

# Occupational Risk Evaluation of Using Bottom Ash and Fly Ash as a Construction Material

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**Abstract:** As a case study, the potential to use bottom ash and fly ash from a large-sized (120 MW) bubbling fluidized bed boiler (BFB) at the power plant of a fluting board mill were assessed to determine their suitability for use as an earth construction agent. In addition, the extractability of heavy metals in the ashes was determined using artificial sweat and gastric fluids to assess the potential occupational risk from ash handling. Owing to the relatively high total concentration of polycyclic aromatic hydrocarbons (PAHs) [23.0 mg/kg; dry weight (d.w.)], and the extractable concentrations of Mo (3.9 mg/kg; d.w.) and Se (0.2 mg/kg; d.w.) in the fly ash, which exceed the Finnish limit values for materials used in covered earth construction (20 mg/kg; d.w. for PAHs, 0.5 mg/kg; d.w. for Mo, and 0.1 mg/kg; d.w. for Se), the utilization of this ash residue fraction in such structures requires an environmental permit. Because of the high extractability of certain heavy metals in fly ash by using an artificial gastric fluid, e.g., Ba (446 mg/kg; d.w.), V (65.6 mg/kg; d.w.), Zn (100 mg/kg; d.w.), Cu (38.3 mg/kg; d.w.), and As (36.7 mg/kg; d.w.), the careful handling of this ash residue is recommended to prevent the ingestion and penetration of ash particles across the human gastrointestinal tract. **DOI: 10.1061/(ASCE)HZ.2153-5515.0000111.** © 2012 American Society of Civil Engineers.

**CE Database subject headings:** Bottom ash; Fly ash; Construction materials; Fluidized bed technology; Heavy metals; Occupational safety.

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## Introduction

The pulp and paper industry is an energy-intensive but also energy efficient industry. Pulp and paper mills generate various types and quantities of energy-rich biomass-derived residues such as black liquor, a by-product from the kraft (sulfate) pulp-making process, and clean bark, wood chips, and sawdust from wood-handling plants, sawmills, and ground-wood mills (Gavrilescu 2008; Mladenov and Pelovski 2010). In Finland, many pulp and paper mills generate more than half of their energy needs from these liquors and solid process wastes.

Wood-derived fuels are a clean and truly renewable, sustainable source of energy. Wood-derived fuels are ecologically relatively unproblematic energy sources, which in every way assist in the move toward sustainability through sustainable development, because they help to reduce the use of fossil fuels. The incineration of wood-derived fuels, in particular, is playing an increasingly important role in the transition toward CO<sub>2</sub>-lean energy systems, because the advantage of wood bioenergy is that it could significantly reduce the use of fossil fuels and the formation of CO<sub>2</sub> emissions (Arbon 2002).

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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 enables the cocombustion of various fuels, even fuels with a high moisture content. Although the incineration of pulp and paper mill residues by 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.

The disposal of ash in landfills conflicts with public efforts to reduce the supply of waste to landfills through increased recycling and reuse. The European Union Directives on the landfilling of waste (EC 1999) and guidance on establishing criteria and procedures for the acceptance of waste at landfills (EC 2003) have resulted in the stricter regulation of landfills. Many landfill sites cannot meet the current demands and are consequently being shut down. The cost of running landfills also has increased because of the new tighter regulations. The large and increasing volume of ash residues arising from Finnish pulp and paper mills is motivating a search for alternative disposal options to landfilling, and there is a growing trend toward the utilization of these ash residues. Careful attention to ash chemistry can maximize the potential of ash residues for beneficial applications instead of the reliance on landfill for their disposal.

Many researchers have described the possible occupational risks to humans when industrial by-products and recycled materials are used in earth construction or are landfilled (Wahlström et al. 2001;

Mroueh and Wahlström 2002). Extraction (leaching) tests are widely used as tools to estimate the release of heavy metals from ash over a range of possible waste management activities, including recycling or reuse, when assessing the efficiency of waste treatment processes, and after disposal. Extraction is not total decomposition, and the extractable recoveries of analytes are generally less than their total concentrations. Recoveries can only reach total values if the element is completely soluble in the extraction solvent. The importance of extraction studies relates to the fact that the potential toxicity of a heavy metal in ash is not dependent on its total concentration, but on its extractability (Filgueiras et al. 2002).

Artificial sweat, gastric/gastrointestinal fluids, and saliva have been used as extractants for *in vivo* and *in vitro* testing in many environmental studies to determine the levels of extractable heavy metals in a range of industrial wastes such as coal fly ash (Twining et al. 2005), chromate copper arsenate-treated wood (Nico et al. 2006), urban roadside and industrial soils (Kim et al. 2002; Wang et al. 2007), air-borne particulate matter (Madrid et al. 2008), and in various mine waste materials such as tailings, heap leach, and waste rock (Bruce et al. 2007). Although *in vitro* tests by using artificial body fluids have been reported to have limitations, for instance because they cannot contain all the constituents of human fluids (e.g., proteins and enzymes), they nevertheless provide a rapid and inexpensive means to determine the bioavailability of heavy metals in wastes and are therefore relatively widely used.

## Experimental

### Bottom and Fly Ash Sampling Procedures

The bottom 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 to operate in 1984, and in 2007 the electrostatic precipitator was replaced and a flue gas cleaning scrubber was installed. Sampling was carried out over a period of 15 days, and five individual samples (kg per sampling day) were combined to give one composite sample with a weight of 5 kg for both the bottom ash and fly ash. The sampling period represented normal process operating conditions for the combustion plant, e.g., in terms of O<sub>2</sub> 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 was clean bark from the mill's wood-handling process, whereas approximately 95% of the barked wood was birch (*Betula verrucosa* and *B. pubescens*), 4% was spruce (*Picea abies*), and 1% was alder (*Alnus incana* and *A. glutinosa*). The peat fuel originated near the fluting mill and was thus of domestic origin, whereas 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 collection system, the fly ash fractions from the three fields of the ESP are collected and combined in one ash silo. Thus, the fly ash investigated in this study was a mixture from all three fields of the ESP. The temperature in the BFB is approximately 900°C, and in the ESP approximately 150°C. After sampling, the samples were stored in plastic bags in a refrigerator (+4°C). A coning and quartering method (Gerlach et al. 2002) was repeatedly applied to reduce the ash sample to a size suitable for conducting laboratory analyses.

### Determination of the Mineral Composition and the Physical and Chemical Properties of the Ashes

To determine the mineralogical composition of the bottom ash and fly ash, X-ray diffractograms of powdered samples were obtained with a Siemens D5000 diffractometer (Siemens, Karlsruhe, Germany) by using CuK $\alpha$  radiation. The scan was run from 5 to 80° (two-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, Karlsruhe, Germany) and the International Center for Diffraction Data (ICDD) PDF-2 Release 2006 software package (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 12,880 at a solid-to-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 12,880. The organic matter content, as measured by the loss-on-ignition (LOI), was determined according to European standard SFS-EN 12,879, and the total organic carbon (TOC) content according to European standard SFS-EN 13,137. A comprehensive review of the standards, analytical methods, instrumentation, and quality control is provided in a previous paper (Dahl et al. 2009).

### Determination of Total Heavy Metal Concentrations in the Ashes

To determine the 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 Matthews, USA) by using USEPA method 3051A. 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 Analyst 700 cold-vapor atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler. A comprehensive review of USEPA method 3051A and the instrumentation is provided in a previous paper (Dahl et al. 2009).

### Determination of Total Polychlorinated Biphenyl and Polycyclic Aromatic Hydrocarbon Concentrations in the Ashes

To determine the total polychlorinated biphenyl (PCB) concentration in the ashes, European standard SFS-ISO 10,382 [Suomen Standardisoimisliitto (SFS-ISO) 2007a] was followed. The sample (10 g) was extracted with a mixture of hexane (5 mL) and acetone (10 mL) for 30 min by ultrasonic-assisted extraction (Bandelin Sonorex). According to the standard methodology (SFS-ISO 2007a), the PCBs were assigned and quantified by comparison of the relative retention times and relative peak height or peak areas with respect to injection standards containing commercial internal standards (PCB-30 and PCB 204).

To determine the total polycyclic aromatic hydrocarbon (PAH) concentration in the ashes, European standard SFS-ISO 18,287 (SFS-ISO 2007b) was followed. The sample (10 g) was extracted with a mixture of hexane (5 mL) and acetone (10 mL) for 30 min by

ultrasonic-assisted extraction (Bandelin Sonorex). According to the standard methodology (SFS-ISO 2007b), the identification and quantification of the PAH compounds were carried out with commercial deuterated PAHs (naphthalene-*d*<sub>8</sub>, acenaphthylene-*d*<sub>10</sub>, phenanthrene-*d*<sub>10</sub>, chrysene, and perylene-*d*<sub>12</sub>) as internal standards. A comprehensive review of the determination of PCB and PAH concentrations is provided in the original standards (SFS-EN 2007a, b).

### Extraction Procedures and Determination of Extractable Concentrations in the Extracts

To determine the extractable concentrations of dissolved organic carbon (DOC), heavy metals, fluoride, sulfate, and chloride in the ashes, European standard SFS-EN 12,457-3 was used. This procedure is a two-stage batch test at a liquid-to-solid (L/S) ratio of 2 L/kg and 8 L/kg, with an extractant containing ultrapure water (H<sub>2</sub>O). The sum of leachable concentrations (i.e., L/S 10 L/kg) is compared to the maximum allowable concentrations, which together with the total element concentrations determine whether the residue may be used as an earth construction agent or whether it needs to be disposed of either to an inert-waste, nonhazardous waste, or hazardous waste landfill. The metal concentrations (i.e., Sb, As, Ba, Cd, Cr, Cu, Hg, Pb, Mo, Ni, V, Zn, and Se) in the extracts were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). Determination of the DOC concentration in the extract was carried out according to European standard SFS-EN 1,484 using a Leco CHN-600 analyzer (Leco, USA). Determination of the fluoride, sulfate, and chloride concentrations in the extract was carried out according to European standard SFS-EN ISO 10,304-1 using a Dionex ICS 2000 ion chromatography system with conductivity detection (Dionex, USA). Comprehensive reviews of the European standards and instrumentation are provided in previous papers (Dahl et al. 2009; Pöyky et al. 2009).

### Procedure for Determining the Extractability of Heavy Metals in Ashes using Artificial Sweat and Gastric Fluids

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

pH to a value of 6.47 with ammonia (Song et al. 2007). Artificial gastric fluid was prepared by dissolving 60.06 g glycine in 2 L of deionized water and adjusting the pH to a value of 1.51 with HCl (Wang et al. 2007). The extraction was carried out in polypropylene bottles by shaking 1 g of ash on a dry weight (d.w.) basis with 100 mL of the extract (i.e., artificial sweat or artificial gastric fluid) for 1 h by end-over-end mixing at 37°C. Thus, the liquid-to-solid ratio (L/S 100 L/kg) in this procedure was the same as those of Wang et al. (2007) and Kim et al. (2002). To minimize possible chemical and/or microbiological changes in the ash during the extraction procedure, extraction was carried out by using an undried ash sample instead of a dried sample, because according to Kosson et al. (2002), 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 0.45 μm 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).

## Results and Discussion

### Mineral Composition, Physical, and Chemical Properties of the Ashes

The most important physical and chemical properties of the ashes are presented in Table 1. Both ashes were strongly alkaline (pH 10.4–10.5). According to Van Herck and Vandecasteele (2001), an alkaline pH indicates that part of the dissolved metals occurs as basic metal salts, oxides, hydroxides, and/or carbonates, as shown in the fly ash by the X-ray diffractogram. Therefore, the proportion of soluble basic metal salts, oxides, hydroxides, and carbonates in the ashes outweighs the proportion of soluble acid components, and the ashes subsequently generate an alkaline pH.

The very low (< 0.5 g/kg; d.w.) total organic carbon value in the bottom ash indicates complete combustion of organic matter in the fluidized bed boiler, which is reasonable because the incineration temperature in the fluidized bed boiler is approximately 900°C. The very low (< 0.5%; d.w.) loss-on-ignition value in the bottom ash also supports this, although according to the findings of

**Table 1.** Physical and Chemical Properties of the Bottom Ash and Fly Ash

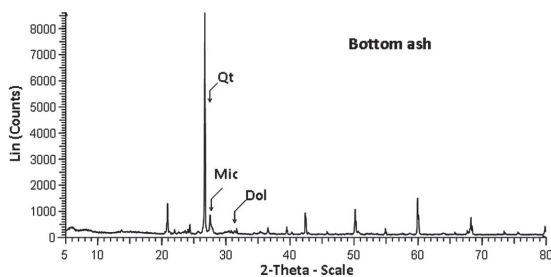
Parameter	Unit	n	Bottom ash	Fly ash	Literature value for concentration in Finnish ashes	
					Coal ash	Wood+peat ash
pH (1:5)		3	10.4	10.5	11.8	
Loss-on-ignition (550°C)	% (dry weight)	3	< 0.5	15.6 ± 0.3	9.1–12.1	1–34
Total organic carbon	g/kg (dry weight)	3	< 0.5	140	115	4.5–10
Dry matter content (105°C)	%	3	94.0–0.2	71.1–0.8		
8.0 ≤ size < 16.0 (mm)	weight%	1	0.18	0		
4.0 ≤ size < 8.0 (mm)	weight%	1	2.8	0		
2.0 ≤ size < 4.0 (mm)	weight%	1	3.0	0		
1.0 ≤ size < 2.0 (mm)	weight%	1	21.4	0		
0.5 ≤ size < 1.0 (mm)	weight%	1	59.7	0		
0.25 ≤ size < 0.5 (mm)	weight%	1	6.9	3.5		
0.125 ≤ size < 0.25 (mm)	weight%	1	2.1	9.4		
0.075 ≤ size < 0.125 (mm)	weight%	1	1.0	21.4		
0.045 ≤ size < 0.075 (mm)	weight%	1	1.2	23.0		
Size < 0.045 (mm)	weight%	1	1.1	42.0		
Sieving loss	weight%	1	0.62	0.70		

Payá et al. (2002) and Ribbing (2007), it does not closely reflect the amount of unburned carbon in ash, but rather the volatile fraction, such as chemically bonded water in  $\text{Ca}(\text{OH})_2$ ,  $\text{CO}_2$  in the form of carbonates such as  $\text{CaCO}_3$ , or chlorides and sulfur. However, 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 volatile fractions and unburned organic material. If the LOI values in the bottom and fly ash are compared to those reported in the literature (Lahtinen 2001; Dahl et al. 2008; Korpijärvi et al. 2009), the observations are in relatively good agreement with the LOI and TOC values in the ashes from Finnish power plants.

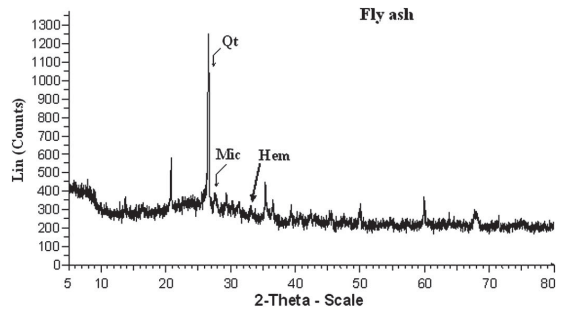
According to Table 1, the particle size distributions of the bottom ash and fly ash differ significantly. No particles of a diameter range between 0.5 and 16.0 mm existed in the fly ash, whereas these particles accounted for approximately 81.1 weight percent (wt%) of the bottom ash. The fly ash consists of small particles with a diameter of less than 0.5 mm. From the utilization point of view, these smaller particle fractions can be of greatest concern because of their dust generation potential during ash handling. Owing to the dry matter content of 94.0% the bottom ash is more likely to generate dust problems than the fly ash, which has a dry matter content of 71.1%. The lower dry matter content of the fly ash is attributed to the fact that before the residue is transferred from the electrostatic precipitator to the ash-collector silo, it is watered in order to prevent dust problems.

The particle size distribution of the fly ash also may be partly the reason for its relatively high LOI and TOC values, because in the fluidized bed boiler the fly ash particles rise with the flue gas into the electrostatic precipitator and so remain in the combustion chamber zone for a shorter period than those particles that are associated with the bottom ash fraction. The sieving losses of 0.62 wt% for the bottom ash and of 0.70 wt% for the fly ash were low.

The X-ray diffraction (XRD) spectra in Figs. 1 and 2 highlight similarities and differences between the mineral composition of the bottom and fly ashes. Both ashes contained silicate minerals such as microcline [ $\text{K}(\text{AlSi}_3\text{O}_8)$ ] and quartz ( $\text{SiO}_2$ ), and their abundances in the ashes were relatively similar. However, hematite ( $\text{Fe}_2\text{O}_3$ ), which is an oxide mineral, and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), which is a carbonate mineral, only existed in the fly ash and bottom ash, respectively. Although X-ray diffraction (XRD) analysis can be useful to identify the chemical species of crystalline particles in ash, in this 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., noncrystallised matter), and its detection limit is normally 1–2% (w/w). This is probably why crystalline compounds containing the metals in Table 2 were not



**Fig. 1.** X-ray diffraction pattern for the bottom ash; mineral abbreviations and their abundances (%) are: Dol = dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ; 2.3%], Mic = microcline [ $\text{KAlSi}_3\text{O}_8$ ; 20.7%], Qt = quartz [ $\text{SiO}_2$ ; 76.6%]



**Fig. 2.** X-ray diffraction pattern for the fly ash; mineral abbreviations and their abundances (%) are: Hem = hematite [ $\text{Fe}_2\text{O}_3$ ; 3.4%], Mic = microcline [ $\text{KAlSi}_3\text{O}_8$ ; 22.9%], Qt = quartz [ $\text{SiO}_2$ ; 73.7%]; a Cu-tube was used to measure the spectra, which energizes the X-rays of Fe in the ash and produces a relatively high background

identified by XRD, despite the fact that the concentrations of these heavy metals could be quantitatively measured by ICP-OES.

The existence 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 also may be partly attributable to sand and soil particle contamination of forest residues during harvesting, transportation, and handling (Steenari et al. 1999). In addition, it partly derives from the decomposition of plant tissue-derived Si-based minerals during incineration, such as phytolith ( $\text{SiO}_2 \times n\text{H}_2\text{O}$ ), which is often a structural component of plant tissues, deposited between and within plant cells (Humphreys et al. 2004).

### Total Concentrations of Compounds in Ashes with Respect to the Finnish Limit Values for Earth Construction Agents

Table 2 presents the total concentrations of PCBs, PAHs, and heavy metals in the ashes and the current Finnish limit values for the total concentration of these compounds in earth construction agents used for covered or paved structures. In Finland and elsewhere in the European Union (EU), national legislation, which is on the basis of EU directives, sets rules and limit values for the use of industrial residues as earth construction agents, e.g., in road construction applications (Sorvari 2003). However, environmental standards, such as leaching tests, differ between countries (Huang et al. 2006). Therefore, although European countries such as Spain (Forteza et al. 2004), France (Bruder-Hubscher et al. 2001), Sweden (Roth and Eklund, 2003), Denmark (Hjelmar et al. 2007), and Germany (Cenni et al. 2001) have established national legislation that enables and controls the recycling of ash as an earth construction agent, the national legislation and limit values of these countries are not possible to discuss in this context because of the complexity of the legislation. However, the statutory limit values of the above mentioned European countries can, if needed, be found in the literature cited previously.

In Table 2, the total concentrations are expressed on a dry weight basis and as means of triplicate samples. However, the standard deviations are not given for all compounds, because in some cases the triplicate samples yielded exactly the same element concentrations. The limit values in Tables 2 and 3 are for the basic characterization of waste material, which is conducted to prove that the waste in question falls within the scope of the Finnish Government Decree 403/2009 (VNa 2009) concerning the recovery

**Table 2.** Total Concentrations (mg/kg; d.w.;  $n = 3$ ) of Polychlorinated Biphenyls, Polycyclic Aromatic Hydrocarbons, and Heavy Metals in Ashes with Respect to Finnish Limit Values for Construction Materials (mg/kg; d.w.) and Values from Power Plants (mg/kg; d.w.)

Compound	Bottom ash	Fly ash <sup>a</sup>	EF <sup>b</sup>	Limit value for the total concentration <sup>c</sup>	Literature value of the total concentration in Finnish ashes	
					Coal ash	Wood + peat ash
PCB	< 0.07	< 0.07		1.0	-0.02	-10
PAH	< 3.0	23.0	(> 7.6)	20/40	-0.1	-250
Sb	< 4.0	< 4.0				0.04-16
As	3.9 ± 0.1	46.9 ± 0.6	12.0	50	-100	1.9-110
Ba	215.7 ± 10.7	741.3 ± 14.4	3.4	3000	-1800	170-1674
Cd	< 3.0	1.7 ± 0.1	(> 0.6)	15	-100	0.06-22
Cr	10.9 ± 0.3	47.1 ± 1.8	4.3	400	-200	12-120
Cu	16.9 ± 1.1	99.4 ± 0.7	5.9	400	-100	13-220
Hg	< 0.04	0.7	(> 0.7)			0.01-0.9
Pb	< 3.0	46.3 ± 1.0	(> 15.4)	300	-100	2.3-310
Mo	< 1.0	15.9 ± 0.6	(> 15.9)	50	-100	-25
Ni	6.3 ± 0.2	45.5 ± 0.9	7.2			21-65
V	16.4 ± 0.6	94.8 ± 3.3	5.8	400	-200	-160
Zn	256.0 ± 6.2	274.7 ± 5.5	1.1	2000	-200	160-10000
Se	< 4	5.2 ± 0.5	(> 1.3)			-20

<sup>a</sup>If the total concentration of a compound exceeds its limit value, it is given in bold type.

<sup>b</sup>EF = (total element concentration in the fly ash/total element concentration in the bottom ash).

<sup>c</sup>The total limit values are for basic characterization of waste material, which is conducted to prove that the waste in question falls within the scope of the Finnish Government Decree 403/2009; the total limit values of 20 and 40 for polycyclic aromatic hydrocarbons are for covered and paved structures, respectively.

**Table 3.** Extractable Concentrations (mg/kg; d.w.;  $n = 1$ ) in Ashes with Respect to Finnish Limit Values for Construction Materials (mg/kg; d.w.) and Values from Power Plants (mg/kg; d.w.)

Compound	Bottom ash <sup>a</sup>	Fly ash <sup>a</sup>	Limit value for the extractable concentration <sup>b</sup>		Literature value of the extractable concentration in Finnish ashes	
			Covered structure	Paved structure	Coal ash	Wood+peat ash
DOC	< 15	30	500	500	16-41	-800
Sb	< 0.5	< 0.05	0.06	0.18	-0.02	-0.8
As	< 0.15	< 0.15	0.5	1.5	< 0.3	-83
Ba	0.68	10.4	20	60	0.9-34	0.13-160
Cd	< 0.015	< 0.015	0.04	0.04	< 0.02	-0.02
Cr	< 0.1	0.4	0.5	3.0	-1.1	-36
Cu	< 0.1	< 0.1	2.0	6.0	< 0.05	-0.2
Hg	< 0.005	< 0.005	0.01	0.01	< 0.001	-0.46
Pb	< 0.15	< 0.15	0.5	1.5	-0.2	-1.9
Mo	< 0.13	3.9	0.5	6.0	0.07-9.7	-6.7
Ni	< 0.1	< 0.1	0.4	1.2	< 0.05	-0.15
V	0.5	0.2	2.0	3.0	-0.94	-3.8
Zn	< 0.1	< 0.1	4.0	12	< 0.05	0.06-110
Se	< 0.08	0.2	0.1	0.5	-1.2	-0.44
Fluoride	< 5	8.6	10	50	-33	-22
Sulphate	< 50	220	1000	10.000	130-2000	-110000
Chloride	< 50	140	800	2400	-1000	-15.000

<sup>a</sup>If the extractable concentration of a compound exceeds its limit value either for a covered or a paved structure, it is given in bold type.

<sup>b</sup>The extractable limit values are for basic characterization of waste material, which is conducted to prove that the waste in question falls within the scope of the Decree 403/2009.

of certain wastes in earth construction. This decree also includes limit values for quality control tests on wastes, which are the same as those for basic characterization, but quality control testing includes fewer compounds than basic characterization. However, a noteworthy distinction between the limit values of the two types

of investigation is that in the case of quality control testing, exceeding of the limit value by a maximum of 30% may be acceptable.

Except for the total concentration of PAH in the fly ash, which exceeded the limit value for an agent used in covered earth construction, the other total concentrations in the ashes were less than

the statutory Finnish limit values for both covered and paved structures. Owing to the elevated total PAH concentration (23 mg/kg; d.w.) in the fly ash, which slightly exceeded the statutory limit value of 40 mg/kg (d.w.) for PAHs for covered structures, this residue cannot be used as an earth construction agent in a covered structure by simply submitting a notification to the competent authority. Instead, an environmental permit is required. In Finland, the environmental authorities responsible for waste management make the final decision on the utilization of wastes in earth constructions. In a case in which basic characterization testing proves that the waste in question falls within the scope of the Finnish Government Decree 403/2009 (VNa 2009) concerning the utilization of certain wastes in earth construction, the competent environmental authority may decide that the maximum limit values for certain compounds can be up to 30% higher than those given in Table 2 on the basis of the local environmental conditions at the site where the residue is planned to be used (VNa 2009). Therefore, if, in suitable locations, the environmental authority relaxes the maximum limit values for PAHs by 30% to the value of 26 mg/kg (d.w.), it is clear that the total concentration of PAHs in the fly ash would no longer restrict the utilization of this residue as an earth construction agent for covered structures.

If the total concentrations of PCBs, PAHs, and heavy metals in both ash fractions are compared with those reported in the literature (Lillman 2009), the observations for total concentrations are in relatively good agreement with the concentrations of these compounds found in ashes from Finnish power plants. Although the findings for the concentration of PAHs in the fly ash and of Zn in both ashes were higher than the maximum values reported in the ashes from Finnish power plants incinerating coal, the total concentrations in the ashes were lower than those reported in the ashes from Finnish power plants incinerating a mixture of wood and peat. The elevated PAH concentration (23.0 mg/kg; d.w.) in the fly ash, which is formed during incomplete combustion, is reasonable when considering that the LOI (15.6%; d.w.), TOC (140 g/kg; d.w.), and DOC (30 mg/kg; d.w.) values in this residue also were elevated and clearly more than those in the bottom ash (see Tables 1–3). This phenomenon also has been reported by Johansson and van Bavel (2003), according to whom, PAHs could potentially be leached into the environment from the ashes, although PAHs are normally relatively strongly bound to the ash matrix. From the exposure assessment perspective, PAHs present a risk to the environment, especially if they enter the food chain through contact, inhalation, or ingestion (Sun 2004).

Table 2 presents 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. An elevated EF value indicates a high degree of element volatilization, whereas a low EF value is indicative of nonvolatile behavior under normal operating conditions and the formation of a heavier mineral phase (Steenari and Lindqvist 1997). In addition to the element volatilization characteristics, element retention in fly ash through other processes (i.e., primarily the condensation process) determines the final fate of volatile 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. Because this phenomenon is well known and has been reported elsewhere (Lind et al. 1999; Lin and Yeh 2010), and as the ratio of various elements between bottom ash and fly ash depends on factors such as the type of boiler, operating conditions, the fuel mix, and the efficiency of flue gas cleaning devices (Steenari et al. 1999; Shoumkova 2006; Siddique 2009), this issue will not be discussed in this paper. In this study, the aim was simply to assess whether the physical and chemical properties, and the total and extractable heavy metal

and other substance concentrations in the ashes, support their utilization as an earth construction agent.

### **Extractable Concentrations of Compounds in Ashes with Respect to the Finnish Limit Values for Earth Construction Agents**

Table 3 provides the extractable concentrations of DOC, heavy metals, fluoride, sulfate, and chloride in the ashes and the limit values for the extractable concentrations of these compounds in earth construction agents used for covered and paved structures. Except for V, the extractable concentrations of all other compounds in the fly ash were more than those in the bottom ash. Although the exact reason for this difference between the ashes in extractable element concentrations cannot be given, according to Ludwig et al. (2005), the release of substances from ash depends on factors such as the chemical and mineralogical characteristics of the ash material. Furthermore, Karlfeldt and Steenari (2007) reported that the extractability of an element depends not only on the speciation of the element itself, but also on the matrix of the material. For example, a very important factor for the extractability of a specific element is whether it is present primarily inside or on the surface of particles. Encapsulation of metal species inside ash particles, and sorption, which refers to processes other than the precipitation/dissolution of pure mineral phases, i.e., adsorption and coprecipitation processes (Meima and Comans 1999; Sarkar et al. 2005), also could explain some of the relatively high extractability values obtained for the fly ash. If the extractable concentrations of DOC and heavy metals in the bottom and the fly ashes are compared to those reported in the literature (Lillman 2009), the observations for extractable concentrations in this study are in good agreement with the concentrations of these compounds in ashes from other Finnish power plants, and lower than the literature values.

Except for the extractable concentrations of Mo and Se in the fly ash, which exceeded the limit value for agents used in covered earth constructions, the other extractable concentrations in the ashes were lower than the statutory Finnish limit values for use in both covered and paved structures. Owing to the elevated extractable Mo (3.9 mg/kg; d.w.) and Se (0.2 mg/kg; d.w.) concentrations in the fly ash, which exceeded the statutory limit value of 0.5 mg/kg (d.w.) for Mo and of 0.1 mg/kg (d.w.) for Se for covered structures, this residue cannot be used as an earth construction agent in a covered structure simply by submitting a notification to the competent authority. Instead, if the fly ash is intended to be used for such purposes, an environmental permit is required.

The competent environmental authority may decide that the maximum limit values for extractable compounds can be up to 30% more than those given in Table 3 on the basis of the local environmental conditions at the site where residue is planned to be utilized (VNa 2009). However, even if the environmental authority were to relax the maximum limit values for the extractable concentration of Mo by 30% to the value of 0.65 mg/kg (d.w.), and that of Se to the value of 0.13 mg/kg (d.w.) for a covered structure, the extractable concentrations of Mo (3.9 mg/kg; d.w.) and of Se (0.2 mg/kg; d.w.) in the fly ash would still exceed the relaxed limits. This means that the extractable concentrations of Mo and Se restrict the utilization of the fly ash residue as an earth construction agent for covered structures. It is likely that this residue could not be utilized for such purposes by simply submitting a notification to the competent authority, but that an environmental permit would be required. The elevated extractability of Mo and Se results from the fact that both of these elements are able to form oxyanions such as  $\text{MoO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$ , and  $\text{SeO}_4^{2-}$ , and the extractability of Mo and Se consequently increases toward extreme alkaline conditions and decreases toward neutral and acidic conditions (Cornelis et al. 2008).

Thus, as long as the pH of the ashes investigated in this study remains clearly alkaline, the leaching of Mo and Se is likely.

From the utilization point of view, determination of the DOC concentration of ash is important. Carbon in waste can occur as elemental, inorganic, and organic carbon. All these carbon forms have distinct chemical properties and possible environmental effects. Elemental carbon is practically insoluble, whereas soluble carbon forms can complex with chemical elements in waste and in natural materials, thereby increasing element leaching (Kumpiene et al. 2011). Ashes are often considered to be suitable as construction materials when the stability of structures and their environmental impacts are crucial factors. Various carbon species might differently affect ash aging, and precise determination of carbon speciation can facilitate more accurate predictions of the long-term stability of such construction. Knowledge of the DOC concentration also is important, because dissolved organic carbon may affect the transport of pollutants from incineration residue when landfilled or used in geotechnical constructions (Ecke and Svensson 2008).

In Finland, the limit values presented in Tables 2 and 3 restrict the utilization of ashes as earth construction agents, not the total or the extractable concentrations of soil where the application of ash is to occur. However, baseline data on the total and extractable heavy metal concentrations in Finnish soils can, if needed, be found in the publication of Tarvainen and Kallio (2002). In addition, the nutrient and heavy metal concentrations in two types of typical Finnish forest soils (i.e., Scots pine and Norway spruce stands) can be found in the publication of Merilä and Derome (2008).

#### Occupational Risk Aspects—Extractable Heavy Metal Concentrations in Ashes using Artificial Sweat and Gastric Fluids

According to Mroueh et al. (2000), the most significant activities that cause potential occupational risks to humans when industrial by-products are used in earthworks are: (1) transport of the by-product, (2) intermediate storage in a pile, (3) preprocessing of by-products, (4) construction, (5) use of the construction, (6) structural maintenance and repairs, and (7) accident risks. According to Mroueh and Wahlström (2002), 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, and ground and surface waters (Mroueh et al. 2000).

In terms of human health risk assessment, the main area of concern is the oral/ingestion pathway, followed by respiratory and dermal exposure routes (Mroueh and Wahlström 2002; Twining et al. 2005). Although the skin provides a large surface area, according to Twining et al. (2005), it is relatively impervious to solids such as ash particles. However, according to Mroueh et al. (2001), the alkaline nature of the ashes (see Table 1) 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 (Twining et al. 2005). 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 only the extractability of certain heavy metals in ashes by artificial sweat and gastric fluids are discussed. However, the extractability (solubility) of metals in artificial body fluids should be determined to understand the possible occupational risks associated with ash handling.

Except for Zn, the extractable concentrations of heavy metals in the artificial gastric fluid were clearly more than those in the artificial sweat fluid (see Table 4). The highest extractable concentrations in the artificial sweat fluid were observed for Ba, which were 16.9 mg/kg (d.w.) and 25.1 mg/kg (d.w.) for the bottom ash and fly ash, respectively. The highest extractable concentrations in the artificial gastric fluid also were observed for Ba, which were 86.6 mg/kg (d.w.) and 446 mg/kg (d.w.) for the bottom ash and fly ash, respectively. In addition, the extractability of Zn in both ashes, and the extractability of Cu, As, V, and Pb for the fly ash were relatively high in the artificial gastric fluid. These results are reasonable considering that the pH of the gastric fluid was extremely acidic both before (i.e., pH 1.49 for both ashes) and after (i.e., pH 1.62 for the bottom ash and 1.79 for the fly ash) extraction. However, for the fly ash, the extractable concentration of Mo was slightly more in the artificial sweat (6.9 mg/kg; d.w.) than that in

**Table 4.** Extractable Concentrations (mg/kg; d.w.;  $n = 1$ ) of Heavy Metals in Ashes by Simulated Body Fluids and Recovery Values (R%)

pH and heavy metal	Extractable concentration in the artificial sweat fluid		R% <sup>a</sup>		Extractable concentration in the artificial gastric fluid		R%	
	Bottom ash	Fly ash	Bottom ash	Fly ash	Bottom ash	Fly ash	Bottom ash	Fly ash
pH (before)	6.50	6.50			1.49	1.49		
pH (after)	8.08	8.81			1.62	1.79		
Sb	< 2.0	< 2.0			< 2.0	< 2.0		
As	< 1.5	5.0		10.7	< 1.5	36.7		78.3
Ba	16.9	25.1	7.8	3.4	86.6	446	40.1	60.2
Cd	< 0.15	< 0.15			< 0.15	1.6		94.1
Cr	< 1.0	< 1.0			< 1.0	6.1		12.9
Cu	< 1.0	< 1.0			4.0	38.3	23.7	38.5
Pb	< 1.5	< 1.5			< 1.5	20.2		43.6
Mo	< 0.5	6.9		43.4	< 0.5	5.2		32.7
Ni	< 0.5	< 0.5			< 0.5	8.4		18.5
V	1.1	2.8	6.7	2.9	10.5	65.6	11.1	69.2
Zn	< 1.5	< 1.5			100	100	36.4	36.4
Se	< 2.0	3.7		71.2	< 2.0	3.9		75

<sup>a</sup>R% = [(Extractable concentration in the artificial sweat fluid)/(Total concentration given in Table 1)] × 100%.

the artificial gastric fluid (5.2 mg/kg; d.w.). For the fly ash, the pH of the artificial gastric fluid was extremely acidic both before (pH 1.49) and after (pH 1.79) extraction, whereas the pH of the artificial sweat fluid was slightly alkaline before (pH 6.50) and after extraction (pH 8.81). The higher extractable concentration of Mo in the artificial sweat is reasonable, because Mo is able to form oxyanions, which means that its extractability clearly increases from acidic pH values to neutral and alkaline conditions (Al-Abed et al. 2006). Although the highest extractable concentration of Se also occurs in strongly alkaline conditions, the extractability of Se for the fly ash was practically the same in the artificial sweat (3.7 mg/kg; d.w.) and gastric (3.9 mg/kg; d.w.) fluids.

The extraction recovery (*R*) values (%) for the metals, which were determined as the ratio of the metal concentration extracted with artificial sweat and gastric fluids (Table 4) to the total metal concentration in the ash (Table 1), varied between 2.9% (V) and 71.2% (Se) in the artificial sweat fluid and between 11.4% (V) and 94.1% (Cd) in the artificial gastric fluid. The *R*% values for metals in Table 4 have not been calculated in those cases in which the total or the extractable concentration of a metal was lower than the limit of detection by ICP-OES. Therefore, taking into consideration the toxicity properties of many of the heavy metals presented in Table 4 (Cenni et al. 2001; Mroueh et al. 2001; Wahlström et al. 2001) and the observation of high extractable concentrations of certain heavy metals in artificial sweat and gastric fluids, we conclude that careful handling of fly ash is recommended to minimize human health risks, especially if it causes dusting.

## Conclusions

Owing to the slightly elevated extractable concentrations of Mo (3.9 mg/kg; d.w.) and Se (0.2 mg/kg; d.w.) in the fly ash, which exceed the limit values for extractable Mo and Se, this residue cannot be utilized in earth constructions only by submitting a notification to the competent authority. However, such utilization for both covered and paved structures is still possible, although an environmental permit would be required. The highest extractable concentrations in the artificial sweat fluid were observed for Ba, which were 16.9 mg/kg (d.w.) and 25.1 mg/kg (d.w.) for the bottom ash and fly ash, respectively. The highest extractable concentrations in the artificial gastric fluid also were observed for Ba, which were 86.6 mg/kg (d.w.) and 446 mg/kg (d.w.) for the bottom ash and fly ash, respectively. Furthermore, the extractability of Zn in both ashes using artificial gastric fluid was high (100 mg/kg; d.w.), as was the extractability of Cu (38.3 mg/kg; d.w.), As (36.7 mg/kg; d.w.), V (65.6 mg/kg; d.w.), and Pb (20.2 mg/kg; d.w.) for the fly ash. Therefore, in terms of human health risk assessment, we conclude that careful handling of fly ash is recommended to prevent ash dusting and 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.

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