

# Release of Elements in Bottom Ash and Fly Ash from Incineration of Peat- and Wood-Residues using a Sequential Extraction Procedure

Risto Poykio, Kati Manskinen, Olli Dahl, Mikko Mäkelä, and Hannu Nurmesniemi

**Abstract**—When the results of the total element concentrations using USEPA method 3051A are compared to the sequential extraction analyses (i.e. the sum of fractions BCR1, BCR2 and BRC3), it can be calculated that the recovery values of elements varied between 56.8-% and 69.4-% in the bottom ash, and between 11.3-% and 70.9-% in the fly ash. This indicates that most of the elements in the ashes do not occur as readily soluble forms.

**Keywords**—Ash, BCR, leaching, solubility, waste

## I. INTRODUCTION

FROM an environmental point of view, it is not the total element concentrations in waste, sludge and other residues such as ash, which are of prime importance, but rather how easily the metals are mobilized in the environment. In order to estimate the bioavailability of elements and their potential mobility, it is necessary not only to determine the total concentrations, but also the different forms or the processes binding the elements to the solid phase of a sample [1-4].

Extraction is a procedure that puts solid and 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 [5-6]. The general principle applied in landfill approval or in the recycling and reuse of materials is that the composition and extractability of waste have to be known. Extraction tests are carried out in the assessment of worst-case environmental scenarios, in which the components of the sample become soluble and mobile.

Sequential extraction procedures apply various successive extractions on a sample with an aim to divide the total extractable concentration of an element into separate fractions to assess the potential forms in which the element occurs in the matrix [5]. Although time consuming, the use of a

sequential extraction procedure is generally a good compromise for attaining information on the risk of environmental contamination in support of environmental policy [7-8].

## II. EXPERIMENTAL

### A. Bottom and fly ash sampling procedures

The bottom ash and fly ash investigated in this study originated from a large-sized (120 MW) bubbling fluidized bed (BFB) boiler at the power plant of a fluting board mill located in Finland [9]. Sampling of a bottom ash and fly ash was carried out over a period of fifteen days. During this period, a total of six sub-samples for both ashes were collected. The six individual sub-samples for both ashes 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 O<sub>2</sub> content and temperature. During the sampling period when bottom ash and fly ash were sampled, approximately 50-% of energy produced by the BFB boiler originated from the incineration of commercial peat fuel, and 50-% from the incineration of clean wood residues (i.e. bark, wood chips and sawdust). Approximately 74-% of the forest residue consisted of clean bark from the wood handling process of the mill. Approximately 98-% of the barked wood comprised birch (*Betula verrucosa* and *B. pubescens*), and 2-% was alder (*Alnus incana* and *A. glutinosa*). The peat fuel originated from near the fluting mill, and was thus of domestic origin.

### B. Determination of the mineral composition and physical and chemical properties of the ashes

For the determination of 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 CuK $\alpha$  radiation. The scan was run from 5 to 80° (2-theta-scale), with increments of 0.02° and a counting time of 1.0 seconds 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 by a pH/EC analyser 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-

Risto Pöykio (Ph.D.) is with the city of Kemi, FI-94100 Kemi, Finland (corresponding author to provide phone: +358-16-259 673; fax: +358-16-259 481; e-mail: risto.poykio@kemi.fi).

Kati Manskinen (M.Sc.) is with the Stora Enso Oyj Heinola Fluting Mill, FI-18101 Heinola, Finland (e-mail: kati.manskinen@storaenso.com).

Olli Dahl (Professor) is with the Aalto University, Department of Forest Products Technology, School of Chemical Technology, Aalto FI-00076, Finland (e-mail: olli.dahl@aalto.fi).

Mikko Mäkelä (M.Sc.) is with the Aalto University, Department of Forest Products Technology, School of Chemical Technology, Aalto FI-00076, Finland (e-mail: mikko.makela@aalto.fi).

Hannu Nurmesniemi (Ph.D.) is with the Stora Enso Oyj Veitsiluoto Mill, FI-94800 Kemi, Finland (e-mail: hannu.nurmesniemi@storaenso.com).

liquid (i.e. ultrapure water) ratio of 1:5. Determination of the dry matter content of the bottom ash and fly ash was carried out according to European standard SFS-EN 12880. 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 according to European standard SFS-EN 13137. A comprehensive review of the standards, analytical methods, instrumentation and quality control is given in our previous paper [10].

#### *C. Determination of total element 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 HNO<sub>3</sub> (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 [11]. The cooled solutions were transferred to 100 mL volumetric flasks and the solutions were diluted to volume with ultrapure water. All reagents and acids were suprapure or pro analysis quality.

Except for Hg, the total element concentrations in the 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.

#### *D. Procedure for determining the extractability of elements in the ashes and element determination in the extracts*

For the partitioning of elements in the bottom ash and fly ash between the exchangeable (CH<sub>3</sub>COOH), easily reduced (NH<sub>2</sub>OH-HCl in nitric acid medium) and oxidisable (H<sub>2</sub>O<sub>2</sub> + CH<sub>3</sub>COONH<sub>4</sub>) fractions, three-stage sequential extraction procedure was used. This extraction procedure, which schematic diagram is illustrated in Pöykiö et al. [10], is widely used for the partitioning of elements in ash [5-6]. In the literature, this three-stage extraction is widely known as "BCR sequential extraction". Therefore, in this manuscript, we have used the abbreviations "BCR1" for the exchangeable (CH<sub>3</sub>COOH) fraction, "BCR2" for the easily reduced (NH<sub>2</sub>OH-HCl in nitric acid medium) fraction and "BCR3" for the oxidisable (H<sub>2</sub>O<sub>2</sub> + CH<sub>3</sub>COONH<sub>4</sub>) fraction.

The sequential extraction was carried out by shaking 5 g of the ash in a polypropylene bottle. In order to minimize possible chemical and/or microbiological changes in the material, the extraction was carried out using the sample as such, instead of a dried sample, since according to Kosson et al. [12], it is preferable to avoid sample drying before extraction. 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 % HNO<sub>3</sub> 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).

### III. RESULTS AND DISCUSSION

#### *A. Mineral composition and physical and chemical properties of the ashes*

According to the XRD-based mineralogy [13], the bottom ash contained only silicate minerals (i.e. anorthite, magnesiohornblende, microcline and quartz). The fly ash contained anorthite, microcline and quartz, but also biotite, which is a silicate mineral, as well as hematite, which is an oxide mineral. The existence of Ca-based minerals in the form of anorthite, magnesiohornblende and anorthite in the ashes is reasonable due to the content of calcium naturally occurring in wood residue [14]. Wood residues were one fuel in this study. In this context it is notable that the acidic ammonium acetate (NH<sub>4</sub>Ac) extractable calcium concentrations in the bottom and fly ash were 10033 mg/kg (d.w.) and 54333 mg/kg (d.w.), respectively [13]. The existence of silicate minerals in the bottom ash is reasonable when considering that the bed material of fluidized bed boiler furnaces usually consists of silica sand. Furthermore, the existence of silicate minerals both in the bottom and fly ash fractions may also partly due to the sand and soil particle contamination of forest residues during harvesting transportation and handling [15]. In addition, it may partly derive from the decomposition of plant tissue-derived Si-based minerals during incineration, such as phytolith (SiO<sub>2</sub> × nH<sub>2</sub>O), which is often a structural component of plant tissue, deposited between and within plant cells [16]. According to Vamvuka and Kakaras [14], hematite could be produced from oxidation of organic iron or siderite during the combustion process.

#### *B. Total element concentrations in the ashes*

Table I and II present the total and extractable concentrations of elements in the bottom and fly ash, respectively. The concentrations of elements were significantly higher in the fly ash than those in the bottom ash. If we disregard the elements whose concentrations were lower than the detection limits, the total element concentrations in the fly ash were within 1.9 (Zn) and 9.3 (Fe) times higher than those in the bottom ash.

TABLE I  
TOTAL AND EXTRACTABLE ELEMENT CONCENTRATIONS (MG/KG; DRY WEIGHT) IN THE BOTTOM ASH

Element	Total	BCR1	BCR2	BCR3
Al	12733	2820	2230	2880
As	< 3.0	< 0.6	< 0.6	< 0.8
Ba	262	80.5	30.2	71.0
Be	< 1.0	< 0.2	< 0.2	< 0.3
Cd	< 0.3	< 0.08	< 0.08	< 0.1
Co	2.3	0.51	< 0.12	0.2
Cr	10.8	< 0.4	< 0.4	1.7
Cu	12.2	2.8	1.3	2.8
Fe	7633	477	812	420
Mn	492	134	65.1	91.7
Mo	< 1.0	< 0.2	< 0.2	< 0.3
Ni	6.3	0.3	< 0.2	0.3
Pb	< 3.0	< 0.6	< 0.6	< 0.8
Sb	< 4.0	< 0.6	< 0.6	< 0.8
Se	< 4.0	< 0.8	< 0.8	< 1.0
V	8.8	0.7	2.7	1.6
Zn	348	151	28.8	20.1

TABLE II  
TOTAL AND EXTRACTABLE ELEMENT CONCENTRATIONS (MG/KG; DRY WEIGHT) IN THE FLY ASH

Element	Total	BCR1	BCR2	BCR3
Al	35333	730	1930	10500
As	41	< 0.6	< 0.6	2.6
Ba	802	12.7	143	413
Be	2.0	< 0.2	0.4	0.9
Cd	3.0	1.3	0.4	0.3
Co	18	2.6	0.8	1.2
Cr	53	0.7	0.7	4.6
Cu	98	2.4	2.2	28.3
Fe	71167	48.0	3330	2960
Mn	2383	373	301	313
Mo	12	0.5	< 0.2	1.7
Ni	57	5.0	1.5	2.4
Pb	33	< 0.6	0.6	8.2
Sb	< 4.0	< 0.6	< 0.6	< 0.8
Se	6.0	< 0.8	< 0.8	4.1
V	81	< 0.4	15.3	17.2
Zn	671	120	51.4	62.2

Note:

Total = USEPA method 3051A

BCR1 = Acid soluble, extractable and carbonate bound

BCR2 = Reducible and bound to Fe/Mn oxides

BCR3 = Oxidisable and bound to organic matter and sulphides

The enrichment of elements in the fly ash is due to the fact that the temperature of the BFB boiler (900 °C) is high enough to vaporize some elements. In addition to the element volatilization characteristics, element retention in fly ash through other process (i.e. primarily the condensation process) determines the final fate of volatilizable elements. 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. Consequently, the bottom ash has an enhanced content of non-volatile components, and frequently contains of melted particles [17]. Since this phenomenon is well known and has been reported elsewhere [17-18], 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.

#### *C. Release of elements in the ashes using a three-stage sequential extraction procedure*

If inorganic materials and by-products such as ash are disposed of in landfills, or used as an earth construction agent, low metal concentrations and the tight binding of element to the matrix are favourable. However, in this context it is worth mentioning that both ashes were strongly alkaline (i.e. bottom ash pH 11.3; fly ash pH 12.0). Furthermore, the dry matter content of both ashes were very high (i.e. bottom ash 92.0%; fly ash 74.8%; see reference 13). This is a disadvantage and dermal contact with these residues should be avoided during disposal or utilization, since according to Mroueh et al. [19], the alkaline nature of the ash may cause skin irritation.

When the sequential extraction procedure is applied for 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 [20]. Thus, 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 the action of chelating agent [5]. However, according to Ludwig et al. [21], the pattern of elements release from ash depends not only on the extraction method and the type of extractant used, but also on the element, the type of matrix and the chemical and mineralogical characteristics of the ash material.

The distribution of elements in the bottom ash and fly ash after three-stage BCR extraction (leaching) between acid soluble ( $\text{CH}_3\text{COOH}$ ), reducible ( $\text{NH}_2\text{OH}\cdot\text{HCl}$  in nitric acid medium) and oxidisable ( $\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$ ) fractions are presented in Table I and II. The BCR1 fraction, which is the fraction after extraction with a weak extractant (i.e.  $\text{CH}_3\text{COOH}$ ) releases acid-soluble, exchangeable and carbonate-bound elements from the matrix (i.e. ash). These metals are usually bound on the surface of the ash particles by relatively weak electrostatic interactions and are thus potentially bioavailable [5]. This fraction corresponds to the form of metals that is most available for plant uptake [22], and can be released by merely changing the ionic strength of the medium [5]. The use of acetic acid as a leachant emulates the organic acids produced from decomposing waste in anaerobic environments such as actively decomposing 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 [23-25]. The use of acetic acid as leachant has been questioned, because it does not occur in nature. However, according to [26], acetic acid is a realistic choice to simulate a plausible worst-case scenario for waste material co-disposed with municipal solid waste. Thus, the elevated concentrations of elements in this fraction may be due to the complexing ability of the mono-dentate organic ligand of acetate [24]. If we disregard elements whose concentrations were lower than the detection limits, only the extractable concentrations of Al (2820 mg/kg; d.w.), Ba (80.5 mg/kg; d.w.), Cu (2.8 mg/kg; d.w.), Fe (477 mg/kg; d.w.) and Zn (151 mg/kg; d.w.) in the bottom ash were higher in the bottom ash than those in the fly ash.

The BCR2 fraction, which is the fraction after extraction with a reducing agent consisting of hydroxylamine hydrochloride (NH<sub>2</sub>OH-HCl) in a nitric acid medium, simulates anoxic conditions that are likely to occur in a natural medium [27]. The use of NH<sub>2</sub>OH-HCl 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 [28]. If we disregard elements whose concentrations were lower than the detection limits, and Al (2230 mg/kg; d.w.), the extractable concentrations of other elements in the bottom ash were lower than those in the fly ash.

The BCR3 fraction, which is the fraction after extraction with a combination of H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>COONH<sub>4</sub>, corresponds to metals that are organically bound or occur as oxidisable minerals, e.g. sulphides. 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<sub>2</sub>O<sub>2</sub>), 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 [5]. Furthermore, hydrogen peroxide also oxidises sulphides to sulphates [27]. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions, although ammonium acetate is a weak extractant [29]. Due to the relatively high TOC value of 97.0 mg/kg (d.w.) in the fly ash [see ref. 13], the release of elements 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. [30], the organic fraction released in the oxidisable step is not considered to be very mobile or available. If we disregard elements whose concentrations were lower than the detection limits, all the extractable concentrations of elements in the bottom ash were lower than those in the fly ash.

When the results of the total element concentrations using USEPA method 3051A are compared to the sequential extraction analyses (i.e. the sum of fractions BCR1, BCR2 and BCR3), it can be calculated that the recovery values of elements varied between 56.8-% and 69.4-% in the bottom ash, and between 11.3-% and 70.9-% in the fly ash (note: the elements whose concentrations were lower than the detection limits were disregarded in this calculation). This indicates that most of the elements in the ashes do not occur as readily soluble forms.

#### IV. CONCLUSION

The concentrations of elements were significantly higher in the fly ash than those in the bottom ash. If we disregard the elements whose concentrations were lower than the detection limits, the total element concentrations in the fly ash were within 1.9 (Zn) and 9.3 (Fe) times higher than those in the bottom ash. The enrichment of elements in the fly ash is due to the fact that the temperature of the BFB boiler (900 °C) is high enough to vaporize some elements.

According to a three-stage sequential extraction procedure, in which elements in the bottom ash and fly ash were fractionated between acid-soluble (CH<sub>3</sub>COOH), reducible (NH<sub>2</sub>OH-HCl) and oxidisable (H<sub>2</sub>O<sub>2</sub> + CH<sub>3</sub>COONH<sub>4</sub>) fractions, the concentrations of most elements were higher in all fractions of the fly ash than those in the bottom ash. If we disregard elements whose concentrations were lower than the detection limits and cadmium, only the extractable concentrations of Al (2820 mg/kg; d.w.), Cu (2.8 mg/kg; d.w.) and Fe (477 mg/kg; d.w.) in the bottom ash were higher than those in the fly ash. However, in the bottom ash, the extractable concentration of Al (2820 mg/kg; d.w.), Cu (2.8 mg/kg; d.w.) and Fe (477 mg/kg; d.w.) in the acid-soluble fraction (CH<sub>3</sub>COOH) were higher than those in the fly ash.

When the results of the total element concentrations using USEPA method 3051A are compared to the sequential extraction analyses, the recovery values of elements varied between 56.8-% and 69.4-% in the bottom ash, and between 11.3-% and 70.9-% in the fly ash. This indicates that most of the elements in the ashes do not occur as readily soluble forms.

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