

Department of Forest Products Technology

Utilisation aspects of ashes and green liquor dregs from an integrated semichemical pulp and board mill

Kati Manskinen



Utilisation aspects of ashes and green liquor dregs from an integrated semichemical pulp and board mill

Kati Manskinen

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Abstract

This thesis investigated the properties of bottom and fly ashes originating from a bubbling fluidised bed boiler (120 MW) using two different fuel mixtures (i.e. Fuel mixture A: coal, wood and peat; and B: wood and peat) and of the green liquor dregs originating from the associated semichemical pulp and board mill in relation to the potential utilisation of these residues from various aspects. The total concentrations of As, Cd, Cr, Cu, Ni, Pb, Zn and Hg in the bottom ashes were lower than the maximum allowable concentrations for these elements in forest fertilisers. The total Ca concentrations in bottom ashes A (2.4%; d.w.) and B (3.4%; d.w.) were lower than the legal requirement of 6.0% (d.w.) for ash used as a forest fertiliser. The total Ca concentrations in fly ashes A (6.4%; d.w.) and B (11.0%; d.w.) were higher than the minimum limit value of 6.0% (d.w.), but the concentration of As in fly ashes A (46.9 mg/kg d.w.) and B (41.3 mg/kg; d.w.) exceeded the maximum limit value of 40 mg/kg (d.w.). Only bottom ash B could be used as a forest fertiliser, provided some additional Ca is used. The bottom ashes both fulfilled the Finnish regulations on waste recovery in earth construction. Due to the elevated total concentration of PAH (23 mg/kg; d.w.) and extractable concentrations of Mo (3.9 mg/kg; d.w.) and Se (0.2 mg/kg; d.w.) in fly ash A, this residue cannot be used in covered structures. Due to the elevated concentration of PAH (90 mg/kg; d.w.) in fly ash B, this residue cannot be used in covered and paved structures. However, the utilisation of these residues as an earth construction agent is still possible, but an environmental permit would be required. According to the sequential extraction studies, extractable concentrations of most of the elements in the fly ash A were higher than those in the bottom ash A. The extractability of various elements, both in the bottom and fly ashes A, varied widely. Most of the elements did not occur as readily soluble and mobile forms in these ashes, which supports their utilisation instead of final disposal. The green liquor dregs were strongly alkaline (pH 11.7) and had a high neutralising capacity (34.2% Ca equivalents; d.w.). These results support the utilisation of this residue e.g. as a soil conditioning agent or pH buffer for acidic soils. The relatively low total concentrations of non-process elements in the green liquor dregs and low partitioning of these elements in the sequential extraction procedure support the re-use of this residue. However, if green liquor dregs are to be utilised, an environmental permit is needed. In terms of human health aspects, the careful handling of fly ash and green liquor dregs is recommended to prevent material dusting problems and the penetration of material particles across the human gastrointestinal tract. In order to promote the utilisation of ashes and green liquor dregs, efforts to develop Finnish legislation on waste utilisation is needed.

Keywords ash, extraction, Finnish legislation, green liquor dregs, heavy metals, SC-fluting

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Tekijä

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Puolikemiallisen sellu- ja kartonkitehtaan tuhkan ja soodasakan hyötykäytön näkökulmia

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Työssä tutkittiin puolikemiallisen sellu- ja kartonkitehtaan leijupetikattilan (120 MW) pohja- ja lentotuhkaa kahdella eri polttoaineseoksella (A: hiili, puu ja turve; B: puu ja turve) ja kemiaalikierron soodasakkaa sekä tarkasteltiin näiden jätejakeiden hyötykäyttömahdollisuuksia eri näkökulmista. Pohjatuhkien raskasmetallien (As, Cd, Cr, Cu, Ni, Pb, Zn, Hg) kokonaispitoisuudet alittivat metsätaloudessa käytettävien tuhkalannoitteiden enimmäispitoisuuksien raja-arvot. Pohjatuhkien kalsiumpitoisuudet (A: 2,4 % ja B: 3,4 %) olivat kuitenkin alhaisemmat kuin sille asetettu vähimmäisvaatimus (6,0 %). Lentotuhkien kalsiumpitoisuudet (A: 6,4 % ja B: 11,0 %) ylittivät vähimmäisvaatimuksen, mutta toisaalta lentotuhkien arseenin kokonaispitoisuudet (A: 46,9 mg/kg ka.; B: 41,3 mg/kg ka.) ylittivät metsätaloudessa käytettävän tuhkalannoitteen arseenin enimmäispitoisuuden raja-arvon (40 mg/kg ka.). Ainoastaan tutkittu pohjatuhka B soveltuisi käytettäväksi metsätaloudessa tuhkalannoitteena, mikäli siihen lisättäisiin kalsiumia vähimmäisvaatimusten täyttämiseksi. Pohjatuhkat täyttivät valtioneuvoston asetuksen vaatimukset jätteiden hyödyntämisestä maarakentamisessa. Sen sijaan lentotuhkan A haitallisten aineiden PAH-pitoisuus (23 mg/kg ka.) sekä molybdeenin (3,9 mg/kg ka.) ja seleenin (0,2 mg/kg ka.) liukoiset pitoisuudet ylittivät peitetulle rakenteelle asetetut raja-arvot ja lentotuhkan B haitallisten aineiden PAH-pitoisuus (90 mg/kg ka.) ylitti päällystetyn rakenteen raja-arvon. Täten lentotuhkaa A ei voida käyttää peitetystä rakenteesta ja lentotuhkaa B päällystetyssä rakenteesta ilmoitusmenettelyllä, vaan erillinen ympäristölupa vaaditaan. Sekventiaalisessa uutossa monien haitallisten aineiden liukoiset pitoisuudet olivat korkeammat lentotuhkassa A kuin pohjatuhkassa A. Lisäksi haitallisten aineiden liukoiset pitoisuudet olivat pohja- ja lentotuhkissa A merkittävästi erilaisia eri alkuaineilla. Suurin osa pohja- ja lentotuhkan A haitallisista aineista ei kuitenkaan ollut helposti liukenevassa muodossa sekventiaalisessa uutossa, mikä tukee tutkittujen tuhkien hyötykäyttöä kaatopaikalle läjittämisen sijaan. Soodasakka oli voimakkaasti alkalista (pH 11,7) ja sen neutraloiva kyky (34,2 % Ca ekv. ka.) oli suuri, jolloin soodasakkaa voidaan käyttää esimerkiksi maanparannusaineena tai pH-puskurina happamassa maaperässä. Soodasakan hyötykäyttö edellyttää ympäristölupaa. Soodasakan haitallisten aineiden suhteellisen alhainen kokonaispitoisuus ja alhainen liukoisuus sekventiaalisessa uutossa tukevat myös tutkitun soodasakan hyötykäyttöä. Työterveydellisestä näkökulmasta tarkasteltuna tutkitun lentotuhkan ja soodasakan huolellinen käsittely on suositeltavaa, jotta työntekijät eivät altistu näiden materiaalien haitta-aineille. Tuhkan ja soodasakan hyötykäytön edistämiseksi Suomen lainsäädäntöä tulee yrittää kehittää.

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Preface

This study was carried out at the Department of Forest Products Technology, Aalto University, Espoo, Finland from 2010 to 2013. I wish to express my deep gratitude to my supervising professor Olli Dahl for giving me the opportunity to work under his expert guidance. I thank him warmly for both guiding me in the academic world and for his inspiration and positive co-operation in the field of interesting process-related research questions during these years.

The idea for this study came about when my colleague Dr. Hannu Nurmesniemi proposed the extensive study of the chemical, physical and extraction properties of solid residues originating from the Stora Enso Oyj Heinola Fluting Mill. I express my sincere thanks to Hannu for his extensive experienced co-authorship and for his guidance of this thesis, and most of all for seeing both the potential in this subject and also in me. I also thank him for introducing me to Dr. Risto Pöykiö, who is also a key person and co-author behind this thesis. I am extremely grateful to Risto for his extensive expertise and interest in this research topic and thank him warmly for guiding and encouraging me throughout the whole process. It has been a pleasure to work with such hardworking and professional scientists.

The experimental part of this study was carried out as part of my work at Stora Enso Oyj Heinola Fluting Mill and in view of this I express my gratitude to my former manager, director Mr. Jarkko Rautaoja who gave me the opportunity to work on this study and for encouraging me and arranging study leave. I am also grateful to my current manager, mill director Mr. Ari Tanninen, for supporting me in the finalising of this thesis. I also express thanks to Vice President of Sustainability Mrs. Marjaana Luttinen for her support of this study.

I express my warm thanks to Mr. Sami Kalmi and Mrs. Eija Liikola for helping me at the mill's power plant and answering my endless questions. I am especially grateful to Mrs. Anja Korhonen, a highly professional colleague who patiently and proficiently took care of the sampling in this study. I also thank her for taking care of my environmental management duties during my study leave. Moreover, I wish to thank Mrs. Kaisa Vuori

and Mrs. Tuija Pouttu at the laboratory department of Heinola Fluting Mill for taking care my product safety and laboratories duties during this study. I am also grateful to all the many personnel of the laboratory department and to my other colleagues at Stora Enso Heinola Fluting Mill – I apologise my absence during this study and thank you for supporting me.

The chemical analyses for this study were conducted in the laboratory of Suomen Ympäristöpalvelu Oy and so the contributions of their technical personnel, especially Mr. Ilkka Välimäki, are gratefully acknowledged. Others I also extend my thanks to are Mr. Gary Watkins for correcting the English language of this thesis, lawyer Mrs. Hanna Puittinen from Stora Enso for checking and correcting the legislation review of this thesis and to Mrs. Taina Kaakinen and Mrs. Ulla Andelin in the Imatra Research Centre of Stora Enso for all their information searching work.

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Finally, I wish to express my warmest gratitude to my husband Jukka - without you it would not have been possible to combine the care of three young children, challenging work, doctoral studies and this thesis. Thank you for being the best father for Otto, Topi and Elias. I am grateful for your support during all these years. I feel lucky to share my life with you.

Heinola, May 2013



Kati Manskinen (née Hämäläinen)

List of original articles

This thesis is based on the following papers, which are referred in the text by their Roman numerals:

- I** K. Manskinen, H. Nurmesniemi, R. Pöykiö, O. Dahl (2010). Comparison of the fertilizer properties of bottom ash and fly ash from the 120 MW power plant of a fluting board mill incinerating different fuel mixtures. *Journal of International Environmental Applications & Science* 5(4): 526-537.
- II*** K. Manskinen, H. Nurmesniemi, R. Pöykiö (2012). Occupational risk evaluation of using bottom ash and fly ash as a construction material. *Journal of Hazardous, Toxic and Radioactive Waste* 16(1): 79-87.
- III** K. Manskinen, R. Pöykiö, H. Nurmesniemi (2011). Comparison of the total and fractionated heavy metal and sulphur concentrations in bottom ash and fly ash from a large-sized (120 MW) power plant of a fluting board mill. *Chemija* 22(1): 46-55.
- IV** K. Manskinen, H. Nurmesniemi, R. Pöykiö (2011). Total and extractable non-process elements in green liquor dregs from the chemical recovery circuit of a semi-chemical pulp mill. *Chemical Engineering Journal* 166(3): 954-961.
- V** K. Manskinen, R. Pöykiö, H. Nurmesniemi (2011). Extractability of heavy metals in green liquor dregs using artificial sweat and gastric fluids. *International Journal of Civil and Environmental Engineering* 3(1): 41-44.

* The ASCE-EWRI Journal of Hazardous, Toxic and Radioactive Waste has selected the paper "Occupational Risk Evaluation of Using Bottom Ash and Fly Ash as a Construction Material" to receive the 2013 Best Practice-Oriented Paper Award, The World Environmental & Water Resources Congress 2013, May 19-23, Cincinnati, Ohio, USA.

Author's contribution

- I** Kati Manskinen was responsible for the research plan and sampling procedure. She interpreted the results and was the main author of the article with the co-operation of Hannu Nurmesniemi and Olli Dahl and with the assistance of Risto Pöykiö.
- II** Kati Manskinen was responsible for the research plan and sampling procedure. Hannu Nurmesniemi and Risto Pöykiö carried out the literature review. Kati Manskinen interpreted the results and wrote the article together with Hannu Nurmesniemi and Risto Pöykiö.
- III** Kati Manskinen was responsible for the research plan and sampling procedure. Risto Pöykiö interpreted the results and wrote the article together with Kati Manskinen and with the assistance of Hannu Nurmesniemi.
- IV** Kati Manskinen was responsible for the research plan and sampling procedure. Kati Manskinen interpreted the results and wrote the article with the assistance of Hannu Nurmesniemi. Risto Pöykiö carried out the literature review together with Kati Manskinen and with the assistance of Hannu Nurmesniemi.
- V** Kati Manskinen was responsible for the research plan and sampling procedure. She interpreted the results and wrote the article with the assistance of Risto Pöykiö and Hannu Nurmesniemi.

List of abbreviations and definitions

BCR	Community Bureau of Reference
BFB	bubbling fluidised bed
CEN	European Committee for Standardization
CFB	circulating fluidised bed
CLC	clean carton clippings
CRM	certified reference material
d.w.	dry weight
DOC	dissolved organic carbon
EOW	end-of-waste
ESP	electrostatic precipitator
EU	European Union
EVIRA	Finnish Food Safety Authority
FAAS	flame atomic absorption spectrometer
FINAS	Finnish Accreditation Service
ICP-OES	inductively coupled plasma optical emission spectrometer
ISO	International Organization for Standardization
LOI	loss-on-ignition
NPEs	non-process elements
NSSC	neutral sulphite semichemical
NV	neutralising value
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
RV	reactivity value
SC	semichemical
SFS	Finnish Standards Association
TOC	total organic carbon
USEPA	US Environmental Protection Agency
w.w.	wet weight
w/w	weight to weight
XRD	X-ray diffraction

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1. Introduction

Various by-products or residues from industry are considered to be valuable as raw materials. The utilisation of these as beneficial products saves natural resources and allows industry to implement the waste hierarchy principles promoting reuse and recycling of residues instead of disposal (Waste Framework Directive 2008). In Finland, approximately 1,526,000 tonnes of ashes were generated in year 2010 (Statistics Finland 2012). Approximately 216,000 tonnes of these originated from the pulp and paper industry and moreover, the industry generated approximately 90,000 tonnes of green liquor dregs in 2010 (Finnish Forest Industries Federation 2012). There is a growing trend to utilise such residues e.g. as a fertiliser (Augusto et al. 2008; Saarinen 2012) or as an earth construction agent (Korpijärvi et al. 2009; Soininen et al. 2010; Ramboll Finland Oy 2012).

Besides the concern of saving natural resources, the economic driver to search for other treatment options than that of landfilling has become more important. The cost of landfilling ashes and green liquor increased at the end of 2007 due to new demands on the construction and environmental monitoring of landfills (VNp 1997). Furthermore, according to the new Finnish Waste Tax Act (2010), a tax of 40 euros per tonne of landfilled ash had been required to be paid from the beginning of 2011 and 50 euros per tonne since the beginning of 2013.

According to the Finnish Waste Decree (2012), ashes and green liquor dregs are regarded primarily as wastes. They may also be regarded as by-products if End-Of-Waste (EOW) criteria are fulfilled (Waste Act 2011). For an institutional or professional utilisation of waste an environmental permit is required (Environmental Protection Act 2000). The environmental permit process has been shown to be time-consuming and laborious, and it has been considered as the main barrier to recycling activities (Sorvari 2008). Therefore, some national regulations have been set up in order to offer exemptions to the environmental permit process and to promote the utilisation of selected wastes as earth construction materials (VNa 2006a; VNa 2009) or as fertilisers (VNa 2006b; MMM 2011; MMM 2012). These national

regulations set the limit values for harmful elements in waste material which may not be exceeded in order to qualify for the exemption to the environmental permit process. However, according to several researchers some of these national limit values are exceeded in the ashes (Lillman 2009; Vuorinen and Suoniitty 2010; Soininen et al. 2010). Sorvari (2008) has reported that the available information on the environmental properties of industrial residues has been inadequate and partly unsuitable during the development process of the national regulations. Ashes and green liquor dregs contain naturally occurring elements, some of which are essential for healthy plant and animal life, while others are toxic for the environment and human health if present in sufficient quantities (Tolvanen 2004). Waste shall not contain any harmful substances in such a way that recovery might cause a danger or hazard to health or to the environment (Finnish Waste Act 2011).

This study generates information about the properties of ashes and green liquor dregs originating from an integrated semichemical (SC) pulp and board mill located in Finland. SC-board is a corrugated board packaging material that is a renewable and recyclable raw material which is widely used in many applications nowadays. This study focuses on the most important chemical, physical and extraction properties of the ashes and green liquor dregs originating from the above-mentioned process and assesses whether the properties of these residues support their re-use. The utilisation of these residues continues the improvement of waste management practice and the environmental performance of the pulp and paper industry. The sequential extraction partition procedure, which has been reported to be a widely applied extraction test for assessing the potential mobility of the harmful elements in solid residues (Smeda and Zyrnicki 2002), is used in this study in order to evaluate potential environmental impacts of residues in utilisation. Furthermore, in order to understand the potential risk associated with ash and green liquor dregs handling, the extractability of heavy metals in the ashes and green liquor dregs is investigated by the use of artificial sweat and gastric fluids (Twining et al. 2005; Wang et al. 2007).

Although ashes are widely studied, this study provides useful information about the chemical, physical and extraction properties of both ashes and green liquor dregs from various aspects, and promotes the reuse and recycling of these residues. This study helps in the development of environmental regulations, by assisting environmental and legislative authorities assimilate accurate and reliable results about the environmental properties of residues. In addition, to the best of our knowledge, such comprehensive research into the extraction properties of green liquor dregs from a SC-pulping process has not yet been published.

2. Literature review

2.1 Review of Finnish environmental legislation on waste utilisation

In Finland, the national environmental legislation is based on EU directives and regulations. The most important Finnish environmental legislation concerning waste recovery and reuse are the Finnish Environmental Protection Act (86/2000), the Finnish Environmental Protection Decree (169/2000), the Finnish Waste Act (646/2011) and the Finnish Waste Decree (179/2012). Industrial residues such as ashes and green liquor dregs are regarded as wastes, and an environmental permit is required for an institutional or professional utilisation of such waste (Waste Decree 2012, Environmental Protection Act 2000).

The environmental process of utilisation of ashes may be exempted if these residues fulfil the requirements of Finnish Government Decrees (591/2006) and (403/2009), which regulate the recovery of ashes in earth construction, or they fulfil the regulations on fertilisers, which are set in the Fertilizer Product Act (539/2006), in the Decree on the operations concerning fertilizer products and their supervision (11/12), and in the Decree on fertilizer products (24/11) (VNa 2006a,b; VNa 2009; MMM 2011; MMM 2012). It is worthwhile to note, that these regulations are not applied to green liquor dregs.

According to the Finnish Waste Act (2011), waste may also be regarded as a by-product if the End-Of-Waste (EOW) criteria given in the legislation are fulfilled. These kinds of by-products are further regarded as products in Finnish national legislation (Punta and Tolvanen 2011). So far, the regulations on by-products given in the Waste Act 646/2011 have not yet been applied to ashes used as earth construction agents (Ramboll Finland Oy 2012).

2.1.1 Regulations of fertiliser products

According to the Decree on fertilizer products (24/11), the industrial ash originating from combustion of peat, wood and agro-biomass is permitted to be used as a raw material for fertiliser or as a fertiliser product (MMM 2011). Furthermore, Decree (24/11) requires that ash needs to be treated in such a way that dusting is minimised (MMM 2011). Ash can also be used as a fertiliser in agriculture, horticulture, forestry and landscaping green areas (MMM 2011). Decree (24/11) does not apply to ashes used in landfills or in the landscaping of closed areas however (MMM 2011).

Decree (24/11) gives the limit values for maximum allowable heavy metal concentrations and minimum values for nutrient content in ashes (MMM 2011). The maximum allowable limit values of heavy metals are set for the total concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni) and zinc (Zn) for ashes used as forest fertiliser and for other fertiliser purposes (MMM 2011). The limit values of heavy metals set in the Decree are higher for forest fertiliser than those for the other fertiliser purposes.

Furthermore, Decree (24/11) also regulates the maximum load of cadmium (Cd) per year, where the allowable maximum load in fertiliser products must not exceed 1.5 g per hectare per year (MMM 2011). In addition, due to the application of fertiliser products as repeat applications in batches and in cycles, the maximum load of Cd applied may be no more than 7.5 g per hectare at an interval of five years in agriculture and horticulture, 15 g per hectare over 10 years in landscaping, and no more than 100 g per hectare over 60 years in forestry (MMM 2011).

Decree (24/11) also sets out minimum values of 2.0% (d.w.) for the sum of phosphorus (P) and potassium (K), and 6.0% (d.w.) for calcium (Ca) in forest fertilisers. In addition, ashes used for fertiliser purpose other than as a forest fertiliser need to have at least a neutralising value (NV) of 10% (d.w.; Ca equivalents) (MMM 2011). The Decree (24/11) also allows the addition of some inorganic nutrients to granulated ashes in order improve their fertiliser properties (MMM 2011). However, if boron (B) is added to ashes, the residues are not allowed to use as fertiliser in groundwater recharge areas or nature reserves (MMM 2011).

Decree (24/11) does not set specific limit values for the major nutrients such as nitrogen (N), phosphorus (P), potassium (K), water soluble phosphorus (P(H₂O)), or for other nutrients such as magnesium (Mg), sodium (Na), sulphur (S), boron (B), cobalt (Co), iron (Fe), manganese (Mn) and molybdenum (Mo), however, their concentration has to be reported to the

environmental authorities (MMM 2011). Furthermore, the concentrations of chloride (Cl) may be reported, but the current Decree does not set any maximum allowable limit value for it (MMM 2011).

According to the Decree on operations concerning fertiliser products and their supervision (11/12), the producer of the fertiliser is liable for organising in-house control to identify factors affecting on the quality of the fertiliser (MMM 2012). In Finland, the Finnish Food Safety Authority (Evira) registers and controls power plants that produce ash for use as fertiliser (MMM 2012). The quality of such ash needs to be investigate at either Evira's research laboratory or other suitable accredited laboratory, i.e. ones which have been evaluated and accepted by the Finnish Accreditation Service FINAS or other corresponding accreditation body (MMM 2012).

The Decree on fertilizer products (24/11) substituted the previous Decree (12/07) in September 2011 and brought some changes in limit values into force (MMM 2007; MMM 2011). The previous Decree on fertilizer products (12/07) was in force during the studies covered by this thesis, i.e. between March 2007 and September 2011 (MMM 2007; MMM 2009; MMM 2011). These minimum and maximum limit values are presented later in this study together with the results (see section 5.1, Table 2) (MMM 2007; MMM 2011).

2.1.2 Regulations on waste recovery in earth construction

The Finnish Government Decree (591/2006) concerning the recovery of waste in earth construction is applicable for waste materials such as concrete chippings and, fly and bottom ashes from the combustion of coal, peat and wood-based material (VNa 2006a). Decree (591/2006) applies to earth construction purposes in the case of roads, streets, bicycle lanes, parking areas, sport grounds and trails, and railway yards (VNa 2006a). However, it does not apply in important water supply or other groundwater zones, and the specified minimum distance for a structure containing ash from a well or spring intended for use as drinking water is 30 m (VNa 2006a).

Furthermore, according to this Decree only the necessary quantity of ash is to be used for the purpose of levelling the soil structure and enhancing its bearing capacity and durability, such that the maximum thickness of the structure containing ash is 150 cm (VNa 2006a). An earth construction structure containing ash also has to be covered or paved, where the 'covering' refers to protecting the emplaced ash with a layer of natural rock, the minimum thickness of which is 10 cm to prevent the spread of waste, and 'paving' refers to protecting with asphalt with a maximum void of 5 per cent,

or with another material with a corresponding level of protection, in order to reduce the seepage of rainwater (VNa 2006a).

The Finnish Government Decree (403/2009) concerning the recovery of waste in earth construction updated the annexes of Decree (561/2006) and gives the current limit values for the total concentrations of Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs) and selected heavy metals (VNa 2009). In addition, the limit values for extractable concentrations of dissolved organic carbon (DOC), selected heavy metals, fluoride, sulphate and chloride are also set (VNa 2009). In addition, waste must not contain any other harmful substances in such a way that recovery might cause a danger or hazard to health or to the environment (VNa 2006a). The quality of waste must be examined through basic characterisations according to standard CEN/TS 14405 and quality control investigations according to standard SFS-EN 12457-3 (VNa 2009). Basic characterisations are conducted to prove that the waste in question falls within the scope of Decree (403/2009) concerning the recovery of waste in earth construction (VNa 2009). This decree also includes limit values for quality control tests on wastes, which are the same as those for basic characterisation, but this quality control testing includes fewer compounds than basic characterisation (VNa 2009). These tests have to be carried out primarily by standardised methods, and secondarily by other methods, which are found to be accurate enough, sensitive and reproducible (VNa 2009).

The environmental authorities responsible for waste management make the final decision on authorisations for the utilisation of wastes in earth constructions. It is notable that in the case of quality control testing, the competent environmental authority may decide that the maximum limit values for certain compounds can be up to 30% higher than those set in the legislation on the basis of the local environmental conditions at the site where the residue is planned to be used (VNa 2009). If the requirements of Decree (591/2006) are fulfilled, the proprietor of the recovery site must submit a notification to a regional environment centre in order to recover ashes by way of utilisation in earth construction (VNa 2006a).

The sampling of ashes has to be carried out in accordance with the standards SFS-EN 932-1, SFS-EN 932-2 and SFS-EN 14899 and collection of samples needs to be carried out by a competent person (VNa 2009). These requirements are not required to be followed if it is not technically and economically possible due to the quality of the waste (VNa 2006a).

2.2 Review of ashes and green liquor dregs

In Finland, the total quantity of ashes from combustion plants and boilers was 1,526,000 tonnes in year 2010 (Statistics Finland 2012). Approximately 477,000 tonnes of the total were fly ashes originating from coal combustion, 426,000 tonnes were fly ashes originated from combustion of peat and untreated wood, 367,000 tonnes were bottom ashes, boiler dusts and slags, 188,000 tonnes were from incineration of waste, and the balance of 68,400 tonnes originated from oil incineration. The combustion plants of the Finnish pulp and paper industry generated approximately 216,000 tonnes of ashes in 2012. In addition, approximately 90,000 tonnes of green liquor dregs were also generated (Finnish Forest Industries Federation 2012). Approximately 61% of the ashes (d.w.) and 16% of the green liquor dregs (d.w.) generated have been reported as utilised instead of having been landfilled in the period 2006-2010 (Finnish Forest Industries Federation 2012).

2.2.1 Origin, properties and utilisation of ashes

A large amount of results concerning the characteristics and utilisation of various ashes have been reported from several aspects. The properties of ashes depend on the fuels used and several other factors such as boiler type, temperatures in the boiler, burning speed, air feeding and age of the boiler and ash collector systems (Steenari et al. 1999; Emilsson 2006; Korpijärvi et al. 2009). This literature review focuses on the most important chemical, physical and extraction properties of ashes from similar origin as the ashes investigated in this study i.e. ashes originating from combustion of coal/wood/peat fuels and especially on the ashes originating from co-combustion and from fluidised bed boilers (BFB). In addition, the aspect concerning whether the properties of the above-mentioned ashes support their utilisation as a forest fertiliser or as an earth construction agent according to the requirements of Finnish environmental legislation is reviewed. For instance, the properties of ashes from municipal waste incineration are provided extensively elsewhere (Quina et al. 2008; Lam et al. 2010; Siddique 2010).

In the pulp and paper industry, the BFB type boiler is a commonly used technology for energy production because it is suitable for biomass fuels (Hupa 2012). More than half of the energy of the pulp and paper industry is produced by burning organic wood-based solid residues originating from the processes themselves (Tarnawski 2004). Besides bark and other wood

residues, a large variety of the other fuels are burnt i.e. peat, coal, oil and municipal waste may be co-combusted in BFB boilers (Tolvanen 2004).

In BFB technology, fuels are fed into the boiler directly above a bed material, which normally consist of silica sand at a temperature of 750-900°C (Enestam 2011). Part of the ash consists of trace elements which occur naturally in fuels (Zevenhoven and Kilpinen 2001). A sub-class of these trace elements are the heavy metals (Zevenhoven and Kilpinen 2001). The term heavy metal has never been defined by the International Union of Pure and Applied Chemistry (IUPAC), however density is in most of the cases taken to be the defining factor, so that heavy metals are commonly defined as those with a density of higher than 5 g/cm³ (Järup 2003; Duffus 2002). Trace elements with a low volatility tend to concentrate in the bottom ash, while more volatile elements concentrate in the fly ash; therefore bottom and fly ashes have different chemical compositions (Zevenhoven and Kilpinen 2001; Tolvanen 2004; Alvarez-Ayuso et al. 2006). In the BFB the bottom ash is removed from the bottom of the boiler together with bed material, and the fly ash is separated from the flue gas by cleaning equipment e.g. by electrostatic precipitator or baghouse filter (Emilsson 2006). Compared to the total ash amount, the portion of fly ash from a BFB boiler may vary between 80% and 100% and the portion representing bottom ash between 0% and 20% (Ramboll Finland Oy 2012).

A large body of research results concerning the properties of ashes derived from different single wood, peat or coal fuels have been published. Wood ashes have been reported to have high pH and neutralising capacity (Etegni and Cambell 1991; Demeyer et al. 2001; Augusto et al. 2008). In addition, high amounts of Ca, K, P and Mg and some other nutrients e.g. Mn, Zn and B have also been detected in wood ashes (Hytönen 2003; Augusto et al. 2008; Ojala 2010). Due to the high pH, neutralising capacity and high content of nutrients, wood ashes are considered to be potential liming agents in acidic soils as a fertiliser (Demeyer et al. 2001; Hytönen 2003; Emilsson 2006; Augusto et al. 2008). However, wood ashes may also often have high levels of Cd, which may limit the utilisation of these residues as forest fertilisers (Rothpfeffer 2007). In addition, many additional factors also have an influence on the properties of ash originating from wood e.g. tree species, part of the tree utilised and soil type where the trees were harvested (Österås et al. 2005; Rothpfeffer 2007).

Peat ashes have been reported to contain in general fewer nutrients, but also mainly less heavy metals than wood ashes (Ojala 2010). However, peat ashes often have higher levels of As than wood ashes (Huotari 2012). According to Hytönen (2003), peat ashes have been shown to contain high amounts of P,

but only small amounts of K and B, which have not been found very suitable for amelioration in connection with field afforestation. Wood and peat ashes do not usually contain N, which is vaporised during combustion if these fuels are well burnt (Ojala 2010). In addition, the ashes from combustion of sludges and barks from pulp and paper mill processes have been reported to contain Cr, Cd, Pb and Ni (Korpijärvi et al. 2009).

Coal ashes have been reported to contain more heavy metals than both wood and peat ashes (Korpijärvi et al. 2009). However, it has also been observed that coal ash contains small amounts of K, but is a good source of B (Hytönen 2003). Respectively, in the research of Adriano et al. (1980), coal ashes have not been found to be practical sources of essential plant nutrients N, P, and K, but they can effectively serve as a supplementary supply of Ca, S, B, Mo, and Se to soils. Furthermore, coal ashes have widely been reported to be potentially suitable for road or earth constructions due to their insensitiveness to changes in moisture content, strength and durability properties, but also due to reason that they have been found environmentally safe (Takada et al. 1995; Lahtinen 2001; Pandian 2004; Lillman 2009; Rifa'i et al. 2009). However, according to Lahtinen (2001), fly ash from biofuel may have even better geotechnical properties as an earth construction agent than the fly ash from coal. The requirements for the geotechnical properties of coal/peat/wood derived ashes have been reported comprehensive elsewhere (Takada et al. 1995; Lahtinen 2001; Pandian 2004; Ramboll Finland Oy 2012).

The ashes originating from co-combustion of peat, wood and biological paper making sludge have been reported to have similar properties to peat and coal fly ashes in terms of composition and leaching properties (Laine-Ylijoki et al. 2002). However, according to the research of Steenari and Lindqvist (1999), the properties of ash originating from co-combustion cannot be predicted based on the properties of the ash formed from each fuel and therefore these types of ashes are important to characterise. The findings of Laine-Ylijoki et al. (2002) support this and they have presented that the evaluation of environmental acceptability of the ashes originating from co-combustion of peat, wood and biological paper making sludge has to be based on environmental properties and compositional variations of representative ash samples.

The research of Laine-Ylijoki et al. (2002) showed that increasing the proportion of wood in BFB combustion of wood and peat resulted in the higher total concentrations of Ca, K, Mg, Zn and sulphate in the ashes. However, increasing the proportion of peat resulted in higher total concentrations of Al and Ni. According to Steenari and Lindqvist (1999), lower

levels of Ca, P and Cl and higher levels of Al, Fe and S were observed when coal or peat was added in the combustion of wood in CFB boilers. Furthermore, Steenari and Lindqvist (1999) reported that due to the lower levels of calcium oxide (CaO), the pH of ashes originating from co-combustion (i.e. coal and wood; peat and wood) were lower than those from the combustion of wood alone.

According to Makkonen et al. (2010), the mineral composition of waste material is important to characterise in order to evaluate environmental characteristics since in some minerals metals might be extracted easily while in the others metals may be bound more tightly. Makkonen et al. (2010) detected quartz (SiO_2), microcline (KAlSi_3O_8), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), gehlenite ($\text{Ca}_2\text{Al}(\text{AlSiO}_7)$), calcium oxide (CaO) and anhydrite (CaSO_4) in the ashes originating from the co-combustion of wood and peat. These results show similarities to earlier results of Steenari and Lindqvist (1999), who have also observed quartz (SiO_2), microcline (KAlSi_3O_8), anhydrite (CaSO_4), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and calcium oxide (CaO), but also e.g. tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$), albite-anorthite ($(\text{Na,Ca})\text{Al}(\text{Si,Al})_3\text{O}_8$), hematite (Fe_2O_3) and magnesium ferrite (MgFe_2O_4) in the ashes from the co-combustion of peat and wood. Furthermore, in the ashes from the co-combustion of coal and wood, Steenari and Lindqvist (1999) have also observed quartz (SiO_2), anhydrite (CaSO_4), calcium carbonate (CaCO_3), gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), calcium oxide (CaO), calcium hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and hematite (Fe_2O_3).

In the reports of Lillman (2009), Soininen et al. (2010) and Vuorinen and Suoniitty (2010), the properties of coal/ peat/ wood/agro-biomass derived ashes have been compared to the limit values given in the Finnish environmental legislation for fertilisers (MMM 2007) and for the recovery of ash as an earth construction agent (VNa 2006a; VNa 2009). According to the results of these studies, the total and extractable concentrations in coal/ peat/ wood/agro-biomass derived ashes showed high variation in those originating from different combustion plants and the limit values of several elements were exceeded in many cases (Lillman 2009; Soininen et al. 2010; Vuorinen and Suoniitty 2010). The study of Lillman (2009) showed that the limit values given for material used as an earth construction agent were exceeded in the peat/wood/coal fly ashes often e.g. due to the elevated total concentrations of As, Cd, Pb, Sb and PAHs but also due to the elevated extractable concentrations of several elements, mostly Mo.

In addition, the research of Vuorinen and Suoniitty (2010) showed that 14 % of wood/peat/agro-biomass ashes exceeded the total concentration limit value of As and 7 % of these ashes exceed the total concentration limit values of Cd

given in the Finnish environmental legislation for fertilisers (MMM 2007). It is worthwhile to note that in the research of Vuorinen and Suoniitty (2010), the ash samples were collected from 162 Finnish power plants which reported utilising ash as a fertiliser although the total number of such power plants nationally was 373. Thus, these results represent the selected ashes which may be the most appropriate for fertiliser products. However, it is also notable that after this research Finnish fertiliser environmental legislation was updated and the limit values for As and Cd are now higher than before.

2.2.2 Origin, properties and utilisation of green liquor dregs

Green liquor dregs are solid residues generated in the chemical circuit of chemical pulping and recovery processes (Jordan et al. 2002; Martins et al. 2007). The main idea of the chemical recovery process is to recover processed pulping chemicals for reuse. The chemical recovery process may vary due to the differences in pulping processes i.e. the sulphate process, where the active cooking chemicals are sodium hydroxide (NaOH) and sodium sulphide (Na₂S), and the sulphite process, where the active chemical is hydrogen sulphite (HSO₃⁻) (BREF 2012). Pulping processes are generally classified as mechanical, chemical or semichemical (SC) processes. In the SC-process, the wood chips are treated partly by cooking chemicals under pressure and partly mechanically to process them into suitable fibres; hence the name semichemical. SC-pulping generally uses sulphite chemistry at neutral or close to neutral pH (Gullichsen 2000). The most common SC-pulping process is Neutral Sulphite Semichemical (NSSC) (BREF 2012). In the NSSC-pulping process, the active pulping chemical is hydrogen sulphite (HSO₃⁻) and sodium or ammonium are the only possible bases due to the neutral pH requirement (Gullichsen 2000). Furthermore, the other specialties of NSSC processes are the different kinds of chemical recovery system compared to other processes, and the fact that NSSC-pulp is not bleached (BREF 2012).

In the pulping process the wood chips are cooked with cooking chemicals, and then washed with hot water. This dirty washing water, i.e. low concentration black liquor, is conducted to an evaporation plant to be concentrated into high concentration black liquor. After this, the concentrated black liquor is fed to a recovery boiler, where the organic matter in the black liquor is burned as a fuel liberating energy and the rest of the non-combustible chemicals yield the molten salt i.e. smelt, which falls to the bottom of the boiler (Rothpfeffer 2007). The smelt is discharged from the bottom of the boiler and dissolved in water to form green liquor. According to Morris et al.

(1995), sodium hydrosulphide gives the solution its green colour; hence the name “green liquor”.

Green liquor contains insoluble impurities and non-reactive metals i.e. non-process elements (NPEs), which have to be taken out of the system, for instance by precipitation in the form of green liquor dregs (Jemaa et al. 1999). The closure of the liquid system increases the concentration of metal ions, which are commonly referred as non-process elements (NPEs). This term usually refers to all of the chemical elements in the system other than sodium, sulphur, carbon, hydrogen, and oxygen (Grace and Tran 2009). According to Wilson (1987), the NPEs are defined as those elements that are not essential to the chemical process, i.e. are neither active pulping chemicals, nor compounds present as a result of the incomplete conversion of make-up chemicals to active pulping chemicals. Accumulation of NPEs in the pulping process have been reported to cause several problems such as build-up of scales, deposits, plugging, decreased boiler performance and corrosion of equipment (Malmberg et al. 2002; Hart et al. 2010; Doldán et al. 2011).

Green liquor dregs are mainly sodium carbonate (Na_2CO_3), calcium carbonate (CaCO_3), sodium sulphide (Na_2S) and a small organic fraction that has not been totally burnt in the recovery boiler (Modolo et al. 2010). According to Martins et al. (2007), green liquor dregs contain calcite (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), whereas Taylor and McGuffie (2007) detected in addition e.g. thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) and silicate and sulphate minerals.

The pH of green liquor dregs originating from sulphate pulping processes, i.e. Kraft mills, have been observed to be alkaline, pH 10-13.1 (Toikka 1998; Jordan et al. 2002; Mahdmoudkhani et al. 2005; Zambrano et al. 2010; Modolo et al. 2010). Toikka (1998) reported that due to the differences between processes and different process conditions, the properties of green liquor dregs may vary significantly. Furthermore, according to Toikka (1998), green liquor dregs have higher levels of heavy metals and lower levels of nutrients than wood ash, and thus cannot be utilised as a fertiliser. These findings are partly supported by Rothpfeffer (2007), who reported that green liquor dregs from a Kraft mill contained (except Ca and Mg) fewer nutrients than wood ash. Jordan et al. (2002) also observed higher levels of Ca and Mg in green liquor dregs originating from Kraft mills than in the fly ashes. In addition, high contents of Ca, P, K and Mg originating from Kraft mills' processes have also been reported by Zambrano et al. (2010) and Mahdmoudkhani et al. (2005). Due to the alkaline pH and high nutrient contents, green liquor dregs have been reported to be potential soil conditioning agents or fertilisers (Mahdmoudkhani et al. 2005; Zambrano et

al. 2010). In addition, green liquor dregs are considered e.g. as a potential neutralising agent for acidic wastewaters (Nurmesniemi et al. 2007), as a raw material in cement clinker production (Castro et al. 2009) and as an earth construction agent (Environmental permit 2011).

2.3 Review of extraction methods

The potential toxicity of harmful elements in residues such as ashes and green liquor dregs is not related to total concentration of the elements, but rather their extractability (Filgueiras et al. 2002.) Various leaching and extraction methods are reported to have been carried out on a wide variety of materials for evaluating the environmental suitability of materials (van der Sloot et al. 1997; Filgueiras et al. 2002) and in human health assessments (Wragg and Cave 2002; Twining et al. 2005). According to van der Sloot et al. (1997), leaching and extraction procedures defined as each test applied to a specific matrix may correspond to a well defined chemical treatment, which may or may not be standardised (e.g. by CEN or ISO).

2.3.1 Extraction methods in environmental studies

In the environmental studies, the main idea of leaching (extraction) procedures is to estimate the short-term or long-term release of contaminants from different matrices in various fields e.g. waste treatment and disposal, burning of waste fuels, soil clean-up and the reuse of cleaned soil, sludge treatment, use of compost from different sources, use of secondary materials in construction (Hjelmar 1996; Quevauviller et al. 1996, van der Sloot et al. 1997; Kosson et al. 2002).

Single leaching tests

The leaching tests are divided into procedures for which equilibrium or equilibrium-like conditions are assumed and test-procedures under non-equilibrium conditions (i.e. dynamic leaching test) (van der Sloot et al. 1997; Vaajasaari 2005). Dynamic tests, or tank tests are used for monolithic and stabilised granulated materials (Vaajasaari 2005). The most commonly used equilibrium-like test methods for granular materials are the column test (i.e. percolation test) and batch leaching test (Vaajasaari 2005). Column tests usually simulate field conditions such as fluid flow, mass transfer and dissolution mechanisms in a more realistic manner (van der Sloot et al. 1997) In order to simulate more real-life long-term environmental scenarios the

modelling and accelerating certain aspects can be combined in batch or column leaching tests (van der Sloot et al. 1997; van der Sloot et al. 2001). This can be accomplished for instance by increasing the throughput of liquid through columns or increasing the volume of liquid used in batch tests. According to Astrup et al. (2006a), column tests require a relatively long time to complete are therefore impractical for evaluating the leaching at high liquid L/S ratios for example above liquid-to-solid (L/S) 100-200 L/kg. Quevauviller et al. (1996) have reported that a single leaching test never assesses the long-term risk and dynamic and sequential extraction procedures are needed.

In national programs, leaching tests are developed in relation to national legislation (van der Sloot et al. 1997). Most countries have adopted simple, short-term agitation tests with one or two extraction stages tests in order to evaluate contaminant leaching of by-products (Sorvari 2003). According van der Sloot et al. (1997), differ leaching procedures are needed; regulatory control and shorter for quality control. In Finland, contaminant release from solid waste material in the environment is studied in accordance with standardised leaching methods, which are the up-flow percolation test in basic characterisation according to standard CEN/TS 14405, and the two-stage batch test in quality control studies according to standard SFS-EN 12457-3 (VNa 2009). In both of the above-mentioned leaching methods water is applied in contact with the solid waste material. Water is an important carrier of harmful substances to the environment, and according to Vaajasaari (2005), the most common extraction liquid used in standardised leaching methods for wastes. However, in the dissertation of Vaajasaari (2005), such standardised leaching methods were not found sufficient in the case of inorganic waste materials with a strong acid neutralising capacity, and pH-controlled leaching experiments are stated to be needed. In cases where a pH is effecting on leaching researchers have been reported to characterise leaching properties by the pH dependent leaching at specific pH values in a range of pH 4-12 (Kosson et al. 2002; Astrup et al. 2006a).

Factors effecting on leaching

Several factors have been observed to effect on leaching of the material. These factors may be physical or chemical and those might be influenced due to biological or environmental changes (van der Sloot et al. 1996; van der Sloot et al. 1997).

The pH value has been reported to be one of the most important chemicals factors influencing the leaching of heavy metals in inorganic waste materials (van der Sloot et al. 1997). Most of the heavy metals tend to increase their solubility under acidic conditions, and reach a minimum solubility above the pH value of 9 (Abbott et al. 2003). However, some heavy metals have higher

solubility under alkaline conditions and some heavy metals both at low and high pH values (Abbott et al. 2003). Respectively, according to Sabbas et al. (2003), three main typical leaching behaviours have been identified, i.e. cation-forming species and non-amphoteric metal ions (e.g. Cd), amphoteric metals (e.g. Al, Pb, Zn) and oxyanion-forming elements (e.g. As, Cr, Mo, V, B, Sb). Sabbas et al. (2003) showed that the concentration of cation-forming species and non-amphoteric metal ions display fairly constant high values at $\text{pH} < 4$, and decreases strongly up to $\text{pH} 8$ to 9 , remaining approximately constant or slightly increasing for higher pH values. Furthermore, the leachability of amphoteric metals increases under both strongly acid and strongly alkaline conditions, resulting in a V-shaped solubility curve. For oxyanion-forming elements solubility usually decreases in alkaline ranges ($\text{pH} > 10$) (Sabbas et al. 2003). A change of pH may occur due to various environmental influences e.g. atmospheric CO_2 , acid rain, buffering capacity of natural waters, microbiological activity and organic matter decomposition (Steenari et al. 1999; van der Sloot et al. 2001; Kosson et al. 2002; Astrup et al. 2006b).

In addition to pH , various other chemical factors effecting on leaching have been reported, including e.g. oxidation/reduction complexation, hydrolysis, hydration, dissolution/precipitation, carbonation, sorption, formation of solid solutions (van der Sloot et al. 1997; Kosson et al. 2002; Polettini and Pomi 2004; Ludwig et al. 2005). Reducing conditions may result from material characteristic (e.g. sediments and soils), biological activity or external inputs and lead to formation of different chemical phases with significantly different solubilities compared to oxidised conditions (van der Sloot et al. 1997; Kosson et al. 2002). Therefore testing of these kinds of materials must be carried out in appropriate conditions (Kosson et al. 2002). Furthermore, it has been found relevant to evaluate the certain complexing agent, which may increase the solubility of some heavy metals (Vaajasaari 2005). Organic matter, chloride and sulphate can form complexes with heavy metals, e.g. cadmium may form complex with chloride the mobile anionic CdCl_4^{2-} complexes (van der Sloot et al. 1997; van der Sloot et al. 2001).

Many solid mineral phases in materials have sorptive properties and are capable of binding dissolved constituents onto the surface (van der Sloot et al. 1997). Sorption reactions can involve the formation of bonds, which may vary from relatively weak to quite strong (van der Sloot et al. 1997). According to Ludwig et al. (2005) the release of heavy metals from ash depends on the chemical characteristics of ash materials in terms of form and solubility. Heavy metals may be present as water soluble salts where dilution determines the concentrations in the solution phase and there is no pH dependency

(Ludwig et al. 2005). Heavy metals may be present also as soluble or moderately soluble phases but trapped in materials which need dissolution with acid make the soluble phases free, e.g., carbonates anoxides (Ludwig et al. 2005). Again the solubility of the heavy metals may not be directly related to proton inputs, but protons are required to dissolve the surface cover. Moreover, heavy metals occur in a form that would be released following dissolution processes (Ludwig et al. 2005). For instance, heavy metals could be present as carbonates, oxides or hydroxides or as surface complexes, sorbed to oxide or hydroxide minerals in the ash matrix (Ludwig et al. 2005).

The physical properties of waste matrices effecting on leaching are e.g. porosity of the solid matrix, homogeneity or heterogeneity of the solid matrix in terms of mineral phases, the geometrical shape and size of materials (van des Sloot et al. 1997). In general, smaller particles, the larger surface areas per mass or volume, allow more rapid dissolution and thus increase leachability of the elements (van der Sloot et al. 1997, Vaajasaari 2005). Furthermore, materials with low values of interparticle porosity and low permeability will not transmit water hence the velocity of flow will be quite low (van der Sloot et al. 1997). Physical changes may occur naturally during the time on the surface mineralogy of material as a consequence of atmospheric contact, which effect on leaching (Polettini and Pomi 2004).

Sequential extraction procedures

In sequential extraction procedures, a series of various chemical extractants is applied to the sample, with each successive treatment being more aggressive than the previous one (Kosson et al. 2002). The principle advantage claimed for sequential extraction over the use of single extractants is that the phase specificity is improved since each extractant has a different chemical nature e.g. a dilute acid, reducing or oxidizing agent (Rao et al. 2008). Sequential extraction procedures are widely used in order to estimate the potential mobility of the heavy metals in solid matter into the environment (van Herck and Vandecasteele 2001; Bruder-Hubscher et al. 2002; Bacon and Davidson 2008; Sivula 2012). According to Filgueiras et al. (2002), the sequential extraction procedure provides detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilisation and transport of trace metals.

The aim of the sequential extraction method is to divide the total extractable concentrations of metals into separate fractions in order to assess the form in which the heavy metals occur in the solid waste material (van Herck and Vandecasteele 2001). The manner in which the heavy metal is bound to the solid waste material influences the mobility and, ultimately, the bioavailability

and toxicity to organisms (van Herck and Vandecasteele 2001; Ludwig et al. 2005; Bacon and Davidson 2008). The most weakly bound heavy metals are generally extracted in an earlier stage of the sequential extraction procedure, and thus have the greater potential mobility in the environment than those released later (Bacon and Davidson 2008). These extraction methods have been reported to be carried out in the assessment of the worst case environmental scenarios, in which the components of the sample become soluble and mobile (Filgueiras et al. 2002). Initially, the procedure was developed by Tessier et al. (1979) to fractionate the heavy metals of river sediments. Since then, several various sequential extraction procedures are reported, the main differences being the extractants used, the operating conditions and number of stages involved (Filgueiras et al. 2002; Rao et al. 2008; Bacon and Davidson 2008).

Various studies on sequential extraction procedures have reported the lack of comparability in results (Fuentes et al. 2004; Bacon and Davidson 2008). According to Filgueiras et al. (2002) small changes in the experimental conditions can give rise to large variations in the fractionation. Sequential extraction procedure has been criticised for poor reproducibility (Rauret et al. 1999, Rao et al. 2008). In addition, according to Bacon and Davidson (2008) one of the major disadvantages of sequential extraction procedures is that they are time-consuming. Comprehensive reviews of the limitations of sequential extraction procedures are provided e.g. in reviews of Filgueiras et al. (2002), Rao et al. (2008) and Bacon and Davidson (2008).

BCR sequential extraction procedure

In order to improve the comparability of the sequential extraction results, the European Standards, Measurement and Testing (SM&T) Program, formerly the European Community Bureau of Reference (BCR), developed a harmonised, three-stage sequential extraction procedure for determining metals in soils and sediments (Ure, 1993). In the literature, this three-stage sequential extraction procedure of SM&T is still widely known as the BCR sequential extraction (Rao et al. 2008; Bacon and Davidson 2008). Also, the revised BCR sequential procedure was developed, and also some certified reference materials were produced, which have resulted in better precision between laboratories (Rauret et al. 1999; Mossop and Davidson 2003; van Hullebusch et al. 2005; Larner et al. 2005). The BCR sequential extraction procedure has been reported as successfully applied to various materials, including soils, sediments (Rauret et al. 1999; Mossop and Davidson 2003), sludges (Fuentes et al. 2004; van Hullebusch et al. 2005) and ashes (Smeda and Zyrnicki 2002; Bruder-Hubscher et al. 2002

With the three-stage BCR sequential extraction of SM&T, the obtained fractions are: Acid-soluble fraction (BCR1: CH_3COOH): This fraction gives an indication of the amount of metals bound on the surface of the particles, as well as those that are released as acid-soluble salts such as carbonates (Ndiba and Axe 2009). The metals in this fraction are generally considered readily and potentially mobile (Filgueiras et al. 2002). The use of acetic acid as a leachant emulates the organic acid produced from decomposing waste in anaerobic environments such as landfills (Townsend et al. 2005) and this fraction indicates the proportion of elements that are capable of being released from the matrix into the environment if the conditions become acidic (Long et al. 2009).

Reducible fraction (BRC2: $\text{NH}_2\text{OH-HCl}$): This fraction represents the amount of metals bound to iron and manganese oxides that would be released if the substrate was subjected to reductive conditions (Yousfi and Bermond 1997) and it simulates anoxic conditions that are likely to occur in a natural medium (Rauret 1999). The elements are strongly bound to these oxides but are thermodynamically unstable in anoxic conditions. The metals in this fraction are considered to be relatively stable under normal soil conditions, but can be mobilised by increasing the reducing or oxidising conditions in the environment, which means that they are potentially bioavailable (Filgueiras et al. 2002)

Oxidisable fraction (BCR3: $\text{H}_2\text{O}_2+\text{CH}_3\text{COONH}_4$): This fraction corresponds to the metals that are organically bound or occur as oxidisable minerals, e. g., sulphides (Smichowski et al. 2005). Metals bound in this fraction can be released under oxidation conditions. The organic fraction released in the oxidisable step is not considered to be very mobile or bioavailable (Filgueiras et al. 2002; Smichowski et al. 2005).

2.3.2 Extraction methods in assessing the possible occupational risks of solid residue handling

According to Mroueh et al. (2002), when using by-products in earthworks direct risks to humans are mostly related to the transportation and handling of the by-products, and the typical exposure pathways for heavy metals in by-products are the inhalation of dust and volatile compounds, dermal contact and ingestion. Oral/ingestion exposure is reported to provide the greatest exposure for contaminants in ash, followed by respiratory and dermal exposure routes (Ruby et al. 1999; Wragg and Cave 2002; Twining et al. 2005). Once the material enters the body via the respiratory and gastrointestinal tracts, it mixes with biological fluids and hence has an

opportunity to be dissolved, absorbed and cause toxic effects in humans (Wragg and Cave 2002; Twining et al. 2005).

The employees at power plants may be exposed to heavy metals from ashes via their respiratory, dermal and gastrointestinal tracts (Finnish Institute of Occupational Health 2011). Traces of As, Cd, Ni and Pb have been found on the hands of employees, and in addition elevated levels of several heavy metals also found in their urine (Finnish Institute of Occupational Health, 2011). Furthermore, in the same study the total concentrations of heavy metals in the ashes from the different kinds of the power plants were determined, and it was concluded that heavy metals with the highest total concentration values are the highest priority in exposure assessment (Finnish Institute of Occupational Health, 2011).

Various in-vitro (i.e. test tube or Petri dish) and in-vivo (i.e. animal model) extraction tests simulating human body fluids have been developed in order to estimate the bioavailability of heavy metals from solid waste to humans (Ruby et al. 1999; Twining et al. 2005). In-vitro tests may vary from simple bioavailability tests, where a simple reagent in a single extraction test is used, to more complicated tests, which mimic the more complex aspects of human physiology (Oomen et al. 2002; Wang et al. 2007). Gastrointestinal processes are stated to be complex and difficult to simulate (Wragg and Cave, 2002). It is notable, that in-vitro tests do not provide absolute bioavailability data, which can only be done by in-vivo tests, and thus in-vitro tests can only be used as predictors to estimate the potential bioavailability of heavy metals in human health risk assessment (Wragg and Cave 2002.)

Comprehensive reviews of the different in-vitro methods have been presented by Ruby et al. (1999), Oomen et al. (2002) and Wragg and Cave (2002). Oomen et al. (2002) concluded that different in-vitro methods can lead to a variety results due to the differences in the methods, and that the best method cannot be specified. However, according to Ruby et al. (1999), in-vitro tests have been reported to be a rapid and inexpensive way to assess bioavailability of heavy metals to humans, compared to in-vivo tests, and therefore relatively widely used. Artificial sweat, gastric/ gastrointestinal fluids, and saliva have been used as extractants to determine the levels of extractable heavy metals in a range of industrial wastes such as coal fly ash (Twining et al. 2005), chromate copper arsenate-treated wood (Nico et al. 2006), urban roadside and industrial soils (Kim et al. 2002; Wang et al. 2007), airborne particulate matter (Madrid et al. 2008), and in various mine waste materials such as tailings, heap leach, and waste rock (Bruce et al. 2007).

3. Aims of the study

The main objective of this study was to determine the chemical, physical and extraction properties of the major solid residues originating from the power plant of an SC-pulp and board mill i.e. bottom and fly ashes originating from the BFB boiler and green liquor dregs from Stora Enso Heinola Fluting Mill, Finland, and to assess the potential utilisation of these residues from various aspects. The specific research questions were:

1. to determine the most important chemical and physical properties of the ashes and green liquor dregs, and to assess whether these properties support the utilisation of these residues (Papers I, II, III)
2. to determine the extractability of heavy metals in the ashes and green liquor dregs by a three-stage BCR sequential extraction procedure and evaluate whether these results support the utilisation of these residues from an environmental perspective (Papers III, IV)
3. to determine the extractability of heavy metals in the ashes and green liquor dregs by artificial sweat and gastric fluids and to assess the potential occupational risk of solid residue handling (Papers II, V).

Research question 1 was studied for ashes originating with two different fuel mixtures (i.e. coal, wood and peat; and wood and peat) and also for green liquor dregs from chemical recovery. Research questions 2-3 were studied for ashes originating from the co-combustion of coal, wood and peat and for the green liquor dregs. The structure of this thesis is shown in Table 1.

Table 1. The structure of this thesis.

Research question	Solid residue	
	Bottom ash and fly ash from BFB boiler	Green liquor dregs from recovery boiler
Number 1: Chemical and physical properties of ashes and green liquor dregs and an assessment of utilisation	Paper I, II	Paper IV
Number 2: Sequential extraction partitioning of elements in ashes and green liquor dregs	Paper III	Paper IV
Number 3: Extractable heavy metals in ashes and green liquor dregs using artificial sweat and gastric fluids	Paper II	Paper V

4. Material and methods

4.1 Ashes and green liquor dregs from Stora Enso Heinola Fluting Mill

The study was carried out at an integrated SC-pulp and board mill, i.e. Stora Enso Heinola Fluting Mill, located in Finland. The mill produces NSSC-pulp in its own pulp mill and SC-fluting at its board mill, which are fully integrated. The annual production capacity of the mill is approximately 300,000 tonnes of SC-fluting, which is the corrugated medium between liners in a corrugated board. In addition to the pulp and board mill, the mill has an own waste water treatment plant and a power plant. Figure 1 illustrates the processes at the integrated mill site.

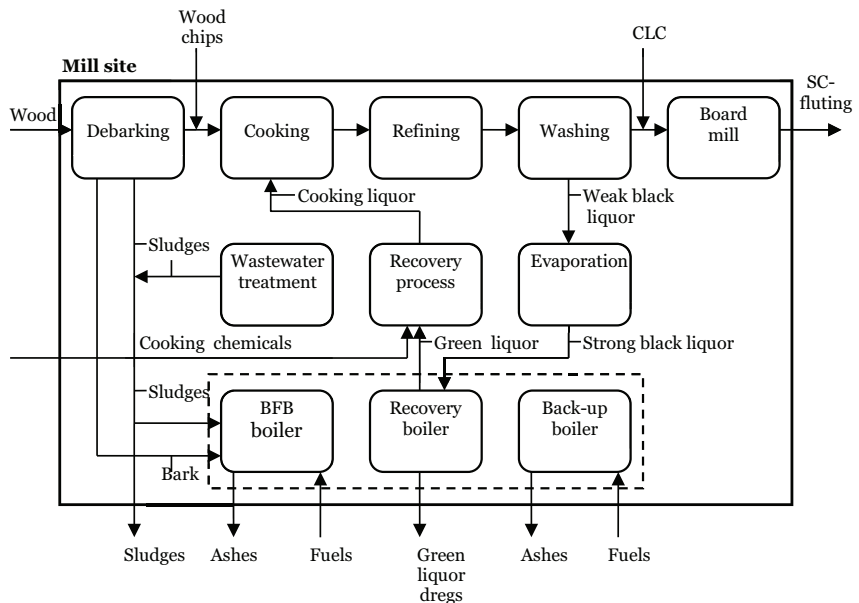


Figure 1. Simplified schema of processes at Stora Enso Heinola Fluting Mill.

The wood raw material is brought to the mill as roundwood or chips. The main wood raw material is birch (*Betula verrucosa* and *B. pubescens*). Other raw

The BFB boiler is mainly fuelled with peat and bark originating from the debarking unit of the mill. During the winter some coal is also used due to the increased need for energy by the district heating load. In addition, part of the sludge originating from the wastewater treatment plant is burnt for energy recovery in the BFB boiler. Some heavy fuel oil and reject from CLC pulping process are also occasionally used as auxiliary fuels. The BFB was commissioned in 1984. In 2007, the flue gas cleaning equipment was upgraded with the electrostatic precipitator (ESP) replaced by a new unit, and a wet-scrubber was installed after the ESP. The particulate matter from flue gas (fly ash) is captured with three fields (i.e. electrodes) of the ESP in the operating temperature below 150°C. Sulphur dioxide emissions are reduced with the wet-scrubber by washing them with an alkaline solution (50% NaOH). The heat energy of the flue gas is also recovered in the wet scrubber using a heat exchanger. The boiler bottom ash is removed together with the bed sand material, and the annual amount of this residue is approximately 600-700 tonnes (w.w.). The fly ash fractions from all three fields of the ESP are collected and combined in one single ash silo resulting in the generation of approximately 5,000-10,000 tonnes (w.w.) of fly ash annually. The washing effluent from the wet-scrubber of the BFB boiler is transferred to the waste water treatment plant of the mill.

Approximately 25% of the energy needed at the mill is produced by the recovery boiler. The recovery boiler is fuelled with black liquor but some heavy fuel oil may also be used as an auxiliary fuel. The recovery boiler started to operate in 1990 and in year 2007, a new ESP with three fields was installed in order to reduce particulate emissions. The particulate matter from the ESP (salt) is collected and mixed together with the black liquor, and after that is fed back to the recovery boiler. The incombustible residue at the bottom of the boiler is taken out in the form of a smelt, then diluted with water and dried under pressure forming green liquor dregs. A pressurised drying unit was installed in 2007 in order to increase the solid content of green liquor dregs. The annual amount of green liquor dregs produced is approximately 1,300-2,000 tonnes (w.w.). The recovery boiler also has a wet-scrubber, which operates in acidic conditions by using the sulphite from the recovery unit. The dirty washing effluent from the scrubber is fed back to the recovery unit for further processing.

The back-up boiler is fuelled with heavy fuel oil and coal, and is used only occasionally, mainly during maintenance of the main boiler. According to the Environmental permit (2004), no more than 2000 annual operational hours are allowed for the back-up boiler starting from 1 January 2008, and the boiler is not allowed to use be used after 31 December 2015. The particulate matter is

cleaned with a cyclone originating from 1960s. The total amount of bottom and fly ash from the back-up boiler is minor, at less than 1 tonne per a year.

4.2 Sampling procedures

4.2.1 Sampling of ashes

The bottom ashes and fly ashes were sampled during periods when two different fuel mixtures were incinerated in the BFB boiler (120 MW). During the first sampling period approximately 50% of the energy originated from the incineration of commercial peat fuel, 25% from the incineration of forest residues i.e. bark, wood chips and sawdust, and 25% from the incineration of coal. Approximately 85% of the volume of forest residues consisted of clean bark from the wood handling process of the mill, with approximately 95% of the barked wood being birch (*Betula verrucosa* and *B. pubescens*), 4% spruce (*Picea abies*) and 1% alder (*Alnus incan* and *A. glutinosa*). The peat fuel originated from near the mill, and was thus of domestic origin, whereas the coal originated from Russia.

During the second sampling period, approximately 50% of the energy originated from the incineration of commercial peat fuel and 50% from the incineration of wood residues. Approximately 74% of the volume of forest residues consisted of clean bark from the wood handling process of the mill, of which approximately 98% of the barked wood was birch (*Betula verrucosa* and *B. pubescens*) and 2% was alder (*Alnus incan* and *A. glutinosa*). The peat fuel originated from near the mill and was thus of domestic origin.

Sampling of bottom ashes (i.e. bottom ash A and B) and fly ashes (i.e. fly ash A and B) was carried out over a period of fifteen days. During this period, a total of six sub-samples for each ash were collected. The six individual sub-samples for each ash were combined to give one composite sample with a weight of 5 kg for each ash. The sampling period represented normal process operating conditions for the combustion plant, for instance in terms of O₂ content and temperature. The temperature in the BFB was approximately 900°C and approximately 150°C in ESP. The bottom ashes were sampled from the outlet of the BFB boiler. The fly ash fractions from three different ESP fields were collected to one ash silo and thus, the fly ash samples studied in this thesis were a mixture from all three fields of the ESP.

After sampling, the samples were stored in polyethylene bottles in a refrigerator (+4°C) until analyses could be carried out. A sample should be analysed as soon as possible after sampling, however, if this is not done according to EPA (2009), the sample should be chemically or physically

preserved as soon as possible after sampling to avoid or minimise biological, chemical and physical changes that can occur between the time of collection and analysis. For this reason the procedure of Sarode et al. (2010) was followed with storage of the sample in a refrigerator (+4°C) until analysis. A coning and quartering method (Gerlach et al. 2002) was repeatedly applied to reduce the sample of ash to a size suitable for conducting laboratory analyses.

4.2.2 Sampling of green liquor dregs

The sampling of the green liquor dregs was carried out at the end of April and in the beginning of the May 2010, over a period of nine days. Six individual daily samples were combined to give one composite sample with a weight of 10 kg. The samples of the green liquor dregs were collected from the pulp mill process, at the outlet of the green liquor pressure filter. The sampling period represented normal process operating conditions of the mill's processes when approximately 73% of the volume of the wood material was birch (*Betula verrucosa* and *B. pubescens*), 23% was aspen (*Populus tremula*) and 4% was spruce (*Picea abies*). The wood material used for cooking mainly originated from Finland, except for roundwood aspen, which originated from Russia. The aspen roundwood was not debarked like the other roundwood tree species. The wood chips were cooked with a mixture of (Na₂SO₃), (NaOH) and (Na₂CO₃). After sampling, the samples were stored in polyethylene bottles in a refrigerator (+4°C) (Sarode et al. 2010). A coning and quartering method (Gerlach et al. 2002) was repeatedly applied to reduce the sample of dregs to a size suitable for conducting laboratory analyses.

4.3 Chemical and physical analyses of ashes and green liquor dregs

4.3.1 Determination of the mineral composition, physical and chemical properties of ashes and green liquor dregs

For the determination of the mineralogical composition of the ashes and green liquor dregs, X-ray diffractograms (XRD) of powdered samples were obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuK α radiation. The scan was run from 5° to 80° (two-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 carried out with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany)

and ICDD PDF-2 Release 2006 software package (PA, USA). Determination of pH and the electrical conductivity (EC) in the ashes and the green liquor dregs was carried out according to European standards SFS-EN 13037 at a solid-to-liquid (i.e. ultrapure water) ratio of 1:5 (SFS-EN 2000c). Determination of the dry matter content of the ashes and dregs 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 (SFS-EN 2000b). The loss-on-ignition (LOI) value was determined according to European standard SFS-EN 12879 at the temperature of 550°C, and the total organic carbon (TOC) content was determined according to European standard SFS-EN 13137 (SFS-EN 2000a; SFS-EN 2001).

The neutralising value (NV) of the ashes and green liquor dregs were determined according to European standard SFS-EN 12945 (SFS-EN 2002b). In this procedure, the dried sample is dissolved in a specific quantity of a standard hydrochloric acid solution and the neutralising value of a sample is determined by back titration with sodium hydroxide. The reactivity value (RV) was determined according to European standard SFS-EN 13971 (SFS-EN 2003). In this procedure, the carbonates of a sample are determined by potentiometric titration with hydrochloric acid.

4.3.2 Determination of the easy soluble plant nutrient concentrations in ashes and green liquor dregs

The determination of the easily soluble plant nutrient concentrations (P, Ca, Na, K, Mg, S, Mn, Cu and Zn) in the ashes and green liquor dregs was carried out according to the procedure of Yli-Halla and Palko (1987). In this procedure, the easily soluble forms of P, Ca, Na, K, Mg and S are extracted with 0.5 M acidic ammonium acetate (pH 4.65), and in the extraction of Mn, Cu and Zn, the acidic (pH 4.65) ammonium acetate extract contains 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na₂EDTA). In both extraction procedures, one volume part of a dry sample was shaken with ten parts of the extraction solution for 1 h. Before analysis, the extract was separated from the solid residue by filtration through a 12.5 mm diameter Schleicher & Schull 589 blue ribbon filter paper (Schleicher & Schull, Dassel, Germany).

The concentrations of Ca, Na, K, Mg and S were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES), and the concentrations of Mn, Cu and Zn by flame atomic absorption spectrometer (FAAS, Perkin Elmer Analyst 700, Norwalk, USA). The concentration of P in the extract was determined spectrophotometrically by the molybdenum blue method using an

automatic Foss-Tecator FIAStar 500 Flow Injection Analyser (Högnäs, Sweden). Before the determination of the nutrients, the sample was dried overnight to a constant mass at 105°C in a drying oven (Termaks) according to European standard SFS-EN 12880 (SFS-EN 2000b).

4.3.3 Determination of the total element and total chloride concentrations in ashes and green liquor dregs

For the determination of the total element concentrations in the ashes and green liquor dregs, the dried sample was digested with a mixture of HCl (3 mL) and HNO₃ (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using USEPA method 3051A (Yafa and Farmer 2006). The cooled solution was transferred to a 100 mL volumetric flask and the solution was diluted to volume with ultrapure water. All reagents and acids were suprapure or pro analysis quality. Except for Hg in the ashes and the green liquor dregs and F in green liquor dregs, the total element concentrations in the ashes and green liquor dregs were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). The concentration of Hg in the ashes and dregs was determined with a Perkin Elmer AAnalyst 700 cold-vapour atomic absorption spectrometer (Norwalk, USA) equipped with a Perkin Elmer FIAS 400 and AS 90 plus autosampler. The concentration of F in the cooled solution was carried out according to European standard SFS-EN ISO 10304-1 using a Dionex DX500 ion chromatography system (Dionex Corp., USA) (SFS-ISO 2009). The concentration of chlorine in the extract was determined with a Dionex DX500 ion chromatography system (Dionex Corp., U.S.A.). For the determination of total Ca, P and K concentrations in Paper I, the lithium tetraborate (Li₂B₄O₇) fusion followed by dissolution in 12.5 mL HNO₃ (65%) and 40 mL H₂O was used (ASTM 2001; CEN ENV 1997). The total Ca, P and K concentrations in the ashes were determined with a Thermo Fisher Scientific iCAP6500 Duo ICP-OES (United Kingdom).

4.3.4 Determination of PCB and PAH in ashes

To determine the total polychlorinated biphenyl (PCB) concentration in the ashes, European standard SFS-ISO 10382 was followed. The sample (10 g) was extracted with a mixture of hexane (5 mL) and acetone (10 mL) for 30 min by ultrasonic-assisted extraction (Bandelin Sonorex) (SFS-ISO 2007a). According to the standard methodology (SFS-ISO 2007a), the PCBs were assigned and

quantified by comparison of the relative retention times and relative peak height or peak areas with respect to injection standards containing commercial internal standards (PCB-30 and PCB 204). To determine the total polycyclic aromatic hydrocarbon (PAH) concentration in the ashes, European standard SFS-ISO 18287 was followed (SFS-ISO 2007b). The sample (10 g) was extracted with a mixture of hexane (5 mL) and acetone (10 mL) for 30 min by ultrasonic-assisted extraction (Bandelin Sonorex). According to the standard methodology (SFS-ISO, 2007b), the identification and quantification of PAH compounds was carried out with commercial deuterated PAHs (naphthalene-d8, acenaphthylene-d10, phenanthrene-d10, chrysene, and perylene-d12) as internal standards. A comprehensive review of the determination of PCB and PAH concentrations are provided in the original standards (SFS-ISO 2007a, b).

4.3.5 Extraction procedure at L/S ratio of 10 and determination of extractable concentrations in the extracts

To determine the extractable concentrations of DOC, heavy metals, fluoride, sulphate, and chloride in the ashes, European standard SFS-EN 12457-3 was used (SFS-EN 2002a). This extraction procedure was chosen due the requirements of Finnish environmental legislation (VNa 2009). This procedure is a two-stage batch test at a L/S ratio of 2 L/kg and 8 L/kg, with an extractant containing ultrapure water (H₂O). The sum of leachable concentrations (i.e. 10 L/kg) is compared to the maximum allowable concentrations, which together with the total element concentrations determine whether the residue may be used as an earth construction agent or whether it needs to be disposed of either to an inert-waste, non-hazardous waste, or hazardous waste landfill. The metal concentrations (i.e. Sb, As, Ba, Cd, Cr, Cu, Hg, Pb, Mo, Ni, V, Zn, and Se) in the extracts were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). Determination of the DOC concentration in the extract was carried out according to European standard SFS-EN 1484 using a Leco CHN-600 analyzer (Leco, USA) (SFS-EN 1997). Determination of the fluoride, sulphate, and chloride concentrations in the extract was carried out according to International standard SFS-ISO 10 304-1 using a Dionex ICS 2000 ion chromatography system with conductivity detector (Dionex, USA) (SFS-ISO 2009).

4.4 Sequential extraction partitioning of elements in ashes and green liquor dregs

The three-stage BCR sequential extraction procedure according to Smeda and Zyrnick (2002) was used for the partitioning of heavy metals in the samples between the exchangeable (BCR1: CH_3COOH), easily reduced (BCR2: $\text{NH}_2\text{OH}\cdot\text{HCl}$ in nitric acid medium) and oxidisable (BCR3: $\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$) fractions. This extraction procedure is harmonised and widely used for the partitioning of heavy metals in ash (Filgueiras et al. 2002). The schematic diagram of the sequential procedure is illustrated in Figure 3.

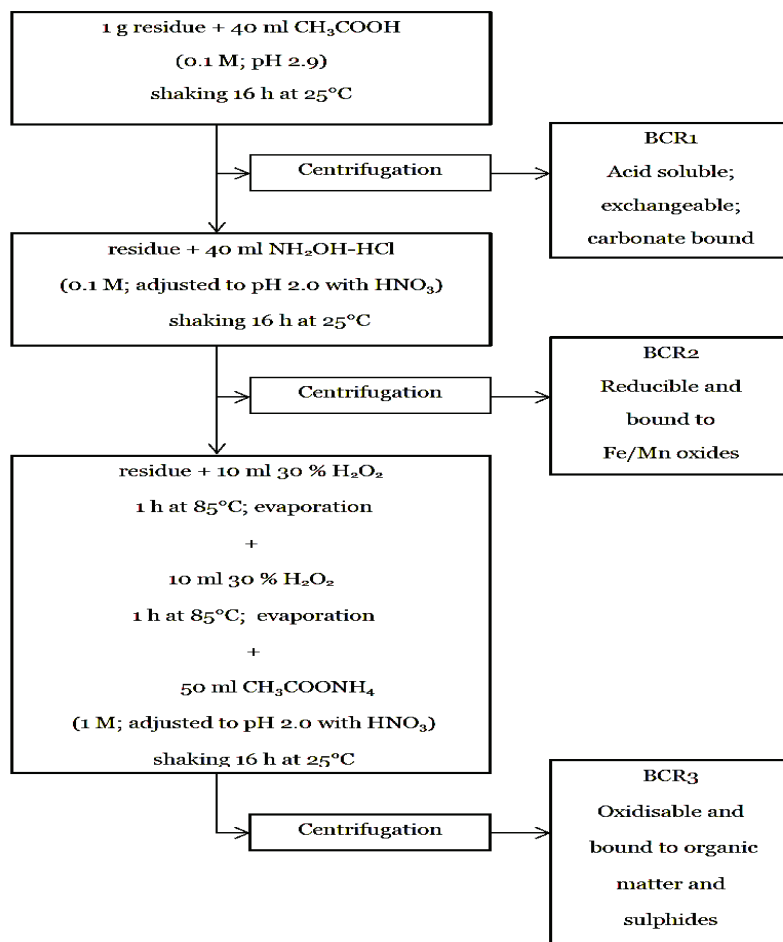


Figure 3. Schematic diagram of the sequential extraction procedure for element partitioning between acid soluble (BCR1), reducible (BCR2) and oxidisable (BCR3) fractions (Smeda and Zyrnick 2002).

Extraction was carried out by shaking 5 g of the sample in a polypropylene bottle. In order to minimise possible chemical and/or microbiological changes

in the material, the extraction was carried out using an undried sample instead of a dried sample since it is preferable to avoid sample drying before extraction (Kosson et al. 2002). After each extraction step the extracts were separated from the solid residue by filtration through a 0.45 µm membrane filter (47 mm diameter; Schleiche Dassel, Germany). In order to avoid losses between the extraction stages, the filters and adhering sample particles from the previous extraction stage were also included in the next stage. After the addition of 200 µL of 65% HNO₃ to the supernatant phase, it was stored in a refrigerator (+4 °C) until the element determinations (Sarode et al. 2010). The element concentrations in the extracts (i.e. extraction stages 1–3) were determined with a Thermo Fisher Scientifici CAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). Validation of the sequential extraction procedures carried out at Suomen Ympäristöpalvelu Oy for ash and green liquor dregs residues have been given in the publications of Nurmesniemi et al. (2005), Nurmesniemi and Pöykiö (2006), Mäkelä (2012) and Pöykiö et al. (2010).

4.5 Procedure for determining the extractability of heavy metals in ashes and green liquor dregs using artificial sweat and gastric fluids

Artificial sweat was prepared by dissolving 5 g NaCl, 1 g lactic acid, and 1 g urea in 1 L of deionised water and adjusting the pH to a value of 6.47 with ammonia (Song et al. 2007). Artificial gastric fluid was prepared by dissolving 60.06 g glycine in 2 L of deionised water and adjusting the pH to a value of 1.51 with HCl (Wang et al. 2007). The extraction was carried out in polypropylene bottles by shaking 1 g of residue (i.e. ash or green liquor dregs) on a dry weight (d.w.) basis with 100 mL of the extract (i.e. artificial sweat or artificial gastric fluid) for 1 h by end-over-end mixing at 37°C. Thus, the liquid-to-solid ratio (L/S 100 L/kg) in this procedure was the same as those of Wang et al. (2007) and Kim et al. (2002). To minimise possible chemical and/or microbiological changes in the residue during the extraction procedure, extraction was carried out by using an undried sample instead of a dried sample, because according to Kosson et al. (2002), it is preferable to avoid sample drying before extraction. After extraction, the extract was separated from the solid residue by filtration through a 0.45 µm membrane filter. The pH of the extract was then measured, and the metal concentrations were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES).

5. Results and discussions

5.1 Chemical and physical properties of ashes (I, II)

5.1.1 The utilisation aspects of ashes as a forest fertiliser (I)

The most important chemical and physical forest fertiliser properties for the bottom and fly ashes from incineration of two different fuel mixtures (i.e. fuel mixture A; coal, wood and peat; fuel mixture B; peat and wood) are summarised in Table 2, and were originally presented in Paper I (Tables 1 and 2). Table 2 also presents the limit values of forest fertiliser given in the current Finnish Decree (24/11) and in the previous Decree (12/07) (MMM 2007; MMM 2001). In the original Paper I (Table 2), the limit values of the previous Decree (12/07) and the results of the ashes investigated that were compared to this earlier Decree (12/07) were presented (MMM 2007). However, after the publication of the original Paper I, the limit values of the current Decree (24/11) came into force and superseded the previous Decree (12/07) (MMM 2007; MMM 2011). Therefore, in addition to the results and conclusions published in the original Paper I, some new conclusions about the fulfilments of the new limits value are also now presented.

The results show that the pH values in the both bottom and fly ashes were alkaline. However, the ashes originating from the incineration of fuel mixture B (i.e. peat and wood) were slightly more alkaline (pH 11.3-12.0) than those (pH 10.4-10.5) from the incineration of fuel mixture A (i.e. coal, peat and wood). These results correspond to the results obtained by Steenari and Lindqvist (1999), who reported that in the ashes originating from the co-combustion of wood with coal, the pH is generally lower than in those originating from the incineration of wood residues only. According to van Herck and Vandecasteele (2001), the alkaline pH of ashes indicates that part of the dissolved metals occurs as basic metals salts, oxides, hydroxides and/or carbonates. Figures 4a-d show the XRD and mineral composition results for bottom and fly ashes A and B.

Table 2. Chemical, physical and forest fertiliser properties of the bottom and fly ashes originating from the co-combustion of different fuel mixtures in a BFB boiler of 120 MW, and previous (Decree 11/07) and the current (Decree 24/11) limit values of Finnish forest fertiliser legislation (Paper I).

Parameter / element	Unit	Bottom ash A	Fly ash A	Bottom ash B	Fly ash B	Limit value of Decree 12/07	Limit value of Decree 24/11
pH (1:5)		10.4	10.5	11.3	12		
EC	ms/m	0.1	1.3	0.5	4.7		
DMC	%	94.0 ± 0.2	71.1 ± 0.8	92.0 ± 0.3	74.8 ± 0.7		
LOI (550°C)	% (d.w.)	< 0.5	15.6 ± 0.3	< 0.5	4.0 ± 0.1		
TOC	g/kg (d.w.)	< 2.0	140	< 1.0	24.3 ± 0.6		
NV	%(Ca; d.w.)	4.4 ± 0.2	7.6 ± 0.1	4.3 ± 0.1	12.3 ± 0.2		10.0 (min) ¹
Cl	% (d.w.)	< 0.01	< 0.01	< 0.01	< 0.01		2.0 (max) ²
Ca	% (d.w.)	2.4	6.4	3.4	11.0		6.0 (min) ²
P+K	% (d.w.)	2.2	1.8	4.1	2.5		1.0 (min) ²
As	mg/kg (d.w.)	3.9 ± 0.1	46.9 ± 0.6	< 3.0	41.3 ± 0.4		30 (max) ²
Cd	mg/kg (d.w.)	< 0.3	1.7 ± 0.1	< 0.3	2.9		17.5 (max) ²
Cr	mg/kg (d.w.)	10.9 ± 0.3	47.1 ± 1.8	10.8 ± 0.5	52.9 ± 1.6		300 (max) ²
Cu	mg/kg (d.w.)	16.9 ± 1.1	99.4 ± 0.7	12.2 ± 0.6	97.6 ± 0.5		700 (max) ²
Hg	mg/kg (d.w.)	< 0.04	0.7	< 0.04	0.3		1.0 (max) ²
Ni	mg/kg (d.w.)	6.3 ± 0.2	45.5 ± 0.9	6.3 ± 0.1	57.1 ± 2.1		150 (max) ²
Pb	mg/kg (d.w.)	< 3.0	46.3 ± 1.0	< 3.0	32.9 ± 0.9		150 (max) ²
Zn	mg/kg (d.w.)	256 ± 6.0	275 ± 6.0	348 ± 7.0	671 ± 5		4500 (max) ²

Fuel mixture A: 50% peat; 25% coal; 25% wood. Fuel mixture B: 50% peat; 50% wood. 1: Other fertiliser than forest fertiliser; 2: Forest fertiliser.

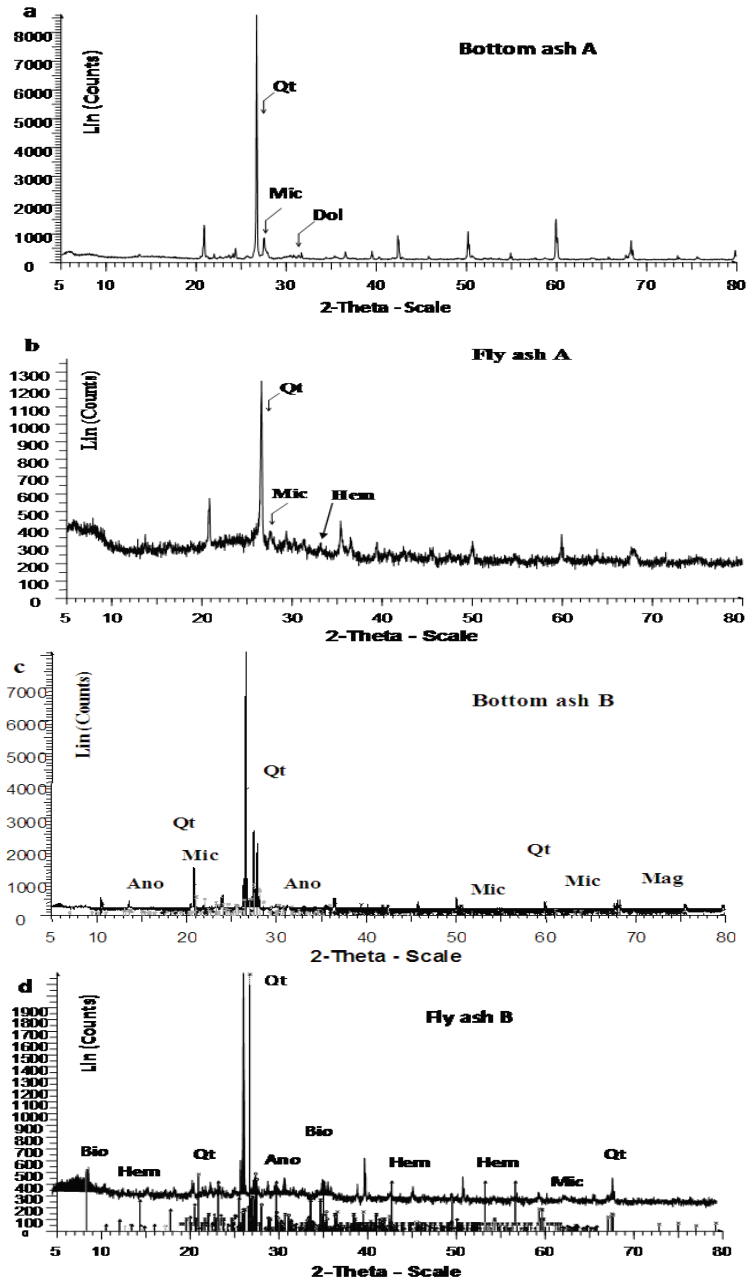


Figure 4. XRD patterns of the bottom and fly ashes. (Paper I)

Mineral abbreviations and their abundances (%) are: a) Bottom ash A: Dol = Dolomite [$\text{CaMg}(\text{CO}_3)_2$; 2.3-%]; Mic = Microcline [KAlSi_3O_8 ; 20.7-%]; Qt = Quartz [SiO_2 ; 76.6-%], b) Fly ash A: Hem = Hematite [Fe_2O_3 ; 3.4-%]; Mic = Microcline [22.9-%]; Qt = Quartz [73.7-%], c) Bottom ash B: Ano = Anorthite [$\text{CaAl}_2\text{Si}_2\text{O}_8$; 31.1-%]; Mag = Magnesiohornblende [$\text{Ca}_2\text{Mg}_4\text{Al}(\text{OH})_2\text{AlSi}_7\text{O}_{22}$; 7.8-%]; Mic = Microcline [32.9-%]; Qt = Quartz [28.2-%], d) Fly ash B: Ano = Anorthite [26.4-%]; Bio = Biotite [$\text{K}(\text{Fe}, \text{Mg})_3\text{AlSi}_3\text{O}_{10}(\text{F}, \text{OH})_2$; 20.8-%]; Hem = Hematite [11.0-%]; Mic = Microcline [16.7-%]; Qt = Quartz [25.1-%].

Note: A Cu-tube was used in the measurement of the XRD spectra, which energises the X-rays of Fe in the ash. Therefore, the background of the XRD spectra in the figures is relatively high.

According to Figures 4a and 4b, bottom and fly ashes A, which originated from the incineration of coal, peat and wood, both contained silicate minerals such as microcline [$K(AlSi_3O_8)$] and quartz (SiO_2). However, hematite (Fe_2O_3), which is an oxide mineral, and dolomite ($CaMg(CO_3)_2$), which is carbonate mineral, existed only in fly ash A and bottom ash A (Figure 4a and 4b). Figure 4c and 4d show that bottom and fly ashes B, which originated from the co-combustion of peat and wood, both contained silicate minerals such as microcline, quartz and anorthite ($CaAl_2Si_2O_8$). In addition, bottom ash B contained magnesio-hornblende ($Ca_2Mg_4Al(OH)_2AlSi_7O_{22}$), which is a silicate mineral, and fly ash B contained hematite (Fe_2O_3) and biotite ($(K(Fe,Mg)_3AlSi_3O_{10}(F,OH)_2)$), which is also a silicate mineral. Thus, the XRD results and alkaline pH partly support the findings of van Herck and Vandecasteele (2001). It is notable, that only a few minerals could be identified. An XRD spectrometer is unable to identify amorphous (glass) phases (i.e. non-crystallised matter), and its detection limit is normally 1–2% (w/w). This is probably why crystalline compounds containing metals (Table 2) were not identified by XRD, although the concentrations of these heavy metals could be quantitatively measured by ICP-OES.

The existence of silicate minerals in the bottom ashes is reasonable since the bed material in the fluidised bed boiler was silica sand. Furthermore, the existence of the silicate minerals both in the bottom and fly ashes may also be partly due to sand and soil particle contamination of forest residues during harvesting, transportation and handling (Steenari et al. 1999).

The results in Table 2 show the loss-on-ignition (LOI) value was relatively high (15.6%; d.w.) in fly ash A and elevated (4.0%; d.w.) in fly ash B. This indicates that fly ashes A and B contain volatile fractions. Respectively, the total organic carbon (TOC) value was high in fly ash A (140 g/kg; d.w.) and elevated in fly ash B (24.3 g/kg; d.w.). However, according to the results (Table 2), the TOC and LOI values were very low in the bottom ashes A (LOI<0.5%; d.w.; TOC<2.0%; d.w.) and B (LOI<0.5%; d.w.; TOC<1.0%; d.w.), which indicates the complete combustion of organic matter in the fluidised bed boiler, and that no volatile fraction remains in the bottom ashes (Paper I).

According to the results in Table 2, the dry matter content of bottom ashes was very high, 94.0% in bottom ash A and 92.0% in bottom ash B. However, the dry matter content of fly ashes was clearly lower, 71.1% in fly ash A and 74.8% in fly ash B, which is due to watering of the fly ash during the process in order to prevent dust problems. If we compare the total concentrations of heavy metals in the ashes to the limit values for use as a forest fertiliser in the Finnish environmental legislation shown in the Table 2, it can be seen that the total concentration of Cd, Cr, Cu, Hg, Ni, Pb and Zn in all bottom and fly ashes

are lower than the current limit values in Decree (24/11), but that the total concentrations of As in fly ash A (46.9 mg/kg; d.w.) and fly ash B (41.3 mg/kg; d.w.) exceeded the maximum limit value (40 mg/kg; d.w.) for forest fertiliser in the current Decree (24/11) (MMM 2011). Therefore, due to the elevated As concentrations in the ash A and B, these residues could not be used as a forest fertiliser as such (MMM 2011). However, they can be used for the landscaping of landfills on industrial and other areas that are closed to the public. However, before fly ashes A and B could be utilised in these types of sites an environmental permit would probably be needed. If the total concentrations of heavy metals in fly ash A and B are compared with those investigated by Vuorinen and Suoniitty (2010), the observations for total concentrations of heavy metals in this study are in good agreement with ashes from other Finnish power plants. Also the elevated total concentrations of As in this study is in accordance with the observations of Vuorinen and Suoniitty (2010), who reported that As is one of the heavy metals exceeding the limit values of forest fertiliser legislation most often, although it is worthwhile to note that in this study the limit values compared were those of the previous fertiliser Decree (11/07) which were stricter limits.

Comparing the total heavy metal concentrations (Table 2) in fly ashes A and B to bottom ashes A and B, it can be seen that the heavy metal concentrations are higher in fly ashes A and B than those in bottom ashes A and B. If we disregard the heavy metals whose concentrations were lower than the detection limits, the total metal concentrations in fly ash A were between 1.1 (Zn) and 12 (As) times higher than those in bottom ash A (Paper I). Respectively, in fly ash B, they were between 1.9 (Zn) and 9.1 (Ni) times higher than those in bottom ash B (Paper I). The enrichment of the heavy metals in the fly ashes is due to the fact that the combustion temperature of 900°C in a BFB boiler is high enough to vaporise these elements.

Furthermore, comparing the total metal concentrations of fly ash A and fly ash B, it can be seen that the total concentrations of Cd, Cr, Ni and Zn were higher in fly ash B than those in fly ash A. However, the total concentrations of As, Cu and Pb were higher in fly ash A than in fly ash B. In contradiction to the observations of Korpijärvi et al. (2009), that coal ashes have significantly higher heavy metal content than wood or peat ashes, in this study it was found that the co-combustion of coal did not clearly increase heavy metal content in the ashes.

The results in the Table 2 show that the Ca concentrations in bottom ashes A (2.4%; d.w.) and B (3.4%; d.w.) were lower than the minimum limit value of 6.0% (d.w.) for Ca. However, the Ca concentrations in fly ashes A (6.4%; d.w.) and B (11.0%; d.w.) exceeded the limit value of 6.0% (d.w.) for Ca.

Furthermore, the results show that the minimum limit value of the current Decree (24/11) for P+K (2.0%; d.w.) was exceeded in all other ashes except in the case of fly ash A (1.8 mg/kg; d.w.) (MMM 2011). The results indicate that if these ashes are used as forest fertiliser some additional Ca is needed for the bottom ashes and some additional P or K for fly ash A. However, according to Emilsson (2006), bottom ashes from BFB boilers should not be applied to forest soil as it consists mainly of bed material.

If comparing these results (Table 2) to the research of Nurmesniemi et al. (2012), who recently researched fertiliser properties of ashes originating from co-combustion of wood (97%) and sludge (3%) in a BFB boiler (120 MW), it can be observed that Ca and P+K concentrations in fly ashes investigated in this study were clearly lower (Table 2) than those (Ca 20%; d.w.; P+K 5.4%) reported by Nurmesniemi et al. (2012). These findings are in accordance with the findings of high amounts of Ca in wood ashes (Hytönen 2003). Furthermore, it can be observed that in the research of Nurmesniemi et al. (2012), the total concentration of Cd in fly ash was clearly higher (12 mg/kg; d.w.) than those in this study (fly ash A 1.7 mg/kg; d.w., fly ash B 2.9 mg/kg; d.w.). These findings are also supported by the earlier findings of elevated Cd levels in wood ashes (Rothpfeffer 2007). In addition, it can be observed that compliance with the limit values for all heavy metals given in the current Finnish fertiliser Decree (24/11) was fulfilled in the case of fly ash investigated by Nurmesniemi et al. (2012), whereas those limits could not be complied with in the fly ashes in this study due to elevated total concentrations of As.

The acid neutralising value (NV) indicates the potential liming effect value of ash in relation to its use as fertiliser. Table 2 shows that fly ash B has the highest NV value of 12.3% (d.w.; Ca equivalents), which exceeds the minimum value of 10% (d.w.; Ca equivalents) given in Decree 24/11 for ashes used in fertiliser purposes other than in forests. The NV values in other ashes investigated were lower than 10% (d.w.; Ca equivalents). However, it is notable that for forest fertiliser there is no limit set for NV value. The NV of 12.3% (d.w.; Ca equivalents) for fly ash B indicates that ca. 3.1 tonnes of this residue would be required to replace 1 tonne of a commercially ground limestone produced by SMA Mineral Ltd, the neutralising value of which is 38% (d.w.; Ca equivalents). The NV values of 4.4% (d.w.; Ca equivalents) for bottom ash B, 7.6% (d.w.; Ca equivalents) for fly ash A and 4.3% (d.w.; Ca equivalents) for bottom ash A indicates that respectively ca. 8.3 tonnes, ca. 5.0 tonnes and ca. 8.3 tonnes of these ashes would correspondingly be required to replace 1 tonne of the above-mentioned commercial limestone product.

In addition, the results in Paper I (Table 1) show that the ratio of the reactivity value (RV) to NV value, which indicate the speed and effectiveness of

the neutralising potential of the liming material in the ash, was highest, RV/NV 72.3%, for fly ash B. The corresponding value for bottom ash B was 48.8%, for fly ash A 55.3% and for bottom ash A 31.8% (Paper I, Table 1). These results indicate that all the ashes investigated in this study are potential soil conditioning agents and pH buffers for acidic soils. However, the fly ashes would be more effective for these purposes than the bottom ashes. Furthermore, the results in Paper I (Table 1) show that the ashes investigated in this study, particularly the fly ashes, had the highest easily soluble plant nutrient concentrations, which indicates that their utilisation as forest fertiliser is a potentially beneficial non-landfill application for these residues.

5.1.2 The utilisation aspects of ashes as an earth construction agent (II)

The total concentrations of PCBs, PAHs and heavy metals in the ashes are presented in Table 3. Extractable concentrations of DOC, heavy metals, fluoride, sulphate and chloride, together with the current Finnish limit values for these compounds in earth construction agents used for covered and paved structures (VNa 2009), are shown in the Table 4. Tables 3 and 4 also show unpublished results for these compounds in the bottom and fly ashes.

Comparing the total concentrations in Table 3 to the limit values given in Finnish Decree (403/2009) (VNa 2009), the results show that the total concentration of PAH in fly ash A (23 mg/kg; d.w.) exceeded the limit value for an agent used in covered earth construction (20 mg/kg; d.w.). Furthermore, the total concentration of PAH in fly ash B (90 mg/kg; d.w.) exceeded both the limit values for covered (20 mg/kg; d.w.) and paved (40 mg/kg; d.w.) construction. Due to the elevated total concentrations of PAHs, fly ash A cannot be used as an earth construction agent in a covered structure and fly ash B neither in covered nor paved structures simply by submitting a notification to the competent authority, instead an environmental permit is required.

Table 3. Total concentrations (mg/kg; d.w.; n=3) of PCBs, PAHs and heavy metals in the bottom and fly ashes originating from the incineration of different fuel mixtures in a 120 MW BFB boiler and the limit values of the Finnish Decree concerning recovery of waste in earth construction (VNa, 2009) (Paper II).

Compound	Total concentration (mg/kg; d.w.)		Total concentration (mg/kg; d.w.) ¹		Limit value
	Bottom ash A	Fly ash A	Bottom ash B	Fly ash B	
PCB	< 0.07	< 0.07	< 0.02	< 0.02	1.0
PAH	< 3.0	23.0	< 0.1	90.6	20/40 ²
As	3.9 ± 0.1	46.9 ± 0.6	< 3.0	41.4 ± 0.4	50
Ba	215.7 ± 10.7	741.3 ± 14.4	262.2 ± 8.1	808.2 ± 8.8	3000
Cd	< 0.3	1.7 ± 0.1	< 0.3	2.9	15
Cr	10.9 ± 0.3	47.1 ± 1.8	10.8 ± 0.5	52.9 ± 1.6	400
Cu	16.9 ± 1.1	99.4 ± 0.7	12.2 ± 0.6	97.6 ± 0.5	400
Pb	< 3.0	46.3 ± 1.0	< 3.0	33.0 ± 0.9	300
Mo	< 1.0	15.9 ± 0.6	< 1.0	11.7 ± 0.3	50
V	16.4 ± 0.6	94.8 ± 3.3	8.8 ± 0.5	81.5 ± 1.2	400
Zn	256.0 ± 6.2	274.7 ± 5.5	347.9 ± 6.8	671.3 ± 4.8	2000

¹ These results are based on the chemical analysis made by Suomen Ympäristöpalvelu Oy in June 2010 (Unpublished data). ² The limit value for paved structure. Fuel mixture A: 50% peat; 25% coal; 25% wood. Fuel mixture B: 50% peat; 50 % wood.

Except for the elevated total concentrations of PAH in fly ashes A and B, total concentrations of other elements in the ashes investigated were lower than the limit values of Decree (403/2009) for both covered and paved structures. Taking into account the elevated LOI (fly ash A 15.6 %; d.w.; fly ash B 4.0 %; d.w.), TOC (fly ash A 140g/kg; d.w.; fly ash B 24.3 g/kg; d.w.) and DOC (fly ash A; 30 mg/kg; fly ash B 34 mg/kg) values in the fly ashes, the high PAH concentrations in fly ash A (23 mg/kg; d.w.) and fly ash B (90.6 mg/kg; d.w.) is reasonable due to incomplete combustion.

According to the results in the Table 4, except for the extractable concentrations of Mo in fly ashes A and B, and Se in fly ash A, the extractable concentration of other elements in the ashes investigated were lower than the limit values of Finnish Decree (403/2009). The extractable concentrations of Mo in fly ash A (3.9 mg/kg; d.w.) and fly ash B (3.2 mg/kg; d.w.) exceeded the limit value of 0.5 mg/kg; (d.w.) for extractable Mo for covered structures (VNa 2009). In addition, the extractable concentrations of Se in fly ash A (0.2 mg/kg; d.w.) exceeded the limit value of 0.1 mg/kg (d.w.) for Se for covered structures. The extractable concentrations of the elements in the all ashes were below the limit values given for the paved structures in Decree (403/2009) (VNa 2009). The elevated extractability of Mo and Se results from the fact that

both of these elements are able to form oxy-anions, and the extractability of Mo and Se thus increases toward alkaline conditions and decreases toward neutral and acidic conditions (Cornelius et al. 2008). Thus, the leaching of Mo and Se is likely as long as the pH of the ashes investigated in this study remains alkaline.

Table 4. Extractable concentrations (mg/kg; d.w.; n=1) in the bottom and fly ashes originating from the incineration of different fuel mixtures in a 120 MW BFB boiler and the limit values of the Finnish Decree concerning recovery of waste in earth construction (VNa, 2009) (Paper II).

Compound	Extractable concentration (mg/kg;d.w.)		Extractable concentration (mg/kg;d.w.) ¹		Limit value	
	Bottom ash A	Fly ash A	Bottom ash B	Fly ash B	Covered structure	Paved structure
DOC	< 15	30	12	34	500	500
Sb	< 0.05	< 0.05	< 0.05	< 0.05	0.06	0.18
As	< 0.15	< 0.15	< 0.15	< 0.15	0.5	1.5
Ba	0.68	10.4	1.1	5.8	20	60
Cd	< 0.0015	< 0.0015	< 0.0015	< 0.0015	0.04	0.04
Cr	< 0.1	0.4	< 0.1	0.13	0.5	3.0
Cu	< 0.1	< 0.1	< 0.1	< 0.1	2.0	6.0
Hg	< 0.005	< 0.005	< 0.005	< 0.005	0.01	0.01
Pb	< 0.15	< 0.15	< 0.15	< 0.15	0.5	1.5
Mo	< 0.13	3.9	0.13	3.2	0.5	6.0
Ni	< 0.1	< 0.1	< 0.1	< 0.1	0.4	1.2
V	0.5	0.2	0.36	0.1	2.0	3.0
Zn	< 0.1	< 0.1	< 0.1	< 0.1	4.0	12
Se	< 0.08	0.2	< 0.08	< 0.08	0.1	0.5
Fluoride	< 5	8.6	< 5	< 5	10	50
Sulphate	< 50	220	< 50	450	1000	10000
Chloride	< 50	140	< 50	330	800	2400

¹ These results are based on the chemical analysis made by Suomen Ympäristöpalvelu Oy in June 2010 (Unpublished data). Fuel mixture A: 50% peat; 25% coal; 25% wood. Fuel mixture B: 50% peat?; 50 % wood.

If the total concentrations of PCBs, PAHs and heavy metals and the extractable concentrations in the ashes investigated are compared with those reported in the literature by Lillman (2009) (Paper II, Table 2 and 3), it can be seen that these are in relatively good agreement with the concentrations of these compounds found in ashes from other Finnish power plants.

5.2 Chemical and physical properties and utilisation aspects of green liquor dregs (IV)

The most important chemical and physical properties of green liquor dregs were presented in the original Paper IV. According to the results in Paper IV (Table 1) the LOI value for the green liquor dregs was 14.5% (d.w.), which indicates that the dregs investigated in this study contained volatile fractions. Furthermore, the results showed that the TOC value was 14.5 g/kg (d.w.). This is consistent with literature values of 3.5-32 g/kg (d.w.) (Toikka 1998; Zambrano et al. 2007), and further indicates that the dregs contain organic material. The results showed that the dry matter content of the green liquor dregs was relatively high at 80.8%, which is reasonable due to the use of an effective pressurised drying unit in the process investigated.

The results in Paper IV (Table 1) show that the pH of the green liquor dregs was strongly alkaline (pH 11.7), which is supported by results of the other researchers (Toikka 1998; Jordan et al. 2002; Mahdmoudkhani et al. 2005; Zambrano et al. 2010; Modolo et al. 2010), who have reported pH values between 10.0 and 13.1 for green liquor dregs. The XRD-spectra in Paper IV (Figure 3) shows that the green liquor dregs contained only pirssonite ($\text{Na}_2(\text{CaCO}_3)_2 \cdot \text{H}_2\text{O}$), which is a carbonate mineral. These findings are consistent with the results of Taylor and McGuffie (2007), who reported the existence of pirssonite in dregs, although they also detected silicate and sulphate minerals. However, Martins et al. (2007) reported the existence of calcite (CaCO_3) in dregs. One reason for the different mineral compositions of the dregs investigated in this study compared to those of Taylor and McGuffie (2007) and Martins et al. (2007) may be differences in the processes carried out at the respective mills. According to Toikka (1998), the physical and chemical properties of green liquor dregs vary significantly depending on the process conditions in which the dregs are formed. The alkaline pH and the existence of calcium carbonate, which is an active ingredient in agricultural lime, mean that green liquor dregs have a liming effect and are therefore a potential soil conditioning or amendment agent (Paper IV).

According to the results obtained in Paper IV (Table 1) the NV value of 34.2% (d.w.; Ca equivalents), which indicates the potential liming effect value of the component in relation to its use as fertiliser, was high. This result indicates that 1.1 tonnes of green liquor dregs would be required to replace 1 tonne of a commercial ground limestone product produced by SMA Mineral Ltd, which has a neutralising value of 38% (Ca equivalents; d.w.). Furthermore the results in Paper IV showed that the RV/NV ratio for the green liquor dregs was high, ca. 95.6%, which indicates that the dregs investigated in this study are a

potential soil conditioning agent and pH buffer for acid soils (Zambrano et al. 2007). Due to the strong alkaline nature and high liming effect value, the dregs are also a potential neutralising agent at the sulphite pulp mill investigated in this study (Paper IV).

The results in Paper IV (Table 1) show that the concentrations of easily soluble plant nutrients (P, Ca, Na, K, Mn, Mg, S, Cu and Zn) in the green liquor dregs were high. Except for the easily soluble Ca concentration in the dregs, the other easily soluble plant nutrient concentrations were ca. 1.8 (P) and 13,430 (Na) times higher than their average concentrations in the local coarse mineral soils (Paper IV). According to Österås et al. (2005), these results indicate that the green liquor dregs are therefore a potential agent for use in counteracting nutrient depletion in forest soils.

The results of the total concentrations of Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, V, Zn, Hg, Si and F in the green liquor dregs are shown in the Paper IV (Table 2) together with the literature values. According to the results in Paper IV (Table 2) except for Al (820 mg/kg; d.w.), Ba (910 mg/kg; d.w.), Fe (600 mg/kg; d.w.), Mn (4150 mg/kg; d.w.), Zn (1320 mg/kg; d.w.) and Si (270 mg/kg; d.w.), the total concentrations of the non-process elements (NPEs) in the green liquor dregs were observed to be low and consistent with the literature values. In addition, in Paper IV the results are compared to the limit values given for the total concentrations of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) in the Finnish fertiliser Decree (12/07), although these limit values are applied only for wood, peat and agro-biomass derived ashes (MMM 2007). According to Finnish environmental legislation, an environmental permit is needed if green liquor dregs are utilised. However, from the environmental point of view new ways to utilise green liquor dregs instead of landfilling them are needed, and therefore, the total heavy metal concentrations of this residue were compared to limit values of the Finnish Fertiliser Decree (12/07) and it was observed that they were clearly lower than those given in the Decree (12/07) (MMM 2007) (Paper IV). In this context it is worthwhile to note that after the publication of the original paper IV, Decree (12/07) (MMM 2007) was substituted by the new Decree (24/2011) (MMM 2011), in which new limit values for As (40 mg/kg; d.w.), and Cd (25 mg/kg; d.w.) came into force and substituted the previous limit values of As (30 mg/kg; d.w.) and Cd (17.5 mg/kg; d.w.). However, the new current legal limit values are now higher than the previous ones and thus, the total heavy metal concentrations in the green liquor dregs are now subsequently also lower than the limit values set by the current fertiliser Decree (24/2011) (MMM 2011).

5.3 Sequential extraction partitioning of elements in ashes (III)

Table 5 summarises the total concentrations and the extractable concentrations of the elements after the three-stage BCR extraction procedure in which elements were fractionated between acid-soluble (BCR1; CH_3COOH), reducible (BCR2; $\text{NH}_2\text{OH-HCl}$) and oxidisable (BCR3; $\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$) fractions in the bottom and fly ashes originating from the co-combustion of coal, peat and wood in a BFB.

According to the results in the Table 5, the total concentrations of the elements were higher in the fly ash than those in the bottom ash. However, the results showed that in the acid soluble fraction (BCR1; CH_3COOH) the extractable concentrations of Al, As, Ba, Cu Fe, Ti, V and Zn were higher in the bottom ash than those in fly ash. The highest extractable concentration in this fraction was observed for Al (3410 mg/kg; d.w.) in the bottom ash, which was ca. 2.3 times higher than that in the fly ash (1490 mg/kg; d.w.), although the total concentration of Al was ca. 4.3 times higher in the fly ash (42500 mg/kg; d.w.) than that in the bottom ash (12200 mg/kg; d.w.). Conversely, the extractability of S in this fraction was clearly lower in the bottom ash (32.0 mg/kg; d.w) than in the fly ash (2090 mg/kg; d.w.), which is consistent with lower total concentrations of S in the bottom ash (59.4 mg/kg d.w.) than in the fly ash (2677 mg/kg; d.w.)

The XRD spectra in Figures 4a-d (see page 33) cannot explain the differences in composition of Al- and S-bearing minerals in bottom ash A and fly ash A and the exact reason for different release of elements between bottom and fly ash is unknown. However, according to Ludwig et al. (2005), the release of metals from ash depends on the chemical characteristics of ash materials in terms of their form and solubility. The different extractability of heavy metals between the bottom and fly ashes may indicate the different binding of elements in these residues. Heavy metals may be present as soluble or moderately soluble phases but trapped in material, as carbonates, oxides and hydroxides, or as surface complexes sorbed to oxides or hydroxide minerals in the ash matrix, which may be dissolved and release by acid.

Furthermore, the results in the Table 5 show that compared to the total concentrations, the partitioning of the elements in the acid soluble fraction (BCR1: CH_3COOH) was highest for S which had partitioning of approximately 53.9% in the bottom ash and 78.1% in the fly ash. If we disregard the elements whose concentrations were lower than the detection limit, the partitioning of the other elements in this fraction varied between 0.9% (Ti) and 33.3% (As) in the bottom ash and between 0.1 % (Ti) and 15.6% (Mn) in the fly ash.

Table 5. The total concentrations of elements and their extractable concentrations in acid-soluble (BCR1), reducible (BCR2) and oxidisable (BCR3) fractions (n=1) in bottom and fly ashes originating from the co-combustion of coal, peat and wood in a BFB boiler of 120 MW (Paper III, Tables 2 and 3).

Element	Total concentration (mg/kg; d.w.) Bottom ash	Extractable concentration (mg/kg; d.w.) Bottom ash			Total concentration (mg/kg; d.w.) Fly ash	Extractable concentration (mg/kg; d.w.) Fly ash		
		BCR1	BCR2	BCR3		BCR1	BCR2	BCR3
Al	12200	3410	3770	2000	42500	1490	5150	7310
As	3.9	1.3	2.2	0.6	46.9	1.3	16.5	6.3
Ba	215.7	52.9	65.4	56.9	741.3	33.0	234	312
Be	1.3	0.8	0.2	<0.3	4.4	0.4	0.9	1.0
Cd	<0.3	<0.1	<0.1	<0.1	1.7	0.8	0.2	0.2
Co	2.9	0.4	<0.1	0.6	15.7	1.4	1.1	1.6
Cr	10.9	<0.4	0.5	3.0	47.1	1.7	2.3	3.8
Cu	16.9	3.8	2.3	2.6	99.4	1.9	2.6	26.2
Fe	8380	360	1070	1930	39833	48.9	3360	1720
Mn	425.0	80.7	58.6	124	977.3	152	166	174
Mo	<1.0	<0.2	<0.2	<0.3	15.9	0.5	0.3	5.2
Ni	6.3	<0.2	<0.2	1.7	45.5	3.3	2.1	4.4
Pb	<3.0	<0.6	<0.6	<0.8	46.3	<0.6	1.3	10.7
S	59.4	32.0	1.2	7.3	2677	2090	183	252
Sb	<4.0	<0.6	<0.6	<0.8	<4.0	<0.6	<0.6	<0.8
Se	<4.0	<0.8	<0.8	<1.0	5.2	<0.8	<0.8	2.2
Ti	233.3	2.0	5.2	44.2	1203.3	0.8	1.9	2.4
V	16.4	1.6	9.7	2.8	94.8	0.9	23.2	25.9
Zn	256.0	74.3	26.3	27.2	274.7	30.9	29.6	25.7

According to Long et al. (2009), this fraction indicates the proportion of elements that are capable of being released from the matrix into the environment if the conditions become acidic. Thus, the high partitioning of S, especially in the fly ash in the acid-soluble fraction indicates that S is able to be mobilised from the ashes into the environment if the conditions become acidic. Consequently, the low partitioning of most elements in the bottom and fly ash indicate that these elements do not occur in readily soluble forms.

The results in Table 5 show that except for Ti, the extractable concentrations for the other elements were higher in the fly ash than in the bottom ash in the reducible fraction (BCR₂; NH₂OH-HCl). The highest difference in the extractability of metals between bottom and fly ash in this fraction was noticed for S, where the extractable concentration was 153 times higher in fly ash than that in the bottom ash, whereas the extractable concentration of Al was only 1.4 times higher in the fly ash than in the bottom ash. As the hydrous oxides of manganese and iron are extracted in this fraction (Filgueiras et al. 2002), the differences in the extractability of heavy metals and sulphur indicate the different binding of elements to these minerals, although hematite (Fe₂O₃) was the only iron oxide observed in the XRD data of the fly ash (Paper III).

Compared to total concentration, the partitioning of the elements in the reducible (BCR₂; NH₂OH-HCl) fraction varied between 2.0% (S) and 29.2% (V) in the bottom ash and between 0.2 % (Ti) and 35.2% (As) in the fly ash. The metals partitioned in this fraction are considered to be relatively stable under normal soil conditions and can be mobilised by increasing the reducing or oxidizing conditions in the environment, which means that they are potentially bioavailable (Filgueiras et al. 2002).

The results in the Table 5 show that except for Fe, Ti and Zn, the extractable concentrations for the other elements were higher in the fly ash than those in the bottom ash in the oxidisable fraction (BCR₃; H₂O₂ + CH₃COONH₄). Due to the high TOC value (140 mg/kg; d.w.) in the fly ash, the release of metals and sulphur, e.g. sulphides, bound to the organic matter of this residue is possible, if conditions become oxidative and the organic matter degrades. Furthermore, the results in the Table 5 show that in this fraction a clearly higher concentration of As was extracted in the fly ash (252 mg/kg; d.w.) than in the bottom ash (7.3 mg/kg; d.w.). As sulphides are extracted in the oxidisable fraction this result is consistent and reasonable with the higher total concentration of As in fly ash (2 677 mg/kg; d.w.) than that in bottom ash (59.4 mg/kg; d.w.).

Comparing the total concentrations of the elements to their partitioning after all stages of the three-stage BCR extraction procedure (i.e. the sum of fractions BCR₁, BCR₂ and BCR₃), the observations are that the highest partitioning in

the bottom ash was for As with a value of 100%, whereas only ca. 51.4% of As was partitioned in the fly ash. In addition, the results show that the highest partitioning in the fly ash was observed for S with a value of ca. 94.3%, while the respective value for S in the bottom ash was ca. 68.2%. The high total partitioning of S in the fly ash together with the high partitioning of S (78.1%) in the acid soluble (BCR1; CH₃COOH) fraction, indicates that S in the fly ash occurs in a readily soluble form.

Furthermore, these results indicate that As is able to become 100% soluble and mobile in the worst-case environmental scenarios in the bottom ash, whereas the lower total partitioning of As in the fly ash, especially together with the low partitioning of As (ca. 3.5%) in the acid soluble (BCR1; CH₃COOH) fraction, indicates that As does not occur in a readily soluble form in this residue. Except for As and S, the partitioning values in the bottom ash varied between ca. 22.0% (Ti) and 86.0% (V), and between 0.4% (Ti) and 78.1% (Ba). Therefore, according to the results of sequential extraction partitioning of elements in the ashes, it can be concluded that most of the elements in the ashes investigated in this study do not occur in readily soluble and mobile forms in these residues.

5.4 Sequential extraction partitioning of elements in green liquor dregs (IV)

Table 6 summarises the total and extractable concentrations of the elements in the green liquor dregs after the three-stage BCR extraction procedure in which elements were fractionated between acid-soluble (BCR1; CH₃COOH), reducible (BCR2; NH₂OH-HCl) and oxidisable (BCR3; H₂O₂ + CH₃COONH₄) fractions.

The results show that in the acid soluble fraction (BCR1; CH₃COOH), most of the extractable concentrations of the non-process elements (NPEs) in the dregs were below the detection limit. If we disregard the elements whose concentrations were below the detection limits, only the extractable concentrations of Al (6.7 mg/kg; d.w.), Ba (5.3 mg/kg; d.w.), Mn (18.7 mg/kg; d.w.), S (6540 mg/kg; d.w.) and Zn (1.1 mg/kg; d.w.) were detected in this fraction.

Table 6. Total and extractable concentrations of elements in acid-soluble (BCR1), reducible (BCR2) and oxidisable (BCR3) fractions (n=1) in green liquor dregs originating from the recovery boiler of a 33 MW NSSC-pulp manufacturing process (Paper IV, Table 2).

Element	Total concentrations (mg/kg; d.w.)	Extractable concentrations (mg/kg; d.w.)		
		BCR1	BCR2	BCR3
Al	820	6.7	<1.0	349
As	< 3.0	<0.6	<0.6	<0.8
Ba	910	5.3	300	490
Be	< 1.0	<0.2	<0.2	<0.3
Cd	3.8	<0.1	0.1	3.4
Co	8.0	<0.1	3.0	2.8
Cr	14.0	<0.4	<0.4	8.2
Cu	61.0	<0.4	<0.4	53.5
Fe	600	<1.0	5.4	9.3
Mn	4150	18.7	1880	2130
Mo	< 1.0	<0.2	<0.2	<0.3
Ni	14.0	<0.2	6.0	4.7
Pb	13.0	<0.6	<0.6	6.0
S	7780 ¹	6540 ¹	270 ¹	560 ¹
Sb	< 4.0	<0.6	<0.6	0.8
Se	< 4.0	<0.8	<0.8	<1.0
Ti	<50 ¹	2.7 ¹	1.2 ¹	1.2 ¹
V	<1.0	<0.4	<0.4	<0.5
Zn	1320	1.1	90.1	877

¹These results are based on the chemical analysis made by Suomen Ympäristöpalvelu Oy in May 2010 (Unpublished data).

Compared to the total concentrations, the highest partitioning was observed for S with partitioning of ca. 84.1%. The partitioning of the other elements in this fraction was low as follows: Al (0.8%), Ba (0.6%), Mg (0.5%) and Zn (<0.1%). The high partitioning of S in this fraction indicates that S is capable of being released into the environment if conditions become acidic (Long et al. 2009). Furthermore, the low partitioning of the other NPEs in this fraction indicates that these NPEs in the green liquor dregs cannot be considered as potentially mobile.

In the reducible fraction (BCR2; NH₂OH-HCl) the highest extractable concentrations of NPEs in the dregs was observed for Mn (2130 mg/kg d.w.).

Compared to the total concentrations, the partitioning of Mn in this fraction was 45.3%. In addition, the relatively high extractable concentrations of S (270 mg/kg; d.w.), Ba (300 mg/kg; d.w.) and Zn (90.3 mg/kg; d.w.), were released in this fraction. Furthermore, if (in addition to above-mentioned elements i.e. Mn, S, Ba, Zn) we disregard the NPEs whose concentrations were lower than the detection limit, only the extractable concentrations of Cd (0.1 mg/kg; d.w.), Co (3.0 mg/kg; d.w.), Fe (5.4 mg/kg; d.w.) and Ni (6.0 mg/kg; d.w.) were extracted by hydroxylamine hydrochloride (NH₂OH-HCl).

Compared to the total concentrations, the partitioning of these elements in this fraction was low and as follows: S (3.4%), Ba (32.9%), Zn (6.8%), Cd (2.6%), Co (37.5%), Fe (0.9%) and Ni (6.8%). The metals portioned in this fraction are considered to be relatively stable under normal soil conditions, but can be mobilised by increasing the reducing or oxidising conditions in the environment, which means that they are potentially bioavailable (Filgueiras et al. 2002).

Furthermore, according to the results in Table 6, except for Co, Ni and S the extractable concentrations of all other NPEs (i.e. Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Se, V, Zn) were higher in the oxidisable fraction (BCR₃; H₂O₂+CH₃COONH₄) than in the previous fractions. The extractable concentrations in this fraction were high for Al (349 mg/kg; d.w.), Ba (490 mg/kg; d.w.), Mn (2130 mg/kg; d.w.), S (560 mg/kg; d.w.) and Zn (877 mg/kg; d.w.), relatively high for Cu (53.5 mg/kg; d.w.) and moderate for Co (2.8 mg/kg; d.w.), Cd (3.4 mg/kg; d.w.), Cr (8.2 mg/kg; d.w.), Fe (9.3 mg/kg; d.w.); Ni (4.7 mg/kg; d.w.) and Pb (6.0 mg/kg; d.w.). According to the TOC value of 14.5 mg/kg (d.w.), the dregs contain organic material. Therefore, the release of metals and sulphur bound to the organic matter in this residue is possible if conditions become oxidative and the organic matter in the green liquor dregs degrades. However, according to Smichowski et al. (2005), the organic fraction released in the oxidisable step is not considered to be very mobile or available. Except for S, the other elements had low partitioning in the sequential extraction procedure which supports the re-use of the green liquor dregs instead of their disposal at landfills.

5.5 Extractable heavy metal concentrations in ashes using artificial sweat and gastric fluids (II)

The total and extractable concentrations of heavy metals in artificial gastric fluid and artificial sweat fluid for bottom and fly ashes originating from the co-combustion of coal, peat and wood are presented in Table 7. The results were originally presented in Paper II (Table 2).

Table 7. Total and extractable concentrations of elements in ashes originating from BFB boiler of 120 MW during the co-combustion of coal, wood and peat ashes, by artificial sweat and gastric fluids, and pH of the extract before (i.e. only extract) and after (i.e. extract and ash) (Paper II).

Element and pH	Total concentration (mg/kg; d.w.)		Extractable concentration in artificial sweat fluid (mg/kg; d.w.)		Extractable concentration in artificial gastric fluid (mg/kg; d.w.)	
	Bottom ash	Fly ash	Bottom ash	Fly ash	Bottom ash	Fly ash
pH (before)	-	-	6.50	6.50	1.49	1.49
pH (after)	-	-	8.08	8.81	1.62	1.79
Al	12200 ¹	42500 ¹	< 2.0 ¹	91.4 ¹	5330 ¹	13700 ¹
As	3.9	46.9	< 1.5	5.0	< 1.5	36.7
Ba	215.7	741.3	16.9	25.1	86.6	446
Cd	< 3.0	1.7	< 0.15	< 0.15	< 0.15	1.6
Cr	10.9	47.1	< 1.0	< 1.0	< 1.0	6.1
Cu	16.9	99.4	< 1.0	< 1.0	4.0	38.3
Ni	6.3	45.5	< 0.5	< 0.5	< 0.5	8.4
Pb	< 3.0	46.3	< 1.5	< 1.5	< 1.5	20.2
Mo	< 1.0	15.9	< 0.5	6.9	< 0.5	5.2
Sb	< 4.0	< 4.0	< 2.0	< 2.0	< 2.0	< 2.0
Se	< 4.0	5.2	< 2.0	3.7	< 2.0	3.9
V	16.4	94.8	1.1	2.8	10.5	65.6
Zn	256.0	274.7	< 1.5	< 1.5	100	100

¹ These results are based on the chemical analysis made by Suomen Ympäristöpalvelu Oy in April 2010 (Unpublished data).

According to the results in the Table 7, the highest extractable concentrations in artificial gastric fluid were observed for Al in both the bottom ash (5330 mg/kg; d.w.) and in the fly ash (13700 mg/kg; d.w.). In addition, high extractable concentrations in the artificial gastric fluid were also observed for

Ba in the bottom ash at 86.6 mg/kg (d.w.) and 446 mg/kg (d.w.) in the fly ash, and for Zn, at 100 mg/kg (d.w.) in both the bottom and fly ashes. Furthermore, the extractability of As, Cu, Pb and V in the fly ash was relatively high in the artificial gastric fluid (Table 7). These results are reasonable due to the extremely acidic pH of the gastric fluid both before (i.e. pH 1.49 for the bottom and fly ash) and after (i.e. pH 1.62 for the bottom ash and pH 1.79 for the fly ash) extraction.

The highest extractable concentrations in the artificial sweat fluid were observed for Al in the fly ashes (91.4 mg/kg; d.w.), and for Ba in the bottom (16.9 mg/kg; d.w.) and fly ash (25.1 mg/kg; d.w.). Except for Mo in the fly ash, the extractable concentrations of heavy metal in the artificial gastric fluid were higher than those in the artificial sweat fluid. The higher extractable concentrations of Mo in the artificial sweat fluid is reasonable, because the pH of the artificial sweat fluid was slightly alkaline before (pH 6.50) and (pH 8.81) after the extraction. Mo is able to form oxyanions, which means that the extractability increases from acidic pH values to neutral and alkaline conditions (Cornelius et al. 2008). Although, the highest extractable concentrations of Se also occurs in strongly alkaline conditions, the extractability of Se in the fly ash was practically same in both the artificial sweat (3.7 mg/kg; d.w.) and gastric (3.9 mg/kg; d.w.) fluids.

If we disregard elements whose concentrations were lower than the detection limits, the extraction recovery (R) values (%) for the heavy metals, which were determined as the ratio of the metal concentration extracted with artificial sweat and gastric fluids to the total metal concentration in the ash, varied between 2.9% (V) and 71.3% (Se) in the artificial sweat fluid and between 11.4 % (V) and 94.1 % (Cd) in artificial gastric fluid.

Although the heavy metals in this study were extracted in the artificial and gastric fluids, this does not necessarily mean that humans working in power plants or in earthworks are necessarily exposed to the heavy metals in ash. The human health risk assessment associated with ash handling is complex, and in this context we only discuss the extractability of certain heavy metals in ashes by artificial sweat and gastric fluids. However, in-vitro tests by artificial sweat and gastric fluids have been reported as being used for assessing occupation risk and safety aspects of material handling (Twining et al. 2005; Kim et al. 2002; Wang et al. 2007; Madrid et al. 2008). Therefore, taking into consideration the fact that many of the heavy metals in the ashes have been reported to have harmful properties (Toikka 1998; Cenni et al. 2001) and due to the relatively high extractability of certain heavy metals in fly ash using an artificial gastric fluid (Table 7), the careful handling of fly ash is recommended in order to minimise human health risks, especially if it causes dusting.

5.6 Extractable heavy metal concentrations in green liquor dregs using artificial sweat and gastric fluids (V)

The total and extractable concentrations of heavy metals in green liquor dregs using artificial gastric fluid and artificial sweat fluid are presented in Table 8..

Table 8. Total and extractable concentrations of elements in green liquor dregs originating from the recovery boiler (33 MW) of a semichemical pulp and board mill by artificial sweat and gastric fluids fractions, and pH of the extract before (i.e. only extract) and after (i.e. extract and ash) (Paper V).

Element and pH	Total concentration (mg/kg; d.w.)	Extractable concentration in artificial sweat fluid (mg/kg; d.w.)	Extractable concentration in artificial gastric fluid (mg/kg; d.w.)
pH (before)	-	6.48	1.53
pH (after)	-	10.3	2.30
Al	820	6.7	730
As	< 3.0	< 1.5	< 1.5
Ba	910	< 1.0	770
Be	< 1.0	< 0.5	< 0.5
Cd	3.8	< 0.15	2.1
Co	8.0	< 0.5	6.2
Cr	14.0	< 1.0	11.4
Cu	61.0	< 1.0	< 1.0
Ni	14.0	1.2	12.0
Pb	13.0	< 1.5	10.3
Sb	< 4.0	< 2.0	< 2.0
Se	< 4.0	< 2.0	< 2.0
V	< 1.0	< 1.0	< 1.0
Zn	1320	1.8	1290

According to the results in the Table 8, the extractable concentrations of heavy metals in the artificial gastric fluid were the highest for Al (730 mg/kg; d.w.), Ba (770 mg/kg; d.w.) and for Zn (1290 mg/kg; d.w.). In addition, the elevated extractable concentrations of Cd (2.1 mg/kg; d.w.), Co (6.2 mg/kg; d.w.), Cr (11.4 mg/kg; d.w.), Ni (12.0 mg/kg; d.w.) and Pb (10.3 mg/kg; d.w.) were observed in the artificial gastric fluid.

The results in the Table 8 show that only the extractability of Al (6.7 mg/kg; d.w.), Ni (1.2 mg/kg; d.w.) and Zn (1.8 mg/kg; d.w.) in the artificial sweat

fluids was higher than the detection limit. According to Table 8, the extractability of these elements in the artificial sweat fluid was significantly lower than in the artificial gastric fluid. The extractable concentrations of heavy metals in the artificial gastric fluid were between 10 (Ni) and 717 (Zn) times higher than those in the artificial sweat fluid (Paper V).

If we calculate the recovery values (R) values (%) for the elements whose extractable concentrations were higher than the detection limits, it can be observed that the extractable recoveries for the metals for green liquor dregs varied between 0.1% (Zn) and 8.6% (Ni) in the artificial sweat fluid and between 55.2% (Cd) and 97.7% (Zn) in the artificial gastric fluid (Paper V). Therefore, taking into consideration the toxicity properties of many of the heavy metals in the green liquor dregs (Toikka 1998; Cenni 2001) and the observation of high extractable concentrations of certain heavy metals in the artificial gastric fluid, the careful handling of the green liquor dregs is recommended in order to prevent ingestion and penetration of green liquor dregs particles across the human gastrointestinal tract.

6. Concluding remarks

6.1 Summary of the results

This study provided comprehensive results of chemical, physical and extraction properties of bottom and fly ashes originating from a BFB boiler (120 MW) using two different fuel mixtures (i.e. Fuel mixture A: coal, wood and peat; Fuel mixture B: wood and peat) and for green liquor dregs originating from the recovery boiler, of a semichemical (SC) pulp and board mill in relation to the potential utilisation of these residues from various aspects.

The results showed that all the ashes investigated, especially fly ashes are a potential fertiliser, soil conditioning agents and pH buffers for acidic soils. However, only the bottom ashes investigated had lower total concentrations of heavy metals than the limit values in Finnish legislation for fertilisers. The elevated As concentration in the fly ashes (A 46.9 mg/kg; d.w.; B 41.3 mg/kg; d.w.), which slightly exceeded the current limit value of As (40 mg/kg; d.w.), restrict the use of these ashes as a forest fertiliser. Furthermore, the results showed that the total Ca concentrations in the bottom ashes (A 2.4%; d.w.; B 3.4%; d.w.) were lower than the minimum limit value (6.0%; d.w.) given for the ashes used as a forest fertiliser, whereas the total Ca concentrations in the fly ashes (A 6.4%; d.w.; B 11.0%; d.w.) exceeded the minimum limit value (6.0%; d.w.). The Finnish fertiliser legislation is applied only for ashes originating from peat, wood and agro-biomass utilisation. Therefore, observing the national regulations for fertiliser products and the results of this study, only the bottom ash B originating from co-combustion of wood and peat investigated here could be used as a forest fertiliser if additional Ca is used.

The bottom ashes investigated fulfilled the Finnish regulations for waste recovery in earth construction. However, due to the elevated total concentration of PAH (23 mg/kg; d.w.) and extractable concentrations of Mo (3.9 mg/kg; d.w.) and Se (0.2 mg/kg; d.w.) in the fly ash A originating from co-combustion of coal, wood and peat, this residue cannot be used as an earth construction agent in covered structures. Due to the elevated concentration of PAH (90 mg/kg; d.w.) in the fly ash B originating from co-combustion of wood

and peat, this residue cannot be used in either covered or paved structures only by simply submitting a notification to the competent authority. However, the utilisation of these fly ashes for such structures is still possible, although an environmental permit would be required.

According to the three-stage BCR sequential extraction studies, most of the elements in the bottom and fly ash A do not occur in readily soluble and mobile forms in these residues, which supports the utilisation of bottom and fly ashes A instead of their final disposal e.g. such as to landfill. The extractability of various elements, both in the bottom and fly ashes A, varied widely. The extractable concentrations of most elements were higher in all fractions in the fly ash A than those in the bottom ash A. However, in the acid soluble (BCR₁; CH₃COOH) fraction, the extractable concentrations of Al, Ba, Be, Cu, Fe, V and Zn, as well as of Fe and Zn in the oxidisable (BCR₃; H₂O₂ + CH₃COONH₄) fraction and Ti in all BCR fractions, were higher in the bottom ash than the those in the fly ash. The different extractability of the various elements between the bottom and fly ashes A may indicate the different binding of the elements in the ashes investigated in this study

The results of this study showed that green liquor dregs originating from the chemical circuit of the integrated semichemical pulp and board mill were strongly alkaline (pH 11.7), had a high neutralising capacity (NV 34.2%; d.w.) and relatively high dry matter content (80.8%). These results support the utilisation of green liquor dregs e.g. as a soil conditioning agent or pH buffer for acidic soils. In addition, the total concentrations of heavy metals in the green liquor dregs were clearly lower than heavy metal limit values for ashes set in current Finnish forest fertiliser legislation. Moreover, the low partitioning of heavy metals in the three-stage BCR sequential extraction procedure support the utilisation of green liquor dregs. The results from the sequential extraction procedure showed that except for S, Co and Ni, the highest extractable concentrations of other non-process elements were in the oxidisable fraction (BCR₃ fraction; H₂O₂ + CH₃COONH₄), although certain non-process elements (NPEs) were also extractable and quantitatively detectable in the acid soluble (BCR₁; CH₃COOH), and the reducible (BRC₂; NH₂OH–HCl) fractions.

In terms of human health aspects, the results of this study showed that the extractability of several elements in fly ash A (i.e. fly ash from the co-combustion of coal, wood and peat) and in green liquor dregs using artificial gastric fluid were elevated. Therefore, taking into consideration the fact that many of these heavy metals are reported to have harmful properties, the careful handling of these residues is recommended to prevent material dusting and penetration of material particles across the human gastrointestinal tract.

6.2 Implications of the results and further recommendations

The results for chemical, physical and extraction properties of the residues obtained in this study support the potential utilisation of the investigated ashes and green liquor dregs instead of their final disposal. However, current Finnish environmental legislation restricts the utilisation of these residues and an environmental permit is required for their further utilisation. The results of this study can be utilised in environmental permit applications and in the decision making process of environmental authorities.

Earlier studies (Steenari and Lindqvist 1999; Laine-Ylijoki et al. 2002) pointed out the importance of evaluation of the environmental properties of industrial residues. The results of this study support these findings and highlight the significance that the acceptability of re-use and utilisation of residues needs to be based on the chemical, physical and extraction properties of specific industrial residues. This study shows e.g. that the NV value of the green liquor dregs investigated was higher and the total concentrations of heavy metal were lower than those of fly ash originating from the co-combustion of wood and peat. In addition, the total metal concentrations of Cd, Cr, Ni and Zn in the fly ash originating from the co-combustion of coal, wood and peat were lower than those in the ash from the incineration of peat and wood. Furthermore, the Ca concentration in the fly ash originating from the co-combustion of coal, wood and peat was higher than the limit values for the residue's use as forest fertilisers set in the regulations on fertiliser products. However, the current Finnish fertiliser regulations (MMM 2011) are applicable only for ashes originating from the incineration of peat, wood and agro-biomass, i.e. not for coal-ashes or green liquor dregs. Thus, the current Finnish environmental legislation restricts the utilisation of coal-derived ashes and green liquor dregs investigated in this study based on the tight criteria concerning the origin of residues. From the environmental point of the view, the properties of residues would seem to be more relevant than the origin or the fuel source-based classification of the residue. Consequently, in order to promote the utilisation of ashes and green liquor dregs, efforts to develop Finnish environmental legislation on waste utilisation is needed.

These results cannot be generalised as such to other similar residues originating from other processes. It is worthwhile to point out that the utilisation acceptability of the ashes and green liquor dregs originating from other processes has to be based on environmental properties of those residue samples. However, this study provided new results for the bottom and fly ashes from co-combustion with two different fuel mixtures (i.e. Fuel mixture A: coal, wood and peat; Fuel mixture B: wood and peat) and for green liquor

dregs. Further, these results are beneficial in assisting the development of national environmental legislation.

The findings of this research support earlier studies that the knowledge of the extractability of the elements in a waste material is important (e.g. Filgueiras et al. 2002). This study provided sequential extraction partitioning results which are useful in the assessment of potential mobility of harmful elements in ashes and green liquor dregs and thus helps to estimate the further utilisation possibilities for these residues from the environmental perspective.

This study also presents completely new results for the extractability of heavy metals in ashes originating from the co-combustion of coal, wood and peat, and in green liquor dregs, in terms of human health aspects. However, more knowledge of the extractability of elements in industrial residues is required in order to better understand occupational risk aspects related to harmful elements in the solid residues originating from various industrial processes. The importance of the occupational health aspects of solid residue management will attract more emphasis in the future due to the fact that ashes may increasingly originate from demanding fuels and treatment processes such as waste incineration.

6.3 Reliability and validity

The sampling of ashes and green liquor dregs investigated in this study was carried out by a competent person and as a part of a compliance testing routine set out in the environmental permit of the mill (Environmental permit 2006). According to this environmental permit, compliance tests need to be carried out every second year. Furthermore, the compliance testing for ashes originating from co-combustion is recommended to be carried out from a composite sample consisting of at least three individual daily samples, where each of them is collected in different weeks (Laine-Ylijoki et al. 2002). In this study the composite sample of the ashes consisted of six individual ash samples collected during three different weeks. Moreover, the composite samples of ashes were collected twice, and thus the bottom and fly ashes collected during one year consisted of twelve individual daily samples in total which is more than required by the permit.

The composite samples of green liquor dregs consisted of six individual daily samples, which were collected during two different weeks. The shorter period of sampling for green liquor dregs than that for ashes has been observed as sufficient since the processes of the mill are stable and the annual amount of green liquor dregs generated at the mill (1,300-2,000 tonnes) is less than the

amount of fly ashes (5,000-10,000 tonnes). In general, the number of individual samples needed in compliance testing depends on the annual amount of waste. It is also notable that Stora Enso Heinola Fluting Mill produces only SC-fluting product, and therefore no remarkable variations occur in the process conditions at the pulp and board mill. However, it is worthwhile to note, that at pulp and board mills there are always unpredictable process variations e.g. in the quality of wood species and in the origin of peat etc. Therefore, there are also variations in the quantity and quality of ashes and green liquor dregs. The analysis of several sub-samples of the ashes and the green liquor dregs would have been useful in this study. However, this was not possible due to practical reasons e.g. interruptions to processes, maintenance shut downs etc. The sampling periods represented the normal process operating conditions at the mill and the local environmental authorities have accepted the sampling procedure used. The environmental authorities will finally decide on the allowable utilisation of the residues investigated in this study based on their physical, chemical and extraction properties.

7. References

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ERRATA FOR APPENDEND PUBLICATIONS

Paper I: The sentence “However, the total Ca concentrations of 2.4 mg/kg (d.w.) and 3.4 mg/kg (d.w) in bottom ashes A and B, respectively, were lower than the requirement of 6.0 mg/kg (d.w.)” in the paragraph conclusions and in the abstract should be “However, the total Ca concentrations of 2.4% (d.w.) and 3.4% (d.w) in bottom ashes A and B, respectively, were lower than the requirement of 6.0% (d.w.)”. In addition, the Latin name (*Alnus insana* and *A. glutinosa*) for alder should be (*Alnus incan* and *A. glutinosa*) in the second and the third paragraph of section material and method.

Paper II: The sentence “Except for Zn, the extractable concentrations of heavy metals in the artificial gastric fluid were clearly more than those in the artificial sweat fluid (see table 4)” in the third paragraph of section Occupational Risk Aspects—Extractable Heavy Metal Concentrations in Ashes using Artificial Sweat and Gastric Fluids should be “Except for Mo in the fly ash, the extractable concentrations of heavy metals in the artificial gastric fluid were clearly more than those in the artificial sweat fluid (see table 4)”. In addition, the total concentration of Cd in the bottom ash < 3.0 mg/kg (d.w.) in Table 2 should be < 0.3 mg/kg (d.w.).

Paper III: The total concentration of Cd in the bottom ash < 3.0 mg/kg (d.w.) in Table 2 should be < 0.3 mg/kg (d.w.).

Paper IV: The sentence “These limit values, which came into force in March 2007, are currently only set for As, Cd, Cr, Cu, Ni, Pb, Zn and Hg, and are applied if wood-, peat and coal-derived ashes are used as a forest fertilizer” in the second paragraph of section 3.2. should be “These limit values, which came into force in March 2007, are currently only set for As, Cd, Cr, Cu, Ni, Pb, Zn and Hg, and are applied if wood-, peat and agrobiomass-derived ashes are used as a forest fertilizer.” In addition, the total concentration of V < 50.0 mg/kg (d.w.) in Table 2 should be < 1.0 mg/kg (d.w.).

Paper V: The total concentration of V < 50.0 mg/kg (d.w.) in Table 1 should be < 1.0 mg/kg (d.w.).

This doctoral dissertation provides new, comprehensive results for the chemical, physical and extraction properties of bottom and fly ashes originating from the co-combustion of different fuel mixtures in a bubbling fluidised bed boiler (120 MW) and for green liquor dregs originating from the recovery boiler of a semichemical pulp and board mill. The potential use of these residues as an earth construction agent or as a fertiliser is reviewed from the Finnish environmental legislation point of view and additional important results concerning environmental and occupational health aspects are also presented.



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