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# Geopolymerization of fly ash as a possible solution for stabilization of used sandblasting grit

Geopolymers are relatively new, environmentally friendly and light weight materials which form as a result of a reaction of aluminosilicate materials with a highly alkaline solution. They are characterised by good mechanical properties and are considered a possible replacement for ordinary Portland cement in construction. In addition, geopolymerization technology is recognized as a possible way of immobilization of toxic waste (nuclear waste, waste water, waste containing heavy metals, etc.). In this paper, we have investigated the possibility of immobilization of used sandblasting grit in fly ash based geopolymers. The results have shown that geopolymerization of fly ash with the addition of used sandblasting grit is possible. Microstructure of synthesized geopolymers is characterised by the presence of aluminosilicate gel and unreacted fly ash. However, compared to fly ash based geopolymers, lower compressive strength is obtained. It is demonstrated that Si/Al ratio determines the compressive strength of geopolymers.

Key words: geopolymerisation, geopolymer, fly ash, sanblasting grit.

## 1. INTRODUCTION

Fly ash is a coal fire by-product material from coal fired power stations. The total amount of coal combustion product produced worldwide is estimated to be about 550 million tonnes, about 68 % of which is from fly ash, and about 117 millions of tonnes of fly ash is valorized into the construction industry and underground mining during 2008. year [1]. Fly ash has already been applied in the civil engineering as an additive to the cement, as raw kiln feed material and as a direct cement replacement, in concrete, in the production of lightweight aggregates and lightweight blocks and road construction.

In addition of red mud, steel slag and used sandblasting grit, fly ash landfill in Pljevlja is indentified as a major environmental problem in Montenegro. It is estimated that about 44 t/h of fly ash is produced in coal fired power station Pljevlja [2], so its valorisation deserves special attention. In recent years, intense studies of the geopolymerization process as an option of fly ash utilisation were studied extensively. Glukhovsky first hypothesized that natural geological transformation which occurs in aluminosilicate minerals may be the basis of structure formation process in a cementitious binder [3]. Later, Davidovits [4] suggested that a reaction of solid. aluminosilicate minerals with strong alkali metal silicate solutions be called "geopolymerization" and useful, environmentally friendly materials produced in such a way - "geopolymers" or inorganic polymers. Raw materials for the synthesis of geopolymers can be either natural aluminosilicate minerals [5,6], or waste with high content of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, such as fly ash and metallurgical slag [7,8]. In the pastten years geopolymers attracted much attention primarily due to good mechanical properties. The geopolymerization mechanism has not yet been clarified and it is assumed that it consists of several steps [9]:

- Dissolution of solid aluminosilicate materials in a strong alkaline aqueous solution
- Formation of Si and/or Si-Al oligomers in an aqueous phase
- Polycondensation of oligomeric species or units in an aqueous phase to form an inorganic polymeric material
- Bonding of undissolved solid particles in the final geopolymeric structure.

Besides, geopolymerization is recognized as a possible technology for immobilization of hazardous waste [10]. In that sense we have investigated the possibility of immobilization of used sandblasting grit through the geopolymerization process. Sandblasting grit is used in shipyards to clean dirt, corrosion, paint or other coatings from ship surfaces and, as a result, it contains organic and inorganic toxic components which may represent an important problem in the environment protection policy.

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In this paper we have investigated the possibility of immobilization of used sandblasting grit in construction materials through its fixation in fly ash based geopolymers.

#### 2. EXPERIMENT

Fly ash used for geopolymerization is supplied from coal fired power station – Pljevlja, Montenegro, and its chemical composition is given in the Table 1.

Composition	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	Na <sub>2</sub> O	ZnO	MgO	MnO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	LOI <sup>*</sup>
%	49.45	5.23	21.77	0.66	13.34	0.46	$4.5 \cdot 10^{-3}$	1.29	0.02	0.24	1.4	4.35

Table 1. Chemical composition of fly ash

<sup>\*</sup>Loss on ignition

Alkali solutions were prepared by mixing of 10 mol·dm<sup>-3</sup> NaOH solution and sodium silicate solution (Na<sub>2</sub>O = 8.5%, SiO<sub>2</sub> = 28.5%, density of 1.4 kg·m<sup>-3</sup>) with a ratio water glass/NaOH of 2. Sodium hydroxide solution is obtained by dissolving of solid NaOH pallets in distilled water and sodium silicate solution was a commercial water glass supplied by Galenika Magmasil, Beograd.

Geopolymers were synthesised by mixing of fly ash or mixture of fly ash and used sandblasting grit with a alkali solution in mass ratio solid/liquid (S/L) of 0.75, 1 and 1.25. Grit is added in a quantity of 10, 20 and 30 % of total solid content in geopolymer mixture.

Used sand blasting grit is supplied from the shipyard Bijela in Montenegro. Geopolymer paste was casted in cylindrical plastic moulds and cured in an oven at the temperature of 65°C for 24 h. After 24 h the moulds have been demolished and the specimens were left at the ambient temperature for a next 6 days and tested for a compressive strength. Scanning electron microscopy investigationsalong with EDX analysiswere done as well.

#### 3. RESULTS AND DISCUSSION

Change of compressive strength as a function of solid to liquid ratio at different percentages of used sandblasting grit is shown in the table 2.

It is evident that compressive strength of geopolymers increases with the increase of solid to liquid ratio from 0.75 to 1.25. This may be explained by the decreasing of water content in the geopolymer mixture. Moreover, addition of used sand blasting grit

decreases compressive strength the higher the percenttage of used sand blasting grit is added. Besides, it is visually observed that addition of used sandblasting grit increases the workability of geopolymer paste, the higher quantity of grit is added. This may be explained by the presence of different organic compounds in the used sandblasting grit which may act in the same way as in the case of mixture of cement and water. As a result of adsorption of these compounds on the surface of fly ash, repulsive forces appear which increase the paste viscosity [11].

Table 2. Change of compressive strength as a function of solid to liquid ratio at different percentages of used sandblasting grit

Demonstrate of added arit	S/L					
Percentage of added grit	0.75	1	1.25			
0	8	10	11			
10	5.6	6.72	9.34			
20	4.44	5.2	8.25			
30	2.17	4.3	7.31			

Results of microstructure investigation are given in Fig. 2 and 3. Microstructure of obtained geopolymer is consisting of unreacted fly ash and gel phase (denoted with arrows) which is formed as a result of polycondensation reaction [9].

In both cases, in pure fly ash based geopolymer and in the case of used sandblasting grit addition, the presence of geopolymer gel is evident. The final strength is dependent of the strength of the gel phase in the geopolymer microstructure, and it depends of the Al /Si ratio.



Fig.2. Fracture surface of fly ash based geopolymer



Fig.3. Fracture surface of fly ash based geopolymer with addition of used sandblasting grit

Table	<i>2. 1</i>	Resu	ılts	of	EDX	quant	tificati	on	of fl	ly ash
	base	ed g	geoj	pol	ymers	with	and	wi	thout	used
	sanc	dbla	stin	g g	rit					

Ratio	Geopolymers without used sandblasting grit	Geopolymers with used sandblasting grit
Al/Si	2.3	3.68

It is previously reported that ideal geopolymers have molar Si/Al ratios in a gel phase of 1, 2, or 3 and that the geopolymers with a Si/Al molar ratio of 2 show the best mechanical properties[4]. The results given in table 2. show that geopolymers prepared without used sandblasting grit have Al/Si molar ratio close to the ideal value while those with the addition of used sandblasting grit posses significantly higher Si/Al ratio which result in decrease of compressive strength.

### 4. CONCLUSIONS

Investigations of the possibility of immobilization of used sandblasting grit in the fly ash based geopolymers have shown that it can be integrated into the fly ash based geopolymers. Addition of used sandblasting grit into the geopolymer mixture results in a decrease of compressive strength of obtained geopolymers compared to the fly ash based geopolymer. The greater the percentage of added used sandblasting grit in a geopolymer mixture, the greater the decrease in compressive strength. In both cases, with and without the addition of the grit, compressive strength increases with the increase of solid to liquid ratio.

Investigations of geopolymer microstructure, with and without used sandblasting grit, have shown that is characterised by the presence of aluminosilicate gel and unreacted fly ash. The Si/Al ratio in the gel phase of fly ash based geopolymers with addition of used sandblasting grit is higher than in geopolymers without the addition of the grit, resulting in deterioration of mechanical properties of geopolymers.

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#### REFERENCES

- [1] Ecoba, 2005, http://www.ecoba.com
- [2] Elaborat o procjeni uticaja na zivotnu sredinu zamjene elektrofilterskog postrojenja TE "Pljevlja" u Pljevljima, JU Institut za razvoj i istrazivanja u oblasti zastite na radu, Maj, 2010

- [3] Glukhovsky VD (1959) Soil silicates. Gosstroyizdat, Kiev, 154pp
- [4] J. Davidovits, Geopolymers, inorganic polymerie new materials, Journal ofThamalAnalysis, Vos 37 (1991)1633-1656.
- [5] H.Xu, Geoplymerisation of alumosilicate materials, PhD Thesis, University of Melbourne, 2002.
- [6] H. Xu, J. S. J. van Deventer, G. C. Lukey, Effect of Alkali Metals on the Preferential Geopolymerization of Stilbite/Kaolinite Mixtures, *Ind. Eng. Chem. Res.* 2001, 40, 3749-3756
- [7] I. Maragkos, I. P. Giannopoulou, D. Panias, Synthesis of ferronickel slag-based geopolymers, Minerals Engineering 22 (2009) 196–203
- [8] J. G. S. van Jaarsveld and J. S. J. van Deventer. Effect of the Alkali Metal Activator on the Properties of Fly Ash-Based Geopolymers, *Ind. Eng. Chem. Res.* 1999, *38*, 3932-3941
- [9] D. Panias, I.P. Giannopoulou, T. Perraki, Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers, Colloids and Surfaces A: Physicochem. Eng. Aspects 301 (2007) 246–254.
- [10] J.G.S. Van Jaarsvald, J. S. J. Van Deventer, L. Lorenzen, "Factors Affecting the immobilization of Metals in Depolymerised Fly ash", Metallurgical and materials transactions, Vol.29 B, 1998, p. 283-291
- [11] M. Criado, A. Palomo, A. Fernández-Jiménez, P. F. G. Banfill, Alkali activated fly ash: effect of admixtures on paste rheology, Rheol Acta (2009) 48:447–455.

## IZVOD

## GEOPOLIMERIZACIJA LETEĆEG PEPELA KAO MOGUĆEG REŠENJA ZA STABILIZACIJU KADA SE KORISTI ZA PESKARENJE

Geopolimeri su relativno novi, ekološki prihvatljivi laki materijali koji se dobijaju kao rezultat reakcije alumosilikatnih materijala i jako alkalnih rastvora. Karakterišu ih zadovoljavajuće mehaničke osobine pa se stoga razmatraju kao moguća zamjena za portland cement u gradjevinarstvu. Osim toga tehnologija geopolimerizacije je prepoznata kao mogući način imobilizacije toksično gotpada (nuklearnog otpada, otpadnih voda i otpada koji sadrži teške metale). U ovom radu ispitivana je mogućnost imobilizacije otpadnog grita u geopolimere na bazi lebdećeg pepela. Rezultati su pokazali da je geopolimerizacija lebdećeg pepela sa dodatkom otpadnog grita moguća. Mikrostrukturu sintetisanih geopolimera karakteriše prisustvo alumosilikatnog gela i neizreagovanih čestica pepela. U poredjenju sa geopolimerima na bazi pepela, u geopolimerima sa otpadnim gritom se dobijaju niže vrijednosti pritisne čvrstoće. Pokazano je da pritisna čvrstoća geopolimera zavisi od odnosa Si/Al.

Key words: geopolimerizacija, geopolimer, leteći pepeo, otpadni grit

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