Extractable Heavy Metal Concentrations in Bottom Ash from Incineration of Wood-Based Residues in a BFB Boiler Using Artificial Sweat and Gastric Fluids

Risto Pöykiö, Olli Dahl, Hannu Nurmesniemi

Abstract—The highest extractable concentration in the artificial sweat fluid was observed for Ba (120mg/kg; d.w.). The highest extractable concentration in the artificial gastric fluid was observed for Al (9030mg/kg; d.w.). Furthermore, the extractable concentrations of Ba (550mg/kg; d.w.) and Zn (400mg/kg: d.w.) in the bottom ash using artificial gastric fluid were elevated. The extractable concentrations of all heavy metals in the artificial gastric fluid were higher than those in the artificial sweat fluid. These results are reasonable in the light of the fact that the pH of the artificial gastric fluid was extremely acidic both before (pH 1.54) and after (pH 1.94) extraction, whereas the pH of the artificial sweat fluid was slightly alkaline before (pH 6.50) and after extraction (pH 8.51).

Keywords—Ash, artificial fluid, heavy metals, *in vitro*, waste.

I. INTRODUCTION

COMBUSTION via a bubbling fluidized bed (BFB) boiler is a widely used technology for energy recovery in the modern pulp and paper industry worldwide. The BFB boiler is especially suitable for inhomogeneous fuels. Fluidized bed combustion technology enables the co-combustion of various fuels even fuels with high moisture contents. Although the incineration of pulp and paper mill residues using fluidized bed combustion is rapidly becoming the ultimate solution for the final disposal of organic wastes, one disadvantage of energy generation from biomass 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. In vitro extraction tests [1] involving synthetic sweat, synthetic gastric/gastrointestinal and synthetic saliva fluids, are widely used for testing of metal release from consumer products such as textile [2] and artificial (polyethylene) turf

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[3] materials, and from items used in an every-day life such as coins or jewellery [4]. Furthermore, synthetic urine-like liquors are applied for studying the solubility of urinary calculi formation in clinic studies [5]. Synthetic human body fluids such as sweat and gastric/gastrointestinal and saliva fluids are also used as extractants to predict the availability of metals for human absorption in a range of industrial wastes such as coal fly ash [6], contaminated soil around old mining area [7] and of municipal solid waste such as compost [8]. Compared to the real human body fluids, which are in *vivo* tests, synthetic fluids are both rapid and inexpensive, requiring only a day to conduct and costing only a small fraction of what *in vivo* tests would cost. Although in *vitro* test by synthetic fluids have reported to have limitations, e.g. due to the fact that they cannot contain all the constituents of human fluids (e.g. proteins, enzymes, etc.), they provide an appropriate mean to determine the bioaccessibility of heavy metals in various materials. Although the real human body fluids have also been applied to study the solubility of heavy metals [9], [10], the application of synthetic body fluids promotes also the fact that real human body fluids may be unhygienic. Furthermore, the real human body fluids have reported to have an unstable nature [11], [12], and in the European Union (EU), their use is strictly regulated by the rules of national ethical committees.

II. EXPERIMENTAL

A. Bottom Ash Sampling Procedure

The bottom ash investigated in this study originated from a large-sized (115 MW) bubbling fluidized bed (BFB) boiler at the power plant of a pulp and board mill complex located in Finland [13]. Sampling of a bottom ash was carried out over a period of three days, and individual sub-samples (1kg per sampling day) were collected and combined to give one composite sample with a weight of 3kg for the bottom ash. The sampling period represented normal process operating conditions for the combustion plant e.g. in terms of O_2 content and temperature. The incineration temperature in a bubbling fluidized bed boiler is ca. 800°C. During the sampling period when bottom ash was sampled from the outlet of the boiler, approximately 97% of energy produced by the BFB boiler originated from the incineration of clean forest residues (i.e. bark, woodchips, and sawdust), and 3% from the incineration of sludge from the primary clarifier of a wastewater treatment

plant of the mill. The forest residues originated from the wood handling plant and sawmill of the pulp and board mill complex investigated in this study, and they were therefore clean residues. Approximately 60% of the forest residues comprised pine (*Pinus sylvestris*) trees, and 30% were willow (*Salix*) and 10% birch (*Betula verrucosa* and *Betula pubescens*).

B. Determination of the Mineral Composition and Physical and Chemical Properties of the Ash

For the determination of the mineralogical composition of the bottom ash, X-ray diffractograms of powdered sample was obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuKα 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 40kV and 40mA. 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 ash 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-liquid (i.e. ultrapure water) ratio of 1:5. Determination of the dry matter content of the bottom 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. A comprehensive review of the standards, analytical methods, instrumentation and quality control is given in our previous paper [13].

C. Determination of Total Element Concentrations in the Ash

For the determination of total element concentrations in the ash, the dried sample was digested with a mixture of HCl (3mL) and HNO$_3$ (9mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using USEPA method 3051A [14]. The cooled solution was transferred to 100mL volumetric flasks and the solution was diluted to volume with ultrapure water. All reagents and acids were suprapure or pro analysis quality.

Apart from Hg, the total element concentrations in the bottom 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 ash 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 Heavy Metals in Bottom Ash Using Artificial Sweat and Gastric Fluids

Artificial sweat was prepared by dissolving 5g NaCl, 1g lactic acid and 1g urea in 1L of deionized water and adjusting

the pH to a value of 6.50 with ammonia [15]. Artificial gastric fluid was prepared by dissolving 60.06g glycine in 2L of deionized water and adjusting the pH to a value of 1.54 with HCl [16]. The extraction was carried out in polypropylene bottles by shaking 1g of ash on a dry weight (d.w.) basis with 100mL of the extract (i.e. artificial sweat or gastric fluid) for 1 hour by end-over-end mixing at 37°C. Thus, the liquid-to-solid ratio (L/S 100L/kg) in our procedure was the same as those of Wang et al. [16] and Kim et al [17]. In order to minimize possible chemical and/or microbiological changes in the ash during the extraction procedure, extraction was carried out using an undried ash sample instead of a dried sample, since according to Kosson et al. [18], it is preferable to avoid sample drying before extraction. After extraction, the extract was separated from the solid residue (i.e. the undissolved ash) by filtration through a 0.45μm membrane filter. The pH of the extract was then measured, and the metal concentrations 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 Bottom Ash

According to the XRD spectra in Fig. 1, the bottom ash contained only silicate minerals (i.e. albite [NaAl$_3$O$_8$; 12.8%], biotite [K(Fe,Mg)$_3$AlSiO$_3$O$_{10}$(F,OH)$_2$; 8.5%], microcline [KAlSi$_3$O$_8$; 44.8%] and quartz [SiO$_2$; 33.9%]). The existence of silicate minerals in the bottom ash originating from the bubbling fluidized bed boiler is reasonable when considering that the bed material of a fluidized bed boiler usually consists of silica sand.

The existence of silicate minerals in the bottom ash may also partly due to the sand and soil particle contamination of forest residues during harvesting transportation and handling [19]. In addition, it may partly derive from the decomposition of plant tissue-derived Si-based minerals during incineration, such as phytolith (SiO$_2$ × nH$_2$O), which is often a structural component of plant tissue, deposited between and within plant cells [20]. The minerals of our bottom ash are partly consistent with the finding of Steenari and Lindqvist [19], who also observed quartz (SiO$_2$) in wood ash. Furthermore, the minerals in our bottom ash correspond with the findings of Meawad et al. [21], who observed albite (NaAl$_3$O$_8$) and quartz, but also with the findings of Holmberg and Claesson [22], who observed microcline (KAlSi$_3$O$_8$) in wood ash. The pH of the bottom ash was strongly alkaline (pH 11.9; see ref. [13]), which according to van Herck and Vandecasteele [23] indicates that part of the dissolved metals occur as basic metal oxides, hydroxides and/or carbonates, although we did not observed any hydroxides or carbonates in the bottom ash (see Fig. 1). The dry matter content of the bottom ash was very high (99.5%; see ref. [13]). This is a disadvantage as it may increase the amount of dust generation during handling of this residue.
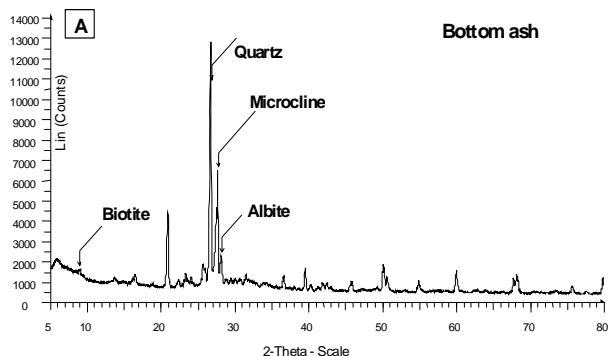
Fig. 1 XRD data of the bottom ash [13]

B. Total and Extractable Heavy Metal Concentrations in the Bottom Ash

According to Mroueh et al. [24], the most significant activities that cause potential occupational risks to humans when industrial by-products are used e.g. in earthworks are: 1) transport of the by-product, 2) intermediate storage in a pile, 3) pre-processing of by-products, 4) construction, 5) use of the construction, 6) structural maintenance and repairs, and 7) accident risks. According to Mroueh and Wahlström [25], the main human exposure pathway in these work activities is the inhalation of dust or volatile compounds, dermal contact and ingestion. In addition, the typical exposure pathways in the environment affect the flora and fauna of the site, as well as ground and surface waters [24].

In terms of human health risk assessment, the main area of concern is the oral/ingestion pathway, followed by respiratory and dermal exposure routes [25], [26]. Although the skin provides a large surface area, according to Twining et al. [26], it is relatively impervious to solids such as ash particles. However, according to Mroueh et al. [27], the alkaline nature of the ash (pH 11.9; see [13]) may cause skin irritation. Once the ash material enters the body via the respiratory and gastrointestinal tracts, it mixes with biological fluids and hence has an opportunity to be dissolved and absorbed [26]. Although the heavy metals in this study were extractable in the artificial and gastric fluids, this does not necessarily mean that humans working in power plants or in earthworks are exposed to the heavy metals in ash. The extractable concentrations of heavy metals in the artificial sweat and gastric fluids cannot be used for assessing the level of human exposure, because we have not carried out any experiments to determine the dose of ash for humans. As human exposure assessment associated with ash handling is complex, in this context we only discuss the extractability of certain heavy metals in bottom ash by artificial sweat and gastric fluids. However, the extractability (solubility) of metals in artificial body fluids should be determined in order to understand the possible occupational risks associated with ash handling.

TABLE I
TOTAL (USEPA 3051A) AND EXTRACTABLE HEAVY METAL CONCENTRATIONS (MG/KG; DRY WEIGHT) IN THE BOTTOM ASH USING ARTIFICIAL SWEAT AND GASTRIC FLUIDS, AS WELL AS THE PH OF THE EXTRACT BEFORE (I.E. ONLY EXTRACT) AND AFTER (I.E. EXTRACT + ASH) EXTRACTION

pH and Metal	Total Concentration	Extractable Concentration	
		Artificial Sweat Fluid	Artificial Gastric Fluid
pH (before)		6.50	1.54
pH (after)		8.51	1.94
Al	20000	< 50	9030
As	< 3.0	< 1.5	< 1.5
Ba	690	120	550
Be	< 1.0	< 0.5	< 0.5
Cd	0.3	< 0.2	0.3
Co	3.1	< 0.5	1.8
Cr	39	1.1	8.8
Cu	18	< 1.0	12
Mo	1.4	< 0.5	< 0.5
Ni	16	< 0.5	5.3
Pb	< 3.0	< 1.5	1.9
Sb	< 3.0	< 1.5	< 1.5
Se	< 3.0	< 1.5	< 1.5
V	18	1.1	9.4
Zn	720	2.4	400

Table I presents the total and extractable concentrations of heavy metals in the bottom ash. If we disregard the metals whose concentrations were lower than the detection limits, the extractable concentrations of heavy metals in the artificial gastric fluid were higher than those in the artificial sweat fluid. These results are reasonable in the light of the fact that the pH of the artificial gastric fluid was extremely acidic both before (pH 1.54) and after (pH 1.94) extraction, whereas the pH of the artificial sweat fluid was slightly alkaline before (pH 6.50) and after extraction (pH 8.51). The relatively high extractable concentration of Ba (120mg/kg; d.w.) in the artificial sweat is reasonable, since Ba is able to form oxyanions, which means that its extractability clearly increases from acidic pH values to neutral and alkaline conditions [28]. In this context it is worth noting that we have also observed this kind of release of barium from ash in our previous study [29]. Therefore, taking into consideration the toxicity properties of many of the heavy metals presented in Table I and our observation of high extractable concentrations of certain heavy metals in artificial gastric fluid, we conclude that, careful handling of this ash fraction is recommended to minimize human health risks, especially if it causes dusting. However, due to the fact that human health risk assessment associated with ash handling is complex question, we are continuing to study the matter in our laboratory.

IV. CONCLUSION

The highest extractable concentration in the artificial sweat fluid was observed for Ba, which was 120mg/kg (d.w.). The highest extractable concentration in the artificial gastric fluid was observed for Al, which was 9030mg/kg (d.w.). Furthermore, the extractable concentrations of Ba (550mg/kg; d.w.) and Zn (400mg/kg: d.w.) in the bottom ash using

artificial gastric fluid were elevated. Therefore, in terms of human health risk assessment, we conclude that careful handling of fly ash is recommended in order to prevent ash dusting and the penetration of ash particles across the human gastrointestinal tract, e.g. through inadvertent wiping of the mouth with dirty hands or through the inhalation of air-borne ash particles. The alkaline nature of the bottom ash (pH 11.9) may cause skin irritation.

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