

## Characterization of fly ash from coal combustion as a precursor for obtaining geopolymers

A. R. Surleva<sup>1\*</sup>, D. M. Ilieva<sup>1</sup>, L. Y. Angelova<sup>1</sup>, G. E. Chernev<sup>2</sup>

<sup>1</sup>Analytical Chemistry Dept., University of Chemical Technology and Metallurgy, 8 "St. Kl. Ohridski" Blvd, 1756 Sofia, Bulgaria

<sup>2</sup>Silicate Technology Dept., University of Chemical Technology and Metallurgy, 8 "St. Kl. Ohridski" Blvd, 1756 Sofia, Bulgaria

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Geopolymerization is a low CO<sub>2</sub> footprint alternative for industrial waste valorization. Along with high content of silica and alumina, raw materials for geopolymer obtaining should contain reactive Si and Al. Additional requirements are fine granulometric composition and low leaching capacity of heavy metals and other components after alkali activation treatment. The paper presents results from the characterization of fly ash from coal combustion in thermal power plant "Bobov dol" as precursor for geopolymer obtaining. High content of silica (52%) and alumina (21%) and a suitable ratio between active Si/Al=2 was found. Distribution of heavy metals in fly ash and geopolymer fractions and their potential bioavailability was assessed by a sequential extraction procedure. The results showed a 30-50 % increase of heavy metals in the nonmobile fraction after the geopolymerization process (Cu, Zn, Pb, Ni, Cr, Pb), except Mn and Fe. The results presented here showed that the studied fly ash is a suitable precursor for geopolymer obtaining, however mechanical and microstructural characteristics of the obtained material should be considered when designing the raw materials mixture.

**Keywords:** fly ash; geopolymers; alkaline reactivity; heavy metals; leaching tests; BCR sequential extraction; raw materials

### INTRODUCTION

Geopolymers present an innovative alternative to ordinary Portland cement offering production technology with low CO<sub>2</sub> footprint [1, 2]. Moreover, flexibility of design of geopolymer materials allows silica- and alumina-rich industrial wastes to be valorized in a green manner.

Geopolymers are alkaline-activated products with low Ca content and high Si and Al. Their structure presents a three-dimensional network of aluminosilicates with an empirical formula  $M_n[-(SiO_2)_z-AlO_2]_n, wH_2O$ , wherein "z" is the Si/Al molar ratio, more often equal to 1-3; "M" is monovalent alkali cation (K<sup>+</sup> or Na<sup>+</sup>); "n" is the degree of polymerization and w is the content of water [1, 3]. The geopolymer network consists in bonding of amorphous or semi-crystalline metal oxides with an alkaline element [4, 5].

Geopolymer obtaining demands raw materials rich in alumina and silica and alkali activators such as Na or K hydroxides and silicates [6]. Different industrial wastes are used as precursors: fly ash, GGBF slag, metakaolin, fibers, volcanic ash, glass wastes, farming wastes, mine tailings, etc. [1, 6-9]. The most widely waste used as a raw material is fly

ash [7, 9-12]. Recent reviews presented the advances in research on fly-ash based geopolymers [1, 2]. Fly ash is a coal combustion byproduct from thermal or electrical power plants with finely grained structure and rich in alumina and silica. The characteristics of the used raw materials govern the technology design and properties of the obtained geopolymer products [8, 9]. Detailed characterization is needed for each raw material. The research efforts are divided in two directions: (a) characterization as a precursor for geopolymer obtaining having in mind the characteristics that govern formation of geopolymer network and (b) characterization as a green material having in mind its behavior and fate in the environment [13]. Along with conventional methods for geopolymer study (XRF, XRD, NMR, FTIR) [1], new chemical approaches are proposed for study specific characteristics of raw and geopolymer materials [1].

This study is aimed at characterization of coal combustion fly ash from a Bulgarian thermal power plant as a precursor for geopolymer obtaining by low CO<sub>2</sub> footprint technology. Chemical, mineralogical and granulometric composition, along with alkaline reactivity of fly ash were studied to assess its suitability as raw material. Leaching characteristics

\* To whom all correspondence should be sent:  
E-mail: [surleva@uctm.edu](mailto:surleva@uctm.edu)

and heavy metals mobility in the fly ash and in the geopolymer obtained by alkali activation were studied to assess environmental footprint of the obtained materials.

## MATERIALS AND METHODS

### Sample description

The studied samples were: (a) fly ash from TTP “Bobov dol” resulting from coal combustion process and (b) geopolymer material based on fly ash. Detailed description of geopolymer obtaining is presented in Ilieva *et al.* [13]. Alkali activation with NaOH and sodium silicate was applied. The samples were cured at room temperature.

### Particle size distribution, pH, EC and Eh

The pH was measured at 1:10 liquid to solid ratio, 10 min after mixing. The pH was measured by a combined glass electrode and Hanna HI5522-02 multimeter. The redox potential (Eh) and electroconductivity (EC) of the suspension were measured using a combined platinum electrode with Ag/AgCl ref. (HI3230B, Hanna Instruments) and conductometric cell (HI-763100, Hanna Instruments), respectively. The particle size analysis of the products was conducted using a laser diffraction particle sizer Mastersizer 3000 (Malvern Instruments).

### Alkaline reactivity

The procedure is presented in detail in Ilieva *et al.* [13]. A sample of one gram ( $\pm 0.0001$  g) was

mixed with 20 mL of 3.0; 6.5 or 10 M NaOH. The samples were agitated on a reciprocal shaker at 100 rpm for 10 min to 72 h. The supernatant was separated by centrifugation for 5 min at 6000 rpm. An aliquot of the supernatant was acidified by HNO<sub>3</sub> and diluted to volume with distilled H<sub>2</sub>O. The concentrations of dissolved Si, Al and Ca were determined by ICP-OES measurement.

### Total heavy metal content and leaching in water

The total heavy metal content was determined by ICP-OES after open acid digestion. A sample of 0.2–0.3 g was digested in *aqua regia* (HNO<sub>3</sub> and HCl 1:3 v/v) (15 mL) and boiled for 25 min in a beaker covered with a watch glass. A total volume of 15 mL of the acid mixture was added in portions of 5 mL. The extract was filtered and diluted up to 50.00 mL with distilled H<sub>2</sub>O. The resulting solution was analyzed by ICP-OES. The leaching characteristics of the studied fly ash were determined by a protocol based on EN 12457-2:2002 [14]. The concentration of the studied elements in the obtained solutions were determined by ICP-OES and the concentration of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> - by UV-Vis spectrometry.

### Sequential extraction of heavy metals

A modified four-step sequential extraction protocol based on the method proposed by the European Community Bureau Reference (BCR) and modified by Gitari *et al.* [15] was applied in the present study (Table 1). The obtained solutions were analyzed by ICP-OES for determination of the heavy metal content.

**Table 1.** Revised BCR sequential extraction scheme [15]

Fraction	Composition of the extracting solution	Experimental conditions	Analytical information
1	40 mL; 0.11 M HOAc	Solid/liquid= 1:40 Agitation 16 h on reciprocal shaker at 30 rpm; t= 25 °C	Exchangeable and water/weak acid-soluble heavy metals. Highly mobile fraction.
2	40 mL; 0.5M NH <sub>2</sub> OH.HCl (pH =1.5 with HNO <sub>3</sub> )	To residue 1; 16 h, t=25 °C	Reducible heavy metals and associated with Fe and Mn oxides. Heavy metals dissolved under anaerobic conditions.
3	10 mL of 8.8 M H <sub>2</sub> O <sub>2</sub> + 50 mL of 1 M NH <sub>4</sub> OAc (pH = 2.0 with HNO <sub>3</sub> )	To residue 2; 1 h at 25 °C, +1 h at 85 °C + 10 mL H <sub>2</sub> O <sub>2</sub> , evaporation till small volume + 50 mL 1 M NH <sub>4</sub> OAc (pH = 2.0 adjusted with HNO <sub>3</sub> )	Oxidizable and associated with sulfides and organic phase. Heavy metals that easy dissolute in oxidizable medium.
4	<i>Aqua regia</i>	Residue 3 was dried and an aliquot was taken and digested for 30 min	Residual fraction, metals incorporated in silicates. Non-mobile (fixed) species.

ICP-OES analysis of leachates

A previously validated method for determination of heavy metals and metalloids in tailing dump materials was applied [16]. An ICP-OES spectrometer (Prodigy high dispersion ICP-OES, Teledyne Leeman Labs, USA) equipped with a dual-view torch, cyclonic spray chamber, and concentric nebulizer was used for metal determination. The wavelengths free from spectral interferences in the studied concentration range were chosen [17].

RESULTS AND DISCUSSION

Chemical and mineralogical composition of fly ash

The chemical composition of the studied sample was determined by XRF spectrometry. The results are presented in Table 2. Based on the chemical composition, the studied fly ash was classified as class F (according to ASTM-C 618) [18]. It

contained CaO of 8.9% (< 10%), total SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub> of 82% (> 70%) and SO<sub>3</sub> of 3.5% (<5%), LOI 3% (<6%).

The mineralogical composition of fly ash was studied by XRD spectrometry. The results are presented in Fig. 1. The results showed that sillimanite (Al<sub>2</sub>SiO<sub>5</sub>) was the predominant aluminosilicate with 48 %, silica was found to be 36 % as α-quartz, hematite, syn (α-Fe<sub>2</sub>O<sub>3</sub>) was 6.3% and anhydrite (CaSO<sub>4</sub>) was 9.2%. The high content of reactive aluminosilicate could determine the successful application of fly ash in the geopolymerization process.

Physico-chemical parameters of fly ash slurry and leachates

The measurements of pH and electrical conductivity in the aqueous solutions were carried out at 23±1°C and liquid-to-solid ratio 1:10.

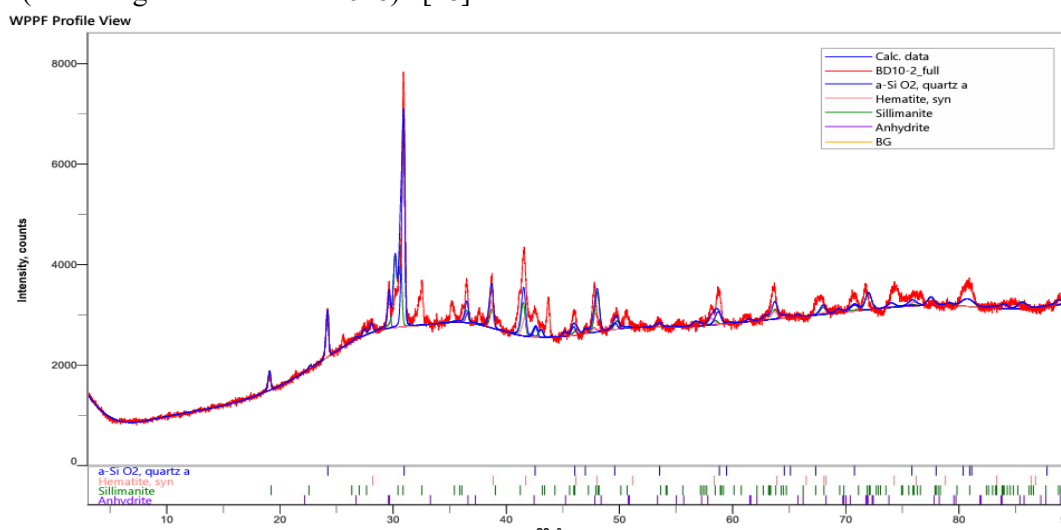


Fig. 1. Mineralogical composition of fly ash from TPP “Bobov dol”, Bulgaria

Table 2. Chemical composition of fly ash (FA)

Oxide	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	K <sub>2</sub> O	TiO <sub>2</sub>	Na <sub>2</sub> O	BaO	MnO	CuO	MgO	SO <sub>3</sub>	LOI	Oth.
FA wt. %	52.5	7.85	21.4	8.89	1.75	1.12	0.70	0.09	0.04	2.04	0.02	3.5	3.34	<0.05

Table 3. Leaching characteristics of fly ash sample

Component	Concentration in leachate, mg/L*	MPL, mg/L	Component	Concentration, mg/L*	MPL, mg/L
Ca	268.4 ± 0.3	150	NO <sub>3</sub> <sup>-</sup>	2.2±0.1	50
Mg	0.790± 0.002	80	SO <sub>4</sub> <sup>2-</sup>	725±1	250
Na	19.41 ± 0.04	200	PO <sub>4</sub> <sup>3-</sup>	< 0.5	0.5
Al	0.320±0.002	0.2	pH**	11.9±0.2	
S	412.1±0.5		EC, mS/cm**	4.4±0.3	
Ni	0.500±0.001	0.020	Eh, mV**	-73±2	
Pb	0.170±0.001	0.005			

\*Standard deviation of measurement is presented (n=3); \*\*standard deviation from 6 replicates.

Fly ash showed high alkalinity of the slurry (pH ~ 12). The electrical conductivity was 4.4 mS/cm and presented the total concentration of dissolved charged ions in distilled water. The trend remained constant within 24 hours. The redox potential of the slurry was -73 mV (vs Ag/AgCl) indicating reductive capacity. The composition of water leachates is presented in Table 3. The maximum permissible limits (MPL) according to Bulgarian drinking water regulation [19] are given for comparison.

Ca, Al, Ni, Pb, and  $\text{SO}_4^{2-}$  exceeded the MPL for drinking water. In contrast, Mg, Na,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  were below MPL. Cu and Zn (< 0.008 mg/L), as well as Fe, Mn and Cr (< 0.005 mg/L), Cd (< 0.007 mg/L), and As (< 0.011 mg/L) were found to be less than the method detection limit [17]. The composition of water leachates gave an indication of the constituents of a generated plume after interaction between fly ash and rainwater [15].

#### Particle size distribution

The particle size distribution of fly ash was studied as received. The particles were finer than 455  $\mu\text{m}$ . The main part of particles (97 %) was below 310  $\mu\text{m}$ . The fraction of particles lower than 100  $\mu\text{m}$  was 51%. The finest fraction (< 63  $\mu\text{m}$ ) was 31 %. The average particle size values were 282, 109, and 16  $\mu\text{m}$  for  $d_{90}$ ,  $d_{50}$ , and  $d_{10}$ , respectively (Fig. 2). The specific surface area of the investigated fly ash was around 161  $\text{m}^2/\text{g}$ .

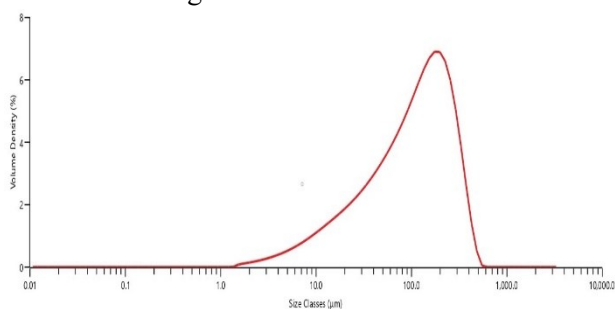


Fig. 2. Particle size distribution of the studied fly ash

#### Alkaline reactivity of fly ash

The presence of Si- and Al-containing minerals in the raw materials is a prerequisite but not enough for geopolymerization. Active Si should be available for reaction in alkaline medium [4] and formation of polymer network to achieve a geopolymer. Al acts as a modifying ion to form chains of -Si-O-Al-O- [4, 5]. Thus, studying alkaline reactivity of raw materials is a crucial step towards their characterization as precursors for geopolymer obtaining.

The results from testing alkaline reactivity of fly ash are presented in Table 4. The dissolution of Ca, Al and Si in 3.0, 6.5 and 10 M NaOH was followed from 10 min up to 72 h by ICP-OES determination of the concentration of studied components in the obtained solutions. The alkaline reactivity is presented as mg dissolved component per kg solid sample.

The results showed that the leachability of Al in the fly ash sample depended on the molarity of the alkali and the contact time. Increasing the alkali concentration resulted in a higher quantity of leached Al at a higher dissolution rate. Prolonging the contact time exerted the same effect, after 72 h no steady state was observed. In contrast, Si was dissolved mainly during the initial contact with alkali and the concentration of Si in the leachates reached a steady value after the first 6 h till 72 h. The concentration of the alkali slightly affected the concentration of dissolved Si. The ratio between dissolved Si:Al was around 2 and didn't change upon increasing the alkali concentration (Table 4). The Si:Al ratio during the initial contact time (< 1h) was less than 1, indicating a lower rate of dissolution of Si compared to Al. After 1 h of contact time, the concentration of dissolved Si was two times higher than the concentration of Al and the ratio was approximately stable till the end of the studied period.

#### Heavy metal content and geochemical fractionation of heavy metals

To assess the total heavy metal content ICP-OES measurement after *aqua regia* digestion was applied. The results showed that the studied fly ash contains 549 mg/kg Fe, 1.6 mg/kg Cu, 3.1 mg/kg Mn; 0.8 mg/kg Mn; 0.8 mg/kg Cr, 0.8 mg/kg Ni; 1.9 mg/kg Pb. As and Cd were below the method limit of detection (MLOD), respectively As < 1 mg/kg and Cd < 0.5 mg/kg.

The modified BCR procedure was applied to assess heavy metal fractionation in fly ash. BCR procedure is well accepted as a method for sequential extraction [20]. The results are presented in Table 5. Our preliminary study on BCR procedure showed the following recovery of pseudo total concentrations (F1+F2+F3+F4) in CRM BCR 701: Cd 105 %; Cr 104 %; Cu 106 %; Pb 116 %; Zn 100 %. The obtained repeatability as RSD was within < 10% (n=3).

The results showed that Cu and Zn were found mainly in the mobile fraction (76 % and 85%, respectively). Less than half of the available Pb, Cr

and Ni were in non-mobile form indicating low mobility potential. Thus, the studied fly ash could be used as a precursor for geopolymer obtaining. Due to the characteristic encapsulation feature of the geopolymerization process, even lower mobility of heavy metals could be expected in geopolymer based products. The results from BCR sequential extraction of heavy metals in fly ash and in a geopolymer are presented in Fig. 3. The results demonstrated that heavy metals were encapsulated in a geopolymer matrix. The content of mobile heavy metals (fractions F1+F2+F3) decreased in the geopolymer material compared to the fly ash. In contrast, the content in the residual fraction increased indicating that heavy metals were firmly embedded in the geopolymer matrix and were available only under *aqua regia* digestion. Pb content in the geopolymer was found to be several times higher than in the pure fly ash (40 mg/kg). It could be due to some impurity during geopolymer

obtaining in the partners' laboratory. However, in both samples the quantity of mobile Pb (F1+F2+F3) was 50% of the pseudo total content (sum of all fractions). Thus, it could be concluded that the geopolymerization process didn't influence the mobility of Pb and it needed further investigation. Twenty percent increase of Cu in the residual geopolymer fraction was observed (Fig. 3). Thus, increased Cu fixation in fly ash-based geopolymer could be supposed. A very high degree of Zn encapsulation was observed: 85 % of Zn was found in mobile fractions (F1+F2+F3) in the fly ash and 57 % - in the geopolymer obtained. A thirty percent lowering in mobility of Cr was observed after geopolymerization. Although the quantity of Fe in the mobile phase decreased two times after geopolymerization, still the main part of Fe in both materials was in mobile form: >85 %. The mobility of Mn wasn't affected by geopolymerization.

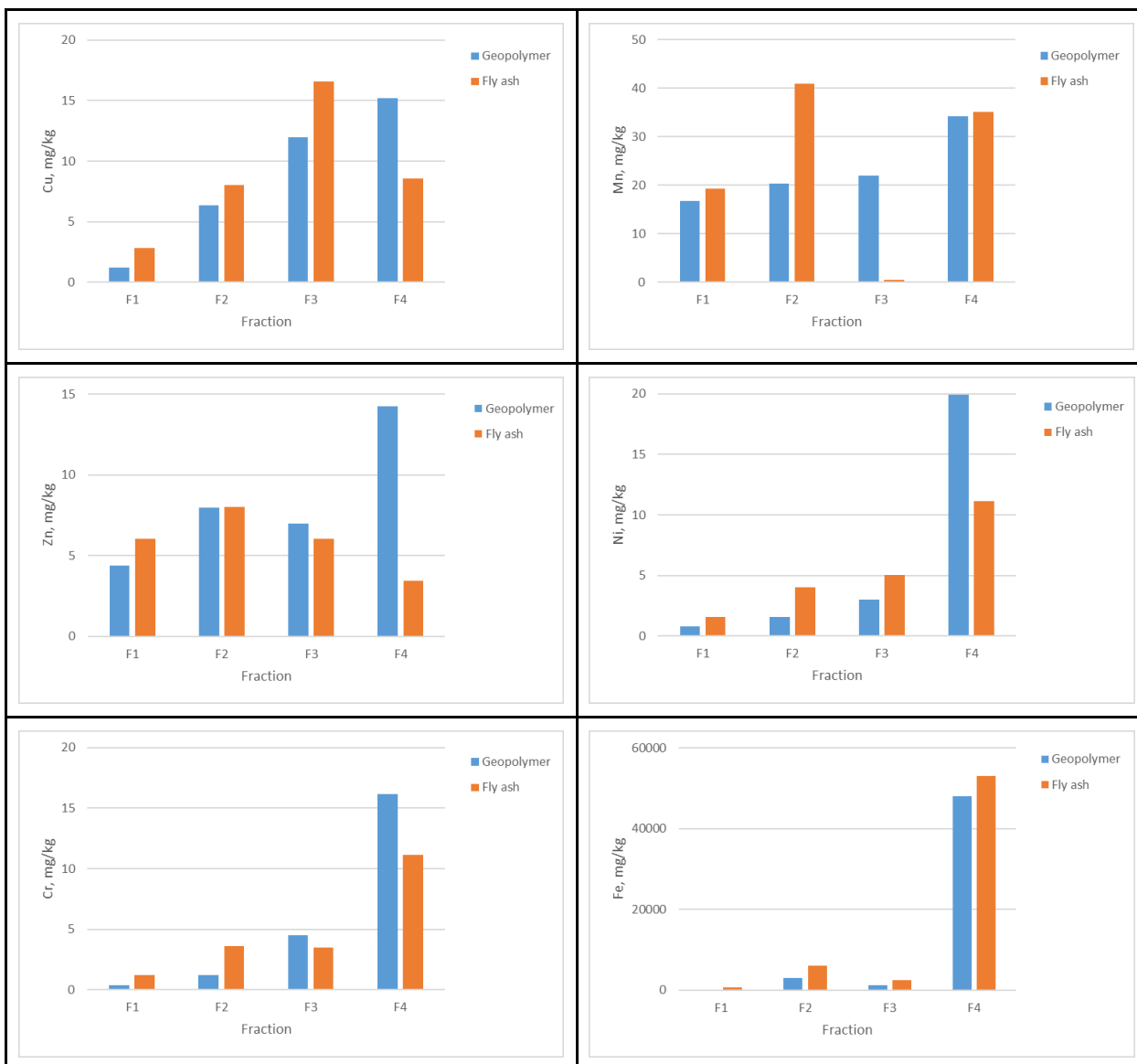
**Table 4.** Alkaline reactivity of fly ash as a function of alkali concentration and contact time.

Concentration of NaOH, M	Time, hours	Ca, mg/kg	Al, mg/kg	Si, mg/kg	Ratio Ca:Al:Si
3	0.17	383.7	230	123.0	1.7/1/0.5
	0.5	268.5	318	428.6	0.8/1/1.3
	1	234.6	1033	912.0	0.2/1/0.9
	4	379.5	4140	1112	0.9/1/2.7
	24	133.6	4120	73834	0.1/1/1.8
	48	73.5	6785	12506	0.1/1/1.8
	72	54.0	10704	17767	0.1/1/1.7
6.5	0.17	315.9	340	146.9	0.9/1/0.4
	0.5	267.3	400	213.7	0.7/1/0.5
	1	255.0	522	439.7	0.5/1/0.8
	4	239.8	806	1151	0.3/1/1.4
	24	220.9	3147	5868	0.1/1/1.9
	48	235.8	5630	10363	0.1/1/1.8
	72	225.9	9604	14475	0.1/1/1.5
10	0.17	230.2	407	281.0	0.6/1/0.7
	0.5	128.0	514	411.7	0.2/1/0.8
	1	280.4	999	931.3	0.3/1/0.9
	4	384.6	1050	1230	0.4/1/1.2
	24	107.5	5394	10262	0.1/1/1.9
	48	82.0	8294	16372	0.1/1/2.0
	72	75.0	11759	25496	0.1/1/2.2

\*Standard deviation of measurement:  $s_{Ca} = \pm 0.3$  mg/kg;  $s_{Al} = \pm 0.3$  mg/kg and  $s_{Si} = \pm 0.4$  mg/kg

**Table 5.** Heavy metals distribution in geochemical fractions of fly ash sample obtained by BCR sequential extraction procedure. Relative standard deviation, %, is presented in brackets (n=2)

Element	Fe	Mn	Cr	Cu	Pb	Ni	Zn
Content, mg/kg							
Exchangeable	617.6 (5.6)	19.3 (1.2)	1.20 (0.5)	2.81 (1.6)	2.81 (0.1)	1.61 (4.1)	6.02 (1.7)
Reducible	6084 (3.8)	40.9 (3.1)	3.61 (6.0)	8.03 (2.6)	9.23 (3.8)	4.01 (5.8)	8.03 (3.7)
Oxidisable	2362 (4.4)	0.50 (0.4)	3.51 (0.4)	16.6 (10)	6.52 (2.7)	5.02 (10)	6.02 (9.8)
Residual	52956 (4.8)	35.1 (3.4)	11.1 (2.2)	8.57 (6.3)	23.1 (3.0)	11.1 (4.1)	3.43 (5.4)
F1+F2+F3	9063	60.7	8.33	27.4	18.6	10.6	20.1
Total	62019	95.8	19.5	35.9	41.7	21.8	23.5



**Fig. 3.** Comparison between content of heavy metals in fly ash (orange) and in the obtained geopolymer (blue). F1: exchangeable fraction; F2: reducible fraction; F3: oxidizable fraction; F4: residual fraction.

### CONCLUSIONS

A fly ash from coal combustion in the thermal power plant “Bobov dol” was studied as a precursor for geopolymer obtaining by alkaline activation. High content of silica (52%) and alumina (21%), along with low content in Ca (9%) and S (<4%), as well as a suitable ratio between active Si/Al=2 was found. Low concentration of heavy metals in the water leachate was observed, except Pb and Ni. Distribution of heavy metals in fly ash and geopolymer fractions and their potential bioavailability was assessed by a BCR sequential extraction procedure. Considering the mobile part of heavy metals in the fly ash sample, the highest part of Cu, Ni, and Cr was released in oxidizable conditions, whereas Pb, Zn, Fe and Mn showed

higher concentration in leachates under reducible conditions. Geopolymerization of fly ash changed the fractionation of the studied heavy metals. The results showed a 30-50 % increase of heavy metals in nonmobile fraction after the geopolymerisation process (Cu, Zn, Pb, Ni, Cr, Pb), except Mn and Fe. The results presented here showed that the studied fly ash is a suitable precursor for geopolymer obtaining, however mechanical and microstructural characteristics of the obtained material should be considered when designing the raw materials mixture.

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