Sodium aluminate activated geopolymers based on natural zeolite clinoptilolite

Натриево-алуминатно активирани геополимери на база природен зеолит клиноптилолит

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Abstract. Geopolymers based on natural zeolite clinoptilolite were activated with different concentration of sodium aluminate and potassium hydroxide and the influence on compressive strength, density and water absorption were evaluated. The microstructure was analyzed by XRD, FTIR and SEM. The obtained geopolymers are comprised of newly formed zeolite phases – phillipsite, zeolite A.

Keywords: geopolymer, natural zeolite, clinoptilolite, sodium aluminate, phillipsite, zeolite A.

Introduction

Geopolymers are synthesized by mixing aluminosilicate precursors and alkali solution, so called activator. The most used alkali activator is a water solution of sodium or potassium silicate and alkali hydroxide. One of the key factors affecting geopolymer synthesis is the ratio Si/Al of the reactants. Most geopolymer applications require Si/Al ratio between 1 and 3 (Davidovits, 2015). In the case of aluminosilicate precursors with lower aluminum content, the Si/Al ratio could be adjusted by using aluminate activators. The natural zeolite clinoptilolite is an example of geopolymer precursor with relatively high Si/Al, about 5–6. Our previous studies showed the potential of natural zeolite from Beli Plast as geopolymer precursor (Nikolov et al., 2017a, b; 2021). However, the prepared geopolymers were characterized by a high shrinkage and low rate of strength gain, probably attributed to low aluminum content of the system. The studies were extended to usage of alternative aluminate activator solution. Thus, the shrinkage of the geopolymer based on natural zeolite and sodium aluminate was reduced 4–5 times compared to silicate activated ones (Nikolov et al., 2020). Sodium aluminate was used successfully with other low aluminum precursors such as perlite (Vance et al., 2009), rice hull ash (Hajimohammadi, van Deventer, 2017), silica fume (Brew, MacKenzie, 2007), geothermal silica (Hajimohammadi et al., 2008), etc.

The aim of the present study is to investigate the influence of different concentration of NaAlO$_2$ and KOH on the properties and microstructure of geopolymers based on natural zeolite clinoptilolite.

Materials and methods of analysis

The geopolymer precursor in the present study is commercially available natural zeolite (particle size < 0.15 mm) from Beli Plast, Bulgaria, provided by Imerys, Bulgaria. The chemical composition is: SiO$_2$ – 78.80, Al$_2$O$_3$ – 11.70, CaO – 3.44, K$_2$O – 3.08, MgO – 1.12, Fe$_2$O$_3$ – 1.12, Na$_2$O – 0.44, others – 0.30, in % determined by XRF. The activator solutions were prepared prior by using solid KOH pellets, powdered NaAlO$_2$, and tap water. The synthesis of the geopolymers was obtained using 5 different concentration of sodium aluminate and KOH (Table 1). The recipes are based on previous studies with solid to water ratio equal to 0.45 (Nikolov et al., 2020). The fresh geopolymer pastes were mixed...
with quartz sand (zeolite:sand = 1:1 by mass) to prepare cubic specimens (3.17 mm) for evaluation of the physical and mechanical properties. The samples were stored in plastic bags for one day at laboratory conditions (20 °C), then on second day were placed at 80 °C for 24 hours. The density was calculated by hydrostatic weighing method. The relative mass loss (Δm) was calculated after weighing the dry specimens before and after soaking in water. The powder XRD patterns were obtained by Bruker D2 Phaser (CuKα radiation, 30 kV and 20 mA). The chemical composition was analyzed by X-ray fluorescence apparatus – Rigaku Supermini 200 using 30 mm pressed tablets. FTIR spectra were collected by Tensor 37 spectrometer (Bruker) with a 4 cm⁻¹ resolution on KBr pallets. The morphology was studied by scanning electron microscopy JEOL 6390 on fractures of samples covered with gold in vacuum.

Results and discussion

The prepared geopolymers showed density in the range 1.33–1.49 g/cm³ (Table 1). Series ZA4 showed highest density and respectively lowest water absorption. The density increased with the increase of sodium aluminate content. On the other hand, when SiO₂/Al₂O₃ is fixed at 4.8, the density decreased with the raise of alkali content. All series were characterized by relatively high water absorption (21–29%), which is a sign for considerable amounts of capillary pores. The series with Al₂O₃/M₂O ≤ 0.77 showed high relative mass loss after watering (> 2%) probably due to unreacted alkalis which were leached out. The 90th day compressive strength of 16.8 MPa for series ZA3 was the highest – at ratio H₂O/M₂O = 12.5 and Al₂O₃/M₂O.

The results from powder XRD showed that the natural zeolite was comprised of mostly clinoptilolite (~ 80%) and opal-cristobalite (Fig. 1 a). After geopolymerization both phases were dissolved (except for series ZA5) and take part of geopolymer gel visible as amorphous halo between 20 and 40° 2θ. The usage of higher amounts of sodium aluminate led to inhibition of clinoptilolite dissolution and crystallization of zeolite A (series ZA5). With the decrease of reactive Al added and substitution of Na with K – we observed change in zeolite formation: zeolite A (ZA5) – phillipsite-Na (ZA4) – phillipsite-K (ZA3, ZA2, ZA1).

The FTIR spectra showed a significant band in all geopolymer series at about 1009–1026 cm⁻¹ associated with asymmetric stretching vibration T-O-Si (T – Si or Al) (Fig. 1 b). A strong peak in this range is characteristic of geopolymers and indicates the extent of polysialation in the geopolymer gel (Zaharaki et al., 2010; Valcke et al., 2005). From series ZA1, ZA2, ZA5, when the ratio H₂O/M₂O is constant, we observe blueshift on the main band with the decrease of SiO₂/Al₂O₃ ratio. Moreover, when ratio SiO₂/Al₂O₃ is constant (series ZA2, ZA3, ZA4), the main band blueshifts to lower wavenumbers by the increase of the ratio H₂O/M₂O, i.e. by lowering the alkalinity of the systems. The last is contradictory to the finding of Phair and van Deventer (2002), that the main band at lower wavenumbers are generally due to geopolymers synthesized at higher pH. The other bands at about 438–465 cm⁻¹ are assigned to the in-plane bending of Al-O and Si-O linkages. For series ZA5 this band was located at much higher wavenumber – 465 cm⁻¹, but this can be explained due to presence of unreacted clinoptilolite in the sample (Nikolov, Rostovsky, 2017). Series ZA5 showed bands at 557 cm⁻¹ and 669 cm⁻¹. These features can be assigned to the external vibrational modes of the tetrahedron rings producing the overtetrahedral form of the zeolite middle range order (Mozgawa, 2001). The bands at about 669 cm⁻¹,

### Table 1. Composition design, physical and hydrophysical properties and compressive strength of the prepared geopolymers based on natural zeolite clinoptilolite (M – sum of Na + K)

<table>
<thead>
<tr>
<th>Series</th>
<th>KOH, g</th>
<th>NaAlO₂, g</th>
<th>SiO₂/Al₂O₃</th>
<th>Al₂O₃/M₂O</th>
<th>H₂O/M₂O</th>
<th>Density, g/cm³</th>
<th>Water absorption, %</th>
<th>Δm, %</th>
<th>Compressive strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZA1</td>
<td>24</td>
<td>13</td>
<td>6.8</td>
<td>0.58</td>
<td>10</td>
<td>1.33 ± 0.00</td>
<td>28.6 ± 0.4</td>
<td>3.5 ± 0.2</td>
<td>10.6 ± 0.6</td>
</tr>
<tr>
<td>ZA2</td>
<td>17</td>
<td>26</td>
<td>4.8</td>
<td>0.77</td>
<td>10</td>
<td>1.37 ± 0.01</td>
<td>24.7 ± 0.3</td>
<td>2.0 ± 0.1</td>
<td>11.7 ± 0.6</td>
</tr>
<tr>
<td>ZA3</td>
<td>8</td>
<td>26</td>
<td>4.8</td>
<td>1.02</td>
<td>12.5</td>
<td>1.43 ± 0.01</td>
<td>22.4 ± 0.2</td>
<td>0.8 ± 0.2</td>
<td>16.8 ± 0.4</td>
</tr>
<tr>
<td>ZA4</td>
<td>4</td>
<td>26</td>
<td>4.8</td>
<td>1.18</td>
<td>14</td>
<td>1.49 ± 0.01</td>
<td>21.3 ± 0.3</td>
<td>0.4 ± 0.1</td>
<td>14.8 ± 0.5</td>
</tr>
<tr>
<td>ZA5</td>
<td>11</td>
<td>38</td>
<td>3.8</td>
<td>0.95</td>
<td>10</td>
<td>1.39 ± 0.01</td>
<td>24.5 ± 0.2</td>
<td>0.8 ± 0.2</td>
<td>8.0 ± 0.4</td>
</tr>
</tbody>
</table>

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557 cm$^{-1}$, 465 cm$^{-1}$ are also observed by Aronne et al. (2002), on synthesized zeolite-A. The peaks at about 1470 cm$^{-1}$ correspond to CO$_3^{2-}$ ions, which are product of natural carbonization processes.

On Figure 1c and d we can observe newly formed phillipsite and zeolite-A submicron crystals. Sodium carbonate hydrate elongated crystals are presented at sample ZA2 which correlates with the high relative mass loss of the sample (2%), i.e. excess alkali used and their afterwards carbonization.

The different compositions of the synthesized geopolymers determines the physical properties and
microstructural characteristics of the final material. The result is geopolymer composite comprised of different zeolite phases – phillipsite, zeolite-A and unreacted clinoptilolite. One of the key properties of the zeolites are their sorption and ion-exchange capability. Geopolymers with their similarity to zeolites, possess certain ion-exchange properties (Skorina, 2014). It is known that the ion-exchange capability is roughly proportional to the number of [AlO₄] tetrahedra in zeolite framework (Dimitrov et al., 2021). Therefore, the respective ion-exchange capability in alumina-enriched geopolymer is expected to be enhanced.

**Conclusion**

Sodium aluminate activation of relatively high silica precursors, such as natural zeolite clinoptilolite, produces geopolymer composite comprised of newly formed zeolite phases – phillipsite and zeolite A. Highest compressive strength (16.8 MPa) showed the geopolymer synthesized at: H₂O/M₂O = 12.5, Al₂O₃/M₂O = 1 and SiO₂/Al₂O₃ = 4.8 ratio. The opal-cristobalite and clinoptilolite presented at the raw zeolite dissolved after geopolimerization. The results from FTIR showed that the main band characteristic for geopolymers at about 1000 cm⁻¹ blueshifts to both: increase of aluminum incorporation in the gel; and lowering of the alkalinity of the system. The presence of zeolite phases in the geopolymer will contribute to special properties like enhanced sorption and ion-exchange of the final geopolymer.

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**References**


