

IRENA NIKOLIĆ<sup>1</sup>, MILENA TADIĆ<sup>1</sup>, DIJANA ĐUROVIĆ<sup>2</sup>,  
RADOMIR ZEJAK<sup>3</sup>, BOBAN MUGOŠA<sup>2</sup>

## STABILIZATION/SOLIDIFICATION OF SPENT GRIT IN FLY ASH BASED GEOPOLYMERS

Stabilization/solidification (S/S) method is a potential solution for immobilization of heavy metals containing waste. Immobilization of heavy metals from spent grit, waste material from the shipbuilding and ship repair industry, into the fly ash based geopolymers using the S/S method was evaluated. Addition of spent grit in the quantity of 10% of total solid content of geopolymer mixture decreased the compressive strength of fly ash based geopolymers but did not affect the change of geopolymer strength in function of synthesis parameters. TCLP and EN 12457-2 leaching test were used for the evaluation of chemical stability of contaminated geopolymers with respect to the leaching of heavy metals. The both, TCLP and EN 12457 leachates fulfill the maximum acceptable limits for landfill disposal with respect to the heavy metals concentration. The highest concentration of Zn is observed in a both, TCLP and EN 12457 leachates due to the synthesis parameters.

### 1. INTRODUCTION

Geopolymerization is an innovative technology that can transform various aluminosilicate materials by alkali activation into useful materials, so called geopolymers [1]. A highly alkali mixture of alkali hydroxide and alkali silicate is mainly used as an alkali activator. Geopolymerization is also recognized as a waste minimization technology because it enables utilization of waste aluminosilicate materials like metallurgical slag [2, 3] and fly ash [4–6]. The mechanism of the geopolymerization process is not fully understood but assumption is that it consists of several processes such as dissolution of starting materials and formation of aluminate and silicate monomeric species and

---

<sup>1</sup>Faculty of Metallurgy and Technology, University of Montenegro, Džordža Vašingtona bb, 81000 Podgorica, Montenegro, corresponding author M. Tadić, e-mail: milenak@ac.me

<sup>2</sup>Institute of Public Health of Montenegro, Džona Džeksona bb, 81000 Podgorica, Montenegro.

<sup>3</sup>Faculty of Civil Engineering, University of Montenegro, Džordža Vašingtona bb, 81000 Podgorica, Montenegro.

polycondensation which lead to the formation of three dimensional aluminosilicate network and the hardening of geopolymer structure [7]. Dissolution process enables breaking of Al–O–Si and Si–O–Si bonds in the starting materials and liberation of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  to form a monomeric  $[\text{Al}(\text{OH})_4]^-$ ,  $[\text{SiO}_2(\text{OH})_2]^{2-}$  and  $[\text{SiO}(\text{OH})_3]^-$  species which further continue to condense leading to the formation of aluminosilicate network [8].

Geopolymerization received attention in two potential applications: as a promising technology for production of environmentally friendly materials which may be successfully used as a replacement for cement based materials and as a possible solution for stabilization/solidification (S/S) of toxic wastes [9, 10]. Solidification is conversion of liquid or semi solid sludge waste to a stable solid material encapsulating toxic materials through isolation, precipitation and/or adsorption while the stabilization involves chemical reaction between toxic materials and binders [11].

Currently, special attention is paid to the immobilization of heavy metals. They are considered to be one of the main pollutants in the environment as they are toxic, non-biodegradable and have a very long half-life in soil [12], having a significant effect on plants and animals and to the humans. This is the reason for arousing public awareness of the need to protect the environment from the effects of these pollutants and in this sense, stabilization/solidification of heavy metals contained in waste by the geopolymerization process is a promising method.

The shipbuilding industry is the one of the potential sources of environmental pollution. In the ship repair industry, abrasive blasting is the most common surface preparation technique used to remove old paint and other surface materials such as rust, mill scale, dirt and salts. Surface preparation techniques such as abrasive blasting are also one of the most significant sources of shipyard wastes and pollution. The paint usually contains heavy metals which act as anti-fouling and anti-corrosion agents and during blast cleaning the paint contaminates the abrasive material – grit, producing the waste – spent grit (SG) which contains heavy metals. Such contaminated spent grit may present a potential risk for both human health and environment and impose the restriction for its dispose. So far, use of spent grit as an aggregate in the production of Portland cement concrete and in the production of asphalt concrete for roadways has been considered [13].

In this paper, the possibility of using the fly ash based geopolymers (FA-geopolymers) for the stabilization/solidification of spent grit has been considered. The aim was to convert the spent grit in the environmentally accepted building materials – fly ash based geopolymers.

## 2. EXPERIMENTAL

High calcium fly ash (FA) was supplied from the coal fired power station Pljevlja and spent grit from the shipyard Bijela in Montenegro. Chemical composition of fly ash and heavy metals content in SG are given in Table 1.

Table 1

Table 1. Chemical composition of FA and heavy metals content in SG

FA		SG	
Component	Content [%]	Component	Content [g/kg]
SiO <sub>2</sub>	49.45	Zn	1.16
Fe <sub>2</sub> O <sub>3</sub>	5.23	Pb	0.18
Al <sub>2</sub> O <sub>3</sub>	21.77	Cr	4.20
TiO <sub>2</sub>	0.66	Cu	1.10
CaO	13.34	Ni	7.80
Na <sub>2</sub> O	0.46	Cd	0.51
ZnO	4.5·10 <sup>-3</sup>		
MgO	1.29		
MnO	0.02		
P <sub>2</sub> O <sub>5</sub>	0.24		
K <sub>2</sub> O	1.4		
LOI <sup>a</sup>	4.35		

<sup>a</sup>Loss on ignition.

The mixture of NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions in the weight ratio of 1, 1.5 and 2 was used as an alkali activator. 7, 10 and 13 M NaOH solution was used for the synthesis of the geopolymer. Geopolymers were prepared at constant solid (S) to liquid (L) ratio of 1.3. Fly ash based geopolymers contaminated with spent grit were prepared by adding spent grit to the starting mixture with fly ash in the quantity of 10% to the total solid content. The initial compositions of geopolymer mixture are given in Table 2.

Fly ash based geopolymers (FA1-5) were prepared by mixing FA with the alkali silicate activator while fly ash based geopolymers contaminated with SG (FG1-5) were prepared by mixing of SG with the NaOH solution for 10 min to enable dissolution of heavy metals from SG and then Na<sub>2</sub>SiO<sub>3</sub> solution was added. Finally, FA was added into the mixture of alkali silicate solution with SG, and mixing was continued for 5 min. Pastes prepared in such a way were cast into cylindrical plastic moulds (28×60 mm) and sealed with a lid to prevent loss of evaporating water. The samples were cured in the oven for 48 h at 65 °C. After that, the specimens were allowed to cool, removed from moulds and left to rest additional 7 days at ambient temperature before any testing was performed. Before compressive strength testing sample, surfaces were polished flat and parallel. Compressive strength measurements were performed using three cylinders of each sample and averaging the obtained experimental values.

Table 2

Composition of initial FA and FG geopolimer mixtures

Mixture	SG [%]	S/L [g/g]	Na <sub>2</sub> SiO <sub>3</sub> /NaOH	c(NaOH) [mol/dm <sup>3</sup> ]
FA1	–	1.3	1.5	7
FA2	–	1.3	1.5	10
FA3	–	1.3	1.5	13
FA4	–	1.3	1	10
FA5	–	1.3	2	10
FG1	10	1.3	1.5	7
FG2	10	1.3	1.5	10
FG3	10	1.3	1.5	13
FG4	10	1.3	1	10
FG5	10	1.3	2	10

The morphological characterization of the FA and FG geopolymers was performed using the low vacuum modus of the FEI environmental scanning electron microscope (ESEM) Quanta 200 equipped with the EDAX Genesis energy dispersive spectrometer.

The immobilization efficiency was evaluated using the TCLP method No. 1311 [14] and EN 12457-2 [15] leaching tests. For the purpose of TCLP and EN 12457-2 reproduction, fragments of specimens after mechanical tests were collected and used as the samples for leaching tests. During TCLP test, the solid was pulverized and mixed with an extraction fluid (acetic acid solution pH = 3) at the solid: liquid ratio 1:20 for 18 h. The method EN 12457-2 is similar to the TCLP test but the extraction fluid is deionized water. In this case, solid phase was mixed with deionized water at the solid to liquid ratio of 1:10 for 24 h. After the tests, solid and liquid phases were separated by filtration and the eluates were acidified with nitric acid to pH < 2. Metals content was determined using ICP-OES.

### 3. RESULTS AND DISCUSSION

The results obtained by the investigation of the dependences of the compressive strength of FA and FG geopolymers on alkali and silicate dosage, i.e. the NaOH concentration and Na<sub>2</sub>SiO<sub>3</sub>/NaOH weight ratio are shown illustrated in Figs. 1 and 2.

The increase of NaOH concentration leads to the increase of compressive strength of FA and FG geopolymers. However, beneficiary influence of alkali dosage to the compressive strength of geopolymers is limited. The maximal values of geopolymers strength were obtained using 10 M NaOH and further increase of concentration of

NaOH to the value of 13 M leads to a slight decrease of compressive strength (Fig. 1). Similar effect of alkali dosage on the mechanical properties of fly ash based geopolymers was observed earlier [16].

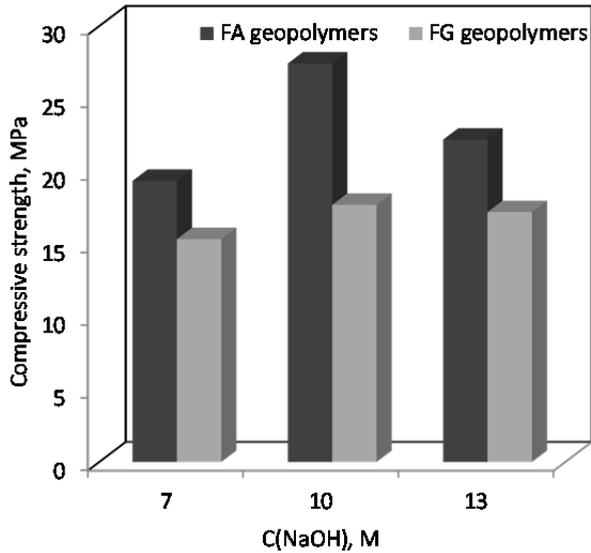


Fig. 1. Dependences of the compressive strength of FA and FG geopolymers on the NaOH concentration

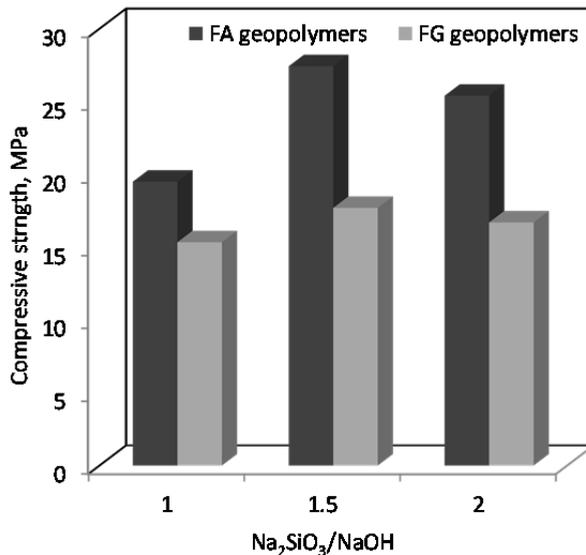


Fig. 2. Dependences of the compressive strength of FA and FG geopolymers on the Na<sub>2</sub>SiO<sub>3</sub>/NaOH weight ratio

The increase of alkali dosage in the range of 7–10 M leads to the faster dissolution of Al and Si from the fly ash providing more Al and Si oligomeric species [17] for the condensation process. This leads to the more effective geopolymerization and higher compressive strength of geopolymers [18]. The increase of the alkali dosage above 10 M results in a more effective Si dissolution [19] in comparison to Al, leading to more probable formation of Si–O–Si polymeric bonds in comparison to the Al–O–Si bonds, which decrease the compressive strength of geopolymers. Addition of spent grit to the geopolymer mixture decreases the compressive strength of geopolymers but does not influence the change of strength with the change of alkali dosage.

Similarly, the increase of silicate dosage, i.e. the increase of  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  weight ratio from 1 to 1.5, leads to the increase of geopolymers strength, while the further increase leads to the reduction of compressive strength (Fig. 2). Silicate dosage strongly influences the viscosity of geopolymer mixture. At the  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  weight ratio higher than 1.5, a very viscous geopolymer paste was obtained which could not be spontaneously casted in the mould. Thus, the increase of geopolymer strength at the  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  weight ratio higher than 1.5 is limited by the paste workability. At the value of this ratio equal to 2, a very bad workability of paste was obtained and obvious fractures on the geopolymers surface were observed which caused the decrease of compressive strength. Moreover, increase of the silicate dosage decreases pH, which inhibits dissolution of Al and Si from the fly ash [20] and hinders geopolymer phase formation leading to the decrease of compressive strength. As in the previous case, the strength of FG geopolymers is lower in comparison to the strength of FA geopolymers but the dependence of geopolymer strength changed in a function of silicate dosage is the same.

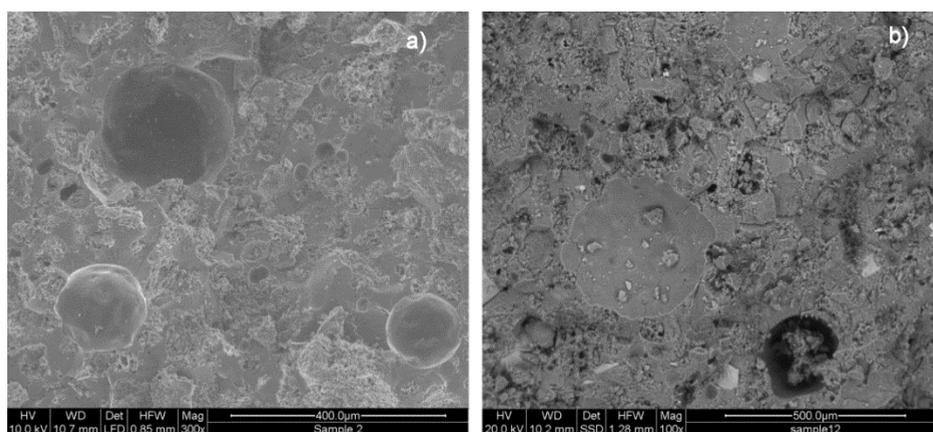


Fig. 3. SEM images of: a) FA and b) FG geopolymers

The samples of FA and FG geopolymers which showed the highest values of compressive strength were subjected to microstructural investigations. In both cases,

FA and FG geopolymers showed the highest value of compressive strength in 10 M NaOH and Na<sub>2</sub>SiO<sub>3</sub>/NaOH weight ratio of 1.5. The SEM images of FA2 and FG2 geopolymers are shown in the Fig. 3. In both cases, separated two phases were clearly observed, the gel phase (geopolymer) and the phase of unreacted FA particles.

The immobilization of heavy metals in geopolymers involves both physical encapsulation and chemical immobilization processes which depend on the total extractable cation concentration [21]. The efficiency of immobilization of heavy metals from SG in the fly ash based geopolymers was evaluated using the TCLP and EN 12457-2 leaching tests, comparing the metals concentration in a TCLP and EN 12457 leachates with the limits established by USEPA (US Environmental Protection Agency) and EULFD (European Landfill Directive). The results are summarized in Tables 3 and 4.

Table 3

Metal content in FG geopolymers [mg/kg] (EN 12457-2) and EULFD limits

c(NaOH) [mol/dm <sup>3</sup> ]	Na <sub>2</sub> SiO <sub>3</sub> /NaOH	Metal content					
		Cd	Cr <sub>(tot)</sub>	Cu	Ni	Pb	Zn
7	1.5	0.17	0.28	0.5	0.23	0.38	1.18
10	1.5	0.18	0.26	0.3	0.23	0.45	1.05
13	1.5	0.17	0.2	0.31	0.25	0.4	0.53
10	1	0.18	0.3	0.35	0.23	0.45	1.01
10	2	0.17	0.27	0.5	0.3	0.4	2.69
Inert waste		0.04	0.5	2	0.4	0.5	4
Non-hazardous waste		1	10	50	10	10	50
Hazardous waste		5	70	100	40	50	200

Table 4

Metal content in FG geopolymers [mg/dm<sup>3</sup>] (TCLP) and USEPA limits

c(NaOH) [mol/dm <sup>3</sup> ]	Na <sub>2</sub> SiO <sub>3</sub> /NaOH	Metal content <sup>a</sup>					
		Cd	Cr <sub>(tot)</sub>	Cu	Ni	Pb	Zn
7	1.5	nd	nd	nd	<0.1	<0.1	0.788
10	1.5	nd	nd	nd	<0.1	<0.1	0.753
13	1.5	nd	nd	nd	<0.1	<0.1	0.493
10	1	nd	nd	nd	<0.1	<0.1	0.258
10	2	nd	nd	nd	0.123	<0.1	0.8
US EPA limits		0.5	5	–	–	5	300

<sup>a</sup>nd – not detected.

EN 12457 leachates are highly alkaline (average value of pH is 11) due to the mobility of Na<sup>+</sup> ions in the aquatic medium. pH of TCLP leachate is somehow lower but the solution is also alkaline (average value of pH is 8.2). The excess of Na<sup>+</sup> ions in the geopolymer mixture remains unreacted after the geopolymerization process and is de-

posited in geopolymer pores [22, 23]. In contact with aquatic environment, ion exchange between  $\text{Na}^+$  and  $\text{H}_3\text{O}^+$  occurs, contributing to the increase of pH [24] which may influence the mobility of heavy metals with a strong pH dependent solubility [25].

The results presented in the Tables 3 and 4 have shown that the concentration of Cd exceeds the EULFD for the inert waste but fulfil the acceptable limits for non-hazardous waste. The concentrations of all other potential hazardous metals are below the EULFD limits for inert waste. The concentrations of all metals in TCLP geopolymer leachates are below the USEPA limits for a hazardous waste. The highest concentrations of all heavy metals in FG geopolymer leachates were observed for Zn ions and the most expressive influence of the synthesis parameters was observed in this case. It is evident that Zn concentration in both EN 12457 and TCLP leachates decreases with the increase of NaOH concentration used for the synthesis of FG geopolymers, i.e. efficiency of Zn immobilization increases with the increase of alkaline dosage in the range of 7–13 M. Adding more alkali is expected to increase the solubility of Zn and also Al and Si from the fly ash, providing the higher concentrations of Al and Si species to bind Zn in a less soluble form or to encapsulate it into the geopolymer matrix. On the other hand, the increase of silicate dosage, i.e. the increase of  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  ratio leads to the increase of Zn concentration in both, EULFD and TCLP geopolymer leachates which indicate the decrease of immobilization efficiency of Zn.

However, as the EN 12457-2 and TCLP leachates are alkaline, these tests are insufficient to address a wide range of possible exposure conditions of waste and additional pH dependence leaching tests should be conducted which will be the meter of further study.

#### 4. CONCLUSIONS

- The addition of spent grit to the fly ash in the quantity of 10% of the total solid content does not change the influence of synthesis parameters on the compressive strength of fly ash based geopolymers. The same effect of alkali and silicate dosage on the compressive strength of FA and FG geopolymers is observed, but the lower values of compressive strength of FG geopolymers in comparison to the strength of FA geopolymers are observed.

- Leaching tests have shown that heavy metals from spent grit can be immobilized in the fly ash based geopolymers. The highest concentration in TCLP and EN-12457 leachates is observed for Zn ion which is affected by the synthesis parameters. Immobilization efficiency of Zn increases with the increase of NaOH concentration and decrease of  $\text{Na}_2\text{SiO}_3/\text{NaOH}$  weight ratio. However, additional pH dependent leaching tests need to be done for a complete consideration of immobilization of heavy metals from spent grit in the fly ash based geopolymers.

## ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the Ministry of Science of Montenegro in the framework of project No. 01-460. The authors especially thank prof dr. Velimir Radmilović from the University of Belgrade, Faculty of Technology and Metallurgy, Nanotechnology and Functional Materials Center for support in microstructure investigations. SEM-EDS analysis was performed at the Austrian Centre for Electron Microscopy and Nanoanalysis, Graz Centre for Electron Microscopy.

## REFERENCES

- [1] DAVIDOVITS J., *Geopolymers, inorganic polymeric new materials*, J. Therm. Anal., 1991, 37 (8), 1633.
- [2] DAVIDOVITS J., *Application of Ca-based geopolymer with blast furnace slag, a review*, 2nd International Slag Valorisation Symposium, Leuven 2011.
- [3] MARAGKOS I., GIANNOPOULOU I.P., PANIAS D., *Synthesis of ferronickel slag-based geopolymers*, Mineral. Eng., 2009, 22 (2), 196.
- [4] BAKHAREV T., *Geopolymeric materials prepared using class F fly ash and elevated temperature curing*, Cement Concrete Res., 2005, 35 (6), 1224.
- [5] ANDINI S., CIOFFI R., COLANGELO F., GRIECO T., MONTAGNARO F., SANTORO L., *Coal fly ash as raw material for the manufacture of geopolymer-based products*, Waste Manage., 2008, 28 (2), 416.
- [6] PALOMO A., GRUTZECK M.W., BLANCO M.T., *Alkali-activated fly ashes. A cement for the future*, Cement Concrete Res., 1999, 29 (8), 1323.
- [7] PANIAS D., GIANNOPOULOU I.P., PERRAKI T., *Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers*, Colloid. Surface. A., 301 (1–3) 246.
- [8] SAGOE-CRENTSIL K., WENG L., *Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis. Part II. High Si/Al ratio systems*, J. Mater. Sci., 2007, 42 (9), 3007.
- [9] LUNA-GALIANO Y., FERNANDEZ PEREIRA C., VALE J., *Stabilization/solidification of a municipal solid waste incineration residue using fly ash-based geopolymers*, J. Hazard. Mater., 2011, 185 (1), 373.
- [10] FERNANDEZ PEREIRA C., LUNA Y., QUEROL X., ANTENUCCI D., VALE, J., *Waste stabilization/solidification of an electric arc furnace dust using fly ash-based geopolymers*, Fuel, 2009, 88 (7), 1185.
- [11] JAARVELD VAN J.G.S., DEVENTER VAN J.S.J., *The effect of metal contaminants on the formation and properties of waste-based geopolymers*, Cement Concrete Res., 1999, 29 (8) 1189.
- [12] RAM M.S., SINGH L., SURYANARAYANA M.V., ALAM S.T., *Effect of iron, nickel, cobalt on bacterial activity and dynamics during anaerobic oxidation of organic matter*, Water Air Soil Poll., 2000, 117 (1–4), 305.
- [13] BURUIANA D.L., BORDE M., *Minimization and use of grit waste from surface cleaning operations*, Metalurgia Int., 2011, 16 (11), 159.
- [14] USEPA, 1990. *Toxicity Characteristic Leaching Procedure TCLP Fed. Regist., Appendix II. Method 1311*, United States Environmental Protection Agency.
- [15] EULFD, 2002.EN 12457. *Characterisation of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. Part 2. One stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm*, European Landfill Directive, European Committee for Standardisation.
- [16] RATTANASAK U., CHINDAPRASIRT P., *Influence of NaOH solution on the synthesis of fly ash geopolymer*, Mineral. Eng., 2009, 22 (12), 1073.
- [17] PANAGIOTOPOULOU C., KONTORI E., PERRAKI T., KAKALI G., *Dissolution of aluminosilicate minerals and by-products in alkaline media*, J. Mater. Sci., 2007, 42 (9), 2967.

- 
- [18] PANIAS D., GIANNOPOULOU I.P., PERRAKI T., *Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers*, Colloid. Surface. A., 2007, 301 (1–3), 246.
- [19] LI C., LI Y., SUN H., LI L., *The composition of fly ash glass phase and its dissolution properties applying to geopolymeric materials*, J. Am. Ceram. Soc., 2011, 94 (6), 1773.
- [20] DUXSON P., PROVIS J.L., LUKEY G.C., MALLICOAT S.W., KRIVEN W.M., VAN DEVENTER J.S.J., *Understanding the relationship between geopolymer composition, microstructure and mechanical properties*, Colloid. Surface A, 2005, 269 (1–3), 47.
- [21] PHAIR J.W., VAN DEVENTER J.S.J., SMITH J.D., *Effect of Al source and alkali activation on Pb and Cu immobilisation in fly-ash based geopolymers*, Appl. Geochem., 2004, 19 (3), 423.
- [22] DUXSON P., LUKEY G.C., SEPAROVIC F., VAN DEVENTER J.S.J., *Effect of alkali cations on aluminum incorporation in geopolymeric gels*, Ind. Eng. Chem. Res., 2005, 44 (4), 832.
- [23] DUXSON P., PROVIS J.L., LUKEY G.C., VAN DEVENTER J.S.J.,  *$^{39}\text{K}$  NMR of free potassium in geopolymers*, Ind. Eng. Chem. Res., 2006, 45 (26), 9208.
- [24] ALY Z., VANCE E.R., PERERA D.S., HANNA J.V., GRIFFITH C.S., DAVIS J., DURCE D., *Aqueous leachability of metakaolin-based geopolymers with molar ratios of  $\text{Si}/\text{Al} = 1.5\text{--}4$* , J. Nucl. Mater., 2008, 378 (2), 172.
- [25] IZQUIERDO M., QUEROL X., DAVIDOVITS J., ANTENUCCI D., NUGTEREN H., FERNANDEZ PEREIRA C., *Coal fly ash–slag based geopolymers. Microstructure and metal leaching*, J. Hazard. Mater., 2009, 166 (1), 561.