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Ultrasound and shaking-assisted water-leaching of anions and cations from fly ash

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Abstract: Two mechanical extraction techniques were used for the extraction of environmentally interesting components of coal fly ash: shaking, during which the extraction process lasted from 6 up to 24 h, and sonication that lasted from 15 up to 60 min, using water as extractant. The concentration of anions in fly ash extracts was determined by ion chromatography, while atomic absorption spectrometry was used for determination of: As, Pb, Cd, Ni, Cr, Zn, Cu, Fe, Mn and Al. The ultrasonication yielded slightly higher amounts of extracted anions as well as Pb, Al, Mn and Fe cations, while shaking-assisted extraction was more efficient for the Cr, As, Zn and Ni ions. The changes in pH value, particle size distribution within colloid solution, zeta potential and conductivity during ultrasound-assisted extraction were measured in order to explain changes that occur on the surface of fly ash particles contacting water and different processes (adsorption, ion exchange and flocculation) that develop under natural conditions. Principal Component Analysis was used for assessing the effect of observed process parameters. It is essential to evaluate quantity of these elements leachable from coal fly ash into the surface waters in natural conditions in order to prevent contamination of the environment.

Keywords: fly ash; environmental impact; aqueous extracts.

INTRODUCTION

Being one of the major fossil fuels for generating electricity, coal is also the important factor in global warming and one of the main contributors to acid

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rain.^{1,2} During coal combustion in thermal power plants a series of physico-chemical transformations of mineral matter present in coal particles occur, leading to dispersion of potentially toxic elements into the environment.^{3,4} The emission of combustion gases includes in part a fly ash that escapes the particulate matter control device. Despite high retention efficiency of these devices in thermal power plants (*e.g.*, electrostatic precipitators), considerable amounts of microparticles are emitted into the atmosphere because of the high overall rate of coal consumption in large power plants. These particles are considered to be highly contaminating, due to their large specific surface areas and the fact that potentially toxic trace elements condense on their surfaces during cooling of combustion gases. Coal fly ash is a highly heterogeneous material usually consisting of silicon dioxide, aluminum oxide and iron oxide as major mineral components.⁵ During coal combustion, various trace elements such as As, Pb, Cd, Mn, Cr, Ni, Zn and Cu could be present in fly ash, depending on coal characteristics and the combustion process.^{4,6,7} Their possible release into the environment could cause many problems. Along with As, Pb, Cd, Mn, Cr and Ni, fluorine and chlorine are among the hazardous air pollutants mentioned in the 1990 Clean Air Act Amendments. Heavy metals can be leached from fly ash and may become a hazard to the environment because of their contribution to the formation of toxic compounds.^{1-3,7}

In order to analyze the elements contained in fly ash, it is necessary to extract the analytes from solid samples and employ an instrumental technique to determine their quantity. The extraction of analytes involves digestion process using strong acids, such as HNO₃, HCl, HF and H₂SO₄ or their combinations.⁶⁻⁹ The use of mineral acids at elevated temperatures can lead to a loss of easily volatile elements, thus making impossible determination of anions in the same solution. Apart from microwave digestion, which is widely used, another technique for sample preparation is ultrasound-assisted extraction (UAE).⁸⁻¹³ UAE can be performed by using ultrasonic baths or probes. The main advantages of the technique are speed of digestion, high sample treatment capacity and low reagent usage. When ultrasonic water bath is used, subsequently samples can be centrifuged instead of filtered if they were placed in plastic screw-top bottles or polypropylene centrifuge tubes.^{14,15} Lower pressure and temperature used during the ultrasonic treatment makes this technique safer than the microwave assisted digestion.

For metal detection, atomic absorption spectrometry (AAS) or inductively coupled plasma/optical emission spectrometry (ICP-OES) have been used.^{3,7-18} Halogens and nonmetals are in most cases determined by ion chromatography (IC) or ion selective electrodes.^{19,20}

In this study, ultrasound-assisted extraction (UAE) for sample preparation was investigated in order to determine metals and nonmetals in coal fly ash and

the results were compared with those obtained by shaking-assisted extraction (SAE) and with the standard ASTM procedure.²¹ Using our extraction techniques, the idea was to employ only water as extractant in order to predict the environmental impact of real leaching process associated with the disposal of fly ash into the ponds.²²

The anion content (fluorides, chlorides, nitrates, nitrites, sulfates and phosphates) was analyzed by IC and the metals (arsenic, lead, cadmium, nickel, chromium, zinc, copper, iron, manganese and aluminum) were measured by AAS. The main criterion for the selection of elements was their natural presence in coal, as well as their potentially negative effects on human health and the environment.

Particle size distribution (PSD) and zeta potential (ZP) measurements were performed, as well as pH value and conductivity estimations of suspension solution during ultrasonic extraction, with the aim of better understanding different processes during exposure of fly ash to the water treatment, under certain conditions.

Experimental results were subjected to analysis of variance (ANOVA) to show relations between samples. Pattern recognition technique (Principal Component Analysis – PCA) was applied on the experimental data (used as descriptors) to characterize and differentiate among the observed samples.^{23,24}

EXPERIMENTAL

Sampling and sample preparation

Fifty individual samples were collected from the Kostolac thermal plant, located approximately 90 km east of Belgrade, Serbia. All individual samples were combined and bigger lumps milled in a grinder to obtain smaller pieces < 1 mm. Subsequently, the samples were thoroughly homogenized, as confirmed by energy dispersive X-ray fluorescence spectrometry (EDXRFS), dried at 50 °C for 24 h, and then micronized in a plate mill for 30 s. Finally, they were sieved through a sieve with 0.212 mm openings which corresponds to US standard mesh 70 and Tyler standard mesh 65. The moisture content determined by the Karl-Fisher coulometric titration method was 1.24 %. All the results were calculated for dried sample.

Homogeneity was confirmed by EDXRFS (in-house developed spectrometer), suitable for non-invasive and non-destructive analysis of various materials. As an excitation source, air cooled X-ray tube (Oxford Instruments, Rh – anode, max. 50 kV, 1 mA) with a pinhole lead-brass collimator and beam size at the exit of the collimator of 0.5 mm was used. For the detection of characteristic X-rays, an AMPTEK X-123 Complete X-ray spectrometer with a Si-PIN detector (6 mm²/500 µm, Be window 12.5 µm thickness) was employed, and for spectra acquisition and peak calculations ADMCA software was used. Two laser pointers mounted on the measuring head enabled repeatable positioning of the samples. Experimental parameters of 40 kV applied voltage, 800 µA current, and a measuring interval of 200 s with no filter were selected and kept constant during all measurements. The geometrical parameters chosen were as follows: detector–sample distance, was 21 mm; X-ray tube collimator tip–

–sample distance, 16 mm; and the angle between the axes of the X-ray tube and the detector, 45°, while the sample surface was perpendicular to the excitation X-ray beam.

The extraction suspensions were prepared by mixing the ash sample with deionized water at a ratio 1:10, *i.e.* 3 g of solid sample to 30 ml in 50 ml volumetric flasks. All chemicals used for the analysis were of analytical grade. Deionized water from a Milli Q unit (SG GmbH) was used for the preparation of all samples. The resistivity of the deionized water was 18.0 M Ω cm at 22.5 °C.

Three shaking-assisted extractions (SAE) were performed for each extraction time of 6, 12 and 24 h at room temperature (20 °C) using a custom made linear shaker. The ultrasound-assisted extractions (UAE), employed a SONIS 2 GT (Iskra PIO d.o.o., Slovenia) ultrasonic bath operated at 40 kHz ultrasonic frequency and 200 W effective ultrasonic power. Three extractions were also performed for each extraction time of 15, 30, 45 and 60 min. The extraction times, for both procedures, were chosen according to earlier investigations of solid sample extractions.^{12,15,19}

After the extraction processes, the resulting suspensions were filtered through a medium pore sized filter paper.

Measurement techniques

The concentration of anions in solutions was determined by ion chromatography using a Dionex ion chromatography instrument. The conductivity detection was performed after the suppression of eluent conductivity using an anion suppressor ASRS 300. The separation column employed was a Dionex Ionpac AS 11. As an eluent aqueous solution of NaHCO₃ (0.5 mM) and Na₂CO₃ (2 mM), at a flow rate of 0.9 mL min⁻¹ was used. Samples were filtered and then injected. Sample volume was 20 μ L for each probe. Three replicate injections of each sample were made and the results averaged. All chemicals were of analytical reagent grade. All standard solutions, eluent and reagents were prepared with Milli-Q water, degassed under vacuum, and then filtered prior to use. A primary multi-anion standard solution (SPEX CertiPrep Group) was used. Calibration standards were prepared by serial dilutions of the multi-component standard with Milli-Q water.

For the determination of metals, an atomic absorption spectrometer (Perkin–Elmer AAnalyst 700) was used. Both flame and electrothermal atomization techniques were employed, depending on the element. The whole system was controlled by means of AA WinLab 32 software. Zn, Mn, Fe and Cu were determined by air-acetylene, while Al by nitrous oxide-acetylene flame AAS. As, Pb, Cd, Ni and Cr were measured using electrothermal AAS, coupled with standard pyrolytic graphite-coated tubes with integrated platforms (Perkin–Elmer Part No. B3 001264) as an atomizer. Graphite platforms significantly improve the instrument performance for the determination of Cd, Pb and As, according to ASTM D 6357.²¹ Graphite tubes are purged with argon as an inert gas. Samples were injected into the graphite furnace (GF) system by an autosampler (Perkin–Elmer AS-800). The deuterium lamp background correction was used for certain elements. Each hollow cathode lamp or electrode discharge lamp, used in these measurements as a radiation source, operated using current recommended by the manufacturer. Calibration solutions for each element were prepared from serial dilutions of 1 g L⁻¹ single element stock solution in 0.2 vol. % nitric acid (Merck, KGaA, Germany). The obtained results were compared to the results obtained by the standard procedure²¹ whereby good agreement was found.

The pH value was determined using a pH meter (pH 1500, P11/BNC, Eutech Instruments, Thermo Fisher Scientific, USA).

Additionally, the UAEs were repeated in order to measure PSD and ZP by dynamic light scattering spectroscopy using a Zeta-Sizer Nano Red ZS, with a 633 nm He-Ne laser (Malvern, UK) and the data were analyzed by the Zetasizer Software, version 6.20 (Malvern, UK). The instrumental conditions were: 30 runs with run duration of 10 s; temperature, 25 °C; refractive index, 1.600 and absorption index of material, 0.09. The measurements were conducted during the extraction process every 15 min for the colloid PSD and ZP.

Statistical analysis

Descriptive statistical analyses for all the obtained results were expressed by means, for each treatment. Collected data were subjected to ANOVA to explore the effects of process variables. Furthermore, pattern recognition technique PCA was applied successfully to classify and discriminate between different samples. The evaluation of ANOVA and PCA of the obtained results was performed using Statistica software version 12.²³⁻²⁶

RESULTS AND DISCUSSION

Homogeneity proof

Homogeneity of the fly ash composite sample, after combining and long-term mixing, was confirmed by EDXRF spectrometry. After the batch was well shaken, 5 subsamples were taken from the bulk and pastilles (0.500 g and 25 mm radius) made for each of them. Every subsample pastille was then analyzed by EDXRF spectrometry at two different measuring spots in each pastille. Almost perfect overlap of the two acquired spectra confirmed the homogeneity of the composite sample (Fig. 1). Grain size distribution is represented in Fig. 2.

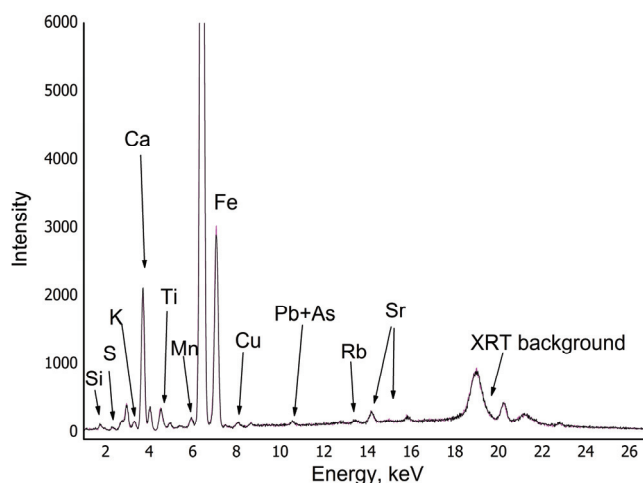


Fig. 1. EDXRF spectra of composite fly ash sample.

Results of anion concentration measurements

The results of the IC analysis of chloride, fluoride, nitrate, nitrite, phosphate and sulfate anions in the samples treated with two different techniques of mech-

anical preparation, SAE and UAE are presented in Table I. Accuracy was determined by measuring each sample in triplicate and expressed as relative standard deviation. It should be noted that the fly ash sample is solid and as such is never perfectly homogenous. Relative standard deviation (*RSD*) of the analytical measurements performed was determined: 1.2 (fluoride), 0.92 (chloride), 4.6 (sulfate) and 7.7 % (nitrate).

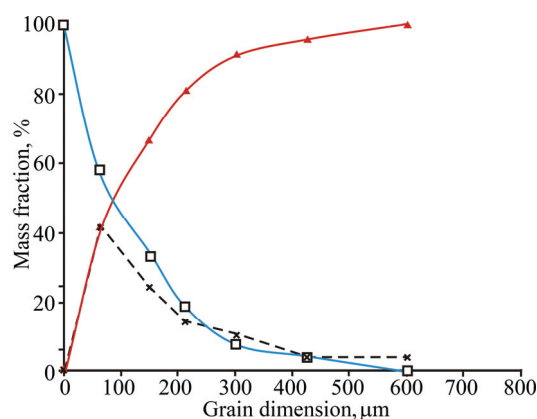


Fig. 2. Grain size distribution of fly ash (□ – sieved fraction, ▲ – unsieved fraction, x – overall).

TABLE I. The results of the anions determination (mg/100g) after UAE/SAE ($n = 3$, uncertainty as standard deviation); a, b, c, letters printed in superscript within the same column in the table show significantly different means of observed data (at $p < 0.05$ level)

UAE / min	Fluoride	Chloride	Nitrate	Sulfate
15	2.87±0.04 ^a	1.99±0.07 ^a	0.12±0.02 ^a	673±50 ^a
30	2.86±0.10 ^a	2.17±0.11 ^a	0.13±0.01 ^a	675±55 ^a
45	2.66±0.04 ^c	2.08±0.07 ^a	0.11±0.01 ^a	678±58 ^a
60	2.46±0.04 ^b	2.37±0.56 ^a	0.10±0.02 ^a	778±4 ^a
SAE / h	Fluoride	Chloride	Nitrate	Sulfate
6	2.83±0.16 ^a	1.90±0.12 ^a	0.12±0.02 ^a	646±17 ^a
12	2.77±0.07 ^a	1.84±0.20 ^a	0.14±0.01 ^a	674±3 ^a
24	2.43±0.07 ^b	1.71±0.04 ^a	0.11±0.01 ^a	707±9 ^b

Nitrites and phosphates were not detected. Nitrites most likely oxidized to nitrates. Macro and micro-analysis of coal confirmed the content of P_2O_5 to be below 0.01 %. The concentration of phosphorus in the ash was even lower and after the extraction it was below the detection limit.²⁰

The results of fluorides extracted by SAE and UAE are shown in Table I. A steady decrease in concentration with time was observed in samples obtained in both procedures (statistically significant at $p < 0.05$ level, according to Tukey's HSD test).²⁷ In the case of UAE, the concentration of fluoride remained the same for the first 30 min, but after 45 min values decreased and after 60 min were

slightly higher than for the samples obtained by SAE after 24 h. It can be noticed that the concentration of fluoride extracted using ultrasound was slightly higher compared to shaker procedure.

The UAE for chloride ions (Table I) results demonstrated the extracted ion amount did not depend on the extraction time. During SAE, however, the concentration of chlorides decreased after 12 h, and even more after 24 h of shaking.

As shown in Table I, the extracted amount of nitrate ions varied with the extraction time. In both cases, the nitrate content initially increased, but finally decreased below the initial values.

The amount of sulfate anions extracted by UAE gradually increased and continued rapid increase after 60 minutes. Monitoring changes in the amount of sulfates with an elapsed time of shaking, the increase in their concentration is much more steady. After six-hour agitation, the extracted sulfate average was approximately 30 mg/100 g and remained at the same level for the next twelve-hour agitation.

Results of cation concentration measurements

The results of As, Pb, Cd, Ni and Cr cation contents in the samples mechanically treated by SAE and UAE, determined by graphite furnace atomic absorption spectrometry (GFAAS) and the results of Zn, Cu, Fe, Mn and Al content determined by flame atomic absorption spectrometry (FAAS), are shown in Table II. For the concentration ranges measured, the relative standard deviation (RSD) was: 2.1 (As), 2.2 (Pb), 6.4 (Cd), 9.7 (Ni), 0.6 (Cr), 9 (Zn), 12 (Cu), 11.8 (Fe), 8.6 (Mn) and 9.5 % (Al).

TABLE II. The results of the cation determination ($\mu\text{g}/100\text{ g}$) after UAE/SAE ($n = 3$, uncertainty as standard deviation); a,b,c – letters printed in superscript within the same column in the table, show significantly different means of observed data (at $p < 0.05$ level)

Element	UAE / min				SAE / h		
	15	30	45	60	6	12	24
As	27.44 \pm 1.19 ^b	31.69 \pm 1.23 ^a	33.35 \pm 0.57 ^a	33.71 \pm 0.48 ^a	25.30 \pm 1.24 ^a	35.77 \pm 1.05 ^b	42.45 \pm 1.36 ^c
Zn	2.67 \pm 1.15 ^a	3.00 \pm 1.00 ^a	3.33 \pm 1.15 ^a	10.67 \pm 2.08 ^b	7.33 \pm 1.53 ^a	10.67 \pm 2.08 ^a	11.33 \pm 1.53 ^a
Pb	1.15 \pm 0.14 ^{ab}	1.02 \pm 0.03 ^a	1.31 \pm 0.11 ^b	1.90 \pm 0.07 ^c	1.10 \pm 0.04 ^a	1.19 \pm 0.04 ^{ab}	1.47 \pm 0.19 ^b
Cu	11.33 \pm 1.53 ^a	11.67 \pm 2.08 ^a	16.67 \pm 2.31 ^{ab}	21.00 \pm 4.00 ^b	11.00 \pm 1.73 ^b	18.33 \pm 1.15 ^a	21.33 \pm 1.53 ^a
Fe	38.33 \pm 2.52 ^b	48.00 \pm 6.56 ^{ab}	58.67 \pm 9.07 ^a	63.33 \pm 5.51 ^a	43.00 \pm 8.19 ^a	56.33 \pm 6.66 ^{ab}	61.33 \pm 5.51 ^b
Mn	14.50 \pm 0.87 ^a	13.67 \pm 1.15 ^a	13.33 \pm 1.15 ^a	13.00 \pm 1.00 ^a	13.00 \pm 1.00 ^b	12.00 \pm 1.00 ^{ab}	11.00 \pm 1.00 ^a
Cd	0.05 \pm 0.01 ^a	0.08 \pm 0.01 ^a	0.13 \pm 0.04 ^{ab}	0.23 \pm 0.09 ^b	0.07 \pm 0.04 ^a	0.19 \pm 0.08 ^a	0.11 \pm 0.02 ^a
Ni	0.52 \pm 0.09 ^b	2.69 \pm 0.28 ^a	2.49 \pm 0.39 ^a	2.56 \pm 0.47 ^a	1.57 \pm 0.41 ^a	2.38 \pm 0.16 ^{ab}	2.70 \pm 0.59 ^b
Cr	34.33 \pm 3.53 ^a	79.5 \pm 9.7 ^{ab}	92.9 \pm 6.3 ^{bc}	128.3 \pm 29.1 ^c	78.8 \pm 3.2 ^a	118.9 \pm 13.0 ^b	162.6 \pm 6.2 ^c
Al	10300 \pm 323 ^c	5620 \pm 86 ^{bc}	2070 \pm 66 ^{ab}	730 \pm 18 ^a	3770 \pm 90 ^b	590 \pm 76 ^a	459 \pm 12 ^a

The increased concentration of some ions is more or less proportional to the extraction time (statistically significant at $p < 0.05$ level, according to Tukey's

HSD test). Also, observed increase was more regular when SAE was applied. In most cases, the amount of cations extracted by SAE for 24 h and UAE for 60 min appeared approximately the same. It can be noticed that the concentrations of As, Ni, Zn and Cr increased in time, but the amounts obtained by SAE were 20–25 % higher than the corresponding values obtained by UAE. The concentration increase for all these elements was gradual, except for Zn extracted by UAE. The obtained values were very low after 45 min, followed by a sudden peak of about 70 % after 60 min.

The concentrations of Cu and Fe ions in fly ash samples were almost the same at the end of the extraction period for both methods of mechanical treatment. The concentration increase was steady in each case, but the results of ultrasound were obtained much faster, so it is clear that UAE accelerated the reactions.

The larger quantity of Pb ion was extracted by UAE, even after an extraction time of 45 min. After 60 min, concentration was about 30 % higher than obtained using SAE.

In the case of Cd ion, the amount extracted by SAE varied with time, contrary to UAE extraction that provided for steady increase. Therefore, it can be concluded that the ultrasound usage secured consistent values of concentration for extracted ions.

The total concentration of Al ion in extracts obtained by UAE contrary to that obtained by SAE was significantly higher. But, the amount of Al, as well as Mn, during the extraction, decreased in both cases.

In order to characterize and differentiate among the observed samples, pattern recognition technique (PCA) was applied on the experimental data (used as descriptors). The PCA method allows a considerable reduction in the number of variables and the detection of structure in the relationship between measured parameters. All samples were produced during different time intervals as shown by experimental design (Tables I and II) and predicted by PCA score plot (Fig. 3a and b, respectively). For visualizing the data trends and the discriminating efficiency of the used descriptors a scatter plot of samples, using the first two principal components (PCs) issued from PCA of the data matrix, was obtained. The quality results for UAE water-leaching of anions and cations from fly ash process (Fig. 3a) show that the first two principal components, accounting for 95.30 % of the total variability can be considered sufficient for data representation. The content of Cu (8.3 % of the total variability), Fe (8.1 %), Cd (8.6 %) and Cr (8.4 %) were the most positively influential variables for the first factor coordinate calculation, while the most evident negative contribution for the first factor component was observed by fluoride (8.3 %). On the other hand, the most positively influential variables for the second factor component calculations

were: As (12.0 %), Ni content (26.0 %) and nitrate (18.8 %), while the negative influence was observed by Pb (9.4 %).

The first two principal components explained 100 % of total variability for SAE process, as seen from Fig. 3b. The content of As (8.7 % of the total variability), Zn (8.1 %), Cu (8.5 %), Fe (8.5 %), Ni (8.5 %), Cr (8.6 %) and sulfate (8.6 %) were the most positively influential variables for the first factor coordinate calculation, while the most evident negative contribution for the first factor component was observed for Mn (8.7 %).

The change in cation and anion concentrations during UAE and SAE can be observed in Fig. 3a and b, respectively, with higher Al and Mn concentrations Fig. 3a, at the beginning of the process (for both UAE and SAE), while the concentration of Pb, Cr, As, Cu, Ni, Fe and Zn, and also the sulfate content is increased with UAE and SAE time (Fig. 3b). The most negatively influential variables for the second factor component calculation were: Cd (32.2 % of the total variability), fluoride (8.2 %) and nitrate content (36.6 %).

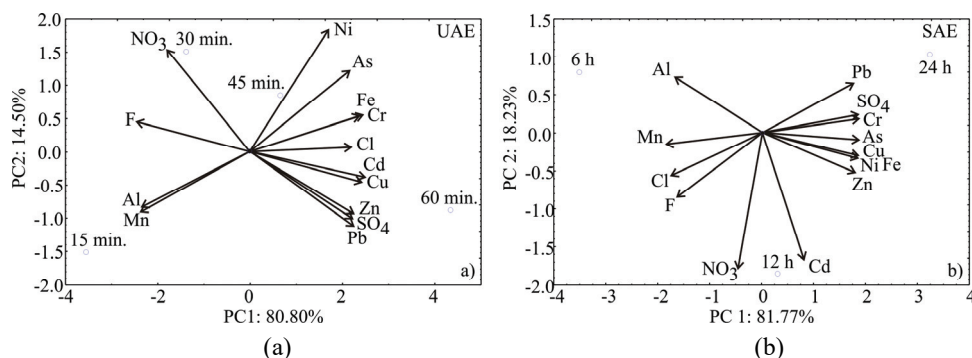


Fig. 3. Biplot graphic of UAE (a) and SAE (b) water-leaching of anions and cations from fly ash.

Our results are in a very good agreement with the results obtained using the standard procedure for GFAAS.²⁴ In Table III the comparison of measured concentrations of As, Pb, Cd, Ni and Cr in fly ash after 60 min of UAE, and those obtained by ASTM D 6357 are shown. The advantage of UAE method is its simplicity, while standard procedure is time-consuming including usage of hazardous substances.

Compared to SAE, UAE technique proved to be more efficient in the case of Al, on average 160 % increased concentration was extracted. It was more efficient in the case of Pb, Mn and Fe ions, also (Fig. 3). Ultrasonic energy, when applied to solutions, causes acoustic cavitation. The collapse of bubbles formed by ultrasonic energy results in the generation of high temperatures and pressures at the interface of the collapsing bubble and another phase, leading to enhanced

chemical reactivity.^{28,29} The surface area available for reactions with the extraction agent could increase because of the possible fragmentation and aggregate disintegration of sample particles. It is well known that the processes of adsorption and desorption could arise, but due to recombination of reactive groups under extreme conditions the formation of new chemical species in the suspension occur at prolonged sonication times.³⁰

TABLE III. A comparison of concentration values ($\mu\text{g}/100\text{ g}$) determined by GFAAS after 60 min UAE with those obtained by a standard test method

Element	UAE	ASTM D 6357
As	33.71 \pm 0.68	34.42 \pm 0.80
Pb	1.90 \pm 0.07	2.01 \pm 0.09
Cd	0.23 \pm 0.09	0.22 \pm 0.07
Ni	2.56 \pm 0.47	2.69 \pm 0.55
Cr	128.3 \pm 29.1	121.9 \pm 27.0

Also, significantly larger amounts of Zn and Cr extracted by SAE contrary to UAE can be noticed. This could be explained either by considerably longer agitation time (24 h) and subsequent dissolution, or by the re-adsorption of extracted cations onto the newly exposed sorption sites due to influence of ultrasound.

As observed in Fig. 3, the extracted amounts of some metals varied a lot with the extension of extraction time, although some metals behaved in the similar way during the extraction. The concentrations of Cu and Zn were slightly elevated, until a sharp increase occurred in both cases, after 30 and 45 min, respectively. Concentrations of Mn and Al showed a steady decline. Mn could be expected to exist as an oxide since MnS forms only under extreme conditions of high sulfur and low oxygen availability. As such, it is very nonvolatile and its wide distribution in the ash could be expected. Small amounts of Ni, Pb and Cd suggest a prior geochemical association of these metals with Mn. Concentration of Fe and As increased with extraction time, but very slowly after 45 min. This can be explained by the presence of As probably as an arsenical pyrite. Both sulfides of As and Fe are volatile and thus could be expected to condense on the surface of cooling ash particles.³¹⁻³³

Changes in pH value, particle size distribution (PSD) in colloid, zeta potential and conductivity during the extraction

The changes of the average particle size distribution, zeta potential, pH value and conductivity of the suspension during ultrasonic extraction of fly ash are presented in Table IV.

The results given in Table IV were analyzed by applying PCA and presented in Fig. 4. The first two principal components explained 98.8 % of total variability for the changes in the average particle size distribution, zeta potential, pH value

and conductivity of the suspension during ultrasonic extraction. Zeta potential (25.2 % of the total variability), pH value (32.1 %) and conductivity (30.6 %) were the most negatively influential variables for the first factor coordinate calculation. The most positively influential variable for the second factor component calculation was the particle size (51.5 % of the total variability), while the negative influence was observed for zeta potential (23.8 %).

TABLE IV. Changes of the average particle size distribution, zeta potential, pH value and conductivity of suspension during ultrasonic extraction

Extraction time min	Average particle size nm	Zeta potential mV	pH value	Conductance $\mu\text{S cm}^{-1}$
15	1418	-11.9	11.00	535.33
30	1390	-8.80	11.41	609.00
45	1416	-10.3	11.32	596.00
60	1262	-10.7	10.48	561.67

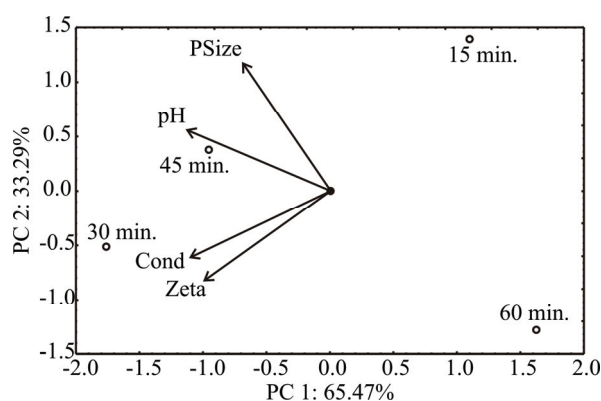


Fig. 4. Biplot graphic of the changes in the average particle size distribution, zeta potential, pH value and conductivity of suspension during ultrasonic extraction.

Once the fly ash particles contact an aqueous environment, solid phase dissolution reactions occur immediately. Hydrolysis of oxide forms of Ca, K, Mg and Na are suspected to cause high initial pH values of the solution. Al, Fe and Si are particularly soluble at elevated pH values.³⁴ The pH value did not change significantly; the largest decline (11.32 to 10.48), occurred from 45 to 60 min of UAE when the concentration of sulfate was the highest (Table I). Large amounts of sulfate are typically released from fly ash, and there is a probability that soluble inorganic complexes are formed.³¹ The total content of acid cations decreased most from 15 to 30 min (Table II) and the corresponding increase in pH value can be observed.

The general dividing line between stable and unstable suspensions is taken at ± 30 mV. Particles with zeta potentials more positive than 30 mV or more negative

tive than -30 mV are normally considered stable.³⁵ In this case, measured zeta potential of colloid particles ranged from -11.9 to -8.8 mV with the largest change observed between 15 and 30 minutes of sonication. The flocculation phenomena increased because the force of electrostatic rejection was low. It could be assumed that due to Al and Mn adsorption processes, the surface charge of colloidal particles slightly increased. The absolute value of zeta potential corresponds to the thickness of diffusion layer of ions. The valence of the ions could also influence double layer thickness. Since the extracted concentration of Al is higher than the concentration of other extracted cations (Table II) it could be assumed that one of the reasons for the low values of zeta potential lies in high concentrations of Al^{3+} in solution that compresses the double layer to a great extent in comparison with a monovalent ion such as Na^+ .³⁶ After 60 min of sonication, concentration of Al^{3+} dropped and absolute value of zeta potential increased, most likely due to Al^{3+} adsorption. Colloidal instability caused the particle size changes during sonication. From 15 to 30 min, average particle size declined and, as is expected, conductivity increased. After 60 min average particle size decreased, most likely because of the impact of ultrasound and consequent increase in the temperature of the solution.

Zeta potential, conductivity and pH values are changing in the same way during exposure to ultrasound (Fig. 4). From 15 to 30 min they increased, which corresponded to an increase of charged particles in the solution and a thinner diffusion layer of ions. After 45 min, the diffusion layer thickness increased, primarily due to Al^{3+} and Mn^{2+} adsorption, as well as other ions to a lesser extent; pH value decreased because of increased concentration of sulfate in solution and decrease in conductivity occurred probably due to readsorption of alkali and alkaline earth metals on smaller diameter particles of fly ash.

In aqueous media, the pH value of the sample is one of the most important factors that affect zeta potential. A zeta potential versus pH value curve will be positive at low pH values and negative at high pH values. Since the range of pH values in this case is alkaline, low negative zeta potentials are expected, which is in accordance with the results presented in Table IV and Fig. 4.

Various cations released into the solution caused the change in pH value, which could further influence the adsorption and desorption processes to some extent. These processes are mainly related to competitive cation interactions for the sorbing phase and the exchange of sorbed cations with those from solution influenced by ultrasound.

Further investigations are required in order to explore in what forms are analyzed ions present during the processes of extraction, what are the relations between them, as well as the compounds they may form in the given range of pH values, which would be substantial for enhancements of extraction procedures.

CONCLUSIONS

From the obtained results it could be concluded that the techniques employed for the mechanical assisted extraction (as a preparation step) of fly ash samples are significant for estimating the concentration of trace elements and pollutants that could be released into the environment. Shaking and ultrasound assisted extractions of aqueous fly ash suspensions were performed. The ultrasonic assisted extraction is less time consuming and our results showed that the prolonged extraction of 15 min did not lead to significant change in the amount of the extracted anions, except in the case of sulfate where concentration readily peaked. Contrary to this, the concentration of the most cations increased over the UAE extraction time and 60 min extraction was found to be optimal. Only amounts of Al and Mn showed decrease. The larger amounts of As, Ni, Zn and Cr, were extracted by SAE, probably due to considerably longer agitation time. The interaction of ultrasonic energy with the aqueous fly ash suspensions, alternately, influenced the processes of cation adsorption and desorption, leading to a change in the extracted amounts of cations as a function of sonication time. UAE was more efficient for Al, Pb and Mn. The concentrations of Cu and Fe ions were almost the same after both extraction procedures, so it was clear that ultrasound accelerated the reactions, while in the case of Cd ions UAE promoted release as well as extracted quantity. It could be concluded that there is no significant difference in the extracted quantities for most of analyzed ions between SAE and UAE, but the 15 min UAE is as efficient as six-hour SAE. The pH value, conductivity, average particle size and zeta potential changed in accordance with extraction times and measured concentrations of cations and anions.

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ИЗВОД

УЛТРАЗВУЧНА И МЕХАНИЧКА ЕКСТРАКЦИЈА У ВОДИ АНЈОНА И КАТЈОНА ИЗ ЛЕБДЕЋЕГ ПЕПЕЛА

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Представљене су технике екстракција анјона и катјона из лебдећег пепела помоћу дејонизоване воде. Извршено је испитивање расподеле величина честица, као и потврда хомогености узорака помоћу рендгенске флуоресцентне спектрометрије. Прва екстракциона процедура је изведена помоћу линеарне мућкалице у току 6, 12 и 24 h, а друга помоћу ултразвука у току 15, 30, 45 и 60 min. Концентрације анјона (сулфати, хлориди,

флуориди, фосфати, нитрати и нитрити) из водених екстраката одређиване су јонском хроматографијом, док су метали који су битни за животну средину (Al, Fe, Mn, Cd, Cr, As, Ni, Zn, Cu и Pb) у раствору одређивани применом атомске апсорпционе спектрометрије. Поређење класичне и ултразвучне екстракције показује већу ефикасност примене ултразвука за екстракцију анјона као и Pb, Al, Mn и Fe, док је за одређивање Cr, As, Ni и Zn класична екстракција ефикаснија. Промена рН вредности, величине колоидних честица, зета потенцијала и проводљивости су током ултразвучне екстракције мерене у циљу објашњења интеракције површине честица лебдећег пепела са водом и различитих процеса (адсорпције, јонске измене, флокулације) који се дешавају у природним условима. Анализа главних компоненти је коришћена за процену утицаја испитиваних параметара. Са аспекта утицаја на животну средину, од посебног значаја је квантитативна анализа испитиваних елемената који процесом испирања доспевају у природне воде.

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