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Comparison of sequential and single extraction in order to estimate the environmental impact of metals from fly ash

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Abstract: The aim of this paper is to simulate leaching of metals from fly ash in different environmental conditions using ultrasound and microwave-assisted extraction techniques. Single-agent extraction and sequential extraction procedures were used to determine the levels of different metals leaching. The concentration of metals (Al, Fe, Mn, Cd, Co, Cr, Ni, Pb, Cu, As and Be) in fly ash extracts were measured by inductively coupled plasma-atomic emission spectrometry. Single-agent extractions of metals were conducted at sonication times of 10, 20, 30, 40 and 50 min. Single-agent extraction with deionized water was also performed by exposing samples to microwave radiation at temperature of 50 °C. The sequential extraction was conducted according to the BCR procedure which was modified and applied to study the partitioning of metals in coal fly ash. The microwave-assisted sequential extraction was performed at different extraction temperatures: 50, 100 and 150 °C. The partitioning of metals between the individual fractions was investigated and discussed. The efficiency of the extraction process for each step was examined. In addition, the results of the microwave-assisted sequential extraction are compared to the results obtained by standard ASTM method. The mobility of most elements contained in the fly ash is markedly pH sensitive.

Keywords: coal fly ash; single-agent extraction; sequential extraction; micro-waves; ultrawaves.

INTRODUCTION

The residual material from coal combustion processes, collectively known as coal combustion residues (CCRs), is solid waste that includes bottom ash and fly

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ash. The coal ash is highly heterogeneous material composed of silicon dioxide, aluminum oxide and iron oxide among other materials.¹ In the process of coal combustion, the ash gets concentrated with various trace toxic elements such as As, Se, Cr, V, Ti and Pb.^{2,3} Studies on the partitioning behavior of the trace elements (As and Pb) during coal combustion have shown their enrichment in the ash particles. This is primarily due to the adsorption on iron oxides and the silicate matrix.⁴ The main quantity of coal ash is disposed in the soil and is used in the cement and concrete industry. Depending on the coal source, the coal ash can vary widely in respect of the pH value of its generated leachate and the trace element content, which generally exceeds this typically present in the soil.⁵ The risk, associated with the reuse of coal ash in natural environmental settings, in terms of their mobility and ecotoxicological significance, is largely determined by: the physicochemical conditions the ash is placed under, the total leachable metal content in the ash, and the distribution or mineralogical fractionation of metals.^{1,5}

In recent years, column-leaching systems, single or sequential chemical extraction techniques have been employed to determine the geochemical association of metals in coal ash and to provide a reasonable estimate of metal availability under environmentally relevant conditions.⁶⁻⁹ Microwave-assisted BCR and Tessier sequential extraction are significantly quicker than the conventional procedures. These methods provide comparable data quality in terms of precision and accuracy.¹⁰ The main advantages of inductively coupled plasma-atomic emission spectrometry (ICP-AES) are multi-element determination and high sample throughput with detection limits low enough for most ash samples.^{11,12} Another useful sample preparation method for solid samples is ultrasound-assisted digestion. The ultrasound-assisted digestion is safer than the microwave method, because as an ultrasound technique is conducted at substantially lower pressure and temperature.^{11,13,14}

There are several extraction procedures for solid samples reported in the literature. They are based on different sequence schemes and are carried out under various operating conditions.¹⁵⁻¹⁷ Sequential batch extraction process may simulate the leaching condition where the disposed fly ash will experience repetitive percolation of rain water and/or a low-pH acid mine drainage solution and the leachate will co-exist with fly ash for a considerable period of time. Repetitive extractions reveal the highest concentrations of each constituent that is likely to leach out into the natural environment.¹⁸ By using a column leaching system to simulate an exposure to water or acid mine drainage, it was found that the release of several metal ions was suppressed in an alkaline leachate until the leachate was turned to acidic one. The leaching of most cationic metals such as Pb, Cu and Ni is lower due to the alkaline nature of the ash.⁶ The potential for surface and ground water pollution through leaching of elements such as As, Zn, Pb and

Ni from coal fly ash was investigated at a pH ranging from 2.0 to 6.5. The principal mechanisms controlling the metal mobility are the dissolutions of primary solids in aggressive environments.¹⁹ The ecosystem appears to be an excellent filtering machine that retains contaminants such as metals in soil profiles. However, the borderless nature of the environment could result in the transfer of pollutants into groundwater and river systems, either in dissolved or particulate form. This may pose a serious threat to the aquatic organisms, while metal inputs in groundwater resources may entail a significant health hazard.²⁰

The objective of this research was to assess the leaching potential of coal fly ash in water environment and to study the mobility of metals by using two single extraction techniques, the ultrasonic bath and microwave-assisted digestion. The deionized water that was used as a soft extraction solvent had hydrolytic and dissolving effect on the coal ash constituents. The concentration of the investigated elements- Al, As, Fe, Mn, Be, Cd, Co, Cr, Ni, Pb and Cu was determined by using ICP-AES. In addition, the efficiency of microwave-assisted extraction on the elements leachability was investigated at three temperatures. Complementary to the primary goal of the study was a sequential extraction analysis, whose purpose was to investigate the availability of potentially toxic metals under different oxidation and pH conditions. This was particularly important in order to make conclusions about the behavior and solubility of the metals. The partitioning of the metals was investigated using microwave sequential extraction procedure. The BCR extraction protocol (Standards, Measurements and Testing Programme of the European Commission, BCR procedure) was modified by adding a third extraction step, according to the Förstner extraction scheme.²¹

EXPERIMENTAL

Samples

Twenty individual samples were obtained from the „Kostolac” power plant, which is located approximately 90 km east of Belgrade, Republic of Serbia. All individual samples were combined and the bigger lumps were milled in a grinder to obtain a fraction of < 1 mm. Then, the samples were well homogenized, 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. Each sample was oven-dried at 105 °C overnight prior to use.

Deionized water from a Milli-Q system (Millipore, USA) was used for the extraction and preparation of all the solutions. The resistivity of the deionized water used was 18.2 MΩ cm at 25 °C. All reagents were of analytical grade. The glassware and plastic containers were cleaned in 10 % HNO₃ in an ultrasonic bath and then were rinsed with deionized water.

The total metal content was determined after acid extraction of metals employing ASTM standard method (acid digestion was done in 5 cm³ of HCl and HF (70:30) mixed acid solution and 2 cm³ of HNO₃).²²

Instrumentation

The type of ultrasonic bath used was Transsonic T 760 DH (Elma, Germany) with an ultrasonic frequency of 40 kHz and an effective ultrasound power of 170 W. The type of microwave digestion system used for fly ash sample preparation was ETHOS 1, advanced microwave digestion system (Milestone, Italy), equipped with 10 PTFE containers. The capacity of the containers was 100 cm³ each, and the maximum pressure and temperature that could be achieved were 10 MPa and 240 °C, respectively.

The ICP-AES measurements were performed using a Thermo Scientific iCAP-6500 DUO ICP spectrometer (Thermo Fisher Scientific, UK), with continuous wavelength coverage ranging from 166 to 847 nm, equipped with a RACID86 charge injector device (CID) detector, a pneumatic cross-flow type nebulizer, a quartz torch and a quartz detector. The instrumental conditions were set to input power of 1150 W and an auxiliary gas flow of 0.5 dm³ min⁻¹, while a coolant gas flow and a nebulizer flow were set to 12 and 0.5 dm³ min⁻¹, respectively. All the concentration measurements were carried out using a five-point calibration. For preparation of the diluted working solutions used in the ICP-AES calibration, a multi-element plasma standard solution 4 (Specpure, Alfa Aesar, Germany) was used. The analytes were determined at the following wavelengths (nm): Al, 308.2; As, 193.7; Be, 234.8; Cd, 226.5; Co, 228.6; Cr, 267.7; Cu, 324.7; Fe, 240.4; Hg, 253.6; Mn, 259.3; Ni, 231.6; Sb, 217.6; Se, 206.3 and Pb, 220.3. The detection limit for Al and Fe was 25 µg dm⁻³, for Cu and Pb 20 µg dm⁻³, for As and Hg 10 µg dm⁻³, for Sb 5 µg dm⁻³ and for Be, Cd, Co, Cr, Mn, Ni and Se 2 µg dm⁻³. The reproducibility of the measurements was about ±8 %.

A 3540 conductivity/pH-meter (Jenway, UK) was used to measure the pH value and the conductivity of the extracts.

Extraction procedure

The first technique involved the use of an ultrasonic bath (ultrasonic-assisted extraction, UAE), with the mixture positioned each time at the same place in the bath and at same initial water temperature of 17 °C. Five extractions were conducted for each of the following extraction times: 10, 20, 30, 40 and 50 min, using a 20 mL:2 g liquid-to-solid ratio. The samples were filtered and the pH value and conductivity of the liquid phase were measured.

The second technique involved the use of a microwave digestion system (microwave-assisted extraction, MAE). The microwave-assisted digestion, using deionized water at temperature of 50 °C, was carried out at a 50 mL:5 g liquid-to-solid ratio. Five samples were simultaneously analyzed to determine the precision of the measurements. Also, five extractions were performed at each of the following temperatures: 50, 100, and 150 °C, for all steps of the microwave sequential extraction procedure. The set temperature was reached in 15 min for each extraction cycle, while the extraction itself lasted 15 min. Subsequently, the samples were cooled to room temperature. Between each stage, the residues were washed with 20 cm³ of deionized water.

The sequential extraction procedure, based on Standards, Measurements and Testing Programme of the European Commission (BCR procedure), is presented in details in our previous paper.²³ The following metal fractions were investigated: water-exchangeable and weakly adsorbed forms (phase I, extracted by acetic acid) easily reducible forms associated with Mn oxyhydroxides (phase II, extracted with NH₂OH·HCl at pH 2.0); moderately reducible forms associated with Fe and Al oxyhydroxides (phase III, extracted by oxalate/oxalic mixture); oxidizable forms associated with organic matter or sulfides (phase IV, extracted by H₂O₂/HNO₃ mixture); while *aqua regia* was used for the residual fraction (phase V).

At the end of each of the extraction procedures, the extract was centrifuged and the resulting supernatant was filtered and stored for metal analysis. A centrifuge was used to separate the solid phase from the extraction liquid. All extracts were decanted, filtered by using 0.45- μm nylon filters (Phenomenex, USA) and, if needed, acidified to pH 2.0. A blank extraction was performed for each of the employed extraction techniques.

RESULTS AND DISCUSSION

The main goal of the sequential extraction procedures is to characterize the distribution of metals within the discrete extraction phases that should be independently dissolved. All sequential extraction techniques have in common three essential stages: speciation of metals extracted in neutral environments, speciation of metals extracted in a reducible acidic environment, and speciation of metals extracted in an oxidizing acidic environment. Sometimes, the last two stages could be performed in several steps. In this research, a modified BCR procedure was applied with a microwave digestion for each of the extraction stages. The extraction steps from phases I to IV represent simple leaching (phase I) and degradation processes under acidic reducible (phases II and III) or oxidative (phase IV) conditions. Step V is exceptional since it is highly aggressive and not easily comparable to natural and urban environments. Any other more aggressive chemical treatment of coal ash that can further influence or degrade the ash samples is not characteristic of the natural environments and therefore not appropriate for our investigations. The effect of temperature on the sequential microwave-assisted digestion was investigated at 50, 100, and 150 °C. The results of microwave-assisted digestion of Fe, Al and Mn as a function of the temperature are shown in Fig. 1.

The Fe and Al concentrations in fraction I (weakly adsorbed) were below 250 and 1000 mg g^{-1} , respectively regardless of the extraction temperature. Under acidic conditions, higher amounts of Fe and Al were extracted, but the highest amount of Fe was extracted in phase III during which a significant rise in the concentration of the extracted Al was observed. This means that forms of Fe and Al oxyhydroxides are dissolved in the oxalic acid/oxalate extracting agent, and the presented results showed that the used extractant was more efficient for Fe than for Al. The presence of Fe in the second extraction phase was indicative of amorphous, highly mobile hydroxides of the element. The extraction of the amorphous and crystalline oxides occurred during phase III. The concentrations of Fe and Al in fraction IV are smaller than the one in the previous phase since this phase is related to oxidizable forms of organic matter and sulfides. The amount of Fe in the residual fraction was almost two times smaller than the amount of Fe in phase III, while this fraction had the highest Al content in comparison to any of the previously extracted fraction. If the amount of the metals in the individual fractions is expressed as a percent relative to the total extracted amount (Table S-I of the Supplementary material to this paper), it can be seen that the percent of

the extracted Al decreased when the temperature changed from 100 to 150 °C for phases I–III and V, while in phase IV this percent decreased continually. The data from the microwave sequential procedure (Table S-I) indicated that the iron appeared to be fractionated predominantly in moderately reducible and residual phases (more than 80 %). The Fe-rich coal ash particles are believed to be a result of magnetite (Fe_3O_4) formation from iron bearing minerals present in the coal during combustion.²⁴

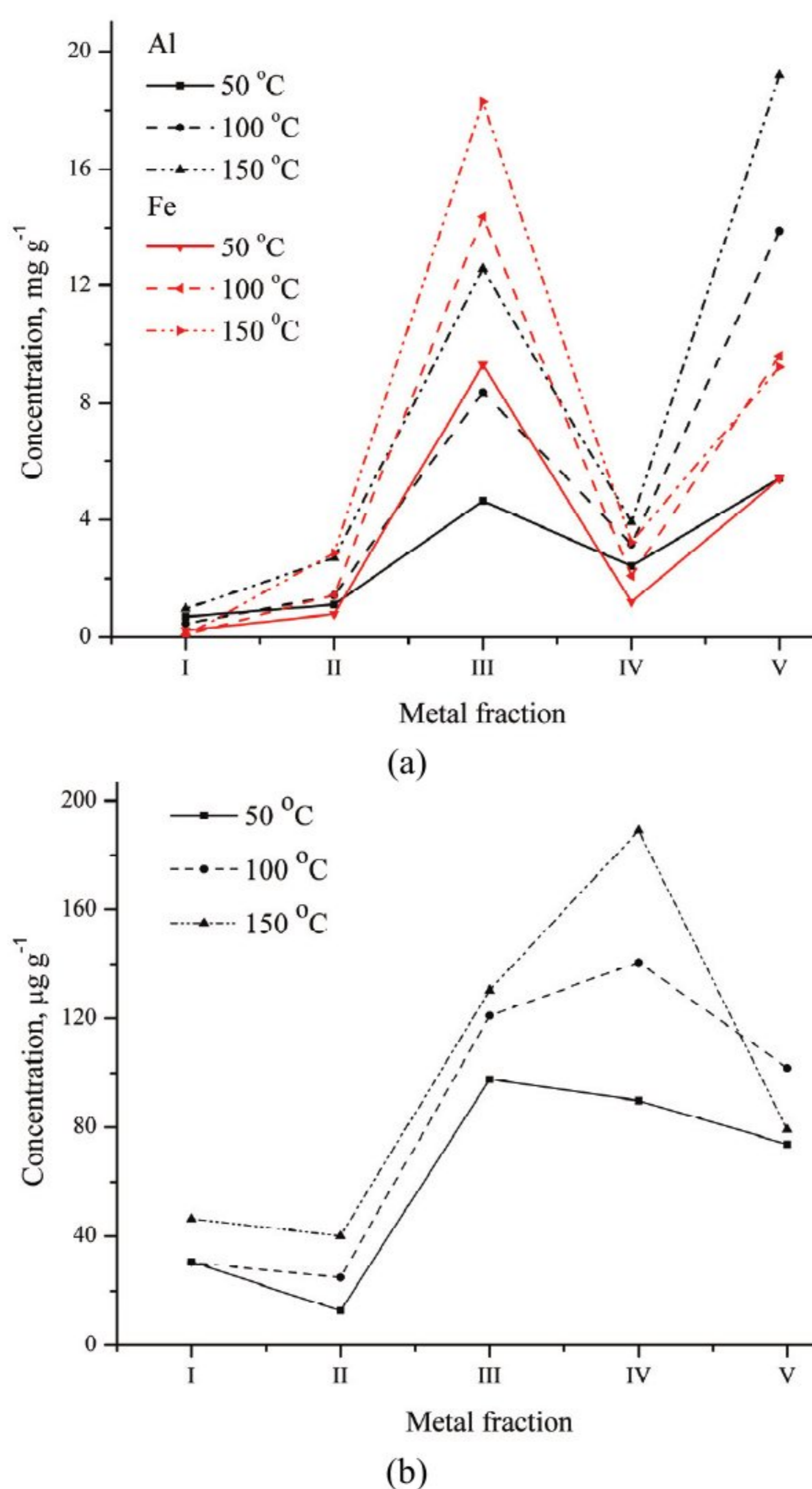


Fig. 1. Distribution of Fe and Al (a) and Mn (b) obtained by sequential MAE at different temperatures.

The extraction and distribution of Mn by MAE as a function of the temperature is shown in Fig. 1b. The manganese is more soluble under slightly acidic (phase I) than under acid conditions (phase II), and contrary to the Fe and Al, the

Mn oxyhydroxide forms, as bearing minerals, were not significantly dissolved in phase II. At 50 °C the highest amount of Mn was extracted in phase III, and comparable amounts were extracted in phases IV and V. With temperature increase of MAE, the concentration of Mn increased in phase III and in phase IV. The influence of the temperature increase on the MAE efficiency is particularly evident for the extraction of oxidizable forms of Mn. In comparison to Fe and Al, the amount of Mn in the residual phase was lower than the one in the previous two phases.

The results of microwave-assisted sequential extraction of Cd, Cr, Co and Ni are presented on Fig. 2a–d.

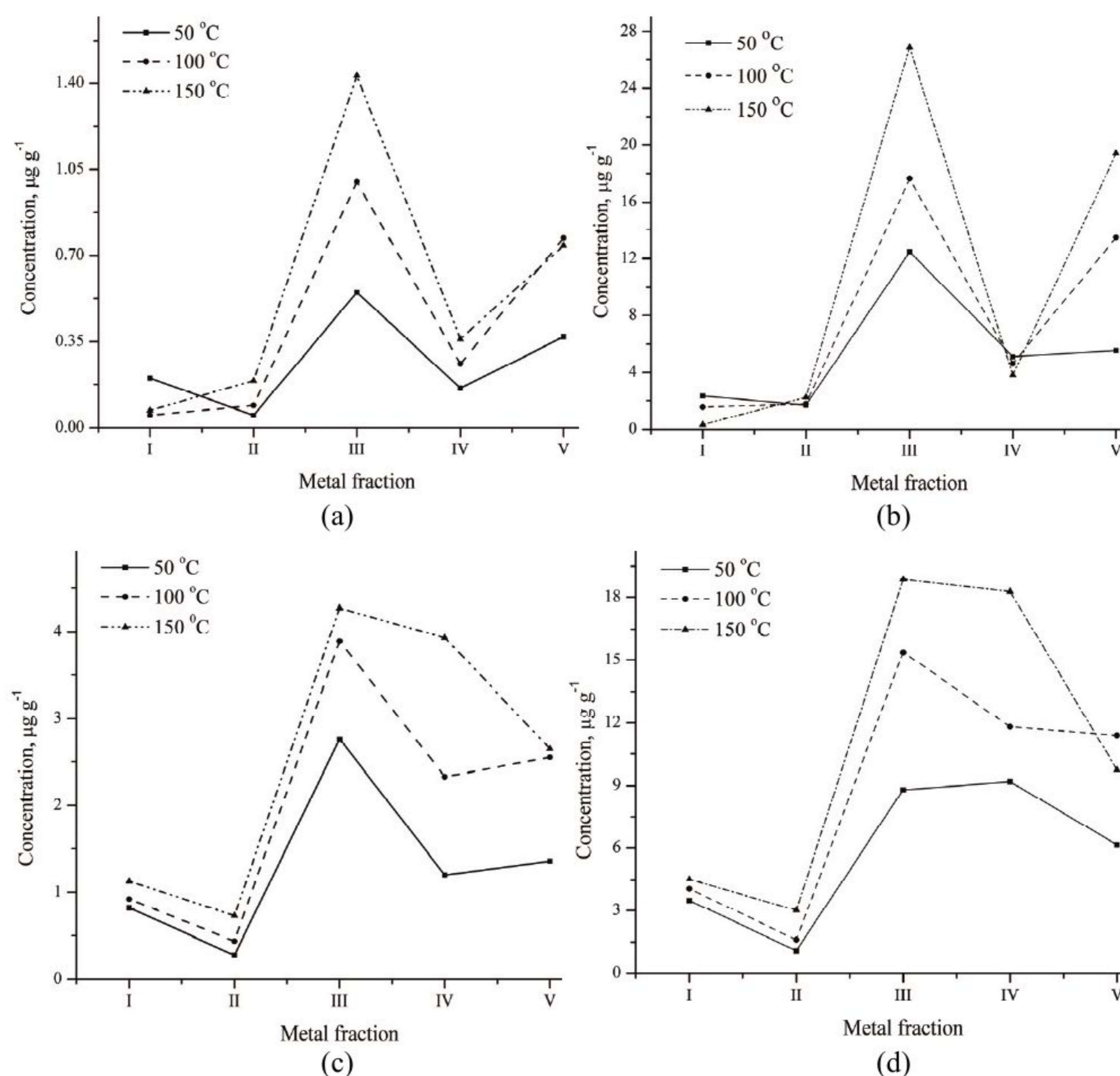


Fig. 2. Distribution of Cd (a), Cr (b), Co (c) and Ni (d) obtained by sequential MAE at different temperatures.

From Fig. 2a–d some similarities between investigated trace elements can be observed. An uniform extraction trend for Cd and Cr for all phases of the sequential extraction was evident. With increase of the temperature, the concentration of Cd and Cr, weakly adsorbed forms fractionated in phase I, decreased. The amount of these two elements extracted in phase II at 50 °C was smaller than the amount extracted in phase I. The efficiency of the Cd extraction, increased with temperature increase during the sequential extraction of forms associated with Fe and Al oxyhydroxides. A primary association with Fe- and Al-bearing species could explain why the Cd was poorly leached under acidic and slightly acidic conditions. The environmental concerns over Cd arise from its potential solubility and toxicity in aquatic systems. This environmentally sensitive element is consistently immobile under near neutral and alkaline conditions. Of particular importance is the effect of Cl on the leaching pattern of Cd. High chloride content may shift the Cd solubility to higher pH values as a result of complexation processes that enhance the mobility.²⁰ The extraction efficiency for moderately reducible Cr forms at 100 and 150 °C was comparable, but increase in temperature influences Cr extraction in residual phase greatly. Chromium in its hexavalent oxidation state, which includes both chromates or dichromates, is widely recognized as potentially carcinogenic and highly soluble in aqueous media, whereas Cr(III) is less soluble and much less hazardous to human health. The presence of oxygen-rich organic matter in the coal may lead to a higher percentage of chromates being formed during combustion. The organic bonds enhance Cr volatilization during combustion, oxidation and precipitation of soluble chromates of coal ash. According to our results, Cr was dominantly leachable only under non-environmental conditions, *i.e.*, very low pH values and reducing conditions. This led to the conclusion that a dominant association with clay minerals in the coal resulted in a primary aluminosilicate association of Cr in the analyzed fly ash.^{20,25}

The concentration change of Co and Ni, extracted in five investigated phases, is shown in Fig. 2c and d, respectively. The amount of these elements in phase II was smaller than the amount presented as weakly adsorbed (phase I). Under acidic condition, the same used for step II of the applied sequential extraction, a precipitation of secondary solids could occur. A rise in the concentration of the extracted Co and Ni occurred in phase III, which means that these elements were mostly associated with Al and Fe oxyhydroxides. This is in accordance with the assumption that the mode of occurrence of Co and Ni, along with Mn in the ash is more dependent on the similarities in the ionic radii than on the chalcophilic or lithophilic nature of the elements. Such similarities would favor their crystallization from the melt into Fe oxides.²⁶ A primary association with Fe-bearing species could explain the fact that Co and Ni were poorly leached under slightly acidic and acidic conditions in relation to the total content (less

than 12 %, Table S-I). Similar trend of the Co distribution in the investigated metal fraction was observed at 50 and 100 °C, while for the Ni the same trend was observed at 50 and 150 °C. The results from the extraction at 50 and 150 °C showed that the nickel was distributed almost evenly between the moderately reducible and oxidizable fraction, due not only to the association with Fe-bearing species, but to the presences of organically associated Ni.²⁷

The results from the sequential extraction of Pb and Cu are presented in Fig. 3. These elements showed an almost regular increase of the extracted amount from fraction I to V. Less than 4 % of the Pb was extracted in fraction I (Table S-I). The extraction of Pb was pronounced under acidic condition, but it was still relatively low since the Pb in the fly ash is dominantly associated with sulfides and silicate.^{28,29} About 6 % of the total extracted Cu was leached at all investigated temperatures in phase I, which is in accordance with the results reported by other authors.³⁰ With temperature increase, the concentration of the extracted Cu, related to the total extracted amount, increased in phases II and V and decreased in phases III and IV (Table S-I). The copper was therefore assimilated within the glass and was not easily released. In contrast, the oxidation of Cu and Fe sulfides in coal leads to a higher mobility of Cu in coal ash.²⁰

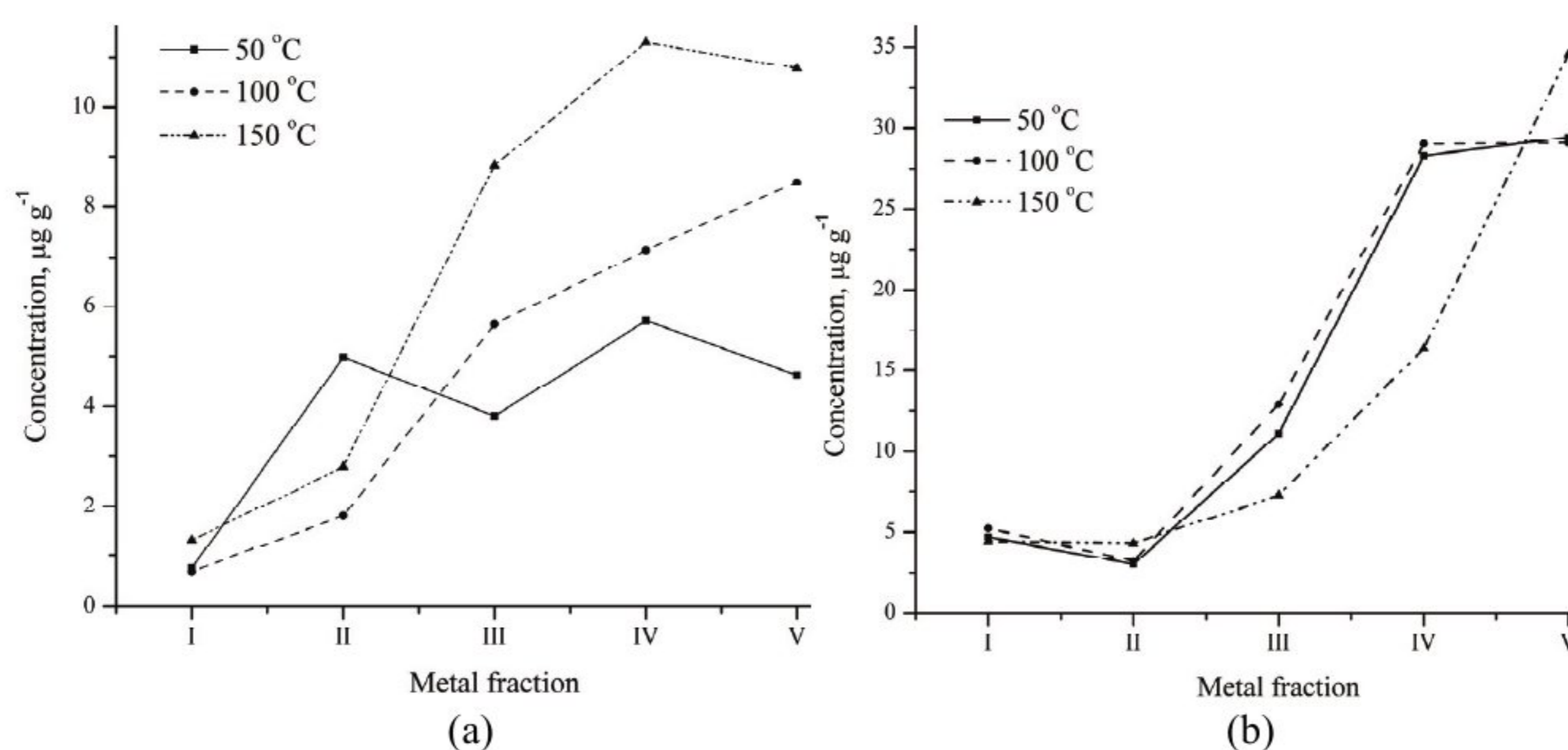


Fig. 3. Distribution of Pb (a) and Cu (b) obtained by sequential MAE at different temperatures.

The results of As and Be determination by sequential extraction are listed in Table I. Analysis of the extraction efficiency as a function of the temperature showed that the lowest investigated temperature was the most efficient for extraction of As from phases I and II. The highest extracted amount for all investigated temperatures was in fraction III, suggesting that the As present in the analyzed sample was mostly associated with iron. This is in accordance with the literature data showing that the As is usually associated with pyrite present in the

coal.³¹ Arsenic is one of the key elements whose excessive concentration in the coal ash may impose restrictions on its use and disposal. An increase in the temperature of the sequential extraction did not lead to an increase in the quantity of the extracted arsenic. On the other hand, arsenic was almost not present in fraction V due to its volatility. The results of Be sequential extraction indicated that most of the Be was associated with Fe and Al oxyhydroxides (phase III) and aluminosilicates (phase V). The concentration of Be in all analyzed fraction increased with increase of the extraction temperature.

TABLE I. Average concentration ($\mu\text{g g}^{-1}$) of As and Be in coal fly ash obtained by sequential microwave digestion at 50, 100 and 150 °C ($n = 5$, uncertainty as standard deviation); n.d. – not detected

| Element | $t / ^\circ\text{C}$ | Phase I | Phase II | Phase III | Phase IV | Phase V | Total |
|---------|----------------------|-----------|-----------|-----------|-----------|-----------|-------|
| As | 50 | 8.14±0.40 | 5.24±0.12 | 32.7±0.60 | n.d. | 0.72±0.30 | 46.8 |
| | 100 | 1.22±0.06 | 4.89±0.20 | 35.7±1.78 | n.d. | n.d. | 41.8 |
| | 150 | 2.66±0.12 | 4.92±0.22 | 35.7±1.97 | 0.25±0.01 | n.d. | 43.5 |
| Be | 50 | 0.11±0.01 | 0.10±0.01 | 0.37±0.01 | 0.12±0.01 | 0.19±0.02 | 0.89 |
| | 100 | 0.08±0.01 | 0.15±0.01 | 0.55±0.02 | 0.17±0.01 | 0.45±0.02 | 1.40 |
| | 150 | 0.14±0.01 | 0.26±0.01 | 0.68±0.03 | 0.14±0.01 | 0.53±0.01 | 1.73 |

The results from Table S-I revealed that for most of the investigated elements, about 10 % of the amount was extracted in the first two phases. Larger amounts were extracted in the last three phases, meaning that the solubility of all elements increased as the extracting solution pH decreased. Fe and Mn oxides are excellent scavengers of trace metals.³¹ Under reducing conditions the quantities of the extracted elements were two to six times higher than those obtained in phases I and II, with arsenic showing the highest increase in its extracted quantity in phase III. These results also indicated that the majority of the metals were distributed in fractions (moderately reducible and residual) which would be unavailable for leaching. The leaching of components is believed to involve both diffusion and dissolution processes, with the efficiency of the solvent extraction process being dependent on a number of factors, including the chemical forms and physical distribution of the components.³² When the first four fractions are removed, the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in the solution over a reasonable time under the conditions normally encountered in nature.¹⁶ The fraction soluble in the phase V of the sequential extraction is the major carrier of all elements present in the ash with exception of the As, binding more than 25 % of the mentioned extracted elements. The concentrations of Ni, Cd and Cr dissolved in the phase III correlate highly with the concentrations of Al and Fe, therefore pointing to the association between these metals with Al and Fe oxyhydroxides. Copper, nickel and lead

were also hardly extracted from the coal ashes (65–90 %, in phases III–V). This indicated that these elements were concentrated in the indissoluble aluminosilicate matrix. Regarding the extraction of all investigated metals, it was observed that an increase in the temperature of the sequential extraction, in particular to 150 °C, led to an increase of their distribution in phases I–III when compared with the one at 50 °C, but still with a considerable presence in phases IV and V (Table S-I).

The data above suggest that the metal release from coal ash is mostly influenced by: 1) extraction techniques, 2) chemical extraction methods and 3) temperature at which microwave-assisted digestion is conducted. Since the metals are mostly associated with Fe-oxides and residual silicate material, minimal metal leaching could be expected under natural conditions (deionized water and weakly adsorbed fractions). Considering the microwave technique, there was a positive correlation between the extracted concentration of metals and the temperature, as expected. The microwave technology provides an opportunity for reducing the extraction times and offers an attractive alternative to the conventional procedures. During the microwave heating of a solution containing ions, the dissipation is initially controlled by dipole rotation and later, as temperature increases, by ionic conduction, which depends largely on the way in which microwaves are delivered to the sample.¹²

The total amount of extracted elements obtained through sequential microwave-assisted extraction at different temperatures was compared to the amount of the elements extracted by using the standard ASTM method.²² The metal concentration determined by standard method are given in the Table II, along with the total metal concentration obtained by sequential extraction expressed as a recovery. The recovery was calculated as a ratio of the total concentration obtained by sequential extraction and the concentration determined by standard method. The content of Al and Fe determined by standard method was 158±5 and 108±3 mg g⁻¹, respectively. The recovery for Al at 50, 100 and 150 °C was 9.04, 17.32 and 24.95, respectively. The recovery for Fe at 50, 100 and 150 °C was 15.62, 25.50 and 31.10, respectively. The concentrations of As, Be, Co and Cr were below the detection limit and were not detected by the standard method.

TABLE II. Comparison of sequential MAE at different temperatures with total metal content obtained by standard ASTM method ($n = 3$, uncertainty as standard deviation)

| Element | Standard metod, $\mu\text{g g}^{-1}$ | Recovery, % | | |
|---------|--------------------------------------|-------------|--------|--------|
| | | 50 °C | 100 °C | 150 °C |
| Mn | 938±45 | 32.47 | 44.63 | 51.72 |
| Cr | 164±3 | 16.90 | 23.84 | 32.10 |
| Ni | 131±3 | 21.90 | 33.77 | 41.52 |
| Pb | 78±8 | 25.51 | 30.46 | 44.89 |
| Cu | 250±5 | 30.62 | 31.79 | 26.80 |

The results listed in Table II showed that the degree of correlation between the standard method and the applied sequential procedure increased with increase of the temperature at which the extraction was conducted. In general, less than 50 % of the total content was determined by sequential extraction. Since most of the analyzed elements were associated in aluminosilicate matrix, the divergence is due to the lack of concentrated HF, which is proven reagent for silica decomposition, in the investigated sequential method.

In order to replicate and simulate the conditions of the environment and to represent the leaching of elements from coal ash into the environment as accurately as possible, the extraction was performed with deionized water by using an ultrasonic bath and microwave-assisted digestion at 50 °C. The leachability of the elements in water was determined in order to estimate the amounts of water-soluble species that may be easily released to the environment. The concentrations of the soluble elements are shown in Table III.

TABLE III. The contents ($\mu\text{g g}^{-1}$) of metals obtained by means of ultrasonic and microwave-assisted extraction at 50 °C with water ($n = 5$, uncertainty as standard deviation); n.d. – not detected

| Element | Ultrasonic extraction, min | | | | | Microwave-assisted extraction |
|---------|----------------------------|-----------|-----------|-----------|-----------|-------------------------------|
| | 10 | 20 | 30 | 40 | 50 | |
| Al | 164±8 | 153±8 | 85.6±7.0 | 86.6±7.8 | 78.4±7.0 | 222±9 |
| Fe | 0.86±0.30 | 0.84±0.31 | 0.82±0.30 | 0.86±0.32 | 1.00±0.30 | 3.42±0.14 |
| Mn | 0.02±0.01 | 0.01±0.01 | 0.01±0.01 | 0.01±0.01 | 0.02±0.01 | 0.04±0.01 |
| As | 0.37±0.10 | 0.35±0.10 | 0.42±0.08 | 0.51±0.08 | 0.57±0.09 | 1.44 ±0.07 |
| Cd | n.d. | n.d. | n.d. | n.d. | 0.15±0.03 | 0.01±0.01 |
| Cr | 0.40±0.01 | 0.34±0.07 | 0.64±0.10 | 0.64±0.11 | 0.65±0.05 | 0.55±0.04 |
| Ni | n.d. | n.d. | n.d. | 0.02±0.01 | n.d. | 0.02±0.01 |
| Pb | 0.05±0.02 | 0.08±0.02 | 0.12±0.02 | 0.47±0.05 | 0.09±0.02 | 0.45±0.03 |
| Cu | n.d. | n.d. | n.d. | n.d. | 0.15±0.02 | 0.39±0.03 |

The results from the ultrasound extraction listed in Table III showed that the concentration of some of the metals varied a lot with the extension of the extraction time, although some of the metals showed a similar behavior during the extraction process. The concentration of Al showed steady decline, while the concentrations of Fe and Mn were almost constant during the ultrasound-assisted extraction. With the extension of the extraction time, the concentration of As constantly increased, while the concentrations of Cr and Pb reached maximum values after 30 and 40 min, respectively. In the extracted suspension Ni was detected after 40 min., while Cd and Cu were detected after 50 min. The single microwave-assisted extraction was more efficient for Al, Fe, As and Cu. Both applied techniques were equally efficient for Cr and Pb, while for Cd the ultrasound extraction was more efficient. The quantities of Be, and Co obtained by ultrasonic bath and single microwave extraction of fly ash in deionized water

were below the detection limit. The mineral fraction in coal undergoes different transformations during and after combustion, namely decomposition, volatilization, fusion, agglomeration or condensation. As flue gas cools down after combustion, some elements condense on the surface of the coal ash particles, while others remain in their core, forming compounds with a variable solubility. The elements enriched in the cores of the coal ash particles are not directly exposed to leaching and therefore their releases are diffusion-controlled and also dependent on the dissolution rates of the surface layers. Surface-associated elements are therefore more susceptible to leaching in an aqueous environment.²⁰

The pH value and conductivity were measured after ultrasound extraction, and the results are presented in Fig. 4. The pH value of the leach extracts for fly ash samples was found to be alkaline and did not significantly change with extension of the extraction time. The conductivity and pH value in leach changed in the same manner until extraction time of 30 min was reached. After this extraction time, they started to change in opposite directions.

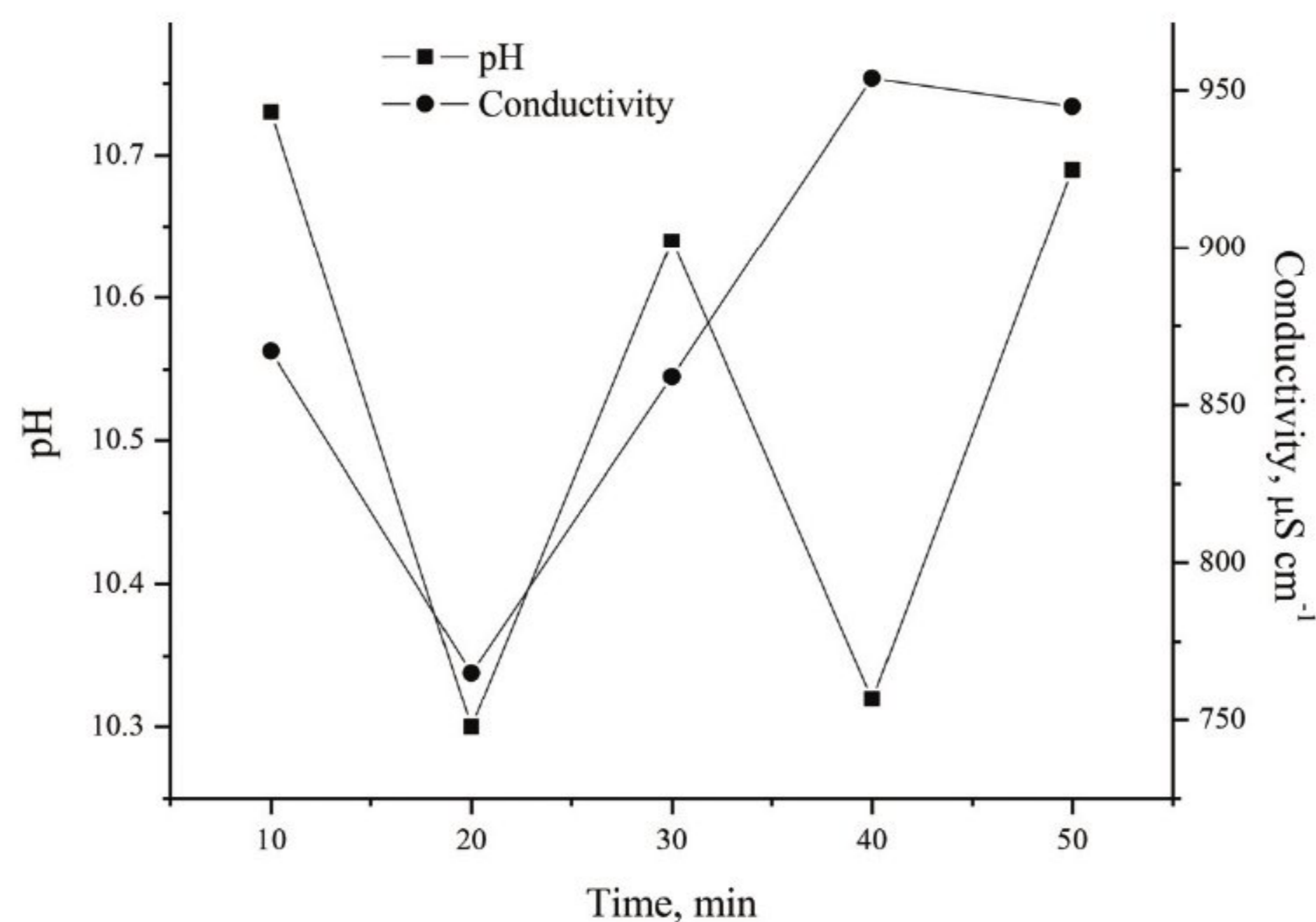


Fig. 4. The change of pH value and conductivity in leach as function of ultrasound extraction time.

When coal ash interacts with water, the principal processes affecting the leaching process are the dissolution of primary solids and precipitation of secondary solids as well as redox conditions, sorption and hydrolysis reactions. The metal mobility is controlled by the dissolution of primary solids and the precipitation/sorption reaction. The soluble salt content in ashes is closely related to the coal properties and the age of the coal ash as well as to the pH and other environmental conditions.³³ The results from the single extraction suggested that Al and Fe are less likely to be released under alkaline pH conditions, due to their dis-

tribution among the less soluble residual silicate and sparingly or acid soluble oxide fractions. Be, Co, Ni, Cd and Mn were insoluble due to the alkaline nature of the ash. Cr, As, Pb and Cu exhibited substantial solubility in deionized water after being exposed to the effect of microwaves and ultrasound. The high sulphate concentrations along with the alkaline pH suppressed the adsorption process of Cr. The arsenic mobilization was due to desorption under high pH condition or dissolution of sparingly soluble arsenate species condensed on the surface of coal ash particles. The leaching of Cu and Pb could be best explained by their surface complexation to Fe and Al oxide (hydroxide) or silicate material. Beyond pH 5, the Cu is likely to be either adsorbed on Fe-oxide or to co-precipitate as hydroxides thus resulting in decreased extract concentrations. Being an amphoteric metal, the solubility of Pb is lowest at around pH 9.²⁰

CONCLUSIONS

The goal of this work was to investigate the availability of metals (Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb) under different oxidation and pH conditions generated within different sequential extraction stages. The characteristics of these stages are recognized as the ultimate possible environmental conditions that may occur in urban surroundings. All of the investigated metals actually became already mobile/available during phases II and III of the microwave sequential extraction with a corresponding pH value ranging from 3 to 5, indicating that whenever an acid rain (pH < 5) precipitates, these elements become mobilized. The proposed modified BCR microwave-assisted procedure significantly reduced the time required for the conventional sequential extraction. The microwave-assisted procedure showed good performance for fly ash analysis in each of the extraction steps, safety and high throughput, which is important for routine analysis. It can be concluded that the extracted amount of each of the analyzed metals by using the sequential microwave-assisted procedure correlated positively with the increase of the extraction temperature.

Also, two different extraction techniques were employed to extract the elements from fly ash using water as an extractant. The ultrasonic extraction was less efficient than the procedures conducted using microwave-assisted techniques. In assays using microwave at constant power, extraction efficiencies were different for the different elements and the standard deviations were higher than those for the extraction using an ultrasonic bath.

Considering the ultrasonic technique, the extracted amount of metals varied with the extraction time. This could be explained with the effect of the ultrasonic energy on the fly ash particles in the suspension, which alternately, is influencing the processes of ion adsorption and desorption.

SUPPLEMENTARY MATERIAL

Participation of metals fraction in total metal content for sequential microwave extraction is available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

УПОРЕЂИВАЊЕ СЕКВЕНЦИЈАЛНЕ И ЈЕДНОСТРУКЕ ЕКСТРАКЦИЈЕ МЕТАЛА ИЗ ЛЕБДЕЋЕГ ПЕПЕЛА У ЦИЉУ УТВРЂИВАЊА УТИЦАЈА НА ЖИВОТНУ СРЕДИНУ

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Циљ овог рада је симулација испирања метала из лебдећег пепела при различитим условима, коришћењем ултразвучне и микроталасне екстракције. Једноструке и секвенцијалне процедуре су коришћене у сврху испитивања ефикасности испирања елемената. Концентрације испитиваних метала (Al, Fe, Mn, Cd, Co, Cr, Ni, Pb, Cu, As и Be) у раствору одређиване су применом атомске емисионе спектрометрије са индуктивно спрегнутом плазмом. Екстракција метала из узорка пепела помоћу једног агенса изведена је коришћењем ултразвука у трајању од 10, 20, 30, 40 и 50 min. Једнострука екстракција помоћу дејонизоване воде изведена је и при дејству микроталасног зрачења на температури од 50 °C. Секвенцијална екстракција је спроведена у складу са BCR процедуром, која је модификована и примењена на проучавање заступљености и расподеле метала у пепелу. Микроталасна секвенцијална екстракција је вршена на температурама од 50, 100 и 150 °C. Испитана је и дискутована заступљеност метала у појединачним фракцијама, као и ефикасност процеса екстракције за сваки појединачни корак. Такође, резултати добијени секвенцијалном микроталасном екстракцијом су упоређени са онима добијеним применом ASTM стандардне методе. Мобилност већине елемената садржаних у пепелу зависи у великој мери од рН вредности.

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