Fly ash classification efficiency of electrostatic precipitators in fluidized bed combustion of peat, wood, and forest residues

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Abstract

The increasing use of biomasses in the production of electricity and heat results in an increased amount of burning residue, fly ash which disposal is becoming more and more restricted and expensive. Therefore, there is a great interest in utilizing fly ashes instead of just disposing of it. This study aimed to establish whether the utilization of fly ash from the fluidized bed combustion of peat, wood, and forest residues can be improved by electrostatic precipitator separation of sulfate, chloride, and some detrimental metals. Classification selectivity calculations of electrostatic precipitators for three different fuel mixtures from two different power plants were performed by using Nelson's and Karnis's selectivity indices. Results showed that all fly ashes behaved similarly in the electrostatic separation process SiO_2 resulted in coarse fractions with Nelson's selectivity of 0.2 or more, while sulfate, chloride, and the studied detrimental metals (arsenic, cadmium, and lead) enriched into fine fractions with varying selectivity from 0.2 to 0.65. Overall, the results of this study suggest that it is possible to improve the utilization potential of fly ashes from fluidized bed combustion in concrete, fertilizer, and earth construction applications by using electrostatic precipitators for the fractionating of fly ashes in addition to their initial function of collecting fly ash particles from flue gases. The separation of the finer fractions (ESP 2 and 3) from ESP 1 field fly ash is recommended.

Keywords: Bioenergy, biomass, fractionating, separation, utilization, valorization,

Highlights

- ✓ Fly ashes from fluidized bed combustion of peat, wood and forest residues.
- ✓ Electrostatic precipitators have ability to work as a classifier for fly ashes.
- ✓ Silica and aluminum concentrated in first electrostatic precipitator unit.
- ✓ Sulfate, chloride and detrimental metals enrich to second and third units.
- ✓ Significantly improved utilization potential for these type of fly ashes.

Graphical abstract

1. Introduction

Biomass is a sustainable energy source used to produce electricity and heat. The use of renewable energy is encouraged by the political goals of European Union, such as “The 2030 climate and energy framework”, which has set the target to increase the share of renewable energy sources to at least 27 % of EU energy consumption by 2030 (European Commission, 2014). Biomass fly ash is the residue produced from the combustion of biomass in power plants, paper mills, and other biomass burning facilities. Biomass, i.e., wood, bark, and other forest residues, is sometimes co-fired with peat. Among combustion methods, fluidized bed combustion (FBC) is efficient and commonly used due to its ability to utilize low-grade fuels with fluctuating quality, composition, and moisture content or mixtures of fuels in situ capture of SO_x and low NO_x emission (Patel et al., 2017). However, the fly ash originating from FBC has limited utilization potential, unlike ashes from pulverized coal combustion, and until recently these types of fly ashes have been disposed of. However, disposal is becoming more and more restricted and expensive; therefore, additional applications in which fly ashes could be utilized efficiently are in demand.

Some fly ashes can be utilized in soil improvement (Lanzerstorfer, 2011; Pedersen, 2003), earth construction (Ohenoja et al., 2016a, 2016b), and as a fertilizer (Budhathoki and Väisänen, 2016; Dahl et al., 2009; Ingerslev et al., 2011; Nurmesniemi et al., 2012) if their properties comply with quality regulations. The regulations are country-specific, although international regulations exist as well. For example, the Finnish national legislation MMM 24/11 (Finnish Ministry of Agriculture and Forestry, 2011), which came into effect in 2011, regulates the utilization of ash as a field or forest fertilizer and sets minimum acceptable content for Ca, the sum of phosphorous and potassium, and the maximum content for detrimental metals. Fly ashes used in earth construction must comply with Government Degree 591/2006 concerning the recovery of certain wastes in earth construction amended by Government Degree 403/2009 (Finnish Ministry of the Environment, 2009, p. 403). For concrete application, the European standard SFS-EN 450-1 (Finnish Standards Association, 2012) sets the maximum values for chloride and sulfate; however, it should be noted that the use of FBC fly ashes in concrete is not standardized in EN 450-1, which applies to ashes originating from pulverized coal combustion where the coal content must be over 60%, or over 50% when coal combustion takes place with pure wood. However, these limit values still provide a guideline for fly ash utilization in concrete. However, FBC fly ash utilization in concrete has been studied in few papers (Rajamma et al., 2015, 2009; Rissanen et al., 2017).

Quite commonly, the excessive content of heavy metals can prevent the use of fly ashes in the aforementioned applications. Manskinen studied the fuel composition of two different ashes and two different ash fractions (bottom and fly ash) originating from FBC and concluded that only bottom ash is able to be utilized as is (Manskinen, 2013). For other ash fractions, the heavy metal content was too high. In particular, the cadmium content in fly ash produced from wood combustion is known to often exceed regulations (Narodoslawsky and Obernberger, 1996; Pedersen, 2003). Cadmium is considered the most harmful of all heavy metals because it remains in the soil, becomes enriched in food chains, and is toxic to organisms (Orava et al., 2006). In addition to heavy metals, the utilization of fly ash in concrete applications is limited by chlorides and sulfates. The presence of chlorides and sulfates in cementitious materials can reduce durability through deterioration of the microstructure (Rajamma et al., 2009).

In the combustion process, electrostatic precipitators are commonly used to collect particles from flue gases using an electrical force (Intra et al., 2010; Jaworek et al., 2013; Van de Velden et al., 2008) due to their relatively inexpensive use and high collection efficiency: typically over 99% (Lind et al., 2003; Mizuno, 2000). Quite often, an electrostatic precipitator consists of two or three units connected in a series to ensure high collection efficiency. The particle size of fly ash is the largest in the first collector chamber and the finest in the last chamber. In a pulverized fuel fired boiler system, the concentrations of environmentally available volatile metals, like cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn), increased towards finer grained ESP fractions (Świetlik et al., 2012). Also, in FBC systems, the concentrations of heavy metals have been found to be at their lowest in the first collector chamber and highest in the last chamber (Orava et al., 2006). Orava et al. found that the heavy metal concentration can be reduced by applying electrostatic precipitation fractionation: for cadmium concentration, the reduction was as high as 70%. Therefore, it can be said that electrostatic precipitation is an acceptable method for fractionating fly ash, in addition to its original function of collecting fly ash particles from flue gases.

Even though there is great potential to use electrostatic precipitators as classifiers and to separate more hazardous fractions, there is no comprehensive study about the classification selectivity of electrostatic precipitator units. In addition, there is no information whether it is possible to separate sulfate and chloride using electrostatic precipitators. This is significant because the separation of those elements is important when fly ash is utilized as a cement replacement material. Therefore, this study aimed to establish whether the utilization of fly ashes from FBC of peat, wood, and forest residues can be improved by electrostatic precipitator separation of sulfate, chloride, and some detrimental metals. Classification selectivity calculations of electrostatic precipitators for two different Finnish power plants were performed by using Nelson's and Karnis's selectivity indices. This paper presents first time the use of these indices for the electrostatic precipitators; the indices have been used previously in screening, cleaning, fractionation, and flotation studies (Hautala et al., 2009; Karnis, 1997; Körkkö, 2012; Nelson, 1981). Fly ash samples were collected from both power plants with three different fuel mixtures to show the potential variations in ash quality: low, average, and high peat content.

2. Materials and methods

2.1 Fly ashes

The work was done using fly ashes from two different Finnish power plants. The fuel of the first power plant consists of a mixture of peat and forest industry residuals, mainly bark, in a 250 MW bubbling fluidized bed boiler (BFBB) while in the other boiler peat is burned together with wood in a 100 MW circulating fluidized bed boiler (CFBB), Fig 1a. No limestone is added in either plant, except that, in the first case, a paper mill sludge containing CaCO_3 is fed into the boiler from time to time. The fly ash samples were collected in both power plants with three different fuel mixtures: low, average, and high peat content. The exact proportion of peat content in the fuel is not known. However, in the "low peat mixture," the peat content is roughly 30%–40% of the total mass of fuel; in the "average peat mixture," it is around 50%; and, in the "high peat mixture," the peat content is around 60% of the mixture. The fly ash samples were collected from three fields of the electrostatic precipitators (ESPs) so that the first field is marked as 1, the second as 2, and the third as 3 (Fig 1b). The mass shares of the ESPs are different depending on the power plant: at the first plant (BFBB), field 1 has a mass share of 84%, field 2 has a mass share of 14%, and field 3 has a mass share of 2 %; at second plant (CFBB), they are 60%, 30%, and 10%, respectively. In total, 18 different fly ashes were studied. The sample names and origin are presented in Table 1.

Table 1. Studied fly ash samples.

Sample name	Low peat1	Low peat2	Ave peat1	Ave peat2	High peat1	High peat2
Boiler type	BFBC	CFBC	BFBC	CFBC	BFBC	CFBC
Fuel type	peat and forest industry residuals	wood and peat	peat and forest industry residuals	wood and peat	peat and forest industry residuals	wood and peat
Fuel mixture	peat content around 30-40%	peat content around 30-40%	peat content around 50%	peat content around 50%	peat content around 60%	peat content around 60%
Electrostatic precipitator (ESP)	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3
Mass share of ESP's (%)	1: 84 2: 14 3: 2	1: 60 2: 30 3: 10	1: 84 2: 14 3: 2	1: 60 2: 30 3: 10	1: 84 2: 14 3: 2	1: 60 2: 30 3: 10

The chemical composition, loss on ignition (LOI), specific surface area (BET), and particle size of all 18 fly ash samples were studied (see supplementary materials, Table S1). The chemical composition of all fly ashes

was mainly made up of CaO, SiO₂, Al₂O₃, and Fe₂O₃. Fly ashes contained also from 3%–12% of sulfate and from 0.1%–0.8% of chloride. Trace elements reported here were arsenic (As), cadmium (Cd), and lead (Pb) since those elements are typically the most critical for these types of ashes.

2.2 Methods

2.2.1 Analysis of fly ashes

The particle size distribution of the fly ash samples reported as a volumetric median size (d_{50}) was measured with the laser diffraction technique (Beckman Coulter LS 13320) using the Fraunhofer model and dry procedure. The main chemical components of fly ash were determined from a melt-fused tablet using XRF (X-ray fluorescence analysis from Omnia Pananalytix, Axiosmax 4 kV). The melt-fused tablet was produced from 1.5 g of fly ash melted at 1150 °C with 7.5 g of X-ray Flux Type 66:34 (66% LiB₄O₇ and 34% LiBO₂). Trace elements were measured with inductively coupled plasma atomic emission spectroscopy (ICP-OES) from wet digested samples. The microwave-assisted wet digestion was performed using a 3:1 ratio of HNO₃ and HCl acid mixture for 0.5 g of fly ash at 175 °C according to EPA3051A (United States Environmental Protection Agency, 2007). Specific surface area measurement was based on the physical adsorption of gas molecules on a solid surface using Micrometrics ASAP 2020 and results were reported as BET isotherm.

2.2.2 Selectivity calculations

Since the aim was to determine whether the utilization of fly ashes could be improved by fractionation with electrostatic precipitator, selectivity calculations were performed for ESP 2 and 3 fields. Typically, fly ashes from 2 and 3 fields are mixed with fly ash from ESP 1 at silos, but, by changing the process slightly, fractions from 2 and 3 fields are possible to separate from field 1. Fly ashes from ESP 2 and 3 fields are referred to as fine material since their particle size is smaller than that of ESP 1 fly ash. The fine material share RR_m , in this case, is the mass share of the ESPs presented in Table 1 (last line). The calculation of removal efficiency E_r was based on the following equation 1:

$$E_r = \left[1 - \left(1 - \frac{RR_m}{100} \right) \cdot \frac{x_C}{x_{tot}} \right] \cdot 100, \quad (1)$$

where E_r is the removal efficiency of a component [%], x is the content of elemental analysis, C stands for coarse, and tot stands for the total amount of the component (sum of 1, 2, and 3 fields). The calculated removal efficiencies were plotted against the fine material share, and the selectivity curve introduced by Nelson (Nelson, 1981) was fitted to them. The curve fitting was done by adjusting Nelson's selectivity index in the following equation so that the best fit was achieved:

$$E_r = \frac{RR_m / 100}{1 - Q_N + Q_N \cdot RR_m / 100} \cdot 100, \quad (2)$$

where Q_N is Nelson's selectivity index. Representative curves can be prepared with Nelson's selectivity index, but the selectivity index shown in this way is not uniform. A positive selectivity index ($0 < Q_N < 1$) refers to enrichment of the component to fine fraction, and the ideal selectivity is described as $Q_N = 1$. In the case of a split flow, $Q_N = 0$, the content values for coarse and fine are equal. A negative selectivity index ($-\infty < Q_N < 0$) is a result of component enrichment in the coarse fraction. To achieve a uniform and infinite range ($0 < Q < 1$) for the selectivity index, Karnis's selectivity index (Karnis, 1997) was used:

$$Q_K = \frac{x_1}{x_2}, \quad (3)$$

where Q_K is Karnis's selectivity index, and x_1 is the content of elemental analysis given for the fraction in which the content is lower, and x_2 is for the fraction in which the content is higher. Karnis's selectivity index

has a finite range, but it does not indicate in which fraction (fine or coarse) a component has been enriched. The interdependence of Nelson's and Karnis's selectivity index is:

$$Q_K = 1 - \frac{1}{1 - Q_N} \quad (4)$$

3. Results and discussion

3.1 Shares of main components

As presented above, fly ashes from ESP 2 and 3 fields are referred to as fines since their particle size is smaller than that of ESP 1 fly ash (see Table S1). Here, the removal efficiencies for different chemical components are presented as a function of fines content that refers either the mass of ash from ESP 3 or ESP 2. For the first plant, mass share of ESP 2 is 14% and for ESP 3 it is 2%, and for the second plant those are, 30% and 10%, respectively (see Table 1).

CaO can be seen to concentrate in ESP 2 and 3 fields for all studied fly ashes with a selectivity from $Q = 0.10$ to $Q = 0.25$ (Fig. 2a). The selectivity of CaO is not really high which refers to the fact that CaO is not highly concentrated to any ESP unit. However, it seems that CaO in High peat1 fly ash samples has higher selectivity to concentrate into ESP 2 and 3 units ($Q=0.25$) compared to other studied samples. Instead, SiO₂ concentrates to the ESP 1 field at both plants and for all studied fuel mixes with a selectivity from $Q = 0.20$ to $Q = 0.33$ (Fig. 2b). It seems that plant 1 has higher selectivity ($Q=0.33$) compared to plant 2 ($Q=0.20$). These results for CaO and SiO₂ selectivity are in well-accordance to literature: it has been noticed in earlier studies that CaO is present in every ash fractions (Lind et al. 2000) and SiO₂ is enriched mostly to coarse fraction (Jaworek et al., 2013; Maenhaut et al., 1999; Yu et al., 2007). It is estimated that approximately 10% of the quartz sand that is fed into the furnace is fragmented to become small enough to escape with the fly ash (Lind et al., 2000) and these quartz particles are presented in ESP 1 fly ash. However, the ash transformation during combustion of biomass is a very complex phenomenon and it can exhibit many essentially different scenarios. Calcium ion can exist in many different mineral forms and probably therefore it can be present in every size fractions (Boström et al., 2012).

Fig. 3a shows the classification ability of ESP units for Al₂O₃, and it can be seen to be slightly concentrated in the ESP 1 field with a low selectivity $Q < 0.20$ for both plants and all studied fly ashes. However, for Fe₂O₃, a higher deviation can be seen (Fig. 3b): for sample Low peat2, selectivity of $Q = 0.35$ to fine fraction was observed. For other samples, selectivity of $Q < 0.20$ to fine fractions was observed. The obtained results for Al₂O₃ are in well-accordance to literature: it is noticed also in earlier studies that Aluminum is existing in every ash size fractions. However, for iron as high selectivity as obtained in this study is not reported in literature. The reason for this could be much higher iron contents in peat fly ashes compared to fly ashes originating from coal, wood or forest residues (Hupa, 2012; Ohenoja et al., 2016b; Zevenhoven-Onderwater et al., 2000). In earlier electrostatic precipitator studies no fly ash originating from peat combustion is studied.

The concentration of SiO₂ and Al₂O₃ in coarse fraction and CaO in fine fractions is an advantage when considering concrete applications according to SFS-EN 450-1 (Finnish Standards Association, 2012) since the sum of Al+Si+Fe increases. However, for fertilization and earth construction purposes, this is a disadvantage since fertilizer should contain more than 6% of Ca (Finnish Ministry of Agriculture and Forestry, 2011), and calcium is an important component of the self-hardening reactions (Illikainen et al., 2014) used in earth construction.

3.2 Shares of sulfate and chloride

Classification of sulfate and chloride into ESP 2 and 3 fields and separating those from the ESP 1 fraction can improve the utilization of fly ash in concrete applications. Chloride content must be less than 0.1% and sulfate less than 3% according to the European standard SFS-EN 450-1 (Finnish Standards Association, 2012). Typically, biomass fly ashes contain significant amounts of chloride and sulfate. It is suggested in the literature that the performance of fly ash–cement binders could be improved by the removal or control of sulfates and

chlorides since their presence in cementitious materials can reduce durability through deterioration of the microstructure (Rajamma et al., 2009). When comparing the chemical composition of the studied fly ashes (Table S1) to the regulations mentioned earlier, it can be seen that the sulfate content is at an acceptable level only for Ave peat2, High peat1, and High peat 2 ESP 1 fly ashes. The chloride content is at the limit level for Ave peat2 and High peat2 fly ashes. However, it should be kept in mind that these limits are only suggestions since the use of FBC fly ashes in concrete has not yet been standardized. EN 450-1 applies to ashes originating from pulverized coal combustion where the coal content must be over 60%, or over 50% when coal combustion takes place with pure wood. However, these limit values still provide a guideline for fly ash utilization in concrete.

Sulfate selectivity to concentrate into a fine fraction, i.e., ESP 2 and 3, is shown in Fig. 4. In all cases, SO_3 enriches into ESP 2 and 3 fields with a high selectivity. Selectivity for High peat1 at ESP 2 and 3 and for Low peat1 and Ave peat1 at ESP 3 was $Q = 0.60$ or a bit higher, and for other samples sulfate selectivity was around 0.40.

Chloride selectivity to concentrate into a fine fraction, i.e., ESP 2 and 3, is shown in Fig. 5. Chloride enriches into a fine fraction with a high selectivity ($Q = 0.60$) for High peat1 at ESP 2 and 3 and for Low peat1 and Ave peat1 at ESP 3, and, for other samples, chloride selectivity was under 0.4. For High peat2 at ESP 2 and 3 and for Low peat2 at ESP 3, no selectivity can be observed since the content at all ESP fields was equal. This is most probably due to the difference in the varying initial chloride content between the ashes: for fly ashes having $Q = 0$, the chloride content was really low, near the XRF measuring limit, at all ESP fields.

The results to remove sulfates and chlorides by ESP fractionation is encouraging and make fly ash fractioning using ESP field reasonable. The reason for good selectivity to fine fractions is ultrafine fly ash formation behavior in the combustion: ultrafine fly ash particles are formed via nucleation of volatilized ash species followed by particle growth via collision and coalescence and via vapor condensation. Sulphur and Chloride are known to be volatile and, they are found to appear dominant in the ash particles smaller than $1\ \mu\text{m}$ so that their concentration decreased with increasing particle size (Jaworek et al., 2013). Typical compounds for S and Cl elements are NaCl , Na_2SO_4 , KCl and K_2SO_4 (Jaworek et al., 2013; Latva-Somppi et al., 1998; Lind et al., 2000). 3.3 Shares of detrimental metals

Fly ash utilization in earth construction or fertilization is limited by regulations, which set minimum concentration values for detrimental metals. The Finnish national legislation MMM 24/11 (Finnish Ministry of Agriculture and Forestry, 2011), which came into effect in 2011, regulates the utilization of ash as a field or forest fertilizer and sets minimum acceptable content for Ca, the sum of phosphorous and potassium, and the maximum content for detrimental metals. Fly ashes used in earth construction must comply with Government Degree 591/2006, which concerns the recovery of certain wastes in earth construction as amended by Government Degree 403/2009 (Finnish Ministry of the Environment, 2009, p. 403). Elements reported here include As, Cd, and Pb since these elements were the most critical for the studied fly ashes according to Finnish regulations. The same components are typically critical for all biomass ashes (Lanzerstorfer, 2017; Nurmesniemi et al., 2012). All those detrimental metals examined in this study enriched in ESP 2 and 3 fields (Figs. 6-8).

The deviation for arsenic selectivity was high (Fig. 6). Arsenic enriched into ESP 3 fraction with a very high selectivity at the first plant, $Q = 0.9$. At ESP 2 at the first plant, the selectivity was around $Q = 0.65$, which is still a very high selectivity. At the second plant, the selectivity was lower, from 0.25 to 0.5, depending on the fuel mix composition. The Low peat2 sample had a selectivity of 0.5 at ESP 2 and 3, Ave peat2 had 0.25, and High peat2 had 0.35. The results do not correlate with the fuel mix composition which can be, for instance, due to the variation in the sampling at the plant or at the laboratory. However, differences between the plants can be explained with the different fuel quality.

Cadmium enriched into ESP 2 and 3 fields with varying selectivity (Fig. 7). Again, the first plant had higher selectivity at both ESP for all fuel mix compositions. At ESP 2 and 3 at the first plant, the selectivity was around $Q = 0.6$. The only exception was Ave peat1 at ESP 2 which had a selectivity of only $Q = 0.30$. At the second plant, the selectivity was lower, from 0.2 to 0.4, depending on the fuel mix composition. The Low

peat2 sample had a selectivity of 0.2, Ave peat2 had 0.4, and High peat2 had 0.35 at ESP 2 and 3. However, again, results do not correlate with fuel mix composition which must be explained with changing fuel quality or sampling at the plant or laboratory.

Lead removal efficiency was quite good for both studied plants and all fuel mix compositions (Fig. 8). The deviation for selectivity was quite high again. Lead enriched into ESP 3 fraction with a high selectivity $Q = 0.70$ at the first plant. At ESP 2 at first plant, the selectivity was around $Q = 0.45$ for Low peat1 and High peat1, but only 0.30 for Ave peat1 sample. At the second plant, generally, the selectivity was lower, from 0.2 to 0.4, depending on the fuel mix composition. Low peat2 sample had a selectivity of 0.3 at ESP 2 and 3, Ave peat2 had 0.2, and High peat2 had 0.4. Again, results do not correlate with fuel mix composition.

Generally, ESP 3 at the plant 1 is really effective to remove all studied detrimental elements. However, significant improvement for all studied fly ashes can be achieved by separating fly ashes from ESP 3 or both ESP 3 and 2 units. As with chloride and sulphur, the reason for the enrichment of these heavy metals in the finest fraction is that they are volatilized to some extent at combustion temperature and re-condensed on the fly ash when the off-gas cools down. (Lanzerstorfer, 2017)

3.4 Utilization potential of the fly ashes after the classification

As shown, the use of electrostatic precipitators is an effective method to separate detrimental elements from fly ashes originating from FBC with different fuel compositions. The separation of ESP 2 and 3 fields (finer ash fraction) from ESP 1 (coarse fraction) is recommended in order to get higher quality fly ash for different end uses. Removal of sulphates and chlorides is important if fly ash is used as a supplementary cementitious material in concrete applications because the presence of these elements can reduce the durability of the materials through deterioration of the microstructure (Rajamma, 2009). On the other hand, fly ash utilization in earth construction or fertilizing requires low concentration for detrimental metals. Since detrimental metals concentrate on fine fraction, the coarse fraction may be suitable for these applications, depending on the local regulations. The amount of coarse fraction is typically high (in the power plants of this study, 82 or 60%), so its utilization would significantly decrease the amount of waste to be landfilled.

4. Conclusions

The electrostatic separation process that is commonly used in power plants to clean flue gases from ash particles can be successfully used to improve ash utilization potential. Sulfate, chloride and the studied detrimental metals (As, Cd and Pb) can cumulate to fine ash fraction and thus be separated by the latter units of electrostatic precipitator (ESP 2 and ESP 3). The coarse ash fraction (from ESP 1) has better utilization potential for concrete, fertilizer and earth construction applications when the harmful substances have been removed.

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References

- Boström, D., Skoglund, N., Grimm, A., Boman, C., Öhman, M., Broström, M., Backman, R., 2012. Ash Transformation Chemistry during Combustion of Biomass. *Energy Fuels* 26, 85–93. doi:10.1021/ef201205b
- Budhathoki, R., Väisänen, A., 2016. Particle size based recovery of phosphorus from combined peat and wood fly ash for forest fhautilaertilization. *Fuel Process. Technol.* 146, 85–89. doi:10.1016/j.fuproc.2016.02.016

- Dahl, O., Nurmesniemi, H., Pöykiö, R., Watkins, G., 2009. Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler. *Fuel Process. Technol.* 90, 871–878. doi:10.1016/j.fuproc.2009.04.013
- European Commission, 2014. Communication from the commission to the European Parliament, The Council, The European Economic and Social Committee and the Committee of the Regions. A policy framework for climate and energy in the period from 2020 to 2030.
- Finnish Ministry of Agriculture and Forestry, 2011. Decree of the Ministry of Agriculture and Forestry on Fertiliser Products 24/11 (in Finnish).
- Finnish Ministry of the Environment, 2009. Government Decree amending the annexes to the Government Decree on the utilization of certain wastes in the earth construction.
- Finnish Standards Association, 2012. SFS-EN 450-1:EN Fly ash for concrete. Definition, specifications and conformity criteria.
- Hupa, M., 2012. Ash-Related Issues in Fluidized-Bed Combustion of Biomasses: Recent Research Highlights. *Energy Fuels* 26, 4–14. doi:10.1021/ef201169k
- Illikainen, M., Tanskanen, P., Kinnunen, P., Kärkkö, M., Peltosaari, O., Wigren, V., Österbacka, J., Talling, B., Niinimäki, J., 2014. Reactivity and self-hardening of fly ash from the fluidized bed combustion of wood and peat. *Fuel* 135, 69–75. doi:10.1016/j.fuel.2014.06.029
- Ingerslev, M., Skov, S., Sevel, L., Pedersen, L.B., 2011. Element budgets of forest biomass combustion and ash fertilisation – A Danish case-study. *Biomass Bioenergy* 35, 2697–2704. doi:10.1016/j.biombioe.2011.03.018
- Intra, P., Limueadphai, P., Tippayawong, N., 2010. Particulate Emission Reduction from Biomass Burning in Small Combustion Systems with a Multiple Tubular Electrostatic Precipitator. *Part. Sci. Technol.* 28, 547–565. doi:10.1080/02726351003758444
- Jaworek, A., Czech, T., Sobczyk, A.T., Krupa, A., 2013. Properties of biomass vs. coal fly ashes deposited in electrostatic precipitator. *J. Electrostat.* 71, 165–175. doi:10.1016/j.elstat.2013.01.009
- Karnis, A., 1997. Pulp fractionation by fibre characteristics. *Pap. Timber* 79, 480–488.
- Lanzerstorfer, C., 2017. Grate-Fired Biomass Combustion Plants Using Forest Residues as Fuel: Enrichment Factors for Components in the Fly Ash. *Waste Biomass Valorization* 8, 235–240. doi:10.1007/s12649-016-9565-6
- Lanzerstorfer, C., 2011. Model based prediction of required cut size diameter for fractionation of fly ash from a grate-fired wood chip incineration plant. *Fuel Process. Technol.* 92, 1095–1100. doi:10.1016/j.fuproc.2011.01.004
- Latva-Somppi, J., Moisio, M., Kauppinen, E.I., Valmari, T., Ahonen, P., Tapper, U., Keskinen, J., 1998. Ash formation during fluidized-bed incineration of paper mill waste sludge. *J. Aerosol Sci.* 29, 461–480. doi:10.1016/S0021-8502(97)00291-7
- Lind, T., Hokkinen, J., Jokiniemi, J.K., Saarikoski, S., Hillamo, R., 2003. Electrostatic Precipitator Collection Efficiency and Trace Element Emissions from Co-Combustion of Biomass and Recovered Fuel in Fluidized-Bed Combustion. *Environ. Sci. Technol.* 37, 2842–2846. doi:10.1021/es026314z
- Lind, T., Vaimari, T., Kauppinen, E., Nilsson, K., Sfiris, G., Maenhaut, W., 2000. Ash formation mechanisms during combustion of wood in circulating fluidized beds. *Proc. Combust. Inst.* 28, 2287–2295. doi:10.1016/S0082-0784(00)80639-6
- Maenhaut, W., Fernández-Jiménez, M.-T., Lind, T., Kauppinen, E.I., Valmari, T., Sfiris, G., Nilsson, K., 1999. In-stack particle size and composition transformations during circulating fluidized bed combustion of willow and forest residue. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* 150, 417–421. doi:10.1016/S0168-583X(98)01068-4
- Manskinen, K., 2013. Utilisation aspects of ashes and green liquor dregs from an integrated semichemical pulp and board mill (PhD thesis). Aalto University.
- Mizuno, A., 2000. Electrostatic precipitation. *Dielectr. Electr. Insul. IEEE TransacIEEE Trans. Dielectr. Electr. Insul.* 7.
- Narodoslawsky, M., Obernberger, I., 1996. From waste to raw material—the route from biomass to wood ash for cadmium and other heavy metals. *J. Hazard. Mater.* 50, 157–168. doi:10.1016/0304-3894(96)01785-2
- Nelson, G., 1981. The screening quotient: a better index for screening performance. *Tappi* 64, 133–134.

- Nurmesniemi, H., Mäkelä, M., Pöykiö, R., Manskinen, K., Dahl, O., 2012. Comparison of the forest fertilizer properties of ash fractions from two power plants of pulp and paper mills incinerating biomass-based fuels. *Fuel Process. Technol.* 104, 1–6. doi:10.1016/j.fuproc.2012.06.012
- Ohenoja, K., Tanskanen, P., Peltosaari, O., Wigren, V., Österbacka, J., Illikainen, M., 2016a. Effect of particle size distribution on the self-hardening property of biomass-peat fly ash from a bubbling fluidized bed combustion. *Fuel Process. Technol.* 148, 60–66. doi:10.1016/j.fuproc.2016.02.023
- Ohenoja, K., Tanskanen, P., Wigren, V., Kinnunen, P., Körkkö, M., Peltosaari, O., Österbacka, J., Illikainen, M., 2016b. Self-hardening of fly ashes from a bubbling fluidized bed combustion of peat, forest industry residuals, and wastes. *Fuel*. doi:10.1016/j.fuel.2015.10.093
- Orava, H., Nordman, T., Kuopanportti, H., 2006. Increase the utilisation of fly ash with electrostatic precipitation. *Miner. Eng.* 19, 1596–1602. doi:10.1016/j.mineng.2006.07.002
- Patel, A., Basu, P., Acharya, B., 2017. An investigation into partial capture of CO₂ released from a large coal/petcoke fired circulating fluidized bed boiler with limestone injection using its fly and bottom ash. *J. Environ. Chem. Eng.* 5, 667–678. doi:10.1016/j.jece.2016.12.047
- Pedersen, A.J., 2003. Characterization and electrodialytic treatment of wood combustion fly ash for the removal of cadmium. *Biomass Bioenergy* 25, 447–458. doi:10.1016/S0961-9534(03)00051-5
- Rajamma, R., Ball, R., Tarelho, L., Allen, G., Labrincha, J., Ferreira, V., 2009. Characterisation and use of biomass fly ash in cement-based materials. *J Hazard Mater* 172, 1049–1060.
- Rajamma, R., Senff, L., Ribeiro, M.J., Labrincha, J.A., Ball, R.J., Allen, G.C., Ferreira, V.M., 2015. Biomass fly ash effect on fresh and hardened state properties of cement based materials. *Compos. Part B Eng.* 77, 1–9. doi:10.1016/j.compositesb.2015.03.019
- Rissanen, J., Ohenoja, K., Kinnunen, P., Illikainen, M., 2017. Partial Replacement of Portland-Composite Cement by Fluidized Bed Combustion Fly Ash. *J. Mater. Civ. Eng.* 04017061. doi:10.1061/(ASCE)MT.1943-5533.0001899
- Świetlik, R., Trojanowska, M., Józwiak, M.A., 2012. Evaluation of the distribution of heavy metals and their chemical forms in ESP-fractions of fly ash. *Fuel Process. Technol.* 95, 109–118. doi:10.1016/j.fuproc.2011.11.019
- United States Environmental Protection Agency, 2007. Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils, part of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods [WWW Document]. URL <https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf> (accessed 12.19.16).
- Van de Velden, M., Dewil, R., Baeyens, J., Jossion, L., Lanssens, P., 2008. The distribution of heavy metals during fluidized bed combustion of sludge (FBSC). *J. Hazard. Mater.* 151, 96–102. doi:10.1016/j.jhazmat.2007.05.056
- Yu, D., Xu, M., Yao, H., Sui, J., Liu, X., Yu, Y., Cao, Q., 2007. Use of elemental size distributions in identifying particle formation modes. *Proc. Combust. Inst.* 31, 1921–1928. doi:10.1016/j.proci.2006.07.115
- Zevenhoven-Onderwater, M., Blomquist, J.-P., Skrifvars, B.-J., Backman, R., Hupa, M., 2000. The prediction of behaviour of ashes from five different solid fuels in fluidised bed combustion. *Fuel* 79, 1353–1361.

Figures

Fig. 1. Ash samples were collected from power plants having bubbling and circulating fluidized bed boilers (Fig 1a) from the different fields of the electrostatic precipitator (Fig 1b)

Fig. 2. Fractionation of a) CaO and, b) SiO₂ at electrostatic precipitators. Flow split, i.e., when the content for fine and coarse fractions are equal, is indicated by a black line ($Q = 0$). At the upper side of this line, elements are concentrating into a fine fraction (ESP 2 and 3) and at the underside of this line elements are concentrating into a coarse fraction (ESP 1).

Fig. 3. Fractionation of a) Al₂O₃ and, b) Fe₂O₃ at electrostatic precipitators. Flow split, i.e., when the content for fine and coarse fractions are equal, is indicated by a black line (Q = 0). At the upper side of this line, elements are concentrating into a fine fraction (ESP 2 and 3) and at the underside of this line elements are concentrating into a coarse fraction (ESP 1).

Fig. 4. Fractionation of sulfate at electrostatic precipitators. Flow split, i.e., when the content for fine and coarse fractions are equal, is indicated by a black line ($Q = 0$). At the upper side of this line, elements are concentrating into a fine fraction (ESP 2 and 3).

Fig. 5. Fractionation of chloride at electrostatic precipitators. Flow split, i.e., when the content for fine and coarse fractions are equal, is indicated by a black line ($Q = 0$). At the upper side of this line, elements are concentrating into a fine fraction (ESP 2 and 3).

Fig. 6. Fractionation of Arsenic at electrostatic precipitators. Flow split, i.e., when the content for fine and coarse fractions are equal, is indicated by a black line ($Q = 0$). At the upper side of this line, elements are concentrating into a fine fraction (ESP 2 and 3).

Fig. 7. Fractionation of Cadmium at electrostatic precipitators. Flow split, i.e., when the content for fine and coarse fractions are equal, is indicated by a black line ($Q = 0$). At the upper side of this line, elements are concentrating into a fine fraction (ESP 2 and 3).

Fig. 8. Fractionation of Lead at electrostatic precipitators. Flow split, i.e., when the content for fine and coarse fractions are equal, is indicated by a black line ($Q = 0$). At the upper side of this line, elements are concentrating into a fine fraction (ESP 2 and 3).

Supplementary material

Table S1. The chemical composition, LOI and particle size of studied fly ashes.

	Particle size d ₅₀ (μm)	BET surface area [m ² /g]	Loss on ignition 950°C (%)	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	SO ₃ (%)	Cl (%)	As (mg /kg)	Cd (mg /kg)	Pb (mg/ kg)
Low peat1												
ESP 1	18.3	3.5	1.4	24.2	30.5	11.7	17.4	4.2	0.3	23	5.6	51
ESP 2	11.0	5.5	1.8	28.8	19.5	12.0	19.2	6.2	0.4	58	12	93
ESP 3	3.6	15.1	3.1	31.5	11.8	10.1	16.4	13.2	0.8	190	21	160
Low peat2												
ESP 1	14.7	3.82	1.0	16.2	42.4	9.4	14.8	3.2	0.2	26	5.7	110
ESP 2	9.6	5.79	1.4	18.3	33.8	8.8	19.8	4.3	0.2	42	7.5	160
ESP 3	7.7	7.49	1.5	17.9	28.5	7.9	26.3	5.9	0.2	60	7.7	170
Ave peat1												
ESP 1	26.6	6.8	1.4	24.1	29.0	10.5	21.5	3.5	0.2	18	8.2	52
ESP 2	17.4	11.5	2.4	28.2	20.7	10.5	22.5	5.2	0.3	35	10	64
ESP 3	3.4	10.5	2.4	31.4	11.2	9.8	17.7	12.6	0.7	170	20	150
Ave peat2												
ESP 1	20.7	3.33	0.5	13.8	40.2	10.1	22.3	2.4	0.1	41	3.6	130
ESP 2	12.5	5.46	0.9	16.0	35.3	9.4	23.0	3.4	0.1	51	5.5	160
ESP 3	9.4	7.33	1.2	17.7	30.7	8.7	23.9	5.2	0.2	62	7.2	170
High peat1												
ESP 1	85.6	15.2	3.0	22.3	38.5	10.5	15.9	2.7	0.2	18	3.7	38
ESP 2	17.8	11.1	2.3	29.9	22.5	10.2	20.2	5.6	0.4	38	7.5	62
ESP 3	5.1	47.1	3.9	31.1	12.7	9.7	17.7	12.3	0.8	130	18	130
High peat2												
ESP 1	18.6	4.62	0.3	9.7	47.9	9.7	24.2	1.6	0.1	22	2.4	62
ESP 2	14.9	6.65	0.6	11.3	42.1	9.6	27.9	2.1	0.1	31	3.2	82
ESP 3	10.3	6.97	0.8	12.9	38.4	9.5	29.0	2.8	0.1	40	4.4	110