

UDK: 676.017.2; 622.785; 621.742.48

## Effect of Sintering Temperature and Calcium amount on Compressive Strength of Brushite-Metakaolin Polymer Materials

Dunja Đukić<sup>1</sup>, Marija Šuljagić<sup>2</sup>, Ljubica Andjelković<sup>2</sup>, Vera Pavlović<sup>3</sup>, Dušan Bučevac<sup>5</sup>, Boško Vrbica<sup>4</sup>, Miljana Mirković<sup>5\*)</sup>

<sup>1</sup>University of Belgrade, Faculty of Biology, Studentski Trg 16, Belgrade, Serbia

<sup>2</sup>University of Belgrade-Institute of Chemistry, Technology and Metallurgy, Department of Chemistry, Njegoševa 12, Belgrade, Serbia

<sup>3</sup>University of Belgrade, Faculty of Mechanical Engineering, Kraljice Marije 16, Belgrade, 11120, Serbia

<sup>4</sup>University of Belgrade, Faculty of Chemistry, Studentski Trg 12-16, Belgrade, Serbia

<sup>5</sup>Department of Materials „Vinča“ Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia

---

### Abstract:

*The effect of  $Ca^{2+}$  amount and sintering temperature on mechanical properties of geopolymer-brushite (GPB) binders was investigated. Brushite and raw abandoned kaolinite clay thermally transformed into metakaolin were used for GPB synthesis. The complete phase and structural analyses were performed by X-ray powder diffraction, and Fourier transforms infrared spectroscopy (FT-IR). The pore-filling effect as a consequence of  $Ca^{2+}$  ions incorporation into the hybrid geopolymer networks improved the compressive strength. On the other hand, the chosen biscuit sintering at 800 and 900°C caused the phase transformation of brushite into calcium pyrophosphate, which negatively affected the compressive strength of such materials. The obtained results indicate that the usage of relatively high sintering temperatures is not always the necessary step for producing geopolymer-based types of cement with prominent mechanical properties.*

**Keywords:** *Geopolymer-based cement materials; Brushite; Biscuit sintering; Mechanical properties.*

---

## 1. Introduction

Manufacturing and the use of Portland cement as a binder are resource-exhausting, energy-intensive processes that release large amounts of greenhouse gas (CO<sub>2</sub>) into the atmosphere.[1] The Production of 1 ton of Portland cement requires about 2.8 tons of raw materials, including fuel and other materials. Moreover, manufacturing 1 ton of cement generates about 1 ton of greenhouse gas.[2] Therefore, the replacement of conventional cement, plastics, and many mineral-based products would have a positive impact effect reducing CO<sub>2</sub> emissions from cement clinkers, limiting toxic metal contamination of freshwater resources resulting from mining operations, and reducing the over-use of common

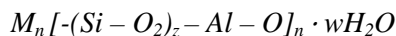
---

\*) **Corresponding author:** miljanam@vin.bg.ac.rs

organic plastics.[3] This motivated many researchers to identify materials that to sustainable development, such as promoting recycling and managing solid waste or the reuse of abandoned raw materials [4–8].

Inorganic polymer concretes, *a.k.a.* geopolymers have emerged as novel engineering materials with the potential to become a substantial element of the construction industry being more environmentally sustainable and presenting a key to the manufacturing-caused pollution minimization.[9] Formation of these types of materials usually involves an alkali activation of industrial aluminosilicate-rich waste materials such as fly ash and blast furnace slag, a process that leaves a very small carbon footprint in comparison to the traditional concretes. Alongside that, such materials can even exhibit better chemical and mechanical properties, in some aspects, compared to ordinary Portland cement, while being cost-effective [3,4,6]. The main attribute of geopolymer technology refers to the robustness and versatility of the manufacturing process. It enables products to be tailor-made from a range of fly ash sources and/or other aluminosilicate raw materials, with specific properties, such as high compressive strength gains, high level of resistance to a range of different acids and salt solutions, and inherent protection of steel reinforcing due to high residual pH and low chloride diffusion rates, for a given application [6,10–12].

Geopolymerization, represents a reaction that chemically integrates minerals and involves naturally occurring silico-aluminates, includes a precursor – any source of silica and alumina that dissolves in the alkaline activator solution. The product of the geopolymer reaction is considered to be an alkali-activated aluminosilicate binder. Mechanism of geopolymerization process involves the polycondensation reaction of geopolymeric precursors i.e. alumino-silicate oxide with alkali polysilicates yielding polymeric Si–O–Al bond:



where  $M$  is the alkaline element,  $z$  is 1, 2, or 3 and  $n$  is the degree of polycondensation [13,14]. Polycondensation of silica and alumina precursors (fly ash, kaolin, metakaolin) and a high alkali content are utilized to attain structural strength of the geopolymer instead of the presence of calcium-silicate hydrate matrix in regular cement [13,15]. Kaolinite ( $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$ ) belongs to the group of clay minerals, widely used in ceramic industries for many years [16]. To enhance the mechanical properties and the compressive strength of the kaolinite, high-temperature heat treatment with an addition of calcium ions is usually used [17,18]. The higher the temperature used during the process, the shorter the time needed to obtain the final product [13,19]. Brushite ( $CaHPO_4 \cdot 2H_2O$ ), an environmentally friendly material, often serves as a source of calcium ions. The formation of Ca-Al-Si units as a consequence of calcium ions incorporation in the geopolymer structure can increase compressive strength due to the microstructural porosity disruption. Besides the improvement in the compressive strength, reaction time can be significantly reduced with calcium source addition [13,20].

This work used raw abandoned kaolinite clay from the Rudovci deposit (Serbia) as Al and Si source for geopolymer binder production. The influence of the brushite addition in different concentrations on the mechanical properties of the geopolymer binder was investigated. Furthermore, different biscuit sintering temperatures were studied as the potential boosters for the compressive strength of the material.

## 2. Materials and Experimental Procedures

Brushite was synthesized by the solution-precipitation reaction, as previously described by Mirković et.al.[21]. The kaolinite clay used in this experiment is of high quality,

localized in abandoned deposit Rudovci, Lazarevac district (Serbia). Physicochemical characteristics of the used kaolinite are previously described by authors [22]. Kaolinite was thermally treated at 750°C for three hours to produce metakaolin. Geopolymer material samples were synthesized using metakaolin mixed with activator solution prepared from 6M sodium hydroxide (analytical grade) and sodium silicate in relation to 1:1.6. In five separate geopolymer mixtures 2 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt% of pure brushite material were added. After the activation reaction step, the obtained geopolymer-brushite (GPB) material samples were put into conic molds and left to age for 28 days at room temperature. All prepared samples were calcined at 800°C (GPB<sub>800</sub>) and 900°C (GPB<sub>900</sub>), with a heat rate of 2°/min and 1h retention time in an air atmosphere using a high-temperature electrical furnace (Elektron Serbia). X-ray powder diffraction (XRPD) analysis was performed to examine phase analysis of synthesized and calcinated materials. Characterization was carried out with Ultima IV Rigaku diffractometer, equipped with CuK $\alpha_{1,2}$  radiations, using a generator voltage (40.0 kV) and a generator current (40.0 mA). For all powdered samples the range of 5–80° 2 $\theta$  was used in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of 10 °/min using D/TeX Ultra high - speed detector. All samples were placed in high-purity a monocrystalline silicon plate, which was used as a sample carrier. Each sample was previously prepared to a grain size of fine powder in a porcelain mortar and sieved through a 0.355 mm sieve. The PDXL2 (Ver. 2.8.4.0) software was used to evaluate the phase composition and identification.[23] All investigated powders were identified using the ICDD data base.[24] The list of selected ICDD card numbers used for identifications contain: brushite: 01-072-0713, quartz: 01-075-8322, muscovite: 01-080-0734, albite: 01-089-6427, nepheline: 00-035-0424, anorthite: 00-041-1486, Calcium Aluminium Silicate: 00-023-0105, beta-Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>: 00-009-0346 and berlinite: 01-076-0233.

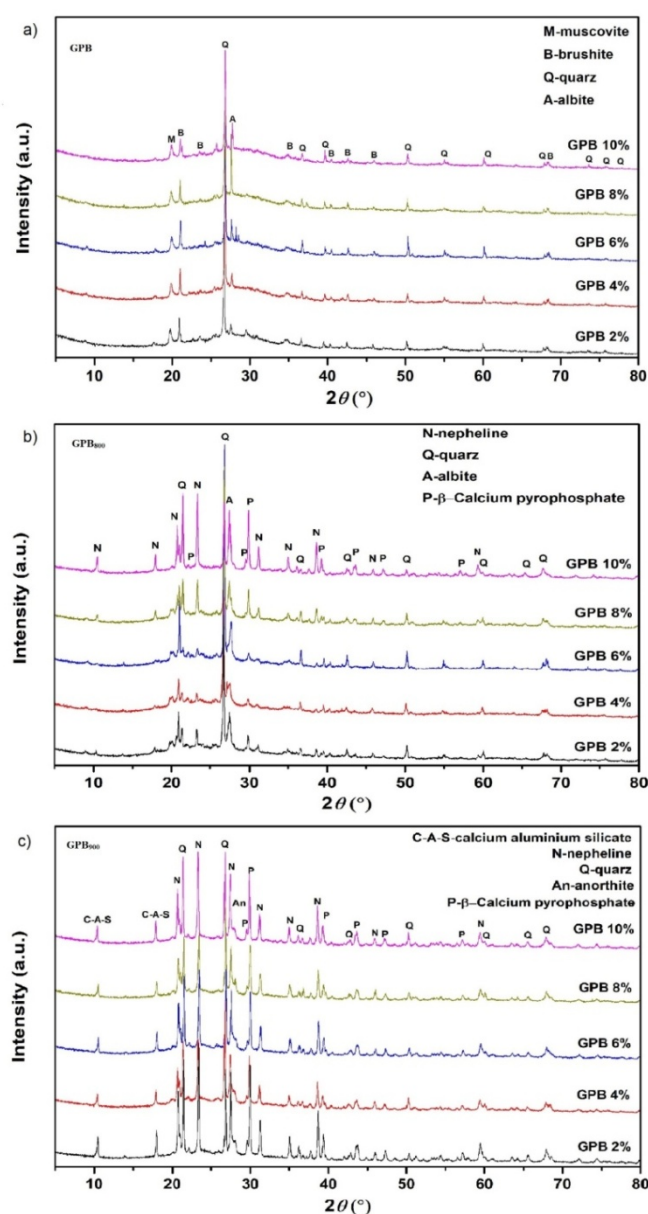
FT-IR spectra for all synthesized GPB, GPB<sub>800</sub> and GPB<sub>900</sub> samples were obtained at Nicolet 6700 FT-IR instrument (Thermo Scientific) in the range between 4000 and 400 cm<sup>-1</sup> using the ATR technique with a Smart Orbit accessory (diamond crystal). The accuracy of FT-IR was 4 cm<sup>-1</sup>. The uncertainty of the method with a 95 % confidence interval was 0.2 cm<sup>-1</sup> recorded for 20 independent measurements of the band at 1601.2 cm<sup>-1</sup> that originates from the certified polystyrene standard. The number of scans for IR sample measurements was 32, while the number of scans for background measurements was 16.

The measurement of compressive strength of cylindrical samples prepared prior to analysis with a height and diameter ratio of 1.6, was carried out on Instron M 1185 testing machine, with a loading rate of 2 mm/min. All compressive strength measurements were conducted in triplicate.

### 3. Results and Discussion

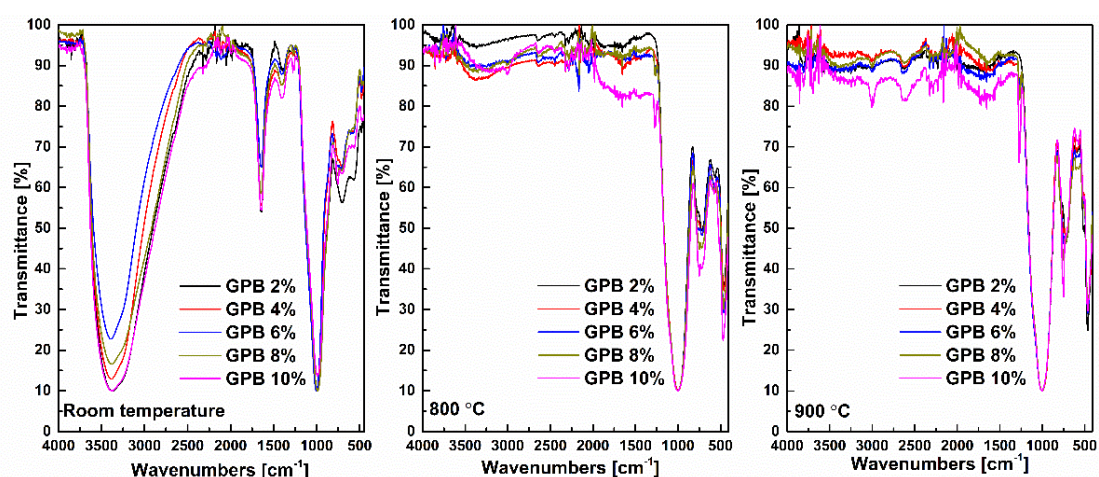
The phase composition of the synthesized GPB samples containing different amounts of brushite (from 2 to 10 wt%) is shown in Figure 1 (a). Since quartz is the main secondary mineral that follows clay minerals and remains undisturbed in the matrix during the alkaline activation process, the peaks originating from quartz were present in all investigated samples. Sharp and narrow peak at about 27° 2 $\theta$ , belongs to sodium-tecto-alumotrisilicate (albite) with the chemical formula NaAlSi<sub>3</sub>O<sub>8</sub>. This phenomenon may be due to the contribution of Na from the alkaline activator solution (sodium hydroxide and sodium silicate) and the possible preferential orientation of the albite. Compared to pure metakaolin,[18] in the case of as-prepared GPB samples wide broad hump region was shifted from 15 to 35 and from 20–40 2 $\theta$  range. This can be explained by the network's modification caused by depolymerization of the raw metakaolin and the polycondensation of precursors. Moreover, the characteristic peaks of kaolinite were not present in the XRPD patterns, indicating formation of the geopolymer matrix. The presence of brushite peaks in the as-prepared samples occurred due

to the formation of hybrid geopolymer material, where brushite phase is incorporated to polymer matrix. The results of XRPD analysis of sintered samples at 800°C (GPB<sub>800</sub>) and 900°C (GPB<sub>900</sub>) are shown in Fig. 1 (b, c). Based on obtained results the peak of quartz and nepheline (NaAlSiO<sub>4</sub>) are indicated as the main phases. The geopolymer samples sintered at 800°C contains mainly quartz with an amount of nepheline, while the increase of sintering temperature to 900°C led to a higher structural order of nepheline phase. These two phases were more pronounced for the GPB<sub>800</sub> and GPB<sub>900</sub> samples with higher amounts of brushite. Anorthite and calcium aluminum silicate were detected in the GPB<sub>900</sub> samples. The most significant difference between XRPD patterns between GPB and GPB<sub>800</sub> and GPB<sub>900</sub> was obtained in the range 25–35 2θ, due to the transformation of brushite to β-calcium pyrophosphate [25,26]. This phase transformation occurred due to the sintering temperature increasing.



**Fig. 1.** a) XRPD spectra of the as-prepared GPB samples; b) GPB<sub>800</sub> samples sintered at 800°C; c) GPB<sub>900</sub> samples sintered at 900°C.

The FT-IR spectra of as-prepared GPB samples and GPB samples biscuit sintered at 800°C (GPB<sub>800</sub>) and 900°C (GPB<sub>900</sub>) are shown in Fig. 2. In the case of non-sintered samples peaks in the region, about 3500 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> originated from stretching vibration of lattice water and surface adsorbed water. These peaks vanished after calcination due to water evaporation, Fig. 2 (b, c). The -P-O-Al-O- vibration in the polymer structure gave rise to absorptions at approximately 560 cm<sup>-1</sup>. The bands at ≈ 710 cm<sup>-1</sup> and ≈ 870 cm<sup>-1</sup> might be attributed to Si-O-Al and Si-O-Si vibrations, respectively. The broad peak at about 1020 cm<sup>-1</sup> for all prepared samples was related to the asymmetric stretching vibration of siloxo, sialate, and phospho-siloxo units in the geopolymer structure. The band at about 530 cm<sup>-1</sup> originated from Si-O-Al vibrations and it was shifted to lower wave numbers compared to the IR spectrum of pure metakaolin. This represents clear evidence that the polycondensation process occurred and GPB structure was formed [18]. A significant difference in IR spectra for non-sintered and biscuit sintered samples can be seen in the region between 1000 cm<sup>-1</sup> and 500 cm<sup>-1</sup>. It can be explained by phase transformation of incorporated brushite into calcium pyrophosphate and deterioration of hybrid phospho-siloxo network structure at used sintering temperatures. The absorptions at approximately 650 cm<sup>-1</sup> and 500 cm<sup>-1</sup> are characteristic for acid phosphates and originate from (H-O-)P=O vibrations and these bands were visible for non-sintered samples. The appearance of intense peaks at 1250 cm<sup>-1</sup> and 480 cm<sup>-1</sup> in the case of GPB<sub>800</sub> and GPB<sub>900</sub> samples might be connected with P-O and P-O-P vibrations of calcium pyrophosphate [22], Fig. 2 (b, c).

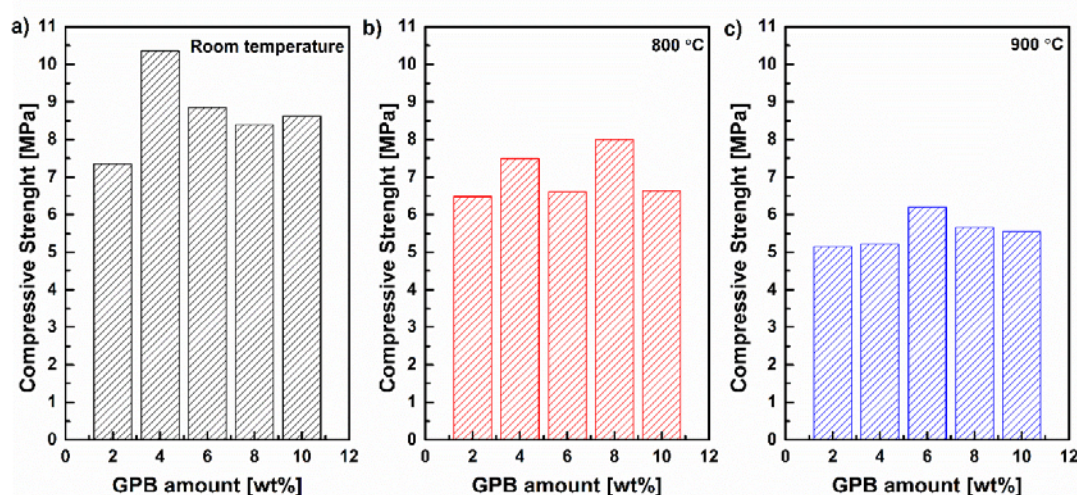


**Fig. 2.** The FT-IR spectra of as-prepared GPB samples and GPB<sub>800</sub> and GPB<sub>900</sub> samples biscuit sintered at 800 and 900°C.

The compressive strength values for all investigated GPB materials are presented in Fig. 3. Unexpectedly, the best results were obtained for non-sintered samples. This can be explained by the phase transformation of brushite to pyrophosphate during the sintering process. This phase change probably disrupts the highly ordered polymer structure of hybrid poly(phospho-siloxo) and poly(siloxo-sialate) Ca-rich networks [18]. Polymer degradation consequently decreased the compressive strength by weakening the structure's density, Fig. 3 (b, c). In all cases, the highest values of compressive strength were achieved for samples with brushite weight amount in the 4-8 % range, although the values are nearly the same. The increase in Ca amount influenced the geopolymer structure due to a pore filling effect of Ca ions, causing higher compressive strengths [18].

The results presented in Fig. 3 undoubtedly suggest that the usage of relatively high sintering temperatures in geopolymer-based cement processing is not always necessary. The

fact that the non-sintered samples showed better mechanical properties in comparison to sintered ones indicates that the energy consumption can be significantly reduced when using such materials as binders.



**Fig. 3.** Compressive strength of as-prepared GPB samples and GPB<sub>800</sub> and GPB<sub>900</sub> samples biscuit sintered at 800 and 900 °C.

#### 4. Conclusion

Geopolymer-brushite binders were successfully synthesized using raw abandoned kaolinite clay with different weight percentages of brushite addition. X-ray powder diffraction and Fourier transform infrared spectroscopy confirmed the formation of geopolymer in all investigated samples. It was found that the presence of brushite improves the compressive strength of the polymer as a result of  $\text{Ca}^{2+}$  ions incorporation into the hybrid geopolymer network. On the other side the sintering process at 800 and 900 °C led to deterioration of compressive strength. It is believed that the structure disruption and appearance of the pyrophosphate phase which take place during sintering are responsible for the low compressive strength of sintered samples. The obtained results point out that the use of high-temperature treatment is not obligatory for the design and the production of geopolymer-based cement materials. Finally, the utilization of raw clay from abandoned site to obtain novel eco-friendly material as a possible manufacturing binder surely has a positive impact on local waste reduction and energy consumption.

#### Acknowledgments

The authors would like to thank the Ministry of Education, Science and Technological Development of Republic of Serbia (Grant Nos. 451-03-9/2021-14/200017, 1702102, 451-03-9/2021-14/200026, and 451-03-9/2021-14/200116) for financial support. This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation (RIS-ALiCE, project no. 18258). This research is a direct result of Training School: Al-rich Industrial Residues for Inorganic Materials, held from May 24<sup>th</sup> – 28<sup>th</sup>, 2021 in Belgrade, Serbia.

## 5. References

1. X. Guo, H. Shi, W.A. Dick, *Cem. Concr. Compos.*, 32 (2010) 142.
2. J. Davidovits, *Ceram. Trans.*, 37 (1993) 165.
3. V.F.F. Barbosa, K.J.D. MacKenzie, C. Thaumaturgo, *Int. J. Inorg. Mater.*, 2 (2000) 309.
4. P. Nuaklong, A. Wongsu, K. Boonserm, C. Ngohpok, P. Jongvivatsakul, V. Sata, P. Sukontasukkul, P. Chindapasirt, *J. Build. Eng.*, 41 (2021) 102403.
5. N. Hamdi, I. Ben Messaoud, E. Srasra, *Comptes Rendus Chim.*, 22 (2019) 220.
6. P. Duxson, J.L. Provis, G.C. Lukey, J.S.J. van Deventer, *Cem. Concr. Res.*, 37 (2007) 1590.
7. A. Terzić, L. Pezo, L. Miličić, N. Mijatović, Z. Radojević, D. Radulović, L. Andrić, *Sci. Sinter.*, 51 (2019) 39.
8. J. Bijeljić, N. Ristić, Z. Grdić, G. Topličić-Ćurčić, D. Đorđević, *Sci. Sinter.*, 52 (2020) 231.
9. M. F. Zawrah, S. E. Abo Sawan, R. M. Khattab, A. A. Abdel-Shafi, *Constr. Build. Mater.*, 246 (2020) 118486.
10. W.K.W. Lee, J.S.J. van Deventer, *Cem. Concr. Res.*, 32 (2002) 577.
11. A. Palomo, M. T. Blanco-Varela, M. L. Granizo, F. Puertas, T. Vazquez, M. W. Grutzeck, *Cem. Concr. Res.*, 29 (1999) 997.
12. J. M. Miranda, A. Fernández-Jiménez, J. A. González, A. Palomo, *Cem. Concr. Res.*, 35 (2005) 1210.
13. D. Khale, R. Chaudhary, Mechanism of geopolymerization and factors influencing its development: a review, *J. Mater. Sci.* 42 (2007) 729-746.
14. D.M.J. Sumajouw, D. Hardjito, S. E. Wallah, B. V Rangan, *J. Mater. Sci.*, 42 (2007) 3124.
15. M. Ivanović, L. Kljajević, J. Gulicovski, M. Petkovic, I. Jankovic-Castvan, D. Bučevac, S. Nenadović, *Sci. Sinter.*, 52 (2020) 219.
16. C. Y. Chen, G. S. Lan, W. H. Tuan, *J. Eur. Ceram. Soc.*, 20 (2000) 2519.
17. H. Xu, J. S.J. Van Deventer, *Miner. Eng.*, 15 (2002) 1131.
18. H. K. Tchakouté, D. Fotio, C. H. Rüschler, E. Kamseu, J.N.Y. Djobo, M. C. Bignozzi, C. Leonelli, *Constr. Build. Mater.*, 163 (2018) 776.
19. B. B. Sabir, S. Wild, J. Bai, *Cem. Concr. Compos.*, 23 (2001) 441.
20. H. Xu, J.S.J. Van Deventer, *Cem. Concr. Res.*, 32 (2002) 1705.
21. M. Mirković, T. Lazarević-Pašti, A. Dosen, M. Čebela, A. Rosić, B. Matović, B. Babić, *RSC Adv.*, 6 (2016) 12219.
22. S. S. Nenadović, L. M. Kljajević, M. A. Nešić, M. Ž. Petković, K. V. Trivunac, V. B. Pavlović, *Environ. Earth Sci.*, 76 (2017) 79.
23. Rigaku, PDXL Integrated X-Ray Powder Diffraction Software, Rigaku, Tokyo, Japan, 2011., (n.d.).
24. International Crystallographical Database (ICDD), in: N.S. 12 Campus Blvd, PA 19073, USA (Ed.) USA, 2012., (n.d.).
25. S. Naga, A. Awaad, H. El-Maghraby, A. El-Kady, *Int. J. Appl. Ceram. Technol.*, 11 (2013) 1.

26. A. D. Anastasiou, C. L. Thomson, S. A. Hussain, T. Edwards, S. Strafford, M. Malinowski, R. Mathieson, C. Brown, A. P. Brown, M. Duggal, A. Jha, Mater. Des., 101 (2016) 346.

---

**Сажетак:** У овом раду испитиван је утицај количине додатог брушита и температуре синтеровања на механичка својства геополимер-брушит везива. Као полазни материјали за синтезу коришћени су каолинитска глина и синтетисани брушит. Комплетна фазна и структурна анализа извршена је дифракцијом рендгенских зрака на праху и инфрацрвеном спектроскопијом са Фуријеовом трансформацијом. Ефекат додатка брушита у геополимерну матрицу побољшао је притисну чврстоћу, док је бисквитно печење изазвало фазну трансформацију брушита у калцијум пирофосфат што је негативно утицало на притисну чврстоћу таквих материјала. Добијени резултати указују да коришћење релативно високих температура синтеровања није увек неопходан корак за производњу цемента на бази геополимера са истакнутим механичким својствима.

**Кључне речи:** геополимерни цементни материјали, брушит, бисквитно синтеровање, механичке особине.

---

© 2022 Authors. Published by association for ETRAN Society. This article is an open access article distributed under the terms and conditions of the Creative Commons — Attribution 4.0 International license (<https://creativecommons.org/licenses/by/4.0/>).

