Chemical and physical properties of cyclone fly ash from the grate-fired boiler incinerating forest residues at a small municipal district heating plant (6 MW)

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ABSTRACT

In Finland, the new limit values for maximal allowable heavy metal concentrations for materials used as an earth construction agent came into force in July 2006. These limit values are applied if ash is utilized, e.g. in roads, cycling paths, pavements, car parks, sport fields, etc. In this study we have determined the most important chemical and physical properties of the cyclone fly ash originating from the grate-fired boiler incinerating forest residues (i.e. wood chips, sawdust and bark) at a small municipal district heating plant (6 MW), Northern Finland. This study clearly shows that elements are enriched in cyclone fly ash, since the total element concentrations in the cyclone fly ash were within 0.2–10 times higher than those in the bottom ash. The total concentrations of 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.) exceeded the limit values, and therefore the cyclone fly ash cannot be used as an earth construction agent. According to the leached amounts of Cr ($38\,mg\,kg^{-1}$; d.w.), Zn ($51\,mg\,kg^{-1}$; d.w.) and sulphate ($50,000\,mg\,kg^{-1}$; d.w.), the cyclone fly ash is classified as a hazardous waste, and it has to be deposited in a hazardous waste landfill.

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1. Introduction

In Finland, the annual heating demand is high, with the share of heating representing 22% of the total energy consumption. In Finland, the biomass-fired power plants in which the total rated thermal input is between 1 and 10 MW, are commonly used for municipal district heating especially in rural areas, as well as in many small towns and urban areas. These so-called small-scale combustion plants, which burn mostly forest residues (i.e. wood chips, sawdust and bark), and peat can be an economically and environmentally advantageous method to exploit locally produced biomass residues [1]. Especially, the use of forest residues for energy production has a number of advantages over other sources—it is renewable, domestic and local, creates jobs and promotes silviculture, and that its sulphur content is very low (ca. 0.02%). The most important justification for the use of wood as a bioenergy, however, is that it could significantly reduce the use of fossil fuels and their carbon dioxide emissions. The use of wood as a biofuel allows the utilization of renewable, natural raw material as an energy source without having any marked effects on the carbon balance in ecosystems [2].

Grate-fired combustion boiler is the oldest method of utilizing coal, solid waste and biomass, but it is still very widely used today, and it is a common combustion technique especially for small-scale combustion plants. The popularity of the grate-firing combustion is due to fact that this technique is appropriate for biomass fuels with high water content, varying particle sizes and high ash content. Furthermore, the advantages of grate furnaces are that this technique has relatively low investment costs for small plants, and in grate furnaces it is possible to use mixtures of wood fuels. However, the disadvantage of energy generation from biomass such as wood residues and bark is that it produces a considerable amount of ash. In the small grate-fired combustion plants two ash flows are produced: the bottom ash remaining on the grate and the fly ash collected in cyclones and bag filters [3,4]. Cyclones and bag filters are used to reduce the emissions of flue gas particles (i.e. fly ash). In Finland, cyclones and multi-cyclones, i.e. several cyclones in series, are used especially in plants whose size is under 10 MW [1].

In the European Union (EU), the properties of solid wastes, especially when they are utilized or taken to a landfill, have to be known.

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In Finland, the new limit values for maximal allowable heavy metal concentrations for materials used as an earth construction agent came into force in July 2007. These limit values, as well as the Finnish national waste legislation is based on the EU directives and regulations [5]. Criteria and procedures for acceptance of at landfills are established in the European Council decision document 2003/33/EC on the landfill of waste [6]. According to EU Landfill Directive 1999/31/EC [7], which is intended to prevent or reduce the adverse effects of direct disposal of untreated waste on human health and on the environment, in particular on surface water, groundwater, soil and air, the waste acceptance criteria impose requirements to waste classification and quality control. The basic requirements for waste classification are: (1) source and origin of the waste, (2) information about the waste production process, (3) information on its composition and on its leaching behaviour and appearance. The European Council Directive 1999/31/EC [7] on landfills classifies all waste into one of three classes: hazardous waste, non-hazardous waste and inert waste. Through classification and characterization, the waste can be related to a class of deposition. The EU Landfill Directive [7], however, to a certain extent does allow for the implementation of national strategies and guidelines within the individual EU member states. At a national level it will be possible to define different sub-classes of non-hazardous waste to prevent co-disposal of waste types with different properties (e.g. organic biodegradable waste and inorganic mineral waste) and different short- and long-term behaviour.

The main purpose of this study was to obtain information about the physical and chemical properties of cyclone fly ash originating from the 6 MW district heating plant of Keminmaan Energia Oy, Northern Finland, which incinerates forest residues (wood chips, sawdust and bark). In this study we have compared the total heavy metal concentrations in the cyclone fly ash to the Finnish heavy metal limit values for materials used as an earth construction agent. We have also evaluated whether the cyclone fly ash should be disposed of either in inert waste, non-hazardous waste or hazardous waste landfill. This study is a part of a major project focusing on the utilization of wastes and by-products from Finnish industry [8,9].

2. Sampling

The cyclone fly ash investigated in this study was obtained from the municipal district heating plant (6 MW) of the Keminmaan Energia Oy, which uses a grate-fired boiler for incinerating forest residues (i.e. wood chips, sawdust and bark). The plant produces about 46 tonnes of cyclone ash per year (dry weight). The incineration temperature inside the boiler (furnace) is ca. 800–1100 °C. After the boiler, the temperature of the flue gas is rapidly cooled, and the flue gas leaves the plant at temperature of between 130 and 150 °C.

Approximately 60% of the wood incinerated in the plant is hardwood such as birch (i.e. *Betula verrucosa*) and willow (i.e. *Saliz* spp.), and approximately 40% is softwood such as Scots pine (i.e. *Pinus sylvestris*). The cyclone fly ash was sampled from the cyclone, which is used for reducing the emissions of flue gas particles. There are no electrostatic precipitators in the plant. The cyclone fly ash is an ash fraction, which has been carried through the flue gas channels into the cyclone and precipitated there [10]. Technically speaking, the cyclone ash is the ash fraction which has been trapped in the cyclone. The ash can be sampled from the cyclone only during maintenance and repair shutdowns at the plant once or twice a year. The ash was sampled at the end of October 2007, and thus the cyclone fly ash investigated in this study is originating from the incineration of wood waste. In Finland, many small municipal district heating plants incinerate wood waste during the

warmer season (ca. April–November) and peat during the winter (ca. December–March). However, some plants, especially the big ones, incinerate the mixture of wood waste and peat all year round. 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 the laboratory analysis. After sampling, the sample was stored in a polyethylene bottle in a refrigerator (+4 °C) until analysis.

3. Experimental

3.1. Determination of the mineral composition, physical and chemical properties

For the determination of the mineralogical composition of the cyclone ash, the X-ray diffractogram of the powdered sample was obtained with a Siemens D 5000 diffractometer using Cu Kα radiation. The scan was run from 2° to 50° (2-theta-scale), with increments of 0.02° and a counting time of 1.5 s per step. Operating conditions were 40 kV and 40 mA. Peak identification was done with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and ICDD PDF-2 Release 2006 package software package (Pennsylvania, USA).

The pH and electrical conductivity (EC) of the cyclone fly ash was determined by a combination pH/EC analyser equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium) and a Phoenix conductivity electrode with a cell constant of 1.0 (Phoenix Electrode Company, USA). Determination of the pH and EC was carried out according to the European standard SFS-EN 13037 [11] at a solid to liquid (S/L) ratio of 1:2.5 (v/v).

Determination of the dry matter content (DMC) of the cyclone fly ash was carried out according to the European standard SFS-EN 12880 [12], in which a sample is dried overnight to a constant mass in an oven at 105 °C. The loss-on-ignition (LOI) value was determined according to the European standard SFS-EN 12879 [13], in which an oven-dried (105 °C) sample is dry-digested overnight in a muffle furnace (Box Furnace, Lindberg, Blue M, Asheville, USA) at 550 °C. Determination of the total organic carbon (TOC) content in the ash sample was carried out according to the European standard SFS-EN 13137 [14] using a LECO CHN-600 analyser (Leco Inc., USA), in which a sample is combusted and the evolved carbon dioxide is measured by infrared spectrometry. The neutralizing (liming effect) and reactivity values were determined according to the European standards SFS-EN 12945 [15] and the SFS-EN 13971 [16], respectively.

3.2. Determination of the easily soluble nutrient concentrations

The determination of easily soluble nutrients such as P, Ca, Na, K, S, Mg, Cu and Zn in cyclone fly ash was carried out according to the procedure of MTT Agrifood Research Finland developed by Yli-Halla and Palko [17]. Easily soluble P, Ca, Na, K, S and Mg were extracted with 0.5 M acidic ammonium acetate (pH 4.65). In the extraction of Cu and Zn, the acidic (pH 4.65) ammonium acetate extract contained 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA). Ammonium acetate extraction is widely used as an indicator of nutrient availability, but it does not give the total concentrations of elements in environmental samples such as waste, sludge or soil [18]. In both extraction procedures, one volume part of a dry sample (i.e. ash) was shaken with 10 parts of extraction solution for 1 h. Before analysis, the extract was separated from the solid residue by filtration through a Schleicher & Schuell 589 (Dassel, Germany) blue ribbon filter paper (12.5 mm diameter).

The concentration of P in the extract was determined spectrophotometrically by the molybdenum blue method [19] using an automatic Foss—Tecator FIAStar 5000 Flow Injection Analyser (Högnes, Sweden). The concentrations of Ca, Na, K, S and Mg were determined by inductively coupled plasma optical emission spectrometer (ICP/OES, Thermo Elemental Iris Interepid II XDL, Franklin, USA), and the concentrations of Cu and Zn by flame atomic absorption spectrometer (FAAS, PerkinElmer Aanalyst 700, Norwalk, USA). Before the nutrient determination on the cyclone fly ash, the sample was dried overnight to constant mass at 105 °C in a drying oven (Termaks) according to the European standard SFS-EN 13137 [12].

3.3. Determination of the total element concentrations

For the determination of total element concentrations in the cyclone fly 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 [20]. The cooled solutions were transferred to 100 mL volumetric flasks and the solutions were 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 suprapure or pro-analysis quality.

Except for Hg, the total element concentrations in the ash sample were determined with a Thermo Elemental IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer (Franklin, USA). The concentration of Hg in the ash was determined with a PerkinElmer Aanalyst 700 cold-vapour atomic absorption spectrometry (Norwalk, USA) equipped with a PerkinElmer FIAS 400 and AS 90plus autosampler.

3.4. Leaching procedures and determination of leachable concentrations in extractants

For the determination of the leachable concentrations of As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn in the cyclone fly ash, the European standard SFS-EN 12457-3 was used [21]. This procedure is a two-stage batch test at a liquid-to-solid ratio (L/S) of 2 and 8 L/kg, and the sum of leachable concentrations (i.e. L/S 10 L/kg) is compared to the maximal allowable concentrations, which in turn, determines whether the cyclone fly ash may be disposed of in inert waste, non-hazardous waste or hazardous waste landfill. The metal concentrations in the extracts were determined with a Thermo Elemental IRIS Intrepid II XDL inductively coupled plasma optical emission spectrometer (Franklin, USA). Determination of the dissolved organic carbon (DOC) content in the extractant was carried out according to the SFS-EN 1484 European standard [22,23] using a Shimadzu TOC-V CPH analyser (Shimadzu Inc., Japan). Determination of the chloride, fluoride and sulphate concentrations in the extractant were carried out according to the SFS-EN ISO 10304-1 European standard [24] using a Dionex ICS 2000 ion chromatography with conductivity detection (Dionex Corp., USA).

4. Results and discussion

4.1. The mineral composition, physical and chemical properties

The XRD pattern shown in Fig. 1 indicates that several distinct peaks were observed and the following mineral classes and minerals were identified in the cyclone ash:oxides (i.e. quartz, hematite and periclase), carbonates (i.e. calcite, siderite and ankerite) and silicates (i.e. albite and kaolinite). Although the mineral composition of cyclone ashes (i.e. fly ash) depends, e.g. on the combustion temperature, the fly ash capturing mechanism, as well as the
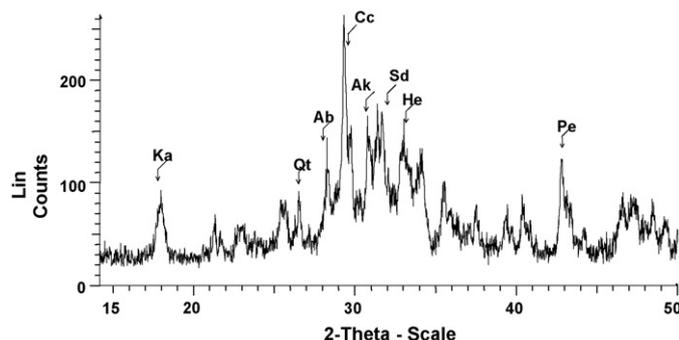

Fig. 1. XRD pattern of the cyclone fly ash. Mineral abbreviations and their abundants (%) are: Ka, kaolinite [(Al$_2$Si$_2$O$_5$)(OH$_4$); 10.5%]; Qt, quartz [SiO$_2$; 5.3%]; Ab, albite [NaAlSi$_3$O$_8$; 21.2%]; Cc, calcite [CaCO$_3$; 14.5%]; Ak, ankerite [Ca(Fe,Mg,Mn)(CO$_3$); 24.8%]; Sd, siderite [FeCO$_3$; 10.8%]; He, hematite [Fe$_2$O$_3$; 6.3%]; Pe, periclase [MgO; 6.6%].

fuels burnt [25], our results agree with the findings of Martins et al. [26], that calcite (CaCO$_3$), especially, is typically observed in wood ash. This is due to the fact that wood chips are abundant in calcium.

According to Table 1, the pH of the cyclone fly ash was strongly alkaline (pH 12.3), which means that it has liming effect. According to Van Herck and Vandecasteele [27], an alkaline pH indicates that part of the dissolved metals occur as basic metal salts, oxides, hydroxides and/or carbonates. Thus, the proportions of soluble basic metal salts, oxides, hydroxides and carbonates in the cyclone fly ash therefore outweigh the proportion of soluble acid components, and the cyclone fly ash subsequently generates an alkaline pH. Furthermore, according to the electrical conductivity value (42.3 mS cm^{-1}), which is an index of the total dissolved electrolyte concentration, the leaching solution of the cyclone fly ash has a relatively high ionic strength, indicating that part of the dissolved metals occurs 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 fly ash contains almost no unburned organic material. Although the LOI is widely attributed to the amount of combustible matter of the sample, according to the findings of Payá et al. [28], it does not represent well the amount of unburned carbon in ash, but rather the volatile fraction.

Table 1
The physical and chemical parameters of the cyclone fly ash, concentrations of easily soluble nutrients in the cyclone fly ash and in the bottom ash [10], as well as the enrichment factor (EF) of the elements

Nutrient/parameter	Unit[a]	Cyclone fly ash (fuel: wood)	Bottom ash (fuel: wood)	EF[b]
Ca	g kg^{-1} (d.w.)	138	84.2	1.6
Mg	g kg^{-1} (d.w.)	19.4	12.4	1.5
Na	g kg^{-1} (d.w.)	3.3	2.3	1.4
K	g kg^{-1} (d.w.)	65.0	22.1	2.9
S	g kg^{-1} (d.w.)	24.1	2.3	10.5
P	g kg^{-1} (d.w.)	3.4	1.2	3.1
Cu	mg kg^{-1} (d.w.)	100	47.5	2.1
Zn	mg kg^{-1} (d.w.)	3500	762	4.6
LOI (550 °C)	% (d.w.)	2.1	6.8	
TOC	g kg^{-1} (d.w.)	16	n.d.	
DMC (105 °C)	%	99.8	69.3	
NV	% (Ca; d.w.)	31.1	30.6	
r_{ac}	% (Ca; d.w.)	29.2	19.0	
pH (1:2.5)	–	12.3	12.0	
EC	mS cm^{-1}	42.3	3.7	

n.d. = not determined.

[a] Concentrations are expressed on a dry weight (d.w.) basis.

[b] EF = [total element concentration in the cyclone fly ash/total element concentration in the bottom ash].

Table 2
Total element concentrations (i.e. microwave oven digestion with a mixture of 3 mL HCl and 9 mL HNO_3 using the USEPA method 3051) in the cyclone fly ash and in the bottom ash [10], the enrichment factor (EF) of the elements and the literature values for heavy metal concentrations in fly ash and bottom ash when forest residues are used as fuel [18,33–35], as well as the Finnish heavy metal limit values for materials used as an earth construction agent

Element	Cyclone fly ash[a] (fuel: forest residues)	Bottom ash[a] (fuel: forest residues)	EF[b]	Literature value[a] (fly ash)	Literature value[a] (bottom ash)	Limit value[a] (earth construction agent)
Cd	25	5.7	4.4	6–40	0.4–0.7	15
Cu	200	196	1.0	−200	15–300	400
Pb	76	29	2.6	40–1000	15–60	300
Cr	290	318	0.9	40–250	>60	400
Zn	3630	950	3.8	3280–4865	15–1000	2000
As	4.0	14	0.3	1–60	0.2–3	50
Co	13	11	1.2	2–300	0–7	
V	39	41	0.9	20–30	10–120	400
Ni	47	46	1.0	20–100	40–250	
Ba	4260	2210	1.9	549–588		3000
Fe	13,200	15,800	0.8	3300–19,500		
Mn	20,000	15,600	1.3	6000–29,000	2500–5500	
Ti	250	1240	0.2	11		
S	24,500	2440	10	4000–23,000		
Hg	1.7	n.d.	n.d.	0–1	<0.4	1.0

n.d. = not determined.

[a] All concentrations ($mg\,kg^{-1}$) are expressed on a dry weight (d.w.) basis.

[b] EF = [total element concentration in the cyclone fly ash/total element concentration in the bottom ash].

The acid neutralizing value (NV) of 31.1% for the cyclone fly ash expressed as Ca equivalents (d.w.) indicates that 1.2 tonnes of cyclone fly ash would be required to replace 1 tonne of a commercial limestone produced by SMA Mineral Ltd., the neutralizing value of which is 38% (Ca equivalents; d.w.). The reactivity value (r_{ac}) was derived in order to assess the speed and effectiveness of the neutralizing potential of the liming material in the ash. The r_{ac}/NV ratio indicates that the so-called "fast acting" capacity is ca. 94% for the cyclone fly ash. This means that the cyclone fly ash has an excellent liming effect.

The easily soluble Ca concentration of $138\,g\,kg^{-1}$ (d.w.) in the cyclone fly ash is 86 times higher than the typical value of $1.6\,g\,kg^{-1}$ (d.w.) in arable land in Central Finland [29]. The DMC of the cyclone fly ash (99.8%) is high compared to that of the bottom ash (69%). This is due to fact that the bottom ash is transferred from the boiler via a conveyor belt which conveys it to the ash-silo (i.e. ash-collector tank) using water. Although most of the water is eliminated before the bottom ash is collected in the silo, it still contains some water which gives it a relatively low dry matter content.

4.2. The total element concentrations and enrichment factors of the element in the cyclone fly ash

Table 2 shows the total element concentrations in the cyclone fly ash compared to those in the bottom ash, as well as the enrichment factors (EF) of each elements. The EF is determined as the ratio of element concentrations in the cyclone fly ash to those in the bottom ash. According to the results in Table 2, the concentrations of elements such as Cd, Pb, Zn and S in the cyclone fly ash were clearly higher than those in the bottom ash. The elevated EF value indicates high element volatilisation during the combustion process and subsequent condensation, whereas a low EF value is indicative of non-volatile behaviour and formation of a heavier mineral phase [3]. The EF value for Hg is not known, because the concentration of mercury in the bottom ash was not analysed. According to our previous studies on the combustion of wood and/or peat, mercury is not generally observed in the bottom ash [29–32]. Thus, our result in Table 2 for low Hg concentration in wood ash agrees with the findings reported in the literature that the concentration of Hg in wood ash is very low. This is due to the fact that, Hg is almost completely volatilised and escapes with the flue gas due to its high

vapour pressure, but also due to the fact that the Hg concentration in forest residues (i.e. wood chips, sawdust and bark) is very low, usually lower than $0.01\,mg\,kg^{-1}$ (d.w.). If we compare our total heavy metal concentrations in the cyclone fly ash to those reported by other researches [18,33–35], we can observe that the concentrations we have obtained for Cd, Cu, Pb, As, Co, Ni, Fe and Mn are in relatively good agreement with the literature values (see Table 2). However, our observation for the concentrations of Cr, V, S and Hg exceeded slightly the literature values, whereas the concentrations of Ba and Ti were clearly higher than the concentrations reported in the literature [18,33–35].

In this context it is also worth noting the low total concentration of mercury ($1.7\,mg\,kg^{-1}$; d.w.) in the cyclone fly ash (Table 2). The low mercury concentration in the cyclone fly ash is a favourable outcome, if it disposed of in landfills. Recently concern has been raised about solid waste disposal and the potential release of mercury from solid waste landfills [36]. In municipal waste landfills, where the mercury concentration is reported to reach values of up to $70\,mg\,kg^{-1}$ (d.w.), mercury diffuses into the atmosphere or can be methylated to methyl mercury. The very high Hg concentration in municipal landfills is due to the fact that mercury-containing material enters municipal landfills from a wide range of sources, including fluorescent lights, batteries, electrical switches, thermometers, and general waste [36]. If the mercury is not stable in the waste and by-products, it will eventually enter the global mercury cycle. It is recognized, however, that the long-term storage of ash containing sorbed or bound mercury might eventually become a host to micro-organisms 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, the biotransformation of mercury and of mercury compounds to methylated species is unlikely [36,37].

The results in Table 2 indicate that the incineration temperature of between 750 and 900 °C in the grate-fired boiler is high enough to vapourise some of the elements. Most of these elements form compounds which condense on the surface of particles in the flue gas, leading to enrichment of some elements in the cyclone fly ash fraction. Consequently, the bottom ash fraction has an enhanced content of non-volatile components, and frequently contains sintered or melted particles [3]. The environmentally

relevant metals like cadmium and lead will concentrate in the fly ash. According to Narodoslawsky and Obernberger [38] the key to this phenomenon is obviously the temperature at which these flows are precipitated.

The enrichment of S in the cyclone fly ash is especially worth noting. During combustion, sulphur sublimates or reacts by forming gaseous compounds such as SO_2 and SO_3. As a result, most of the S passes to the vapour phase, and reacts with inorganic components to form sulphates. According to Obernberger [4], the efficiency of S—fixation in the ash depends on the concentrations of alkaline earth elements, and especially of Ca in the ash, as well as on the efficiency and technology used for dust precipitation. However, this is beneficial from the environmental point of view, because SO_2 is removed from the flue gases, thus decreasing the SO_2 emissions from the plant. During combustion the solid organic matter is decomposed and elements that form ash such as alkali metals and alkaline earth metals are released. In the part of the boiler (i.e. in the cyclone) where the flue gas is rapidly cooled, the sulphates condense on the particles of fly ash or on the tube surfaces [4,5]. In this context it is worth noting that in our previous study [22] we observed that the concentration of sulphur in the fly ash was ca. 25 times and for other elements ca. 2–7 times to those in the bottom ash from the co-combustion of wood and peat at a large-scale fluidized-bed combustion boiler (267/315 MW) of the municipal district heating plant. Thus, the quality of ash varies significantly depending on, e.g. the ratio of the fuels burnt, tree species, growing site, climate and tree component, e.g. bark, wood and leaves. Other factors which affect the ratio of various elements between the bottom ash and fly ash depends on the type of boiler, operating conditions and the efficiency of the flue gas cleaning devices [25].

From the environmental point of view, in Table 2 we have compared the total heavy metal concentrations in the cyclone fly 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 Cd, Zn, Ba and Hg concentrations in the cyclone fly ash exceeded the new Finnish limit value for materials used as an earth construction agent.

We would like to point out, that caution must be exercised if application is to occur in the natural environment and the utilization of ash and other industrial residues always need approval by the competent authority. Although many European countries, e.g. France [39], Denmark [40], Germany [41], Finland [42], Spain [43] and Sweden [44], have established legislation that enables and controls the recycling of biomass-derived ash in the forest environment, or allow the its use as an earth construction agent, the existing legislation must always be applied [45]. If ashes are used as a fertilizer in agriculture and in forestry, limit values for heavy metal concentrations are naturally much more lower than the limit values for material used as an earth construction agent. Thus, it is clear that the cyclone fly ash investigated in this study is not suitable for a fertilizer in agriculture and in forestry.

4.3. Hazard classification of the cyclone fly ash for landfill disposal

Due to elevated concentrations of heavy metals in the cyclone fly ash, it is difficult to utilize and therefore the landfill disposal for the cyclone ash is a favourable alternative. In the EU, the hazardous classification of wastes should be done before decisions are made on waste landfill disposal. In this study, the chemical classification of the cyclone fly ash was done by comparing the leached amounts of substances with the leaching limit values of

Table 3
Leachable concentrations of heavy metals, chloride, fluoride, sulphate and dissolved organic carbon (DOC) at a liquid-to-solid (L/S) ratio of 10 L/kg (mg kg^{-1}; d.w., $n = 1$) in the cyclone fly ash and the current European limit values (mg kg^{-1}; d.w.) of these compounds for acceptance of waste at landfills [6]

Element	Cyclone fly ash (fuel: wood)	Inert waste landfill	Non-hazardous waste landfill	Hazardous waste landfill
As	<0.2	0.5	2.0	25
Ba	2.7	20	100	300
Cd	<0.02	0.04	1.0	5.0
Cr	38	0.5	10	70
Cu	<0.1	2.0	50	100
Hg	<0.005	0.01	0.2	2.0
Mo	5.4	0.5	10	30
Ni	<0.1	0.4	10	40
Pb	2.1	0.5	10	50
Sb	<0.05	0.06	0.7	5.0
Se	1.5	0.1	0.5	7.0
Zn	51	4.0	50	200
Cl$^-$	7220	800	15,000	25,000
F$^-$	28	10	150	500
SO$_4^{2-}$	50,000	1000	20,000	50,000
DOC	29	500	800	1000

the EU [6]. According to Table 3, the leached amount of sulphate concentration (50,000 mg kg^{-1}; d.w.) was very high, and leached amounts of Cr (38 mg kg^{-1}; d.w.) and Zn (51 mg kg^{-1}; d.w.) were elevated. The leached amount of Cr exceeded clearly and Zn slightly the limit values for a non-hazardous waste landfill. The leached amount of sulphate was equal to the limit value for a hazardous waste landfill in European Union. Therefore, the cyclone fly ash has to be deposited of in a hazardous waste landfill. However, in this context it is worth noting that the so-called "after-treatment methods of ash" such as thermal plasma treatment [46], and pelletizing together with re-burning [47] have in some cases successfully used to reduce the leachability of heavy metals in ash; these may be tools for environmental protection for ashes with high metal concentrations such as cyclone fly ash.

5. Conclusions

This study clearly shows that combustion acts like a thermodynamic separation process for different inorganic materials in the fuel, and most of the heavy metals are enriched in cyclone fly ash. According to the enrichment factors, which is the ratio of element concentrations in the cyclone fly ash to those in the ash from the outlet of the biomass-fired system (i.e. bottom ash), the concentrations of most of the elements in the cyclone fly ash were within 1.0–10 times higher than those in the bottom ash when wood is used as a fuel. The total 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.) concentrations in the cyclone fly ash exceeded the new Finnish limit values for materials used as an earth construction agent. Therefore, the cyclone fly ash cannot be used as an earth construction agent, e.g. in roads, cycling paths, pavements, car parks, sport fields, etc., where the limit values are applied.

Chemical classification of the cyclone fly ash was done by comparing the leached amounts of substances with the leaching limit values of the European Union. The leached amount of sulphate concentration (50,000 mg kg^{-1}; d.w.) was very high, and leached amounts of Cr (38 mg kg^{-1}; d.w.) and Zn (51 mg kg^{-1}; d.w.) were elevated. The leached amount of Cr exceeded clearly and of Zn slightly the limit values for a non-hazardous waste landfill. The leached amount of sulphate was equal to the limit value for a hazardous waste landfill in European Union. Therefore, the cyclone fly ash has to be deposited of in a hazardous waste landfill.

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