

Chemical fractionation method for characterization of biomass-based bottom and fly ash fractions from large-sized power plant of an integrated pulp and paper mill complex

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Abstract: The aim of this study was to extract the biomass-based bottom and fly ash fractions by a three-stage fractionation method for water-soluble (H_2O), ammonium-acetate ($\text{CH}_3\text{COONH}_4$) and hydrochloric acid (HCl) fractions in order to access the leaching behaviour of these residues. Except for Mo, S, Na and elements whose concentrations were lower than the detection limits, the extractable element concentrations in both ash fractions followed the order $\text{H}_2\text{O} < \text{CH}_3\text{COONH}_4 < \text{HCl}$. The elements concentrations in this study were also lower than those in our previous studies, in which certain extraction stages followed the BCR extraction procedure.

Key words: ash; extraction; forest industry; landfilling; leaching; heavy metals; waste

1 Introduction

Pulp and paper mills are intensive energy users, as pulp and paper production requires a considerable amount of energy in the forms of heat, steam and electricity. Due to the large amount of energy needed at pulp and paper mills, this industry has a long tradition of utilizing its by-products, such as a black liquor, wood spill, pulp chips, bark residue and sawdust, in energy production. The use of wood-based residues as fuel allows the utilization of renewable, natural raw material as an energy source without any marked effects on the carbon balance of the wider ecosystem. Consequently, the use of wood residue-based biofuels, such as bark, woodchips and sawdust, is exempted from electricity tax and carbon dioxide (CO_2) emissions trading in the European Union (EU) [1,2]. Peat is an internationally poorly known fuel, but it has a significant role in the Finnish energy system, especially in the power plants of the forest industry [3,4].

The bubbling fluidized bed (BFB) combustor is a proven technology for co-combustion of different kinds of biomass at the power plants of the pulp and paper mills. The advantages of BFB technology include fuel flexibility, the ability to burn fuels with high moisture contents and low heating value, and the reduction of emissions of SO_x and NO_x [5]. However, one disadvantage of energy generation from biomass is that it produces a considerable amount of ash residues (i.e. bottom ash and fly ash), which are traditionally disposed of at landfill sites. Incineration and landfilling are integrated components of waste management in many countries. Ensuring the safe disposal and long-term storage of ash and other industrial residues represents a primary environmental task of industrial societies [6]. During storage at landfills, the ash is subjected to leaching by rainwater and comes into contact with other substances, such as chlorides, sulphates, and organic matter, which can form complexes with heavy metals [7]. The pH in a landfill environment may also change due to natural acid formation arising from anaerobic microbial

degradation. During the re-use and long-term storage of wastes, acidification might result from sulphide oxidation, the buffering capacity of natural waters, acid rain and atmospheric CO₂ [8]. Therefore, the main environmental concern with respect to these residues is the release of contaminants by leaching. To assess the environmental impacts from residue disposal, it is necessary to quantify this leaching [9]. The extraction of metals-containing wastes by different solvents, also known as sequential extraction or sequential fractionation, is a good practice to evaluate the mode of metals binding within solid matrix and to evaluate metal mobility in different environments. In sequential extraction, the solid material is successively exposed to different and increasingly aggressive solvents in order to collect the extracts in different fractions, which is essential to assess the mode of metals binding with the solid matrix [10]. These extraction tests are carried out in the assessment of worst-case environmental scenarios, in which the components of the sample become soluble and mobile [11]. The aim of this study is to extract the biomass-based bottom and fly ash fractions using a three-stage fractionation method between water-soluble (H₂O), ammonium-acetate (CH₃COONH₄) and hydrochloride acid (HCl) fractions in order to access the leaching behaviour of these residues. The extraction method used follows the procedure of PETTERSSON et al [12]. This extraction procedure has also been used by ZEVENHOVEN-ONDERWATER et al [13] and HUPA [14]. The extraction procedure predicts the leaching behaviour of heavy metals in ashes and explains the potential release of elements in the ashes under changing environmental conditions.

2 Experimental

2.1 Bottom ash and fly ash sampling

The bottom ash and fly ash investigated in this study originated from the large-sized (246 MW) power plant of an integrated pulp and paper mill complex, comprising a pulp mill and a paper mill located at the same site [15]. The mill investigated in this study produced elemental chlorine-free (ECF) bleached soft and hardwood pulp (ca. 350000 t/a), uncoated fine paper (ca. 490000 t/a), coated printing papers (ca. 360000 t/a), and sawn goods (ca. 150000 t/a), and for this, consumed ca. 48 m³ process water per ton of pulp and 8 m³ process waste per ton of paper produced. The pulping in the mill was based on the sulphate (Kraft) process, in which the active cooking (digestion) chemicals were sodium hydroxide (NaOH) and sodium sulphide (Na₂S). The wastewaters from pulp and paper mill were treated at a biological wastewater treatment plant and at a chemical wastewater treatment plant.

The power plant of the mill used a bubbling fluidized bed (BFB) boiler for energy production. During the sampling period, when the bottom ash was sampled from the outlet of the boiler and the fly ash from the boiler's electrostatic precipitator (ESP), approximately 70% of the energy produced by the BFB boiler originated from the incineration of clean forest residues (i.e., bark, woodchips and sawdust), and 30% originated from the incineration of commercial peat fuel. These forest residues originated from the wood handling plant of the pulp and paper mill complex investigated in this study, and they were therefore clean residues. The bark, woodchips and sawdust were derived from pine (*Pinus sylvestris*), willow (*Salix*) and birch (*Betula verrucosa* and *B. pubescens*), which were all of domestic origin. However, their relative proportions were unknown.

Sampling of the ashes was carried out over a period of 3 d, and the individual samples (1 kg per sampling day) were combined to give one composite sample with a mass of 3 kg for both the bottom ash and fly ash. The sampling period represented the normal process operating conditions for the power plant, e.g., in terms of O₂ content and temperature. The incineration temperature in a bubbling fluidized bed boiler was ca. 800 °C, while in the electrostatic precipitator it was ca. 176 °C. After sampling, the samples were stored in plastic bags in a refrigerator (4 °C) until analyses. The sample should be analyzed as soon as possible after sampling. However, if this is not done, according to EPA [16], the sample should be chemically/physically preserved as soon as possible after sampling to avoid/minimise biological, chemical or physical changes that can occur between time of collection and analysis. For the above-mentioned reason, we decided to follow the procedure of SARODE et al [17] and to storage the samples in a refrigerator (4 °C) until analysis. A coning and quartering method [18] together with sieving was repeatedly applied to reducing the ash samples to a size (< 2 mm) suitable for conducting laboratory analyses.

2.2 Determination of mineral composition and physical and chemical properties of ashes

To determine the mineralogical composition of the bottom ash and fly ash, X-ray diffractograms of powdered samples were obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using Cu K_α radiation. The scan was run from 2° to 80° (2θ), with increments of 0.02° and a counting time of 1.0 s per step. The operating conditions were 40 kV and 40 mA. Peak identification was carried out with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and the software package ICDD PDF-2 Release 2006 (Pennsylvania, USA). The pH of the ashes was determined using a pH/EC analyzer

equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium). The determination of pH was carried out according to European standard SFS-EN 12880 at a solid-to-liquid (i.e. ultrapure H₂O) ratio of 1:5. Determination of the dry matter contents of the ashes was carried out according to European standard SFS-EN 12880, in which samples were dried overnight to a constant mass in an oven at 105 °C. The organic matter content as measured by the loss-on-ignition (LOI) was determined according to European standard SFS-EN 12879, and the total organic carbon (TOC) content was determined according to European standard SFS-EN 13137. The neutralizing (liming effect) value was determined according to European standard SFS-EN 12945. A comprehensive review of the standards, analytical methods and instrumentation was provided in Ref. [19].

2.3 Determination of total nutrient and heavy metal concentrations in ashes

To determine the total nutrient (Ca, Na, Mg, P and K) and total heavy metal concentrations in the ashes, the dried samples were digested with a mixture of HCl (3 mL) and HNO₃ (9 mL) in a CEM Mars 5 microprocessor-controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using USEPA method 3051A [20]. The cooled solutions were transferred to a 100 mL-volumetric flask and the solutions were diluted with ultrapure water. The ultrapure water was generated by an ion exchange water purification system. All reagents and acids were suprapure or pro analysis quality. The total heavy metal concentrations in ashes were determined with a Thermo Fisher Scientific iCAP6500 Duo ICP-OES (United Kingdom). A more comprehensive review of the standards, analytical method and instrumentation was provided in Ref. [19].

2.4 Chemical fractionation of elements in ashes and element determination in extracts

For the fractionation of elements in the bottom ash and fly ash for the water-soluble (H₂O), ion exchangeable (1 mol/L CH₃COONH₄), and hydrochloric acid (1 mol/L HCl) fractions, we used the three-stage sequential extraction procedure of PETTERSSON et al [12]. In this procedure, which was fully described in Refs. [12,13], about 5 g of ash was transferred to a 50 mL polypropylene bottle and sequentially extracted in the following way: once in 30–50 mL ultra-pure H₂O for 24 h under stirring (65 r/min), three times in 3×25 mL 1.0 mol/L CH₃COONH₄(aq) for 3×24 h under stirring, and twice in 2×25 mL 1.0 mol/L HCl(aq) for 2 × 24 h under stirring and heating (80 °C).

According to PETTERSSON et al [12], the first

extraction step (H₂O) was intended to soak the ash and to dissolve the water-soluble compounds such as alkali metal salts. In the second step (CH₃COONH₄), ion exchangeable elements, such as organically associated sodium, calcium and magnesium, were replaced with ammonium ions and thus released to the liquid phases. The third extraction step (HCl) removed acid-soluble compounds, such as carbonates and sulphates.

After each extraction step, the solids were rinsed two times for 2×10 min with 2×25 mL ultra-pure H₂O. After each extraction step, the extracts were separated from the solid residue by filtration through a 0.45 µm-membrane filter (47 mm diameter; Schleicher & Schuell, Dassel, Germany). In order to avoid losses between the extraction stages, the filters and adhering ash particles from the previous extraction stage were also included in the next stage. After the addition of 200 µL of 65% HNO₃ to the supernatant phase, it was stored in a refrigerator (4 °C) until element determination [17]. The element concentrations in the extracts were determined with a Thermo Fisher Scientific iCAP6500 Duo ICP-OES (United Kingdom).

3 Results and discussion

3.1 Mineral composition and physical and chemical properties of ashes

The XRD patterns of bottom ash and fly ash with the identified mineral phases are presented in Fig. 1. According to Fig. 1(a), only silicate minerals such as albite (NaAlSi₃O₈ 33.1%), anorthoclase (KAlSi₃O₈; 20.5%), calcium silicate (CaSi₂O₅ 4.3%), phlogopite (KMg₃AlSi₃O₁₀(OH)₂ 19.2%) and quartz (SiO₂ 22.9%) existed in the bottom ash. The dominant minerals in the fly ash (Fig. 1(b)) were also silicates: albite (40.4%) and quartz (37.3%). Furthermore, the fly ash contained anhydrite (CaSO₄ 11.4%), which is a sulphate mineral, as well as hematite (Fe₂O₃ 7.8%) and lime (CaO 3.1%), which are oxide minerals. The existence of silicate minerals in the bottom ash is reasonable when considering that the bed sand material of the fluidized bed boiler at the mill investigated in this study consists of silica sand. Woody biomass is frequently also contaminated with sand and/or clay. Because these compounds often contain Al, the formation of alkali aluminosilicate can possibly occur. Furthermore, silicate minerals in ash may also be partly derived from the decomposition of plant tissue-derived Si-based minerals during incineration, such as phytolith (SiO₂·nH₂O), which is often a structural component of plant tissues, deposited between and within plant cells [21]. In addition, the existence of silicate minerals both in the bottom ash and fly ash fractions may also be partly due to sand

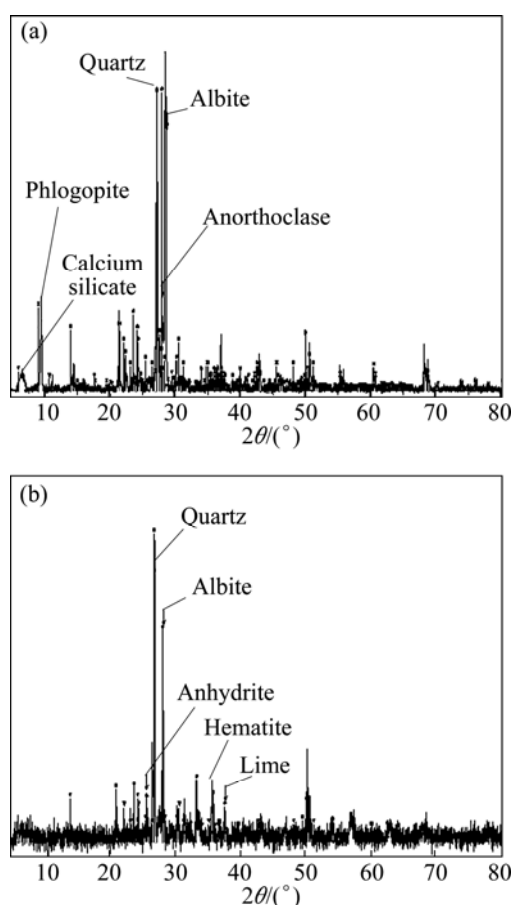


Fig. 1 XRD patterns of bottom ash (a) and fly ash (b)

and soil particle contamination of forest residues during harvesting, transportation and handling [22].

The minerals observed in the ashes investigated in this study correspond with the findings of STEENARI and LINDQVIST [22] who also recorded anhydrite, lime and quartz in wood ash. Furthermore, our XRD spectra are consistent with the findings of MEAWAD et al [23] who observed albite, hematite and quartz in wood ash. However, we did not detect any fairchildite ($(K_2Ca(CO_3)_2)$, as LIODAKIS et al [24], and SERAFIMOVA et al [25] did, or calcite ($CaCO_3$) observed by STEENARI and LINDQVIST [22], although these minerals are common phases identified in biofuel ashes. The differences between the minerals observed in our ashes and those in other studies are due to significant variation in the physical and chemical quality as well as the mineral composition of ashes depending on factors such as the ratio of the fuel sources burnt, the tree species, growing site, climate and tree component (e.g. bark, wood, leaves). Other factors that affect the physical and chemical quality of the ash include the size and age of the trees, the logging technique, collection and storage, as well as the burning technique, such as the combustion temperature and type of boiler [26,27].

As presented in Table 1, both ashes were strongly alkaline (pH 12.0 and 12.6). This is consistent with the findings of CABRAL et al [28] who reported pH values between 12.5 and 13.0 for pure wood ash. The slightly lower pH of our ashes than that reported by CABRAL et al [28] is probably due to the fact that our ashes originated from the incineration of a mixture of wood (forest residues) and peat fuel, and sulphur in peat fuel decreases the pH value of ash. However, the strongly alkaline pH value of the ash fractions investigated in this study indicates their buffering and acid neutralizing capacity. According to the results of HERCK and VANDECASTEELE [29], the alkaline pH of the ash indicates that part of the dissolved metals occur as basic metal salts, oxides, hydroxides and/or carbonates. However, the minerals in our XRD spectra (Figs. 1(a) and (b)) only partially support the findings of HERCK and VANDECASTEELE [29], since we could not observe any hydroxides and/or carbonates minerals in our ashes.

Table 1 Physical and chemical properties of bottom ash and fly ash ($n=1$)

Parameter	Unit	Bottom ash	Fly ash
Total organic carbon (TOC)	$g \cdot kg^{-1}$ (d.w.)	< 2.0	< 2.0
Loss-on-ignition (LOI, 550 °C)	% (d.w.)	< 0.5	< 0.5
Dry matter content (105 °C)	%	99.9	99.9
pH (1:2.5)	–	12.0	12.6
Electrical conductivity (1:2.5)	mS/cm	1.4	13.4
Neutralizing value (NV)	% (Ca, d.w.)	3.4	14.7

The acid neutralizing value (NV) of 3.4 (Ca equivalents; d.w.) for the bottom ash indicates a poor capacity of this residue to act as a liming agent, since about 11.2 t of this residue is required to replace 1 t of a commercial ground limestone product produced by SMA Mineral Ltd. (Finland), which has an NV of 38% (Ca equivalents; d.w.). However, the NV of 14.7 % (Ca equivalents; d.w.) for the fly ash indicates a relatively moderate capacity of this residue to act as a liming agent, since about 2.6 t of this residue is required to replace 1 t of a commercial ground limestone product produced by SMA Mineral Ltd. (Finland). The better acid neutralizing value of the fly ash is reasonable, since the total Ca concentration (122000 mg/kg; d.w.) in the fly ash was ca. 6.1 times higher than that in the bottom ash (20000 mg/kg; d.w.; see Table 2). The acid neutralizing capacity (NV) describes the resistance of a material to acid attack. A change in the pH of a landfill environment may occur due to natural acid formation arising from anaerobic

Table 2 Total (USEPA 3051) and extractable concentrations of elements in bottom ash (BA) and fly ash (FA) using H₂O, CH₃COONH₄ (abbr. NH₄Ac in table) and HCl extraction

Element	Total concentration/ (mg·kg ⁻¹)		Extractable concentration in bottom ash/(mg·kg ⁻¹)			Extractable concentration in fly ash/(mg·kg ⁻¹)		
	BA	FA	H ₂ O	NH ₄ Ac	HCl	H ₂ O	NH ₄ Ac	HCl
Al	7400	27700	60	< 15	7300	< 8	< 15	22400
As	11	57	< 0.2	2.3	3.7	< 0.2	2.0	37
Ba	170	1340	1.5	44	83	3.0	24	370
Be	< 1	< 1	< 0.1	< 0.2	< 0.4	< 0.1	< 0.2	0.8
Cd	< 0.3	3.2	< 0.02	< 0.05	< 0.1	< 0.02	1.2	1.4
Co	2.5	14	< 0.1	< 0.2	2.3	< 0.1	< 0.2	5.0
Cr	37	110	0.9	1.9	27	1.9	2.8	33
Cu	77	110	< 0.2	29	48	< 0.2	11	57
Fe	7840	85700	< 3	< 5	7770	< 3	< 5	40400
Mn	560	3300	< 0.4	9.7	450	< 0.4	15	2350
Mo	< 1	6.0	< 0.1	< 0.2	< 0.4	2.3	1.3	1.4
Ni	6.6	55	< 0.1	0.7	5.9	< 0.1	3.9	18
Pb	< 3	120	< 0.2	< 0.5	2.9	2.9	< 0.5	64
Sb	< 3	< 3	< 0.2	< 0.5	< 1	< 0.2	< 0.5	< 1
Se	< 3	3.3	< 0.2	< 0.5	< 1	< 0.2	1.0	< 1
S	260	7820	48	55	42	3290	3860	190
V	16	85	0.4	1.0	12	< 0.2	1.3	54
Zn	200	660	< 0.2	5.7	190	1.1	27	300
Ti	260	1100	< 4	< 8	260	< 4	< 8	700
Ca	20000	122000	860	5930	7490	11500	33200	69600
Na	2370	4260	31	76	2250	710	220	2910
Mg	5180	16500	< 2	520	3140	< 2	2710	8380
P	800	8780	< 2	83	500	< 2	66	6720
K	3030	11500	< 30	< 30	3000	3860	330	7030

microbial degradation. During the re-use and long-term storage of wastes, acidification might result from sulphide oxidation, the buffering capacity of natural waters, acid rain and atmospheric CO₂ [8]. According to the NV values, the fly ash has a better resistance than the bottom ash to external stress factors that cause H⁺-ion attack, for example, in the form of infiltration leachate, acidic rain, the uptake of atmospheric CO₂, biochemical processes, or oxidation/reduction conditions [8].

The total organic carbon (TOC) value of ash is indicative of the combustion efficiency, with a higher content indicating poorer combustion [30]. The TOC values (<2.0 g/kg; d.w.) in the bottom and fly ash fractions indicate the incomplete combustion of organic matter in these residues. The loss in ignition values (LOI) of 0.5% (d.w.) in the ash fractions also supports this. In this context, it is notable that although LOI is widely used to indicate the unburned material in ash, according to the findings of PAYÁ et al [31], the LOI

instead indicates the volatile fractions. Due to the very high dry matter contents of 99.9%, the bottom ash and the fly ash are likely to cause dust problems during handling. However, from an environmental perspective, the very high dry matter contents of ash fractions are favourable. Completely dry ash reacts very slowly with atmospheric CO₂; the CO₂ must first dissolve into pore water [32]. According to SIVULA et al [33], the initially dry ash is not very reactive until rainwater seeps into the ash heap. According to the electrical conductivity value, which is an index of the total dissolved electrolyte concentration, the leaching solution of the fly ash (13.4 mS/cm) has ca. 9.6 times higher ionic strength than that in the bottom ash (1.4 mS/cm).

3.2 Total and fractionated element concentrations in ashes

Table 2 presents the total and fractionated concentrations of elements in the ashes expressed on a

dry mass (d.w.) basis. If we disregard elements whose concentrations were lower than the detection limits, the total element concentrations in the fly ash were between 1.4 (Cu) and 30.1 (S) times higher than those in the bottom ash. According to OBERNBERGER et al [34], during combustion, a proportion of the ash-forming compounds in the fuel are volatilised (especially S) and to some degree also refractory species, such as Ca and Mg, are released in the gas phase. This leads to the enrichment of certain elements in the fly ash. The volatilised fraction depends on the chemical composition of the fuel, the surrounding gas atmosphere, the temperature of the boiler and the combustion technology used [34], and on the chemical form and binding of the ash-forming materials [35].

It is not uncommon that ash is exposed in heaps to ambient conditions (e.g. atmospheric carbon dioxide and precipitation) for several months before utilization. Weathering is a naturally occurring process that changes the composition of the ash and leachate during pre-treatment or disposal. Weathering consists of a series of geochemical processes caused by atmospheric gases and rain. The main chemical and physical processes of weathering are complexation, precipitation, dissolution, sorption and redox potential changes [36]. Carbonation is one of the important weathering process in which atmospheric CO_2 is absorbed by ash and consequently reduces the initially high pH of the ash through a change in the mineral composition [33]. Thus, if inorganic materials and by-products such as ash are disposed of in landfills, low metal concentrations and the tight binding of elements to the matrix are favourable [37].

When the sequential extraction procedure is applied to the fractionation of metals in environmental samples, the ability of different extraction agents to release metal ions depends on their association with specific fractions in the sample. Extractants such as electrolytes, weak acids and chelating agents release metals from the coordination sites, while strong acids and redox agents are capable of releasing additional quantities of metals as a result of the decomposition of the solid matrix [38]. Therefore, consecutive extraction techniques allow us to obtain information on the mobility and thus the bioavailability of major and trace elements under different environmental conditions, such as acidic, alkaline, oxidizing or reducing conditions or through the action of a chelating agent [11].

Water is a suitable extraction solvent if we wish to determine the bioavailability of the compounds in the environment, because water is the most important carrier of contaminants in the field conditions [8,39]. The elements extracted in the water-soluble (H_2O) fraction are relatively labile, mobile and thus may be potentially bioavailable [11]. If we disregard elements whose

concentrations are lower than the detection limits, only the extractable concentrations of Al (60 mg/kg; d.w.) and V (0.4 mg/kg; d.w.) in this fraction are higher in the bottom ash than those in the fly ash. For the bottom ash, the highest individual extractable element concentration in this fraction was observed for Ca (860 mg/kg; d.w.). For the fly ash, the highest individual extractable element concentration in the H_2O fraction was observed also for Ca (11500 mg/kg; d.w.). However, the H_2O extraction most effectively released sulphur from both the bottom ash and fly ash. If we compare the extractable concentrations of elements in the ash fractions with their total concentrations determined using USEPA 3051 digestion [20], the ratio of the extractable S concentration in the H_2O fraction in the bottom ash to its total concentration was 18.5%, whereas in the fly ash it was 42.1%. Although the total phosphorous content in the fly ash fraction was relatively high (8780 mg/kg; d.w.), the water-soluble phosphorous content in this ash residue was negligible (< 2 mg/kg; d.w.). This minimises the risk of phosphorous leaching.

In ammonium-acetate ($\text{CH}_3\text{COONH}_4$) extraction, ion exchangeable elements are replaced with ammonium ions and thus released to the liquid phase. This fraction includes weakly adsorbed elements retained on the solid surface by relatively weak electrostatic interaction and elements that can be released by ion-exchangeable processes [11]. According to SABIENÉ et al [40], ammonium-acetate (1 mol/L) used in this extraction stage is perhaps the most preferred reagent for exchangeable elements because of its relatively high concentration and the metal-complexing power of the acetate ion, which prevents the re-adsorption or precipitation of released metal ions. Furthermore, the use of ammonium acetate as an extractant is reasonable, because during the anaerobic degradation of organic matter, in the acetogenesis phase, volatile fatty acids and ethanol are produced and transformed, for instance into acetate, by acidogenic bacteria [8]. Besides the extraction of cations by acetate ions (CH_3COO^-), partial removal of some elements in this extraction stage may occur due to complexation with ammonium ions (NH_4^+) [41]. If we disregard elements whose concentrations are lower than the detection limits, all extractable element concentrations in $\text{CH}_3\text{COONH}_4$ fraction are higher in the bottom ash than those in the H_2O fraction. However, for Mo, Pb, Na and K in the fly ash, the reverse was observed, since the extractable concentrations of these elements in the H_2O fraction were higher than those in the $\text{CH}_3\text{COONH}_4$ fraction. If we disregard elements whose concentrations are lower than the detection limits, only the extractable concentrations of As (2.3 mg/kg; d.w.), Ba (44 mg/kg; d.w.), Cu (29 mg/kg; d.w.) and P (83 mg/kg; d.w.) in the $\text{CH}_3\text{COONH}_4$ fraction are higher

in the bottom ash than those in the fly ash. The very high extractable concentrations of nutrients such as Ca both in the bottom (5930 mg/kg; d.w.) and fly ash (33200 mg/kg; d.w.), as well as Mg (2710 mg/kg; d.w.) and S (3860 mg/kg; d.w.) in the fly ash are reasonable because $\text{CH}_3\text{COONH}_4$ releases the easily soluble forms of these elements from the ash material. However, if we compare the extractable concentrations of elements in the ash fractions with their total concentrations determined using USEPA 3051 digestion [20], Cu in the bottom ash and S in the fly ash are the elements released most easily from the ash fractions by ammonium acetate extraction. The ratio of extractable Cu concentration in $\text{CH}_3\text{COONH}_4$ fraction in the bottom ash to its total concentration is 37.6%, while for S in the fly ash this ratio was 49.4%. According to ZEVENHOVEN-ONDERWATER et al [13], the elements leached out by ammonium acetate are also believed to be organically associated. Although the TOC values in the bottom and fly ash fractions are low (2%=2.0 mg/kg; d.w.; see Table 1), the release of elements bound to the organic matter of these residue is possible if the organic matter degrades.

Dilute hydrochloric acid (1 mol/L HCl) is one of the more common partial extractants used. It extracts labile metals, but has little effect on breaking up the silicate lattice and residual phase metals, hence leaving metals bound to these phases untouched [42]. Hydrochloric acid is in full dissociation, does not oxidize metals but forms chelated complexes with metals, especially with cadmium [40]. The use of HCl as extractant is reasonable, if we wish to determine the leachability of heavy metals in ash fraction under extremely acidic conditions. According to VAAJASAARI [8], naturally acidic lakes and humic waters in mires are examples of naturally acidic solutions in which the originally pH is lower than 5.3. Taking into account of the complexation of chloride anions with heavy metal ions, hydrochloride acid appears to be one of the most potential candidates for an effective lixiviant [43]. In our study, the extractable cadmium concentrations in bottom ash (<0.1 mg/kg; d.w.) and fly ash (1.4 mg/kg; d.w.) are very low, and thus our results are not consistent with the findings of SABIENE et al [40]. If we disregard elements whose concentrations are lower than the detection limits, the extractable concentrations of S (42 mg/kg; d.w. in the bottom ash and 190 mg/kg; d.w. in the fly ash) in the HCl fraction are lower than those in the $\text{CH}_3\text{COONH}_4$ or H_2O fraction. Furthermore, the extractable concentration of Mo (1.4 mg/kg; d.w.) in the HCl fraction is higher in the fly ash than that in the H_2O fraction. The extraction of labile metals from solid media is environmentally more meaningful than a total digestion [44]. The total element concentrations only represent a source term for the unrealistic environmental scenario in which the entire

mineral structure of the ash is dissolved [45]. For the bottom ash, the highest individual extractable element concentrations in the HCl fraction were observed for Fe (7700 mg/kg; d.w.), Ca (7490 mg/kg; d.w.), Al (7300 mg/kg; d.w.), Mg (3140 mg/kg; d.w.), K (3000 mg/kg; d.w.) and Na (2250 mg/kg; d.w.). For the fly ash, the extremely high extractable element concentrations in the HCl fraction were observed for Ca (69600 mg/kg; d.w.), Fe (40400 mg/kg; d.w.) and Al (22400 mg/kg; d.w.). However, if we compare the extractable concentrations of elements in the ash fractions with their total concentrations determined using USEPA 3051 digestion [20], titanium (Ti) in the bottom ash and Al in the fly ash are elements most easily released from the ash fractions using HCl extraction. The ratio of extractable Ti concentration in the HCl fraction in the bottom ash to its total concentration was 100%, while for Al in the fly ash this ratio was 80.9%. It is worth noting that several factors have been observed to affect on leaching of the ash material. These factors may be physical or chemical and those might be influenced due to biological or environmental changes. These factors and experimental errors are not possible to discuss in this context but were presented in Ref. [46].

4 Comparison with BCR extraction studies

One of the main commonly used sequential extraction procedures is that of the BCR (Community Bureau of Reference of the European Commission, now the Standards, Measuring and Testing Program) [42]. The BCR sequential extraction procedure allows the separation of extractable metals into three fractions, namely acid soluble (CH_3COOH), reducible ($\text{NH}_2\text{OH-HCl}$) and oxidizable ($\text{H}_2\text{O}_2/\text{CH}_3\text{COONH}_4$). If we compare the extractability of heavy metals in this study with those in our previous studies [47,48], in which the certain extraction stages followed the BCR extraction procedure, we notice that the BCR procedure released most of the heavy metals from the bottom and fly ash more effectively than the extraction procedure used in this study.

5 Conclusions

In order to assess the potential release of elements in the ashes under changing environmental conditions, the elements in ash fractions were extracted using a three-stage fractionation method for water-soluble (H_2O), ammonium-acetate ($\text{CH}_3\text{COONH}_4$) and hydrochloride acid (HCl) fractions. Except for Mo, S, Na and elements whose concentrations are lower than the detection limits, the extractable element concentrations in both ash fractions follow the order $\text{H}_2\text{O} < \text{CH}_3\text{COONH}_4 < \text{HCl}$. The

elements concentrations in this study are also lower than those in our previous studies in which certain extraction stages followed the BCR extraction procedure.

The water (H₂O) extraction most effectively released sulphur both from the bottom ash and fly ash. If we compare the extractable concentrations of elements in the ash fractions with their total concentrations determined using USEPA 3051 digestion, the ratio of extractable S concentration in H₂O fraction in the bottom ash to its total concentration was 18.5%, whereas in the fly ash it was 42.1%. Furthermore, Cu in the bottom ash (37.6%) and S (49.4%) in the fly ash was element most easily released from the ash fractions using CH₃COONH₄ extraction. From environmental perspective, when these ashes are disposed of in a landfill or utilized, the above-mentioned metals are most likely to be released from the ash fractions. The most effective extraction solution was 1 mol/L hydrochloric acid (HCl). The ratio of extractable Ti concentration in HCl fraction in the bottom ash to its total concentration was 100%, while for Al in the fly ash this ratio was 80.9%.

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化学分离法分析大型纸浆发电厂废渣中 生物质底灰和飞灰成分

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摘要: 采用三步分离法, 其中第一步用水, 第二步用乙酸铵, 第三步用盐酸, 提取纸浆发电厂生物质飞灰和底灰的组分, 以评估这些残渣的浸出行为。除了 Mo、S、Na 以及那些浓度低于检测范围的元素外, 在这两种灰份中, 对于其他元素这三种浸出剂的浸出能力从弱到强的顺序为: 水、乙酸铵和盐酸。采用三步分离法处理的废渣中元素浓度比前期用 BCR 连续提取法得到的低。

关键词: 灰份; 提取; 林业; 垃圾填埋; 浸出; 重金属; 废渣

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