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Leaching of heavy metals from wood biomass ash, before and after binding in cement composite

DIJANA M. DRLJAČA[1]*, LJILJANA M. VUKIĆ[1], DAJANA M. DRAGIĆ[1], ALEKSANDRA P. BORKOVIĆ[1], TATJANA T. BOTIĆ[1], PERO T. DUGIĆ[1], SAŠA V. PAPUGA[1], MARKO D. ŠOLIĆ[2#], SNEŽANA P. MALETIĆ[2#], PETAR M. GVERO[3] and JELENA R. SAVKOVIĆ[1]

[1]*Faculty of Technology, University of Banja Luka, V. S. Stepanovića 73, Banja Luka, Bosnia and Herzegovina,* [2]*Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, Novi Sad, Serbia and* [3]*Faculty of Mechanical Engineering, V. S. Stepanovića 71, Banja Luka, Bosnia and Herzegovina*

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Abstract: Wood ash is a complex mixture of inorganic and organic compounds. It is heterogeneous in composition, which can vary considerably. Ash is mainly disposed of in landfills, which creates a risk for air, soil and groundwater contamination by trace elements. In order for wood biomass ash to be used as a secondary raw material, it is necessary to perform leaching tests, to determine which microelements it contains, and which of them could be released into the environment during the ash disposal. Sequential extraction (SE) showed that in the exchangeable and carbonate fraction, the most volatile metals As, Cd, Zn and Pb are released the most from the ash of deciduous trees, while the leaching of ash from coniferous trees is significantly lower. The evaluation of risk assessment code (RAC) for the tested biomass ash samples, indicates that Pb is a high-risk leaching element due to its condensation on the ash particles. By performing toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) tests, it was established that the released concentrations of tested metals are below the maximum allowable concentration, given by the regulation. The leaching tests of composites, prepared from wood ash in combination with cement, indicate that the leaching of ash is reduced to a minimum, and that all heavy metals are bound in a cement matrix, which indicates the possibility of using wood ash for construction purposes.

Keywords: biomass ash; sequential extraction; TCLP test, SPLP test, tank test.

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* Corresponding author. E-mail: dijana.drljaca@tf.unibl.org
\# Serbian Chemical Society member.

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INTRODUCTION

The most commonly used form of biomass for the production of thermal energy is wood biomass. Ash from wood biomass is a non-combustible, solid residue that is formed after complete combustion, and contains most of the mineral fractions derived from biomass. Wood ash is a complex mixture of inorganic and organic composition, consisting of a large number of compounds. In addition to the macronutrients P, K, Ca and Mg, necessary for plants, wood ash also contains microelements. Nutrients such as Cu, Zn, Mn, Fe and Ni are essential substances for plants. However, their excessive amounts (especially Cu, Zn and Ni) can have toxic effects.[1] Currently, 70 % of the produced wood biomass ash is disposed of, 20 % is used as a supplement for agricultural land, and 10 % is used for other purposes.[2]

For ash, which is generated by burning wood biomass, to be safely deposited it is necessary to perform leaching tests in order to determine which microelements it contains, and which of them could be released into the environment during the disposal. Numerous studies regarding this subject have been performed.[3–5]

Sequential extraction procedure was used to examine wood ash from thermal power plants in Croatia, and it was found that leaching of Ni and As can have a significant environmental impact.[3] Tessier's sequential extraction on wood ash from Poland, found high mobility of Co (28.44 %), Cr (20.49 %) and Pb (16.51 %), which poses a risk for environmental pollution during disposal.[4] An international study, involving researchers from Finland, Japan and Sweden, points out that heavy metals, present in wood ash, give rise to a very high risk for the environment contamination. High-risk metals in the ash from the bottom of the furnace are Cd, and in fly ash Cd and Se.[5]

It is believed that the disposal of fly ash will soon be too expensive, and possibly completely banned. Today, the intensive research is carried out on the chemical and mineralogical composition of ash from biomass of various origins. In accordance with that, biomass ash can be classified, and recommendation for its use as secondary raw material can be made on the basis of this classification[6]. The use of wood biomass ash in construction is an environmentally motivated choice, with the aim of reducing disposal costs, but also the preservation of natural resources and reducing greenhouse gas emissions.[2]

In order to consider the impact of biomass ash on environmental media in the case of its disposal or use as a raw material in construction, it is necessary to further investigate the potential migration of heavy metals from wood ash, conducting standard leaching tests. Given that there are very few papers in this region dealing with the issue of leaching of wood biomass ash, as well as leaching from cement composites, this paper represents pioneering research in the mentioned area in our region.

EXPERIMENTAL

Materials

In order to obtain comprehensive and relevant results, the research was carried out on two types of ash, which came from two different sources of wood biomass:

1. The ash generated by the combustion of different types of hardwood (spruce and fir) – source: a heating plant, Toplana AD, Prijedor, Bosnia and Hertzegovina.
2. The ash generated by the combustion of wood bark – source: ENSA BH d.o.o., Srbac, Bosnia and Hertzegovina (biomass processing factory, pellet and briquette production).

Samples of biomass ash from heating plant in Prijedor were collected from two sampling sites: electrostatic precipitators – fly ash (Pd-FA) and boiler ash – bottom ash (Pd-BA).

Samples of ash from biomass processing factory ENSA BH differed according to the type of wood, of which ash was created: E_1 (fir/spruce with bark content of 45 wt. %) and E_2 (oak with bark content of 14.7 wt. %).

Biomass ash characterization

The chemical analysis of the ash was determined by X-ray fluorescent spectrophotometry (Bruker, WDXRF "S8 Tiger"), and the mineralogical analysis was determined by X-ray diffractometry (XRD).

Leaching tests

Leaching tests on ash samples were performed in order to establish the amounts of heavy metals found in ash, which can be found in the environment after the ash disposal.

In order to simulate the real conditions of ash deposition from the city heating plant, two mixtures were prepared:

1. Pd_1 (fly ash and bottom ash mixed in mass. ratio 10 FA:90 BA);
2. Pd_2 (fly ash and bottom ash mixed in mass. ratio 20 FA:80 BA).

Ash samples from ENSA BH factory are used as they are: E_1 and E_2, unchanged.

The following tests were performed: pseudo-total metal content, Tessier sequential extraction, as well as standard TCLP and SPLP tests.

After the leaching tests were done, the separation of solid and liquid phase was performed on membrane filtration unit (Sartorius, Membranfilter GMBIH, Goffingen, Germany), through 0.45 μm membrane filter paper. The filtrates were acidified with HNO_3 (1:1) to pH 2 and were kept in the refrigerator until determination of the trace metals on the ICP-MS (Agilent).

Pseudo-total metal content

Pseudo-total metal content (PTMC) was determined in raw samples of biomass ash, where 0.5 g of ash was extracted with 12 cm^3 mixture of HNO_3 and HCl (volume ratio 3:1).[5] Extraction was performed on a water bath with reflux, for 4 hours. Filtrates were not acidified due to extremely acidic nature of the extraction agent.

Sequential extraction

Sequential extraction (SE) was performed, according to the Tessier procedure.[7] All ash samples were pre-dried at 105 °C for 24 h, and weighted (1 g) in plastic centrifugal cuvettes. After each extraction step, the samples were centrifuged (15 min at 3500 rpm), filtered and washed with 30 cm^3 of deionized water (2×), centrifuging after each wash, to minimize sample losses during filtration. The filtrates after one extraction step were combined. The solid residue that was left after the filtration was stored in a refrigerator until the next extraction step. The conditions of performed SE are shown in Table I.

TABLE I. SE conditions performed on biomass ash samples

Fraction	Extraction agent	Extraction conditions	
		Stirring time, h	t / °C
Exchangeable fraction (EF)	15 cm^3 $MgCl_2$ (c = 1 mol dm^{-3}), pH 5.80	2	25±1
Carbonate fraction (CF)	15 cm^3 NaOAc (c = 1 mol dm^{-3}), pH 5.00	5	25±1
Fe and Mn fraction (Fe&MnF)	40 cm^3 $NH_2OH·HCl$ (c = 0.04 mol dm^{-3}) in 25 % HAc, pH 2.00	5	94±1
Organic fraction (OF)	6 cm^3 HNO_3 (c = 0.02 mol dm^{-3}) + 10 cm^3 30 % H_2O_2, pH 2.00, acidified with HNO_3	5	85±1
	10 cm^3 NH_4OAc (c = 3.2 mol dm^{-3}) in 20 % HNO_3	1	25±1

Single leaching tests

Single leaching tests were performed in 50 cm^3 plastic cuvettes with lids. The necessary stirring was provided using an orbital shaker (Laboratory Instruments, WiseShake SHO-2D witeg, Wertheim, Germany). pH value of tested samples was measured (Multi Line P4, WTW), before and after the extraction. After stirring time, the samples were filtered on membrane filtration unit (Sartorius, Membranfilter GMBIH, Goffingen, Germany), through 0.45 µm membrane filter paper. The filtrates were acidified with HNO_3 (1:1) and were kept in the refrigerator until the determination of the trace metals.

Toxicity characteristic leaching procedure (TCLP) test

The test was performed according to US EPA method 1311, 2003, at liquid and solid phase ratio 20:1 (L:S = 40 cm^3:2 g). In this test, the choice of extraction fluid depends on the alkalinity of the tested material. During the selection process of the extraction agent, it was found that a solution of CH_3COOH, with pH value of 2.88±0.05, is to be used for TCLP test.

synthetic precipitation leaching procedure (SPLP) test

The test was performed according to US EPA Method 1312, 2003, at liquid and solid phase ratio 20:1 (L:S = 40 cm^3:2 g). As an extraction fluid, a mixture of acids composed of H_2SO_4 and HNO_3 (60:40 mass ratio) at pH 4.2, was used.

Preparation of cement composites

The ash samples used for preparation of cement composites are:

1. Pd_1 (sample obtained by mixing fly and boiler ash from heating plant Prijedor in mass ratio FA:BA = 10:90)
2. E (combined sample ENSA, obtained by mixing ash samples in mass ratio E_1:E_2 = = 50:50.

The preparation of cement composites involved the preparation of mixtures of ash and cement. The mass ratio of cement to ash was 65C:35A. Silica sand (granulation 0.1–0.65) was added in the mixture at mass ratio sand/cement = 3, with the addition of water (water/cement = 0.66). First, all dry components were homogenized in plastic cups. Then, the water was added during the mixing with propeller stirrer. The obtained mixture was used to fill moulds, whose dimensions were 3×3×3 cm^3. The samples were kept in the moulds for 48 h to harden. The hardened cubes were removed from the moulds and stored at a temperature of 20 °C in plastic bags for 28 days to prevent losing moisture. After 28 days, the cement composites were exposed to tests of monolith leaching in the tank, as previously described in PTMC test.

Monolith leaching test in the tank (NSF/ANSI 61–2009)

The leaching test was performed in glass jars with lids, using distilled water as an extraction agent. The samples of cement composites were placed in inert polyamide meshes, and then immersed in a vessel with deionized water (Fig. 1).

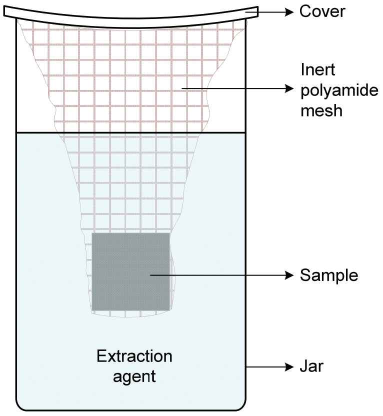

Fig. 1. Semi-dynamic leaching test.

Leaching was performed by immersing the same cement composite in a fresh solution of deionized water after 1, 2, 4 and 7 days, at a temperature of 20 °C, which was provided by an incubator (Velp Scientifica 120l). After each series of tests, the pH value and electrical conductivity of extraction agents were measured. Later, filtration was performed through membrane filter paper (0.45 μm). The filtrates were acidified and the concentration of heavy metals in them was determined by ICP-MS technique.

RESULTS AND DISCUSSION

The results of the chemical analysis of biomass ash are presented in the Supplementary material to this paper, Table S-I.

The results of chemical analysis show that the dominant component of boiler ash from the Prijedor heating plant (Pd-BA) is SiO_2 (53.9 %), while the dominant component of fly ash (Pd-FA) is CaO (46.0 %). In the sample E_1, the dominant components are SiO_2 (36.3 %) and CaO (36.4 %), while in the sample E_2, the dominant component is CaO (43.07 %).

The results of the mineralogical analysis of the examined biomass ashes are presented in Supplementary material, Table S-II.

Alite sum is the sum of clinker minerals tricalcium silicate (C_3S) and dicalcium silicate (C_2S) formed by the reaction of CaO and SiO_2 during combustion in a furnace, at temperatures above 1150 °C. A significant alite sum content of 24.5 % for Pd-BA and 27.5 % for Pd-FA was found in the ash samples from the Prijedor district heating plant (Table S-II). In the case of ENSA biomass ash, the alite sum content is significantly lower, 7.94 % for E_1 and 11.3 % for E_2, so it can be asserted that the temperature in the furnace at ENSA is lower than the temperature in the Prijedor heating plant. This statement is confirmed by a significantly lower concentration of free lime, for sample E_1 3.86 %, and for E_2 1.18 %, but also a high content of Calcite, especially for E_2 in a concentration of 70.1 %. Free lime is formed by decarbonization of carbonates (calcite) at temperatures above 850 °C.[8] Table S-II shows that iron is present mainly in the form of hematite Fe_2O_3, and not magnetite. Mullite appears only in sample E_1.

For sample E_1 an amorphous (glassy) phase was detected in a significant concentration of 18.9 %. E_1 is a mixture of coniferous wood ash (spruce/fir) with a high content of bark (45 %). The bark of the tree is characterized by a lower content of cellulose, and a higher content of lignin.[9] During the burning of wood with a higher content of bark, its calorific value decreases, and a larger amount of ash, with lower melting temperature, is generated.[10] The glass phase was not detected in samples originating from deciduous trees. To prevent the ash from melting in the furnace, it is recommended that the biomass combustion temperature does not exceed 1100 °C.[9]

Leaching tests

The determination of the physicochemical composition was followed by the leaching of heavy metals from ash samples, in order to identify and quantify the amounts of metals that could potentially be found in the environment after the ash disposal. This was performed using the following standard leaching tests.

Pseudo-total metal content

The results of leaching tests on PTMC for the examined ash samples are presented in Supplementary material, Table S-III.

The metal concentration values from leaching tests were compared with the maximum acceptable concentrations (*MAC*) of heavy metals and potentially toxic elements in agricultural land, expressed in mg kg^{-1} of dry clay soil.[11] The test results show that pseudo-total content of metals As, Co and Pb, in all of the examined ash samples, are lower than the *MAC* of heavy metals for clay soil, prescribed by the regulation (Table S-III).

In contrast, the metals Ba, Cr, Ni were leached in concentrations far higher than the *MAC*. Leaching of Cd and Zn is also higher than the concentrations prescribed by the regulation for the samples Pd_1, Pd_2 and E_1, as well as leaching of Cu for the sample E_1.

These results indicate a possibility for leaching of heavy metals, but not necessarily the induced toxicity. To exert toxic effects, heavy metals must be bound to compounds from which they can be easily released, or leaching will occur if the physical and chemical conditions in the environment change, which will increase the solubility of the metal.[12]

Since the leaching tests of PTMC do not provide insight into the forms of heavy metals bounding in the ash, neither their mobility, leaching was also performed by SE tests.

Leaching tests – sequential extraction

Sequential extraction (SE) is a process in which the same sample is transferred to a number of different extraction agents under different leaching conditions, resulting in selective dissolution of metals from different fractions. Tessier sequential extraction was originally developed for soil analysis, but it is widely used to test many materials, with appropriate adjustment of extraction conditions.[7,13]

SE enables the isolation of five metal fractions from biomass ash: exchangeable fraction (leached metals directly available for exchange), carbonate fraction (soluble in acetate buffer, and potentially available for leaching in neutral conditions), Fe and Mn fraction (oxide fraction, potentially available in acidic medium), organic fraction (metals bound to organic matter and sulphides, soluble in acidic medium), and residual fraction (metals bound in silica matrix and completely inaccessible for leaching).

The residual fraction of SE was determined by subtracting all tested fractions of one metal from the experimentally obtained pseudo-total metal content for the same metal.

The results obtained by phases of SE, expressed as mg kg^{-1}, are presented in Supplementary material (Table S-IV). These results are also shown graphically in Figs. 2 and 3, expressed as percentages by SE phases relative to the pseudo-total metal content.

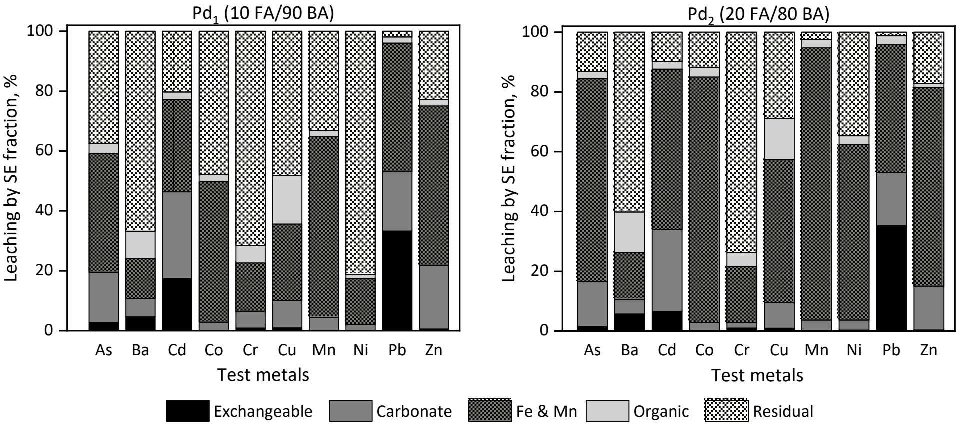

Fig. 2. Leaching of metals by SE fractions in relation to PTMC for ash mixture samples Pd$_1$ and Pd$_2$.

Fig. 2 shows the increased leaching of the sample Pd_2 (20 FA/80 BA) compared to the sample Pd_1 (10 FA/90 BA). The reason for this is the higher proportion of fly ash in the Pd_2 mixture. The type of ash (boiler or fly ash) has a great influence on the leached concentrations of heavy metals. The differences are more noticeable for easily volatile metals As, Cd, Zn and Pb for the samples Pd_1 (10 FA:90 BA) and Pd_2 (20 FA:80 BA) in the exchangeable and carbonate fraction, because, with the higher content of fly ash in mixtures, the concentration of heavy metals increases, which is in accordance with numerous authors' findings.[5,14,15]

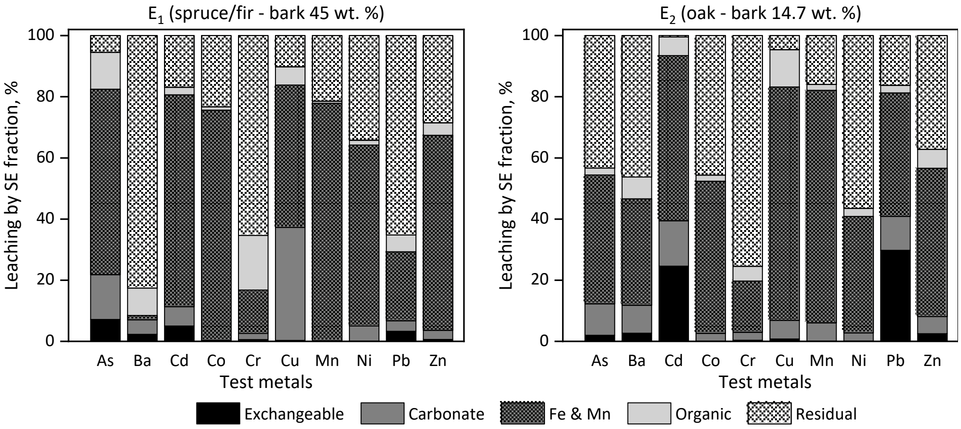

Fig. 3. Leaching of metals by SE fractions in relation to PTMC for ash mixture samples E_1 and E_2.

As, Ba, Cd and Pb appear in exchangeable fractions of both tested ash mixtures, which indicates direct leaching after disposal, and higher the leaching the smaller ash particles are.[16] Pb was released the most from the Pd_1 sample, in a concentration of 33.3 %, while 35.2 % of Pb was leached from the Pd_2 sample. The appearance of Ni in exchangeable fraction of tested samples, in a very small amount (Pd_1 – 0.07 % and in Pd_2 – 0.33 %), indicates possible condensation of Ni on fly ash particles, because its concentration increases with higher FA content in the mixture.[17] In the exchangeable fraction, in addition to heavy metals, Na, K, and Ca are also released, most often in the form of chlorides, but also in the form of well-soluble Na- and K- carbonates.[18]

The residue of Ca, K, Mg and Na carbonates is released in the carbonate fraction.[18] In addition to these "non-hazardous" elements, the most noticeable leaching in this fraction is that of As, Cd, Pb and Zn, for both tested ash samples. It could be concluded that some of these elements are bound in the form of chlorides and carbonates in these ash samples.

The residual fraction of sample Pd_1 mostly consists of Ni (81.2 %), Cr (71.5 %), and Ba (66.8 %), and for sample Pd_2, Cr (73.8 %) and Ba (60.2 %), which indicates that these elements are mostly bound in the form of silicates.

The results of sequential extractions for wood biomass samples E_1 and E_2 are shown in Fig. 3.

The samples E_1 (spruce/fir with bark content 45 wt. %) and E_2 (oak with bark content 14.7 wt. %) are quite complex, and differ both in wood type and bark content, which significantly complicates the interpretation of the results.

In the sample $E_{1,}$ the leaching of individual metals is significantly higher in percentage. As is released in exchangeable and carbonate fractions at concentration of 7.18 and 14.66 %, respectively. In the residual fraction, As retains in concentration of 5.48 %, while the total concentration of As, obtained by the pseudo-total metal content test, is the lowest in relation to all tested samples, and amounts to 2.26 mg kg^{-1} (Table S-III).

Leaching of As in sample E_2 is significantly lower, in exchangeable fraction (2.00 %), in carbonate fraction (10.33 %), while the residual fraction remains with 43.33 %, for the established PTMC of 6.75 mg kg^{-1}. Large differences in concentrations are also visible in the leaching of Cd, Cu, and Pb.

Generally, metal leaching in the sample E_2 is quite similar to leaching in sample Pd_1 and Pd_2, since the E_2 ash sample originates from deciduous trees. The ash of the E_1 sample originates from coniferous trees, so the differences in leaching between the E_1 and E_2 samples are expected, due to the different biomass composition. Differences in heavy metal concentrations are visible and can be tied to the type of tree – coniferous or deciduous. Lower average concentrations of Pb, Cd, Hg and As are emitted by spruce combustion, compared to the combustion of wood briquettes from deciduous trees.[15] Due to the increased emission of these elements, there is a risk that occurs during combustion in open fireplaces in households.

In the Fe and Mn fractions, many metals (As, Cd, Co, Cu, Mn, Ni, Zn) are released in higher concentrations, most likely because they are present in the form of pure or mixed oxides in these ash samples.[18]

In the organic fraction, the leaching of metals is mostly low, because it is a material that does not contain much of residual organic matter.

The residual fraction of sample E_1 mostly consists of Ba (82.6 %), Cr (65.4 %) and Pb (65.2 %), and for sample E_2 Cr (75.4 %), Ni (56.5 %) and Ba (46.3 %).

The results of the obtained SE leaching of heavy metals are difficult to compare with those by other authors due to the numerous modifications performed by the authors. Differences in the performance of fractions, from author to author, are reflected in the use of the aqueous phase, as the first extraction step, then in the duration of extractions, temperature, extraction agent, but also in the method of filtration, which is usually not emphasized. In recent years, mandatory centrifugation of the sample before filtration on membrane filter paper has been introduced, in order to reduce the loss of the sample during filtration, with rinsing of the precipitate.[19] Therefore, in order to compare the obtained results, it is necessary to present the detailed data on the manner of performing individual SE fractions, which is often not the case.

Table II presents an overview of the results obtained from wood biomass ash, with the conditions of SE performance by fractions. Also, it is necessary to emphasize that the metals analysed in the mentioned works were not the same.

TABLE II. Literature review of the obtained results from wood biomass ash, with the conditions of performing SE by fractions

SE Fraction	SE Conditions	Leached metals	Literature
Aqueous	Fraction not performed	–	This paper
	Deionized water, pH 7, τ = 1 h, t = 20 °C	Co, Cr, Mn, Pb	4
	Fraction not performed		18
	Fraction not performed		1
	Fraction not performed		5
Exchangeable	15 cm^3 1 M $MgCl_2$, pH 5.80, τ = 2 h, t = 25 °C	As, Ba, Cd, Co, Cr, Cu Mn, Ni, Pb, Zn	This paper
	1 M $MgCl_2$, pH 7, τ = 1 h, t = 20 °C	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb	4
	50 cm^3 1M NaOAc, τ = 0.5 h at room temperature	As, Cd, Cr, Cu, Ni, Pb, Zn	18
	Fraction not performed		1
	Fraction not performed		5
Carbonate	15 cm^3 1 M NaOAc, pH 5.0, τ = 5 h, t = 25 °C	As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	This paper
	CH_3COOH/CH_3COONa, pH 5, τ = 5 h, t = 20 °C,	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb	4
	50 cm^3, CH_3COOH/CH_3COONa, pH 5, τ = 1 h at room temperature	As, Cd, Cr, Cu, Ni, Pb, Zn	18
	0.11 M CH_3COOH, pH 7.0, τ = 16 h, t: 20–25 °C	Cu, Zn, Mn	1
	20 cm^3 0.11 M CH_3COOH, τ = 16 h at room temperature	Al, As, Ba, Be, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, Zn	5
Fe–Mn oxide	40 cm^3 0.04 M $NH_2OH\cdot HCl$ in 25 % HAc, pH 2.00, τ = 5 h, t = 94°C	As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn	This paper
	0.04 M $NH_2OH\cdot HCl$ in 25% CH_3COOH, τ = 5 h, t = 96 °C,	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	4
	20 cm^3 0.04M $NH_2OH\cdot HCl$ in 25% Hac, τ = 1 h, t = 96 °C	As, Cd, Cr, Cu, Ni, Pb, Zn	18
	30 cm^3 0.04M $NH_2OH\cdot HCl$ in 25% Hac, τ = 1 h, t = 96 °C		

TABLE II. Continued

SE Fraction	SE Conditions	Leached metals	Literature
Fe–Mn oxide	0.5M NH_2OH-HCl, pH 1.5, τ = 16 h, *t:* 20–25 °C	Cu, Zn, Mn	1
	20 cm^3 0.1 M NH_2OH-HCl in HNO_3, τ = 16 h	Al, As, Ba, Be, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, Zn	5
Organic	6 cm^3 0.02 M HNO_3 +10 cm^3 30 % H_2O_2 acidified by HNO_3 up to pH 2; τ = 5 h, *t* = 96 °C 10 cm^3 3.2 M NH_4OAc in 20% HNO_3, τ = 5 h, *t* = 85 °C	As, Ba, Cd, Co, Cr, Cu Mn, Ni, Pb, Zn	This paper
	30% H_2O_2, pH 2, τ = 5 h, *t* = 85 °C, 3.2 M CH_3COONH_4 in 20 % HNO_3, τ = 1 h, *t* = 20 °C	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	4
	20 cm^3 30 % H_2O_2 acidified by HNO_3 up to pH 2, *t* = 1 h, *t* = 85 °C, 20 cm^3 30 % H_2O_2, τ = 1 h, *t* = 85 °C, 20 cm^3 3.2 M CH_3COONH_4 in 20 % HNO_3, τ = 0.5 h at room temperature	As, Cd, Cr, Cu, Ni, Pb, Zn	18
	30 % H_2O_2, pH 2.0, τ: 1–2 h, *t:* 20–25 °C 1.0 M CH_3COONH_4, pH 2.0, τ = 16 h, *t*: 20–25 °C	Cu, Zn, Mn	1
	5 cm^3 9.8 M H_2O_2, pH 2–3, *t* = 85 °C 25 cm^3 1 M CH_3COONH_4, τ=16 h	Al, As, Ba, Be, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, Zn	5
Residual	HNO_{3conc}/HCl_{conc} = 3:1 (volume ratio), τ = 4 h, *t* = 96 °C	As, Ba, Cd, Co, Cr, Cu Mn, Ni, Pb, Zn	This paper
	$HNO_{3conc}/HClO_{4conc}$ = 2:1 (volume ratio), τ = 5 h, *t* = 96 °C	Cr, Cu, Fe, Mn, Ni, Zn	4
	HNO_3/HCl/HF	As, Cd, Cr, Cu, Ni, Pb, Zn	18
	HF/HNO_3/HCl	Cu, Zn, Mn	1
	$HNO_{3\ conc}/HCl_{conc}$ = 3:1 (volume ratio)	Al, As, Ba, Be, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, V, Zn	5

The exact concentrations of metals obtained by leaching may differ from those by other authors, but the importance of SE is that they allow us to observe the behaviour of metals in different fractions of SE depending on the type of sample.

Risk assessment of leaching of heavy metals from the tested ashes

The mobility and stability of heavy metals depends primarily on the form of metal bonding in the material, which is determined by different fractions of SE. From the presented results it is evident that heavy metals are bound to different fractions, which indicates different forms of binding. Risk assessment code

(*RAC*) is a method that evaluates the potential risk of heavy metals leaching from a material.[5] The method involves application of the ratio of sum of exchangeable and carbonate fractions (because they are considered the most unstable compared to other phases) and pseudo-total metal content. According to the *RAC*, the following classification can be made: when the ratio of exchangeable fraction+carbonate fraction/pseudo-total metal content is <1 %, heavy metal has no harmful effect on the environment; if the ratio is between 1 % and 10 % metal has the low risk; at a ratio from 11 to 30 % the metal has a medium risk; a ratio from 31 to 50 % indicates a high risk, while a ratio of more than 50 % indicates a very high risk for leaching, and represents an extremely high risk to the environment.

The risk assessment levels, according to Pöykiö *et al.*,[5] for the tested ash samples are shown in Table III.

TABLE III. Category and risk assessment over the value of the risk assessment code (RAC) for the tested biomass ash samples

Category	*RAC* (EF+CF/PSUM)	Risk	Pd_1	Pd_2	E_1	E_2
I	< 1	No	–	–	Co, Mn	–
II	1–10	Low	Co, Cr, Cu, Mn, Ni, Ba	Co, Cr, Cu, Mn, Ni, Ba	Cr, Ni, Ba, Pb, Zn	Co, Cr, Cu, Mn, Ni, Zn
III	11–30	Medium	As, Zn	As, Zn	As, Cd, Cu	As, Ba
IV	31–50	High	Cd	Cd	–	Cd, Pb
V	> 50	Very high	Pb	Pb	–	–

The results in Table III show a very high risk of Pb leaching from samples Pd_1 and Pd_2. Also, there is a high risk of Cd leaching for samples Pd_1, Pd_2 and E_2, although the total Cd concentration of these samples was lower compared to other metals (Table S-III). Ash metals, which have an extremely low total concentration, can pose a high or even extremely high risk to the environment if they are bound to the ash matrix by weak bonds. In general, the greatest danger is presented by easily volatile metals, which condense on its surface by cooling the ash, and are very easy to leach. This statement coincides with those of many authors.[5,20]

Risk-free or low-risk metals may not pose a potential hazardous effect to the environment and human health, but should not be neglected. Given their relatively low concentrations, it is necessary to take into account the long-term effects they may have on soil, groundwater and surface water.[21] The increased concentrations of As and Cu were found in mixtures of wood ash with soil, but also in plants growing in the area where ash is deposited.[22]

Single leaching tests – TCLP test

The TCLP test is widely used, and was developed with the aim of simulating the conditions prevailing at the landfill where the waste material is disposed of.

Comparison between values for leached metals obtained by TCLP test and limit values given by the regulation[23] is shown in Fig. 4.

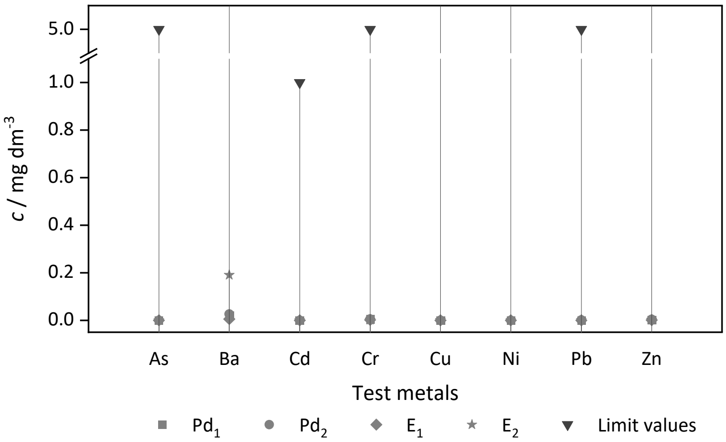

Fig. 4. Concentrations of leached metals obtained by TCLP test from wood ash compared to limited concentrations given by the regulation.

Fig. 4 shows that no sample of wood ash exceeds the limited values given by the Regulation. The leaching of the tested metals by the TCLP test is extremely low, which is in accordance with Sano *et al.*[14]

Single leaching tests – SPLP test

The SPLP test was developed as an alternative to the TCLP test when waste disposal is done outside municipal landfills. This test aims to simulate the impact of acid rain on waste material, and to monitor the leaching that occurs under these conditions. The obtained values of leached metals are compared with The Regulation on the conditions for discharging wastewater into surface waters. The comparison between the values for leached metals obtained by SPLP test and limited concentrations given by the Regulation[24] is shown in Fig. 5.

Fig. 5 shows that the leaching of the tested metals from wood ash samples does not exceed the limited values given by the regulation, although the limit values prescribed for this SPLP test are significantly lower compared to the limited values for the TCLP test.

Change in pH before and after leaching tests

One of the key factors for leaching is the pH value, and therefore it is very important to know the pH value of the initial solutions as well as the final pH values.[25] Fig. S-1 of the Supplementary material shows the change in pH before and after performing single leaching tests.

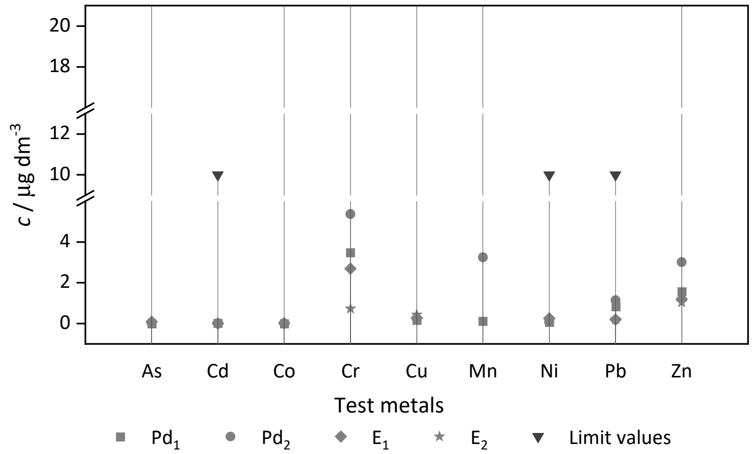

Fig. 5. Concentrations of leached metals obtained by SPLP test from wood ash compared to limited concentrations given by the regulation.

From the presented results, it can be established that the change in pH value during the tests is strongly influenced by the nature of the extraction fluid, while the type of ash does not have a significant effect. The change in pH value during leaching is greatly influenced by the content of Ca^{2+}.[26] Since high concentration of CaO was found in the tested samples by chemical analysis (Table S-I), the high pH values after the test were expected, which is in accordance with the findings by authors who, apart from the modified TCLP test, also used other individual leaching tests.[14]

Monolith leaching test in the tank

Ash, as a waste material, due to its specific composition can be used for many purposes. One of the possibilities is the use of ash in construction as a partial replacement for cement. However, due to the presence of heavy metals which ash carries with it, it is necessary to determine which heavy metals and in what concentration can be leached during the practical application of such composites. Tank leaching test is used for the testing of monolithic material.

The change in pH value and electrical conductivity of the extraction agent, caused by the leaching of cement composites in the tank for 7 days is given in Fig. S-2 of the Supplementary material.

The results show high pH values (Fig. S-2a) and electrical conductivity (Fig. S-2b) during leaching. High pH values (pH > 11) indicate that the extraction agent enters the pores of the monolith, comes into contact with hydrated cementitious material, and affects the leaching of alkaline cations, primarily Ca^{2+} and K^+. The main product of cement hydration, $Ca(OH)_2$, is additionally added with biomass ash, which is also extremely alkaline, resulting in a high pH value during leaching,[27,28] even after 7th day of leaching (for sample with Pd_1 mixture, pH 11.83; for sample with E mixture, pH 11.84).

The conductivity measurements during leaching completely match pH values. Extremely high values of electrical conductivity after the first day of leaching for the sample Pd_1 (1303 μS cm^{-1}) and the sample E (1983 μS cm^{-1}) decreased significantly during the experiment, and on 7th day had the following values: sample Pd_1 (726 μS cm^{-1}) and sample E (779 μS cm^{-1}).

For easier observation and interpretation, the results are presented in percent relative to the pseudo-total metal content, and shown graphically in Fig. 6. The results in mg kg^{-1} can be found in Supplementary materials (Table S-V of the Supplementary material).

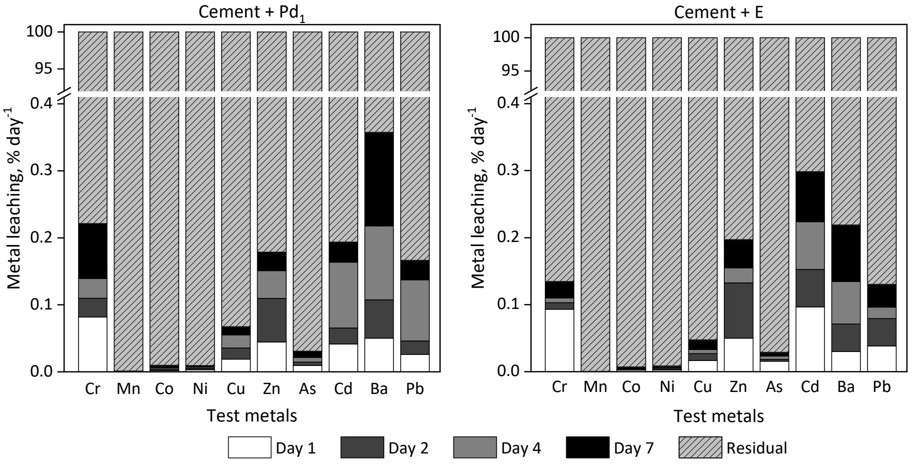

Fig. 6. Percentage of metal leaching per day in relation to pseudo-total metal content for tested ash samples in cement composites (65C: 35A).

With a high proportion of ash in cement mixtures (65C:35A), heavy metal leaching is reduced to a minimum after the first day. The results shown in the figure are confirmed by the authors.[16] In addition to the useful components in the ash (primarily silicon) that participate in hydration and hardening together with cement, the ash also has components that do not have pozzolanic activity. As the proportion of ash in the mixture increases, so does the proportion of unwanted components, which can impair the strength of the cement composite. Therefore, in order for the ash to be used as a partial replacement for cement, it is necessary to further test the compressive strength. The compressive strength test, as well as tests of other required properties of hardened cement composite, must be performed at different weight ratios of cement and ash, in order to determine which mixture ratio of cement and ash gives the best results.[29]

CONCLUSION

Based on this research, it can be concluded that the tested ash produced by wood biomass combustion, according to standard leaching tests (TCLP and SPLP), does not exceed the limit values of heavy metal content given by the regulation. However, regardless of their relatively low concentrations, it is necessary to take into account the long-term effects they can have on soil, groundwater and surface water. On the other hand, the possibility of using wood biomass ash in cement composites solves the problems of long-term impact of heavy metals, because their leaching, even with a relatively large share of ash in the composite, is minimized. Also, finding the optimal cement/ash ratio is extremely important, so the required strength of cement composites is not reduced due to the use of ash.

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ИЗВОД

ИЗЛУЖИВАЊЕ ТЕШКИХ МЕТАЛА ИЗ ПЕПЕЛА ДРВНЕ БИОМАСЕ, ПРИЈЕ И ПОСЛИЈЕ ВЕЗИВАЊА У ЦЕМЕНТНИ КОМПОЗИТ

ДИЈАНА М. ДРЉАЧА[1], ЉИЉАНА М. ВУКИЋ[1], ДАЈАНА М. ДРАГИЋ[1], АЛЕКСАНДРА П. БОРКОВИЋ[1], ТАТЈАНА Т. БОТИЋ[1], ПЕРО Т. ДУГИЋ[1], САША В. ПАПУГА[1], МАРКО Д. ШОЛИЋ[2], СНЕЖАНА П. МАЛЕТИЋ[2], ПЕТАР М. ГВЕРО[3] и ЈЕЛЕНА Р. САВКОВИЋ[1]

[1]*Технолошки факултет, Универзитет у Бањој Луци, В.С. Степановића 73, Бања Лука, Босна и Херцеговина,* [2]*Природно–математички факултет, Нови Сад, Трг Доситеја Обрадовића 3, Нови Сад и* [3]*Машински факултет, Универзитет у Бањој Луци, В.С.Степановића 71, Бања Лука, Босна и Херцеговина*

Дрвни пепео представља комплексну мјешавину неорганских и органских једињења, хетерогеног је састава и његов састав може знатно варирати. Углавном се одлаже на депоније, што представља ризик од загађења ваздуха, земљишта и подземних вода елементима који су присутни у траговима. Да би се пепео дрвне биомасе могао примијенити као секундарна сировина, неопходно је извршити тестове излуживања, како би се утврдило које микроелементе садржи, те установити који од њих би се могли излужити у животну средину током депоновања. Секвенцијалном екстракцијом установљено је да се у измјењивој и карбонатној фракцији највише излужују лако испарљиви метали As, Cd, Zn и Pb за пепео листопадног дрвећа, док су излуживања пепела који потиче од четинарског дрвећа знатно нижа. Процјена ризика преко вриједности кода за оцјењивање (*RAC*) за узорке пепела биомасе, указује да је Pb високо ризичан елемент за излуживање због кондензовања на честицама пепела. Извођењем TCLP и SPLP тестова установљено је да су излужене концентрације испитиваних метала испод граничних концентрација прописаних правилником. Тестови излуживања композита, припремљених од дрвног пепела са цементом, указују да су излуживања пепела сведена на минимум, и да су сви тешки метали везани у цементну матрицу, што упућује на могућност кориштења дрвног пепела у грађевинске сврхе.

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