

Comparison of The Fertilizer Properties of Ash Fractions from Medium-Sized (32 MW) and Small-Sized (6 MW) Municipal District Heating Plants

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Abstract—Due to the low heavy metal concentrations, the bottom ash from a 32 MW municipal district heating plant was determined to be a potential forest fertilizer as such. However, additional Ca would be needed, because its Ca concentration of 1.9-% (d.w.) was lower than the statutory Finnish minimum limit value of 6.0-% (d.w.) for Ca in forest fertilizer. Due to the elevated As concentration (53.0 mg/kg; d.w.) in the fly ash from the 32 MW municipal district heating plant, and Cr concentration (620 mg/kg; d.w.) in the ash fraction (i.e. mixture of the bottom ash and fly ash) from the 6 MW municipal district heating plant, which exceed the limit values of 30 mg/kg (d.w.) and 300 mg/kg (d.w.) for As and Cr, respectively, these residues are not suitable as forest fertilizers. Although these ash fractions cannot be used as forest fertilizer as such, they can be used for the landscaping of landfills or in industrial and other areas that are closed to the public. However, an environmental permit is then needed.

Keywords—Ash, fertilizer, peat, forest residue, waste

I. INTRODUCTION

ALL extraction of biomass from the forest removes nutrients. During the combustion of forest residues and peat, the nutrients and acid-buffering substances are concentrated in the ash. This makes the ash potentially suitable as a compensatory fertilizer to replace the lost nutrients and acid-buffering capacity in forest soil. For the sustainable utilisation of biomass in dedicated combustion plants, the most beneficial approach involves the return of the ash discards to the field or the forest as a relatively low-grade fertiliser, based principally on the lime, potassium and phosphorus contents of the ash [1]. The dumping of ash in landfills conflicts with public efforts to reduce waste disposal to landfills through increased recycling and reuse. The EU Landfill Directive (1999/31/EC) has resulted in the stricter regulation of landfills [2]. Many of

these cannot meet the current requirements and are consequently being shut down. The cost of running landfills has also increased because of the new regulations. This has made it economically feasible to return forest fuel ash to the forest and in so doing complete the cycle of nutrients and restore the acid-buffering capacity. The large and increasing volume of ash residues arising from Finnish pulp and paper mills is motivating a search for alternative disposal options to landfill. The utilization of solid wastes and residues, such as ash, allows industry to implement the 3R principle of the reduction, reuse and recycling of materials as beneficial products [3]. Therefore, there is a growing trend towards the utilization of ash residues in Finnish pulp and paper mills. Careful attention to ash chemistry can maximize the potential of ash residues for beneficial application instead of the relying on landfills for their disposal.

II. BACKGROUND

A. An overview of Finnish national legislation on ash utilization in forestry

In Finland, national legislation regulates the utilization of ash in forestry. The Fertilizer Product Act (539/2006), the Degree on fertilizer products (12/07 and 9/09) and the Degree on the operations concerning fertilizer products and their supervision (13/07) set guidelines for ash recycling and fertilizing in forestry [4-7]. According to these regulations, only wood, peat or agrobiomass ash is permitted to be used as a raw material for agroash and forest ash. Air pollution control (APC) residues are not allowed to be used as fertilizer products. According to Finnish legislation, “agroash” refers to ash 1) to be used as such as a fertilizer product, 2) to be used in agriculture, horticulture, landscaping and forestry, and 3) having a minimum P+K content of 2-% and at least 8-% of Ca. “Forest ash” refers to ash 1) to be used as such as a fertilizer product, 2) to be used only in forestry, 3) having a minimum P+K content of 1-% and at least 6-% of Ca, and 4) having a maximum Cl content of 2-% [8]. According to the procedures of the Finnish Ministry of Agriculture and Forestry [4-6], which sets statutory rules for fertilizer products in Finland, the average maximum load of cadmium due to the use of fertilizer products must not exceed 1.5 g of cadmium per hectare per year. The maximum load of cadmium due to the application of fertilizer products as used batches and as cycles of use may be: 1) no more than 6 g per hectare at an

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interval of four years in agriculture and horticulture; 2) 15 g per hectare at an interval of 10 years in landscaping; and 3) no more than 60 g per hectare at an interval of 40 years in forestry [4-8]. Furthermore, the Finnish legislation on fertilizer products set rules for the spreading of ash and the levels of cadmium and phosphorous in the ash. The width of the buffer zone around lakes and alongside rivers has to be at least 25 m. The maximum permissible cadmium concentration in fertilizer is 22 mg Cd per kg P_2O_5 . In addition, possible municipal environmental regulations have to be taken into account during ash spreading [4-5].

III. EXPERIMENTAL

A. Ash sampling procedures

The bottom ash and fly ash fractions originating from a large-sized (32 MW) municipal district heating plant were sampled during the period when approximately 70-% of the energy produced by the bubbling fluidized bed boiler (BFB) originated from the incineration of commercial peat fuel, and 30-% from the incineration of clean forest residues (i.e. 15-% stumps and 15-% sawdust). The peat fuel was of domestic origin. The tree species of stumps and sawdust were pine (*Pinus sylvestris*) and spruce (*Picea abies*), which were both of domestic origin. However, their relative proportions were not known. The bottom ash was sampled from the outlet of the boiler and the fly ash from the boiler's electrostatic precipitator. Sampling was carried out over a period of three days, and three individual samples (1 kg per sampling day) were combined to give one composite sample with a weight of 3 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_2 content and temperature. The incineration temperature in the bed sand of the boiler varies between 810 and 830 °C and that in the upper zone of the boiler between 1100 and 1200 °C. After the boiler, the temperature of the flue gas entering the combination of wet scrubber and heat exchange is ca. 142 °C, and decreases to around 50 °C, when it is emitted from the plant [9]. After sampling, the samples were stored in plastic bags in a refrigerator (+4 °C). A coning and quartering method [10] was repeatedly applied to reduce the ash sample to a size suitable for conducting laboratory analyses.

The ash fraction originated from a small-sized (6 MW) municipal district heating plant was sampled from the ash silo after clean forest residues (i.e. woodchips and sawdust) had been incinerated. This ash fraction is actually a mixture of ash from the moving grate (i.e. bottom ash) and that which has been carried through the flue gas channels into the cyclone (i.e. fly ash) and precipitated from there. The tree species of the woodchips and sawdust were pine (*Pinus sylvestris*), spruce (*Picea abies*), willow (*Salix*) and birch (*Betula verrucosa* and *Betula pubescens*), which were all of domestic origin. However, their relative proportions were not known. Sampling was carried out over a period of three days, and three individual samples (1 kg per sampling day) were

combined to give one composite sample with a weight of 3 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_2 content and temperature. The incineration temperature inside the boiler is ca. 800 - 1100 °C. After the boiler, the flue gas rapidly cools, and the flue gas leaves the plant at a temperature of between 130 - 150 °C [11]. After sampling, the samples were stored in plastic bags in a refrigerator (+4 °C). A coning and quartering method [10] was repeatedly applied to reduce the ash sample to a size suitable for conducting laboratory analyses.

B. Determination of the mineral composition, dry matter content and neutralizing value of the ashes

To determine the mineralogical composition of the ash, X-ray diffractogram of powdered sample was obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using $CuK\alpha$ radiation. The scan was run from 2 to 80° (2-theta-scale), with increments of 0.02° and a counting time of 1.0 second 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 software package (Pennsylvania, USA).

Determination of the dry matter content of the ashes was carried out according to European standard SFS-EN 12880, in which a sample is dried overnight to a constant mass in an oven at 105 °C. The neutralizing (liming effect) value was determined according to the European standard SFS-EN 12945. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous paper [11].

C. Determination of the total chloride and water soluble phosphorous concentrations of the ashes

Determination of the total chloride concentration in the ashes was carried out according to European standard CEN/TS 15289 [12]. In this procedure, the ash is extracted with HNO_3 in a CEM Mars 5 microprocessor-controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) at 120 °C for 1 hour. The concentration of chlorine in the extract was determined with a Dionex DX500 ion chromatography system (Dionex Corp., U.S.A.). Before the nutrient determination, samples were dried overnight to constant mass at 105 °C in a drying oven (Termaks) according to European standard SFS-EN 12880. A more comprehensive review of the standards, analytical methods and instrumentation is provided in our previous paper [11]. Determination of the water soluble phosphorous concentration in the ashes was carried out according to European standard CEN/TS 15105 [12]. In this procedure, the ash is heated with water in a closed container at 120 °C for 1 hour. The concentration of phosphorous in the extract was determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES).

D. Determination of the total Ca, Mg, K and P concentrations in the ashes

Determination of the total Ca, Mg, K and P concentrations in the ashes were carried out according to the ASTM method C 1301-95 [13]. In this procedure, the ash sample is digested by the lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) fusion followed by dissolution in 65 % HNO_3 . The cooled solution was transferred to a 100 mL volumetric flask and the solution was 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 (Elga, Ltd; Bucks, England). All reagents and acids were suprapure or pro analysis quality. The Ca, Mg, K and P concentrations in ashes were determined with a Thermo Fisher Scientific iCAP6500 Duo ICP-OES (United Kingdom).

E. Determination of the total heavy metal concentrations in the ashes

To determine the total heavy metal concentrations (B, As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) in the ashes, the dried sample was digested with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a CEM Mars 5 microprocessor-controlled microwave oven with a CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using USEPA method 3051A [11]. The cooled solution was transferred to a 100 mL volumetric flask and the solution was 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 (Elga, Ltd; Bucks, England). All reagents and acids were suprapure or pro analysis quality. Except for Hg, the total heavy metal concentrations in the ashes were determined with a Thermo Fisher Scientific iCAP6500 Duo ICP-OES (United Kingdom). The concentration of Hg in the ash was determined with a Perkin Elmer Analyst 700 cold-vapour AAS equipped with a Perkin Elmer FIAS 400 and AS 90 plus auto-sampler.

IV. RESULTS AND DISCUSSION

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

The XRD spectra in Figure 1(A - C) show similarities and differences in the mineral composition of the ashes. Bottom ash (Fig. 1A) and fly ash (Fig. 1B) that were obtained from the incineration of peat and clean wood residues (i.e. stumps and sawdust) in the bubbling fluidized bed boiler (32 MW), both contained silicate minerals such as microcline (KAlSi_3O_8) and quartz (SiO_2). Muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), which are silicate minerals, only existed in bottom ash (Fig. 1A), whereas oxide minerals such as calcium aluminium oxide (CaAl_2O_4), srebrodolskite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) and lime (CaO), as well as anhydrite (CaSO_4), which is a sulphate mineral, only existed in fly ash (Fig. 1B).

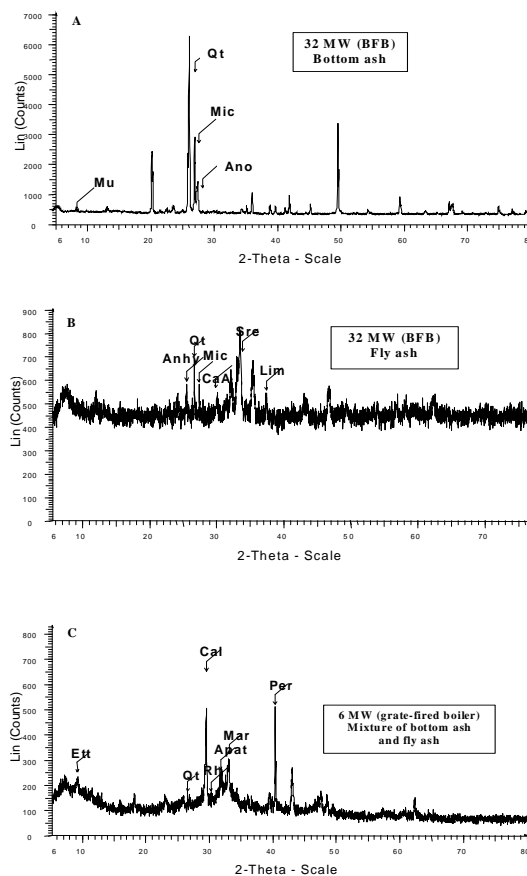


Fig. 1 XRD patterns of the ashes originating from the medium-sized (32 MW; spectra A and B) and small-sized (6 MW; spectra C) municipal district heating plants

Mineral abbreviations and their abundances (%) are:

Spectra A: Mu = Muscovite [$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$; 5.2-%]; Qt = Quartz [SiO_2 ; 58.4-%]; Mic = Microcline [KAlSi_3O_8 ; 16.1-%]; Ano = Anorthite [$\text{CaAl}_2\text{Si}_2\text{O}_8$; 20.3-%].

Spectra B: Anhy = Anhydrite [CaSO_4 ; 8.7-%]; Qt = Quartz [6.8-%]; Mic = Microcline [10.3-%]; CaA = Calcium Aluminium Oxide [CaAl_2O_4 ; 12.6-%]; Sre = Srebrodolskite [$\text{Ca}_2\text{Fe}_2\text{O}_5$; 58.7-%]; Lim = Lime [CaO ; 2.9-%].

Spectra C: Ett = Ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}(\text{H}_2\text{O})_{26}$; 6.7-%]; Qt = Quartz [1.5-%]; Cal = Calcite [CaCO_3 ; 28.1-%]; Rh = Rhodonite [$(\text{Mn},\text{Fe},\text{Mg},\text{Ca})_5(\text{SiO}_3)_5$; 8.4-%]; Apat = Hydroxylapatite [$\text{Ca}_4(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$; 22.8-%]; Mar = Marokite [$\text{Ca}(\text{Mn}_2\text{O}_4)$; 10.1-%]; Per = Periclase [MgO ; 22.3-%].

The mineral composition of the mixture of bottom ash and fly ash (Fig. 1C) from the grate-fired boiler (6 MW) contained ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}(\text{H}_2\text{O})_{26}$), which is a sulphate mineral, quartz (SiO_2), calcite (CaCO_3), which is a carbonate mineral, rhodonite ($(\text{Mn},\text{Fe},\text{Mg},\text{Ca})_5(\text{SiO}_3)_5$), which is a silicate mineral, hydroxylapatite ($\text{Ca}_4(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$), which is a phosphate mineral, as well as oxide minerals such as marokite ($\text{Ca}(\text{Mn}_2\text{O}_4)$) and periclase (MgO). In this context, it is worth

noting that although X-ray diffraction (XRD) analysis can be useful in identifying the chemical species of crystalline particles in ash, an XRD spectrometer is unable to identify the amorphous (glass) phase (i.e. non-crystallised matter), and its detection limit is normally 1 - 2-% (w/w). In this context it is worth to mention that, a Cu-tube was used in the measurement of the XRD spectra, which energizes the X-rays of Fe in the ash. Therefore, the background of the XRD spectra in the figures is relatively high (see Fig. 1A-C).

The existence of silicate minerals in the ashes originating from the bubbling fluidized bed boiler (32 MW) is reasonable when considering that the bed material of fluidized bed boiler furnaces usually consists of silica sand. Furthermore, the existence of silicate minerals in these ash fractions as well as in the ash originating from the grate-fired boiler (6 MW) may also be partly due to sand and soil particle contamination of forest residues during harvesting, transportation and handling [14]. In addition, it may partly derive 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 [15].

B. Physical and chemical properties of the ashes - the total chlorine, calcium and heavy metal concentrations in the ashes and their potential as forest fertilizers

Table I shows the most important properties and heavy metal concentrations in the ashes, as well as the current Finnish minimum or maximum limit values for ashes used as a forest fertilizer. If the concentration of certain element is below or exceeds its limit value, it is given in bold type.

The dry matter content of the ash originated from a 6 MW municipal district heating plant was relatively low (60.8%). This is due to the fact that the 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 ash is collected in the silo, it still contains some water which gives it relatively low dry matter content. This is an advantage, since dust problems during dandling are not very likely.

The acid neutralizing value (NV) is one of the most important indices in evaluating the liming effect value of the ash in relation to its use in forestry. The capacity of a liming agent to neutralize soil acidity depends on the levels of soluble and hydrolysable bases such as oxides, hydroxides, carbonates and silicates. Cations such as calcium, magnesium, and potassium are the interactive counter-ions. According to the NV values, the mixture of the bottom and fly ash from a 6 MW municipal district heating plant has the best capacity as a liming agent to neutralize soil acidity and act as a soil amendment agent compared to the other ashes. This is because the Ca concentration (30.5-%, d.w.), Mg concentration (5.3-%; d.w.) and the sum of P+K concentration (8.1-%; d.w.) in this ash fraction were higher than in the other ashes. The NV of 32.3-% (d.w.) for the ash originating from a 6 MW municipal district heating plant indicates that ca. 1.1 tonnes of this residue would be required to replace 1 tonne of a commercially ground limestone product produced by SMA

Mineral Ltd., the neutralizing value of which is 38-% (Ca equivalents; d.w.). In the bottom ash and fly ash originating from a 32 MW municipal district heating plant, the respective NV values are 4.2-% Ca (d.w.) and 23.1-% Ca (d.w.), indicating that ca. 9.0 tonnes and 1.6 tonnes of these ashes would correspondingly be required to replace 1 tonne of the above-mentioned limestone product.

TABLE I
THE DRY MATTER CONTENT (DMC), NEUTRALIZING VALUE (NV), CHLORIDE (CL), CALCIUM (CA), MAGNESIUM (MG), SUM OF PHOSPHOROUS (P) AND POTASSIUM (K), WATER SOLUBLE PHOSPHOROUS (P (H₂O)), AS WELL AS BORON (B) AND HEAVY METAL (AS, CD, CR, CU, HG, PB, NI AND ZN) CONCENTRATIONS IN ASHES, AND THE CURRENT MAXIMUM (MAX) OR MINIMUM (MIN) FINNISH LIMIT VALUES FOR ASHES USED AS A FOREST FERTILIZER

Metal/ parameter	Unit	BA (32 MW)	FA (32 MW)	BA+FA (6 MW)	Limit value
DMC	%	99.5	99.5	60.8	
NV	% (Ca; d.w.)	4.2	23.1	32.3	
Cl	% (d.w.)	< 0.01	0.04	< 0.01	2.0 max
Ca	% (d.w.)	1.9	24.2	30.5	6.0 min
Mg	% (d.w.)	0.3	2.2	5.3	
P+K	% (d.w.)	1.6	2.0	8.1	1.0 min
P (H ₂ O)	% (d.w.)	< 0.01	< 0.01	< 0.01	
B	mg/kg (d.w.)	21.0	41.0	260	
As	mg/kg (d.w.)	5.0	53.0	< 3.0	30 max
Cd	mg/kg (d.w.)	< 0.3	3.3	3.5	17.5 max
Cr	mg/kg (d.w.)	14.0	56.0	620	300 max
Cu	mg/kg (d.w.)	8.0	92.0	150	700 max
Hg	mg/kg (d.w.)	< 0.04	0.3	< 0.04	1.0 max
Pb	mg/kg (d.w.)	4.0	51.0	7.0	150 max
Ni	mg/kg (d.w.)	6.0	49.0	100	150 max
Zn	mg/kg (d.w.)	79	280	560	4500 max

Note: BA(32 MW) = Bottom ash from the 32 MW municipal district heating plant; FA(32 MW) = Fly ash from the 32 MW municipal district heating plant; BA+FA(6 MW) = Ash (i.e. mixture of the bottom ash and fly ash) from the 6 MW municipal district heating plant.

The chloride content in all ash fractions was clearly lower than the maximum limit value (2.0-%; d.w.). The Ca concentration of 1.9-% (d.w.) in the bottom ash from the 32 MW municipal district heating plant was lower than the minimum limit value of 6.0-% (d.w.) for Ca. Therefore, this residue may not be used as a forest fertilizer without the addition of auxiliary Ca. Comparing the bottom ash and fly ash from the 32 MW municipal district heating plant, all nutrient and heavy metals were evidently enriched in the fly ash. The enrichment of nutrients and metals in the fly ash is due to the fact that the combustion temperature of between 800 and 1200 °C is high enough to vaporize elements. In addition to element volatilization characteristics, element retention in fly ash through other process (i.e. primarily the condensation process) determines the final fate of volatilizable elements [16]. Most of these species form compounds that condensate on the surface of particles in the flue gas, leading to the enrichment of elements in the fly ash fraction. Since this phenomenon is well known and has been reported elsewhere [17], we did not focus on it in the present context. The concentrations of heavy metals (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) in the bottom ash from the 32 MW municipal district

heating plant did not restrict the utilization of this residue as a forest fertilizer. However, from the utilization point of view, it is notable that in the fly ash from this same plant, the As concentration of 53.0 mg/kg (d.w.) exceeded its maximum limit value of 30.0 mg/kg (d.w.). Furthermore, in the ash originating from the 6 MW municipal heating plant, the Cr concentration of 620 mg/kg (d.w.) exceeded its maximum limit value of 300 mg/kg (d.w.). These results imply that these ash fractions cannot be used as a forest fertilizer as such, but they can be used for the landscaping of landfills or in industrial and other areas that are closed to the public. However, before these residues could be utilized in these types of sites, an environmental permit would be needed. Although there are no minimum or maximum limit values for the dry matter content (DMC), neutralizing value (NV), magnesium (Mg), water soluble phosphorous ($P(H_2O)$) or boron (B) in the ash used as a forest fertilizer (see Table 1), their content has to be reported to the environmental authorities when ash is used for such a purpose.

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