Extractability of heavy metals in cyclone ash

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Abstract. Landfill disposal is the only reasonable option for cyclone ash due to its elevated concentrations of the heavy metals Cd (25 mg kg^{-1}; d.w.), Zn (3630 mg kg^{-1}; d.w.), Ba (4260 mg kg^{-1}; d.w.), and Hg (1.7 mg kg^{-1}; d.w.). The distribution of heavy metals (i.e. Cd, Cu, Pb, Cr, Zn, As, V, and Ba) after a three-stage BCR sequential extraction procedure between the exchangeable (CH$_3$COOH), easily reduced (NH$_2$OH–HCl), and oxidizable (H$_2$O$_2$ + CH$_3$COONH$_4$) fractions showed that the highest concentrations of most of the heavy metals occurred in the oxidizable fraction. This indicates that a major part of the heavy metals retained in the cyclone ash originating from a small-scale (6 MW) municipal district heating plant incinerating forest residues (i.e. wood waste and bark) are not easily liberated under the conditions normally found in nature.

Key words: environmental research, air pollution, ash, cyclone, extraction, heavy metals, waste.

INTRODUCTION

Air contaminants from the energy production plants, e.g. municipal district heating plants, are emitted into the atmosphere as particulates, aerosols, vapours, or gases. The most common methods of eliminating or reducing pollutants to an acceptable level are destroying the pollutant by thermal or catalytic combustion, changing the pollutant to a less toxic form, or collecting the pollutant by use of equipment to prevent its escape into the atmosphere. Fly ash removal from flue gas by using electrostatic precipitators (ESP), cyclones, fabric filters, or wet scrubbers will result in a dry fine solid particulate material, which is commonly called an air-pollution-control (APC) residue [1,2].

During combustion most of the heavy metals in the fuel are retained in the ash. The various ash fractions, such as bottom ash, cyclone ash, filter ash, and fly ash, may contain relatively high concentrations of nutrients and heavy metals. Combustion acts like a thermo-dynamic separation process for the different inorganic materials in the fuel. Elements with a low volatility will concentrate in the bottom ash, while more volatile elements will concentrate in the fly ash. The consequence of this separation effect in combustion plants is that the different ash fractions have a different chemical composition. Flue gas treatment residues may be solids (e.g. dust from cyclones and ESP) or spent adsorbent materials (e.g. saturated resins). Appropriate options for disposal or reuse of these residues will depend on the type and degree of contaminants as well as the waste matrix [3].

Before ash residue can be utilized or disposed of in a landfill, its chemical as well as extraction (leaching) characteristics must be known. During transport, disposal, and storage, it is possible that the APC residues are subjected to leaching effects of rain and to other substances, e.g. chloride, sulphate, and organic matter, which may form complexes with heavy metals. The change of the pH in a landfill environment may also occur, e.g. due to sulphide oxidation, buffering capacity of natural waters, acid rain, and atmospheric CO$_2$. Thus,

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the total elemental concentrations represent a source term only 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 real bioavailability of metals and their potential toxicity, it is necessary not only to determine the total concentrations but also the different chemical forms or processes binding the heavy metals to the solid phase of the sample [4].

Extraction tests are widely used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including recycling or reuse, for assessing the efficacy of a waste treatment process, and after disposal. Sequential extraction tests are being designed to treat the material with different solutions, resulting in the allocation of constituents into separate fractions. Such an approach gives information on which chemical conditions are needed to obtain different extraction efficiencies. Extraction is a procedure that is widely applied for the recovery of elements from various environmental samples such as soil, sediment, airborne particulate matter, sludge, waste, etc. Extraction studies are carried out in the assessment of worst-case environmental scenarios, in which the components of the sample become soluble and mobile [5].

The main purpose of this study was to obtain information about the extractability of heavy metals in the cyclone ash originating from the small-scale (6 MW) municipal district heating plant at Keminmaa, Northern Finland. In Finland and elsewhere in the European Union, the properties of solid wastes and by-products, especially when they are taken to a landfill, have to be investigated. The general principle applied in landfill approval is that the composition and extractability of the waste have to be known. This study is part of a major project in which the sequential extraction procedure is used for assessing the metal partitioning in different types of ash originating from a large-scale (246 MW) fluidized bed co-combustion boiler of a pulp and paper mill complex [6] and from a coal-fired power plant (660 MW) [7], as well as from a small-scale (6 MW) municipal district heating plant [8].

MATERIALS AND METHODS

Sampling

The cyclone ash investigated in this study was obtained from the municipal district heating plant (6 MW) of Keminmaan Energia Oy, Northern Finland, which uses a grate-fired boiler for incinerating forest residues (i.e. wood waste, wood chips, sawdust, and bark). Approximately 60% of the wood incinerated in the plant is hardwood such as birch (*Betula verrucosa*) and

willow (*Salix* spp.), and approximately 40% is softwood such as Scots pine (*Pinus sylvestris*). The cyclone ash was sampled from the cyclone, which is used to reduce the emissions of the flue gas particles. Technically speaking, the cyclone ash is the fly ash fraction that has been trapped in the cyclone. The incineration temperature in the combustion chamber is between 800 and 1100 °C. However, after the boiler, the flue gas is rapidly cooled, and it leaves the plant at temperatures between 130 and 150 °C. The sampling period represented normal process conditions for the plant. A coning and quartering method was applied repeatedly to reduce the ash sample to a size suitable for laboratory analysis. After sampling, the sample was stored in a polyethylene bottle in a refrigerator (+4 °C) until analyses.

Determination of the physical and chemical properties in cyclone ash

The pH and electrical conductivity (EC) of the cyclone ash were determined by a combination pH/EC analyser equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium) and a Phoenix conductivity electrode (Houston, USA) with a cell constant of 1.0. The pH and EC were determined at a solid to liquid (S/L) ratio of 1 : 2.5 (v/v) [9]. Determination of the dry matter content of the cyclone ash was carried out according to the SFS-EN European standard [10], in which a sample is dried overnight to a constant mass in an oven at 105 °C. The organic matter content, expressed as the loss-on-ignition (LOI), and total organic carbon (TOC) were determined according to the SFS-EN European standards [11,12], respectively.

Determination of the total element concentrations in cyclone ash

For the determination of total element concentrations (Cd, Cu, Pb, Cr, Zn, As, V, Ba, and Hg) in the cyclone ash, the dried sample was decomposed (digested) with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM corp., Matthews, USA) using USEPA method 3051 [13]. The cooled solutions were transferred to 100 mL volumetric flasks and the solutions diluted to volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and Elgastat Maxima ion exchange water purification system. All reagents and acids were suprapur or pro analysis quality.

The total mercury concentration was determined with a Thermo Elemental X7 inductively coupled plasma mass spectrometer (Winsford, England). The total element concentrations of the other heavy metals (i.e. Cd, Cu, Pb, Cr, Zn, As, V, and Ba) in the cyclone ash were determined either with a Thermo Elemental

X7 inductively coupled plasma mass spectrometer (Winsford, England) or with a Perkin Elmer Aanalyst 700 cold-vapour atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90plus autosampler.

Sequential extraction procedure and element determinations in the extracts

For the partitioning of heavy metals (i.e. Cd, Cu, Pb, Cr, Zn, As, V, and Ba) between the exchangeable (CH_3COOH), easily reduced ($NH_2OH–HCl$), and oxidizable ($H_2O_2 + CH_3COONH_4$) fractions, we used the three-stage BCR sequential extraction procedure, which is described completely in our previous studies [6–8]. The extraction was carried out in polypropylene bottles by shaking 4 g of ash with the extractant. In order to minimize possible chemical and/or micro-biological changes in the ash during the extraction procedure, cyclone ash as such was used instead of dried samples because, according to Kosson et al. [5], 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 Schleicher and a Schuell (Dassel, Germany) membrane filter (0.45 mm and 47 mm diameter). In order to avoid losses between the leaching stages, the filters and adhering ash particles from the previous extraction stage were also included in the next stage. After addition of 200 μL of 65% HNO_3 in the supernatant phase, it was stored in a refrigerator (+4 °C) until the element determinations. For the determination of the total element concentrations of the heavy metals (i.e. Cd, Cu, Pb, Cr, Zn, As, V, and Ba) in the extracts (i.e. stages 1–3) the same instruments were used as for their determination in cyclone ash.

RESULTS AND DISCUSSION

The physical and chemical properties of the cyclone ash

According to Table 1, the pH of the cyclone ash was strongly alkaline (pH 12.3). According to Van Herck and Vandecasteele [14], an alkaline pH indicates that part of the dissolved metals occur as basic metal salts, oxides, hydroxides, and/or carbonates. Therefore, the proportions of soluble basic metal salts, oxides, hydroxides, and carbonates in the cyclone ash outweigh the proportion of soluble acid components, and the cyclone ash subsequently generates an alkaline pH. However, it is not self-evident that the water fraction of ash is alkaline. The pH of coal fly ash can vary from 4.5 to 12.5 depending largely on the S content of the parent coal. The coals found in the eastern part of the United

Table 1. Physical and chemical parameters of the cyclone ash (concentrations are expressed on a dry weight (d.w.) basis) from Keminmaan Energia Oy

Parameter	Cyclone ash
Loss on ignition (550 °C)	2.1%
Total organic carbon (TOC)	16 g kg^{-1}
Dry matter content (105 °C)	99.8%
pH (1 : 2.5)	12.3
Electrical conductivity (EC)	42.3 mS cm^{-1}

States, e.g. in Pennsylvania and West Virginia, may produce an acidic water fraction, since they have a high sulphur concentration (ca 0.2 wt %). The coals found in the western part of the United States tend to be lower in sulphur; moreover, they have a high calcium concentration. These ashes produce an alkaline water fraction, and from an environmental point of view, this may increase metal leachability [15].

Furthermore, according to the electrical conductivity value (42.2 mS cm^{-1}), which is an index of the total dissolved electrolyte concentration, the leaching solution of the cyclone ash has a relatively high ionic strength, indicating that part of the dissolved metals occur as dissolved basic metal salts, e.g. oxides and hydroxides. The low TOC value of 1.6% (16 g kg^{-1}; d.w.) indicates that the cyclone ash contains almost no unburned organic material. The LOI value (2.1%) also supports this statement. The low content of unburnable material in the cyclone ash indicates the efficiency of incineration in the grate-fired boiler. In our previous studies [6,16] we observed that the unburnable organic material content is usually higher in the fly ash than in the bottom ash. This phenomenon is probably due to the fact that the fly ash particles that rise with the flue gases into the APC devices (e.g. cyclone, electrostatic precipitator) remain for a shorter time in the combustion chamber than those particles associated with the bottom ash fraction.

Total concentrations of heavy metals in the cyclone ash

Table 2 shows the total concentrations of heavy metals in the cyclone ash. From the utilization point of view, we compared the total heavy metal concentrations in the cyclone ash to the maximal allowable heavy metal concentrations for materials used as an earth construction agent, set on the basis of the Finnish legislation. These limit values, which came into force in July 2007, are applied if the ash is utilized e.g. in roads, cycling paths, pavements, car parks, sport fields, etc. According to Table 2, the total Cu, Pb, Cr, As, and V concentrations in the cyclone ash were lower than the Finnish limit value for materials used as an earth construction

Table 2. Total heavy metal concentrations in the cyclone ash determined using USEPA method 3051, extractable concentrations in stages 1–3, the sum of metal concentrations in extraction stages 1–3, recoveries (%), and the Finnish heavy metal limit values for materials used as an earth construction agent

Heavy metal	Total concentration, mg kg^{-1}; d.w.	Extractable concentration, mg kg^{-1}; d.w.			Sum of extraction at stages 1–3, mg kg^{-1}; d.w.	R[a], %	Limit value, mg kg^{-1}; d.w.
		Stage 1	Stage 2	Stage 3			
Cd	25	0.2	2.6	18	21	84	15
Cu	200	0.2	8.0	97	105	52.5	400
Pb	76	0.2	0.2	5.5	5.9	7.7	300
Cr	290	32	2.2	18	52	17.9	400
Zn	3630	0.2	14	3880	3894	107	2000
As	4.0	0.2	0.7	2.6	3.5	87.5	50
V	39	0.3	3.8	1.7	5.8	14.9	400
Ba	4260	36	73	520	629	14.7	3000
Hg	1.7	0.2	0.2	0.3	0.7	41.1	1.0

[a] The recovery (R) = [sum of metal concentrations in extraction stages 1–3/total metal concentration] ×100.

agent. However, the total Cd, Zn, Ba, and Hg concentrations in the cyclone ash exceeded the limit values. Therefore, the cyclone ash cannot be used as an earth construction agent, and it has to be disposed of in landfills.

In this context it is worth noting the relatively low total concentration of mercury (1.7 mg kg^{-1}; d.w.) in the cyclone ash. The low mercury concentration is a favourable outcome, if the cyclone ash is disposed of in landfills. Recently concern has been raised about solid waste disposal and the potential release of mercury from solid waste landfills [17]. It is recognized that the long-term storage of ash containing sorbed or bound mercury might eventually become a host to microorganisms that could form methylated mercury species or could cause the reduction of mercury compounds to elemental mercury. This could enhance vapour transport and some forms of mobility, such as liquid transport with colloids. However, if the ash is strongly alkaline as in this study (pH 12.3), the biotransformation of mercury and of mercury compounds to methylated species is unlikely [17].

Partitioning of heavy metals in the cyclone ash

The distribution of heavy metals in the cyclone ash after a three-stage BCR sequential extraction procedure between the exchangeable fraction (CH$_3$COOH), easily reduced fraction (NH$_2$OH–HCl), and oxidizable fraction (H$_2$O$_2$ + CH$_3$COONH$_4$) is shown in Fig. 1. No partitioning for mercury is shown in Fig. 1 because its total concentration in the cyclone ash was very low.

If inorganic materials and by-products, e.g. wastes, are disposed of in a landfill, tight bounding of the heavy metals to the matrix is favourable. Sequential extraction helps to evaluate the extractability of different heavy metals. Sequential extraction tests are designed to treat

the material with different solutions, resulting in the allocation of constituents into separate fractions. When the sequential extraction procedure is applied for the partitioning of heavy metals in environmental samples (e.g. ash, sludge, sediment, soil, etc.), the ability of different extracting agents to release metal ions depends on their association with specific fractions in the sample. Extractants like electrolytes, weak acids, and chelating agents release metals from coordination sites, while strong acids and redox agents are capable of
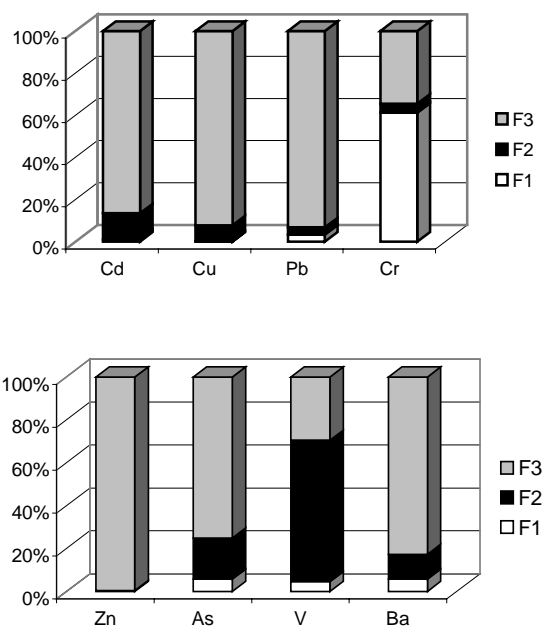

Fig. 1. Partitioning of heavy metals in cyclone ash between the exchangeable (F1; CH$_3$COOH), easily reduced (F2; NH$_2$OH–HCl), and oxidizable (F3; H$_2$O$_2$ + CH$_3$COONH$_4$) fractions.

releasing additional quantities of metals as a result of the decomposition of the solid matrix [18]. Validation of the extraction procedure carried out using reference materials is presented in our previous studies [19,20].

The exchangeable fraction (F1), which is extractable with CH_3COOH, gives an indication of the amount of metals bound on the surface of the particles, as well as of metals that are released as acid-soluble salts such as carbonates. This fraction is bioavailable and corresponds to the forms of metals that are most available for plant uptake, and can be released by merely changing the ionic strength of the medium. The use of acetic acid as an extractant emulates the organic acids produced from decomposing waste in anaerobic environments such as landfill 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 acidogeneous bacteria. Therefore, according to Svensson et al. [21], acetic acid is a realistic choice to simulate a plausible worst-case scenario for waste material co-disposed with municipal solid waste. Among the potentially toxic metals only chromium (61.3%) showed a clear partitioning in this fraction, whereas lead (3.4%), arsenic (5.8%), vanadium (4.5%), and barium (5.7%) showed only a slight tendency to be partitioned in this fraction, and the proportions of cadmium (0.9%), copper (0.2%), and zinc (<0.01%) in this fraction were negligible.

The use of hydroxylamine hydrochloride ($NH_2OH–HCl$), which is a strong reducing agent, as extractant in the easily reduced fraction (F2) simulates anoxic conditions that are likely to occur in the natural medium [22]. The Fe and Mn oxides act as a 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 mobilized with increasing reducing or oxidizing conditions in the environment [4]. Vanadium, especially, showed a clear partitioning in this fraction as its proportion was 65.9%. In addition, cadmium, arsenic, and barium, which are all potentially toxic metals, showed also a clear tendency to be partitioned in this fraction. The proportion of cadmium in this fraction was 12.5%, of arsenic 19.1%, and of barium 11.6%. The proportion of zinc (<0.4%) in this fraction was very low.

The oxidizable fraction (F3), in which the combination of H_2O_2/CH_3COONH_4 is used, corresponds to metals that are organically bound or occur as oxidizable minerals, e.g. sulphides [4]. As metals bound to this fraction can be released under oxidizing conditions, an oxidation process is usually applied to leach out metals associated with the above-mentioned phases. Hydrogen peroxide (H_2O_2), which is used as an oxidizing reagent in this fraction, is a strong oxidant ($E° = 1.77$ V). In general, hydrogen peroxide applied to a heated medium (e.g. 85 °C) is the reagent preferred 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. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions [4]. According to the low TOC (16 g kg^{-1}; d.w.) and LOI (2.1%; d.w.) values (see Table 1), the cyclone ash contains almost no unburnable organic material. From the environmental point of view, the low organic matter in ash is a favourable phenomenon if the ash is disposed of in a landfill. If an ash contains high amounts of organic material, the degradation of the organic matter under oxidizing conditions in a landfill can lead to the release of the metals bound to these organic components. Furthermore, if present, the organic matter may form complexes with toxic heavy metals [23]. However, according to Smichowski et al. [24], the organic fraction released in the oxidizable step is not considered to be very mobile and available. Although heavy metals were extractable in all fractions, the highest concentrations of most of the metals (i.e. Cd, Cu, Pb, Zn, As, and Ba) occurred in the oxidizable fraction (F3), which indicates that these heavy metals in the cyclone ash are not easily liberated under the conditions normally found in nature. The proportion of Cd, Cu, Pb, Zn, As, and Ba in this fraction varied between 75% and 99% (see Fig. 1), whereas the proportions of vanadium and chromium were only 29.5% and 34.5%, respectively.

According to the results given in Table 2, the total heavy metal concentrations are clearly higher than the sum of the three extraction stages (fractions). This can be explained by the fact that extraction does not necessarily mean total decomposition, and the extractable recoveries of analytes are generally lower than the total concentrations. Recoveries can only reach the total values if an element is completely soluble in the extraction solvent [4,5].

CONCLUSIONS

In Finland, the new limit values for materials used as an earth construction agent came into force in July 2006. Because of the elevated total concentrations of the heavy metals Cd (25 mg kg^{-1}; d.w.), Zn (3630 mg kg^{-1}; d.w.), Ba 4260 mg kg^{-1}; d.w.), and Hg (1.7 mg kg^{-1}; d.w.), which exceed the Finnish limit values for material used as an earth construction agent, landfill deposition is the only reasonable alternative for cyclone ash. According to the three-stage BCR sequential extraction procedure (i.e. exchangeable fraction (CH_3COOH), easily reduced fraction ($NH_2OH–HCl$), and oxidizable fraction ($H_2O_2 + CH_3COONH_4$)), the highest con-

centrations of most of the metals occurred in the oxidizable fraction, which indicates that a major part of the heavy metals retained in cyclone ash are not easily liberated under the conditions normally found in nature.

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Raskmetallide ekstraheeritavus tsüklontuhast

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Tingituna kõrgest raskmetallide kontsentratsioonist (Cd 25 mg kg^{-1}, Ba 4260 mg kg^{-1}, Zn 3630 mg kg^{-1} ja Hg $1{,}7$ mg kg^{-1} kuivkaalu kohta) on prügimägedele ladustamine ainus vastuvõetav alternatiiv tsüklontuha jaoks. Raskmetallide Cd, Cu, Pb, Cr, Zn, As, V ja Ba jaotumine pärast kolmeastmelise BCR-i järjestikust ekstraktsiooniprotsessi vahetuva (CH$_3$COOH), kergesti taanduva (NH$_2$OH–HCl) ning oksüdeeruva (H$_2$O$_2$ + CH$_3$COONH$_4$) fraktsiooni vahel näitab, et enamikul raskmetallidel on kõige kõrgem kontsentratsioon oksüdeeruvas fraktsioonis. Sellest järeldub, et põhiosa raskmetallidest, mis tekivad väikestes munitsipaalsoojusjaamades (6 MW) puidujäätmete ja puukoore põletamisel ning mis jäävad tsüklontuha sisse, ei vabane normaalsetes looduslikes tingimustes kergesti.