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ALKALI-ACTIVATED FLY ASH CONCRETE (CONCRETE WITHOUT CEMENT)

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Preliminary notes

In this work, alkali-activated fly ash was used as a binder instead of Portland cement at the preparation of concrete. Sodium hydroxide and water glass were used as alkali activators. Fractions of natural aggregate of 0-4 mm, 4-8 mm and 8-16 mm were replaced by air-cooled granulated steel slag fraction of 4-8 mm and 8-16 mm and the fraction of river sand was replaced with silica fume. The obtained samples were cured at 2 different temperatures. The first was cured at room temperature and the other was steam-cured for 8 hours and left at room temperature until the tested date. The compressive strength test was investigated by using cube samples 150 ×150 ×150 mm after 3 and 28 days. The results of the present work have shown that low-calcium fly ash-based geopolymer concrete can substitute the use of Portland cement in concrete.

Keywords: *fly ash, geopolymer, silica fume, slag, sodium hydroxide, water glass*

Beton od alkalijski aktiviranog elektrofiltarskog pepela (Beton bez cementa)

Prethodno priopćenje

U ovom radu pri pripremi betona kao vezivo umjesto portland cementa korišten je alkalijski aktiviran elektrofiltarski pepeo. Kao alkalijski aktivatori korišteni su vodeno staklo i natrijev hidroksid. Frakcije prirodnog agregata od 0-4 mm, 4-8 mm i 8-16 mm zamijenjene su frakcijama zrakom hlađene granulirane šljake od 4-8 mm i 8-16 mm, a frakcija pijeska zamijenjena je s amorfnom SiO_2 prašinom. Dobiveni uzorci sušeni su na dvije različite temperature. Prvi su sušeni na sobnoj temperaturi a drugi su zaparivani 8 sati i zatim sušeni na sobnoj temperaturi do ispitivanja. Tlačna čvrstoća dobivenih uzoraka ispitana je na kockama 150 ×150 ×150 mm nakon 3 i 28 dana. Dobiveni rezultati su pokazali da geopolimerni beton dobiven alkalijskom aktivacijom elektrofiltarskog pepela može zamijeniti portland cement u betonu.

Ključne riječi: *amorfna SiO_2 prašina, elektrofiltarski pepeo, geopolimerni beton, granulirana šljaka, natrijev hidroksid, vodeno staklo*

1 Introduction
Uvod

Geopolymers are a class of inorganic polymer materials formed by the reaction between a strongly alkaline solution and an aluminosilicate fine binder (with a particle size in the range 1 μm to 30 μm). Commonly used binders include class F fly ash, granulated slags or metakaolin, but any fine amorphous aluminosilicate material can be used. The most common activator is a mixture of water, sodium hydroxide and sodium silicate but other alkali metal systems or mixtures of different alkalis can be used, as can any waste source of concentrated alkali. The solution needs to be concentrated otherwise the end product will be a crystalline zeolite rather than a geopolymer. The hardened material has an amorphous 3-dimensional structure similar to that of an aluminosilicate glass. However unlike glass these materials are formed at low temperature and as a result can incorporate an aggregate skeleton.

Geopolymerization process is based on a complicated heterogeneous reaction that takes place between a solid material rich in aluminosilicate oxides and an alkali metal silicate solution under highly alkaline conditions.

The best mechanism proposed for geopolymerization process includes the following four stages [1, 2, 3]:

- dissolution of Si and Al from the solid aluminosilicate materials in the strong alkaline solution
- formation of Si and Si-Al oligomers in the aqueous phase
- polycondensation of oligomers to form a three-dimensional aluminosilicate framework
- bonding of the undissolved solid particles into the geopolymeric framework and hardening of the whole geopolymeric system.

According to Glukhovsky [4] the first steps consist of a breakdown of the covalent bonds Si-O-Si and Al-O-Si which happens when the pH of the alkaline solution raises, so those groups are transformed in a colloid phase. Then an accumulation of the destroyed products occurs, which interacts among them to form a coagulated structure, leading in a third phase to the generation of a condensed structure. The empirical formula of geopolymer is:

$$M_n\left[(-SiO_2)_z - AlO_2\right]_n \cdot wH_2O$$

where

M is monovalent cation, usually an alkali (K^+, Na^+)

n is the degree of polycondensation

z is (the $\frac{SiO_2}{Al_2O_3}$ ratio) = 1, 2 or 3

z can also be larger than 3, up to 32.

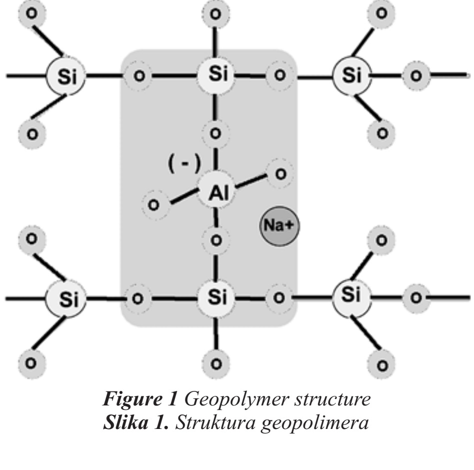

Figure 1 *Geopolymer structure*
Slika 1. *Struktura geopolimera*

The inorganic polymer network is in general a highly-coordinated 3-dimensional aluminosilicate gel, with the negative charges on tetrahedral Al(III) sites charge-balanced by alkali metal cations (Fig. 1).

Geopolymers possess excellent physico-chemical and mechanical properties, including low density, micro-porosity, negligible shrinkage, high strength, great surface hardness and significant thermal stability, fire and chemical resistance [5, 6, 7, 8].

2 Experimental program
Eksperimentalni dio

2.1 Materials
Materijali

The fly ash with specific surface area of 0,29 m^2/g from the Tuzla Thermal Power Station was used as the binder instead of Portland cement.

Due to the relatively low calcium content, this fly ash should be classified as Class F according to the ASTM C 618 definitions [9].

The sodium hydroxide in the form of tiny granules with 98 % purity and water glass (Na_2O = 14,7 %, SiO_2 = 29,4 % and H_2O = 55,9 %) were used as alkali activators.

For the preparation of the MIX 1 were used fractions of the natural gravel of 0-4 mm, 4-8 mm, 8-16 mm and river sand. In the MIX 2 fractions of the natural gravel have been replaced with granulated air-cooled steel slag fractions of 4-8 mm and 8-16 mm from the steel production in Split. In the MIX 3 fractions of the river sand have been replaced with silica fume produced by Elkem in Norway.

The chemical compositions of the fly ash, slag, and silica fume are shown in Tab. 1.

***Table 1** The chemical composition of the fly ash, blast furnace slag and silica fume*
***Tablica 1.** Kemijske analize letećeg pepela, šljake i amorfne SiO_2 prašine*

Components	Fly ash, mass %	Slag, mass %	Silica fume, mass %
CaO	5,29	31,52	2,55
SiO_2	55,80	14,24	91,50
Al_2O_3	19,20	7,40	1,75
Fe_2O_3	8,85	25,74	-
MgO	2,88	7,42	1,00
MnO	-	3,80	-
SO_3	-	0,44	-
Na_2O	2,00	0,13	0,85
K_2O	0,26	0,08	0,70
LOI	5,60	4,71	1,60
Total	99,88	95,48	99,85
Density, kg/m^3	1910	3410	2210
Blaine, m^2/kg	2930,00		11334,00

2.2 Designing of composition samples
Projektiranje sastava uzoraka

Geopolymer concrete can be manufactured by adopting the conventional techniques used in the manufacture of Portland cement concrete.

Mass of components for 1 m^3 of geopolymer concrete

Assuming that the density of concrete is 2400 kg/m^3 and mass fraction of aggregate 77 % of the mass of concrete, the total mass fraction of aggregates in concrete is:
$0,77 \times 2400\ kg/m^3 = 1848\ kg/m^3$.

Mass of individual fractions of aggregate is:

15 % aggregate, fraction 8-16 mm:	277 kg
20 % aggregate, fraction of 4-8 mm:	370 kg
35 % aggregate, fraction of 0-4mm:	647 kg
30 % sand:	554 kg
Total:	1848 kg

The mass of fly ash and alkaline solution is:
$2400 - 1848 = 552\ kg/m^3$.

The ratio of mass alkaline solution and fly ash is 0,35, so the mass of fly ash is

$$\frac{552}{(1+0,35)} = 408\ kg/m^3,$$

and the mass of alkaline solution is: $552 - 408 = 144\ kg/m^3$.

The water glass to sodium hydroxide mass ratio was fixed as 2,5 and the mass of sodium hydroxide solution is

$$\frac{144}{(1+2,5)} = 41\ kg/m^3,$$

and the mass of water glass is: $144 - 41 = 103\ kg/m^3$.

Mass fractions of components for the four concrete cubes volume 13,5 dm^3 ($1,5 \times 1,5 \times 1,5\ dm \times 4$) are shown in Tab. 2. The concentration of 18 M sodium hydroxide was prepared by mixing of tiny granules with water.

2.3 Mixing and curing of geopolymer concrete
Miješanje i sušenje geopolimernog betona

Fly ash and aggregates were dry mixed in an 80 litre capacity pan mixer for 3 minutes. This was followed by the addition of the activator solutions, extra water and superplasticizer followed by a final mixing of another 3 minutes. Extra water was added to adjust their slump test to about 40±10 mm. High range water reducing super-plasticizer Glenium at 1 % by mass of fly ash was added in order to improve the workability. Immediately after mixing, the slump test of fresh geopolymer concrete was determined. After the determination of slump, the fresh concrete was placed in the mould 150 × 150 × 150 mm and was vibrated by hand-held vibrator. Six concrete specimens were cured at room temperature and the other six were steam-cured for 8 hours then left at room temperature until the day of testing.

3 Results and discussion
Rezultati i rasprava

The obtained results of investigation of compressive strength of prepared 3-mixtures of geopolymer concrete are shown in Tab. 3 and presented by diagram in Fig. 2.

The influence of chemical ratios SiO_2/Al_2O_3 on the compressive strength of geopolymer concrete is shown in Tab. 4.

Each chemical ratio is calculated from both solid and liquid parts of the paste. For example, SiO_2 for MIX 2 was obtained from fly ash, slag and water glass.

Table 2 *The proportions of 3 different geopolymer concrete mixtures*
Tablica 2. *Maseni udjeli sastojaka za 3 različite mješavine geopolimernog betona*

Components	MIX 1 Mass		MIX 2 Mass		MIX 3 Mass	
	%	kg	%	kg	%	kg
Aggregate, fraction 8-16 mm	11,50	3,74	-	-	-	-
Aggregate, fraction 4-8 mm	15,45	5,00	-	-	-	-
Aggregate, fraction 0-4 mm	27,00	8,70	-	-	-	-
Sand	23,01	7,47	22,97	7,47		
Fly ash	17,02	5,51	16,94	5,51	16,94	5,51
Slag, fraction 4-8 mm	-	-	27,06	8,80	27,06	8,80
Slag, fraction 8-16 mm	-	-	27,06	8,80	27,06	8,80
Silica fume	-	-			23,00	7,47
Sodium hydroxide, 18 M	1,70	0,55	1,69	0,55	1,69	0,55
Water glass	4,29	1,39	4,27	1,39	4,29	1,39
Total	99,97	32,36	99,99	32,52	100,00	32,72

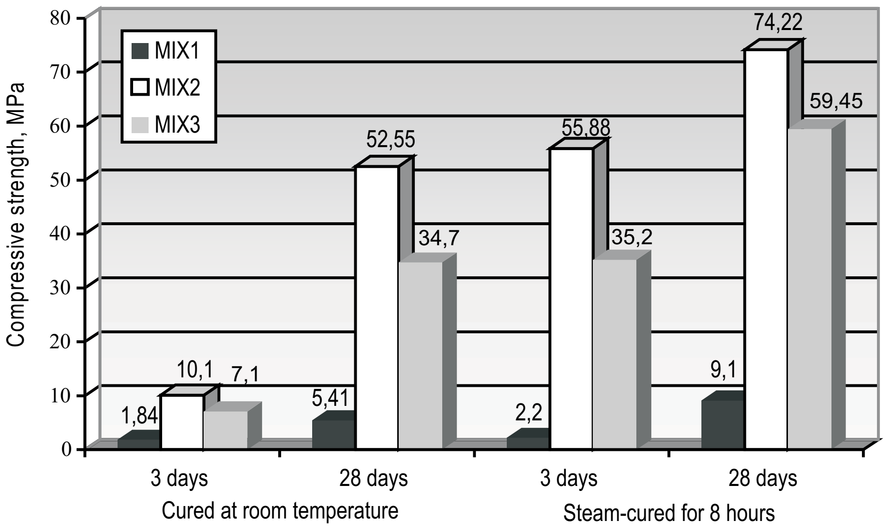

Figure 2 *Relationship between compressive strength and curing time of the geopolymer concrete (MIX1, MIX2 and MIX3).*
Slika 2. *Ovisnost tlačne čvrstoće (Mješavine 1, 2 i 3) geopolimernog betona o načinju sušenja*

Table 3 *Compressive strength of geopolymer concrete samples*
Tablica 3. *Postignute tlačne čvrstoće uzoraka geopolimernog betona*

Samples	Compressive strength, MPa			
	Cured at room temperature		Steam cured (8 hours)	
	3-days	28-days	3-days	28-days
MIX 1	1,84	5,41	2,2	9,10
MIX 2	10,10	52,55	55,88	74,22
MIX 3	7,20	34,70	35,20	59,45

Table 4 *Chemical ratios of SiO_2/Al_2O_3 in geopolymer concrete mixtures*
Tablica 4*. Omjer SiO_2/Al_2O_3 u geopolimernim betonskim mješavinama*

Samples	Chemical ratios
	SiO_2/Al_2O_3
MIX 1	3,3
MIX 2	2,5
MIX 3	5,2

Samples of MIX 1 with a fraction of natural aggregate and mass ratio of silica to alumina of 3,3 had a low compressive strength after 3 and 28 days cured at room temperature. Samples of MIX 1 which were steam-cured for 8 hours then left at room temperature had also low compressive strength after 3 and 28 days.

Samples of MIX 2 with the mass ratio of silica to alumina of 2,5 in which the fraction of natural aggregate was replaced with fraction of slag had good compressive strength after 3 and 28 days cured at room temperature. Samples of MIX 2 which were steam-cured for 8 hours then left at room temperature had a very high compressive strength after 3 and 28 days.

Samples of MIX 3 where the fraction of natural aggregate was replaced by fraction of slag and sand fraction of silica fume, with mass ratio of silica to alumina of 5,2 had good compressive strength after 3 and 28 days curing at room temperature.

Samples of MIX 3 which were steam-cured for 8 hours then left at room temperature had a high compressive strength after 3 and 28 days.

4 Conclusions
Zaključci

1) MIX 1 exhibited very low compressive strength and it is not suitable for use as concrete.
2) With a double alkali activation of fly ash and granulated slag in the MIX 2 excellent compressive strength has been achieved after 3 and 28 days (Fig. 2). MIX 2 has the potential to replace Portland cement in concrete.
3) Higher steam-cured temperature significantly affects the early strength of geopolymer concrete more than that of the late strength.

5
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