GEOPOLYMERIZATION OF LOW-GRADE BAUXITE

GEOPOLIMERIZACIJA REVNEGA BOKSITA

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In terms of quality, bauxite ore can be classified as high- or low-grade ore. High-grade bauxite ores are used for alumina extraction using the Bayer process, while low-grade bauxite ores have a limited application. In this paper we investigate the possibility of evaluating low-grade bauxite ores with the geopolymerization process. The influence of the synthesis parameters, i.e., alkali and silicate dosages and alkali cations (Na^+ and K^+) on the compressive strength of bauxite-based geopolymers is evaluated. The results show that an increase in the alkali dosage has a beneficial effect on the strength of bauxite-based geopolymers, while the strengthening of geopolymers by increasing the silicate dosage is limited by the viscosity of the geopolymer paste. Moreover, Na-geopolymers reach higher values of the compressive strength than K-geopolymers.

Keywords: geopolymerization, low-grade bauxite, alkali-cation geopolymerization degree, compressive strength

Glede na kvaliteto delimo boksitne rude na revne in bogate. Bogate se uporabljajo za pridobivanje glinice po Bayerjevem postopku, medtem ko ima revna boksitna ruda le omejeno uporabnost. V tem članku opisujemo preiskavo možnosti za oceno revne boksitne rude s postopkom geopolimerizacije. Ocenjeni so bili parametri sinteze, to je dodatek alkalij in silikatov ter alkalnih kationov (Na^+ in K^+) na tlačno trdnost geopolimera na osnovi boksita. Rezultati so pokazali, da povečanje dodatka alkalij ugodno vpliva na trdnost geopolimera na osnovi boksita, medtem ko je utrjevanje geopolimera z dodajanjem silikatov omejeno z viskoznostjo geopolimerne paste. Poleg tega doseže Na-geopolimer večjo tlačno trdnost v primerjavi s K-geopolimerom.

Ključne besede: geopolimerizacija, revni boksit, stopnja alkalijske kationske geopolimerizacije, tlačna trdnost

1 INTRODUCTION

Bauxite ore is the most important Al-bearing ore, comprised of aluminium, silica, titania, iron oxides and traces of impurities. It is mainly used for alumina extraction with the Bayer process. The efficiency of aluminium extraction from bauxite ore greatly depends on the content of reactive silica. With respect to alumina and silica contents, bauxite ores can be of high (metallurgical) or low (non-metallurgical) grade. The Bayer process only utilizes the high-grade (metallurgical) bauxite with high alumina and low reactive-silica contents. On the other hand, low-grade bauxite is characterised by a higher content of reactive silica. Reactive silica includes silica phases in the form of clay or quartz, which restrict its processing with the traditional Bayer process because of a loss of soda and alumina. Effective processing of low-grade bauxite for alumina production includes a pre-treatment which renders the silica unreactive during the Bayer digestion or allows a separation of silica from bauxite.[1] The soda-sinter process or a combination of Bayer-sinter processes are mainly used to produce alumina from low-grade bauxite.[2] Nevertheless, these processes are characterised by high energy consumption which does not qualify them as efficient methods for alumina production. Chemical pre-treatments of low-grade bauxite with a selective flocculation[3]

and direct or reverse flotation[4,5] are promising methods for de-silicating low-grade bauxite and hydrometallurgical processing for alumina extraction.

On the other hand, a high silica content in low-grade bauxites makes them suitable for the geopolymerization process. Geopolymerization is a relatively new technology that can transform natural or waste aluminosilicate materials, with alkali activation, into an amorphous to semi-crystalline inorganic polymer – the geopolymer.[6] The process includes several steps: dissolution of the starting material in a highly alkaline silicate solution and formation of aluminate and silicate monomeric species, formation of Si and/or Si–Al oligomers in an aqueous solution, condensation of oligomeric species in an aluminosilicate network – geopolymer, and hardening.[7] Mixtures of sodium or potassium hydroxide solutions and alkaline silicate solutions (water glass) are mainly used as activators in the geopolymerization process. The role of alkali cations in the geopolymerization process is twofold:

- the Si^{4+} and Al^{3+} cations in geopolymer gels are tetrahedrally coordinated as $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ and are linked by oxygen bridges;[8] the negative charge on the AlO_4^- group is charge-balanced by alkali cations,[9]
- alkali cations also influence the dissolution step of the geopolymerization process by acting as catalysts

in the dissolution of Al and Si from the starting materials[10].

In this paper we investigate the influence of synthesis parameters and alkali cations on the geopolymerization process.

2 EXPERIMENT

2.1 Materials and the geopolymer synthesis

Low-grade bauxite from the Paklarica deposit in Montenegro, with its granulation below 100 μm, was used for a geopolymer synthesis. Its chemical composition is given in **Table 1**.

Table 1: Chemical composition of low-grade bauxite
Tabela 1: Kemijska sestava revnega boksita

Component	w/%
SiO_2	15
Fe_2O_3	13
Al_2O_3	54
TiO_2	2
CaO	0.45
Na_2O	0.2
MgO	0.15
MnO	0.1
Cr_2O_3	0.09
K_2O	0.1
LOI*	14.9

*Loss on ignition

A mixture of sodium- or potassium-based alkaline and silicate solutions was used as an activator. The alkaline silicate solution was prepared by mixing MOH and M_2SiO_3 (M represents the Na or K ion) solutions with the mass ratios of 1, 1.5 and 2. Commercial sodium and potassium silicate solutions ($w(Na_2O) = 8.5$ %, $w(SiO_2) = 28.5$ %, the density of 1.39 kg/m³; $w(K_2O) = 13.18$ %, $w(SiO_2) = 26.38$ %, the density of 1.39 kg/m³) were used.

Geopolymer paste was prepared by mixing bauxite with the alkaline silicate solution at the solid to liquid (*S/L*) ratio of 2.5. The paste was cast in a closed, plastic cylindrical mould, with the dimensions of 28 mm × 60 mm and cured for 72 h at 65 °C (24 h in a closed mould, 24 h in an open mould and after the samples were removed from the moulds, they were left to cure for another 24 h). The geopolymer samples were left for 14 days at ambient temperature before any testing was performed.

2.2 Characterisation techniques

Compressive strength measurements were performed according to the MEST EN 1354:2011 standard using two cylinders of each sample and averaging the obtained experimental values.

Microstructural investigations were carried out using the FEI 235 DB focussed ion-beam system, equipped with an EDAX energy dispersive spectrometer (EDS). The SEM images were recorded with various electron detectors, including a secondary electron detector (SED) and through-the-lens back scattered detector (TLD-B).

The pore-size distribution and surface area were evaluated using N_2 adsorption/desorption isotherms that were measured with an ASAP 2020 instrument. Degassing of the geopolymer samples was performed at 100 °C for 24 h to ensure the removal of the moisture in the samples. Surface areas were calculated using the Brunauer-Emmet-Teller (BET) method,[11] while the pore-size distribution and cumulative pore volumes were determined with the Barret-Joyner-Halenda (BJH) method.[12]

The degree of geopolymerization reaction for the bauxite-based geopolymers was investigated with chemical processes using the method described by Rattanasak et al.[13]

A geopolymer powder sample (3 g) was dissolved using 30 ml of 2 M HCl and stirred for 20 min at 60 °C. After this, a separation of the solid and liquid phases was performed with filtration and the remaining solid was washed with warm water to completely remove HCl. In the final filtration step, acetone was applied to remove the water before drying the sample at 70 °C for 2 h. After this treatment, dissolution of the remaining solid with 30 ml of 3 % $w(Na_2CO_3)$ was carried out for 20 min at 80 °C. Finally, another separation of the solid and liquid phases was performed; the residual sample was washed with water and acetone and dried at 70 °C for 2 h. The mass of the solid residue (the unreacted bauxite) was determined and the geopolymerization degree (*GD*) was calculated using the following equation 1:

$$GD = \frac{m_{sample} - \left[m_{residue} \cdot (1-LOI)\right]}{m_{sample}}, \% \qquad (1)$$

where m_{sample} is the mass of the powder sample in grams, $m_{residue}$ is the mass of the residual solid in grams and LOI is the loss on ignition of the powder sample of the bauxite-based geopolymer.

3 RESULTS AND DISCUSSION

3.1 Compressive strength

A change in the compressive strength of bauxite-based geopolymers as a function of synthesis parameters is given in **Figures 1** and **2**. It is evident that an increase in the NaOH concentration from 7 M to 13 M leads to an increase in the compressive strength of bauxite-based geopolymers (**Figure 1**), with the maximum value (27.36 MPa) achieved with 13 M NaOH. Additionally, this sample is characterized by the highest *GD* value (32.6 %). The role of NaOH in the geopolymerization process is to provide sufficient concentration of OH⁻ ions for breaking the Al–O–Si and Si–O–Si bonds in bauxite and freeing Al^{3+} and Si^{4+}, which in an alkali-silicate solution form aluminate $[Al(OH)_4]^-$ and silicate
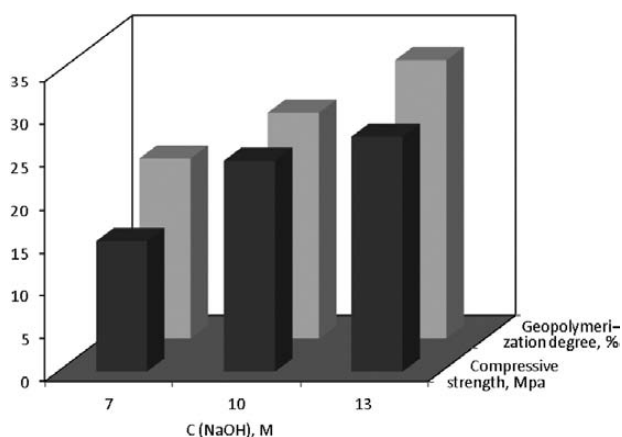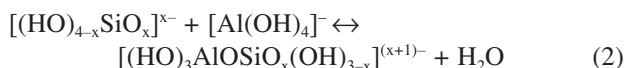
Figure 1: Change in the compressive strength of bauxite-based geopolymers as a function of the NaOH concentration with the $w(Na_2SiO_3)/w(NaOH)$ mass ratio of 1.5
Slika 1: Spreminjanje tlačne trdnosti geopolimerov iz boksita v odvisnosti od koncentracije NaOH pri masnem razmerju $w(Na_2SiO_3)/w(NaOH)$ 1,5

Figure 2: Change in the compressive strength of bauxite-based geopolymers as a function of the $w(Na_2SiO_3)/w(NaOH)$ mass ratio for the C (NaOH) of 13 M
Slika 2: Spreminjanje tlačne trdnosti geopolimerov iz boksita v odvisnosti od masnega razmerja $w(Na_2SiO_3)/w(NaOH)$; C (NaOH) je 13 M

$[(HO)_{4-x}SiO_x]^{x-}$ monomeric species.[14] An increase in the NaOH concentration from 7 M to 13 M results in a higher dissolution of Al and Si from the starting materials, a higher availability of the monomeric species for the condensation process and a formation of geopolymer oligomers (dimers, trimers) following Equation 2.[15] The increase in the NaOH concentration leads to an increase in the number of oligomers in the system which results in the formation of a gel and, consequently, a higher geopolymerization degree (**Figure 1**) as well as a higher strength of the bauxite-based geopolymers.

$$[(HO)_{4-x}SiO_x]^{x-} + [Al(OH)_4]^- \leftrightarrow$$
$$[(HO)_3AlOSiO_x(OH)_{3-x}]^{(x+1)-} + H_2O \qquad (2)$$

On the other hand, the compressive strength of bauxite-based geopolymers increases with an increase in the $w(Na_2SiO_3)/w(NaOH)$ mass ratio from 1 to 1.5, while a further increase leads to a decrease in the compressive strength (**Figure 2**). A change in the $w(Na_2SiO_3)/w(NaOH)$ mass ratio controls the influence of the soluble silicate dosage (the water glass dosage) on the geopolymerization process. The role of the said dosage is to provide sufficient concentration of the silicate species for the initiation of the polycondensation between silicate and aluminate species.[16]

The presence of soluble silicates in a geopolymer mixture influences both, the dissolution of Al and Si from the starting materials and the polycondensation of aluminate and silicate species. The presence of soluble silicates influences the polycondensation process by changing the nature of the silicate species present in alkaline silicate solutions. In the systems with a lower soluble-silicate concentration, monomeric chains and cyclic trimmers are the dominant silicate species, while in the systems with a higher concentration of soluble silicate, larger rings, complex structures and polymers are present, giving rise to a three-dimensional polymer
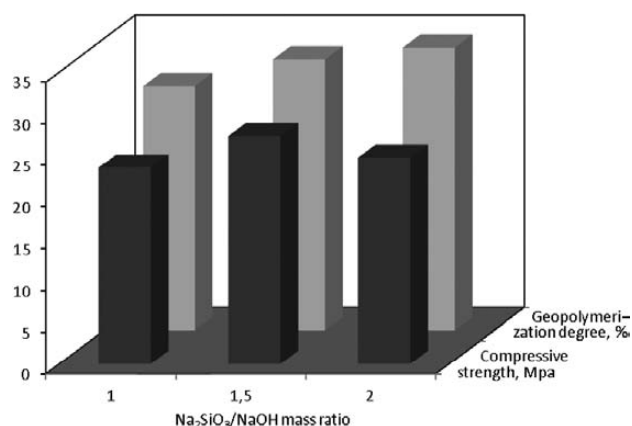
framework, leading to an increase in the mechanical properties of the resulted geopolymeric materials.[7] An increase in the compressive strength with an increase in the silicate dosage is limited by the viscosity of the geopolymer mixture. With the $w(Na_2SiO_3)/w(NaOH)$ mass ratio of 2, the geopolymer paste was extremely difficult to mould and visible cracks were observed on the surface after the curing period, resulting in a slight decrease in the compressive strength.

The investigation of the alkali-cation influence on the compressive strength of bauxite-based geopolymers was focused on the samples prepared using 13 MOH with the $w(M_2SiO_3)/w(MOH)$ ratio of 1.5, exhibiting the highest value of the compressive strength. The results have shown that Na-geopolymers are characterized by a considerably higher compressive strength and *GD* in comparison to K-geopolymers (**Figure 3**).
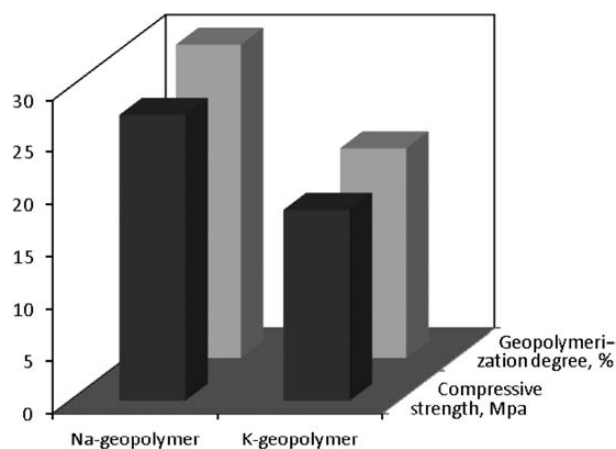

Figure 3: Compressive strength and geopolymerization degree of Na- and K-bauxite-based geopolymers
Slika 3: Tlačna trdnost in stopnja geopolimerizacije Na- in K-geopolimera na osnovi boksita

3.2 Microstructural investigations

SEM-EDS analyses were made on the broken fragments of the samples left behind after the compressive-strength tests and the results are given in **Figure 4** and **Table 2**. It is evident that the microstructure of both Na- and K-geopolymers is uniform without a distinctly separated gel phase and unreacted bauxite particles. The unreacted bauxite particles are covered with a layer of gel that forms as a result of the geopolymerization reactions. The results of the EDS microanalysis have shown that the main constituents of the bauxite-based geopolymers are Al, Si and O. The presence of Na and K is detected in the Na- and K-geopolymers, respectively. Previous investigations showed that the strength of geopolymers is strongly affected by the ratio of Si/Al in the gel phase and that an increase in the compressive strength is accompanied by an increase in the $w(\text{Si})/w(\text{Al})$ ratio.[17] The results presented here show that the values of the $w(\text{Si})/w(\text{Al})$ and $w(\text{alkali metal})/w(\text{Si})$ (or Al) ratios for both Na- and K-geopolymers are very close, which indicates that alkali cations do not affect the values of these ratios, and the difference in the strength of Na- and K- geopolymers is not accompanied by a difference in the $w(\text{Si})/w(\text{Al})$ ratio.

3.3 Porosity analysis

A porosity analysis was performed on Na- and K-based geopolymers. The results are summarized in **Table 3** and the obtained adsorption/desorption isotherms are presented in **Figure 5a**. According to the IUPAC (International Union of Pure and Applied Chemistry) the classification of the adsorption/desorption isotherms,[18] both Na- and K-geopolymers may be considered as mesoporous materials (the pore size from 2 nm to 50 nm). The isotherms of Na- and K-geopolymers are the type IV isotherms with the hysteresis loops associated with the capillary condensation taking place in the mesopores. However, the initial sections of the iso-
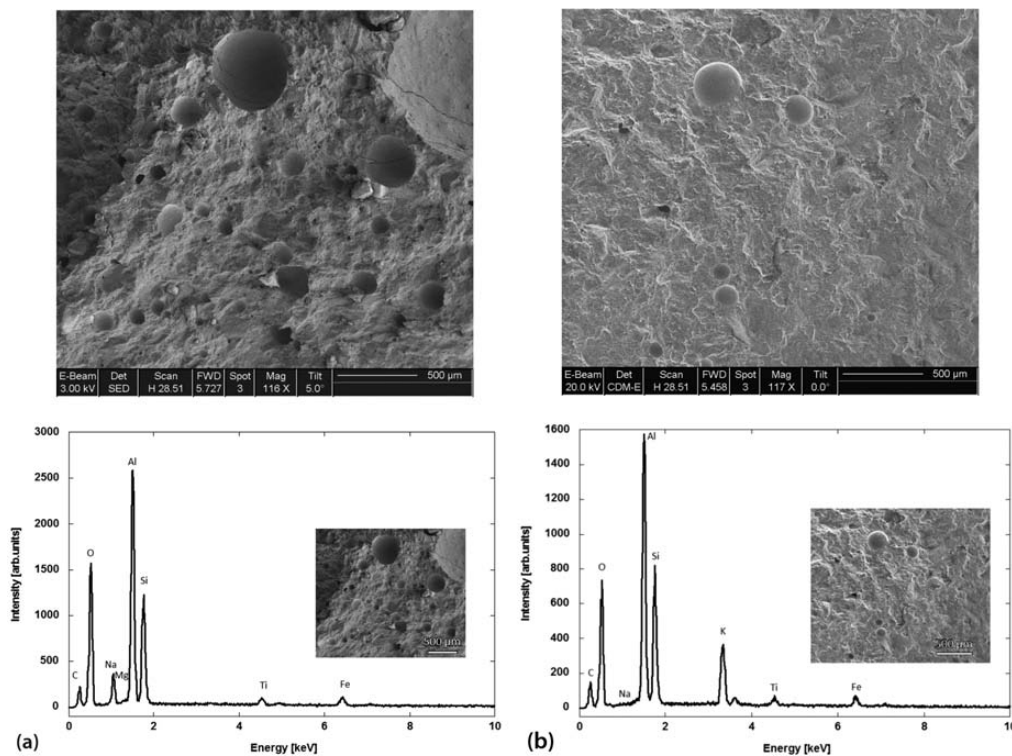

Figure 4: SEM-EDS of: a) Na- and b) K-bauxite-based geopolymers
Slika 4: SEM-EDS: a) Na- in b) K-geopolimera na osnovi boksita

Table 2: Contents of the elements ($w/\%$) and their ratios in Na- and K-geopolymers
Tabela 2: Vsebnost elementov ($w/\%$) in njihov masni delež v Na- in K-geopolimerih

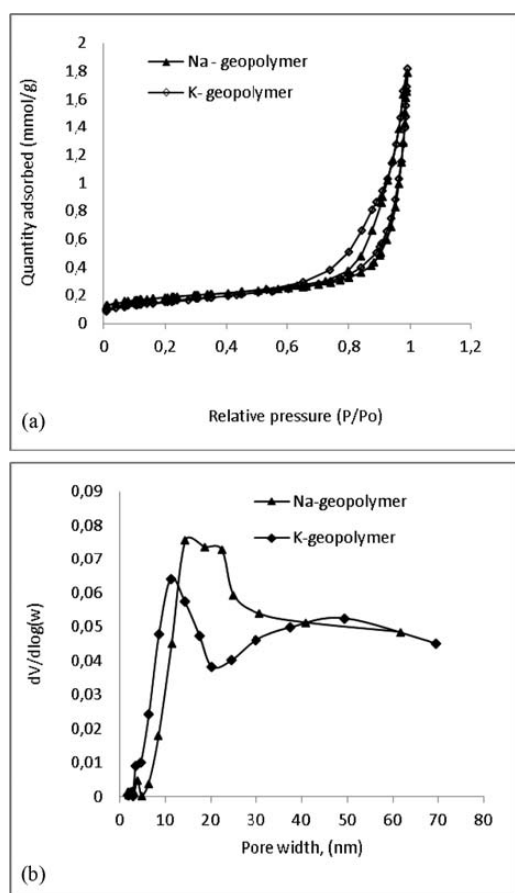| Element	Element content ($w/\%$)		ratio	Na-geopolymer	K-geopolymer
	Na-geopolymer	K-geopolymer			
Al	24.62	20.3	$w(\text{Na})/w(\text{Al})$	0.17	–
Si	14.97	12.57	$w(\text{K})/w(\text{Al})$	–	0.35
Na	4.35	–	$w(\text{Si})/w(\text{Al})$	0.60	0.56
K	–	7.29	$w(\text{Na})/w(\text{Si})$	0.29	–
			$w(\text{K})/w(\text{Si})$	–	0.57

Figure 5: a) Adsorption/desorption isotherms and b) pore-size distribution of Na- and K-bauxite-based geopolymers
Slika 5: a) Izoterme adsorpcije/desorpcije in b) razporeditev por pri Na- in K-geopolimeru na osnovi boksita

Figure 6: *t*-plots of Na- and K-geopolymers
Slika 6: *t*-odvisnosti poroznosti Na- in K-geopolimerov

therms indicate the contributions of the micropores (the pore size less than 2 nm) to the total porosity of a geopolymer.

The results presented in **Table 3** indicate that the difference in the strength of Na- and K-geopolymers must be considered with respect to the pore structure, i.e., the contribution of the micro- and mesoporosity to the total porosity of geopolymers must be evaluated.

The method of *t*-plot is used to estimate the micropore volume according to the intercept at the *y*-axis deduced from the extension of the linear part of a *t*-plot. The *t*-plots of Na- and K-geopolymers are given in **Figure 6**. They are characterized by a steep slope and a small intercept, which is indicative of a high mesoporosity.[19] However, the intercept at the *y*-axis for the
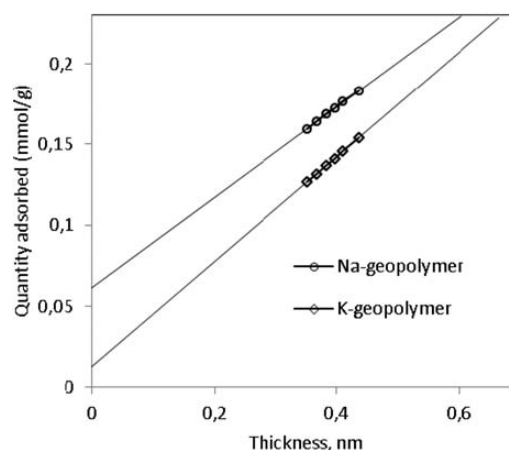
Na-geopolymer is higher than that of the K-geopolymer, indicating that more micropores contribute to the porosity of the Na-geopolymer than to the K-geopolymer. It is also indicative that the presence of microporosity in a geopolymer structure is almost eliminated by introducing K^+ instead of Na^+ in the geopolymerization reaction. Moreover, the hysteresis loop of the K-geopolymer is more pronounced than that of the Na- geopolymer (**Figure 5a**) which also indicates a development of the mesoporosity in the K- geopolymer. As the mesopores are characterized by a higher pore size, it seems reasonable that the development of mesoporosity leads to a decrease in the strength of a geopolymer structure.

The results of the porosity analysis have shown that Na-geopolymers are characterized by a higher percentage of microporosity (8.74 %) in comparison to that of K-geopolymers (0.76 %). Although K-geopolymers are characterized by a somewhat lower average pore size compared to Na-geopolymers, they are 99.24 % mesoporous materials and thus characterized by a lower compressive strength.

Moreover, as both Na- and K-geopolymers are considered as mesoporous materials, the mesopore structure is very important with respect to the geopolymer strength. It is evident that both differential curves of the pore-size distribution (**Figure 5b**) are characterized by the two peaks reflecting different pore sizes. The differential curve of the Na-geopolymer is characterized by the two close peaks, one around 14.2 nm and the other one around 22.4 nm. On the other hand, the differential curve for the K-geopolymer is characterized by two regions:

Table 3: Porosity of bauxite-based geopolymers
Tabela 3: Poroznost geopolimerov iz boksita

C (NaOH)/(mol dm^{-3})	V_{tot}/(cm^3/g)	V_{mes}/(cm^3/g)	V_{mic}/(cm^3/g)	P_{mes}/%	P_{mic}/%
Na-geopolymer	0.056539	0.051596	0.004943	91.25	8.74
K-geopolymer	0.057570	0.057132	0.000438	99.24	0.76

V_{tot} – total porosity, V_{mes} – mesopore volume calculated by subtracting the total pore volume and micropore volume, V_{mic} – micropore volume calculated using *t*-plot method, P_{mes} – fraction of mesoporosity calculated as V_{mes}/V_{tot}, P_{mic} – fraction of mesoporosity calculated as $1 - V_{mes}/V_{tot}$

the narrow region with the peak corresponding to the smaller pore width of around 11.2 nm and the broad one with the peak around 48 nm. It is evident that introducing the K$^+$ cation to a geopolymer system leads to the development of a bimodal pore-size distribution and the development of higher pores (around 49 nm) resulting in a decrease in the geopolymer strength of K-geopolymers in comparison to the strength of Na-geopolymers.

4 CONCLUSIONS

From the results of investigating the geopolymerization of low-grade bauxite, we have drawn the following conclusions:

- The compressive strength of bauxite-based geopolymers is strongly affected by alkali and silicate dosages. Their strength may be increased with an increase in the NaOH concentration. The maximum value of the compressive strength is reached with the use of 13M NaOH.
- On the other hand, the beneficial influence of an increase in the silicate dosage is limited. In this case, the maximum value of the compressive strength was observed for the $w(Na_2SiO_3)/w(NaOH)$ mass ratio of 1.5. A decrease in the strength of a geopolymer structure with a further increase in the silicate dosage is accompanied by an increase in the viscosity of the geopolymer paste and moulding difficulties.
- Moreover, the strength of bauxite-based geopolymers is strongly affected by the nature of alkali cations. Generally, Na-geopolymers are characterized by a higher compressive strength in comparison to K-geopolymers which is influenced by their porosity.
- Alkali cations do not affect the $w(Si)/w(Al)$, $w(M)/w(Si)$ and $w(M)/w(Al)$ ratios (M represents the Na or K ion) in a gel phase of a geopolymer and the difference in the strength of Na- and K-geopolymers is not affected by the proportion of the main constituent of a gel phase.

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