

Comparison of the total and fractionated heavy metal and sulphur concentrations in bottom ash and fly ash from a large-sized (120 MW) power plant of a fluting board mill

Kati Manskinen¹,

Risto Pöykkiö^{2*},

Hannu Nurmesniemi³

¹ *Stora Enso Oyj,
Heinola Fluting Mill,
FI-18101 Heinola, Finland*

² *City of Kemi, Valtakatu 26,
FI-94100 Kemi, Finland*

³ *Stora Enso Oyj, Veitsiluoto Mill,
FI-94800 Kemi, Finland*

According to the XRD spectra, both ashes contained microcline ($K(AlSi_3O_8)$) and quartz (SiO_2). However, hematite (Fe_2O_3) and dolomite ($CaMg(CO_3)_2$) only existed in fly ash and bottom ash, respectively. The total element concentrations were 1.1 (Zn) to 45.1 (S) times higher in fly ash than those in bottom ash. According to three-stage sequential extraction procedure of the European Standards, Measurement and Testing (SM & T) Program (formerly the Community Bureau of Reference (BCR), in which elements in bottom ash and fly ash were fractionated among acid-soluble (CH_3COOH ; BCR 1), reducible ($NH_2OH-HCl$; BCR 2) and oxidizable ($H_2O_2 + CH_3COONH_4$; BCR 3) fractions, the concentrations of most elements were higher in all fractions of fly ash than those in bottom ash. However, in the BCR 1 fraction, the extractable concentrations of Al, Ba, Be, Cu, Fe, V and Zn, as well as of Fe and Zn in the BCR 3 fraction and Ti in all BCR fractions, were higher in bottom ash than the corresponding heavy metal concentrations in the fly ash. The results are discussed in relation to observations in the literature concerning heavy metals and sulphur release from a sample matrix under different extraction conditions.

Key words: ash, sequential extraction, heavy metals, leaching, waste

INTRODUCTION

Combustion via a bubbling fluidized bed boiler (BFB) is a widely used technology for energy recovery in the modern pulp and paper industry worldwide. The BFB is especially suitable for inhomogeneous fuels. Fluidized bed combustion technology is suitable for the co-combustion of various fuels, even those with a high moisture content. Although the incineration of pulp and paper mill residues using fluidized bed combustion is rapidly becoming the ultimate solution for the final disposal of wastes, the disadvantage of energy generation from solid fuels such as coal, peat and forest residues is that it produces a considerable amount of ash residue. Ash residue fractions such as bottom ash, which accumulates at the bottom of the fluidized bed boiler, and fly ash, which is collected from the flue gas by methods such as electrostatic precipitation, wet scrubbing, fabric filters, or a mechanical device such as a multicyclone or a baghouse,

constitute a major fraction of the solid residues produced by the power plants of pulp and paper mills. Elements with a low volatility are concentrated in bottom ash, while more volatile elements concentrate in fly ash. Consequently, individual ash fractions differ in their chemical composition [1–3].

During transport, disposal and storage, ash is most probably subjected to leaching by rainwater and comes into contact with other substances such as chlorides, sulphates, and organic matter that can form complexes with heavy metals [4, 5]. At landfills, pH is a major factor influencing metal mobility. Due to sulphide oxidation, microbial activity, the buffering capacity of natural waters, acidic deposition and atmospheric CO_2 , changes in the pH of ash may occur in a landfill environment which is the most common disposal option for ashes [6–8]. According to Li et al. [9], the pH of ash in landfills may drop to a value as low as 3 to 5. Due to the variety of processes occurring at landfills, which may affect the leachability of heavy metals in ash, various chemical extraction methods have been developed to predict the

* Corresponding author. E-mail: risto.poykio@kemi.fi

fractionation of heavy metals in wastes [10], since the total metal content is a poor indicator of metal bioavailability, mobility and toxicity [11]. The total element concentrations only represent a source term for the unrealistic environmental scenario in which the entire mineral structure of the solid material is dissolved. Measurement of the total concentration of metals provides relatively misleading information for assessing the possible bioavailability and mobility of metals. In order to estimate the bioavailability of metals and their potential toxicity, it is necessary not only to determine the total concentrations, but also the different forms or processes binding the heavy metals to the solid phase of a sample [9–11].

Extraction is a procedure that puts solids and a liquid in contact with each other under defined conditions. Extraction tests are widely used as tools to estimate the potential release of constituents from waste materials over a range of possible waste management activities, including recycling or reuse, in assessing the efficacy of waste treatment processes, and after disposal. Sequential extraction tests are being designed to treat test materials with different solutions, resulting in the allocation of constituents among separate fractions. Such an approach provides information on the chemical conditions needed to obtain different extraction efficiencies. In the sequential extraction procedure, chemical extractants of various types are applied to a sample, each successive treatment being more extreme than the previous one [10]. The goal of this method is to divide the total extractable concentration of metals into separate fractions in order to assess the form in which metals occur in waste material. Extraction studies are carried out on the assessment of worst-case environmental scenarios in which the components of a sample become soluble and mobile [10–13].

EXPERIMENTAL

Bottom and fly ash sampling procedures

Bottom ash and fly ash investigated in this study originated from a large-sized (120 MW) bubbling fluidized bed boiler (BFB) at the power plant of a fluting board mill located in Finland. The bubbling fluidized bed boiler started operating in 1984, and in 2007 the electrostatic precipitator was replaced with a new one and a flue gas cleaning scrubber was installed. Sampling was carried out over a period of 15 days, and six individual samples were combined to give one composite sample with a weight of 5 kg for the bottom ash and fly ash. The sampling period represented normal process operating conditions for the combustion plant in terms of O₂ content and temperature. During the sampling period, approximately 50% of the energy produced by the BFB originated from the incineration of commercial peat fuel, 25% from the incineration of coal, and 25% from the incineration of clean forest residues (i. e. bark, wood chips and sawdust). Approximately 85% of the forest residue consisted of clean bark from the mill wood handling process.

Approximately 95% of the barked wood comprised birch (*Betula verrucosa* and *B. pubescens*) trees, 4% was spruce (*Picea abies*) and 1% was alder (*Alnus insana* and *A. glutinosa*). The peat fuel originated near the fluting mill and was thus of domestic origin, while the coal originated from Russia.

Bottom ash was sampled from the outlet of the boiler. The electrostatic precipitator (ESP) at the power plant has three fields (i. e. electrodes), and in the current configuration of the plant's fly ash collected system, fly ash fractions from three fields of the ESP are collected and combined into one ash silo. Thus, the fly ash investigated in this study was a mixture from three fields of the ESP. The temperature in the BFB was ca. 900 °C and in the ESP ca. 150 °C. After sampling, the samples were stored in plastic bags in a refrigerator (+4 °C). The coning and quartering method [14] was repeatedly applied to reduce the ash sample to a size suitable for conducting laboratory analyses.

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

To determine the mineralogical composition of bottom ash and fly ash, X-ray diffractograms of powdered samples were obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuK α radiation. The scan was run from 5 to 80° (2-theta-scale), 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 ICDD PDF-2 Release 2006 software package (Pennsylvania, USA).

The pH of the ashes was determined with a pH/EC analyser equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium). The determination of pH was carried out according to the European standard SFS-EN 12880 at a solid- to-liquid (i. e. ultrapure water) ratio of 1 : 5. The determination of dry matter content in bottom ash and fly ash was carried out according to the European standard SFS-EN 12880. The organic matter content, as measured by the loss-on-ignition (LOI), was determined according to the European standard SFS-EN 12879 and the total organic carbon (TOC) content according to the European standard SFS-EN 13137. A comprehensive review of the standards, analytical methods, instrumentation and quality control is given elsewhere [15].

Determination of total heavy metal and sulphur concentrations in the ashes

For the determination of total element 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 the USEPA method 3051A [15]. The cooled solutions were transferred to 100 mL volumetric flasks and diluted to a volume with ultrapure

water. All reagents and acids were of suprapure or pro-analysis quality.

Except for Hg, the total element concentrations in bottom ash and fly ash were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). The concentration of Hg in the ashes was determined with a Perkin Elmer AAnalyst 700 cold-vapour atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler.

Sequential extraction partitioning of elements in the ashes and element determination in the extracts

For the partitioning of heavy metals and sulphur in bottom ash and fly ash between the exchangeable (CH_3COOH), easily reduced ($\text{NH}_2\text{OH-HCl}$ in nitric acid medium) and oxidiz-

able ($\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$) fractions, we used the three-stage sequential extraction procedure illustrated in Fig. 1. This extraction procedure was developed by the European Standards, Measurement and Testing (SM & T) Program, formerly the European Community Bureau of Reference (BCR) in an attempt to harmonize the different extraction schemes [16]. Although the harmonization project was launched as far back as in 1987 [17], in the literature this three-stage extraction procedure is still widely known as the BCR sequential extraction [17, 18].

Extraction was carried out by shaking 5 g of ash in a polypropylene bottle. In order to minimize possible chemical and / or microbiological changes in the material, the extraction was carried out using a sample as such, instead of a dried sample since, according to Kosson et al. [19], it is preferable to avoid sample drying before extraction. Af-

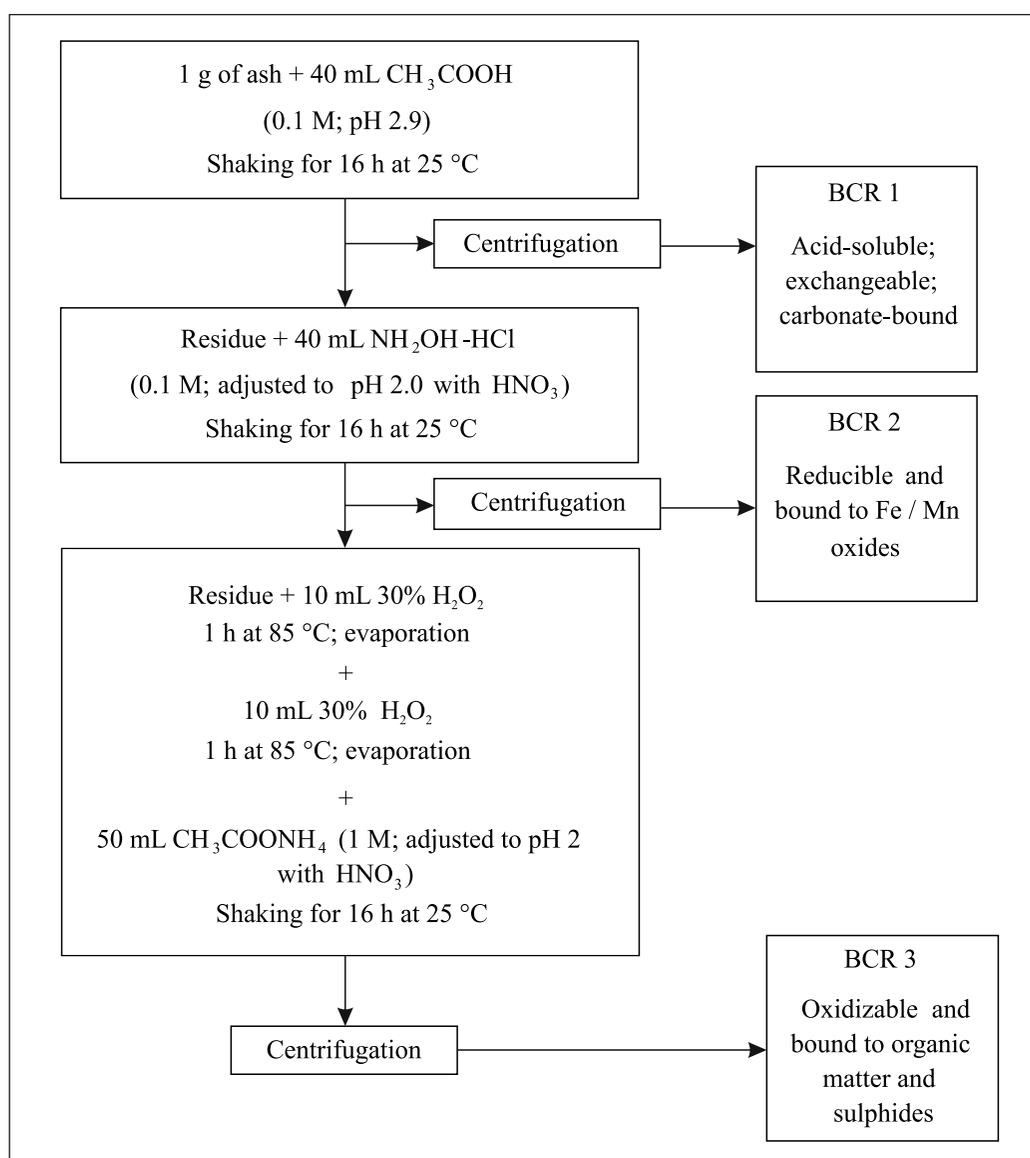


Fig. 1. Schematic diagram of the three-stage BCR extraction procedure for element partitioning between acid-soluble (BCR 1), reducible (BCR 2) and oxidizable (BCR 3) fractions [10, 13, 33]

ter 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 determinations. The element concentrations in the extracts (i. e. extraction stages 1–3) were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES).

RESULTS AND DISCUSSION

Mineral composition and physical and chemical properties of the ashes

The most important physical and chemical properties of the ashes are given in Table 1. Both ashes were strongly alkaline (pH 10.4–10.5). According to Van Herck and Vandecasteele [20], an alkaline pH indicates that part of the dissolved metals occur as basic metal salts, oxides, hydroxides and / or carbonates, as shown in the fly ash by the X-ray diffractogram. It is well known that the pH of ash from the combustion of forest residues is alkaline. However, the pH of ash resulting from the combustion of coal varies from 4.5 to 12.0, largely depending on the sulphur content of the parent coal [21]. According to Van Herck and Vandecasteele [20], if the proportion of soluble basic metal salts, oxides, hydroxides and carbonates in ashes outweighs the proportion of soluble acid components, the ashes subsequently generate an alkaline pH, as they did in our case.

The very low (<0.5 g/kg; d. w.) total organic carbon (TOC) value in the bottom ash indicates a complete combustion of organic matter in the fluidized bed boiler, which is reasonable because the incineration temperature in the fluidized bed boiler is ca. 900 °C. The very low (<0.5%; d. w.) loss-on-ignition value (LOI) in the bottom ash also supports this. The high LOI (15.6%; d. w.) and TOC (140 g/kg; d. w.) values in the fly ash indicate that this ash fraction contains both a volatile fraction and unburned organic material. In this context, it is worth noting that although LOI is widely used to indicate the unburned material in ash, according to the findings of Payá et al. [22], the LOI value rather indicates the volatile fractions. According to Ribbing [23], the LOI is not a good

method for measuring unburned material in ashes that contain chemically bonded water, e. g., in Ca(OH)₂ or CO₂ in the form of carbonates as CaCO₃, or chlorides and sulphur. Furthermore, it has been reported [24] that if fly ash includes significant quantities of volatile organic compounds (VOC), then LOI overestimates the amount of unburned carbon. Therefore, on the grounds of the above-mentioned finding, it is reasonable to expect that the high LOI (15.6%; d. w.) and TOC (140 g/kg; d. w.) values in the fly ash indicate the presence of both a volatile fraction and unburned organic material in this residue.

The dry matter content of the bottom ash was 94.0% and that of the fly ash 71.1%. The fly ash has a lower dry matter content because the residue is transferred from the electrostatic precipitator to the ash-collector silo and is watered in order to prevent dust problems. The XRD spectra in Fig. 2 (a, b) show the similarities and differences between the mineral composition of bottom ash and fly ash. Both ashes contained silicate minerals such as microcline (K(AlSi₃O₈)) and quartz (SiO₂), and their abundance in the ashes was relatively similar. However, hematite (Fe₂O₃), which is an oxide mineral, and dolomite (CaMg(CO₃)₂), which is a carbonate mineral, only existed in fly ash and in bottom ash, respectively. In this context, it is worth noting that although X-ray diffraction (XRD) analysis can be useful for identifying the chemical species of crystalline particles in ash, in our case only a few minerals as well as carbonates in the fly ash could be identified. An XRD spectrometer is unable to identify the amorphous (glass) phase (i. e. non-crystallised matter), and its detection limit is normally 1–2% (w/w). This is probably why crystalline compounds containing metals (Table 2) were not identified by XRD, despite the fact that the concentrations of these heavy metals could be quantitatively measured by ICP-OES.

The presence of silicate minerals in the bottom ash is reasonable when considering that the combustion bed material of fluidized bed boiler furnaces usually consists of silica sand. Furthermore, the existence of silicate minerals both in the bottom ash and fly ash fractions may also be partly due to sand and soil particle contamination of forest residues during harvesting, transportation and handling [6]. In addition, it may be partly derived from the decomposition of plant tissue-derived Si-based minerals during incineration, e. g., phytolith (SiO₂ × nH₂O) which is often a structural component of plant tissues deposited between and within plant cells [25].

Table 1. Physical and chemical properties of bottom ash and fly ash (n = 3)

Parameter	Unit	Bottom ash	Fly ash
pH (1 : 5)		10.4	10.5
Loss on ignition (LOI; 550 °C)	% (d. w.)	<0.5	15.6 ± 0.3
Total organic carbon (TOC)	g/kg (d. w.)	<0.5	140
Dry matter content (105 °C)	%	94.0 ± 0.2	71.1 ± 0.8
Electrical conductivity (EC; 1 : 2.5)	mS/cm	0.1	1.3

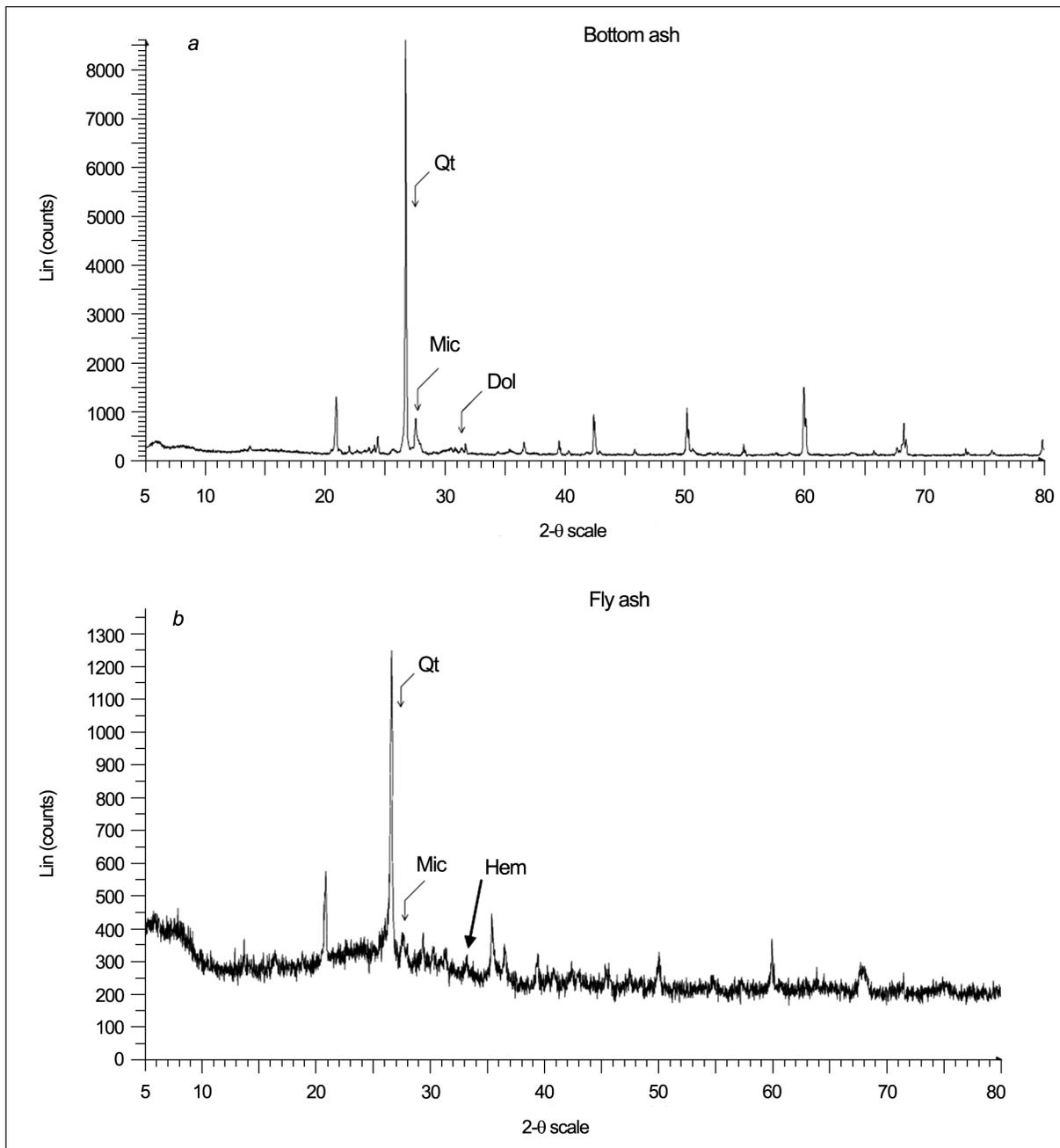


Fig. 2. XRD patterns for bottom ash and fly ash

Notes. 1. Mineral abbreviations and their abundances (%) are: 1) bottom ash: Dol = dolomite [$\text{CaMg}(\text{CO}_3)_2$; 2.3%]; Mic = microcline [KAlSi_3O_8 ; 20.7%]; Qt = quartz [SiO_2 ; 76.6%], 2) fly ash: Hem = hematite [Fe_2O_3 ; 3.4%]; Mic = microcline [KAlSi_3O_8 ; 22.9%]; Qt = quartz [SiO_2 ; 73.7%].

2. In measuring XRD spectra, a Cu tube, which energizes the X-rays of Fe in the ash, was used. Therefore, the background of XRD spectra in the figures is relatively high.

Total heavy metal and sulphur concentrations in the ashes
Table 2 presents the total concentrations of heavy metals and sulphur in the ashes. The total concentrations are expressed on a dry weight (d. w.) basis and as means of triplicate samples. However, the standard deviations are not given for all compounds, because the triplicate samples in some cases had exactly the same element concentrations. Table 2 also shows the enrichment factors (EF) for each element. The EF value is determined as the ratio of element concentrations in the

fly ash to those in the bottom ash. The total element concentrations were 1.1 (Zn) to 45.1 (S) times higher in the fly ash than those in the bottom ash. An elevated EF value indicates a high degree of element volatilization, whereas a low EF value is indicative of non-volatile behaviour under normal operating conditions and the formation of a heavier mineral phase [26]. The ratio of various elements between bottom ash and fly ash depends on the type of a boiler, the fuel mix and the efficiency of flue gas cleaning devices. The EF values for Cd,

Table 2. Total concentrations of elements in bottom ash and fly ash determined using USEPA 3051A ($n = 3$), as well as the enrichment factor (EF) of elements, the literature values [28] for the total concentrations (mg/kg; d. w.) of these elements in ashes from Finnish power plants incinerating coal or a mixture of forest residues and peat, and the literature values [29, 30] for the total concentrations (mg/kg; d. w.) of these elements in Finnish soil (fine till <0.06 mm)

Element	Total concentration, mg/kg; d. w.		EF ¹	Literature value for the total concentration mg/kg; d. w. in Finnish ashes	Literature value for the total concentration mg/kg; d. w. in Finnish soil (fine till <0.06 mm)
	Bottom ash	Fly ash			
Al	12200 ± 265	42 500 ± 2 088	3.5		
As	3.9 ± 0.1	46.9 ± 0.6	12.0	1.9–110	–139
Ba	215.7 ± 10.7	741.3 ± 14.4	3.4	170–1 800	400–900
Be	1.3 ± 0.1	4.4	3.4		
Cd	<3.0	1.7 ± 0.1	(>0.6)	0.06–100	0.01–0.90
Co	2.9 ± 0.2	15.7 ± 0.4	5.4		–30
Cr	10.9 ± 0.3	47.1 ± 1.8	4.3	12–200	5.0–300
Cu	16.9 ± 1.1	99.4 ± 0.7	5.9	13–220	2.0–126
Fe	8 380 ± 236	39 833 ± 643	4.8		
Mn	425.0 ± 3.6	977.3 ± 13.6	2.3		
Mo	<1.0	15.9 ± 0.6	(>15.9)	–100	–2.0
Ni	6.3 ± 0.2	45.5 ± 0.9	7.2	21–65	2.5–121
Pb	<3.0	46.3 ± 1.0	(>15.4)	2.3–310	0.1–24.7
S	59.4 ± 3.5	2 677 ± 91	45.1		
Sb	<4.0	< 4.0	n.d.	0.04–16	0.1–0.9
Se	<4.0	5.2 ± 0.5	(>1.3)	–20	
Ti	233.3 ± 23.1	1 203.3 ± 11.5	5.2		
V	16.4 ± 0.6	94.8 ± 3.3	5.8	–200	9.0–180
Zn	256.0 ± 6.2	274.7 ± 5.5	1.1	–10.000	6.9–400

¹ EF = total element concentration in the fly ash / total element concentration in the bottom ash.

Mo, Pb and Se are given in parentheses, because the concentrations of these elements in the bottom ash were below the detection limit. The enrichment of elements in fly ash is due to the fact that the temperature of the fluidized bed boiler (900 °C) is high enough to vaporize some elements. In addition to the element volatilization characteristics, element retention in fly ash through other processes (primarily the condensation process) determines the final fate of volatilizable elements [27].

Most of these species form compounds that condense on the surface of particles in the flue gas, leading to the enrichment of some elements in the fly ash fraction. Since this phenomenon is well known and reported elsewhere [26, 27], and as the ratio of various elements between bottom ash and fly ash depends, for instance, on the type of boiler, operating conditions, the fuel mix and the efficiency of flue gas cleaning devices [1, 3], we do not focus on it in the present context. If we compare our total concentrations of heavy metals in bottom ash and fly ash to those reported in the literature [28], our observations for total concentrations are in relatively good agreement with the concentrations of these compounds in ashes from Finnish power plants. Furthermore, except for Cd (1.7 mg/kg; d. w.), Mo (15.9 mg/kg; d. w.) and Pb (46.3 mg/kg; d. w.) in the fly ash, the total concentrations of other elements in the ashes agree relatively well with those in Finnish soil (i. e. fine till <0.06 mm) reported in the literature [29, 30] and for many elements were lower

than the maximum element concentrations reported in the literature.

Partitioning of heavy metals and sulphur in the ashes

If inorganic materials and by-products such as ash are disposed off in landfills or utilized as an earth construction agent, low heavy metal concentrations and the tight binding of element to the matrix are favourable [31]. When the sequential extraction procedure is applied in the fractionation of heavy metals in environmental samples, the ability of different extraction agents to release metal ions depends on their association with specific fractions in a 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 [32]. Thus, consecutive extraction techniques allow us to obtain information about the mobility and thus the bio-availability of major and trace elements under different environmental conditions, such as acidic, alkaline, oxidizing or reducing, or the action of a chelating agent [10, 12].

The distribution of heavy metals and sulphur in bottom ash and fly ash after three-stage BCR extraction (leaching) between acid-soluble (CH_3COOH), reducible ($\text{NH}_2\text{OH-HCl}$ in nitric acid medium) and oxidizable ($\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$) fractions is presented in Table 3. This extraction procedure is widely used for partitioning metals in ashes [10, 13, 33].

Table 3. Extractable concentrations of elements in acid-soluble (BCR 1), reducible (BCR 2) and oxidizable (BCR 3) fractions (n = 1), as well as the sum (i. e. Σ 1–3) of fractions BCR 1, BCR 2 and BCR 3

Element	Extractable concentration mg/kg; d. w. in bottom ash				Extractable concentration mg/kg; d. w. in fly ash			
	BCR 1	BCR 2	BCR 3	Σ (1–3)	BCR 1	BCR 2	BCR 3	Σ (1–3)
Al	3 410	3 770	2 000	9 180	1 490	5 150	7 310	13 950
As	1.3	2.2	0.6	4.1	1.3	16.5	6.3	24.1
Ba	52.9	65.4	56.9	175.2	33.0	234	312	579
Be	0.8	0.2	<0.3	(<1.3)	0.4	0.9	1.0	2.3
Cd	<0.1	<0.1	<0.1	(<0.3)	0.8	0.2	0.2	1.2
Co	0.4	< 0.1	0.6	(<1.1)	1.4	1.1	1.6	4.1
Cr	<0.4	0.5	3.0	(<3.9)	1.7	2.3	3.8	7.8
Cu	3.8	2.3	2.6	8.7	1.9	2.6	26.2	30.7
Fe	360	1 070	1 930	3 360	48.9	3 360	1 720	5 129
Mn	80.7	58.6	124	263.3	152	166	174	492
Mo	<0.2	<0.2	< 0.3	(<0.7)	0.5	0.3	5.2	6.0
Ni	<0.2	<0.2	1.7	(<2.1)	3.3	2.1	4.4	9.8
Pb	<0.6	<0.6	< 0.8	(<2.0)	< 0.6	1.3	10.7	(<12.6)
S	32.0	1.2	7.3	40.5	2 090	183	252	2 525
Sb	<0.6	<0.6	< 0.8	(<2.0)	< 0.6	< 0.6	< 0.8	(<2.0)
Se	<0.8	<0.8	< 1.0	(<2.6)	< 0.8	< 0.8	2.2	(<3.8)
Ti	2.0	5.2	44.2	51.4	0.8	1.9	2.4	5.1
V	1.6	9.7	2.8	14.1	0.9	23.2	25.9	50.0
Zn	74.3	26.3	27.2	127.8	30.9	29.6	25.7	86.2

The acid-soluble fraction (i. e. BCR 1 fraction), extractable with acetic acid (CH_3COOH), gives an indication of the amount of metals bound on the surface of the particles, as well as the metals that are released as acid-soluble salts such as carbonates [16, 33]. This fraction is potentially bioavailable and corresponds to the form of metals that is most available for plant uptake, and can be released by merely changing the ionic strength of the medium [10]. The use of acetic acid as a leachant emulates the organic acids produced from decomposing waste in anaerobic environments such as landfills, since in the acetogenesis phase during the anaerobic degradation of organic matter, carboxylic acids (e. g., acetic acid), volatile fatty acids and ethanol are produced and transformed into acetate, carbon dioxide and hydrogen by acidogenic bacteria. Thus, the elevated concentrations of elements in this fraction may be due to the complexing ability of the monodentate organic ligand of the acetate [34, 35]. The use of acetic acid as a leachant has been questioned because it does not occur in nature. However, according to Svensson et al. [36], acetic acid is a realistic choice to simulate a plausible worst-case scenario for waste material co-disposed with municipal solid waste.

In real-world leaching scenarios, the pH of ashes originating from the power plants of pulp mills is very alkaline (pH ~10–12.5), and the ashes have a very high acid-neutralizing capacity. However, in the long term, the acid neutralizing capacity of ash in a landfill decreases [9]. Thus, ash disposal at landfill sites may cause contaminant release into the environment as the pH decreases, even though it has been demonstrated that many types of ash are likely to

maintain alkaline pH values for very long periods of time, e. g., for many thousands of years [8]. Therefore, this fraction also indicates the proportion of elements that are capable of being released from the matrix into the environment if the conditions become acidic [37]. According to the results in Table 3, the greatest differences in the solubility of metals between bottom ash and fly ash in the acid-soluble fraction (BCR 1 fraction) were found for Al and S. The extractable concentration of Al in the bottom ash (3 410 mg/kg; d. w.) was ca. 2.3 times higher than that in the fly ash (1 490 mg/kg; d. w.), whereas the extractability of S (32.0 mg/kg; d. w.) in the bottom ash was clearly lower than that in the fly ash (2 090 mg/kg; d. w.). Although the exact reason for the different release of metals from ashes is unknown, according to Ludwig et al. [38], the release of metals from ash depends on the chemical characteristics of ash materials in terms of form and solubility. Heavy metals may be present as soluble or moderately soluble phases but trapped in materials that need dissolution, such as carbonates and oxides which, when dissolved by acid, release soluble phases. The solubility of heavy metals may not be directly related to the input of protons, but protons are required to dissolve the surface cover. For example, heavy metals could be present as carbonates, oxides or hydroxides, or as surface complexes, sorbed to oxides or hydroxide minerals in the ash matrix. Although the XRD spectra in Fig. 2 (a, b) are not able to clarify the differences in the composition of Al- and S-bearing minerals in bottom ash and fly ash, the observations of Ludwig et al. [38] could provide reasons for the different solubility of Al and S in our ashes.

The reducible fraction (i. e. BCR 2 fraction), extractable with a strong reducing agent consisting of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in a nitric acid medium, simulates anoxic conditions that are likely to occur in a natural medium [10, 39]. According to Sabbas et al. [40], under disposal conditions, redox reactions can occur as a result of microbiologically mediated processes due to the presence of organic matter or abiotic transformations leading to the formation of reducing gases (H_2). For bottom ash monofills, the presence of unburned organic material and H_2 generally leads to reducing conditions. According to Sabbas et al. [40], abiotic gas is produced in the presence of water by the chemical oxidation of elemental metals, including Al, Fe and Cu. Due to its high solubility in alkaline conditions ($\text{pH} > 9.5$), aluminium is regarded as the main element responsible for abiotic gas production at landfill sites. This is due to the alkaline nature of ash, which alters the glassy phases so that aluminium particles come into contact with hydration water, although a significant number of ash particles are enclosed in glassy phases formed during incineration which act as a barrier against the reaction between water and aluminium [40]. However, in a well-constructed landfill with a top layer, no oxygen or surface water will be available below the top-most layer. Thus, heavy-metal leaching might be slightly affected by an influx of surface water and of oxygen. Leachates consisting of various types of dissolved organic matter and inorganic salts are the only carriers of heavy metal migration in landfill sites [37].

The use of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in a nitric acid medium as an extractant for this fraction influences the complexation of metals with chloride [5]. This fraction also represents the content of metals bound to iron and manganese oxides that would be released if the substrate was subjected to reductive conditions [37, 39]. The Fe and Mn oxides act as "cement" or are present as nodules between the particles or coating them. The elements are strongly bound to these oxides but are thermodynamically unstable in anoxic conditions. The metals in this fraction can be mobilised by increasing the reducing or oxidising conditions in the environment, which means that they are potentially bioavailable [10]. According to the results presented in Table 3, the differences in the extractability of metals between bottom ash and fly ash in this fraction were greatest for Al, Ba, Fe, Mn, S and V. The extractability of these elements was 1.4 (Al) to 153 (S) times higher in fly ash than in bottom ash. As the hydrous oxides of manganese and iron are extracted in this fraction [10], the differences in the extractability of heavy metals and sulphur indicate the different binding of elements to these minerals, although hematite (Fe_2O_3) was the only iron oxide observed in the XRD data of the fly ash.

The oxidizable fraction (i. e. BCR 3 fraction), in which a combination of H_2O_2 / $\text{CH}_3\text{COONH}_4$ is used for extraction, corresponds to the metals that are organically bound or occur as oxidizable minerals, e. g., sulphides [10, 37]. As metals bound to this fraction can be released under oxidising

conditions, an oxidation process is usually applied to extract metals associated with the above-mentioned phase. Hydrogen peroxide (H_2O_2), which is used as an oxidising reagent in this fraction, is a strong oxidant. In general, hydrogen peroxide applied to a heated medium (i. e. 85°C) is the preferred reagent for dissolving organic matter as a compromise between the complete degradation of organic matter and the minimum alteration of silicates. Heating promotes the oxidation process [10]. Furthermore, hydrogen peroxide also oxidises sulphides to sulphates [41]. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions [42].

The low total organic carbon (TOC) value (< 0.5 g/kg; d. w.) of the bottom ash indicates that the amount of organic matter in this residue is relatively low (Table 1). It is therefore not very likely that the degradation of organic matter under oxidizing conditions could lead to a significant release of the metals bound to these organic components of the bottom ash. Due to the high TOC value (140 mg/kg; d. w.) in the fly ash, the release of metals and sulphur bound to the organic matter of this residue is possible, if conditions become oxidative and the organic matter degrades. However, according to Smichowski et al. [43], the organic fraction released in the oxidizable step is not considered to be very mobile or easily available. Except for Ti and Zn, the extractable concentrations for most of the metals were higher in fly ash than those in bottom ash. As sulphides are extracted in this fraction, the clearly higher sulphur concentration in the extract of fly ash (252 mg/kg; d. w.) compared to that of the bottom ash (7.3 mg/kg; d. w.) is reasonable and consistent with the higher total sulphur concentration in fly ash (2 677 mg/kg; d. w.) than that in bottom ash (59.4 mg/kg; d. w.).

CONCLUSIONS

Both bottom and fly ashes were strongly alkaline ($\text{pH} 10.4\text{--}10.5$). The very low (< 0.5 g/kg; d.w.) total organic carbon (TOC) and loss on ignition value (LOI) values in the bottom ash indicate the complete combustion of organic matter of this fraction in the fluidized bed boiler. The LOI (15.6%; d. w.) and TOC (140 g/kg; d. w.) values in the fly ash indicate that it contains both a volatile fraction and unburned organic matter. According to the extraction of elements by acetic acid (CH_3COOH), the extractable concentration of Al in the bottom ash (3 410 mg/kg; d. w.) was ca. 2.3 times higher than in the fly ash (1 490 mg/kg; d. w.), whereas the extractability of S (32.0 mg/kg; d. w.) in the bottom ash was clearly lower than in the fly ash (2 090 mg/kg; d. w.). According to the extraction of elements by hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in a nitric acid medium, the differences in the extractability of metals between bottom ash and fly ash in this fraction were greatest for Al, Ba, Fe, Mn, S and V. The extractability of these elements was 1.4 (Al)

to 153 (S) times higher in fly ash than in bottom ash. According to the extraction of elements with a combination of $\text{H}_2\text{O}_2 / \text{CH}_3\text{COONH}_4$, the extractable concentrations of Ti and Zn were higher in bottom ash than in fly ash. However, except for those elements with concentrations below the limit of quantitation, the extractable concentrations of other elements were higher in fly ash than in bottom ash. As sulphides are extracted in this fraction, the clearly higher sulphur concentration in the extract of fly ash (252 mg/kg; d. w.) compared with that of bottom ash (7.3 mg/kg; d. w.) is reasonable and consistent with the higher total sulphur concentration in fly ash (2 677 mg/kg; d. w.) than in bottom ash (59.4 mg/kg; d. w.).

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Kati Manskinen, Risto Pöykiö, Hannu Nurmesniemi

**VISUMINĖS IR FRAKCIONUOTOS SUNKIŲJŲ
METALŲ IR SIEROS KONCENTRACIJŲ Paly-
ginimas didelės galios (120 MW) jėgainės
nuosėdiniuose ir lakiuose pelenuose**

S a n t r a u k a

Abiejų rūšių pelenuose rasta mikrokline ($K(AlSi_3O_8)$) ir kvarco (SiO_2). Lakiuose pelenuose rasta hematito (Fe_2O_3), o nuosėdiniuose – dolomito ($CaMg(CO_3)_2$). Visuminė elementų koncentracija lakiuose pelenuose yra didesnė nei nuosėdiniuose. Atitinkamas koncentracijų santykis kinta nuo 1,1 (cinkui) iki 45,1 (sierai).