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# Properties of Alkali Activated Aluminosilicate Material after Thermal Load[1]

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The porosity, bulk density, compressive strength, bending strength, thermal conductivity, and specific heat capacity of a material based on alkali activated slag are determined at room temperature conditions for samples subjected to a thermal load up to 1200°C prior to the measurements and compared to reference material data. The results are discussed using material characterization experiments, namely, X-ray diffraction analysis and scanning electron microscopy. Experimental results show a remarkable high-temperature resistance of the studied material, which after pre-heating to 1200°C exhibits mechanical properties comparable to the reference material not exposed to any thermal load.

**KEY WORDS:** aluminosilicates; mechanical properties; thermal load; thermal properties.

## 1. INTRODUCTION

Portland or blended cement as a traditional binder in concrete is the most universal binder to date although it has a number of disadvantages, such as high energetic demand for its production, low resistance against aggressive substances, and instability at high temperatures. At the end of the 20th century a trend of low-energy binders appeared, based on the utilization of secondary raw materials. In this respect, slag is one of the possibilities to expand the range of concrete and mortars by other materials

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that meet the requirements of binders, and in many aspects, have better properties than ordinary Portland cement. Granulated blast furnace slag is used as a component of blended cements. However, in this case its hydraulic properties (i.e., its ability to form a solid structure due to the reaction with water, or, in other words, to incorporate water into a solid structure) are not fully utilized because in grinding together with clinker and gypsum, a part of the grains remains unreacted due to its difficult grindability. Alkali activation (i.e., using alkali ions for activation, mainly for the sake of increasing the hydraulic activity) of granulated blast furnace slag makes possible a more suitable and more economic utilization of its hydraulic properties.

Alkali-activated slags form high-strength materials [1]. The strength depends on the type of slag, its physical state, the activator used, and the method in which the building material is cured. The composition of the hardened product and its microstructure were studied, e.g., in Refs. 2 and 3. The reaction products have a low content of calcium and are mostly of an amorphous character.

Alkali-activated slags exhibit remarkable high-temperature resistance which makes them perspective materials for high-temperature applications, for instance as fire protecting layers in buildings and tunnels. The behavior of alkali-activated slag at high temperatures up to 1200°C was analyzed in Ref. 4.

The properties of materials on the basis of alkali-activated slag were only seldom studied to date. Mostly just mechanical properties at normal temperatures were measured (see, e.g., Refs. 5–7). Thermal parameters such as thermal conductivity and specific heat capacity were not yet measured even in normal conditions.

The effect of high temperatures on mechanical properties of aluminosilicate materials was studied in Ref. 8 where the compressive strength of mortars on the basis of alkali-activated slag after heating up to 600°C was measured. A similar effect on thermal properties was not yet studied at all. However, information on the effect of high temperatures on the properties of aluminosilicate materials might be very useful in practical applications. The high temperature resistance of these materials could be so high that they possibly could survive the conditions of fire. Then, their properties after thermal load would become a very important factor because they could be used even after high temperature exposure.

In this paper, the compressive and bending strength, the thermal conductivity and specific heat capacity of an alkali activated aluminosilicate material are determined at room temperature conditions for samples subjected to a thermal load up to 1200°C prior to the measurements and compared to reference material data.

## 2. MATERIALS AND SAMPLES

Fine-ground slag of Czech origin (Kotouè Štramberk, Ltd.) was used for sample preparation. Its chemical composition is shown in Table I, its granulometry in Table II. As an alkali activator, a water glass solution ($Na_2O{\cdot}x SiO_2 \cdot y H_2O$) was used. It was prepared using Portil-A dried sodium silicate ($Na_2SiO_3$) preparative (Cognis Iberia, s.l. Spain). The sand aggregates were normalized according to EN 196-1 with granulometry PG1, PG2, PG3. The composition of the mixture for sample preparation is presented in Table III.

The technology of sample preparation was as follows. First, the silicate preparative was mixed with water. The solution was then mixed in the homogenized slag–sand mixture. The final mixture was put into 71 × 71 × 71 mm molds (for thermal parameter measurements) or 40 × 40 × 160 mm molds (for mechanical parameter measurements) and vibrated. The specimens were demolded after 24 h and then stored for additional 27 days in a water bath at laboratory temperature.

After the 28-day curing period, the specimens were dried at 110°C, and after drying, subjected to a thermal load. Heating of the samples to

**Table I.** Chemical Composition of Applied Slag (in mass%)

| $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | MgO | MnO | Cl− | $Na_2O$ | $K_2O$ | $SO_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 38.6 | 0.52 | 7.22 | 38.77 | 12.90 | 0.50 | 0.06 | 0.21 | 0.38 | 0.36 |

**Table II.** Slag Granulometry

| Sieve residue | | |
|---|---|---|
| 0.045 mm (%) | 0.09 mm (%) | Specific surface ($cm^2{\cdot}g^{-1}$) |
| 12.4 | 1.9 | 3920 |

**Table III.** Composition of Mixture for Sample Preparation

| Sand (g) | | | | | |
|---|---|---|---|---|---|
| PG1 | PG2 | PG3 | Slag (g) | Alkali-activation silicate admixture (g) | Water (ml) |
| 450 | 450 | 450 | 450 | 90 | 190 |

the predetermined temperature was always done at the rate of $10\,\mathrm{K\cdot min^{-1}}$, then the specimens remained at that temperature for a time period of 2 h and finally they were slowly cooled at the rate of $1\,\mathrm{K\cdot min^{-1}}$. The chosen pre-heating temperatures were 200, 400, 600, 800, 1000, and 1200°C. Three specimens were investigated for each thermal state.

## 3. EXPERIMENTAL METHODS

First, the basic properties of the material were studied. The water vacuum saturation method and mercury porosimetry were used for the investigations.

In the water vacuum saturation measurements, the bulk density and the open porosity were determined. 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 de-aired water. For a period of 3 h air was evacuated with a vacuum pump from the desiccator. The specimen was then kept under water not less than 24 h.

From the mass of the dry sample $m_\mathrm{d}$, the mass of the water saturated sample $m_\mathrm{w}$, and the mass of the immersed water saturated sample $m_\mathrm{a}$, the volume $V$ of the sample was determined from the equation,

$$V = \frac{m_\mathrm{w} - m_\mathrm{a}}{\rho_\mathrm{l}}, \tag{1}$$

where $\rho_\mathrm{l}$ is the density of water. The open porosity $\psi_0$ and the bulk density $\rho$ were calculated according to the equations,

$$\psi_0 = \frac{m_\mathrm{w} - m_\mathrm{d}}{V\rho_\mathrm{l}} \tag{2}$$

$$\rho = \frac{m_\mathrm{d}}{V}. \tag{3}$$

The error in the water vacuum saturation measurements is estimated to be less than 5%, based on the differences within a set of measurements on different specimens.

The mercury porosimetry measurements were performed using the porosimeter Micromeritics Pore Sizer 9310—maximum working pressure 200 MPa, pore distribution in the range of 300–0.006 $\mu$m. Both global characteristics of the porous space and the pore distribution curves were measured.

The compressive strength and the bending strength were determined as the mechanical properties are the most characteristic for aluminosilicates. The bending strength was measured by the standard 3-point bending test using a 500 kN testing device. The compressive strength was determined by a compression test using the same device. It was carried out on the parts of the specimens broken in the bending test. The measurement error in the determination of the compressive strength and the bending strength is estimated to be less than 5%, based on the differences within a set of measurements on different specimens.

The thermal conductivity and specific heat capacity were the thermal properties determined for the studied material. The thermal conductivity was measured in laboratory conditions using the commercial device Isomet 2104 (Applied Precision, Ltd.). Isomet 2104 is equipped with various types of optional probes; needle probes are for porous, fibrous or soft materials, and surface probes are suitable for hard materials. The measurement is based on an analysis of the temperature response of the analyzed material to heat flow impulses. The heat flow is induced by electrical heating using a resistor heater having a direct thermal contact with the surface of the sample.

The measurements were carried out as a function of moisture content. The specimens were first dried at 110°C. Then, they were partially water saturated and placed into a 100% relative humidity environment for 3 days so that moisture could be homogenized inside a specimen.

Measurement errors in the determination of the thermal conductivity using the impulse method described above can be determined only indirectly because a commercial device was used, which is, in fact, a "black box" from the point of view of data evaluation. The calibration error can be estimated on the basis of a comparison of measured values with the declared values of the etalons provided by the producer. In the particular case of measurements in this paper, the differences from the declared values were less than 3.5%. Naturally, there were also random errors due to the nonhomogeneity of the samples that had to be added to this error. These were estimated to be less than 5%, based on the differences within a set of measurements on different specimens.

The specific heat capacity of dry materials was determined by the mixing calorimeter method in a water calorimeter. Calibration of the water calorimeter (tight Dewar flask) was carried out using warm water of a similar heat capacity as that of the sample. To determine the specific heat capacity of wet materials, we used the mixing rule. The content of moisture in a porous material does not significantly change its volume. So, we can write for the volumetric specific heat capacity $\rho_{\text{wet}} c_{\text{wet}}$ [in $\text{J}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$]

$$\rho_{\text{wet}} c_{\text{wet}} = \rho_{\text{dry}} c_{\text{dry}} + \rho_{\text{w}} c_{\text{w}} w \tag{4}$$

$$\rho_{\text{wet}} = \rho_{\text{dry}} + \rho_{\text{w}} w, \tag{5}$$

where $\rho_{\mathrm{wet}}$ is the apparent bulk density of the wet material, $\rho_{\mathrm{dry}}$ is the bulk density of the dry material, $\rho_{\mathrm{w}}$ is the density of water [in kg·m$^{-3}$], $w$ is the moisture content by volume [m$^3$/m$^3$], and $c_{\mathrm{wet}}$, $c_{\mathrm{dry}}$, and $c_{\mathrm{w}}$ are the specific heat capacities of the wet material, the dry material, and water, respectively [in J·kg$^{-1}$·K$^{-1}$].

## 4. EXPERIMENTAL RESULTS AND DISCUSSION

Table IV shows the basic characteristics of the studied aluminosilicate material determined by a water vacuum saturation method after thermal load. The porosity began to increase significantly after pre-heating to 600°C, achieved its maximum at 800°C, and at 1000°C and 1200°C, it was not changed significantly.

The values of porosity determined by mercury porosimetry shown in Table V were systematically lower than those determined by the water vacuum saturation method. This is an expected result in general because the dimensions of the samples are significantly lower for mercury porosimetry

**Table IV.** Dependence of the Basic Properties of the Studied Material on Thermal Load as Measured by the Water Vacuum Saturation Method

| Thermal load (°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 |

**Table V.** Dependence of the Basic Properties of the Studied Material on Thermal Load as Measured by Mercury Porosimetry

| Thermal load (°C) | Total intrusion volume (cm$^3$·g$^{-1}$) | Total pore area (m$^2$·g$^{-1}$) | Median pore diameter ($\mu$m) | Bulk density (kg·m$^{-3}$) | Porosity (m$^3$/m$^3$) |
|---|---|---|---|---|---|
| 25 | 0.053 | 1.53 | 5.09 | 2170 | 0.12 |
| 200 | 0.061 | 3.02 | 4.97 | 2130 | 0.13 |
| 600 | 0.096 | 7.92 | 5.53 | 2040 | 0.20 |
| 1200 | 0.113 | 2.01 | 32.6 | 2050 | 0.23 |

so that big pores and cracks may not be included in the resulting porosity value. However, the basic trend concerning the increase of porosity with temperature was confirmed and the values of porosity determined by both methods were closer to each other with an increase of temperature. The most dramatic increase in porosity was for mercury porosimetric measurements observed again at 600°C. The values of porosity at 1200°C were the same for the water vacuum saturation method and mercury porosimetry. This indicates a significant change of structure and disappearance of major cracks not detectable by mercury porosimetry.

In Fig. 1 the pore distribution curves show that while for lower temperatures the main peak was at about 3 $\mu$m, after pre-heating to 1200°C it was shifted to about 30 $\mu$m where it already appeared in a less notable form after pre-heating to 600°C. This indicates again a remarkable change in the structure of the material after pre-heating.

Table VI shows that the dependence of mechanical properties on the pre-heating temperature was not monotonic as is usual for many other building materials. Both the compressive strength and bending strength achieved their minimum values at 800°C where the compressive strength was about 5 times and the bending strength 2.5 times lower than for reference specimens, and then they began to increase. After pre-heating to 1200°C, the compressive strength was only about 12% lower and the bending strength 18% lower than those of reference specimens.

The effect of the pre-heating temperature on thermal conductivity of the studied aluminosilicate material in the dry state is presented in Table VII. Similarly as with the porosity and the mechanical properties, the first

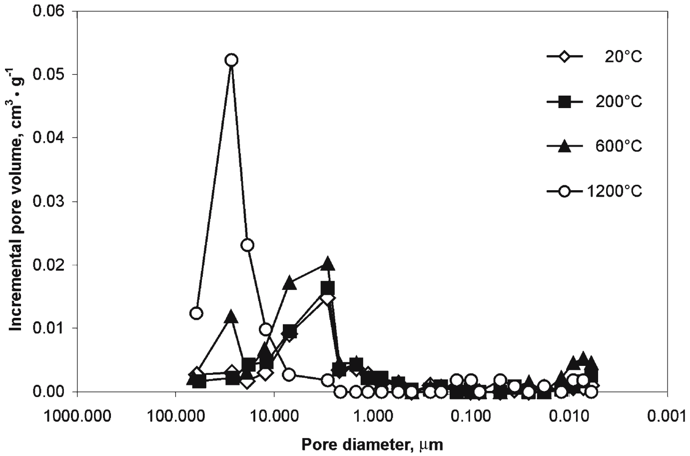

**Fig. 1.** Dependence of the pore distribution curves of the studied material on thermal load.

**Table VI.** Dependence of the Mechanical Properties of the Studied Material on Thermal Load

| Thermal load (°C) | Bending strength (MPa) | Compressive strength (MPa) |
|---|---|---|
| 25 | 4.4 | 55.8 |
| 200 | 4.4 | 44.6 |
| 400 | 3.8 | 45.6 |
| 600 | 2.6 | 31.4 |
| 800 | 1.7 | 9.9 |
| 1000 | 2.2 | 14.8 |
| 1200 | 3.6 | 48.7 |

**Table VII.** Dependence of the Thermal Properties of Dry Material on Thermal Load

| Thermal load (°C) | Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$) | Specific heat capacity ($J \cdot kg^{-1} \cdot K^{-1}$) | Thermal diffusivity ($10^{-6} m^2 \cdot s^{-1}$) |
|---|---|---|---|
| 25 | 1.59 | 798 | 0.92 |
| 200 | 1.60 | 781 | 0.99 |
| 400 | 1.67 | 743 | 1.04 |
| 600 | 1.09 | 754 | 0.70 |
| 800 | 0.94 | 777 | 0.59 |
| 1000 | 1.10 | 789 | 0.67 |
| 1200 | 1.16 | 738 | 0.77 |

remarkable change was observed for pre-heating to 600°C. The thermal conductivity decreased here by about 30% in comparison with the reference material and the decrease continued at 800°C where it was about 40%. For higher pre-heating temperatures, the thermal conductivity was stabilized approximately at the values measured for 600°C pre-heating.

The pre-heating temperature was also an important factor for the shape of the thermal conductivity vs. moisture relation as is shown in Fig. 2. The almost linear $\lambda(w)$ function characteristic for pre-heating temperatures up to 400°C was suddenly changed into a convex-type function at 600°C and then again into a concave-type function for higher pre-heating temperatures. Another interesting feature of the thermal conductivity measurements was that the maximum values achieved for the highest moisture content were very similar for all pre-heating temperatures taking into account the typical ±10% error range of the applied measuring method. These changes in the effect of water content on thermal

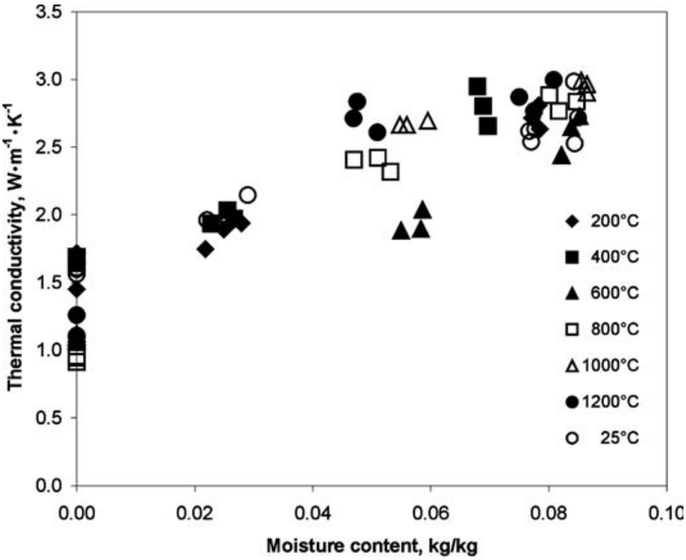

**Fig. 2.** Dependence of the thermal conductivity of the studied material on moisture content and thermal load.

conductivity indicate again significant structural changes in the material due to high-temperature exposure.

The changes in the specific heat capacity of the dry aluminosilicate material due to pre-heating (Table VII) were much less important than the changes in thermal conductivity. The typical differences were less than 5%, which is on the edge of the error range of the measuring method. Therefore, we can conclude that the pre-heating process did not lead to any detectable changes in the specific heat capacity. The dependence of the specific heat capacity on moisture content in Fig. 3 was also found to be quite regular, with no detectable differences between the cases corresponding to the particular pre-heating temperatures.

The measurements of basic, mechanical, and thermal parameters of the studied aluminosilicate material as a function of the pre-heating temperature revealed three important temperatures from the point of view of parameter changes. The first was 600°C when the first remarkable reduction of mechanical parameters appeared accompanied by an increase in porosity and a decrease in thermal conductivity. Here, the changes in all studied properties corresponded well in a qualitative sense. The main reason for the reduced mechanical properties of the material was probably the transition of $SiO_2$ in the aggregates from the $\beta$-form to the $\alpha$-form,

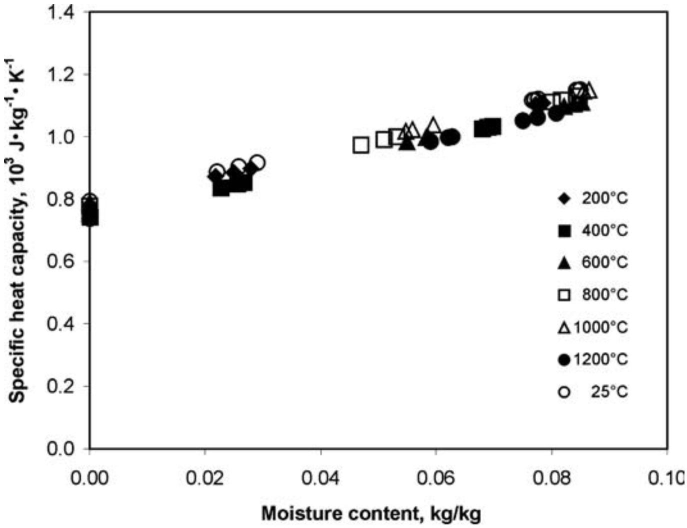

**Fig. 3.** Dependence of the specific heat capacity of the studied material on moisture content and thermal load.

which takes place at 573°C and is accompanied by volume changes. The damage of the interfacial zone is illustrated on the SEM image in Fig. 4. The X-ray diffraction analysis performed on the same material without aggregates for a better identification of main features did not show any changes in the phase composition in the temperature range up to 600°C as is documented in Fig. 5. The relatively high X-ray-amorphous background can be attributed to the CSH gels, i.e., to the main reaction product which maybe surprisingly was not yet decomposed at 600°C. The highest peaks on Fig. 5 correspond to the mineral akermanite, $Ca_2MgSi_2O_7$.

The second important temperature from the point of view of the properties of the studied aluminosilicate material was 800°C where the minima of mechanical properties and thermal conductivity and the maximum of porosity were achieved. Here, the main factor was the CSH gels decomposition as is shown in XRD results in Fig. 6 where the X-ray-amorphous background practically disappeared. It should be noted that the amount of akermanite in Fig. 6 dramatically increased compared to lower temperatures which probably indicated the beginning of its crystallization but this behavior was not yet reflected in an improvement in mechanical properties.

The third significant temperature was 1200°C where the mechanical properties were remarkably improved but the porosity remained at its high

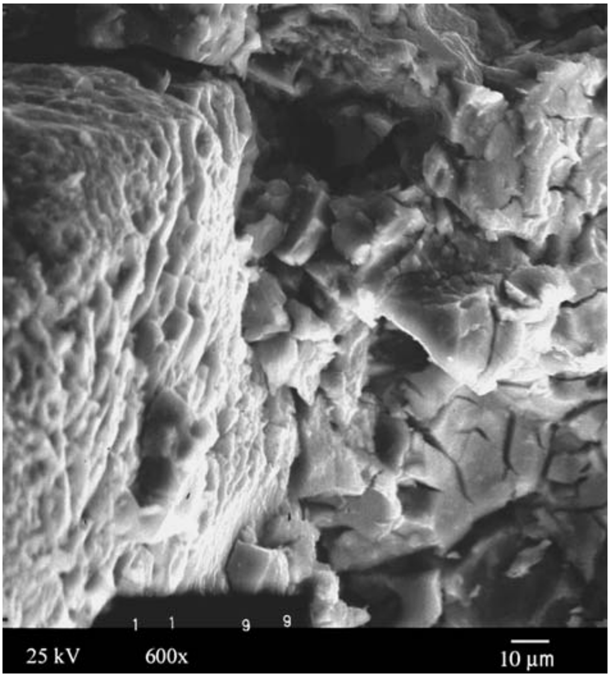

**Fig. 4.** SEM image of the aggregate-binder interface after pre-heating to 600°C.

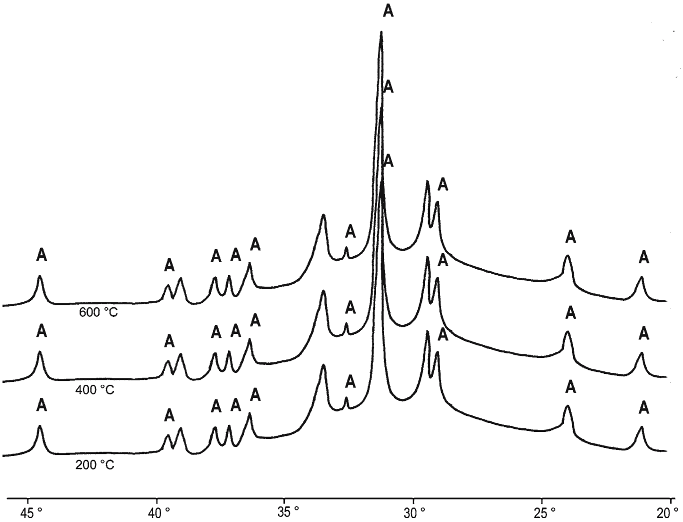

**Fig. 5.** X-ray diffraction analysis of the studied aluminosilicate material without aggregates pre-heated to 200, 400, and 600°C.

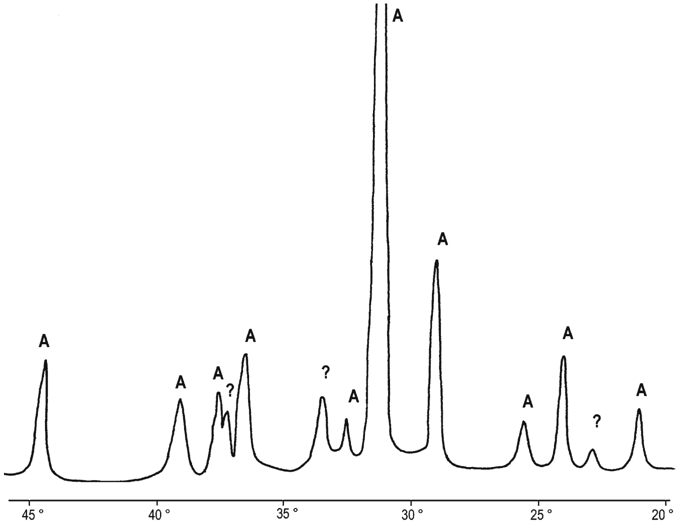

**Fig. 6.** X-ray diffraction analysis of the studied aluminosilicate material without aggregates pre-heated to 800°C.

value and the thermal conductivity at its correspondingly low value. The most probable reason for this behavior was the growth of akermanite crystals on the seeds formed at lower temperatures, which was promoted by the high temperature environment. This statement is supported by XRD results in Fig. 7 where the amount of the akermanite phase was remarkably increased. The transition of the binder phase was apparently completed after pre-heating to 1200°C. As is documented in the SEM image of the binder-aggregate interface in Fig. 8, the cracks in the binder phase disappeared due to a sintering process and the contact between aggregates and the new binder phase was re-established. Therefore, the improvement of mechanical properties was quite logical. The difference in porosity and thermal conductivity as compared to the reference material was due to the appearance of a new binder phase on the basis of akermanite which had different properties than the original CSH structure.

## 5. CONCLUSIONS

The results of measurements of basic, mechanical, and thermal parameters of the aluminosilicate material based on slag alkali activated by water glass after a thermal load up to 1200°C revealed good potential use of this material in practical applications. The original CSH structure

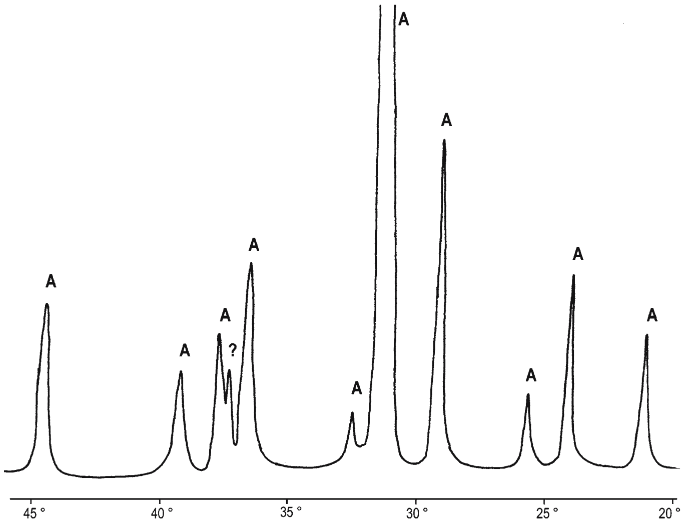

**Fig. 7.** X-ray diffraction analysis of the studied aluminosilicate material without aggregates pre-heated to 1200°C.

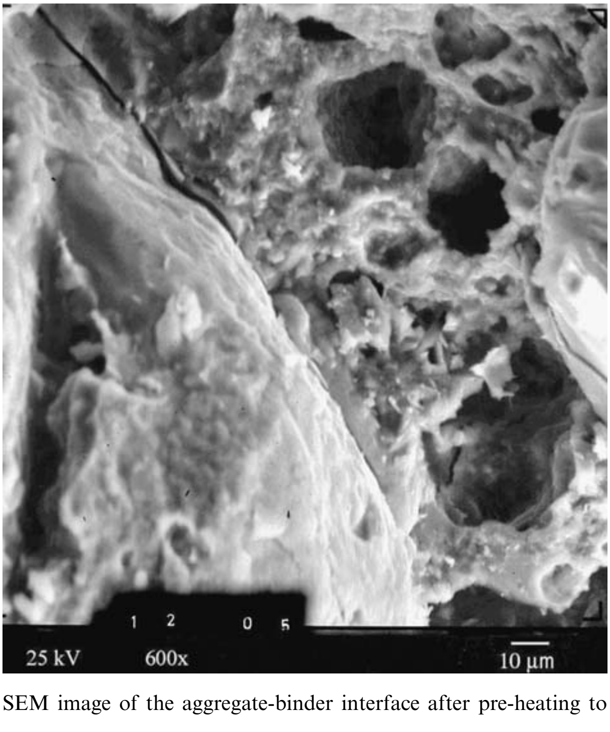

**Fig. 8.** SEM image of the aggregate-binder interface after pre-heating to 1200°C.

of the binder was, after high-temperature exposure, found to be gradually replaced by a new structure based on akermanite which, after preheating to 1200°C, exhibited superior mechanical properties comparable with the properties of the original material not subjected to any thermal load. In addition, the porosity of the material increased significantly after pre-heating to 1200°C. This makes very good pre-requisites for using the material in such applications where traditional cement-based materials fail, for instance, as fire protection materials, or using it in the form of protective layers for the current reinforced concrete structures, for instance, in tunnels. Taking into account that the material is partially based on waste materials, which serve as secondary raw materials for the forming of the binder system, it is possible to consider it as a low-energy material, so that it meets a trend common in recent production processes.

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