0} \int_0^x \frac{du}{dx} d\eta \]  

(24)

which is more convenient for the immediate solution.

Materials and Technologies for Sample Preparation

Fine-ground slag of Czech origin (12.4% residue on 0.045 mm sieve and 1.9% on 0.09 mm sieve, the specific surface 3920 cm² g⁻¹) produced by Kotouč Štramberk, Ltd., CZ was used for sample preparation. It consisted of 38.6% SiO₂, 7.2% of Al₂O₃, 38.8% of CaO, 12.9% of MgO and some minority compounds. As alkali activator, water glass solution was used. It was prepared using Portil-A dried sodium silicate preparative (Cognis Iberia, s.l., Spain). Electrical porcelain provided by P-D Refractories CZ, Velké Opatovice, was used instead of commonly used sand aggregates because of its more convenient high-temperature properties. It consisted of 48.6% SiO₂, 45.4% of Al₂O₃, 1.0% of Na₂O, 2.9% of K₂O and some minority compounds. The granulometry of the electrical porcelain is shown in Table 1. Its porosity was 0.3%, water absorption at saturation 0.1%, bulk density 2350 kg m⁻³.

The technology of sample preparation (the exact composition of the mixture (Table 2) was as follows. First, the silicate preparative was mixed with water. The solution was then mixed in the homogenized slag-electrical porcelain mixture. The final mixture was put into molds and vibrated. The specimens were demolded after 24 h and then stored for further 27 days in water bath at laboratory temperature.
Table 1: Granulometry of electrical porcelain aggregates

<table>
<thead>
<tr>
<th>Sieve mesh (mm)</th>
<th>4.00</th>
<th>2.50</th>
<th>1.00</th>
<th>0.50</th>
<th>0.25</th>
<th>0.125</th>
<th>0.090</th>
<th>0.063</th>
<th>0.045</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sieve residue (%)</td>
<td>4.00</td>
<td>2.50</td>
<td>1.00</td>
<td>0.50</td>
<td>0.25</td>
<td>0.125</td>
<td>0.090</td>
<td>0.063</td>
<td>0.045</td>
</tr>
<tr>
<td>0-1 mm fraction</td>
<td>-</td>
<td>-</td>
<td>0.69</td>
<td>45.24</td>
<td>70.76</td>
<td>89.98</td>
<td>93.40</td>
<td>98.99</td>
<td>99.99</td>
</tr>
<tr>
<td>1-3 mm fraction</td>
<td>-</td>
<td>4.12</td>
<td>78.33</td>
<td>99.57</td>
<td>99.94</td>
<td>99.94</td>
<td>99.95</td>
<td>98.98</td>
<td>100.00</td>
</tr>
<tr>
<td>3-6 mm fraction</td>
<td>69.31</td>
<td>95.52</td>
<td>99.97</td>
<td>99.98</td>
<td>99.99</td>
<td>100.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2: Composition of mixture for sample preparation

<table>
<thead>
<tr>
<th>Electrical porcelain (g)</th>
<th>Alkali-activation silicate admixture (g)</th>
<th>Water (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1 mm fraction</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>1-3 mm fraction</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>3-6 mm fraction</td>
<td>450</td>
<td>450</td>
</tr>
</tbody>
</table>

After the 28 days curing period, the specimens were dried at 110°C and after drying subjected to thermal load. Heating of the samples to the predetermined temperature was always done with the rate of 10 K min⁻¹, then the specimens remained at that temperature for the time period of two hours and finally they were slowly cooled. The chosen pre-heating temperatures were 200, 400, 600, 800, 1000 and 1200°C.

In the experimental work, the following samples were used for every pre-treatment: basic properties-3 specimens 50×50×23 mm, water absorption-3 specimens 50×50×23 mm, moisture profiles-3 specimens 20×40×300 mm. The samples for determination of water absorption and moisture profiles were provided on all lateral sides by water- and vapor-proof plastic foil insulation.

RESULTS AND DISCUSSION

The porosity and bulk density (Table 3) were changed only moderately for heating up to 600°C. However, heating to 800 and 1000°C led to a decrease of bulk density as high as 10% and increase of porosity of about 13% which indicates structural changes and/or chemical reactions in the material. After heating to the temperature of 1200°C the studied material exhibited very similar basic properties to those at room temperature.

Figure 2 shows the moisture diffusivity κ as function of moisture content calculated using the Matano method from the measured moisture profile for all pre-treatment conditions. The values of κ were relatively high already in the reference state, about one order of magnitude higher than ceramic brick, for instance. This indicates substantial amount of capillary pores in the μm range in the material. The increase of moisture diffusivity was up to 600°C moderate only, a more remarkable increase was observed at 800 and 1000°C and the most significant it was after heating to 1200°C. This was except for 1200°C in a qualitative agreement with the porosity measurements in Table 3.

The sudden increase in moisture diffusivity after heating to 1200°C indicated formation of different type of structure in the material with high amount of large capillary pores. Therefore, additional material characterization experiments were performed using Mercury Intrusion Porosimetry (MIP) and Scanning Electron Microscopy (SEM). The increase of moisture diffusivity after heating to 1200°C was found to be in a very good agreement with the global characteristics of the pore space of the studied composite measured by MIP in dependence on thermal load in Table 4. While for lower heating temperatures the median pore radius was between 1 and 10 μm, for 1200°C thermal pre-treatment it was as high as 33 μm. Formation of a different type of structure in the material subjected to thermal pre-treatment of 1200°C was confirmed by SEM results in Fig. 3a, b. The reference specimen in Fig. 3a presented relatively compact structure with small cracks about 2-3 μm wide. After heating to 1200°C, a completely new microstructure with high amount of large pores up to 100 μm appeared as it was shown in Fig. 3b.
Table 3: Basic properties of the studied aluminosilicate composite

<table>
<thead>
<tr>
<th>Thermal load (°C)</th>
<th>Bulk density (kg m⁻³)</th>
<th>Matrix density (kg m⁻³)</th>
<th>Porosity (m³ m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15°C</td>
<td>2101</td>
<td>2659</td>
<td>0.21</td>
</tr>
<tr>
<td>200°C</td>
<td>2184</td>
<td>2835</td>
<td>0.23</td>
</tr>
<tr>
<td>400°C</td>
<td>2105</td>
<td>2756</td>
<td>0.24</td>
</tr>
<tr>
<td>500°C</td>
<td>2164</td>
<td>2860</td>
<td>0.24</td>
</tr>
<tr>
<td>800°C</td>
<td>1977</td>
<td>2726</td>
<td>0.28</td>
</tr>
<tr>
<td>1000°C</td>
<td>1048</td>
<td>2752</td>
<td>0.29</td>
</tr>
<tr>
<td>1200°C</td>
<td>2117</td>
<td>2685</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Fig. 2: Moisture diffusivity as function of moisture content

Fig. 3: SEM images of the studied alkali activated aluminosilicate composite, (a) reference specimen, (b) specimen subjected to thermal pre-treatment of 1200°C.

One of the reasons for the observed changes in pore size and in the character of microstructure observed in MIP and SEM measurements was most probably crystallization of alermanite Ca₂MgSi₅O₁₄, and the subsequent growth of its crystals after heating to higher temperatures. This was
Table 4: Global characteristics of the studied aluminosilicate composite measured by mercury intrusion porosimetry

<table>
<thead>
<tr>
<th>Thermal load</th>
<th>Total intrusion volume (cm$^3$ g$^{-1}$)</th>
<th>Total pore area (m$^2$ g$^{-1}$)</th>
<th>Median pore diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>0.059</td>
<td>3.96</td>
<td>3.46</td>
</tr>
<tr>
<td>200°C</td>
<td>0.080</td>
<td>6.62</td>
<td>4.94</td>
</tr>
<tr>
<td>400°C</td>
<td>0.059</td>
<td>3.41</td>
<td>5.84</td>
</tr>
<tr>
<td>600°C</td>
<td>0.071</td>
<td>10.48</td>
<td>1.46</td>
</tr>
<tr>
<td>800°C</td>
<td>0.125</td>
<td>0.82</td>
<td>2.61</td>
</tr>
<tr>
<td>1000°C</td>
<td>0.164</td>
<td>1.09</td>
<td>2.31</td>
</tr>
<tr>
<td>1200°C</td>
<td>0.049</td>
<td>3.33</td>
<td>33.60</td>
</tr>
</tbody>
</table>

**Fig. 4:** Apparent moisture diffusivity as function of thermal load

indicated in Zuda et al. (2006) where similar aluminosilicate composite with quartz sand aggregates was investigated using XRD method. The sudden change in the microstructure after heating to 1200°C may, however, be also related to the use of electrical porcelain aggregate. Electrical porcelain is produced at the temperature of approximately 1400°C but its stability in alkali environment is only up to 1150°C. At higher temperature it starts to melt and forms a ceramic bond with an AAS matrix (Bayer, 2005).

Figure 4 shows the apparent moisture diffusivity $\kappa_a$ calculated from the water absorption experiment. The increase of $\kappa_a$ with increasing load temperature was achieved already at 600°C but later $\kappa_a$ was stabilized at almost the same values which is a significant difference from the moisture diffusivity vs. moisture functions calculated using the Matano method in Fig. 2. This is a surprising result because for many other materials a good coincidence between the apparent moisture diffusivity and moisture dependent moisture diffusivity was achieved (Drehalová and Černý, 2003). The most probable reason for the observed differences in this study was the different space orientation of the experiments in both cases. While the water absorption experiment resulting in apparent moisture diffusivity was performed in vertical position, the moisture profiles leading to the determination of moisture dependent moisture diffusivity were measured in horizontal position. Therefore, the measurement in vertical position was probably affected by the gravity. This argument can be supported by the substantial increase of the amount of large capillary pores after heating to higher temperatures which was observed in MIP measurements in Table 4.

**CONCLUSIONS**

Water transport properties of alkali activated aluminosilicate material with electrical porcelain aggregates were studied in dependence on previous thermal treatment up to 1200°C in the paper. Moisture diffusivity $\kappa_a$ as the main water transport parameter was calculated by two methods. One of them was well established method based on measurement of moisture profiles and Boltzmann-Matano
analysis, the second was simple method based on sorptivity concept. The application of the method based on Boltzmann-Matano analysis, although more complicated and laborious, was for the studied material clearly a better choice. The sorptivity method for calculation of apparent moisture diffusivity was not found very suitable, the reason being mainly the effect of gravity on moisture transport.

Moisture diffusivity of the studied aluminosilicate composite was found to depend on moisture content in very significant way. The differences in corresponding to the lowest and highest moisture values were almost two orders of magnitude. In the reference state without thermal treatment, the moisture diffusivity values were relatively high already, about one order of magnitude higher than for ceramic brick. The thermal treatment led to further enhancement of the fast water transport capability of the material. One-order-of-magnitude increase in moisture diffusivity was observed after heating to 120°C compared to reference specimens. This feature is advantageous for a material which can potentially be utilized as fire-protecting layer. After heating to high temperatures, water evaporation and the accompanying pore pressure increase is the most frequent source of damage of composite materials, besides the thermal decomposition processes. Therefore, the studied aluminosilicate may have good prerequisites for future use in fire protection of building structures.

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