# Utilization of Waste-Based Geopolimers for Radionuclide Immobilization – A Review

Slavko Dimović, Ivana Jelić and Marija Šljivić-Ivanović

***Abstract* — The aim of this article is to review the utilization of waste components for radionuclides immobilization by geopolymerization. The geopolymers represent a wide range of alkaline-activated aluminosilicates. Synthesis of geopolymers from waste provides less raw material consumption and addresses issues regarding the disposal of waste. Fly ash, red mud, construction and demolition waste, or slags are the most utilized waste types. The advantage of these waste materials represents the possibility of utilization of any aluminosilicate-containing waste that could be dissolved in an alkaline solution to produce a matrix for radionuclide immobilization. Despite many publications and investigations concerning the usage of waste components in geopolymerization, the utilization of waste-based geopolymers in the disposal of radionuclides has not yet been developed enough.**

***Keywords* — radionuclides; waste; geopolymers; recycle; reuse.**

## I. Introduction

The fast technological progress led to a realization of a large amount of waste to the environment, increased non-renewable natural resource extraction, and energy consumption [1-3]. The safe disposal of different kinds of waste and industrial by-products has become a key concern worldwide [4]. Problems arising from a substantial amount of waste have gained great social and environmental importance [1]. The investigation of waste reusing to produce new products has been expansively carried out [5-6].

The term geopolymer and its description as cement-free green cementitious material were introduced in the late 70s [7]. In past years, geopolymerization technology has been shown advantages in reusing various types of waste for the production of the new materials for many purposes. These so-called inorganic polymers [7], have been proposed for the utilization of solid aluminosilicate waste and the development of new materials [8]. Geopolymers have gained attention primarily due to the ease of synthesis with little or zero-emission of greenhouse gases [9]. Hence, the utilization of geopolymers could show many advantages such as usage of low-cost waste materials in production (e.g. slags, fly ash, various clays, and even agricultural wastes), saving natural resources, ambient temperature production, and high compressive and flexural strengths, in particular as compared to cement [7-8]. All these characteristics are placing them in a category of new eco-friendly and sustainable materials.

Geopolymers are structurally and chemically comparable to rocks and are synthesized by condensation mechanisms similar to organic polymers [7]. The geopolymerization represents a process comprising of the dissolution of aluminosilicate solids in a strongly alkaline medium followed by condensation of free alumina-silica oligomers to form a tetrahedral polymeric structure [7,10]. During this process, activated aluminosilicate is dissolved in an alkaline solution to form free $SiO4^-$ and $AlO4^-$ ions charge-balanced by hydrated alkali cations. Ions are tetrahedrally coordinated, forming amorphous or semi-crystalline oligomers. Finally, geopolymer gel is created by polymerization and hardening of oligomers [11] (Fig.1).

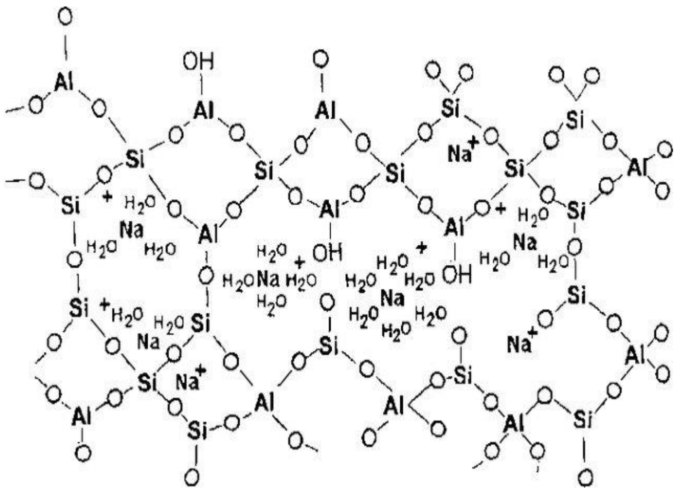

Fig. 1. Model of geopolymer structure [12]

The empirical formula of geopolymer could be shown as [7,12-13]:

$$Mn[-(SiO_2)_z-AlO_2^-]_n\cdot\cdot\ wH_2O$$

where:
M – alkaline or alkaline-earth cation;
n – degree of poly-condensation;
z – number, generally <3 for three-dimensional structure;
w – number of crystalline water molecules.

Slavko Dimović – Vinca Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11000 Belgrade, Serbia (e-mail: sdimovic@vin.bg.ac.rs).

Ivana Jelić – Vinca Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11000 Belgrade, Serbia (e-mail: ivana.jelic@vin.bg.ac.rs).

Marija Šljivić-Ivanović – Vinca Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11000 Belgrade, Serbia (e-mail: marijasljivic@vin.bg.ac.rs).

Compared to conventional construction materials, e.g. concrete, the synthesized geopolymers show adequate physicomechanical properties, such as high strengths [14]. Likewise, geopolymers are fire resistant up to 1400°C, heat, and acid-resistant materials. They exhibit high early compressive strength, low porosity, and freeze-thaw resistance, e.g. long-term durability [7-8,12]. However, their most important advantage is that, depending on their design, they acquire properties tailored to the needs of the end-user [8].

The aim of this article is to review the utilization of waste components for radionuclides immobilization by geopolymerization. However, the immobilization of radionuclides in the waste-based geopolymers was rarely investigated, according to available data, unlike very comprehensive research on heavy metals [15]. Geopolymerization technology has been proposed to stabilize and solidify a simulated residue containing hazardous metals [16]. Although, a few studies from the past several years have pointed out that radionuclides could be immobilized in the geopolymer matrix. Also, the results for some heavy metals immobilization by geopolymers could be used for these purposes.

## II. Radionuclide Immobilization Practice

The usual procedures for the immobilization of radioactive waste are technological operations of converting these materials into stable insoluble forms using matrix materials (solidification). Standard matrices for immobilization of radioactive waste are cement, mortar, concrete, bitumen, polymers (e.g. plastics) or borosilicate glass, etc. [17-18]. Conditioning processes such as cementation and vitrification are often used to convert waste into a stable solid form insoluble and prevent dispersion to the surrounding environment.

A systematic approach typically incorporates the identification of a suitable matrix material that will ensure the stability of the radioactive materials for the period necessary. The type of waste being conditioned determines the choice of matrix material and packaging. Conditioning of radioactive waste implies operations of transformation into forms suitable for later manipulation (handling, transport, temporary storage, and permanent disposal).

Also, investigation of the sorption process in order to prevent the interaction of radionuclides with living tissue and their accumulation (since these ions are not biodegradable like most organic substances [19], while radionuclides emit extremely dangerous radioactive radiation [20]), as well as monitoring the process of their migration in the environment and finding technological innovations for their immobilization is currently expanding. A large number of researches are based on finding sorbents of the highest efficiency, i.e. sorption capacity, and the lowest possible production costs. Due to the topicality, numerous studies have examined various sorbent materials that are readily available locally and whose economic viability can justify their widespread usage.

Sorption of radionuclides from liquid radioactive waste (LRW), i.e. from a suspension or solution, onto waste materials is based on finding the sorbents with as much higher sorption capacity while reducing the cost of their production [21]. For example, the immobilization of LRW (and heavy metals) using stony C&DW or its components has been increasingly investigated over the last few years [21], due to the similarity of the cement matrix usually used for radionuclide immobilization. Various types of cementitious material, namely concrete and facade material, clay-based materials such as bricks, ceramic and roof tiles, as well as waste asphalt, were consistently investigated [22-24].

Studies have shown that the immobilization of ions in geopolymer matrixes also includes the sorption processes. Sorption on a synthesized geopolymer could be studied as a function of the geopolymer dosage, ions initial concentration, contact time, pH, and temperature [25-27].

## III. Radionuclide Immobilization by Waste-based Geopolymers

The very high costs of immobilization, temporary storage, and final disposal of LRW and wastewater heavy metals treatment, stimulate research into the development of cost-effective materials, which during production or after usage represent final waste [28]. Particular attention should also be paid to European legislation that encourages the development of a "circular economy", which implies the efficient use of materials [29]. However, the thermal stability and acid corrosion resistance of cement-based materials are relatively low [30]. Moreover, the utilization of other materials, such as glass and resin, is limited by their high cost and complex preparation [31]. Because of its excellent mechanical performance, such as compressive strength, acid/alkaline resistance, and heat resistance, geopolymers have become ideal materials for solidifying toxic waste [15].

In recent studies, the waste aluminosilicates were used to synthesize different geopolymers as heavy metal, as well as radionuclides immobilizing matrixes. The raw materials mainly used in geopolymerization are clays or pozzolanic materials such as kaolin, calcined kaolin, different fly ashes, and blast furnace slags partially dissolve in the alkali solution [16]. Conversion of fly ash to an amorphous aluminosilicate sorbent, i.e. geopolymer has been investigated under different conditions and was paid great attention as a potential material for removal of Ni(II), Pb(II), Cu(II), and radionuclides: $^{137}$Cs and $^{90}$Sr [32]. The geopolymer testing also included key radionuclides such as Tc, I, Sr, and Cs [33-39], as well as $^{152}$Eu, $^{60}$Co, and $^{59}$Fe isotopes [40], which dominate the risk to the environment. For example, 20 – 30 years after the nuclear reactor shutdown, taking into account fission and corrosion products, the most abundant radionuclides in contamination residues generally include $^{63}$Ni, $^{137}$Cs, $^{60}$Co, and $^{90}$Sr [41]. In solidification systems made by geopolymerization, geopolymers exhibit different immobilization efficiencies toward different ions, and the mechanisms vary. Zhang et al. [26] reported that Pb(II) could be immobilized in geopolymers more effectively compared to Cd(II) and Cr(VI). Wang et al. [27] determined that solidification of Pb(II), Cd(II), Mn(II), and Cr(III) in a fly ash-based geopolymer occurs by exchange with ions including Na(I) and Ca(II). However, El-Eswed et al. [33] argued that rather than ion exchange, ions including Pb(II), Cd(II), Cu(II), Th(IV), and U(VI) are immobilized by forming chemical bonds between $Si–O^{−}$ and $Al–O^{−}$. Xu et al. [34] and Peng et al. [35] compared the immobilization efficiency of Sr(II) and metakaolin geopolymer with cement and found that Sr(II) showed a higher leaching resistance. They concluded that the geopolymer matrix appeared more compact and dense, which encapsulated Sr more tightly. Among the studies on Co(II) immobilizing, metakaolin is generally used as the starting material. Kara et al. [42] studied the performance of the metakaolin geopolymer for Co(II) removal, but the immobilization rate for Co(II) was lower than for Mn(II). El-Naggar [43] improved the immobilization effect of 60Co by adding blast furnace slag to Egyptian kaolinite and reported that this geopolymer's compressive strength was significantly enhanced. In recent research, Q. Yu et al. [44] compared the performance of immobilizing Co with the Mn slag-based geopolymer and an ordinary metakaolin-based geopolymer. The results strongly suggested that divalent Co was oxidized to trivalent Co in the Mn slag-based geopolymer matrix, resulting in enhanced Co solidification capacity compared to a metakaolin-based geopolymer. The results in this study indicate that the Mn slag-based geopolymer's oxidation environment played an important role in Co immobilization [44].

Although geopolymers are considered as promising matrixes for waste solidification, the effects of the Si/Al molar ratio of geopolymer on the immobilization efficiencies for metal ions have not been fully studied and understood. Q. Tian et al. [37], were synthesized and investigated geopolymers with different Si/Al ratios from coal fly ash and silica fume. Sorption tests were conducted to evaluate their immobilization efficiencies for $Cs^{+}$. The results indicated that a geopolymer with a low Si/Al ratio could have a better immobilization performance for $Cs^{+}$ than that with a high Si/Al ratio. A high Si/Al ratio could contribute to a more compact structure of geopolymer and better sorption process [37].

Likewise, in novel investigations, a geopolymer was applied to convert ion exchange resins contaminated with radionuclides into a solid waste form. It was found that a geopolymer has superior properties to enable the encapsulation of spent resins [45-46]. However, there is limited understanding of the chemical interactions between encapsulated spent ion-exchangers, used for decontaminating wastewater, and aluminosilicate matrix. This fact makes it difficult to predict the long-term stability of the waste form [46].

Radionuclides Cs and Sr are two of the most difficult radionuclides to immobilize and are therefore suitable elements to study in assessing geopolymers as matrices for immobilization of radioactive wastes [39,47].

## IV. Conclusion

With the increasing depletion of natural raw materials, their sustainable usage is an important topic for consideration. Therefore, the development of sustainable and low carbon footprint materials is an important task for the future. Thus, waste-based geopolymers have found a possible application in the immobilization of radionuclides. This paper aims to review so far knowledge related to the utilization of waste-based geopolymers in radionuclides immobilization. All results from cited studies suggest that waste-based geopolymers represent promising matrix materials for the solidification of radioactive wastes, but more precise investigations are needed.

## Acknowledgments

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

## References

[1] C.S. Vieira, P.M. Pereira, "Use of recycled construction and demolition materials in geotechnical applications: A review", *Res. Resour. Conserv. Recycl.*, vol. 103, pp. 192-204, 2015.

[2] C. Zou, Q. Zhao, G. Zhang, B. Xiong, "*Energy revolution: from a fossil energy era to a new energy era*", Nat. Gas Ind. B, vol. 1, pp. 1-11, 2016.

[3] O. Blanchard, "Energy consumption and modes of industrialization: Four developing countries", *En. Policy*, vol. 20, pp. 1174-1185, 1992.

[4] S.S. Amritphale, P. Bhardwaj, R. Gupta, "Advanced Geopolymerization Technology", in *Geopolymer Science and Applications*, ch. 1, pp. 1-11, London, UK: Intech Open, 2019.

[5] European Commission, Waste Framework Directive 2008/98/EC, Off. Journal of the European Union, L 312, https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX: 32008L0098& from=EN

[6] Environment Action Programme EU 2013, Living well, within the limits of our planet, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32013D1 386

[7] J. Davidovits, "Geopolymers", *J. Thermal Anal.*, vol. 37, pp. 1633-1656, August, 1991.

[8] J.L. Provis, "Geopolymers and other alkali activated materials: why, how, and what?", *Mater.Struct.*, vol. 47, pp. 11-25, January, 2014.

[9] A. Noorul, M. Faisal, K. Muhammad, S. Gul, Synthesis and characterization of geopolymer from bagasse bottom ash, waste of sugar industries and naturally available China clay. *J. Clean. Prod.*, vol. 129, pp. 491-495, 2016.

[10] J.L. Provis, A. Palomo, C. Shi, "Advances in understanding alkali-activated materials", *Cem. Concr. Res.*, vol. 78, pp. 110-125, 2015.

[11] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer. "Geopolymer Technology: The Current State of the Art", *J. Mater. Sci*., vol. 42, no. 9, pp. 2917-2933, 2007.

[12] J. Davidovits, *Geopolymers-Inorganic polymeric new material*, Reprint of Journal of Thermal Analyses (1991), Saint-Quentin, France, Institut Géopolymère, 1997.

[13] Y. Hu, S. Liang, J. Yang, Y. Chen, N. Ye, Y. Ke, S. Tao, K. Xiao, J. Hu, H. Hou, W. Fan, S. Zhu, Y. Zhang, B. Xiao, "Role of Fe species in geopolymer synthesized from alkali-thermal pretreated Fe-rich Bayer red mud", *Constr. Build. Mater*., vol. 200, pp. 398-407, 2019.

[14] J.S.J. Van Deventer, J.L. Provis, P. Duxson, G.C. Lukey, "Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products", *J. Hazard. Mater*., vol. 139 pp. 506-513, 2007.

[15] T. Cheng, M. Lee, M. Ko, T. Ueng, S. Yang, S. The heavy metal adsorption characteristics on metakaolin-based geopolymer. *Appl. Clay Sci*., vol. 56, pp. 90-96, 2012.

[16] C. Fernández-Pereira, Y. Luna-Galiano, M. Pérez-Clemente, C. Leiva, F. Arroyo, R. Villegas, L.F. Vilches, Immobilization of heavy metals (Cd, Ni or Pb) using aluminate geopolymers, *Mater. Lett.*, vol. 227, pp. 184-186, 2018.

[17] M. I., Ojovan, W. E., Lee, *An Introduction to Nuclear Waste Immobilization*, Second edition. Elsevier, 2014.
[18] S., Stefanovsky, S., Yudintsev, R., Giere, G., Lumpkin, *Nuclear waste forms*, The Geological Society of London, London, UK, 2004.
[19] D. Nies, S. Silver, *Molecular Microbiology of Heavy Metals*. Springer. Berlin, Germany, 2007.
[20] C. Grupen, M. Rodgers, *Radioactivity and Radiation*, Springer, Berlin, Germany, 2016.
[21] I. Jelic, M. Sljivic-Ivanovic, S. Dimovic, D. Antonijevic, M. Jovic, M. Mirkovic, I. Smiciklas, The Applicability of Construction and Demolition Waste Components for Radionuclide Sorption, *J. Clean. Prod*., vol. 171, pp. 322-332, 2018.
[22] I. Jelic, M. Sljivic-Ivanovic, S. Dimovic, D. Antonijevic, M. Jovic, R. Serovic, I. Smiciklas, Utilization of Waste Ceramics and Roof Tiles for Radionuclide Sorption, Process Saf Environ, 105, pp. 348-360, 2016.
[23] M. Sljivic-Ivanovic, I. Jelic, A. Loncar, D. Nikezic, S. Dimovic, B. Loncar, The application of experimental design methodology for the investigation of liquid radioactive waste treatment. Nucl Technol Radiat, vol. 32, no. 3, pp. 281-287, 2017.
[24] M. Sljivic-Ivanovic, I. Jelic, S. Dimovic, D. Antonijevic, M. Jovic, A. Mrakovic, I. Smiciklas, Exploring innovative solutions for aged concrete utilization: treatment of liquid radioactive waste, Clean Technol Envir, vol. 20, no. 6, pp. 1343-1354, 2018.
[25] K. Al-Zboona, M. S. Al-Harahshehb, F.B. Hani, Fly ash-based geopolymer for Pb removal from aqueous solution, *J. Hazard. Mater*., vol. 188, pp. 414-421, 2011.
[26] J. Zhang, J.L. Provis, D. Feng, J.S. van Deventer, Geopolymers for immobilization of Cr(VII), Cd(II), and Pb(II). *J. Hazard Mater*., vol. 157, no. (2-3), pp. 587-598, 2008.
[27] Y. Wang, F. Han, J. Mu, Solidification/stabilization mechanism of Pb(II), Cd(II), Mn(II) and Cr(III) in fly ash based geopolymers, *Constr. Build. Mater.*, vol. 30, no. 160, pp. 818-827, 2018.
[28] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage*., vol. 92, pp. 407-418, 2011.
[29] M. Grace, E. Clifford, M. Healy, The potential for the use of waste products from a variety of sectors in water treatment processes, *J. Clean. Prod*., vol. 137, pp. 788-802, 2016.
[30] R. Malviya, R. Chaudhary, Factors affecting hazardous waste solidification/stabilization: A review. *J. Hazard Mater.*, vol. 137, no. 1, pp. 267-276, 2006.
[31] J. Li, J., Wang, Advances in cement solidification technology for waste radioactive ion exchange resins: A review. J. Hazard Mater., vol. 135, no. (1-3), pp. 443-448, 2006.
[32] M. Ahmaruzzaman, A review on the utilization of fly ash, *Prog. Energy Combust. Sci.*, vol. 36, no. 3, pp. 327-363, 2010.
[33] B.I. El-Eswed, O.M. Aldagag, F.I. Khalili, Efficiency and mechanism of stabilization/solidification of Pb(II), Cd(II), Cu(II), Th(IV) and U(VI) in metakaolin based geopolymers, *Appl. Clay Sci*., vol. 140, pp. 148-156, 2017.
[34] Z. Xu, Z. Jiang, D. Wu, X. Peng, Y. Xu, N. Li, Y. Qi, P. Li, Immobilization of strontium-loaded zeolite A by metakaolin based-geopolymer. Ceram. Int., vol. 43, no. 5, pp. 4434-4439, 2017.
[35] X. Peng, Y. Xu, Z. Xu, D. Wu, D. Li, Effect of simulated radionuclide strontium on geopolymerization process, *Procedia Environ. Sci*., vol. 31, pp. 325-329, 2016.
[36] N. Deng, H. An, H. Cui, Y. Pan, B. Wang, L. Mao, J. Zhai, Effects of gamma-ray irradiation on leaching of simulated 133Cs+ radionuclides from geopolymer wasteforms, *J. Nucl. Mater*., vol. 459, pp. 270–275, 2015.
[37] Q. Tian, S. Nakama, K. Sasaki, Immobilization of cesium in fly ash-silica fume based geopolymers with different Si/Al molar ratios, Science of the Total Environment, vol. 687, pp. 1127–1137, 2019.
[38] X. Liu, Yi D. Lu, X. Lu, Immobilization of Simulated Radionuclide $^{90}$Sr by Fly Ash-Slag-Metakaolin–Based Geopolymer, *Nucl Technol*, vol. 198, no. 1, pp. 64-69, 2017.
[39] B. Walkleya, X. Kea, O.H. Hussein, S.A. Bernal, J.L. Provis, Incorporation of strontium and calcium in geopolymer gels, *J. Hazard Mater*, vol. 382, no. 121015, 2020.
[40] T. Hanzlicek, M. Steinerova, P. Straka, Radioactive Metal Isotopes Stabilized in a Geopolymer Matrix: Determination of a Leaching Extract by a Radiotracer Method, J. Am. Ceram. Soc., vol. 89, no. 11, pp. 3541-3543, 2006.
[41] International Atomic Energy Agency (IAEA), Radiological Characterization of Shut Down Nuclear Reactors for Decommissioning Purposes, Technical Reports Series No. 389, Vienna, 1998.
[42] I. Kara, D. Tunc, F. Sayin, S.T. Akar, Study on the performance of metakaolin based geopolymer for Mn(II) and Co(II) removal, *Appl. Clay Sci.*, vol. 161, pp. 184-193, 2018.
[43] M.R. El-Naggar, Applicability of alkali activated slag-seeded Egyptian Sinai kaolin for the immobilization of 60Co radionuclide. *J. Nucl. Mater.*, vol. 447, pp. 15-21, 2014.
[44] Q. Yu, S. Li, H. Li, X. Chai, X. Bi, J. Liu, T. Ohnuki, Synthesis and characterization of Mn-slag based geopolymer for immobilization of Co, *J. Clean. Prod*, vol. 234, 97-104, 2019.
[45] W.H. Lee, T.W. Cheng, Y.C. Ding, K.L. Lin, S.W. Tsao, C.P. Huang, Geopolymer technology for the solidification of simulated ion exchange resins with radionuclides, *J Environ Manage*, vol. 235, pp. 19-27, 2019.
[46] X. Ke, S.A. Bernal, T. Sato, J.L. Provis, Alkali aluminosilicate geopolymers as binders to encapsulate strontium-selective titanate ion-exchangers, *Dalton Trans*., vol. 48, pp. 12116-12126, 2019.
[47] N. Vandevenne, R.I. Iacobescu, R. Carleer, P. Samyn, J. D'Haen, Y. Pontikes, S. Schreurs, W. Schroeyers, Alkali-activated materials for radionuclide immobilisation and the effect of precursor composition on Cs/Sr retention, *J. Nucl. Mater.*, vol. 510, pp. 575-584, 2018.

APSTRAKT

Cilj ovog rada je pregled upotrebe otpadnih komponenti za imobilizaciju radionuklida geopolimerizacijom. Geopolimeri predstavljaju širok spektar aluminosilikata koji se aktiviraju u alkalnoj sredini. Sinteza geopolimera iz otpada ne samo da omogućava manju potrošnju sirovina, već se bavi i pitanje odlaganja otpada. Leteći pepeo, crveni mulj, građevinski otpad i šljaka su najčešće korišćene vrste otpada. Prednost ovih otpadnih materijala predstavlja mogućnost upotrebe bilo kog aluminosilikatnog otpada koji može da se rastvori u alkalnom rastvoru kako bi se proizveo matriks za imobilizaciju radionuklida. Uprkos mnogim publikacijama i istraživanjima u vezi korišćenja otpadnih komponenti u geopolimerizaciji, upotreba geopolimera na bazi otpada pri odlaganju radionuklida još uvek nije razvijena.

**Upotreba geopolimera na bazi otpada za imobilizaciju radionuklida - Pregled**

Slavko Dimović, Ivana Jelić i Marija Šljivić-Ivanović