Impact of leaching procedure on heavy metals removal from coal fly ash

Andrija Z. Janković[1], Mirjana R. Ćujić[2], Milica D. Stojković[1], Maja B. Đolić[1], Dragana Z. Živojinović[1], Antonije E. Onjia[1], Mirjana Đ. Ristić[1] and Aleksandra A. Perić Grujić[1]

[1]University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia
[2]University of Belgrade, Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, Belgrade, Serbia

Abstract
In this work, removal of heavy metals (Cr, Mn, Co, Ni, Cu, Zn, As, Cd, and Pb) from fly ash has been studied using acid leaching and wet oxidation methods. In parallel, microwave-assisted acid digestion was applied for determination of pseudo-total concentrations of heavy metals to estimate the leaching efficiency. Multivariate statistics (Pearson correlation, principal component analysis, and hierarchical cluster analysis) have shown two dominant groups of elements, depending on their characteristics and affinity towards the ash solid phase. Thus, Cr, Zn, Mn, Co, and Ni belong to the group I, while Pb, As, Cd, and Cu belong to the group II. It was demonstrated that the wet oxidation method was more suitable than acid leaching since the reduction in metal concentration was 30 to 75 % compared to 12 to 25 % obtained by acid digestion. The influence of fly ash treatment on the residue characteristics was investigated by X-ray diffractometry and scanning electron microscopy. The analyses revealed surface and structure changes of fly ash after the wet oxidation treatment. Overall, wet oxidation could be an appropriate treatment for heavy metal removal from fly ash, providing a material that could be further used, thus reducing the risk of pollution caused by the disposal of coal combustion fly ash.

Keywords: Waste utilization; wet oxidation; acid leaching; material characterization.

Available on-line at the Journal web address: http://www.ache.org.rs/HI/

1. INTRODUCTION

Ash, bottom and fly presents one of the waste streams generated in the coal combustion process. The amount, characteristics, and potential usage of this waste depend on the coal type and properties of the combustion process. The Republic of Serbia (RS) is dominantly dependent on coal as a resource for electric energy production; the installed capacity is 4,437 MW, and about 24 billion kilowatt hours are generated annually. Nikola Tesla Thermal Power Plants Branch (TENT) is the largest electricity producer in Southeast Europe. The plant has 14 units with a total installed capacity of 3,430 MW. Annually, TENT generates more than 50 % of electricity in Serbia. In line with the waste management hierarchy, which highlights the reuse and recycling of waste, in particular, both in the EU and RS, research is still being carried out regarding the reuse of waste in the process of making construction products containing certain amounts of waste [1]. Approximately 7 million tons of fly ash and slag are produced in thermal power plants in Serbia every year, only 3 % of which is used in the cement industry [2].

Threats to human health and quality of the environment have been mostly the subject of studies/research focusing on coal fly ash (CFA) from Serbian power plants. Single-agent extraction and sequential extraction procedures were used to determine the leaching levels of different metals (Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Pb) [3]. In a previous study, analysis of CFA, taken from the ash dumps located in the vicinity of the power plant Kostolac using the method of sequential dissolution has been performed to determine the influence aspects of selected heavy metals (V, Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb) on working and living environments [4]. The isotopic ratios $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ determined in CFA from Serbian coal-fired power plants present an important contribution to a lead isotopic database fundamental for interpreting different pollution sources [5]. Determination of rare earth elements in CFA leachate from

five Serbian coal-fired thermoelectric power has recently been investigated using dispersive solid-liquid microextraction based on a poly(1,6 hexanediol diacrylate)/graphene sorbent followed by inductively coupled plasma mass spectrometry, ICP-MS [6].

Pollutant emissions from coal and coal waste combustion plants and fly ash landfilling from electricity production were evaluated regarding the environmental risks [7]. This study compared power plants in Serbia Kolubara A, Kostolac B, and Nikola Tesla A, as well as a semi-industrial fluidized bed boiler, as combustion facilities with different combustion regimes, fuel types, and capacities.

In recent research [8], human health risk assessment of potentially harmful substances in fly ashes has been performed by estimating the carcinogenic and non-cancer risks for trace elements and the incremental life cancer risk of seven carcinogenic polycyclic aromatic hydrocarbons (PAHs) associated with different exposure routes.

Samples of coal fly ash from two coal-fired power plants in Serbia (Nikola Tesla and Kostolac) were analyzed and examined as neutralization agents of acid mine drainage [9]. Cotton, cotton/polyester yarn, and fly ash as waste materials from Serbia were used as adsorbents for the removal of certain heavy metals from water [10].

Enhanced coal fly ash leaching can be used to extract valuable element(s) from CFA and to remove toxic element(s) [11]. In the present study, the effect of two methods, acid leaching and wet oxidation, on the removal efficiency of some toxic/hazardous heavy metals from fly ash originating from two Serbian thermal power plants, Nikola Tesla A and Nikola Tesla B, has been investigated. Wet oxidation has been proposed for the first time for this purpose. With this approach, reuse of CFA could be provided, thus reducing the risk of contamination caused by CFA disposal. Bottom ash has been studied, as well, in order to determine fractionation of trace pollutants during the combustion process.

2. MATERIALS AND METHODS

In this work, bottom and fly ash were collected from coal-fired power plants (CPP) in Serbia, Nikola Tesla A and B, located near the Serbian capital, Belgrade. They use lignite as a fuel obtained from the Serbian coal mining complex, RB Kolubara. The CPP Nikola Tesla A, the Serbian largest thermal power plant, has a capacity of 1765 MW and six generation units, while CPP Nikola Tesla B has a total capacity of 1320 MW and two generation units.

Determination of the chemical composition of fly ash and bottom ash was performed by using inductively coupled plasma-optical emission spectrometry (ICP-OES). In specific, prior to the digestion, bottom and fly ash samples were oven-dried at 60 °C for 8 h and then homogenized by using a ball mill. A portion of 0.5 g of the homogenized coal fly ash sample is mixed with 3.0 g lithium tetraborate (≥99.995 %, Sigma-Aldrich, USA) as a fluxing agent, in a platinum crucible. The mixture is then placed in a laboratory furnace and subjected to a controlled temperature ramp up to 1000 °C, a then hold at 1000 °V for 2 h. The obtained homogeneous glass bead is dissolved in a 0.3 % acid solution HCl (ACS reagent grade, Sigma-Aldrich, USA). The resulting solution is analyzed by using the instrument Agilent ICP-OES model 5800 (Agilent Technologies, Santa Clara, CA, USA).

2. 1. Coal ash treatment procedures

Three procedures were used for coal ash treatment: 1) microwave-assisted digestion; 2) acid leaching; and 3) wet oxidation.

In the first method (i.e. microwave-assisted digestion) bottom and fly ash samples (0.5 g) were digested by using high-purity ACS reagent grade mineral acids (nitric, hydrofluoric, and boric) purchased from Sigma-Aldrich (USA). Two-step microwave digestion (Milestone ETHOS LEAN, Milestone Srl, Sorisole, Italy) was carried out. In the first step, 6 mL of concentrated nitric acid and 2 ml of concentrated hydrofluoric acid were added to a Teflon vessel. The digestion conditions for the microwave system were as follows: constant power of 800 W, 10 min at 552 kPa, then 15 min at 827 kPa. The Teflon vessels were then cooled to room temperature and, in the second digestion step, 20 ml of boric acid (5 % w/v) and 20 ml of high purity water (resistivity 18.2 MΩ·cm) were added. In the second step, digestion conditions for the microwave system were as follows: constant power of 800 W, 10 min at 552 kPa, then 15 min at 827 kPa. After digestion, the solution was filtered, and the clear filtrate was diluted to 50 mL with high-purity water obtained from a Milli Q water system (Merck, Darmstadt, Germany).

In the acid leaching method, 1 g of fly ash was burned at 360 °C for 1 h first followed by 650 °C for 1 h. Then 3 ml of concentrated HNO_3 and 5 ml of concentrated $HClO_4$ (ACS reagent grade, Sigma-Aldrich, USA) were added. The beakers were kept on a hot plate (56 to 58 °C). Next, 10 ml of concentrated HCl was added. The solid phase was then separated from the solution. The solution was diluted to 50 ml with high-purity water, while the solid phase was analyzed by X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

For wet oxidation, approximately 0.2 g of fly ash was weighed (the weight was recorded to the nearest 0.1 mg), and approximately 0.2 g of V_2O_5 (ACS reagent grade, Sigma-Aldrich, USA), 8 ml of concentrated HNO_3, and 2 ml of concentrated H_2SO_4 (ACS reagent grade, Sigma-Aldrich, USA) were added. The vessel was placed in a heated sand bath and covered with a watch glass. The temperature was gradually increased to reach 150 °C, which was then maintained for 24 h. After heating, the vessel was cooled and then diluted to a volume of 20 ml with water. The solid phase was separated by centrifuge and further analyzed by XRD and SEM. The liquid phase was transferred into a 100 ml volumetric flask and made up to volume with high purity water.

Bottom ash and fly ash were subjected to microwave digestion to determine distribution of the examined heavy metals between these phases. Only fly ash was treated by acid digestion and wet oxidation, due to the harmful impact on human health and the environment. All experiments were performed in triplicate.

The element concentration in the leachate samples was measured by either ICP-OES, Agilent ICP-OES model 5800 with SPS 4 autosampler (Agilent Technologies, Santa Clara, CA, US) or inductively coupled plasma mass spectrometry (ICP-MS), Thermo Fisher iCAP Q ICP-MS (Thermo Fisher Scientific Inc., Waltham, MA, US). The analysis was repeated three times and the mean was reported as the concentration of heavy metal. All chemicals were of reagent grade. The applied procedure was run without a sample, and the obtained blank values were subtracted from the ICP-OES/ICP-MS measurements of the elements evaluated.

2. 2. Fly ash and residues characterization

Fly ash and leaching/oxidation residues were examined by XRD and SEM.

Diffraction measurements were performed by using a SmartLab Rigaku powder diffractometer (Rigaku Corporation, Tokyo, Japan) that works on the principle of Bragg-Brentan geometry, using an X-ray tube with a copper anticathode, that is, using CuKα radiation with a wavelength of λ = 0.1542 nm. The voltage on the X-ray tube was 40 kV, and the current was 30 mA. Measurements were made in the range of diffraction angles 2θ from 5 to 90° with an angle step of 0.02° and a measurement speed of 2°/min. X-ray phase analysis of the samples was performed on the obtained diffractograms by using the EVA v.9.0 program package [12] and with the help of the PDF-2 crystallographic database [13]. Morphology of fly ash samples before and after leaching/oxidation was observed by TESCAN MIRA 3 XMU field emission scanning electron microscope, FESEM (Tescan, Brno, Czech Republic) operated at 20 keV.

The main steps of applied coal ash treatment procedures are illustrated in Figure 1.
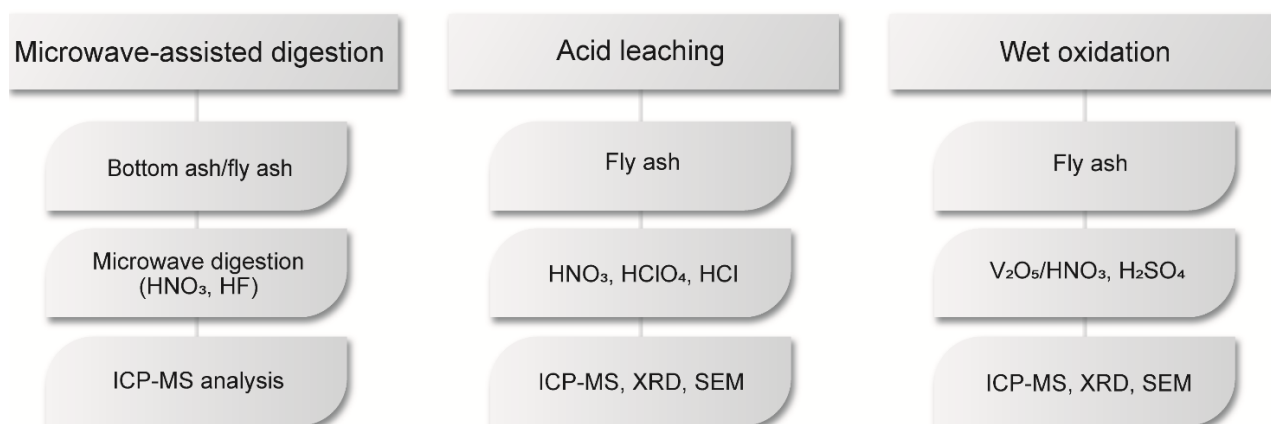

Figure 1. Main steps of applied procedures

3. RESULTS AND DISCUSSION

3. 1. Composition of bottom ash and fly ash

Chemical compositions of examined fly ash and bottom ash are presented in Table 1.

Fly ash from both CPPs is characterized by a high concentration of silica and alumina and a low concentration of calcium. It belongs to class F, according to ASTM C618 [14], since the sum of the percentages of $SiO_2 + Al_2O_3 + Fe_2O_3$ is 76.13 % (TENT A) and 84.63 % (TENT B), higher than a minimum of 70 %.

Table 1. Chemical composition and loss on ignition (LOI) of the investigated fly ash and bottom ash

CPP / ash	Content, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	LOI
TENT A / fly ash	48.1	25.6	2.36	7.1	4.6	6.2	0.7	0.8	3.0
TENT A / bottom ash	27.3	19.4	3.09	3.9	2.0	3.4	0.6	0.5	41.8
TENT B / fly ash	54.3	24.9	5.4	4.0	2.1	4.2	0.7	0.8	1.4
TENT B / bottom ash	41.1	23.2	6.22	2.1	1.4	3.7	0.6	0.7	14.6

Fly ash samples from CPPs TENT A and TENT B were shown to be very similar (Table 1) implying negligible effects of burning conditions; both CPPs use lignite from the RB Kolubara basin. Concerning chemical composition, minor differences in concentrations of Si and Al oxides and Na_2O and TiO_2 concentrations are noticed. TENT A fly ash is slightly enriched in CaO, MgO, and Na_2O and has a slightly higher LOI.

The concentrations of major oxides in fly ashes (Table 1) are similar to those determined in fly ashes sourced from European coal-burning power plants (from Spain, the Netherlands, Italy, and Greece), except for K_2O, which is at a higher concentration in fly ashes examined in this research (6.2 for TENT A and 4.2 for TENT B) compared to 0.4 to 4.0 for fly ashes examined in the research of Moreno *et al*. [15].

The influence of combustion conditions is observed in the bottom ash chemical composition, where the SiO_2 concentration and LOI are significantly different in the two CPP ash samples and indicate incomplete coal combustion in TENT A. LOI of bottom ash from TENT A is almost 3 times higher compared to TENT B / bottom ash.

3. 2. Heavy metal concentration

Contents of selected heavy metals in both fly ash and bottom ash samples originating from coal-fired power plants TENT A and TENT B is presented in Figure 2.
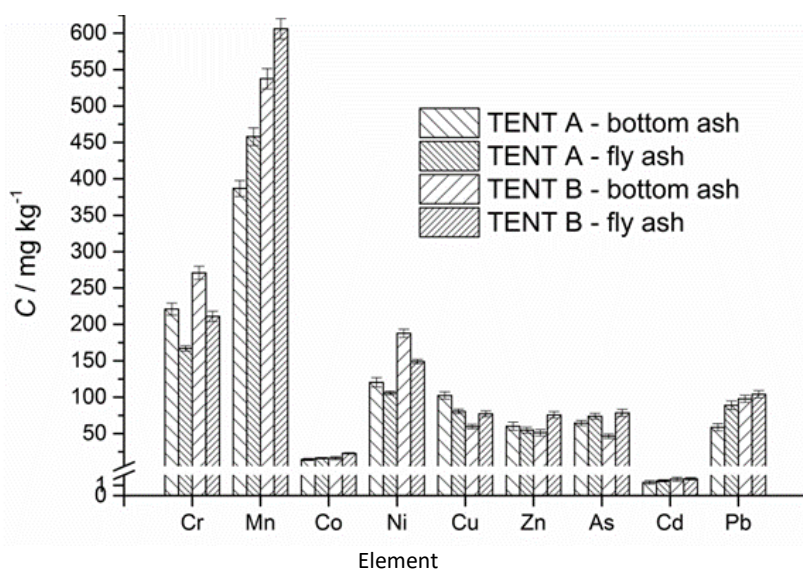

Figure 2. Concentrations of selected heavy metals (triplicate average) in fly ash after microwave-assisted digestion (the error bars represent the standard deviation of the triplicates)

The heavy metal concentration decreases in the order Mn > Cr > > Ni > Cu > As > Pb > Zn > Co > Cd (TENT A) and Mn > Cr > Ni > Cu > Pb > As > Zn > Co > Cd (TENT B), indicating similar patterns. All samples are enriched with Mn, in a concentration range of 386.9 (TENT A bottom ash) and 606 mg kg^{-1} (TENT B fly ash). Concentrations higher than 100 mg kg^{-1} were noticed for Cr and Ni in all samples, while other elements were present at lower concentrations. Elements at the lowest concentrations are Cd, ranging from 1.3 (TENT A bottom ash) to 1.6 mg kg^{-1} (TENT B fly ash) and Co, ranging from 14.6 (TENT B bottom ash) to 23 mg kg^{-1} (TENT B fly ash).

All elements are present in low to middle contents compared to the data reported for European coal combustion fly ashes [15]. The examined fly ashes have the lowest content of Cd (1.4 (TENT A) and 1.6 mg kg^{-1} (TENT B)) and Co (16.3 and 23 mg kg^{-1} in TENT A and TENT B fly ashes, respectively). The range of these heavy metals in European fly ashes is 1-6 mg kg^{-1} for Cd and 20 to 112 mg kg^{-1} for Co [15]. Previously, it has been emphasized that the basic factor influencing the chemical composition of fly ash is the type of basic fuel used [16]. Based on the data presented in Figure 2, trace element concentrations in the native fly ashes studied, it was concluded that the values are similar.

Generally, elements and their compounds can evaporate during coal combustion, and they can be adsorbed and condensed on the surface of coal combustion particles when the temperature decreases [17]. Distribution of various elements between the bottom ash and fly ash depends on the type of boiler, operating conditions, the fuel mix, and the efficiency of flue gas cleaning devices [18] and is greatly influenced by the temperature in the combustion boiler, retention time of feed coal and air supply to the combustion grate [19]. In order to describe the element distribution between fly ash and bottom ash, *f/b* value (ratio of element concentration in the fly ash to that in the bottom ash) is calculated. This index is used to detect elements that are volatilized and subsequently condensed totally or partially in the flue gas (high *f/b* ratio) or heavy and low-volatile elements that preferably are enriched in bottom ash [20]. For both TENT A and TENT B, the *f/b* value for Cr is lower than 0.8 (0.76 and 0.78, for TENT A and TENT B, respectively), suggesting its enrichment in bottom ash in comparison to fly ash. Cr has relatively low vapor pressures and a higher boiling point, so it was retained in the slag or bottom ash [21]. Nickel is depleted in TENT B fly ash (*f/b* = 0.79), while Zn is depleted in TENT A fly ash, with the same value of *f/b* = 0.79. The results obtained concerning the bottom ash of TENT A enrichment with even 4 elements (Cr, Ni, Cu, and Zn) are in accordance with TENT A bottom ash characteristics; namely, a high value of LOI is an indication of a high amount of unburned carbon, which is the reason for its adsorption affinity.

The concentrations of examined elements in residuals obtained after acid leaching and wet oxidation are presented in Figures 3 and 4, respectively. To easily compare values for different methods, the concentration scale was the same as in Figure 2.
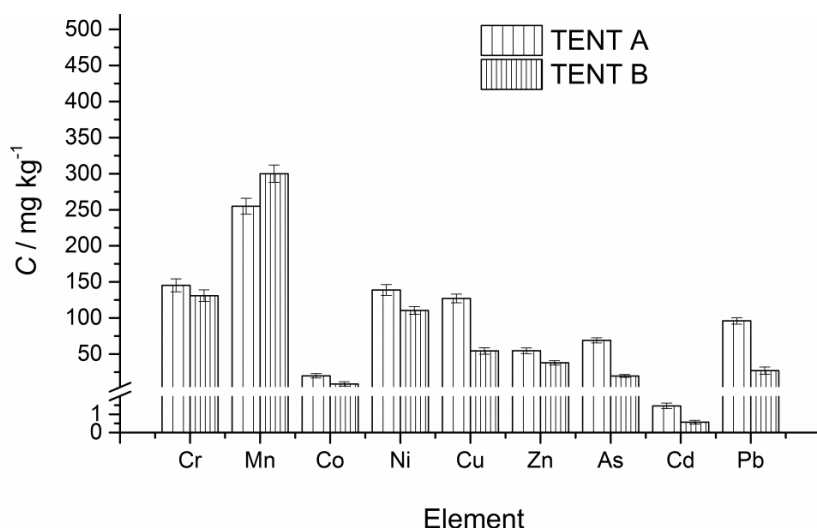

Figure 3. Concentrations of heavy metals (triplicate average) remained in residuals after acid (the error bars represent the standard deviation of the triplicates)

A decrease in the concentration of all examined elements is observed after acid treatment (Figure 3). The highest removal degree by acid digestion is obtained for Mn and for fly ash from both CPPs, 25 % for TENT A and 19.5 % for TENT B. The lowest removal efficiency is obtained for Pb (12.4 %, TENT A).
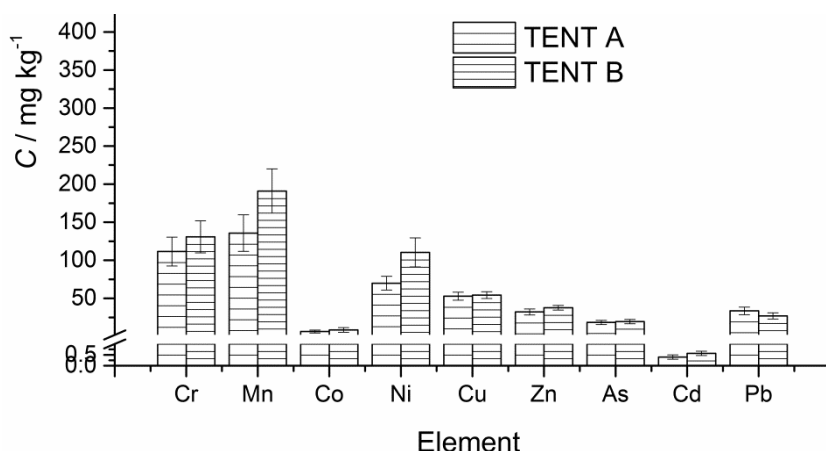

Figure 4. Concentrations of heavy metals remained in residuals after wet oxidation (triplicate average); the error bars represent the standard deviation of the triplicates)

Applying the wet oxidation method showed a significant decrease in the concentration of the examined heavy metals in all tested samples from both CPPs (Figure 4). Considering the degree of concentration decrease, two groups of elements are distinguished: one group in which the degree of removal is from 30 to 50 % (Cr, Ni, Cu, Zn), and the second group in which this degree is in the range 60 to 75 % (Mn, Co, As, Cd and Pb).

In general, wet oxidation showed 2-6 times higher extraction for analyzed heavy metals than acid leaching. Previously, it has been observed that the effect of different acids and acid combinations on fly ash digestion and metal dissolution is metal-dependent [22].

3. 3. Fly ash and residual characterization

Surface compositions of fly ash from TENT A and TENT B, and of residuals obtained after acid leaching and wet oxidation were investigated *via* XRD. Detailed information on the morphology, shape and surface texture of individual particles was obtained using SEM. The phases found in fly ashes and their chemical formulas and symbols are shown in Table 2, while XRD profiles are presented in Figure 5.

Table 2. Mineral name, chemical formula, and symbol

Name of mineral	Chemical formula	Symbol
Quartz	SiO_2	Q
Cristobalite	SiO_2	Cr
Anhydrite	$CaSO_4$	An
Mullite	$Al_{4.64}Si_{1.36}O_{9,68}$	Mu
Anorthoclase	$(Na_{0.7}K_{0.3})(Al_{1.0}2Si_{2.98}O_8)$	Ano
Albite	$(Na,Ca)Al(Si,Al)_3O_8$	Al
Hematite	αFe_2O_3	He
Calcite	$CaCO_3$	C

Fly ashes from both CPPs have shown similar patterns in mineralogical characterization, which is expected considering the same origin of the fuel (lignite, RB Kolubara). The phase analysis results show that in all samples, a few crystalline phases and probably one amorphous phase are present. The dominant crystalline phase in the fly ashes was made of silicates and alumosilicates, such as quartz, mullite, albite, and anorthoclase. Carbonates (calcite), oxide of iron (hematite), and sulfate mineral (anhydrite) were also detected. The types and proportions of metal minerals in coal ash vary depending on their origin [23]. Previously, it was published that magnetite was present in coal fly ash from TENT B [24]. In this research,

as well as in the research of Šešlija *et al.* [25], this mineral was not detected while only weakly magnetic hematite was present. A considerable amount of amorphous matter is present, which is confirmed in results published previously [9,25].
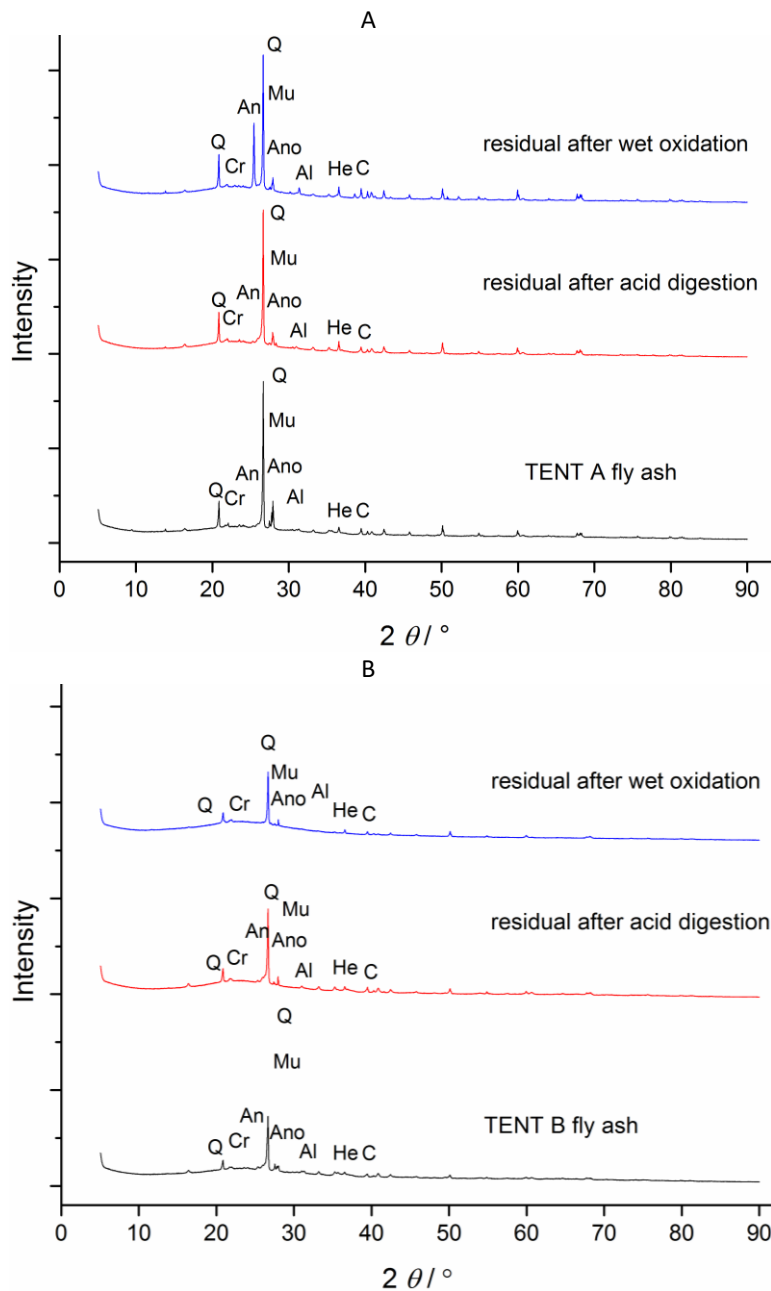

Figure 5. Mineral identification of the initial coal fly ash and the residual after the treatment from: A) TENT A; B) TENT B

Diffraction peak intensities of crystalline phases in the residuals after acid digestion did not change significantly compared to the initial fly ashes, indicating that the crystalline phase types did not change significantly. After wet oxidation, the quartz phase remained the main mineral phase, as it is difficult to dissolve under applied conditions. Also, the crystal phase diffraction peaks of cristobalite and calcite in the residual after this treatment did not change compared to those of the initial fly ash. On the other hand, the XRD analysis of wet oxidation residuals has shown changes in the anorthoclase, albite, and hematite contents.

SEM images of the fly ashes are shown in Figures 6 (TENT A) and 7 (TENT B) together with residuals of acid-treated and wet oxidized fly ash.
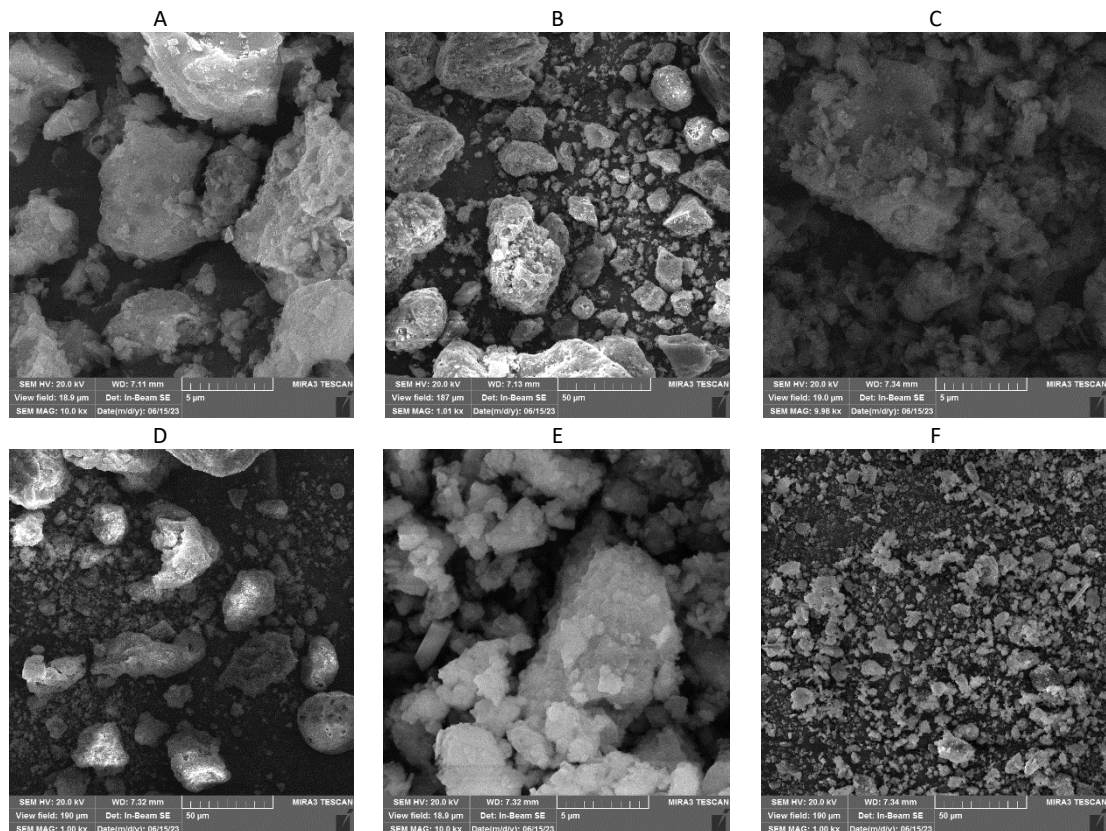
*Figure 6. SEM micrographs of TENT A samples: A,B) initial fly ash; C,D) residual after acid digestion;
E,F) residual after wet oxidation; (A, C and E: scale bar = 5 μm; B, D and F: scale bar = 50 μm)*
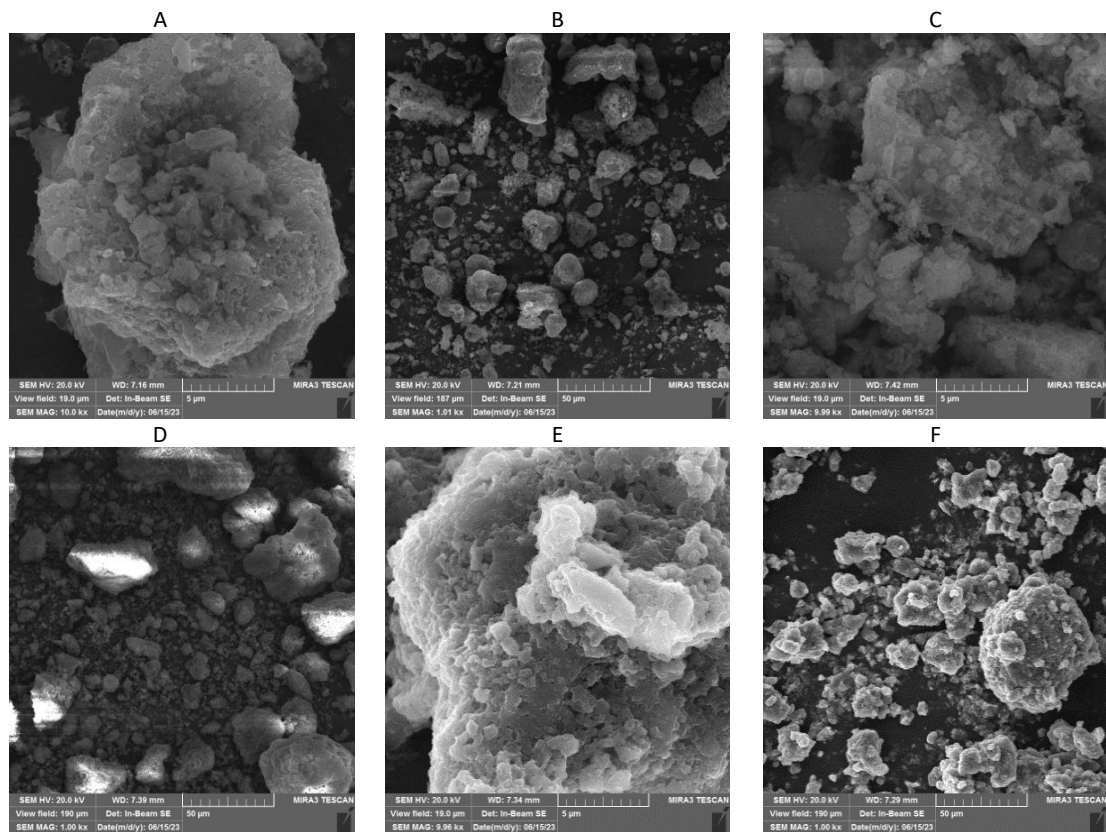

*Figure 7. SEM micrographs of TENT B samples: A,B) initial fly ash; C,D) residual after acid digestion;
E,F) residual after wet oxidation; (A, C and E: scale bar = 5 μm; B, D and F: scale bar = 50 μm)*

SEM images of fly ashes from TENT A and TENT B are similar (Figs 6A and 7A, respectively) showing particles of different sizes and shapes. Similar results were obtained previously by Wang *et al.* [11], where three typical CFA particles were found: spherical, oval, and irregular. For TENT A, the fly ash sample contains few 5 μm particles, while in the TENT B sample, one large particle is noticed, with many small fine particles packed inside and on its surface. The residual of TENT A fly ash after acid digestion had the same morphological pattern as the ash, while wet oxidation resulted in particle structure degradation.

3. 4. Correlation analysis

The experimental data from the chemical analysis after treatment (wet oxidation, acid leaching and microwave digestion of bottom ash/fly ash, TENT A/TENT B) have been used for the correlation analysis. The calculated correlation coefficients are listed in Table 3.

Table 3. Pearson correlation matrix between heavy metal concentrations in coal fly ash samples

	Cr	Mn	Co	Ni	Cu	Zn	As	Cd
Mn	0.997							
Co	0.990	0.987						
Ni	0.972	0.968	0.995					
Cu	0.747	0.767	0.616	0.525				
Zn	0.997	0.988	0.990	0.974	0.707			
As	0.881	0.902	0.821	0.769	0.716	0.848		
Cd	0.968	0.975	0.927	0.888	0.566	0.951	0.970	
Pb	0.968	0.961	0.924	0.884	0.538	0.965	0.925	0.983

Typically, a high correlation was found among all heavy metals because all fly ash samples were obtained by burning the lignite of the same origin. The strongest correlation was found between Pb, Cd, and As, while a very high correlation exists between Cr, Mn, Ni, Zn, and Co.

After performing the correlation analysis, the correlation matrix was checked (*i.e.* the correlation matrix of variables has to have the sufficient number of correlation coefficients above 0.3 to apply factor analysis [26]). Also, justification for performing the factor analysis was confirmed (*i.e.* the Kaiser-Meyer-Olkin (KMO) indicator takes values between 0 and 1, and the smallest value acceptable for good factor analysis (FA) is 0.5 to 0.6 [26,27] and the Bartlett's test of sphericity should be statistically significant, *i.e.* that $p < 0.05$ [28]). Consequently, the principal component analysis (PCA) was applied to the original data set. Two main components were obtained, which can explain the largest variance, over 90 % (Fig. 8). Most heavy metals with very strong correlations are in the first component.
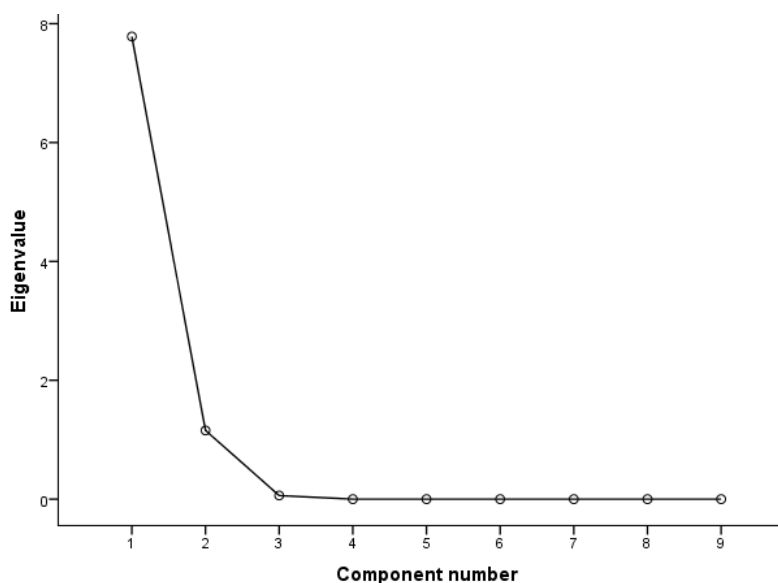

Figure 8. Scree plot of eigenvalues

This scree plot shows that the eigenvalues start to form a straight line after the second principal component. Therefore, the remaining principal components account for a very small proportion of the variability (close to zero) and are probably unimportant. Similar results were obtained by applying cluster analysis to z-transformed data. The dendrogram in Figure 9 shows clusters that coincide with and confirm the result obtained by the PCA analysis. The tested parameters were grouped into two clusters based on their characteristics and affinity towards the solid phase. In cluster I, there are predominantly Cr, Zn, Mn, Co, and, at a slightly greater Euclidean distance, Ni; in the second cluster, Pb, As, and Cd, and as a special one at a slightly greater Euclidean distance, Cu.
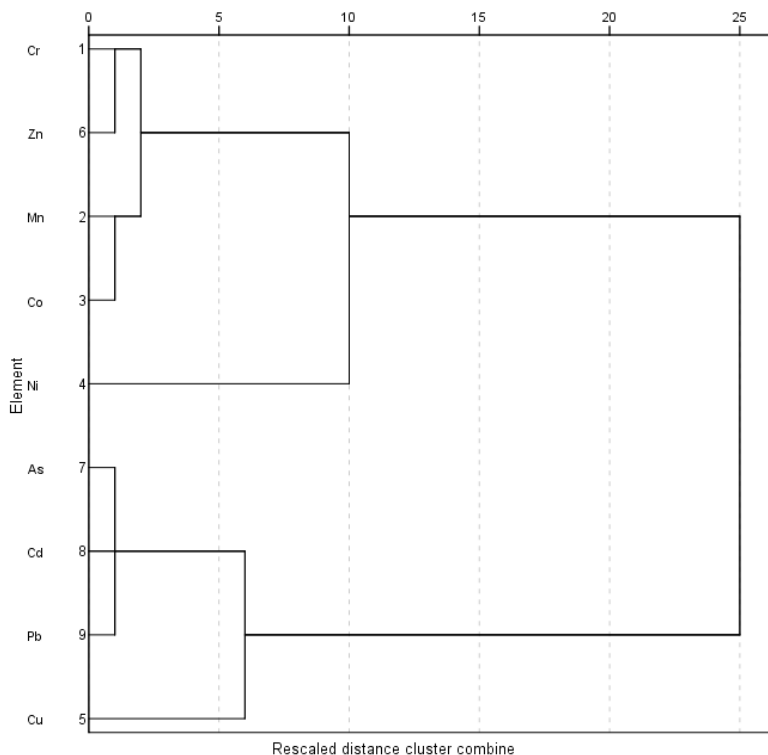

Figure 9. Dendrogram (using Ward linkage) of element grouping in fly ash samples

4. CONCLUSION

The present study investigated contents of selected heavy metals (Cr, Mn, Co, Ni, Cu, Zn, As, Cd, and Pb) in coal bottom and fly ash in samples collected from two Serbian coal-fired power plants, TENT A and TENT B, both using lignite from RB Kolubara. Microwave-assisted acid digestion was applied for sample preparation. The obtained results indicate that burning conditions did not significantly influence the chemical composition, nor the concentration of heavy metals. These concentrations were in the range reported for European coals. A decrease in heavy metal concentration in the fly ash residue has been observed during the heavy metal removal experiments using acid leaching and wet oxidation. The results indicate that wet oxidation is more efficient, with the removal degree in the range of 30 to 75 %; after this treatment, particle structure and surfaces were changed. In this way, material for possible further application can be prepared, and consequently, contamination caused by large amounts of disposed CFA can be reduced.

REFERENCES

[1] Šerović R, Jelić I, Matić B, Savić A. Utilization of solidified industrial hazardous waste in construction: A case study. *Hem Ind.* 2023; 77(2): 137-146 https://doi.org/10.2298/HEMIND222610001S.

[2]   Vukićević M, Popović Z, Despotović J, Lazarević L. Fly ash and slag utilization for the serbian railway substructure. *Transport.* 2018; 33(2): 389-396 https://doi.org/10.3846/16484142.2016.1252427.

[3]   Tasić AM, Sredović Ignjatović ID, Ignjatović LM, Ilić MA, Antić MP. Comparison of sequential and single extraction in order to estimate the environmental impact of metals from fly ash. *J Serb Chem Soc.* 2016; 81(9): 1081-1096 https://doi.org/10.2298/JSC160307038T.

[4]   Đorđević D, Stanković M, Krstić N, Dimitrijević V, Anastasijević N, Đorđević M, Nikolić M. Geochemical analysis of Kostolac power plant fly ash: working and living environment influence aspect. *Saf Eng*. 2018; 8(1): 15-20 https://doi.org/10.7562/SE2018.8.01.03.

[5]   Đolić M, Ćujić M, Stanišić T, Čičkarić D, Ristić M, Perić Grujić A. Contribution to the Serbian coal ranking and fly ash characterization using Pb isotopic ratio. *Metall Mater Eng*. 2022; 28(4): 675-684 https://doi.org/10.56801/MME931.

[6]   Slavković-Beškoski L, Ignjatović L, Bolognesi G, Maksin D, Savić A, Vladisavljević G, Onjia A. Dispersive Solid-Liquid Microextraction Based on the Poly(HDDA)/Graphene Sorbent Followed by ICP-MS for the Determination of Rare Earth Elements in Coal Fly Ash Leachate. *Metals (Basel)*. 2022; 12(5): 791 https://doi.org/10.3390/met12050791.

[7]   Buha Marković JZ, Marinković AD, Savić JZ, Mladenović MR, Erić MD, Marković ZJ, Ristić MĐ. Risk Evaluation of Pollutants Emission from Coal and Coal Waste Combustion Plants and Environmental Impact of Fly Ash Landfilling. *Toxics*. 2023; 11(4): 396 https://doi.org/10.3390/toxics11040396.

[8]   Buha-Marković J, Marinković A, Savić J, Krstić A, Savić A, Ristić M. Health risk assessment of potentially harmful substances from fly ashes generated by coal and coal waste combustion. *J Serb Chem Soc.* 2023; 88(11): 1161-1173 https://doi.org/10.2298/JSC220130048M.

[9]   Petronijević N, Radovanović D, Štulović M, Sokić M, Jovanović G, Kamberović Ž, Stanković S, Stopić S, Onjia A. Analysis of the Mechanism of Acid Mine Drainage Neutralization Using Fly Ash as an Alternative Material: A Case Study of the Extremely Acidic Lake Robule in Eastern Serbia. *Water (Switzerland)*. 2022; 14(20): 3244 https://doi.org/10.3390/w14203244.

[10]   Trivunac K, Vukčević M, Maletić M, Karić N, Pejić B, Perić-Grujić A. Waste materials as adsorbents for heavy metals removal from water: Comparative analysis of modification techniques. *Tekst Ind*. 2023; 71(1): 4-10 https://doi.org/10.5937/tekstind2301004T.

[11]   Wang N, Sun X, Zhao Q, Yang Y, Wang P. Leachability and adverse effects of coal fly ash: A review. *J Hazard Mater*. 2020; 396: 122725 https://doi.org/10.1016/j.jhazmat.2020.122725.

[12]   Bruker-AXS (2013). Crystallography Open Database for DIFFRAC.EVA. https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/x-ray-diffraction/xrd-software/eva/cod.html

[13]   Powder Diffraction File: PDF-2 (Database), International Center for Diffraction Data (ICDD), Newtown Square, Pennsylvania, USA, 2008.

[14]   ASTM-C 618-15: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete. 2015

[15]   Moreno N, Querol X, Andrés JM, Stanton K, Towler M, Nugteren H, Janssen-Jurkovicová M, Jones R. Physico-chemical characteristics of European pulverized coal combustion fly ashes. *Fuel*. 2005; 84(11): 1351-1363 https://doi.org/10.1016/j.fuel.2004.06.038 .

[16]   Strzałkowska E. Morphology, chemical and mineralogical composition of magnetic fraction of coal fly ash. *Int J Coal Geol*. 2021; 240: 103746 https://doi.org/10.1016/j.coal.2021.103746.

[17]   Wei Q, Song W. Mineralogical and chemical characteristics of coal ashes from two high-sulfur coal-fired power plants in Wuhai, Inner Mongolia, China. *Minerals* 2020; 10(4): 323 https://doi.org/10.3390/min10040323.

[18]   Dahl O, Nurmesniemi H, Pöykiö R, Watkins G. Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. *Fuel Process Technol*. 2010; 91(11): 1634-1639 https://doi.org/10.1016/j.fuproc.2010.06.012.

[19]   Tang Q, Liu G, Zhou C, Sun R. Distribution of trace elements in feed coal and combustion residues from two coal-fired power plants at Huainan, Anhui, China. *Fuel*. 2013; 107: 315-322 https://doi.org/10.1016/j.fuel.2013.01.009.

[20]   Dai S, Zhao L, Peng S, Chou C-L, Wang X, Zhang Y, Li D, Sun Y. Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China. *Int J Coal Geol*. 2010; 81(4): 320-332 https://doi.org/10.1016/j.coal.2009.03.005.

[21]   da Silva EB, Li S, de Oliveira LM, Gress J, Dong X, Wilkie AC, Townsend T, Ma LQ. Metal leachability from coal combustion residuals under different pHs and liquid/solid ratios. *J Hazard Mater*. 2018; 341 (September): 66-74 https://doi.org/10.1016/j.jhazmat.2017.07.010.

[22]   Ramanathan T, Ting YP. Selection of wet digestion methods for metal quantification in hazardous solid wastes. *J Environ Chem Eng*. 2015; 3(3): 1459-1467 https://doi.org/10.1016/j.jece.2015.05.006.

[23]   Ramakrishna C, Thenepalli T, Nam SY, Kim C, Ahn JW. The brief review on coal origin and distribution of rare earth elements in various coal ash samples. *KSEE*. 2018; 27(2): 61-69 https://doi.org/10.5855/ENERGY.2018.27.2.061.

[24]   Hredzák S, Tomanec R, Matik M, Šepelák V, Václavíková M. Magnetic separation and analysis of products obtained from coal-fired power plant fly ashes of Nikola Tesla B (Serbia). *J Min Met*. 2006; 42 A: 55-68 https://www.jmma.tfbor.bg.ac.rs/Volumes/2006/06.pdf.

[25] Šešlija M, Rosić A, Radović N, Vasić M, Đogo M, Jotić M. Physiproperties of fly ash and slag from the power plants. *Geol Croat.* 2016; 69(3): 317-324 https://doi.org/10.4154/gc.2016.26.

[26] Tabachnick BG, Fidel SL. Using multivariate statistics. 7th ed., New York, NY: Pearson; 2018. ISBN 978-0134790541

[27] Kaiser HF, A second generation little jiffy. *Psychometrika*. 1970; 35(4): 401-415 https://doi.org/10.1007/BF02291817.

[28] Bartlett MS. A note on the multiplying factor for various chi square approximations. *J R Stat Soc, B:Stat*. 1954; 16: 296-298 https://doi.org/10.1111/j.2517-6161.1954.tb00174.x.

Uticaj metode izluživanja na uklanjanje teških metala iz letećeg pepela

Andrija Z. Janković[1], Mirjana R. Ćujić[2], Milica D. Stojković[1], Maja B. Đolić[1], Dragana Z. Živojinović[1], Antonije E. Onjia[1], Mirjana Dj. Ristić[1] i Aleksandra A. Perić Grujić[1]

[1]*Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Beograd, Srbija*
[2]*Univerzitet u Beogradu, Institut za nuklearne nauke Vinča – Institut od nacionalnog značaja za Republiku Srbiju, Beograd, Srbija*

(Naučni rad)

Izvod

Uklanjanje teških metala (Cr, Mn, Co, Ni, Cu, Zn, As, Cd i Pb) iz elektrofilterskog pepela proučavano je korišćenjem metoda kiselog luženja i vlažne oksidacije. Paralelno je primenjena i kisela digestija uz pomoć mikrotalasne pećnice za određivanje pseudoukupnih koncentracija teških metala u cilju procene efikasnosti luženja. Multivarijantna statistika (Pearsonova korelacija, analiza glavnih komponenti i hijerarhijska klaster analiza) pokazala je dve dominantne grupe elemenata u zavisnosti od njihovih karakteristika i afiniteta prema čvrstoj fazi pepela. Grupe I (Cr, Zn, Mn, Co i Ni) i II (Pb, As, Cd i Cu) su međusobno diskriminisane. Pokazalo se da je metoda vlažne oksidacije prikladnija od kiselog luženja jer je smanjenje koncentracija metala bilo 30-75 % u poređenju sa 12-25 % dobijenih kiselom digestijom. Takođe je ispitan uticaj tretmana letećeg pepela na karakteristike čvrstog ostatka metodama rendgenske difrakcije i skenirajuće elektronske mikroskopije. Ovim metodama su otkrivene promene na površini i u strukturi letećeg pepela nakon tretmana vlažnom oksidacijom. Vlažna oksidacija se može smatrati kao moguća metoda za tretman u cilju uklanjanje teških metala iz letećeg pepela, obezbeđujući materijal koji bi se mogao dalje koristiti i smanjujući rizik od zagađenja izazvanog odlaganjem letećeg pepela.

Ključne reči: iskorišćenje otpada; vlažna oksidacija; izluživanje kiselinom; karakterizacija materijala