



TAMPEREEN TEKNILLINEN YLIOPISTO
TAMPERE UNIVERSITY OF TECHNOLOGY

ALEKSI AUTIO
EFFECT OF AIR CLASSIFICATION ON UTILIZATION POTENTIAL
OF FLY ASHES FROM CO-COMBUSTION

Master of Science Thesis

Examiner: University Lecturer Henrik
Tolvanen
Examiner and topic approved in the
Faculty of Natural Sciences council
meeting on 1.11.2017

ABSTRACT

Aleksi Autio: Effect of air classification on utilization potential of fly ashes from co-combustion

Tampere University of Technology

Master of Science Thesis, 78 pages

July 2018

Master's Degree Programme in Environmental and Energy Engineering

Major: Energy and Biorefining Engineering

Examiner: University Lecturer Henrik Tolvanen

Keywords: fly ash, air classification, ash utilization, heavy metal

Circular economy is an upward trend that applies also to ashes. It will be increasingly important to change the status of ash from a waste that has to be landfilled to a useful product. The main driving force behind this change are the high landfilling costs but utilization of ash saves also natural resources. However, the Finnish legislation sets limit values for heavy metals and other harmful substances for several utilizations. High heavy metal content can therefore prevent the utilization of some ashes. Options for these ashes are disposal of at a landfill or a refining process to reduce the heavy metal content.

The aim of this thesis was to examine the functionality of air classification as an ash refining technology. A test run was conducted with an air classifier pilot equipment to investigate the effect of air classification on the utilization potential of fly ashes. The fly ashes used in the experiments were received from five power plants combusting different mixtures of fuels to cover an extensive section of ashes produced in Finland. These power plants used either bubbling or circulating fluidized bed technology. In air classification process, ash feed was divided into three size fractions. The basic idea was that the heavy metals enrich in the fine ash fractions so the coarse fraction was more easily utilized due to the reduced heavy metal concentrations. This study is limited to the utilization of ashes as fertilizers and in earth construction since there is exact legislation for the properties of ash used in these applications.

The thesis attained its aim of evaluating the functionality of the air classifier pilot. Mechanically the classifier functioned adequately. However, air classification had no effect on the utilization potential of the test ashes despite the lowered heavy metal concentrations in the coarse ash fractions. This is because, most of the test ashes were already utilizable as fertilizers or in earth construction so there was no need for the refining process. One of the test ashes was originally hazardous waste but the air classification could not improve its properties enough to remove the status of a hazardous waste. The profitability analysis revealed that air classification would be profitable if ash could be transferred from a landfill to utilization. Therefore, a specific type of ash should be found for the air classification to be feasible. Overall, the low availability of suitable ashes and the limitations in profitability restrict the use of air classification technology in the refinement of fly ash.

TIIVISTELMÄ

Alexi Autio: Ilmaluokituksen vaikutus yhteispolton lentotuhkien hyötykäyttökelpoisuuteen

Tampereen teknillinen yliopisto

Diplomityö, 78 sivua

Heinäkuu 2018

Ympäristö- ja energiatekniikan diplomi-insinöörin tutkinto-ohjelma

Pääaine: Energia- ja biojalostustekniikka

Tarkastaja: Yliopiston lehtori Henrik Tolvanen

Avainsanat: lentotuhka, ilmaluokitus, tuhkan hyötykäyttö, raskasmetalli

Kiertotalous on nouseva trendi, joka koskee myös tuhkia. Tuhkan aseman muuttaminen kaatopaikalle sijoitettavasta jätteestä hyötykäytettäväksi tuotteeksi tulee olemaan entistä tärkeämpää. Ajavana voimana tämän muutoksen takana ovat korkeat kaatopaikkamaksut, mutta tuhkan höytykäytöllä säästetään myös luonnonvaroja. Suomen lainsäädäntö asettaa raja-arvot raskasmetalleille ja muille haitallisille aineille useissa tuhkan hyötykäyttökohteissa. Korkeat raskasmetallipitoisuudet voivat siis estää joidenkin tuhkien hyötykäytön. Vaihtoehtoina näillä tuhkillä ovat kaatopaikkasijoitus tai jalostusprosessi raskasmetallipitoisuuksien vähentämiseksi.

Tämän työn tavoitteena oli selvittää ilmaluokituksen soveltuminen tuhkan jalostusteknologiaksi. Pilotti kokoluokan ilmaluokittimella suoritettiin koeajo, jossa tutkittiin ilmaluokituksen vaikutusta lentotuhkien hyötykäyttökelpoisuuteen. Koeajossa käytetyt lentotuhkat saatiin viideltä voimalaitokselta, jotka käyttävät erilaisia polttoaineseoksia. Polttoprosessi näissä voimalaitoksissa perustui joko kerros- tai kiertoileijutekniikkaan. Testituhkat edustavat laajasti erilaisia tuhkia, joita syntyy yhteispolttolaitoksissa Suomessa. Ilmaluokitusprosessissa tuhkasyöte jaetaan kolmeen kokojakeeseen. Perusidea on, että raskasmetallit rikastuvat hienojakeisiin, joten karkea jae voidaan helpommin ottaa höytykäyttöön madaltuneiden raskasmetallipitoisuuksien ansioista. Tässä työssä keskityttiin tuhkan hyötykäyttöön lannoitteena ja maanrakennuksessa, koska näille käyttökohteille on olemassa täsmällinen lainsäädäntö, joka asettaa tavoitteet tuhkan ominaisuuksille.

Tutkimuksen avulla voitiin arvioida ilmaluokitinpilotin soveltuvuutta lentotuhkan jalostamiseen. Luokitin toimi mekaanisesti riittävän hyvin. Ilmaluokituksella ei kuitenkaan ollut vaikutusta testituhkien hyötykäyttökelpoisuuteen, vaikka raskasmetallipitoisuudet laskivatkin karkeassa tuhkajakeessa. Useimmat testituhkat olivat valmiiksi lannoite- tai maanrakennuskelpoisia, jolloin tuhkan jalostamiselle ei ollut tarvetta. Yksi tuhkista oli puolestaan alun perin vaarallista jätettä, mutta tuhkan ominaisuudet eivät parantuneet ilmaluokituksella riittävästi tuhkan jätestatuksen poistamiseksi. Taloudellisen kannattavuusarvion mukaan ilmaluokitus on kannattavaa, jos tuhka saadaan siirrettyä kaatopaikalta hyötykäyttöön. Ilmaluokitus soveltuu siis vain tietyn tyyppisille tuhkillä. Tällaisten tuhkien vähäisen saatavuuden ja taloudellisten rajoitteiden vuoksi mahdollisuudet ilmaluokitusteknologian käyttöön lentotuhkien jalostamisessa ovat rajalliset.

PREFACE

This master's thesis was made for the department of Chemistry and Bioengineering in Tampere University of Technology (TUT). The research was funded by Valmet Technologies. The experimental part of the thesis was conducted at Valmet's Energy R&D Center in Tampere.

Juha Roppo and Erkki Välimäki were the coordinators of my thesis in Valmet. I would like to thank them for their continuous support throughout the thesis work. Especially Juha's ash related expertise and Erkki's help in the project management were invaluable. Henrik Tolvanen was the examiner of my thesis from TUT. I thank him from giving an academic perspective to this work and offering valuable feedback that elevated the thesis to this final state.

The experiments with the air classifier pilot had an important role in this thesis. I thank Jouko Niemi and Seppo Jounela for their advice relating to the air classifier as well as the planning of the experiments. The personnel of the R&D Center provided me assistance in any subject related to the ash classification experiments. Therefore, special thanks to Sakari Kulmala, Juha Sutinen, Hannu Lehtinen, Kari Hoikkala and Raine Järvinen. Additionally, thanks to Marko Palonen for helping to arrange me this thesis work and Aino Vettenranta for proofreading and feedback on the thesis.

Finally, I would like to thank my family for their ongoing support and friends for making the student years unforgettable.

Tampere, 30.7.2018

Alexi Autio

CONTENT

1.	INTRODUCTION	1
2.	BACKGROUND	3
2.1	Composition of ashes	3
2.1.1	Major and minor elements	3
2.1.2	Trace elements	7
2.2	Behaviour of ash during combustion process	7
2.2.1	General principles of ash formation.....	7
2.2.2	Behaviour of trace elements.....	8
2.2.3	Ash formation in fluidized bed combustion.....	9
2.3	Ash utilization	11
2.3.1	Introduction to ash utilization	11
2.3.2	Ash utilization as fertilizers	12
2.3.3	Ash utilization in earth construction	15
2.3.4	Ash utilization in concrete applications	16
2.4	Legislation concerning ash utilization and disposal.....	17
2.4.1	Legislation on ash utilization as fertilizer	17
2.4.2	Legislation on ash utilization in earth construction	18
2.4.3	Legislation on ash disposal at landfills	20
2.5	Cyclone separators	22
2.6	Profitability calculation methods	25
3.	EXPERIMENTAL	28
3.1	Air classifier	28
3.2	Fly ashes used in the experiments	30
3.3	Ash classification experiments.....	32
3.4	Laboratory analysis methods.....	34
3.5	Methods for analysing the results.....	35
3.5.1	Error evaluation.....	35
3.5.2	Cost estimation.....	36
4.	RESULTS AND DISCUSSION	39
4.1	Functionality of test equipment.....	39
4.1.1	Mechanical functionality.....	39
4.1.2	Classification of fly ash.....	42
4.1.3	Elemental compositions of test ashes.....	50
4.1.4	Enrichment characteristics of elements.....	54
4.1.5	Mass balance calculations and error evaluation.....	58
4.2	Effect of air classification on ash utilization.....	59
4.2.1	Utilization possibilities of ashes used in experiments	59
4.2.2	Cost estimations of selected utilization scenarios.....	66
5.	CONCLUSIONS.....	70
	REFERENCES.....	73

NOMENCLATURE

BFB	bubbling fluidized bed	
BHF	backhouse filter	
BTEX	benzene, toluene, ethylbenzene and xylenes	
CAPEX	capital expenditure	
CFB	circulating fluidized bed	
DOC	dissolved organic carbon	
EF	enrichment factor	
ESP	electrostatic precipitator	
GEC	grade efficiency curve	
ICP-MS	inductively coupled plasma mass spectrometry	
ICP-OES	inductively coupled plasma optical emission spectrometry	
L/S	liquid to solid ratio	
LOI	loss on ignition	
NCF	net cash flow	
NPV	net present value	
OPEX	operational expenditure	
PAH	polycyclic aromatic hydrocarbons	
PCB	polychlorinated biphenyls	
PMT	periodic payment	
TDS	total dissolved solids	
TOC	total organic carbon	
VAT	value-added tax	
C	concentration	
c_o	solids loading	[kg, solids/kg, gas]
c_{oL}	limit loading	[kg, solids/kg, gas]
I_0	initial investment	
i	interest rate	
I_n	salvage value of an investment	
m	mass	[kg]
M	molar mass	[g/mol]
n	holding period of an investment	
x_{50}	cut-size	[μm]
x_{med}	average particle size	[μm]
η	efficiency, grade efficiency	

1. INTRODUCTION

Ash is a waste produced from inorganic and unburned substances in the fuel during a combustion process. According to the targets of circular economy, it will be increasingly important to turn these ashes from a waste that has to be landfilled to a useful product. The quality of ash varies significantly depending on the fuel, the combustion technology and the flue gas cleaning system. The elemental composition, mechanical properties and origin of an ash define the utilization possibilities for this ash. The Finnish legislation defines the properties required for several applications. Legislation concerning ash utilization as fertilizers and in earth construction sets the limit values for heavy metals and other harmful substances. Some ashes have high heavy metal content that prevent the utilization and must, therefore, be disposed of at a landfill. Another possibility is to refine these ashes so that they meet the limit values.

In this thesis, a test run with an air classifier pilot equipment was carried out to evaluate whether air classification technology could be used to reduce the content of heavy metals in fly ashes and improve their utilization potential. Five test ashes were received from power plants using co-combustion of biomass and several other fuels. The fuel mixtures varied from biomass-peat to biomass-peat-coal-waste to cover a wide section of co-combustion ashes produced in Finland. Ashes originating from co-combustion was chosen as subject because these ashes were identified most likely to benefit from air classification. Ashes from the combustion of purely wood-based biomass seldom have elevated heavy metal contents. Power plants combusting only coal are scarce in Finland and their ashes can often be utilized in concrete applications that are beyond the scope of this research. Ashes from waste incinerators have probably too high heavy metal contents for air classification to be sufficient to improve their utilization. Also, bottom ashes were excluded from this research since they usually have lower heavy metal concentrations than fly ashes. This is due to the behaviour of heavy metals and other trace elements during the combustion process, which is further described in Ch. 2.2.2.

The ash composition, formation as well as the behaviour of trace elements during combustion are discussed in the literature survey in Ch. 2. The volatilization and subsequent condensation of trace elements during the combustion process causes them to enrich in the fine fly ash particles. This enrichment is the reason that air classification affects the heavy metal content in ashes. Other topics of the literature survey are related to ash utilization, the legislation governing the utilization and the technology behind the air classification.

In the experimental section of this thesis in Ch. 3, a series of experiments are conducted with an air classifier pilot. Ash is divided into three size fractions in the air classification process. The idea is that heavy metals enrich in the fine fractions so that the coarse fraction can be more easily utilized. The target of this research is to examine the functionality of the air classifier as an ash refiner. The following aspects relating to the air classifier pilot are considered:

- Mechanical functionality
- Classification performance
- Enrichment characteristics of elements in different ash fractions
- Effect on the utilization potential of the test ashes
- Profitability

Mechanical functionality is evaluated based on the information gathered during ash classification experiments. Laboratory analyses of particle size distribution, elemental composition and leachability of different ash fractions have a vital role in determining the functionality. Particle size distribution analysis is used in evaluating the classification performance that basically signifies the effectiveness of the separation of coarse and fine particles. Investigating the enrichment characteristics of elements in fine and coarse fractions is based on the elemental composition analyses. Elemental composition and leachability analyses are both needed for the evaluation of the effect of air classification on the utilization potential of ashes. Finally, the calculation of the profitability of an air classifier investment is made for a few utilization scenarios based on the cost estimations of the capital and operational costs of the pilot as well as the costs related to ash utilization.

2. BACKGROUND

This chapter discusses the topics related to the utilization of ashes as well as the other background information needed for the analysis of the results acquired during the experimental section of this research. The typical elemental composition of ash originating from the combustion of biomass is in spotlight in the first subchapter but the compositions of coal and peat ashes are also discussed. The formation and behaviour of ash during a combustion process are presented to provide information about the conditions affecting the quality of ash. Ash utilization as fertilizer and in earth construction were chosen as the utilization targets in this research due to the exact legislation available for those applications. Both the suitability of different ashes in these utilizations and the relevant Finnish legislation are discussed in the following subchapters. Also, the utilization of ash in concrete applications is briefly introduced. The air classification technology is based on the cyclone separators. Therefore, the fundamentals of the cyclone operation are described in Ch. 2.5. Finally, the profitability calculation methods used for the evaluation of the profitability of an air classifier investment are presented.

2.1 Composition of ashes

2.1.1 Major and minor elements

The elements that cover over one weight -% of an ash are considered major elements whereas minor elements are the ones that cover 0.1-1 weight -%. Typically, the elements in biomass ash are in decreasing order of abundance O – Ca – K – Si – Mg – Al – Fe – P – Na – S – Mn – Ti [1, p. 72]. For coals, the similar list is O – Si – Al – Ca – Fe – C – K – Mg – H – Na – Ti – N – P [2, p. 1491]. The element abundance varies considerably depending on the fuel origination especially for biomass so the lists are only directional. However, the first few elements in the lists are almost always major elements whereas the last few are almost always minor elements.

The composition of biomass based fuels and their ashes varies considerably depending on the source of the biomass. Biomass is generally classified into five main classes: *Wood and woody biomass* comprises chips, sawdust, bark, branches, stems and leaves of different wood species; *Herbaceous and agricultural biomass* includes many kinds of straws and agricultural plant residues such as bagasse and rice husks; *Aquatic biomass* is mainly algae and other aquatic vegetation; *Animal and human biomass wastes* are for example bones and various manures. The fifth biomass class is considered semi-biomass as it does not consist entirely of biological substances. This class is called *Contaminated biomass and industrial biomass wastes* that comprises of various wood and wood product wastes as well as municipal solid waste. This thesis focuses on wood and woody biomass class

as it is the most utilized biomass class in energy production in Finland. Table 1 summarizes the chemical composition of general biomass classes and presents also composition for peat and different types of coal. [3, p. 915]

Table 1 Mean ash content and compositions (weight-%, dry matter) for different types of biomass, peat, and coal, adapted from [4, pp. 387-389].

Fuel	Ash	SiO ₂	CaO	K ₂ O	MgO	P ₂ O ₅	Al ₂ O ₃	SO ₃	Fe ₂ O ₃	Na ₂ O	TiO ₂
Wood and woody biomass	4.3	21.99	39.20	12.44	6.42	4.99	4.57	4.85	3.24	2.04	0.26
Herbaceous and agricultural biomass	8.0	33.09	14.82	26.81	5.69	6.30	3.43	4.09	2.77	2.78	0.22
Aquatic biomass	25.1	31.09	8.20	15.79	3.98	1.36	1.61	24.52	2.24	10.99	0.22
Animal and human biomass wastes	31.8	39.12	20.04	10.58	4.23	14.94	2.42	2.74	1.35	3.53	1.05
Contaminated biomass and industrial biomass wastes	17.9	39.67	19.57	2.60	4.03	2.18	16.15	3.16	6.27	2.62	3.75
Peat	4.9	37.53	9.97	1.12	2.14	2.75	20.14	12.11	13.83	0.10	0.31
Lignite	34.6	44.87	13.11	1.48	2.50	0.20	17.11	8.64	10.80	0.48	0.81
Sub-bituminous coal	26.4	54.74	7.05	1.67	2.14	0.08	22.86	4.07	5.30	1.09	1.00
Bituminous coal	15.7	56.14	4.90	1.61	1.55	0.22	24.82	2.16	6.68	0.77	1.15

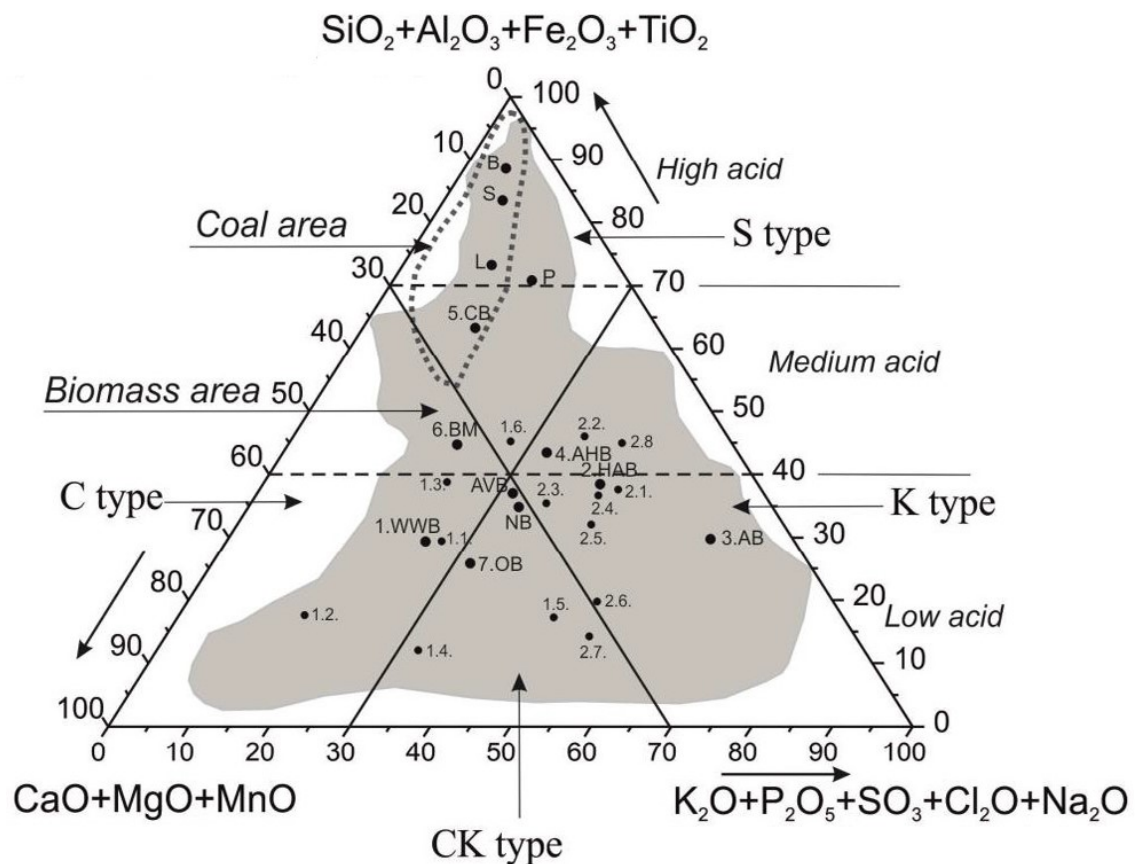
The elemental compositions of different ashes in Table 1 are mean values gathered from a total of 141 biomass varieties, some of which with multiple samples, and 38 samples of peat and coals [4, pp. 387-389]. The elements are presented as their most common oxides. However, the elements seldom exist in the ash only as common oxides (SiO₂, CaO...) but also as various other compounds. Presenting concentrations as oxides helps to evaluate the oxygen content in the ash. Furthermore, weight percentages in Table 1 are normalized so that their sum is 100%. This is a quite accurate assumption if the composition of all the relevant elements are analysed. [5, pp. 4-5].

Some observations about the enrichment and depletion of major elements in different fuels can be made based on Table 1. Generally, biomass has lower ash content and higher Ca, K, P and Mg contents than coals, whereas coals have higher Si, Al, Fe and Ti contents. However, there is considerable variation between the biomass classes and inside the classes between biomass varieties as well. In summary, wood and woody biomass has lower ash and higher Ca contents than other biomass classes. Other biomass classes, on the other hand, generally higher concentrations of K and/or P. Contaminated biomass and industrial

biomass wastes class is an exception as its composition has similarities with both the coals and the other biomass classes.

There are connections between elements in biomass and biomass ash. Some elements exist more probably with certain elements than others. Vassilev et al. [3] introduced a biomass and biomass ash classification system that is based on three main connections. These connections are: (1) Si – Al – Fe – Ti; (2) Ca – Mg – Mn; and (3) K – P – S – Cl – Na. The biomass types formed based on these associations are S, C and K type, respectively. The fourth class is CK type that is a combination of C and K type biomasses. Those four types are further divided into six subclasses based on their acidic tendencies (high acid, medium acid, low acid). The classification system is illustrated in Figure 1. The data, on which Table 1 is based on, is inserted in the figure and the grey area represent all the 141 biomass varieties gathered. Peat and coal samples are also included for comparison. Mean values of each biomass class and subclass are presented with black dots. Here is an example how to read the triangular diagram: 1. WWB (average of wood and woody biomass samples) include 30% of Si, Al, Fe and Ti oxides, 46% of Ca, Mg and Mn oxides, and 24% of K, P, S, Cl and Na oxides.

The top of the triangle in Figure 1 represents the coal area. Peat and S type biomasses and their ashes, such as contaminated biomass, have often similar composition as coals regarding the major elements. As mentioned before, the elements enriched in S type biomasses are usually Si, Al, Fe and Ti. They are typically the least mobile elements which means that they have low solubility and leachability. The S type biomasses are also less volatile and reactive than other biomass classes. C type biomasses include mainly wood and woody biomasses that are rich with elements like Ca and Mg. Mn is also often enriched in the C type compared to other biomass classes. These elements are considered moderately mobile, less volatile and highly reactive. Herbaceous, agricultural and aquatic biomasses as well as animal and human biomass wastes are typically K type biomasses. Element association for this class is K – P – S – Cl – Na. These elements are highly mobile, highly volatile and highly reactive. Mobility affects the leaching behaviour of ash during utilization, whereas volatility and reactivity affect the behaviour of ash during combustion (see Chs. 2.2 and 2.3). Classification system helps to predict these factors and thus also fuel performance during combustion, ash composition and ash utilization applications. [4]



- | | |
|--|--|
| 1. WWB – Wood and woody biomass | 3. AB – Aquatic biomass |
| 1.1. Stems | 4. AHB – Animal and human biomass wastes |
| 1.2. Barks | 5. CB – Contaminated biomass and industrial biomass wastes |
| 1.3. Branches | 6. BM – Biomass mixtures |
| 1.4. Pruning | |
| 1.5. Leaves | |
| 1.6. Others | |
| 2. HAB – Herbaceous and agricultural biomass | OB – Other biomasses |
| 2.1. Grasses | AVB – All varieties of biomass |
| 2.2. Straws | NB – Natural biomass |
| 2.3. Stalks | P – Peat |
| 2.4. Shells | L – Lignite |
| 2.5. Husks | S – Sub-bituminous coal |
| 2.6. Pits | B – Bituminous coal |
| 2.7. Residues | |

Figure 1 Different biomass species in biomass and biomass ash classification system, [4, p. 400].

2.1.2 Trace elements

The elements covering < 0.1 weight-% of the ash are considered trace elements. Most of the elements in ash are trace elements even though they form only a small fraction of the ash. Despite the low concentrations of trace elements in ash, they may produce serious health and environmental hazards. To prevent this, flue gas cleaning equipment, such as electrostatic precipitators and baghouse filters are designed to efficiently capture the fly ash particles. Potentially hazardous trace elements are often referred to as heavy metals in literature, although they usually contain also light metals, heavy non-metals and semi-metals. In this thesis, the term heavy metal designates elements that are considered harmful concerning the utilization of ash (see Chs. 2.3 and 2.4). The term trace elements, on the other hand, designates all the elements that fit in the definition based on the concentration, and thus includes also heavy metals. [6]

Concentrations of different trace elements vary depending on the fuel type. Toxic trace elements are usually more abundant in coals than biomass. However, certain trace element concentrations may be significantly larger in some biomasses than for coals. These elements are typically Ag, Au, Be, B, Cd, Cr, Cu, Ni, Rb, Se, and Zn. This list contains both harmful heavy metals, such as cadmium, and valuable noble metals such as silver and gold. Valuable metals offer utilization possibilities if they are separated from the biomass ashes but, on the other hand, heavy metals cause increased health and environmental risk. Furthermore, some harmful trace elements tend to occur in more mobile and hazardous compounds in biomass ashes than in coal ashes. Therefore, the evaluation of environmental impacts is an important part of biomass ash utilization. [6]

2.2 Behaviour of ash during combustion process

2.2.1 General principles of ash formation

A basic method for analysing the combustibility of solid fuels is the proximate analysis. It divides the fuel into fixed carbon, volatile matter and ash. The proximate analysis is usually performed on dry matter but includes occasionally also the moisture content of the fuel. The combustion of a solid fuel particle can be divided into a few phases. At the beginning, the temperature of the fuel particle rises and it dries as the moisture vaporizes. After the drying phase, pyrolysis occurs. The volatile matter in the particle evaporates and burns rapidly. The fixed carbon is left behind, and it burns considerably more slowly than the volatile matter. The fuel particle diminishes until only the incombustible, inorganic and unburned organic matter, ash, remains. Large ash particles remain in the furnace and are collected from the bottom of the furnace. The smaller particles are transported from the furnace with the flue gases. These ash fractions are called bottom ash and fly ash, respectively. This thesis focuses mainly on fly ash since its utilization is generally

more challenging so there is larger need for a refining process, such as air classification examined in this thesis. [7]

The ash forming substances in the fuel, the combustion technology and temperature are the key factors that define the composition of ash and its distribution between fly and bottom ashes. As presented in Ch. 2.1, the major ash forming elements in biomass are alkali and alkali earth metals, such as K and Ca. Coal ash, on the other hand, consists mainly of Si, Al and Fe. These elements and their compounds behave in various ways during combustion. Most of the ash forming substances stay in the burning fuel particle and form one or several ash particles that can agglomerate producing larger particles. These ash particles are transported either to the bottom ash or the fly ash depending on their size. Typical elements in ash produced by this mechanism are Si, Al, Fe, Ca, and Mg. Another important ash forming mechanism is volatilization. Especially alkali chlorides volatilize easily and can react with other ash forming compounds. In reducing atmosphere also some oxides that stay usually in solid phase, such as SiO₂, CaO and MgO, may volatilize. When these volatilized gases condense in the lower temperatures in the flue gas duct, they form particles with a diameter less than 1 µm. [8, p. 273-274], [9]

Ash is responsible for many malfunctions in boiler operation. Slagging in the furnace, fouling of the heat exchangers and some corrosion issues are caused by deposition of ash particles or melting of ash [10]. These ash related issues do not have a direct effect on ash utilization and are not discussed in this thesis. However, a considerable part of ash-related research focuses on describing and preventing fouling and slagging problems. These studies affect the boiler designs, operation parameters and fuel mixtures, thus affecting also the composition and utilization potential of ashes.

2.2.2 Behaviour of trace elements

Trace elements are especially important considering the utilization of ashes since they may produce serious environmental risks. Understanding their behaviour during combustion helps to predict the concentrations of trace elements in ash. Generally, elements can be divided into three classes based on their behaviour. These classes are non-volatile elements, elements that volatilize in the furnace but condense in the flue gas duct, elements that volatilize but do not condense. Most harmful trace elements, or heavy metals as they are called in the rest of this thesis, belong in the middle class so they volatilize and subsequently condense forming submicron particles that may adhere to the surface of larger particles or stay in the flue gas stream on their own. Typical trace elements in this category are, for example, As, Cd, Mo, Ni and Sb. Some trace elements, such as Br, Hg and Se, volatilize but do not condense. However, the combustion technology and more importantly the combustion temperature affects the volatility of elements. For example, Reinik et al. reported that Cd was less volatile in circulating fluidized bed combustion than in pulverized combustion of shale oil due to the lower combustion temperature [11]. As mentioned in the introduction, the aim of this research is to examine the technology

to separate heavy metals from fly ash (see Ch. 3.1). The separation is based on classifying the ash by its particle size distribution. Substances that go through the volatilization and condensation enrich in the fine fraction of the ash, unless they are stuck on the larger particles as mentioned in Ch. 2.2.1. Larger fly ash particles, that are formed during the combustion of fixed carbon, enrich in the coarse fraction. [12], [13]

The enrichment of heavy metals in the fine ash fraction can be seen, for instance, in the heavy metal distribution between bottom and fly ash. Fly ash consists naturally of lighter (i.e. smaller) particles and, therefore, has higher heavy metal concentrations than bottom ash [14], [15], [16]. Another example can be found during the flue gas cleaning process. Electrostatic precipitators (ESP) are commonly used to capture the fly ash particles from the flue gas using electric fields. ESPs have usually two to three stages to ensure the high efficiency of particle removal. The first stage collects the coarser particles and the rest of the stages separate the fine fraction from the flue gas. The first field of an ESP has thus lower concentrations of heavy metals than the other fields. Therefore, an electrostatic precipitator could be used as a classifier to separate the coarse ash fraction to enhance the its utilization potential. However, this requires a few changes in the general operational practices in power plants. Firstly, the ashes from different stages of ESP are usually mixed and transported into the same ash silo. They should be collected separately to utilize the classification capability of ESP. Secondly, the first stage of ESP typically collects most of the particles. Therefore, the enrichment of heavy metals in the latter stages may not have a sufficient effect on the composition of the coarse fraction. Mass distribution of fly ash between the stages could be altered by changing the power of the electric fields in each stage.[17], [18]

2.2.3 Ash formation in fluidized bed combustion

Combustion technology affects also significantly to the formation of ash during combustion. Only ash formation characteristics for fluidized bed combustion are presented here because all the ashes examined during this thesis work are from fluidized bed boilers (see Ch. 3.2). In fluidized bed combustion, fuel is combusted in a sand bed fluidized by primary air that is fed to the boiler from the bottom of the furnace. The fluidized bed provides efficient mixing of the fuel and combustion air, and balances the temperature differences caused from the varying quality of the fuel. Therefore, fluidized bed combustion is especially well suited for biomass combustion and co-combustion of biomass and other solid fuels. The combustion technology is called either bubbling fluidized bed combustion (BFB) or circulating fluidized bed (CFB) combustion depending on the boiler design. In CFB, the size of sand particles is smaller and velocity of fluidizing air is higher than in BFB. Consequently, the large part of the sand in CFB combustion is transported from the furnace with the flue gas. These particles are separated from the flue gas stream with a cyclone and returned to the furnace. [19, p. 490].

The formation of ash in fluidized bed combustion is similar to the general ash formation that is described in Ch. 2.2.1, apart from the influence of the bed sand. Bottom ash is formed from the non-volatilizing ash compounds that collide with the sand particles. CFB combustion produces less bottom ash than BFB because CFB boilers have higher fluidizing velocity. Fly ash can be divided usually to the fine fly ash fraction and the coarse fraction. Simplified ash formation mechanisms in CFB are presented in Figure 2. Lind et al. [20, p. 2291] found also that during CFB combustion, 10% of the bed sand that was fed into the furnace was fragmented and transported into coarse fly ash, raising its SiO₂ concentration. [20]

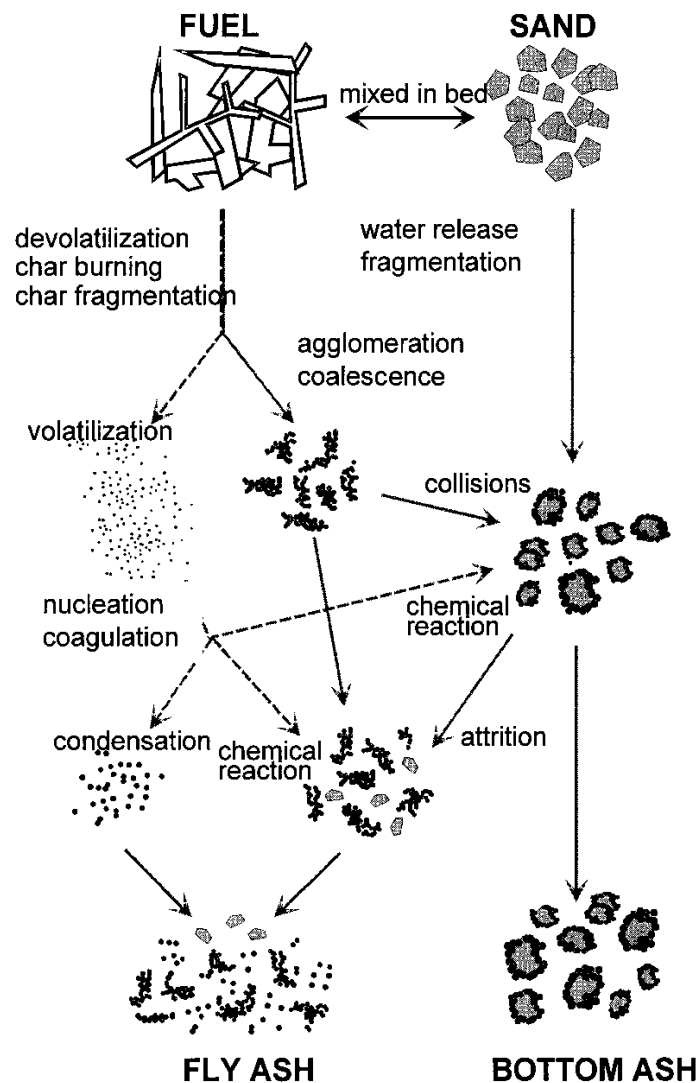


Figure 2 Simplified ash formation mechanisms during circulating fluidized bed combustion of biomass based fuels [20, p. 2292].

A typical ash related issue during fluidized bed combustion of different biomasses is the agglomeration of sand particles caused by the melting of ash. This mechanism is similar to the other ash related issues briefly mentioned in Ch. 2.2.1. Bed agglomeration may lead to defluidization of the bed and shutdown of the plant. To prevent this, the bed material

needs to be replaced regularly, the bed temperature is moderate (750-950 °C) [19, p. 490], and ash concentration is kept low in comparison with bed material. [21, p. 261]

2.3 Ash utilization

2.3.1 Introduction to ash utilization

Ash utilization is the main theme in this research. Promoting the utilization of ashes is important in both environmental and economical point of view. The change in the status of the ash from waste to be disposed to the utilizable product is a part of the concept of circular economy. The main idea behind circular economy is looking for closed loops, i.e., someone's waste may be somebody's else's resource [22, p. 526]. This reduces the consumption of virgin natural resources and can also provide economic benefits in resource and waste management. This research focuses on the utilization of fly ashes from biomass and co-combustion, although, various bottom ashes and fly ashes from coal combustion can also be utilized in some applications presented in this chapter.

In a survey by Finnish Energy in 2015 [23], Finnish power plants were quizzed about the utilization of their ashes. The survey had a good coverage since 79% of power plants answered, including the largest producers of ash. The total produced quantity of ash in 2014 was 1.34 Mt/a, of which about 230 kt/a was fly ashes from biomass and co-combustion. The fly ashes from coal combustion and bottom ash from waste incineration had the largest shares with 330 kt/a and 200 kt/a, respectively. The utilization of ash produced in Finland in 2014 is presented in Figure 3.

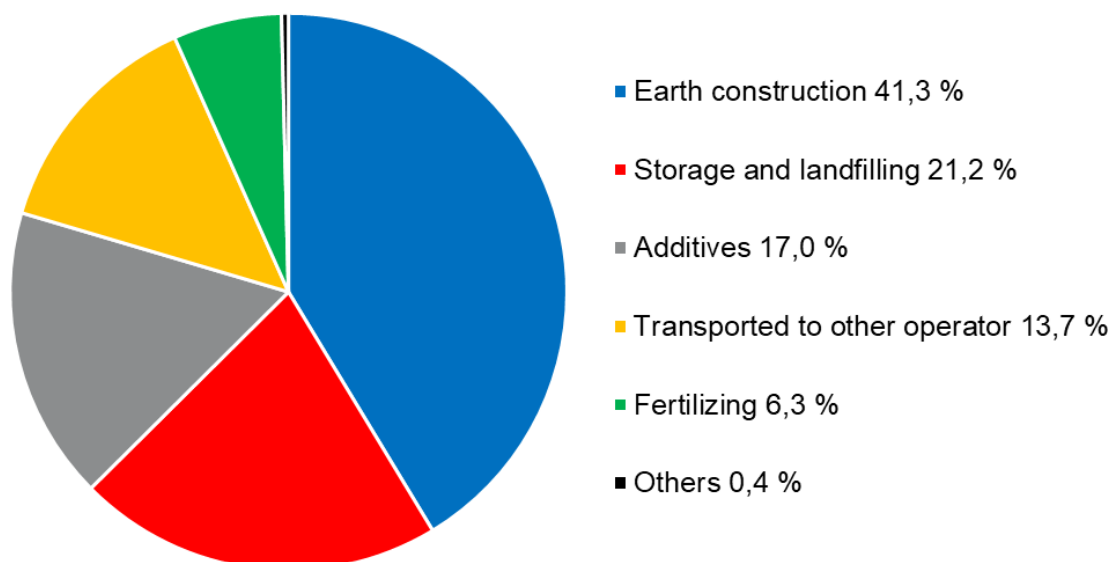


Figure 3 Ash utilization in Finland in 2014, adapted from [23, p. 8]

Based on the information in Figure 3, ash utilization in earth construction is common in Finland. Ashes from coal, peat and co-combustion are typically used in various earth construction applications. Fly ashes from coal combustion are also used as additives in concrete and cement products. About 20% of ash is either stored or landfilled. Those ashes are mainly from waste incineration but also from coal combustion. The utilization of ashes transported to other operators is not fully known but it is also often related to earth construction. Only 6.3% of ashes are utilized as fertilizers. Those ashes are mainly originated from biomass combustion. [23]

Most ashes produced in Finland are already utilized excluding ashes from waste incineration [23]. However, there are still possibilities to improve by reducing the amount of landfilled ash or by changing the low value earth construction ashes into fertilizer or concrete additive products with added value. The following subchapters discuss the most relevant utilizations concerning biomass and co-combustion ashes. Those are fertilizer and earth construction use. Also, ash utilization in concrete applications is briefly discussed, although, the utilization capability of the test ashes analysed during this thesis cannot be verified for these applications due to the lack of legislation.

2.3.2 Ash utilization as fertilizers

Recycling the nutrients from ashes back to soil is circular economy at its best. During harvesting nutrients and other minerals are removed from forest or field ecosystems but they can be returned to soil with ashes. Ash has also other beneficial effects to soil in addition to nutrients: it optimizes pH, improves texture, reduces bulk density, improves aeration and water holding capacity [24, p. 22]. Ash utilization as fertilizers is relevant for ashes originating from biomass combustion or co-combustion with large share of biomass since biomass ashes have usually higher concentrations of valuable nutrients than ashes from coal or peat combustion (see Ch. 2.1.1). These nutrients, mainly K and P, but also S, Ca, Cu, Mg, Mn and Zn, are beneficial for plant growth [25, p. 108]. Nitrogen is the only nutrient missing from ashes because it escapes in the atmosphere after the combustion as gaseous N_2 or, to a lesser extent, NO_x . Therefore, mixture of biomass ash and some nitrogen rich waste, such as sewage sludge or manure, is a viable option to improve the fertilization potential [26]. Otherwise, an additional nitrogen fertilizer has to be used alongside an ash fertilizer at least in agriculture. In Finland, other inorganic fertilizer products can also be used as additives in ash fertilizers to increase their nutrient content [27].

Continuous harvesting during conventional forestry and especially agriculture may lead to acidification of soil that lowers the availability of nutrients to plants. Biomass ashes have an important neutralizing effect in acidic soils due to their highly alkaline nature that derives mainly from the high Ca content [28]. As a result, biomass ashes are most beneficial to acidic soils. Considering ash utilization in agriculture, the concentrations of the most important nutrients, K and especially P, are often too low that the ash could be used

as the only fertilizer. Therefore, other inorganic fertilizer products are usually needed in addition to ashes. Consequently, ash can be seen firstly as a liming agent replacing commercial lime and secondly as a fertilizer in agriculture. In forestry, where regular fertilization is uncommon, ash products that have both liming and fertilizing potential are more suitable without additional fertilizers. The replacement of lime with ash is an environmentally friendly option since the calcination of natural limestone in production of lime has high power consumption and CO₂ emissions. Additional environmental benefits occur when replacing some of the commercial fertilizers with ash, saving nutrient resources. Especially phosphorus resources are limited globally [29, p. 18].

There are some limitations before extensive utilization is viable. Environmental impacts need to be evaluated profoundly before using ashes as fertilizers especially in agriculture where food is produced. The risks include uncertain bioavailability of nutrients, accumulation of harmful trace elements into plants and fauna, contamination of ground water, health issues caused by dust, and uncertainties about technology for ash pre-treatment. It is typically beneficial that nutrients are in water-soluble phase, i.e., have high leachability so that they are easily bioavailable to plants. On the other hand, harmful trace elements or heavy metals should have as low water solubility as possible to prevent contamination. However, nutrients are often in water-insoluble compounds such as glass, silicates and phosphates, and heavy metals (As, Bi, Br, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, Zn) occur in the surface of water-soluble compounds such as chlorides, sulphates and carbonates. Furthermore, the occurrence of different elements varies between ashes, which makes the prediction of functionality of specific ash as fertilizer challenging. The evaluation of utilization potential needs to be done, therefore, separately for each variety of ash. [30, p. 22]

The pH has naturally large impact on leachability of water-soluble fraction in ashes. Leachability of most elements increases significantly when pH decreases. High alkalinity of ashes has therefore positive effect on utilization of ashes on this point of view. However, leachability of some elements, mainly Cr, Mo, Se, V, increases with increasing pH [31, p. 57]. There are some legislative limitations on heavy metal concentrations in ashes used as fertilizers. Limit values for heavy metals in Finnish legislation are presented in Ch. 2.4.1. Limit values for concentrations may not be enough to assure the safe fertilizer use of ashes because bulk concentration does not give information about the behaviour of an element in soil and plants [30, p. 22]. Legislative restrictions will possibly shift towards limiting the leachability of elements as it better describes the effects of elements on ecosystems.

Other barriers for fertilizer use of ashes are related to productization. Converting fly ash from combustion waste to a fertilizer product is challenging. The varying quality of ashes is one of the most difficult issues to solve. End users expect and the legislation [32] demands almost constant nutrient concentrations so that the fertilizing and liming effects

can be predictable. Concentrations of harmful elements also need to stay below limit values. This can be achieved with unchanging fuel mixture and combustion conditions, which can be difficult to accomplish in practice. Another solution is a pre-treatment technology that stabilizes quality variations. Furthermore, regular analyses of the element concentrations in the ash product is necessary to ensure that the quality fulfils the requirements.

Granulation of ashes is a common pre-treatment method of fly ash that does not improve the elemental quality of ash but contributes to other issues. It turns the ash from fine powder to spherical granules. This removes the health risk of dusting and thus facilitates the transportation, storage and application of ash. Granulation affects also the leachability and thus the bioavailability of elements. Pesonen et al. [33] discovered that granulation of ash from co-combustion of wood and peat lowers the leachability of nutrients Ca, K, Mg, P and S. This means that fertilizing effect is slower than with untreated ash. Moreover, the total bioavailability of Ca, K, Mg and S reduces after granulation which therefore lowers the total fertilizing potential of ash. However, slower fertilizing effect means also longer fertilizing effect that can be beneficial especially in forestry where application intervals of fertilizers are usually from several years to a few decades. Granulation had no clear impact on the bioavailability of heavy metals. They were nevertheless below the limit values and, thus, had no effect on ash utilization. Granules of biomass ash are the most suitable in nitrogen rich peatlands where a lack of K and P limits the growth [34]. In mineral soils where there is a shortage of nitrogen, ash fertilizers have a weaker fertilizing effect.

There is a considerable difference between fertilizer markets in agriculture and forestry. Conventional fertilizers and other soil amelioration agents are in extensive use in commercial food production but only emerging in forestry. As a result, it is easier for ash fertilizers to gain market share in forestry segment than in agriculture. This can be seen, for example, in the difference in the number of producers for ash fertilizers for forests and fields in Finland. There are a few companies that manufacture granulated biomass ashes that are complete products for forest fertilizing [35, 36] but only one plant that is marketing their untreated ash to be utilizable as field fertilizer [37]. Figure 4 depicts ash granules for forest fertilizing.



Figure 4 Granulated ash fertilizer for forest soils, diameter 10-40 mm [36].

Ash utilization as fertilizer has substantial growth potential both in Finland and globally. Goals towards environmentally friendly and circular economy as well as increasing consumption of solid biofuels advance the development of ash utilization. Application of fly ash on soil has potentially several positive but also a few negative effects on plant growth and environment in general. They are summarized in Table 2. In addition to these listed negative environmental effects, there are challenges in quality variation and productization of ashes that need to be solved before extensive ash utilization in fertilizer markets is possible.

Table 2 Positive and negative aspects of ash fertilizers

Positive:	Negative:
1) Provides nutrients like K, P, Ca etc.	1) Uncertain nutrient bioavailability
2) Optimizes soil pH	2) Leachability of heavy metals
3) Improves the texture of soil	3) Dusting and other handling issues
4) Reduces the consumption of other fertilizers	

2.3.3 Ash utilization in earth construction

Fly ash is widely utilized in different applications in earth construction. As described in Ch. 2.3.1, earth construction applications are the most common utilization methods for ash in Finland. Earth construction applications include, for example, sub-bases of roads and fields. Utilized ash needs to fulfil certain environmental and mechanical requirements set by legislation. The Finnish legislation concerning ash utilization in earth construction is discussed in detail in Ch. 2.4.2.

Typical earth construction applications, where ash can be used to replace gravel or sand, are paved roads and car parks or other paved fields. Their structure can be generally divided into five layers. These are, from top to bottom, surface, base, sub-base, sub-grade and embankment. The surface, that is usually paved with tarmac, is flat, wear resistant and prevents the water from reaching the sub-layers. Base is the load-bearing layer that also distributes the load to a wider area. The sub-base improves the load distribution and freeze resistance of the structure. It also leads the water, that may trickle through the surface and the base, out of the structure. The sub-grade prevents the embankment and the other layers from mixing with each other and intercepts any capillary water from rising. The embankment is the bottom of the structure. Fly ash can be used in sub-base and the lower layers. There are some mechanical requirements concerning each layer. In the sub-base, the water permeability and the freezing and thawing endurance of the ash layer need to be adequate. In the sub-grade, the rise of capillary water has to be low. Additional ash free layer may be needed under the ash structure to prevent the rise of capillary water in especially wet conditions. [38]

The utilization of ash in earth construction applications can reduce the construction costs and save the resources that are conventionally used in earth construction (mainly gravel and sand). Economic savings depend on the costs of the resources and the transportation [39]. Ash is usually received free of charge for construction purposes because ash producers would otherwise have to pay the landfilling fee for the disposing of the ash. Therefore, transportation costs and availability and price of alternative resources define whether the ash utilization is economically feasible. Ahmaruzzaman [40, p. 355] estimates that 10-20% reduction in the construction costs can be achieved with the ash utilization if ash is produced within a reasonable distance of the construction site. If also environmental benefits from resource savings and reduction of disposal of ash are considered, transportation distances up to 100 km can be feasible.

2.3.4 Ash utilization in concrete applications

Concrete is the most commonly used building material mainly because it has good durability and mechanical properties, and it is inexpensive. The main ingredient of concrete is Portland cement. The production of Portland cement causes considerable CO₂ emissions and use of natural resources, mainly limestone. Fly ash can be used to replace Portland cement which decreases the environmental impact of concrete manufacturing. Typical share of fly ash of the total amount of cement is 15 to 35% [25, p. 110]. Especially fly ash from coal combustion is vastly utilized in cement replacement because it is widely available and good pozzolan, i.e., it reacts with Ca(OH)₂, in the presence of water, forming compounds with cementitious properties [41, p. 1525]. Biomass fly ashes also have similar properties although they considered less suitable for concrete applications because they tend to be less pozzolanic (less silica and aluminium) and have more alkali metals [30, p. 24]. The European standard SFS-EN 450-1 [42] defines the properties of ashes

that can be utilized in manufacturing of concrete. The standard applies only for pulverized coal combustion but it gives a guideline also for other combustion technologies and fuels. The maximum share of biomass ashes is also defined in the standard. EN 450-1 states that ashes from combustion of fuel containing at least 60% of coal, or 50% in co-combustion with pure wood, can be used in concrete manufacturing. The lack of legislation concerning ashes from biomass and co-combustion delays the growth of utilization of these ashes in concrete applications. [43]

Fly ashes have many advantages compared to regular cement: ash replaces virgin natural resources, has lower heat of hydration (releases less heat when mixed with water), and is generally less expensive. However, there are also disadvantages that impede wider ash utilization. Especially varying chemical and mechanical properties of ash produces challenges for ash utilization. The high concentration of unburned carbon poses the most serious concern for the quality of concrete. According to EN 450-1 [42], content of unburned carbon must be below 5%. Another issue disturbing the utilization of fly ashes in cement manufacturing is that the production of fly ash and the demand for cement in the construction industry are seasonal [44, pp. 333-334]. Most fly ashes are produced on the cold winter months, whereas peak activity of construction projects is on the summer months. These challenges create a need for quality control of ashes, storage facilities and technology development to remove unburned carbon from the ash to improve ash utilization in concrete applications. [43]

2.4 Legislation concerning ash utilization and disposal

2.4.1 Legislation on ash utilization as fertilizer

Finnish legislation provides guidelines for the utilization of ashes as fertilizers or soil ameliorants both in forestry and agriculture. The Fertilizer Product Act [32] sets general boundaries for manufacturing, marketing, transportation, use, import and export of fertilizers. The purpose of this Act is to ensure the quality of fertilizer products and thus prevent the hazards towards the environment, plant production and foodstuffs.

The Fertilizer Product Decree [27], on the other hand, addresses directly the utilization of ash as fertilizer. The Decree defines that ash from combustion of biomass, peat and untreated waste wood can be used as fertilizer or raw material for fertilizer products. This means, for example, that ashes from co-combustion with coal or waste cannot be utilized in soils. The decree determines also upper limits for concentrations of harmful elements and lower limits for concentrations of beneficial nutrients. Table 3 presents the limit values for harmful elements in ash fertilizers. The element-specific limit concentrations have been chosen to correspond to their toxicity in forest and agricultural environment. Especially mercury and cadmium have strict constraints. The column *Other utilizations* refers to fertilizer use in agriculture, horticulture and landscaping. The limit values for these

utilizations are more restrictive than those concerning utilization in forestry due to the concern for accumulation of contaminants in cultivated plants and foodstuffs. The unit of concentration signifies milligram of the harmful elements in kilogram of dry ash.

Table 3 *The limit values for harmful elements in ash fertilizers, according to [27].*

Element	Utilization in forestry mg/kg	Other utilizations mg/kg
Arsenic (As)	40	25
Cadmium (Cd)	25	2.5
Chromium (Cr)	300	300
Copper (Cu)	700	600
Mercury (Hg)	1.0	1.0
Nickel (Ni)	150	100
Lead (Pb)	150	100
Zinc (Zn)	4500	1500

The Fertilizer Product Decree defines also the minimum amount of nutrients in ash used as fertilizer. In forest fertilizers, the sum of the phosphorus and potassium contents has to be over 2.0% ($P + K > 2.0\%$) and the calcium content over 6.0%. In agriculture, the calcium content has to be over 10% but there is no lower limit for other nutrients. Ash can be, therefore, used in agriculture only as a neutralizing agent. Other fertilizers are then used to provide the nutrients required. It is also allowed to add other inorganic fertilizer products to ash to enhance its fertilizing properties or to achieve the required nutrient concentrations. [27]

The national legislation is based on the Regulation by European Parliament and Council relating to fertilizers [45]. At the moment, ash fertilizers are not regulated by EU but the national legislations. However, the EU Regulation is subject to a change due to EU's target to promote circular economy [46]. This concerns mainly the waste legislation but also the fertilizer use. Later, Finland will need to adjust its own legislation according to the changes in EU directives. The fertilizer regulation is possibly going towards restricting the leachability in exchange of the bulk concentrations of elements since the leachability analyses provide more accurate description of the bioavailability of nutrients and heavy metals than composition analyses. Additionally, the restriction that the origin of ash must be biofuels or peat may also change. Then, the properties of ash would define its utilization potential rather than its origin.

2.4.2 Legislation on ash utilization in earth construction

Earth construction is a common practice to utilize ash. The Government Decree on the Recovery of Certain Wastes in Earth construction [47] determines boundaries for this

utilization in Finland. The Decree defines the limit values for concentration and leachability of harmful substances for different earth construction sectors. The new Decree came into force on 1.1.2018. In this update, ash utilization was facilitated for some earth construction applications by removing the need for an environmental permit in accordance with the Environmental Protection Act [48]. The fly and bottom ashes that can be utilized in earth construction can originate from combustion of coal, peat, wood and wood-based fuels. [47]

Table 4 *Limit values for harmful substances in ash used in earth construction, adapted from [47].*

Harmful substance	Earth construction application					
	Road thickness of the waste layer $\leq 1,5$ m		Field thickness of the waste layer $\leq 1,5$ m		Base of an industrial and storage building thickness of the waste layer $\leq 1,5$ m	Graveled ash road thickness of the waste layer $\leq 0,2$ m
	Covered	Paved	Covered	Paved		
	Leachability (mg/kg L/S¹ = 10 l/kg)					
Arsenic (As)	1	2	0.5	1.5	2	2
Barium (Ba)	40	100	20	60	100	80
Cadmium (Cd)	0.04	0.06	0.04	0.06	0.06	0.06
Chromium (Cr)	2	10	0.5	5	10	5
Copper (Cu)	10	10	2	10	10	10
Mercury (Hg)	0.03	0.03	0.01	0.03	0.03	0.03
Molybdenum (Mo)	1.5	6	0.5	6	6	2
Nickel (Ni)	2	2	0.4	1	1	1
Lead (Pb)	0.5	2	0.5	2	2	1
Antimony (Sb)	0.7	0.7	0.3	0.7	0.7	0.7
Selenium (Se)	1	1	0.4	1.2	2	2
Vanadium (V)	2	3	2	3	3	3
Zinc (Zn)	15	15	4	12	15	15
Chloride (Cl ⁻)	3200	11000	800	2400	11000	4700
Fluoride (F ⁻)	50	150	10	50	150	100
Sulphate (SO ₄ ²⁻)	5900	18000	1200	10000	18000	6500
DOC ²	500	500	500	500	500	500
	Concentration (mg/kg dry matter)					
PAH ³	30	30	30	30	30	30

¹Liquid to solid ratio

²Dissolved organic carbon

³Polycyclic aromatic hydrocarbons

The limit values for harmful substances in different earth construction sectors are presented in Table 4. Almost every limit value is for leachability, since it gives more information of the behavior of a substance in environment. If these values in ash are below limits for a specific utilization application, only a notification to authorities is required. Otherwise, an earth construction project must apply for an environmental permit that may be granted on case-by-case basis. This is also the case when power plant producing the ash uses waste as a fuel, even if the leachabilities are below the limit values. [47]

As seen in Table 4, some earth construction locations using ash need to be covered with ground or stone material or paved with tarmac. This decreases the leaching of the harmful substances and thus, their impact on environment. The test procedure for identifying the harmful elements is evaluated with compilation samples that cover a maximum of 50000 tons of ash. Each compilation sample consists of at least 50 subsamples. Continuous sampling and analyzing of the produced ash is required to ensure that environmental hazards are prevented during ash utilization in earth construction. [47]

In addition to environmental requirements, ashes used in earth construction need to fulfil the technical and functional requirements needed for a specific application. Considering earth construction, the most important technical properties are optimal water content, maximum dry bulk density, strength and freezing properties [49, p 14]. Additionally, ash content in ash gravel mixture used in earth construction cannot exceed 30% [47]. If utilized ash originates from the combustion of peat and wood-based fuels, also instructions considering radioactive elements by Radiation and Nuclear Safety Authority need to be applied [50].

2.4.3 Legislation on ash disposal at landfills

If ash cannot be utilized, it is disposed of as waste at a landfill. Wastes are classified to inert, non-hazardous and hazardous waste by the amount of harmful substances they contain. For each class of waste there is a corresponding landfill where the wastes can be disposed. In practice, there are no landfills for inert waste that would accept ash so ash is disposed of as either non-hazardous or hazardous waste depending on its properties. The limit values of harmful substances for each landfill are presented in Government Decree on Landfills [51].

Most of the substances in Table 5 are the same as in the legislation for ash utilization in earth construction presented in Table 4. The same leachability analysis can therefore be used to evaluate whether the ash can be utilized in earth construction or if it needs to be disposed of at a landfill. Many of the limit values for non-hazardous landfill are the same as the highest values in Table 4 (paved road construction). A few values are higher but the limit values of Se and DOC are actually lower for landfills than for earth construction. If the amount of harmful substances exceeds the limit values for hazardous substances, ash cannot be disposed of at any landfill. In that case, it has to be sent to a waste handling station that is specialized in treatment of hazardous wastes. The limit values for inert

landfills are, for the most part, lower than the limit values in Table 4. Furthermore, it is common that landfill owners do not have a separate inert landfill but ash is disposed of at a landfill for non-hazardous or hazardous waste depending on its properties.

Table 5 *Limit values for harmful substances in ash disposed of at landfills for different waste classes, adapted from [51].*

Harmful substance	Limit value, mg/kg		
	Leachability (L/S = 10 l/kg)		
	Inert	Non-hazardous	Hazardous
Arsenic (As)	0.5	2	25
Barium (Ba)	20	100	300
Cadmium (Cd)	0.04	1	5
Total Chromium (Cr _{tot})	0.5	10	70
Copper (Cu)	2	50	100
Mercury (Hg)	0.01	0.2	2
Molybdenum (Mo)	0.5	10	30
Nickel (Ni)	0.4	10	40
Lead (Pb)	0.5	10	50
Antimony (Sb)	0.06	0.7	5
Selenium (Se)	0.1	0.5	7
Zinc (Zn)	4	50	200
Chloride (Cl ⁻)	800	15000	25000
Fluoride (F ⁻)	10	150	500
Sulphate (SO ₄ ²⁻)	1000	20000	50000
DOC ¹	500	800	1000
TDS ²	4000	60000 (6%)	1000000 (10%)
	Limit value, mg/kg		
	Inert	Non-hazardous	Hazardous
TOC ³	30000 (3%)	50000 (5%)	60000 (6%)
BTEX ⁴	6		
PCB ⁵	1		
Mineral oil ⁶	500		
PAH ⁷	40		
LOI ⁸			10%

¹Dissolved organic carbon

⁵ Polychlorinated biphenyls

²Total dissolved solids

⁶C₁₀-C₄₀

³Total organic carbon

⁷ Polycyclic aromatic hydrocarbons

⁴Benzene, toluene, ethylbenzene and xylenes

⁸Loss on ignition

2.5 Cyclone separators

Cyclones are used in various industrial processes mainly to separate solid particles from gas flows. Cyclone installations are common, for example, in power plants, food processing, chemical and mining industries. The ash classification experimented in this research is also based on cyclone technology as described in Ch. 3.1. In this thesis, the cyclones are not used to remove solid particles from gas flow but to classify the ash particles based on their aerodynamic properties, such as size and mass. Some strengths of the cyclone technology in particle separation are low capital and operational costs, robust structure without moving parts, constant pressure drop, and the possibility to be designed for high variety of process conditions and particle feeds. The disadvantages include higher pressure drop than many other particle removal technologies, wearing or fouling of the cyclone and low performance if poorly designed or operated. Besides the cyclones, the most common technologies to separate particles from gas flows are filtration and wet scrubbers. These technologies have usually their specific applications but also compete with cyclones as a separation technology in some processes. [52, p 4-11]

The principle of operation of cyclones is based on the swirling motion of dust-heavy gas. The basic design and operation principle are illustrated in Figure 5. The dusty gas enters the cyclone tangentially at the top part of the cyclone. The cross section of the inlet is typically rectangular as depicted in the figure. Swirl is developed inside the cyclone due to the cylindrical shape of the separation space and the design of the gas inlet. This swirl of the outer vortex transports the particles to the walls of the cyclone due to the centrifugal force and conveys them downward to the dust outlet at the bottom of the cyclone. An upward moving inner vortex is formed in the centre of the cyclone due to the conical shape of the bottom part of the cyclone. Some separation of particles occurs also in the inner vortex. Gas and the smallest particles exit the cyclone in the inner vortex through the vortex finder extending downwards from the cyclone roof. [52, pp. 12-13]

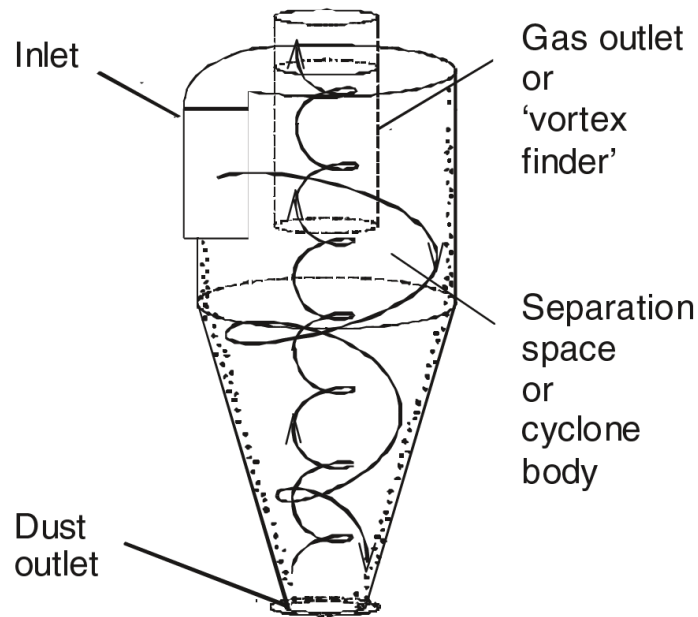


Figure 5 Sketch of a typical cyclone design and operation [52, p 12].

The mass fractions forming the particle flows related to the cyclone operation are the feed, the underflow (captured particles) and the overflow (emitted particles). If their masses are denoted with m_f , m_u , m_o , respectively, the mass balance of the particles in the cyclone is

$$m_f = m_u + m_o. \quad (1)$$

The separation efficiency η of the cyclone is defined as a mass fraction of the underflow:

$$\eta = \frac{m_u}{m_f} = 1 - \frac{m_o}{m_f} = \frac{m_u}{m_u + m_o}. \quad (2)$$

In most industrial processes, the separation efficiency is beneficial to be as high as is practically possible to achieve the limits for particle concentration or to protect the downstream equipment. High overall efficiency is, therefore, an essential target for the design and operation of a cyclone. However, this efficiency is not a very good measure of the operation of a cyclone. [52, p. 51]

A grade efficiency curve (GEC) is used to describe how the separation efficiency changes for different particle sizes. As a result, the suitability of a cyclone for a specific process is best evaluated with a GEC. Grade efficiency is the separation efficiency of a specific particle size or, in practice, a narrow range of particle sizes. A GEC can be estimated with various models or computed with measured particle size distributions of the feed, underflow and overflow fraction. The particle size distribution can be either volume or mass density distribution. If differential distributions for these fractions are $f_f(x)$, $f_u(x)$, $f_o(x)$ respectively, the grade efficiency $\eta(x)$ for particle diameter range $[x - 1/2 dx; x + 1/2 dx]$ is

$$\eta(x) = \frac{m_u f_u(x) dx}{m_f f_f(x) dx} \quad (3)$$

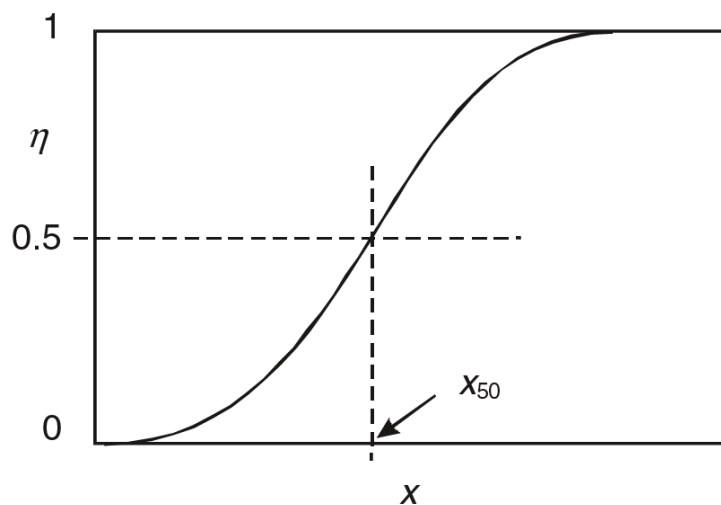
Combining equations (2) and (3) we get

$$\eta(x) = \eta \frac{f_u(x) dx}{f_f(x) dx} = \eta \frac{dF_u(x)}{dF_f(x)} = 1 - (1 - \eta) \frac{dF_o(x)}{dF_f(x)}, \quad (4)$$

where $F_f(x)$, $F_u(x)$, $F_o(x)$ are particle size distributions of the feed, underflow and overflow for particles with diameters less than x . In practice, particle size distributions are in discrete form. To compute a GEC, a discrete equivalent of equation (4) is also needed:

$$\eta \left(\frac{x_i + x_{i+1}}{2} \right) = \eta \frac{F_u(x_{i+1}) - F_u(x_i)}{F_f(x_{i+1}) - F_f(x_i)} = 1 - (1 - \eta) \frac{F_o(x_{i+1}) - F_o(x_i)}{F_f(x_{i+1}) - F_f(x_i)}. \quad (5)$$

A typical, s-shaped grade efficiency curve of a cyclone is sketched in Figure 6. It illustrates how the separation efficiency increases when particle diameter increases. This enables the cyclones to be used to classify particles with different diameters. The figure features also the cut-size, x_{50} , of a cyclone. Particles with the diameter of x_{50} are separated with an efficiency of 50%. The sharpness of the cut, i.e., the slope of the GEC curve around the cut-size is the measure of the quality of a cyclone. Ideally, the GEC would be a vertical line at x_{50} . However, this is not possible due to the various reasons. A few of those reasons are uneven particle distribution at the cyclone inlet, turbulence, design flaws, and agglomeration and attrition of particles. The reliability of a computed GEC is heavily dependent on the accuracy of the analysed particle size distributions. Even minor errors, especially in the fine end of the distribution, affect the curve shape. [52, pp. 51-52, 57-58]



A typical s-shaped grade efficiency curve featuring the separation efficiency of a cyclone on different particle diameters.

Figure 6 Sketch of a typical grade efficiency curve [52, p. 52].

One of the features affecting the performance of a cyclone is solids loading, c_o . It is a ratio of the mass of solid particles to the mass of gas entering the cyclone. At high solids loadings, a mass loading effect, also referred to as saltation effect, will occur. This means that part particles are separated from the gas stream already at the entrance of a cyclone with limited or no sensitivity to particle size. High solid loadings can mean c_o to be as low as 0.01 or even lower. The limit loading, c_{oL} , tells if the mass loading effect will occur and a cyclone becomes a two-stage separator. The mass fraction of the particles exceeding the limit loading will be separated by mass loading effects and the rest of the particles will be classified in the inner vortex. The limit loading can be calculated with a model by Muschelknautz (cited by Hoffmann et al. [52, p. 122]):

$$c_{oL} = 0.025 \left(\frac{x_{50}}{x_{med}} \right) (10c_o)^{0.15} \quad \text{for } c_o \geq 0.1 \quad (6)$$

and

$$c_{oL} = 0.025 \left(\frac{x_{50}}{x_{med}} \right) (10c_o)^k \quad \text{for } c_o < 0.1, \quad (7)$$

where

$$k = -0.11 - 0.10 \ln c_o. \quad (8)$$

The parameters needed for the calculation of the limit loading are the median particle size of the feed, x_{med} , the cut-size of the inner vortex (cut-size with low solids loading), x_{50} , and the solids loading itself, c_o . The efficiency of a cyclone increases with high solids loading due to the higher number of fines separated near the cyclone inlet. For the same reason, the classification capability is impaired as more fines exit the cyclone with under-flow. A grade efficiency curve moves upwards with increasing solids loading due to the increased efficiency and lowered cut-size. At the same time, the sharpness of the cut flattens due to the impaired classification. [52, pp, 112-128]

There are multiple other parameters affecting the efficiency and performance of a cyclone. Some physical parameters, besides the particle diameter are, the density and shape of particles as well as the density and viscosity of gas. The geometry and size of particles have also significant effect on the performance of a cyclone but they are beyond the scope of this research. All these parameters should be considered in a cyclone design to ensure good performance.

2.6 Profitability calculation methods

Profitability is almost always the most important factor defining whether an investment is worth making. Every technology needs to be both technically and economically feasi-

ble. There are several methods to evaluate the profitability of an investment. In this subchapter, a few common methods for estimating the profitability are presented. The calculation methods described here are the net present value method, annuity method and payback method. These methods are used in this thesis for estimating the profitability of an air classifier investment (see Ch. 4.2.2).

The net present value (NPV) method is popular and one of the most reliable profitability calculation methods. The present value of an investment is estimated by discounting the approximated net cash flow (NCF, the annual profits or losses of an investment) to present time, which takes the time value of money into account. Money has more value at present than in the future as it can be invested to produce additional value [53, pp. 82-83]. NPV of an investment is then calculated with the following equation:

$$NPV = \sum_{t=1}^n \frac{NCF_t}{(1+i)^t} + \frac{I_n}{(1+i)^n} - I_0, \quad (9)$$

where I_n is the salvage value, I_0 the initial investment, i the interest rate and n the holding period of an investment. The first term in the equation is the discounted present value, where the NCF may change each year (t). The second term is the discounted salvage value. Salvage value is the estimated resale value of the investment after the holding period. The interest rate can be also considered as the expected rate of return, i.e., the target for the profitability of an investment. According to the net present value method, an investment is profitable if NPV is positive. [53, p. 308-309]

In the annuity method, the initial investment is divided into equal periodic payments (PMT), annuities, for each year of the holding period of an investment. The annuity method is, in a way, an opposite to the NPV method. The initial investment is considered as the present value of an investment and the calculated PMT is the target for annual NCF. The discounted salvage value can also be included in the annuity method by subtracting it from the initial investment as in the following equation:

$$PMT = \left[\sum_{t=1}^n \frac{1}{(1+i)^t} \right]^{-1} \left(I_0 - \frac{I_n}{(1+i)^n} \right). \quad (10)$$

The annual return of an investment is

$$\text{annual return} = NCF - PMT, \quad (11)$$

where the NCF is the estimated annual net cash flow. The investment is profitable if annual return is positive. [53, pp. 93-94], [54, pp. 203-204]

The payback method is the simplest of the profitability calculation methods. It is used to give a quick approximate of the profitability of an investment. The payback period is a

time in which the profits of an investment equal the initial investment. It can be calculated as follows:

$$\textit{payback period} = \frac{I_0}{NCF}. \quad (12)$$

An investment is profitable if the payback period is shorter than the payback period target. Payback period has some limitations since it does not take time value of money into account. Furthermore, the revenue after the payback period is complete, is not considered in this method. The payback method is therefore best used with other profitability calculation methods, such as NPV or annuity methods. [53, p. 319]

3. EXPERIMENTAL

This chapter describes the experimental section of this thesis covering the test equipment, ashes used in the experiments and test methods. The test equipment is a pilot scale air classifier that utilizes multiple cyclones to separate the fine particles from the coarser fraction of ash. The ashes used in the research were gathered from five Finnish power plants that use either bubbling or circulation fluidized bed combustion technology. These ashes were classified with the test equipment in a series of test runs. Between the series, the classified ash fractions were analysed, and based on the analysis results, the new test runs were planned and executed. The analyses were ordered from a commercial laboratory and, therefore, the analysing methods are described only briefly. Additionally, the methods used for analysing the results of the experiments are presented.

3.1 Air classifier

Bulk utilization of fly ash in earth construction or as fertilizer (see Ch. 2.3) is usually the first option to the power plant producing the ash. If concentrations or leachabilities of harmful elements exceed the limit values determined in the legislation for utilization (see Ch. 2.4), the options are limited to the costly disposal at a landfill, changes in fuel mixture or combustion process, or some kind of pre-treatment to improve the quality of ash. The test equipment used in this research is one possible answer for the pre-treatment technology to lower the heavy metal concentrations in ash. It is a pilot-scale air classifier that is based on cyclone technology. The principle of separation of solid particles with cyclones is presented in Ch. 2.5. This classifier is used to split the ash, fed in the system, into three fractions of different particle size distribution. These fractions are referred in this research as coarse, medium and fine fraction. The heavy metals are supposed to enrich in the finer fractions (fine and medium) while the heavy metal concentrations in coarse fraction will decrease (see Ch. 2.2.2). The utilization potential of the coarse fraction will, therefore, improve.

The air classifier consists of a feeding system, two classification units with cyclones, two silos for the products and two fans producing the classification air. Classification process is automatized and can be controlled from a touch screen in the control unit that is attached to the classifier. Air fans are external components and cannot be controlled through the control unit. Instead, they are controlled with separate frequency converters. A simplified process diagram of the air classification process is presented in Figure 7.

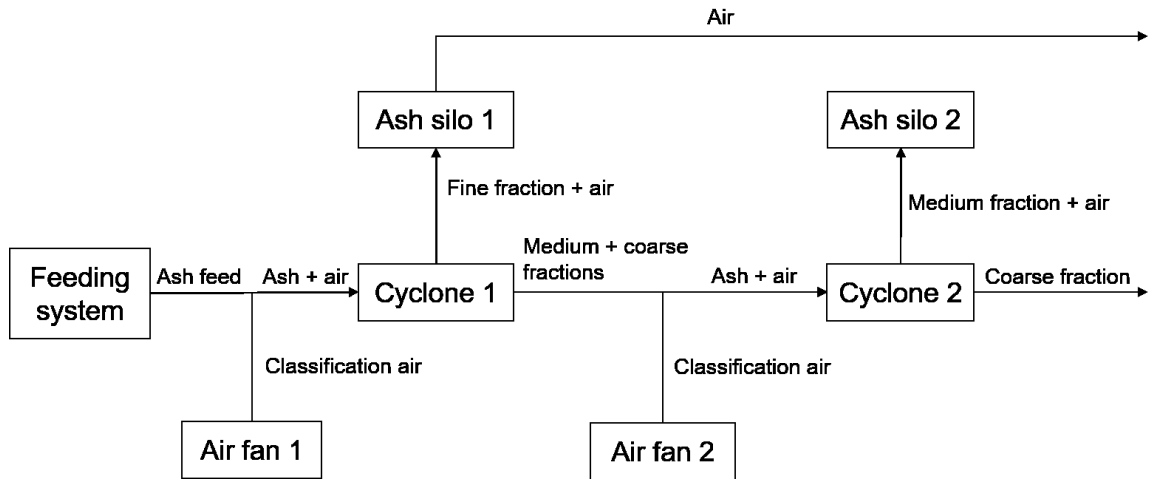


Figure 7 Simplified process diagram of the air classification process.

The operation principle of the air classifier is described based on Figure 7. Ash is fed into the process with a screw feeder. Mass flow of the ash is adjustable as is the rotation frequency of the feed screw. Classification air from the air fan 1 is mixed with the ash feed and the mixture enters cyclone 1, where medium and coarse fractions are separated from the air flow. Fine fraction is collected with backhouse filter inside the ash silo 1. The rest of the process is just repetition. Classification air from air fan 2 is mixed with the medium and coarse fractions. The coarse fraction is then separated in cyclone 2 and the medium fraction in ash silo 2. The fine and medium fractions can be collected after the test period from the bottom of the silos, whereas the coarse fraction is collected continuously during the operation of the classifier.

Cyclone technology is widely used by a variety of industries, and the parameters that affect the separation efficiency of solid particles are well known. As presented in Ch. 2.5, those parameters are the sizing of the cyclone, the particle concentration in the flow and the particle size distribution of the solid particles. The air classifier used in this research has a few additional features that are designed to change the separation efficiency of the cyclones and thus alter the mass distribution between the fine, the medium and the coarse fraction. One of these features is the two classification rotors that are installed at the top of each cyclone. The rotation frequency of motors controlling the classification rotors can be adjusted. The increase in the frequency is supposed to lower the amount of fine fraction that exits the cyclone with classification air and vice versa.

Another instrument to manipulate the separation efficiency of the cyclones is secondary air. The inlet for secondary air is at the bottom of the cyclone. This additional air flow creates a counter swirl in the cyclone, the purpose of which is to increase the amount of the fine particles collected. Increasing the secondary air flow increases also the transportation of the coarser particles into the finer fractions, thus raising the cut-size of the cyclones. The third parameter that affects the separation efficiency of the cyclones is the ash-feed-to-classification-air ratio or simply the solids loading (kg,ash/kg,air). The more

solid particles there are in the air stream, the higher the separation efficiency, i.e., the more of the ash feed goes into the coarse fraction. Figure 8 describes one of the two similar cyclones used in the test equipment. Ash and air flows as well as other components affecting the cyclone operation are presented in the figure.

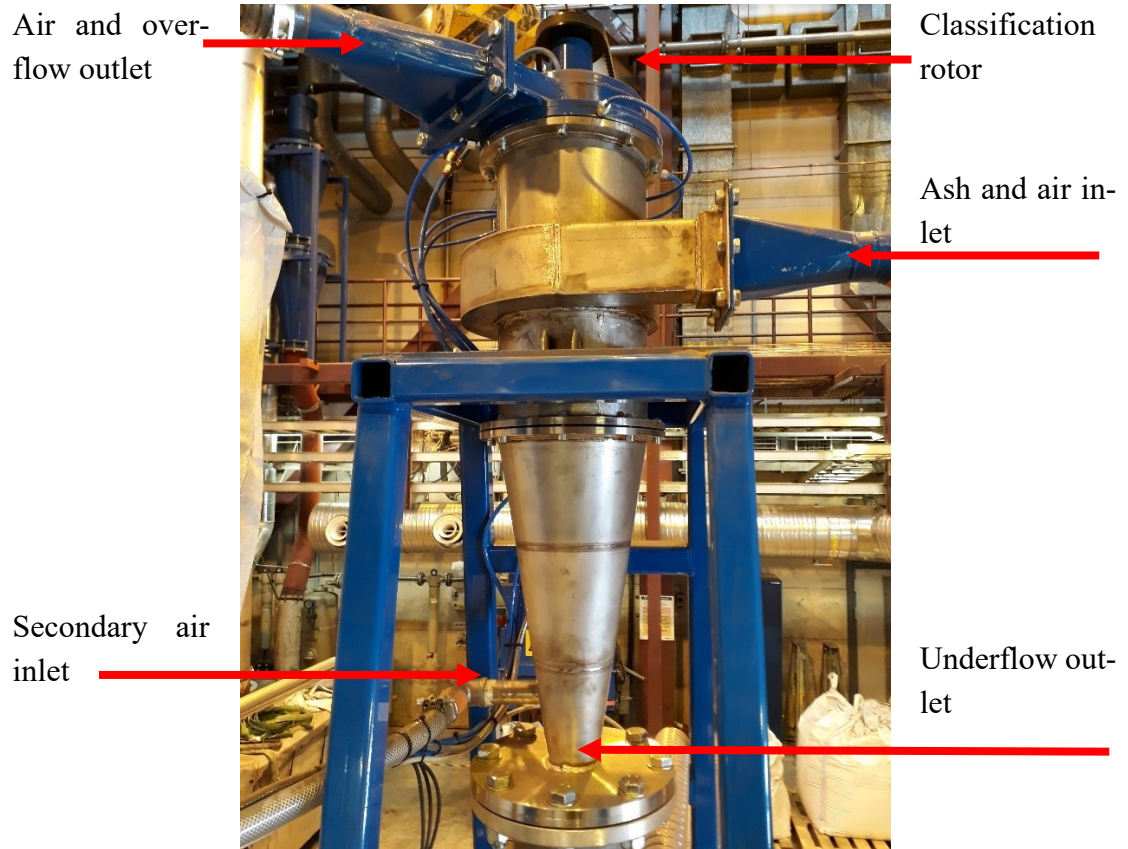


Figure 8 One of the two cyclones in the air classifier.

The cyclones in this air classifier are common cylinder-on-cone type of cyclone. The separation space is cylindrical and bottom part of the cyclone is conical. The ash and air inlet is a so-called wrap-around or scroll inlet. This means that the inlet is not directly connected to the cyclone body but there is a rectangular inlet scroll that connects the inlet to the separation space [52, p. 19]. The inlet for the secondary air is tangentially connected to the bottom of the cyclone. The purpose of the secondary air is to break the layer of solid particles on the cyclone walls so that they are entrained in the inner vortex (see Ch. 2.5). Thus, the overflow of solids should increase with increasing secondary air flow. Other cyclone related design aspects, such as the geometry, are not discussed in this thesis.

3.2 Fly ashes used in the experiments

Fly ashes used in the experimental part of this thesis were gathered from five Finnish power plants. Two of them utilize bubbling fluidized bed (BFB) combustion technology, whereas the other three uses circulating fluidized bed (CFB) technology. Although, the

combustion technologies are similar, the fuel used in these power plants and therefore their ashes differ from each other. They all use co-combustion of bio-based and other fuels. The other fuel consists of peat, coal and waste depending on the power plant. It is important that there are a wide range of ashes with different characteristics in the experiments since the ash quality can have a significant effect on the functionality of the air classifier pilot. Additionally, the test ashes cover a wide section of the co-combustion ashes produced in Finland. In this thesis, the power plants and their respective ashes are named with letters from A to E. Some details of the chosen power plants are presented in the following table.

Table 6 *Power plants that produced the ashes used in the research*

Power plant	Combustion technology	Fuel mixture (energy-%)	Sources of bio based fuels	Capacity	Sources of fly ash
A	BFB	60% peat, 40% bio	Wood chips	medium	ESP ⁵ , 2. and 3. pass
B	BFB	65% bio, 30% peat, 5% DIP- sludge ¹	Bark, forest residue	medium	BHF ⁶ , 2. and 3. pass
C	CFB	65% bio, 35% coal	Bark, forest residue, wood chips, stump chip- pings, sawdust	large	BHF, 2. and 3. pass
D	CFB	42% ² bio, 42% ² peat, 15% ² REF ³	Wood chips, sawdust, bark, forest residue	very large	BHF, 2. pass
E	CFB	32% peat, 27% coal, 25% bio, 10% SRF ⁴ , 5% recycled wood	Stump chip- pings, bark, forest residue	very large	ESP

¹De-inking-pulp -sludge

⁴Solid residue fuel

²Percentage of volume flow of the fuel

⁵Electrostatic precipitator

³Recovered fuel

⁶Backhouse filter

As seen in Table 6, power plants A and B use only bio based fuels or peat, which means that their ashes can be utilized as fertilizers in agriculture or forestry if they meet the requirements for elemental composition according to Finnish legislation (see Ch. 2.4.1). On the other hand, power plants C, D and E use coal or waste in addition to biomasses which prevents the utilization of their ashes as fertilizers. Different earth construction

applications are best suited for ash C if the concentrations of harmful elements are below the limit values set by Finnish legislation (see Ch. 2.4.2). Ashes D and E can also be utilized in earth construction, although, it requires an environmental permit, since the power plants combust waste. Other utilization possibilities can also be contemplated especially for ashes C, D and E. Similarities between power plants A and B, and on the other hand C to E, beside the possible utilization applications, are combustion technology and the capacity of the plant. Plants A and B have medium sized BFB boilers, whereas plants C, D and E have large or very large CFB boilers. The capacity difference is typical for these combustion technologies: BFB boilers are generally smaller than CFB boilers [55].

Every power plant chosen for this research utilizes co-combustion but power plants D and E have proper multi-fuel boilers. They use a wide variety of fuels including fuels produced from municipal solid waste (MSW) such as solid residue fuel (SRF) and recovered fuel (REF). The difference between SRF and REF is that characteristics of SRF are standardized [56], whereas REF is a generic term for any pre-treated non-hazardous waste. Wastes vary significantly in quality which makes it difficult to predict the composition and utilization potential of produced ashes. Therefore, pre-treatment, such as air classification, could be especially beneficial for the ashes D and E.

3.3 Ash classification experiments

The purpose of the experimental part of this research is to investigate the functionality of the pilot equipment in the classification of ash, and to provide sufficient data that can be used to further analyse the utilization potential of the test ashes. Key indicators evaluated are mechanical functionality of the classifier, typical mass distribution between the different ash fractions and their particle size distributions, the controllability of the mass distribution and the enrichment of heavy metals in fine and medium fractions. Several experiments were conducted with ashes A-E to evaluate these indicators. This test run process can be divided into separate sectors: commissioning of the air classifier, primary tests and secondary tests with readjusted process parameters.

An important part of the test run process was commissioning of the test equipment because it had not been used anywhere before. During commissioning, the basic operation of the classifier and the functionality of different inputs were evaluated. In this context, the basic operation includes automatized functions such as operation of the feeding screw and control valves. External inputs to the process were electricity, classification air produced with two fans, instrument air, secondary air and air pulses for filter cleaning from compressed air network. Especially the functionality of the fans providing classification air was uncertain before commissioning since their pressure production capability was lower than the recommended value. Low pressure of the classification air led to some changes in valve control limits. Furthermore, it was estimated that the installed fans would restrict the ash feed since they could not respond to the increasing the pressure drop across

the classifier. Therefore, most of the experiments were performed with a relatively low ash feed of about 40 kg/h.

The next step was to find adequate process parameters to acquire the desired mass distribution between coarse, medium and fine ash fractions. The primary tests were performed with these process parameters for all five ashes. An average test duration was about one and a half hour including some usage without ash feed. Total ash feed in each test was between 40 - 60 kg. Ash analyses made for samples gathered from the primary tests included particle size distribution and composition analyses. These analyses were made for each ash fraction and they were ordered from a commercial laboratory. A flow chart of the test run process is presented in Figure 9.

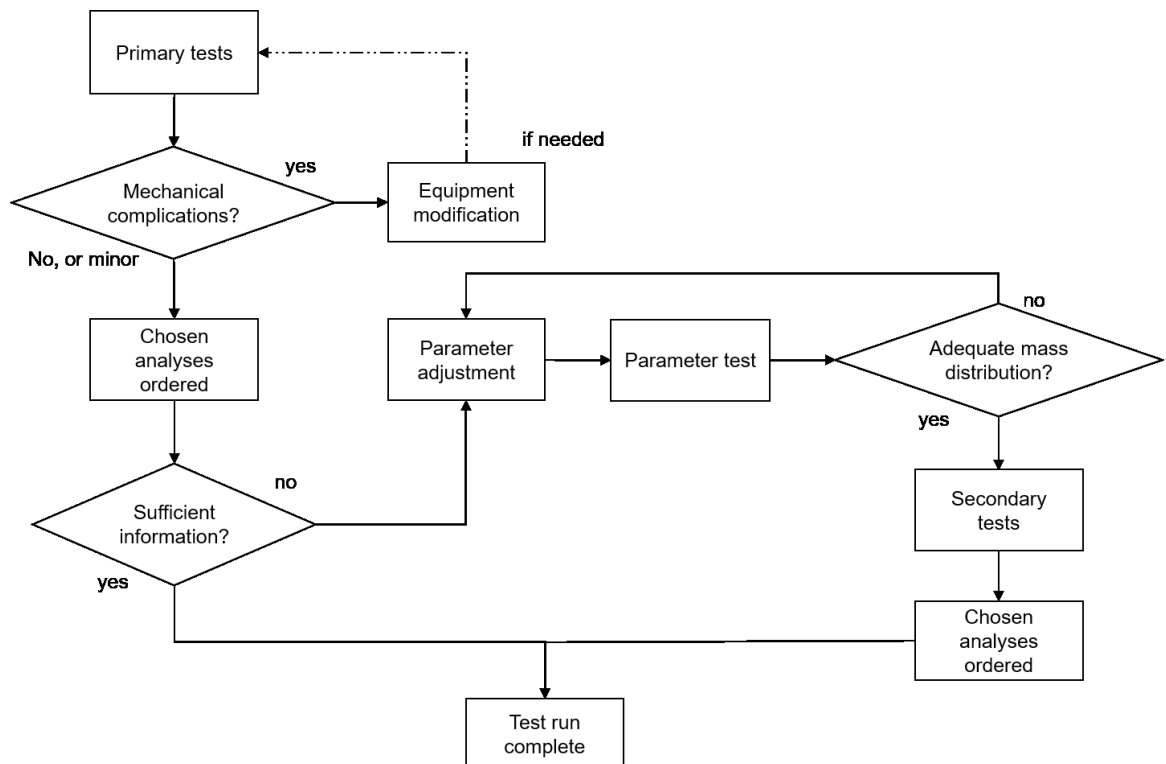


Figure 9 Flow chart of the test run process.

During the test run, a few mechanical complications occurred, some of which required changes to the test equipment. It was estimated separately for each test whether these malfunctions required a repetition of this test. Leaking of ash from different sections of the test equipment was the most common issue during the commissioning and the first experiments. The leaks posed some dusting challenges but were generally easily blocked. More serious complications were related to clogging of the backhouse filters in the product silos. The clogging of the filters led to a gradually increasing pressure drop across the filters and thus, decreasing classification air flow. Different kinds of modifications were experimented before the filter cleaning system was identified as the reason for the complications. At the beginning of the test run, it was unclear that the classifier even had a filter cleaning system that functions during the operation of the equipment. Changes to

wiring and operation settings were needed to fix the filter cleaning system but afterwards the equipment functioned significantly better. Despite the mechanical complications, the operation of the test equipment was sufficiently stable and predictable by the end of the test run.

The analysis results from the primary tests provided sufficient information for ashes A and B (see Ch. 3.2). However, a few additional tests were conducted with ash A because of operational malfunctions. For the other ashes, the secondary tests were planned based on analysis results from the primary tests. The aim for the secondary tests was to optimize the mass distribution between coarse, medium and fine ash fractions. The basic idea behind this optimization was to minimize the amount of fine and medium fractions so that the reduction of heavy metals in the coarse ash fraction is sufficient to improve its utilization potential when compared to the unclassified ash. The hypothesis was that the finer fractions (fine and medium) are expensive to dispose of due to elevated heavy metal concentrations.

The effect of different process parameters on the mass distribution were first evaluated in a series of experiments with ash C. The secondary tests were then performed for ashes C-E with the most suitable process parameters. Chosen samples from these experiments were analysed. In addition to the particle size distribution and composition analyses, leachability analyses were made on ashes A, C and D. Leachability analysis is needed for evaluating properties for landfilling or utilization in earth construction (see Chs. 2.3.3 and 2.4). After the secondary tests and the analysis results, satisfactory information of all ashes was acquired, and the test run was complete.

3.4 Laboratory analysis methods

Extensive analyses were conducted on ash samples gathered during the experiments. Particle size distribution and composition analysis were carried out for nearly every sample from primary and secondary tests (see Ch. 3.3). Additionally, leachability analyses were made on some samples. All analyses were ordered from one commercial laboratory. Next, the basic principles of analysis methods are described briefly.

Particle size distribution analyses were carried out with Malvern Mastersizer 2000 apparatus. These analyses are hereafter referred to as Malvern-analyses for simplicity. The apparatus utilizes optical bench to capture the light scattering pattern of the sample [57]. The particle size distribution that created this scattering pattern can be calculated using different theories. The preparation of the sample is an important part of the analysis since an unrepresentative or agglomerated sample gives incorrect results. Two sample dispersion units were used to prepare the samples. Hydro 2000S accessory was used on most of the samples, and Scirocco 2000 accessory was used on some especially coarse samples. Difference between these dispersion units is that a sample is dissolved in a liquid medium in Hydro 2000S [58], whereas Scirocco 2000 uses air as a medium [59].

Inductively coupled plasma (ICP) spectrometry was used to acquire the composition analyses. These analyses are hereafter referred to as ICP-analyses for simplicity. Plasma used in the analysis is usually produced from argon gas that is heated with electromagnetic field [60, p. 420]. High temperature plasma breaks all chemical bonds in a sample so elemental contents can be detected accurately with a spectrometer connected to ICP. Two versions of ICP-spectrometry were used to find all the relevant elements in ash samples, ICP- mass spectrometry (ICP-MS) and ICP- optical emission spectrometry (ICP-OES). ICP-MS generates the elemental composition from a mass spectrum [60, p. 420], whereas ICP-OES calculates the results from an emission spectrum [61, p. 332]. The trace element concentrations were determined with ICP-MS, since it can detect lower concentrations than ICP-OES. The major and minor element concentrations were determined with ICP-OES. The elements searched with each ICP-technique are presented in the following list.

ICP-MS: As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Se, Sb, Sn, Tl, V, Zn

ICP-OES: Ca, Mg, Na, K, P, Fe, Al, Si, Ti, Mn, Ba

Leachability analysis gives information about the mobility of elements in environment and it is therefore a beneficial tool to evaluate the utilization potential of ashes. Furthermore, it is required by the Finnish legislation in earth construction applications and land-filling (see Ch. 2.4.2 and 0). The two-stage batch leaching ('shake-flask') test was used as an analysis method in accordance with the standard SFS-EN 12457-3 [62]. In the first stage of the analysis ashes are leached with water at liquid to solid ratio (L/S) of 2 l/kg for 6 hours. The water is then separated and the solids are leached again with water at L/S = 8 l/kg for 18 h. The cumulative L/S for the leachability analysis is therefore 10 l/kg. Elemental concentrations are analysed from leachates for example with ICP-OES or ICP-MS.

3.5 Methods for analysing the results

3.5.1 Error evaluation

An important part of an experimental research is to evaluate error sources of the experiments. If there is a way to confirm the degree of errors, it gives credibility to the results of the experiments. In this research, mass balance calculations are performed to determine the errors between the results of elemental composition analyses. Calculating this error helps to evaluate whether the results are reliable. The sources of error affecting the results of the composition analyses and this calculation can be divided into analysis errors, sampling errors and errors related to the test equipment. Analysis errors depend on the accuracy of the analysis method and equipment. They were not provided by the laboratory that conducted the analyses so the accurate evaluation of these errors was not possible. In case of elements with low concentrations, the analysis errors may have a major impact on the total error. The lower concentration of an element, the more the inaccuracies affect

the results. Sampling errors are related to the representativeness of the samples. Main source of sampling errors are the possible differences of actual ash feed and the corresponding sample. Samples of the other ash fractions represent probably well the actual ash fraction because the mixing during the air classification process. The equipment related errors are due to the minor accumulation of ash particles in different parts of classifier as well as the inaccuracy of mass measurement of the ash fractions. The equipment related errors affect only the mass balance calculations and not the actual analysis results so significance of these errors is low considering the effect of air classification on the utilization potential of the test ashes.

The magnitude of all these errors cannot be separately evaluated so the total error is calculated based on the mass balance calculation. The results of the composition analyses for the feed ashes were compared to the calculated sums of the coarse, medium and fine fractions. Sum concentrations of different elements were calculated as mass balanced averages of concentrations in different ash fractions. Therefore, the equation for the calculated concentration is

$$C_{calculated} = \frac{C_{coarse}m_{coarse} + C_{medium}m_{medium} + C_{fine}m_{fine}}{m_{coarse} + m_{medium} + m_{fine}}, \quad (13)$$

where C_i is an elemental concentration in different ash fractions in percentages or in mg/kg, and m_i is a measured mass of the ash fractions. The error percentage was then calculated using analysed concentration as a reference value so the error equation was

$$error = \frac{C_{calculated} - C_{analysed}}{C_{analysed}} * 100\%. \quad (14)$$

Neither the analysed nor the calculated concentration is the actual concentration. Generally, the analysed concentration should better represent the actual concentration as it is not affected by the equipment related errors. If the error between analysed and calculated value is high, it has to be estimated on case-by-case basis which value is more accurate.

3.5.2 Cost estimation

An important aspect of any technology is its economic feasibility. Even though technology would function otherwise perfectly but it is not profitable, it will not be successful. In this chapter, methods for estimating the costs of an air classifier investment are discussed. Two utilization scenarios were chosen for the basis of the cost estimation. These utilization scenarios are described in Table 7.

Table 7 *The utilization scenarios for the cost estimation.*

Ash Fraction	Scenario 1	Scenario 2
Ash feed	landfill	earth construction
Coarse fraction	earth construction	fertilizing
Fine and medium fractions	landfill	landfill

In scenario 1, ash is disposed of at a landfill but with air classification the coarse fraction can be utilized in earth construction. In scenario 2, ash is utilizable in earth construction but air classification improves the quality of the ash so that it can be utilized as fertilizer. In both scenarios, the utilization potential of ash improves since the classification is automatically unprofitable if there is no improvement in utilization potential. The fine and medium fractions are landfilled in both scenarios due to the elevated heavy metal concentrations. The chosen scenarios are estimated to be the most probable and thus represent the most the actual scenarios that can be achieved with air classification. For example, the change from landfilling to fertilizer use is not included in the cost estimation since the ashes from biomass and peat combustion seldom exceed the earth construction limit values.

The air classifier pilot used in this research was the starting point of this cost estimation. The ash feed can be increased to 300 kg/h by replacing of the classification air fans and the ash feeding system. The availability of this equipment is estimated to be 80%, which corresponds to 292 days a year. The annual ash classification capacity is therefore 2100 tons. The coarse fraction accounts for 75% of the ash feed so the share of the fine + medium fraction is 25%. The capital, operational and ash related costs are included in the estimation. The capital expenditures (CAPEX) include rough estimations of the price of the classifier, the air fans or compressors, ash feed and automation system, external equipment such as piping and ash silos and installation work. Electricity consumption and employee costs were considered in operational expenditures (OPEX). Other operational costs include, for example, maintenance and sampling costs. The cost of electricity is a sum of energy and electricity transfer fees. The energy cost, 3.32 c/kWh, is an average of year 2017 as presented by Nordpoolspot [64]. Electricity transfer cost, 2.75 c/kWh, is a transfer cost for mid-sized industry (electricity consumption ~2000 MWh/a) in June 2018 provided by Finnish Energy Authority [65]. The electricity taxes and value-added taxes (VAT) are not included in the electricity costs. Total employee costs are estimated to be 50 €/h per person. It is approximated that one person uses 20% of his/her work hours controlling the classifier besides his/her other tasks so the actual classifier related employee cost is 10 €/h.

The capital and operational costs are the same in both scenarios but the difference between the utilization scenarios comes from the ash related costs. The cost for disposing the ash at a non-hazardous landfill is 130 €/t including the waste tax (70 €/t) but not including VAT (24%). This cost is based on the price list from three waste management

companies [66-68]. These companies do not provide information about costs for land-filling of hazardous ash so landfilled ashes in the cost estimation are expected to be non-hazardous. Ash is estimated to have zero value in earth construction applications and 50 €/t as fertilizer not distinguishing forest and field fertilizing. Transportation costs are approximated to be 15 €/t but they are payed only for ash disposed at a landfill. If ash is utilized, the end user pays for ash transportation. The cost estimations and profitability calculations for the two utilization scenarios are presented in the results section of the thesis, in Ch. 4.2.2.

4. RESULTS AND DISCUSSION

The functionality of the classification test equipment is evaluated based on the experience and the ash analyses gathered during the experimental phase of this research. The most important indicators that define whether the equipment is technically feasible for ash refining, are mechanical functionality, classification properties and enrichment characteristics of heavy metals and other elements between different ash fractions. An important question is: does the air classification change the utilization potential of ash? If the utilization possibilities for classified ash does not improve, for example from landfilling to earth construction, the test equipment is not feasible for that specific ash. Therefore, ash quality affects significantly to the feasibility of the test equipment. The utilization possibilities for each test ash is discussed based on the comparison of analysis results and limit values in legislation. In addition to technical feasibility, the test equipment also has to be economically feasible. Therefore, cost estimations for a few selected utilization scenarios are presented.

4.1 Functionality of test equipment

4.1.1 Mechanical functionality

The mechanical functionality is an important aspect in any technology that is attempting a market breakthrough. Although, the mechanical design is often easily improved, it may not necessarily be cost effective. Ash is usually considered as waste, and even in the best-case scenario its market value is low. Because the value of the ash cannot be raised considerably, ash refining technologies such as air classification need to be mechanically very simple, robust and automatized. Additional maintenance of the equipment and monitoring of the process increase the operational costs that directly affects the feasibility of the equipment.

The air classifier used in this research has the potential to reliably classify ashes by their particle sized distribution. Cyclone technology is used for decades in different industries and it has been proven to efficiently separate coarse particles from various gas streams. The equipment has its own automation system that should be relatively easy to connect into a larger system of a power plant or an ash refining facility. However, some changes need to be made to the current configuration before the classifier can be used extensively in ash refining. Primarily, the piping in the test equipment is made from plastic that would probably wore out in continuous operation. Although, the transparent plastic piping aided in process supervision, it needs to be replaced with steel piping for an actual industrial process. Obviously, the capacity of the classifier needs to be increased from the pilot scale

to match the ash production of a power plant. In this research, the maximum ash feed was 67 kg/h, whereas the full-scale process would need an ash feed of at least 500 kg/h.

There were some malfunctions during the test run that are described in Ch. 3.3. However, by the end of the test run, the classifier functioned rather reliably. Apart from the basic operation, there were a few features that did not work optimally or as expected. Firstly, the ash feeding screw did not have the feeding capacity that was expected. The low bulk density of ash is obviously the reason for the low feeding capacity. During the primary tests that was not a hindrance as an ash feed was set intentionally at 45 kg/h. However, during the second tests the set point of ash feed was set to 90 kg/h but depending on the ash type, the maximum feed was only 59-67 kg/h. Before the test run, the maximum ash feed was expected to be 300 kg/h based on the manufacturer's information. However, in addition to the ash feeding system, the fans providing classification air should also be replaced to correspond to the ash feed of 300 kg/h.

Secondly, the control of the mass distribution between fine, medium and coarse fraction did not function optimally. This mass distribution, or more specifically, the cut-size of the cyclones, is designed to be controlled with classification rotors, secondary air, ash feed and classification air. These features are described in Ch. 3.1. To summarize, an increase in the rotational frequency of the classification rotor, a decrease in the secondary air flow and an increase in the mass fraction of ash in classification air (solids loading) should increase the mass share of coarse fraction and vice versa. However, all these features had only a little effect to the mass distribution. Instead, it was primarily defined by the original particle size distribution of the ash feed and naturally the sizing of the cyclones.

The goal of the test run was to find an optimal mass distribution for each ash type. The basic idea was to minimize the amount of fine and medium fractions so that the reduction of heavy metals in the coarse ash fraction is sufficient to improve its utilization potential when compared to the unclassified ash. The limited effect of the controlling options reduced the results of optimization of the mass distributions from the optimal to the best achievable.

The mass distributions and key process parameters from the primary and the secondary tests and are presented in Table 8. Frequency of classification rotors and secondary air flow values in the table are ratios between the actual process parameters and the parameters used in the first test with ash A. This approach does not reveal the process parameters but gives an idea on the effect of process parameters on the mass distribution. Differences in process parameters between the primary tests with different ash types are consequences of the limited ash feed capacity, minor malfunctions or inaccuracy of control of those parameters. The tests are labelled so that letters A-E refer to an ash type and a numbers 1 or 2 refer to a primary or secondary test respectively. For example, the test C2 is a secondary test with ash C. Ash feeds are averages for each test calculated from the total mass

of the ash fractions and the test duration. The primary tests provided sufficient information from ashes A and B so the secondary tests were not needed.

Table 8 *The effect of process parameters on mass distributions.*

Test	Ash feed (kg/h)	Solids loading (kg,ash/kg,air)	Classification rotor	Secondary air flow	Coarse fraction (%)	Medium fraction (%)	Fine fraction (%)
A1	39	0.18	1	1	90.4	4.8	4.8
B1	35	0.14	1	1.7	68.3	20.2	11.6
C1	39	0.17	1	1.8	70.0	12.6	17.4
C2	67	0.34	4	0.2	74.3	12.1	13.6
D1	44	0.16	1	1.8	64.2	15.3	20.5
D2	59	0.31	4	0.2	74.7	15.8	9.5
E1	45	0.18	1	1.5	69.9	12.8	17.3
E2	61	0.30	4	0.2	74.1	11.2	13.9

Based on the information in Table 8, the behaviour of ash A differs significantly from the other ashes. The coarse fraction for ash A comprises 90% of the mass of the ash feed, whereas the corresponding value is 64-70% for the other ash types. This is due to the fact that ash A is coarser than the other ashes as will be presented later. After the primary tests, a series of experiments was conducted to evaluate the effect of process parameters on the mass distribution. The secondary tests were performed for ashes C-E with the most suitable process parameters. The aim for these tests was to lower the share of the finer fractions (fine and medium) because it was estimated that they are expensive to dispose of due to elevated heavy metal concentrations. Process parameters were adjusted accordingly: ash feed was increased to maximum for each ash, classification air flow reduced by 21-24%, frequency of the classification rotor increased four times and secondary air flow was reduced to minimum without completely stopping the flow. The effect of all these parameters combined on the share of the coarse fraction was 10.5 percentage points for ash D and about 4.3 percentage points for ashes C and E. There are no clear reasons for the differences between ash types. The reasons are related to the original particle size distributions, morphology and the maximum ash feed variation with each ash as well as the minor inaccuracies of the measurements.

The control of the classification rotor and secondary air flow were nearly maximized for the secondary tests but the classification air to ash feed ratio could still be set a little lower. As the ash feeding capacity was at its maximum, lowering the classification air flow is the only option to raise the share of the coarse fraction further compared to the secondary tests. However, determining the absolute minimum value for the classification air flow includes a risk of a blockage formation inside the equipment. Clogging would require shutting down the classifier and might damage the equipment. In summary, it is not possible to make radical changes in the mass distribution with these controlling options.

In the secondary tests, based on the mass distribution data in Table 8, the share of the fine fraction is lowered, whereas the share of the medium fraction remains almost at the same level as in the primary tests and even increases for ash D. Apparently, the first cyclone is affected more by the changes in process parameters than the second cyclone. This is probably due to the changes in solids loadings between the cyclones. Solids loadings in general have significant effect on cyclone performance as described in Ch. 2.5.

The solids loadings are relatively high in every test so some of the solid particles are separated at the cyclone entrance with limited to no classification. This certainly affects the classification performance since fine particles are partly separated with coarse fraction. Reducing the solids loading would probably improve the classification but it would require a heavy increase in classification air flow and/or decrease in the mass flow of ash. The former is probably impossible with current air fans. Reduced solids loading would also lead to an increase in the mass share of fine and medium fractions that would be against the goal of minimizing those fractions. Furthermore, the solids loading effect was not considered during the initial planning of the test run and, thus, was not taken into account during the tests. The effects of solids loading to the classification of the test ashes is discussed later in more detail.

4.1.2 Classification of fly ash

The classification performance of the test equipment is one of the indicators of its functionality. This performance is directly connected to the performance of the cyclones in the equipment. The effectiveness of the cyclones in separating the coarse particles from the fine primarily defines this classification performance. The cut-size and sharpness of the cut are the key factors that define whether these cyclones perform adequately in classification of ash. These parameters are defined in detail in Ch. 2.5. Ideally, the cut-size could be controlled with the classification rotors and the secondary air flow. However, as explained in the previous chapter, these control features had little effect on the mass distribution i.e. the cut-size of the cyclones. In this chapter, the classification performance of the cyclones for each test ash and the features affecting it are evaluated.

The classification performance is evaluated for each ash based on the particle size distribution analyses presented in the following charts. Based on these distributions some further analysis is conducted about the cyclone performance for each ash type. These results are mainly from the primary tests since secondary tests were only performed for ashes C-E. Furthermore, there were no major changes in particle size distributions in the secondary tests. Particle size distributions are presented as volume distributions for each ash fraction. Therefore, larger particles contribute substantially on the distribution as volume is proportional to the third power of the particle diameter. Particle size on the x-axis is on a logarithmic scale to clarify the effect of the cyclone on the distribution. On the right side of the figures are the values for average particle diameters, $d(0.5)$. This marking states that 50 volume percent of an ash fraction are smaller than this diameter. Average

particle diameter gives little information about the particle size distribution but provides a quick outlook on the effect of classification. Similarly, other characteristic diameters $d(0.1)$ and $d(0.9)$ are used to give together a rough estimation about the particle size distribution.

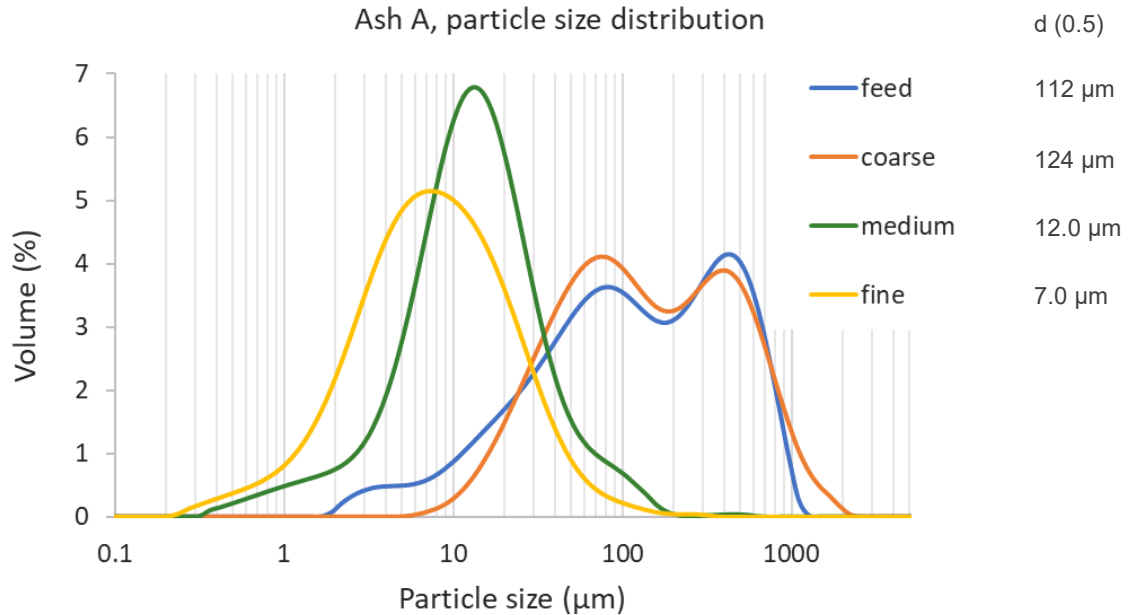


Figure 10 Particle size distribution of ash A from a primary test

Ash A is the has the largest particle size average from the test ashes. As seen in Figure 10, the average particle diameter is 112 μm . The particle size distribution of the feed ash is also quite wide as the other characteristic diameters are: $d(0.1) = 15.4 \mu\text{m}$ and $d(0.9) = 526 \mu\text{m}$. The feed ash has two separate peaks at about 80 and 400 μm . One explanation for this may be that the ash feed includes sand particles that have larger average particle size than ash itself. This sand could come from fractioning of the bed material or along the biomass and peat combusted in power plant A. Relatively small amount of sand could cause the effect seen in Figure 10, since large particles contribute significantly to the volume distribution. This issue is further discussed in Ch. 4.1.4.

Based on the mass distribution data in Table 8, the mass share of the fine and the medium fraction are both 4.8%. This means simply that there are not as many fine particles to be separated. The share of the fine and the medium fractions can be seen in the difference in the particle size distributions of the feed ash and the coarse ash. For example, about 90% of particles below 10 μm are transferred from the feed ash to the fine and the medium fractions. Another observation that can be made from Figure 10, is that the medium and the fine ashes have quite similar particle size distributions. The reason is that the process parameters and the cyclones are similar. The second cyclone is basically collecting the particles that the first cyclone left behind.

In Figure 10, fine and medium fractions seem to include fine particles and coarse ash large particles that do not exist in the feed ash. These differences may be partly due to analysis errors but attrition and agglomeration of particles during the classification have undoubtedly more significant effect. Attrition is caused by cross-particle collisions and collisions between particles and inner walls of cyclones and other components. Agglomeration is also caused by cross-particle collisions but instead of wearing the particle are stuck to each other. Particle attrition and agglomeration had some effect on performance of the cyclones as explained later but they did not have major impact on particle size distributions or other test results.

The cyclone performance is further analysed by computing the grade efficiency curve (GEC) for each ash. The theory behind cyclone performance is presented in Ch. 2.5. GEC shows the cyclone efficiency for each particle size. In this context, the cyclone efficiency is the volume ratio of the underflow and the ash feed. The GECs are computed from the particle size distribution data using equation (5). The sum of the overflow and underflow was used instead of the ash feed data to minimize the effect of sampling and analysing errors on the results. Furthermore, the fine end of the particle distribution data was cut out from the charts because it inflicted unnatural fluctuation on the grade efficiencies for the particles with a diameter below $0.6\ \mu\text{m}$. A reason for that may be the attrition of ash particles during the classification process. Despite the effect on the GECs, the particle attrition did not have a major effect on other results. Another reason for this fluctuation in GECs, are errors in particle size distribution analysis. Minor inaccuracies in volume shares of small particles affect the calculation much more than the inaccuracies in the analysis of the larger particles.

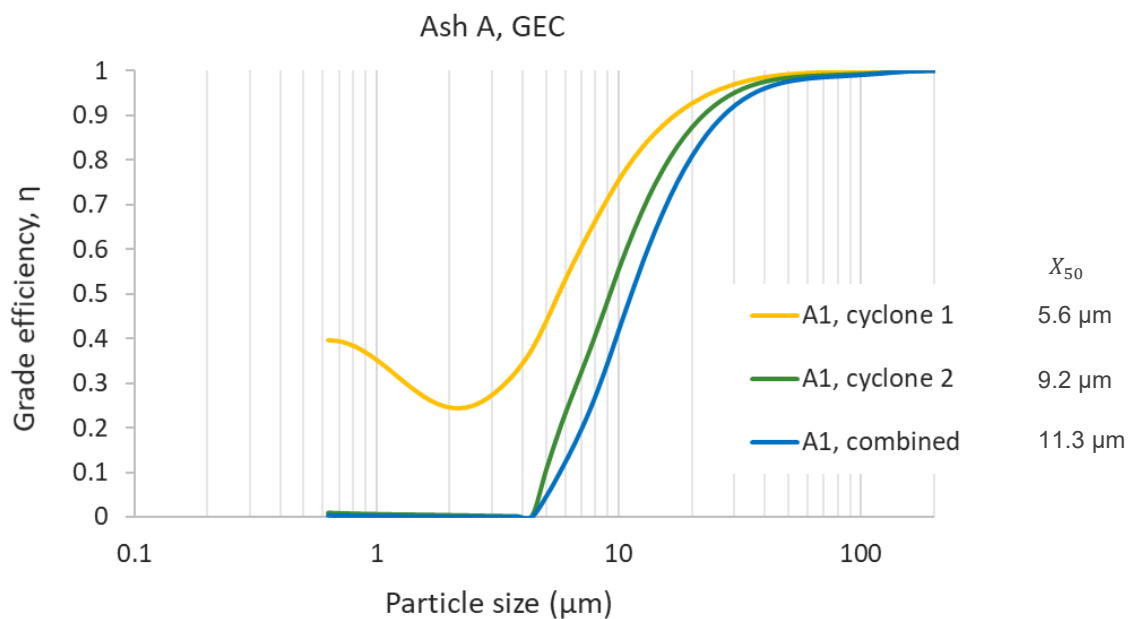


Figure 11 Cyclone grade efficiency curves for ash A

Grade efficiency curves for the primary test with ash A are presented in Figure 11. GECs are computed separately for both cyclones and in the third curve the effects of the cyclones are combined. The cut-size x_{50} for each curve is visible on the right side of the figure. This cut-size corresponds to the particle size that is separated by 50% efficiency. For clarification, the ash fractions (feed, coarse, medium and fine) forming the overflow, the underflow and the ash feed for each cyclone or their combination are depicted in the following table.

Table 9 *Ash fractions forming the mass flows in cyclones*

	Cyclone 1	Cyclone 2	Combined
Feed	feed	medium + coarse	feed
Overflow	fine	medium	fine + medium
Underflow	medium + coarse	coarse	coarse

Cyclone 2 and combined cyclones have a proper GEC shape. The grade efficiency goes from 0 to 1 and the incline is relatively steep. On the other hand, cyclone 1 has considerably flatter curve and elevated grade efficiencies for the smallest particles. Hoffman et al. [69] explain this phenomenon by agglomeration of fine particles in the piping before cyclone inlet. The finest particles tend to stay in the agglomerates as the surface forces that keep them bound are stronger than the inertial forces trying to break the agglomerates. The difference in x_{50} of cyclones 1 and 2 is mainly explained by the coarser particle size distribution of the ash feed for cyclone 2. Solids loadings differences could also be a reason for this difference since increasing solids loadings would move the GEC to the left and thus improve the separation efficiency of the coarse fraction. However, solids loadings hardly affect in this test as they are very similar for the cyclones 1 and 2, 0.174 and 0.183 kg,ash/kg,air, respectively.

The effect of solids loading to the classification performance could be estimated with a limit-loading calculated with equation (6). As described in Ch. 2.5, if the solids loading of the cyclone is larger than the limit loading, a mass loading effect will occur. There, part of the ash feed is separated in the cyclone inlet and exits with the underflow with limited or no classification. However, using equation (6) requires the cut-size of the inner vortex that cannot be calculated from the data obtained in this test run. The information about particle densities would also be needed for an accurate calculation of average particle size of the ash feed, x_{med} . Some estimations can still be made if cut-size of the inner vortex is replaced with the final cut-size of a cyclone presented in the GEC-charts, and the x_{med} is calculated assuming uniform particle density.

Limit-loadings calculated with these assumptions vary from 0.0014 to 0.0049 kg,ash/kg,air for all primary and secondary tests performed during the test run. Corresponding solids loadings vary from 0.14 to 0.36 kg,ash/kg,air so the mass loading effect is certainly occurring, although its magnitude cannot be accurately evaluated. Based on

these limit-loading values over 95% of the ash feed of all the test ashes should be separated by mass loading effect rather than classification based on swirling flow. However, the mass loading effect of this magnitude was not observed in this research. This is due to either the solids loadings simply not having a significant effect in these tests, widely inaccurate limit-loadings, or the Muschelknautz Model, that introduced the limit-loading, not fully applying for these tests. For example, the mass loading effect does not cause the flattening of the GECs as reported by Hoffmann et al. [69].

A reference classification test with low solids loading (about 0.001 kg,ash/kg,air) would be needed for the evaluation of the actual effect of the solids loading on the classification. However, this would require much larger production of classification air and/or much lower ash feed. The minimum achievable solids loading with the current classifier is about 0.03 kg,ash/kg,air. Lower solids loadings would require at least new air fans and larger diameter piping. Keeping in mind the final target of the large-scale air classifier, such changes into process design are not feasible since the increase in ash feed would require even larger air production capacity and other components.

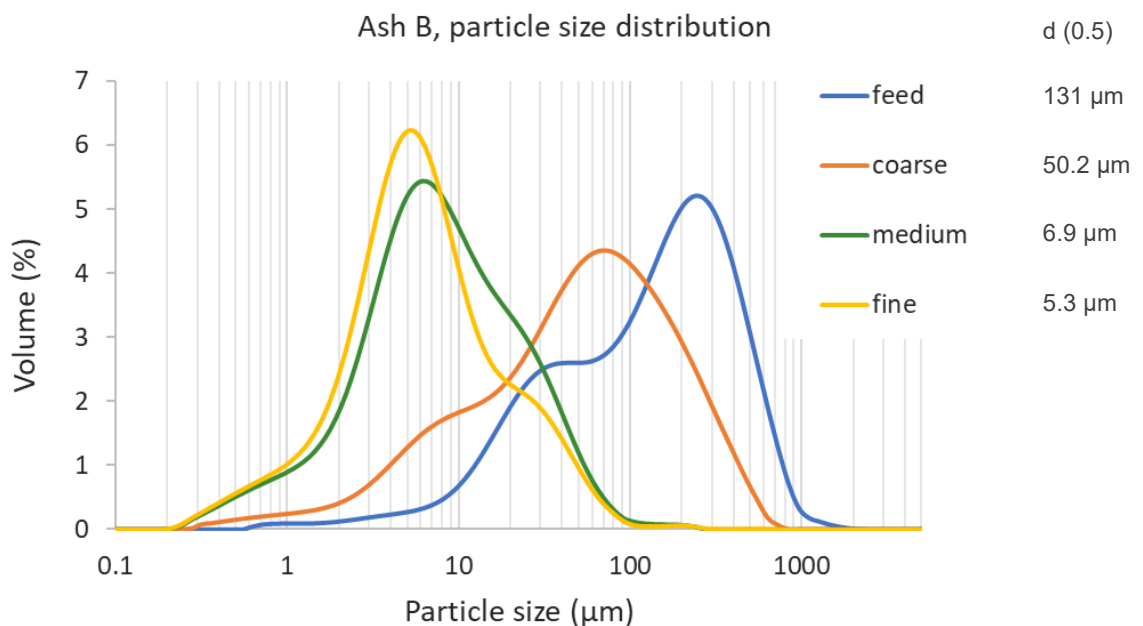


Figure 12 Particle size distribution of ash B from a primary test

Particle size distribution of ash B in Figure 12 is not correct. Based on the figure, the average particle size of the feed ash is much larger than that of the coarse fraction. When fine particles are separated from the feed ash, the volume share of larger particles should naturally increase for the coarse ash. The reason for the mismatch of size distributions is probably due to particle agglomeration. This agglomeration may have happened during the particle size analysis but the ash particles were more likely already agglomerated during initial sampling. The rigorous flow in the classifier then separated the agglomerated particles from each other. Another option is that the large particles were ground into finer

particles during the classification. However, the ash felt somewhat sticky during the sampling, which supports the dispersing of the agglomerates rather than the grinding of the large particles. This stickiness may be due to the de-inking-pulp -sludge (DIP-sludge, see Ch. 3.2) combusted in the power plant B. Similar stickiness was not encountered with other test ashes and DIP-sludge was only used in power plant B. Overall, the classification performance was rather poor for ash B, possibly due to the stickiness. The sharpness of the cut is not optimal and the coarse fraction has a large number of particles below 10 μm , about 17%. Poor classification performance was one of the reasons why secondary tests were not performed for ash B. Other reasons are discussed in Ch. 4.2.1.

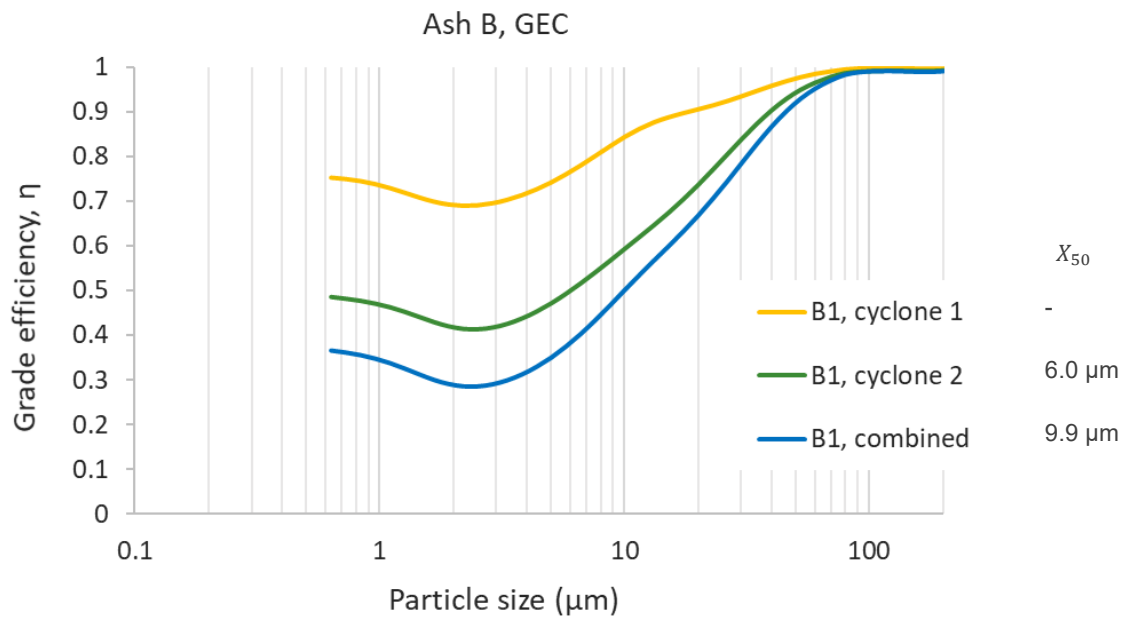


Figure 13 Cyclone grade efficiency curves for ash B

The Grade efficiency curves for ash B are presented in Figure 13. The GECs are much flatter compared to those of ash A. It could be seen already from particle size distributions in Figure 12 that classification performance for ash B was poor and the GECs confirm this observation. The cut-size for cyclone 1 could not even be calculated because the separation efficiency for all particles was above 50%. The reason for flat GECs may be partly caused by high solids loadings. However, the solids loadings were not any higher than for other ashes. In fact, they were 0.14 kg,ash/kg,air for both the cyclones, whereas the average in the primary tests of the other ashes was 0.17 kg,ash/kg,air. This implies that the observed stickiness of the ash B had greater impact on the classification performance. The stickiness of ash particles probably causes them to stay bound in the agglomerates more easily than was observed with other ashes.

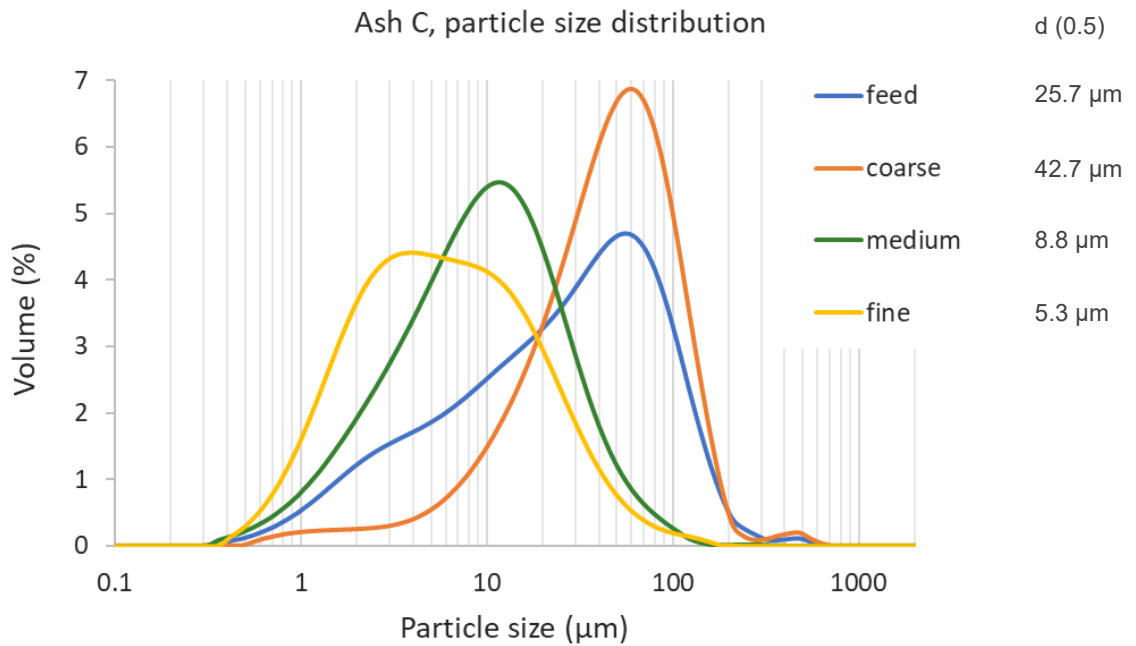


Figure 14 Particle size distribution of ash C from a primary test

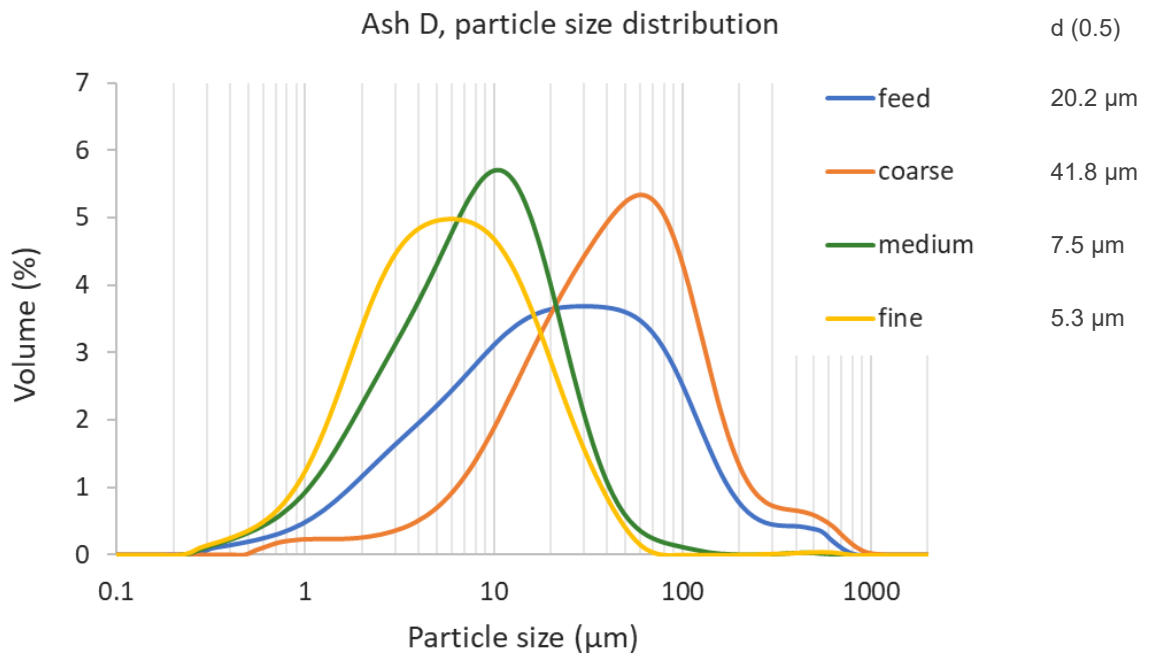


Figure 15 Particle size distribution of ash D from a primary test

Ashes C-E are all from CFB boilers with similar combustion conditions. This can be seen in the similarity of the particle size distributions in Figures 14-16. The average particle size of feed ashes varies from 20.2 μm of ash D to 28.1 μm of E. The other characteristic diameters had also little variance, $d(0.1)$ of ash feeds C-E was 2.7-3.8 μm and $d(0.9)$ was 94-116 μm . Cyclones are functioning steadily because the distributions of the other ash fractions are also similar. However, coarse fractions of ashes C-E include about 10% of particles below 10 μm . The separation efficiency of those particles is only about 65%.

Compared to the ash A, the efficiencies of the cyclones are significantly worse. This is partly due to the finer particles of ashes C-E but there are also other factors affecting cyclone performance that are discussed next.

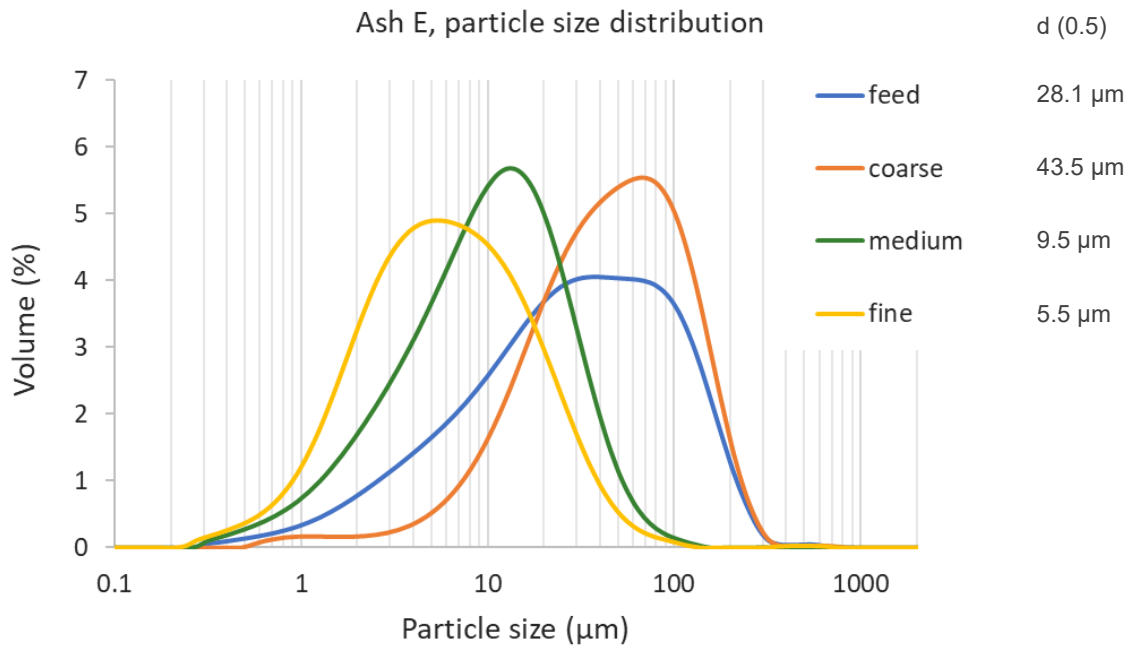


Figure 16 Particle size distribution of ash E from a primary test

Grade efficiency curves for ash E are presented in Figure 17. GECs of ash E were chosen to represent also ashes C and D since they were very similar. The curve from the secondary test is also added to the figure for comparison. The curve shapes of these GECs are the same as the cyclone 1 curve of ash A in Figure 11. Grade efficiencies have a low limit at 2-3 μm and they rise for the smallest particles. As explained before, this implies that agglomeration of the smallest particles occurs inside the classifier. Otherwise, the cyclone performance of the ashes C-E is worse than for ash A but significantly better than for ash B. The difference compared to ash A is basically due to the finer initial particle size distribution of the ashes C-E. This can be already seen from the mass distributions in Table 8 and GECs support this conclusion. The combined cut-size is dropped from 10.4 μm of the primary test to 7.6 μm of the secondary test which was the goal of the secondary tests. However, this did not have significant effect on the mass distribution as can be seen in Table 8. Flatter curve shapes suggests that the solids loading has more significant effect on classification performance for ashes C-E that can also be due to the finer particle size distribution of the ash feed. The effect of increasing solids loading can be seen when comparing combination curves from the primary and the secondary tests. The curve of the secondary test moved slightly upward which is probably due to the increased solids loading. The solids loadings for the primary and the secondary tests are 0.18 and 0.30 kg,ash/kg,air respectively. Similar effect can be seen with ashes C and D as well.

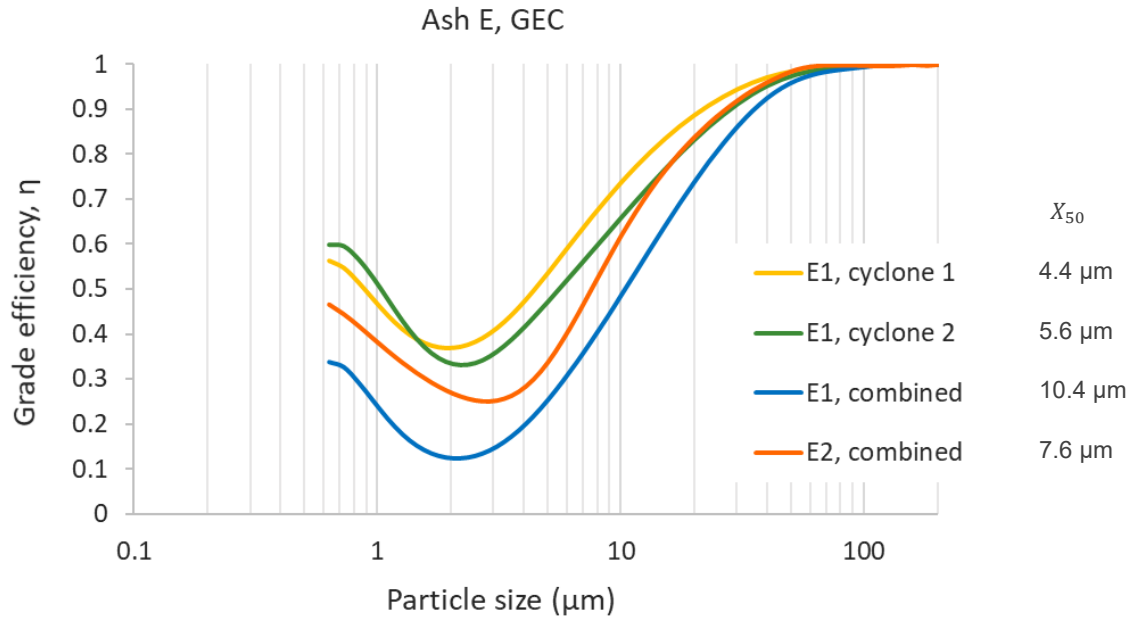


Figure 17 Cyclone grade efficiency curves for ash E

Based on the particle size distributions and grade efficiency curves, the original particle size distribution of a test ash was the most important feature affecting the classification performance. Ash A had clearly the largest average particle diameter and the classification efficiency was clearly the highest. Furthermore, the grade efficiency curves were the closest to the optimal besides the classification of the smallest particle in cyclone 1. The classification performance for ash B was poor overall. This was probably due to the stickiness of the ash particles that was most likely caused by DIP-sludge combusted in the power plant B. The other test ashes had very similar particle size distributions that resulted in similar classification performances. The high solids loadings had some effect on the classification but the magnitude of the effect is unsure due to a lack of a reference test with low solids loading. The Ch. discusses how classification performance affects the enrichment characteristics of different elements.

4.1.3 Elemental compositions of test ashes

The elemental compositions of the test ashes were analysed with either ICP-MS or ICP-OES method as described in Ch. 3.4. The results of the analyses for each ash are presented in the following tables. These results are from primary tests and it is separately discussed, what effects the secondary tests had to the elemental concentrations for ashes C-E. The composition tables are divided into two: one for major and minor elements (> 0.1 weight-%) and another for trace elements. It is worth noting that major and minor elements are expressed in percentages and trace elements in mg/kg.

Concentrations of all ashes in the tables are compared to the limit values of Finnish legislation concerning ash utilization as fertilizers (see Ch. 2.4.1). The concentration values

are highlighted if they exceed, or in case of nutrients, are below the limit values. The values that exceed limit values for fertilizing in agriculture but are below the limits for forestry are highlighted in orange, the values exceeding both limits are in red and the values that are below any of the Ca or K+P limits are in blue. These blue values do not prevent the ash utilization because other fertilizer products may be mixed with ash to increase the nutrient concentrations. This comparison to fertilizer limit values is relevant only for ashes A and B as fuels (coal and/or waste) used in power plants C-E prevent the fertilizer use of their ashes. However, there are no concentration based limit values in earth construction or landfilling, and it is easier to compare ashes with each other when all the values are marked in the same manner. The utilization potential of different ash fractions are further discussed in Ch. 4.2.1.

Table 10 Concentrations of major and minor elements in ash (%) for each ash type.

Ash type	Ca	Mg	Na	K	P	Fe	Al	Si	Ti	Mn	Ba	
A	feed	5.4	1.1	1.6	2.8	0.6	5.9	7.4	20	0.27	0.18	0.14
	coarse	5.0	1.1	1.9	3.0	0.5	5.9	8.1	23	0.28	0.16	0.13
	medium	11	2.0	1.3	3.1	1.3	9.5	8.5	18	0.35	0.46	0.21
	fine	13	2.4	1.1	2.9	1.8	9.5	8.1	15	0.32	0.55	0.23
B	feed	41	0.83	0.35	0.95	0.23	1.3	5.0	8.0	0.14	0.12	0.04
	coarse	41	0.73	0.41	1.0	0.19	1.3	5.1	8.8	0.16	0.10	0.04
	medium	44	0.86	0.29	0.98	0.3	1.5	4.7	6.6	0.16	0.15	0.06
	fine	43	0.94	0.30	1.0	0.38	1.7	4.4	6.0	0.18	0.18	0.07
C	feed	18	1.1	0.68	2.0	0.36	2.9	4.9	15	0.27	0.21	0.21
	coarse	17	0.95	0.70	1.9	0.22	2.8	4.6	16	0.22	0.13	0.15
	medium	17	1.4	0.70	2.3	0.64	3.6	5.9	14	0.32	0.33	0.30
	fine	18	1.4	0.73	2.3	0.73	3.1	5.9	13	0.34	0.38	0.31
D	feed	20	1.8	1.1	2.4	0.63	5.1	6.3	13	0.38	0.28	0.12
	coarse	20	1.5	1.1	2.2	0.35	4.5	5.9	14	0.29	0.18	0.09
	medium	20	2.3	1.1	2.7	1.0	5.8	6.2	12	0.5	0.42	0.17
	fine	21	2.5	1.2	2.8	1.2	6.4	6.4	11	0.55	0.47	0.17
E	feed	9.8	1.4	1.8	2.9	0.63	3.8	8.4	20	0.51	0.23	0.19
	coarse	8.5	1.3	1.8	2.9	0.45	3.5	8.2	23	0.4	0.17	0.15
	medium	14	1.8	1.5	2.6	0.97	4.6	8.0	17	0.69	0.34	0.23
	fine	14	1.9	1.6	2.6	1.2	4.7	8.2	16	0.85	0.40	0.30

The major and minor elements concentrations in the test ashes are presented in Table 10. The most common elements in the test ashes are Ca, Si, Al and Fe apart from oxygen that is not included in the composition analyses. Naturally, the fuel determines primarily the concentrations of major elements in ash. Elemental compositions of test ashes vary surprisingly little despite the differences in the fuel mixtures (see Ch. 3.2). All power plants providing ash for this research, except for the plant C, use a large share

of biomass and peat in their fuel mixture that might explain the similarity in the elemental compositions. However, there are some significant concentration differences between ashes and a few reasons for this are easy to distinguish. For example, Ca content in ash A is only 5.4%, whereas it is 41.3% in ash B. Power plant A uses a fuel mixture with 60 energy-% (share of the total heating value for the fuel) peat that has low Ca content and power plant B uses fuel with 5 energy-% of DIP-sludge with high Ca content but low heating value. This means that DIP-sludge has much higher mass share than 5%. This sludge is also a reason for low nutrient (K and P) concentrations in ash B.

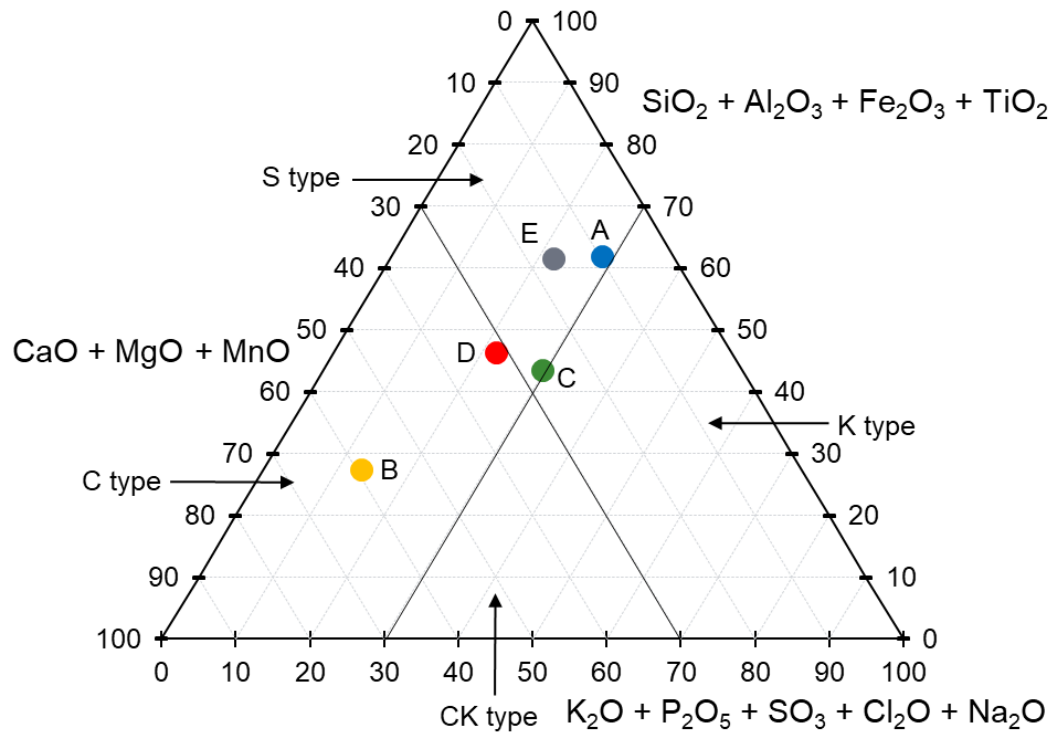


Figure 18 The test ashes presented in an ash classification system.

Besides the classification by particle size, ash can be classified by type as presented in Ch. 2.1.1. The classification system introduced by Vassilev et al. [3] was applied to the test ashes in Figure 18. Although, the classification system was intended for biomass ashes, it can also be used to classify co-combustion ashes. Based on Figure 18, ashes A, E are clearly S type ashes, and B is C type ash. Ashes D and C are in the middle of the diagram so they have a mixture of elements from all ash types. When comparing these results to Figure 1, it can be seen that ashes A and E resemble coal and peat ashes somewhat and ash B resembles wood and woody biomass ash. The data points in the figure are based on the elemental concentrations of the feed ashes from Table 10. Some modifications were made to those concentrations since the classification system requires concentrations as oxides. For example, the Ca content in ash A is 5.4% and CaO content is then $5.4\% \cdot M_{CaO}/M_{Ca} = 7.6\%$, where M is the molar mass. Furthermore, S and Cl concentrations were not included in the analyses so the SO_3 and Cl_2O contents were obtained by subtracting the sum concentrations of other oxides from 100%. This is a quite

accurate assumption since the total content of Ba and all the trace elements were between 0.1-0.5 % for the test ashes. Unburned carbon is also left out of the analyses and may produce some error to the SO₃ and Cl₂O concentrations.

Table 11 Concentrations of trace elements in ash (mg/kg) for each ash type.

Ash type	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Sb	Sn	V	Zn	
A	feed	33	2.2	17	62	75	0.36	8.7	43	39	26	1.2	2.3	100	310
	coarse	14	0.78	16	66	54	0.03	5.3	44	21	18	0.6	1.3	82	170
	medium	130	8.2	31	180	200	1.1	32	120	130	45	18	11	130	1100
	fine	230	16	40	140	250	2.5	48	96	190	57	21	17	140	1800
B	feed	7.7	1.3	5.8	33	120	0.13	4.6	21	16	5.5	0.61	3.5	24	300
	coarse	5.8	1.1	7.3	30	98	0.02	3.9	23	18	6.9	1.3	3.7	25	250
	medium	11	2.3	6.7	32	140	0.17	6.3	27	32	9.4	6.8	5.4	31	380
	fine	17	3.1	13	35	160	0.4	7.6	33	40	11	12	6.7	37	500
C	feed	20	2.5	15	83	43	0.21	35	150	29	8.6	2.3	2.7	130	380
	coarse	10	1.1	11	79	28	0.06	20	130	22	7.7	1.1	2	81	230
	medium	44	4.9	20	140	72	0.51	58	190	49	15	4.6	4.3	160	580
	fine	49	6.2	25	110	80	0.45	67	200	48	13	5.5	4.9	210	750
D	feed	26	6.2	41	150	750	0.65	11	120	200	15	95	27	83	930
	coarse	15	3.2	55	160	500	0.35	8.1	130	160	11	50	18	61	750
	medium	47	10	29	170	1100	0.95	19	130	230	23	150	39	120	1300
	fine	55	12	43	170	1300	1.3	21	140	250	26	180	45	140	1500
E	feed	38	4.5	29	110	510	0.66	9.6	79	150	11	72	27	97	1500
	coarse	28	2.6	28	100	410	0.35	6.6	76	100	7.9	41	20	78	1300
	medium	60	8.2	38	160	760	1.3	17	110	240	19	110	35	140	1900
	fine	80	10	57	190	910	1.6	21	140	290	20	160	45	180	2700

The trace element concentrations in the test ashes are presented in Table 11. It can be clearly seen that the waste combusted in power plants D and E raises the concentrations of trace elements significantly. Most of the elements have higher concentrations in these ashes than in others. Especially Cu, Pb and Sb contents are significantly elevated due to the waste combustion. An exception is ash C that has highest concentrations in Ni, Mo and V. Especially Mo content is surprisingly high as it is over three times higher than the second highest concentration in ash D. The coal used in the plant C has probably high Mo content as well. Ash B has overall the lowest trace element concentrations. This is due to the high biomass share in the fuel mixture of plant B. In Tables 10 and 11, there are some values that appear to be clearly inaccurate. For example, Cr in ash A in Table 11 seems to enrich in all ash fractions which is obviously not possible. These inaccuracies are results of errors during the analyses, sampling and possible differences in the compositions of the analysed ash feed and the actual ash feed. These error sources are evaluated with mass balance calculations in Ch. 4.1.5.

4.1.4 Enrichment characteristics of elements

The basis of this research is the theory of enrichment of heavy metals in the fine ash particles. Those fine particles are then separated with the air classifier. The improvement of the utilization potential of the coarse fraction of ash depends heavily on whether the enrichment of heavy metals in the fine ash fractions is efficient enough. As mentioned in Ch. 2.2.2, this enrichment is due to the volatilization of heavy metals in the furnace and subsequent condensation in the flue gas duct. In this chapter, the enrichment characteristics of all analysed elements are evaluated. These include major, minor and many of the trace elements. It is also discussed whether more accurate classification could improve the enrichment.

The enrichment of elements is illustrated in the following figures. The enrichment in the combination of fine and medium fractions is chosen to represent also the other enrichment characteristics. The combination concentration is simply a mass-weighted average of the two fractions. This combination ash fraction is called hereafter as fine + medium ash. There are a few reasons for this combination. The enrichment characteristics of different elements in fine and medium fractions are quite similar based on the data in Tables 10 and 11. Trace elements enrich generally a little more to the fine fraction than the medium fraction since the fine fraction is indeed a little finer than the medium fraction as seen in Ch. 4.1.2. In practice, however, both fractions are most likely utilized or disposed of together to avoid unnecessary transportation and search for an additional utilization target.

The enrichment characteristics can also be estimated from the same figures as the elements enriching in fine and medium fractions, are reduced from the coarse fraction. Enrichment factor (EF) is used to measure the quantity of the enrichment. EF is calculated simply as a ratio of an element concentrations in fine + medium ash and in the feed ash. However, the concentration in the feed ash is the mass-weighted average of the fine, medium and coarse ashes to minimize the effect of errors made during sampling and analysis. When $EF > 1$, the element enriches in the fine + medium fraction and is therefore reduced from the coarse fraction. If $EF = 1$, no enrichment or reduction occurs. When $EF < 1$, the element is reduced from the fine + medium fraction and enriches in the coarse fraction.

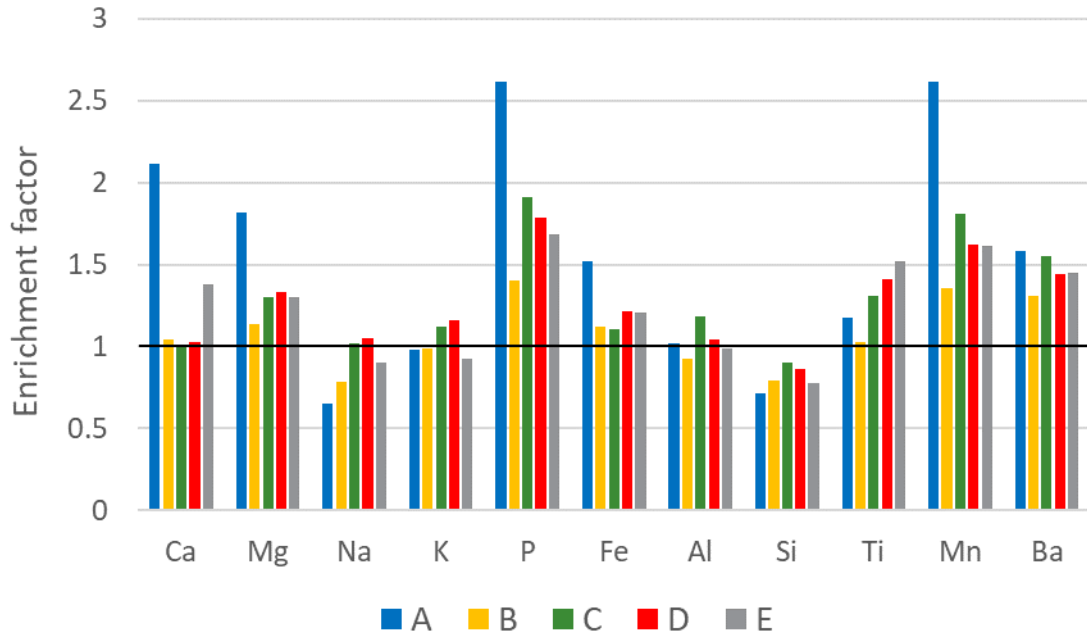


Figure 19 The enrichment of the major and minor elements in fine + medium ash fraction for each test ash

The enrichment of major and minor elements in fine + medium ash is illustrated in Figure 19. The elements that clearly enrich in the finer fractions are in the order of decreasing EF P, Mn, Ba, Mg and Fe. Si is the only element that clearly enriches in the coarse fraction for all the ashes. Also, Ti enriches slightly in fine + medium ash in all other ashes except B. The other elements have EF close to 1 or mixed results between ashes. For example, EF of Ca for ashes B, C and D are very close to 1, whereas it is 1.4 for ash E and 2.1 for ash A. K and Al have very similar enrichment characteristics as neither of them enriches significantly in any ash fraction. Similar enrichment characteristics for Ca, Fe, Si were reported by Ohenoja et al. [18]. However, the accurate comparison with this study is not possible, since their research is about the classification in electrostatic precipitator instead of air classification, and their paper is lacking the values of actual concentrations.

Another observation can be made from Figure 19. EFs of Ca, Mg, P, Fe, and Mn are much higher for ash A than for the other ashes. Different modes of occurrence of elements in the test ashes might explain part of this phenomenon. In other words, different compounds of the same element enrich in different ash fractions as Ohenoja et al. [18, p. 611] also estimated referring to the research by Boström et al. [70]. This is most likely seen in case of Ca as it shows enrichment only for ashes A and E. However, the classification performance is probably the most important reason for this difference between the ashes. As described in Ch. 4.1.2, the classification performance for ash A was better than for other ashes mainly due to the larger particle size distribution. If fine particles are separated with the coarse fraction, it naturally lowers the EF of elements that tend to enrich in the finer ash fractions. Lowered EF is actually an asset when considering only major and minor

elements since Ca, Mg and P have beneficial effects in ash fertilizers (see Ch. 2.3.2). On the other hand, lowered enrichment of trace elements in fine + medium fraction leads to higher heavy metal concentrations in the coarse ash.

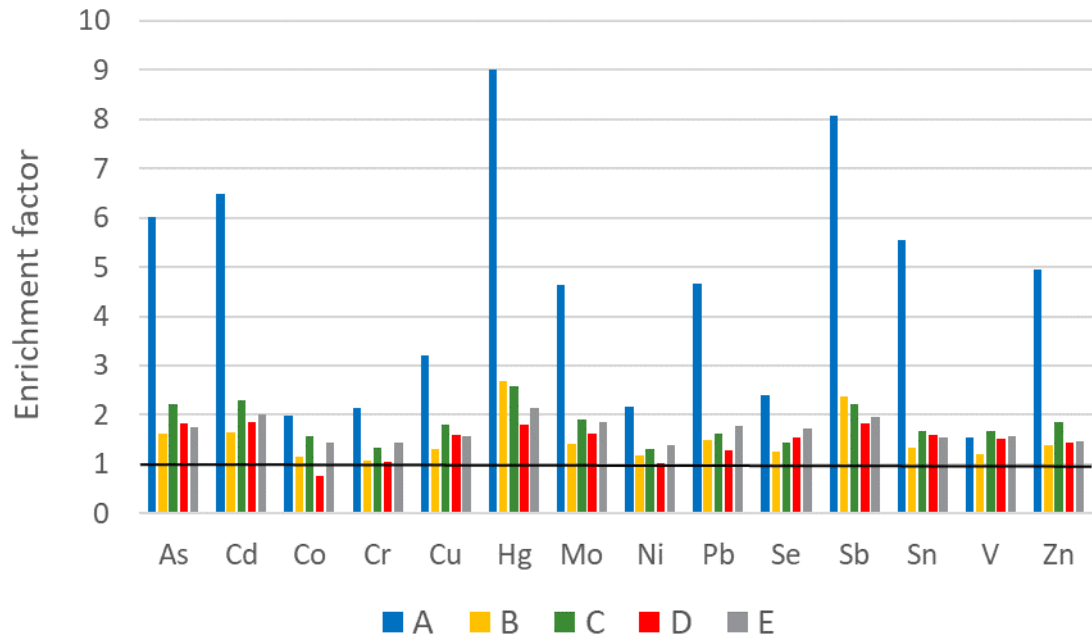


Figure 20 The enrichment of the trace elements in fine + medium ash fraction for each test ash

The enrichment of the trace elements in fine + medium ash is presented in Figure 20. The enrichment factors of the trace elements are generally higher compared to the major and the minor elements in Figure 19. Especially As, Cd, Hg and Sb have high EFs. On the other hand, Co, Cr and Ni have very low EFs. Most of the EFs are between 1.5-2.5 and only Co in ash D enriches in the coarse fraction. Ash A is an exception as mentioned in the previous paragraph. The difference of ash A and other ashes is clearly more significant with the trace elements compared to the major and the minor elements. Only enrichment factor of V is at the same level and many EFs are multiple times higher compared to other ashes. The probability that the utilization potential of an ash improves with air classification is directly connected to the enrichment of heavy metals in fine + medium fraction, i.e., the reduction in the coarse fraction. This is critical since air classification is not feasible without the change in the utilization potential of classified ash. Another feature affecting this probability is naturally the mass share of the fine + medium fraction. Enrichment factors and this mass share define the total reduction of heavy metals in the coarse fraction. For example, 58% of As in ash A enriched in the fine + medium fraction that has mass share of 9.6%. For ash E, 52% of As enriched in fine + medium fraction with mass share of 30%. The effect of air classification in the utilization potential of test ashes is discussed in Ch. 4.2.1.

It was mentioned in Ch. 4.1.2 that ash A had two separate peaks in its particle size distribution (Figure 10) as if the feed ash included sand particles in top of ash. Sand consists mainly on SiO_2 , and ash A has relatively high Si content of 20% based on Table 10. Therefore, sand could cause the high average particle size of ash A, thus improving also the classification performance as well as the EFs. However, addition of coarse sand particles into ash feed to improve classification is not feasible since it would reduce the ash feeding capacity of the classifier.

The classification performance affects certainly the enrichment characteristics. Information about the classification performance for each test ash is presented in Ch. 4.1.2. The better classification performance of ash A is mainly a consequence of considerably larger particle size distribution compared to the other ashes. The solids loading was identified to affect the classification performance. Lowering the solids loading would therefore probably increase the enrichment factors. As mentioned in the previous chapter, major changes in solids loading requires equipment modification that was not possible in this research and, additionally, is probably not feasible in a large-scale classifier.

The enrichment factors presented in figures 19 and 20 are from the primary tests. The effect of the secondary tests on the EFs was found insignificant and, therefore, are not presented in more detail. The changes between primary and secondary tests were quite small, 4.5% on average. Some patterns in changes of EFs between primary and secondary tests were expected due to the lowered cut-size of the cyclones in the secondary tests. For example, if an element enriches efficiently in the fine + medium fraction and the cut-size of a cyclone is decreased in the secondary test compared to the primary test, the EF of this element should increase. This behaviour can be seen in Table 11 in the enrichment characteristics between medium and fine fractions. The EFs of the fine fractions are generally higher than the EFs of corresponding medium fractions. However, no such pattern was observed between the primary and secondary tests. There are a few reasons for this. Firstly, the changes in the mass distributions of different ash fraction between primary and secondary tests were small as discussed in Chs. 4.1.1 and 4.1.2. Secondly, the increased solids loading in the secondary tests may lead to lowered EFs and thus balance the changes. Also, inaccuracy of analyses, sampling and possible differences in the compositions of ash feeds between tests affects the EFs. These sources of error are discussed more in Ch. 4.1.5.

Overall, the enrichment of elements in coarse and fine + medium fractions was similar to what could be predicted based on the literature [14, 15, 18]. However, an exact comparison was not possible since these studies considered the enrichment of elements between and bottom ash fly ash or between different stages of the electrostatic precipitator. There are no relevant studies about air classification of ash. Enrichment characteristics varied between the elements but in summary, the trace elements enrich more efficiently in the fine + medium fraction than the ash forming elements and only Si enrich clearly in the coarse fraction. The classification performance had significant impact on the enrichment factors of elements. Ash A had much higher EFs than the other test ashes which is due

the better classification performance. EFs and the mass share of fine + medium fraction define the total reduction of heavy metals in the coarse fraction and affect, therefore, significantly to the possible improvement of the utilization potential of ashes.

4.1.5 Mass balance calculations and error evaluation

Mass balance calculations were performed separately for each ash type to evaluate the error of the elemental composition analysis. This error evaluation is based on the methods presented in Ch. 3.5.1. The results of composition analyses from the primary tests (see Tables 10 and 11 in Ch. 4.1.3) are used for the calculation. Analysed and calculated elemental compositions and their errors are presented in the following tables. The calculated concentrations are computed using equation (13) and the errors with equation (14).

Table 12 *The result of mass balance calculations for the major and minor elements. Analysed and calculated compositions (%) of feed ash and their errors (%).*

Ash type	Ca	Mg	Na	K	P	Fe	Al	Si	Ti	Mn	Ba
A analysed	5.4	1.1	1.6	2.8	0.60	5.9	7.4	20	0.27	0.18	0.14
A calculated	5.7	1.2	1.8	3.0	0.60	6.2	8.1	23	0.29	0.19	0.14
A error (%)	4.6	8.6	15	7.2	0.61	5.3	9.0	16	5.7	7.3	-0.97
B analysed	41	0.83	0.35	0.95	0.23	1.3	5.0	8.0	0.14	0.12	0.04
B calculated	41	0.78	0.37	1.0	0.23	1.4	4.9	8.0	0.16	0.12	0.05
B error (%)	0.41	-6.0	6.6	6.6	1.8	3.6	-1.0	0.78	16	-1.1	20
C analysed	18	1.1	0.68	2.0	0.36	2.9	4.9	15	0.27	0.21	0.21
C calculated	18	1.1	0.71	2.0	0.36	3.0	4.9	15	0.25	0.20	0.20
C error (%)	-1.6	-0.74	3.7	1.4	0.43	4.3	0.14	2.5	-6.1	-5.4	-6.3
D analysed	20	1.8	1.1	2.4	0.63	5.1	6.3	13	0.38	0.28	0.12
D calculated	20	1.8	1.1	2.4	0.62	5.1	6.0	13	0.38	0.28	0.12
D error (%)	-2.1	-2.1	-3.2	-2.8	-0.91	-0.9	-3.3	-0.18	-1.2	-1.4	-1.7
E analysed	9.8	1.4	1.8	2.9	0.63	3.8	8.4	20	0.51	0.23	0.19
E calculated	10.0	1.5	1.7	2.8	0.64	3.9	8.2	21	0.52	0.23	0.19
E error (%)	3.7	0.76	-4.2	-2.9	1.5	1.8	-2.3	7.3	1.0	0.71	-2.0

The results of mass balance calculations for the major and minor elements are presented in Table 12. The calculated concentrations are primarily very close to analysed concentrations but there are some exceptions. The most notable are the errors of Na and Si concentrations of ash A and Ti and Ba of ash B. Errors for ashes A and B are generally little higher than for ashes C-E. It is difficult to evaluate the actual reasons for this difference. Some of the differences are probably due to the errors related to the test equipment since there were some malfunctions during the first tests as described in Ch. 3.3. Many analysed and calculated concentrations seem to be the same but this is due to the rounding of the values.

Table 13 *The result of mass balance calculations for the trace elements. Analysed and calculated compositions (mg/kg) of feed ash and their errors (%).*

Ash type	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Se	Sb	Sn	V	Zn
analysed	33	2.2	17	62	75	0.36	8.7	43	39	26	1.2	2.3	100	310
A calculated	30	1.9	18	75	70	0.2	8.6	50	34	21	2.4	2.5	87	290
error (%)	-9.3	-15	5.1	21	-6.1	-44	-0.79	17	-12	-19	100	9.5	-13	-5.5
analysed	7.7	1.3	5.8	33	120	0.13	4.6	21	16	5.5	0.61	3.5	24	300
B calculated	8.1	1.6	7.8	31	110	0.09	4.8	25	23	7.9	3.6	4.4	28	310
error (%)	5.8	21	35	-6.1	-5.3	-28	4.6	19	46	43	500	25	15	1.7
analysed	20	2.5	15	83	43	0.21	35	150	29	8.6	2.3	2.7	130	380
C calculated	21	2.5	15	92	43	0.18	33	150	30	9.5	2.3	2.8	110	360
error (%)	5.3	-1.4	-2.9	11	-0.98	-12	-5.8	-0.19	3.2	11	0.24	3.5	-13	-4.1
analysed	26	6.2	41	150	750	0.65	11	120	200	15	95	27	83	930
D calculated	28	6	49	160	760	0.64	12	130	190	16	92	27	86	990
error (%)	8.1	-2.5	18	9.1	0.78	-2.1	13	10	-5.4	6.1	-3.2	-0.93	3.9	6.2
analysed	38	4.5	29	110	510	0.66	9.6	79	150	11	72	27	97	1500
E calculated	41	4.6	34	120	540	0.69	10	91	150	11	70	26	100	1600
error (%)	8.2	2.2	18	12	6.2	4.3	8.6	16	0.58	3.8	-2.1	-2.8	6.8	8.0

The results of mass balance calculations for the trace elements are presented in Table 13. Most of the errors between the analysed and the calculated concentrations are at a moderate level but they are more significant for trace elements than for the major and minor elements. The effect of errors during the analysis is probably the main reason for this difference. As mentioned earlier, the minor inaccuracies make larger impact when elemental concentrations are low. Hg is a good example of this. There are also a few significant errors. Sb has error of 100% and 500% in ashes A and B respectively. These values cannot be reliably used in estimating the utilization potential of these ashes. Luckily, these concentrations are very low and Sb concentrations, in general, are not limited by the Finnish legislation. In addition, the errors for some elements, for example Cr, are surprisingly high for all ashes despite the relatively high concentrations. Based on this observation, there might be some variance in accuracy of the analysis method (ICP, see Ch. 3.4) for different elements. In summary, the composition analyses are relatively accurate based on the mass balance calculations. However, it is important to keep in mind that there is always some error involved in the analysis results.

4.2 Effect of air classification on ash utilization

4.2.1 Utilization possibilities of ashes used in experiments

The effect of air classification on utilization potential of ashes defines whether this technology is feasible in ash refining. If the utilization potential of an ash does not improve

with air classification, the process is automatically unprofitable with this ash. On the other hand, if the utilization potential improves, air classification might be highly profitable. In this chapter, the utilization possibilities of the test ashes are evaluated before and after the classification. This estimation is done by comparing the results of the composition and the leachability analyses on the limit values presented in the Finnish legislation (see Ch. 2.4). The comparison is relevant for fertilizer and earth construction applications since there is no guiding legislation concerning other utilizations. For example, it not possible to determine whether the test ashes are suitable for different concrete application based on these analysis results and the legislation. Moreover, leachability analysis gives information of whether an ash or an ash fraction need to be disposed of at a landfill.

Fuel has a significant effect on utilization potential of ashes formed during combustion. The origin of ash may restrict its utilization. As described in Ch. 2.4.1, only ashes originating from combustion of biomass, peat and untreated waste wood can be used as fertilizer or raw material for fertilizer products. This means that only ashes A and B could be utilized as fertilizers if they meet the other requirements. Considering earth construction, utilizable ashes can originate from combustion of coal, peat, wood and wood-based fuels. Test ashes A-C fall into this category. Power plants D and E use also waste in their fuel mixture so an environmental permit is required if their ashes are used in earth construction applications. In this chapter, the properties of the test ashes are compared only to the relevant utilizations due to the fuel restrictions. Concentrations of elements in ashes A and B are compared to the fertilizer limit values in Table 14. The Fertilizer Product Decree [27] limits the concentrations of harmful trace elements and also sets lower limits for Ca and nutrients (K+P). Concentrations of trace elements are in mg/kg whereas Ca and K+P concentrations are in percentages. The *Other utilizations* in the table refer to use of ash fertilizers in agriculture, horticulture and landscaping. The values that exceed limit values for fertilizing in agriculture but are below the limits for forestry are highlighted in orange and the values that exceed, or in case of nutrients are below, the both limits are in red. The concentration values of ash fractions are the same as in Tables 10 and 11.

Based on the concentrations in Table 14, ash A can be utilized as fertilizer in forestry if some Ca is added so that the lower limit of 6% is exceeded. Only As exceeds the limit concentration for other utilizations and most of the concentrations are relatively low compared to the limit values. The air classification lowers the As concentration in the coarse fraction below the limit, so it is utilizable in agriculture with Ca addition. However, As and Hg concentrations in medium and fine fractions are clearly above the limits. A different utilization target needs to be found for these fractions. This minor improvement of the fertilizer potential of ash A is not enough to make air classification feasible for this ash type when only fertilizer use is considered. Utilization in earth construction is discussed later.

Table 14 Comparison of concentrations of elements (mg/kg) in ashes A and B to the fertilizer limit values.

Ash type and utilization	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Ca (%)	K+P (%)	
A	feed	33	2.2	62	75	0.36	43	39	310	5.4	3.4
	coarse	14	0.78	66	54	0.03	44	21	170	5.0	3.5
	medium	130	8.2	180	200	1.1	120	130	1100	11	4.4
	fine	230	16	140	250	2.5	96	190	1800	13	4.7
B	feed	7.7	1.3	33	120	0.13	21	16	300	41	1.2
	coarse	5.8	1.1	30	98	0.02	23	18	250	41	1.2
	medium	11	2.3	32	140	0.17	27	32	380	44	1.3
	fine	17	3.1	35	160	0.4	33	40	500	43	1.4
Utilization in forestry	40	25	300	700	1.0	150	150	4500	6.0	2.0	
Other utilizations	25	2.5	300	600	1.0	100	100	1500	10	-	

Ash B is ready to be utilized, for example, as a liming agent in agriculture based on the data in Table 14. All concentrations of the trace elements are clearly below the limit values and Ca content is considerably high. The liming agents are used in agriculture to raise pH of the soil to the optimal level for cultivation as described in Ch. 2.3.2. However, nutrient concentrations are very low so other fertilizer products are necessary to provide the fertilizing effect. Inorganic fertilizer products can also be mixed with ash to increase the fertilizer potential. Air classification does not have any positive effect on the utilization of ash B. Cd concentration in fine + medium fraction exceeds the limit values for field fertilizers. Some nutrient addition is needed (K+P > 2%) for this fraction to be utilized as forest fertilizer. As discussed in Ch. 4.1.2, also the classification performance of ash B was poor due to its sticky nature. Overall, air classification was found unsuitable for ash B.

The comparison of the leachabilities in the test ashes to the limit values in the legislation is presented in Tables 15 and 16. The leachability analyses were made of ashes A, C and D. This analysis was found unnecessary for ashes B and E. Ash B is utilizable in agriculture and ash E was very similar to ash D based on the composition and particle size distribution analyses. Fine and medium ash fractions were combined for the same reasons as described in Ch. 4.1.4. However, all ash fractions were analysed for ash C to ensure that there is no major variation in leachabilities between medium and fine fractions. The same leachability analysis can be used to evaluate the suitability of ash to different earth construction applications and the need for the disposal of at a landfill. Covered field and paved road were chosen to represent also the other earth construction applications. Limit values for a covered field are the lowest, and for a paved road the highest, in the Government Decree on the Recovery of Certain Wastes in Earth Construction [47]. The complete

table of those limit values is in Ch. 2.4.2. The limit values for inert landfills are also left out of the tables since, in practice, ash is not disposed of at an inert landfill. The colors green, blue, orange and red highlight the limit values and concentrations that exceed those limits. In order of increasing limit values, covered field is in green, paved road in blue, non-hazardous landfill in orange and hazardous landfill in red. Leachabilities are in mg/kg with liquid to solid ratio being 10 l/kg.

Table 15 Comparison of leachabilities of elements (mg/kg, L/S = 10 l/kg) in ashes A, C and D to the limit values of earth construction and landfilling.

Ash type and utilization	As	Ba	Cd	Cr	Cu	Hg	Mo	Ni	Pb
A feed	<0.05	19	<0.005	0.1	<0.05	0.006	3.2	<0.05	<0.05
A coarse	<0.05	8.1	<0.005	0.09	<0.05	<0.005	1.5	<0.05	<0.05
A fine + medium	<0.05	3.3	0.009	2.5	<0.05	<0.005	12	<0.05	<0.05
C feed	<0.05	3.9	0.02	0.92	<0.05	<0.005	17	<0.05	<0.05
C coarse	<0.05	4.6	0.01	0.5	<0.05	<0.005	11	<0.05	<0.05
C medium	<0.05	2.8	0.03	2	<0.05	<0.005	34	<0.05	<0.05
C fine	<0.05	3.1	0.03	2.2	<0.05	<0.005	37	<0.05	<0.05
D feed	<0.05	33	<0.005	0.26	<0.05	<0.005	1.9	<0.05	<0.05
D coarse	<0.05	28	<0.005	0.07	<0.05	<0.005	0.75	<0.05	<0.05
D fine + medium	<0.05	3.2	0.007	4.6	0.05	<0.005	8.2	<0.05	0.35
Earth construction									
Covered field	0.5	20	0.04	0.5	2	0.01	0.5	0.4	0.5
Paved road	2	100	0.06	10	10	0.03	6	2	2
Landfilling									
Non-hazardous	2	100	1	10	50	0.2	10	10	10
Hazardous	35	300	5	70	100	2	30	40	50

Based on the data in Tables 15 and 16, the leachabilities for most of the elements and other substances in the ash feeds are low and most of the leachabilities increase in the fine + medium fraction. As discussed in Ch. 2.3.2, leachability of most elements is highly dependent of pH. The high pH of test ashes is a probable explanation for low leachabilities as leachability of most elements decreases with increasing pH. The pH of ash feeds in ashes A, C and D were 11.8, 12.3 and 11.0 respectively. However, the leachability of some elements increases with increasing pH. Especially Mo, Cr, Ba, Se and V show higher leachabilities than what could be expected based on composition analyses. Also, chlorides, sulphates and fluorides have relatively high leachabilities. Overall, Mo, Cr, Cl⁻, F⁻ and SO₄²⁻ cause the most concern to the utilization of the test ashes. Pohjala [23] also reported SO₄²⁻ and Mo to be the most limiting substances for the utilization in earth construction in the survey about utilization of ashes in Finland in 2014.

Table 16 Comparison of leachabilities of substances (mg/kg, L/S = 10 l/kg) in ashes A, C and D to the limit values of earth construction and landfilling. PAH values are concentrations (mg/kg).

Ash type and utilization	Sb	Se	V	Zn	Cl ⁻	F ⁻	SO ₄ ²⁻	DOC	PAH
A feed	<0.05	0.12	<0.05	<0.05	120	14	160	19	NA
A coarse	<0.05	0.06	0.09	<0.05	110	8	570	27	0.248
A fine + medium	<0.05	0.23	0.27	<0.05	3540	11	3980	25	NA
C feed	<0.05	0.11	0.29	0.19	570	20	11900	110	0.278
C coarse	<0.05	0.09	0.19	0.28	460	24	9470	85	0.617
C medium	<0.05	0.17	0.58	0.09	870	13	15600	170	1.79
C fine	<0.05	0.16	2.3	0.05	810	10	16800	180	0.849
D feed	0.08	0.07	<0.05	<0.05	8220	2	230	21	0.164
D coarse	<0.05	<0.05	<0.05	<0.05	5680	2	170	18	<0.16
D fine + medium	<0.05	0.38	<0.05	0.21	19600	14	11500	61	NA
Earth construction									
Covered field	0.3	0.4	2	4	800	10	1200	500	30
Paved road	0.7	1	3	15	11000	150	18000	500	30
Landfilling									
Non-hazardous	0.7	0.5	-	50	15000	150	20000	800	-
Hazardous	5	7	-	200	25000	500	50000	1000	-

Several factors affect the leachability results in Tables 15 and 16. Leachabilities are only vaguely connected to the actual concentrations. It is not possible to make accurate prediction of leachability based solely on the element concentration. Therefore, the differences between test ashes and ash fractions are not merely due to the different concentrations but also other factors. As mentioned in the previous paragraph, the pH has significant effect on the leachabilities. All the test ashes were highly alkaline but the pH changed a little between the ash fractions. The pH of the feed and the coarse fraction was the same with all the ashes but it was increased or decreased in fine + medium fractions depending on the ash. For example, in ash D the pH of the feed ash was 11 and in the fine + medium fraction 12.4.

Additionally, elements may occur in various compounds that have different solubilities. The changes of leachabilities of Ba and SO₄²⁻ between ash fractions are probably due to the difference in elements occurrence in compounds. Ba has relatively high leachability in feed ashes and coarse fractions but considerably lower in fine + medium fractions. On the contrary, the leachability of SO₄²⁻ is significantly lower in the feed ashes and coarse fractions than in the fine + medium fractions. Ash C is an exception because the changes in leachabilities between the ash fractions are not so significant as in other ashes. The pH and the molecular occurrence of elements have certainly some effect on the differences of the leachabilities between test ashes and ash fractions but it is not in the scope of this

research to accurately evaluate the reasons for these differences. Another factor influencing the leachabilities are errors during the analysis and sampling. The error sources are the same as described in Ch. 4.1.5. However, it is not possible to estimate the errors with mass balance calculations due to the effect pH and variation in elemental occurrence on the leachabilities.

The laboratory conducting the analyses reported some problems during the leachability analyses of feed and coarse fractions of ash D. As explained in Ch. 3.4, the two-stage batch leaching test was used as analysis method in accordance with standard SFS-EN 12457-3 [62]. However, samples of feed and coarse fractions of ash D had to be analysed using one-stage test defined in standard SFS-EN 12457-2 [63]. The analysis method was changed due to foaming of samples during the leaching. The one-stage analysis was also done at L/S of 10 l/kg. This change of analysis method may explain some of the differences in leachabilities in ash fractions of ash D. Also, the concentration analyses of polycyclic aromatic hydrocarbons (PAH) were not successful for feed and fine + medium fractions of ash A and fine + medium fraction of ash D. However, PAH concentrations were low compared the limit values so the issues during the analyses do not affect the evaluation of utilization of ashes.

Ash A can be utilized in some earth construction applications based on the leachabilities in Tables 15 and 16. The leachabilities of Mo and F⁻ limit the possible earth construction applications to paved roads, paved fields and bases of industrial or storage buildings. However, the technical properties of ash need to also be suitable for these applications. The required properties are introduced in Chs. 2.3.3 and 2.4.2 but they are not evaluated in more detail in this research. Air classification reduces the leachability of Mo so that the coarse fraction can also be used in covered roads. The fine + medium fraction, however, must be disposed at a landfill for hazardous waste since leachability of Mo 12 mg/kg exceeds the limit value 10 mg/kg. Therefore, air classification is not feasible for ash A as was discovered already in the comparison of the concentrations of elements to the fertilizer limit values.

Surprisingly, ash C was the most harmful of the test ashes when considered only the leachabilities of substances. The leachability of Mo is 17 mg/kg which forces the ash to be disposed of at a landfill for hazardous waste. Ash C has the highest Mo concentration of the test ashes as seen in Table 11 that correlates well to the leachability. Ironically, based on the concentrations in Table 11, ash C would be suitable for forest fertilizing if it was not originated partly from coal combustion. This is an example of incomplete state of the legislation concerning ash utilization, which is discussed in Ch 5. Leachability of Mo decreases in the coarse fraction to 11 mg/kg but it is still over the limit value of a landfill for non-hazardous wastes so the utilization potential does not improve. Furthermore, leachability of Mo exceeds the limit values of hazardous wastes in medium and fine fractions. These fractions need to be stabilized prior to disposal. Air classification is not beneficial for ash C because the utilization potential does not change. Also,

the Cr, Cl⁻, F⁻ and SO₄²⁻ have relatively high leachabilities but they are all below the limit values for paved roads.

Ash D is suitable for some earth construction applications based on the data in Tables 15 and 16. These applications are paved roads and bases of industrial or storage buildings. However, the earth construction projects utilizing ash D need to apply for an environmental permit, since the power plant D uses waste in its fuel mixture. The application process may hinder the utilization of ashes that originate at least partly from waste combustion. Cl⁻ is the most limiting substance for utilization of ash D but also leachabilities of Ba and Mo are relatively high. As the feed ash is already suitable for earth construction, no major changes can be achieved with air classification, which makes the process infeasible also for ash D. The utilization potential of ash E can be estimated to be similar to ash D because they had very similar compositions and particle size distributions. The summary of the effect of air classification on the utilization possibilities of the test ashes is presented in Table 17.

Table 17 *The effect of air classification on the utilization potential of the test ashes.*

Test ash	Feed	Coarse	Fine + medium
A	Earth construction, forest fertilizer with Ca addition	Earth construction, forest or field fertilizer with Ca addition	Landfill for hazardous waste
B	Liming agent in agriculture	Liming agent in agriculture	Forest fertilizer with nutrient addition
C	Landfill for hazardous waste	Landfill for hazardous waste	Landfilling after stabilization
D	Earth construction	Earth construction	Landfill for hazardous waste

Most of the test ashes were utilizable in earth construction or as fertilizer without any additional refining. An exception was ash C, which is considered as hazardous waste due to the high leachability of Mo. However, these test ashes do not represent the average ash quality of power plants A-E. The analyses for the official utilization evaluation should be made from the representative compilation samples. Air classification lowered the heavy metal concentrations and most of the leachabilities in the test ashes. However, the test ashes had already adequate utilization potential or the change in leachabilities were not sufficient as seen with ash C. In summary, air classification had not enough effect on the utilization potential of the test ashes. Therefore, this technology is not feasible for these ashes. Although, the test ashes covered a significant section of co-combustion fly ashes produced in Finland, there are probably some ashes that would benefit from air classification.

4.2.2 Cost estimations of selected utilization scenarios

The air classifier used in this research does not function perfectly and is not necessarily suitable for ash refinement as discussed in the previous chapters. In any case, the classification needs to also be economically feasible if there is an ash that would benefit from air classification. In this chapter, cost estimations for the two utilization scenarios are presented. These utilization scenarios and the input values for the cost estimation are described in Ch. 3.5.2. In scenario 1 ash is initially landfilled but after air classification, the coarse fraction can be utilized in earth construction. In scenario 2, ash is initially used in earth construction and the coarse fraction can be used as a fertilizer. Fine + medium fraction is landfilled in both the scenarios. Based on the cost estimations, profitability calculations of an air classifier investment are also presented. In addition to this cost estimation, sensitivity of the profitability of these scenarios to different input values is evaluated. The profitability calculations in this chapter provide only a rough estimation about the actual profitability. More thorough cost estimations are needed before any decisions about an actual investment to an air classifier can be made.

The profitability on an air classifier investment is evaluated using three methods: net present value method, annuity method and payback method. The details of these methods are presented in Ch. 2.6. The net present value of an investment, annual return and payback period are calculated using equations (9), (11), (12) respectively. The input values for the annuity and the net present value methods are interest rate, holding period and salvage value of an investment. In this cost estimation, the interest rate is 6%, holding period 15 years and salvage value 20% of the capital costs of the investment. Using multiple calculation methods gives a better understanding of the profitability of an air classifier in different scenarios.

Based on the profitability indicators in Table 18, scenario 1 is profitable but scenario 2 is not. The net present value of the investment in scenario 1 is nearly 850 k€, annual return about 87 k€ and payback period 3.3 years. These are very good numbers for a pilot scale classifier since the profitability will increase with increasing ash feeding capacity as will be explained later. The scenario 2, however, is highly unprofitable. Therefore, the payback time cannot be calculated and the annual return is 140 k€ negative. The difference in value addition of ash between the scenarios explains this. In scenario 1, the increase in value from ash feed to coarse ash is 130 €/t whereas in scenario 2, it is only 50 €/t. Furthermore, fine + medium fraction that accounts for 25% of the ash is disposed at a landfill in any case. In fact, revenue from ash fertilizer sales barely covers the landfilling costs in scenario 2. An increase in fertilizer price or decrease in the quantity of the landfilled fraction would be highly beneficial in scenario 2. It is worth noting that although scenario 1 is profitable, it does not provide any income. It is just less expensive to classify the ash and utilize it in earth construction than to landfill it.

Table 18 Cost estimation of air classification for selected utilization scenarios.

	Constants	Scenario 1	Scenario 2
Capacity			
Maximum ash feed		300 kg/h	300 kg/h
Availability		80%	80%
Annual capacity		2100 t/a	2100 t/a
CAPEX		420000 €	420000 €
OPEX			
Electricity costs	-6,1 c/kWh	-17000 €/a	-17000 €/a
Employee costs	-10 €/h	-70100 €/a	-70100 €/a
Other operational costs		-15000 €/a	-15000 €/a
Total		-102000 €/a	-102000 €/a
Ash related costs			
Landfilling costs	-130 €/t	-68300 €/a	-68300 €/a
Earth construction value	0 €/t	0 €/a	0 €/a
Fertilizer value	50 €/t	0 €/a	78800 €/a
Transportation costs	-15 €/t	-7900 €/a	-7900 €/a
Ash related costs without air classification		-305000 €/a	0 €/a
Savings/profit		229000 €/a	2600 €/a
Profitability indicators			
Net present value		844000 €	-1350000 €
Annual return		86900 €/a	-139000 €/a
Payback period		3.3 a	NA

The profitabilities of the utilization scenarios are naturally highly dependent on the different inputs presented in the previous paragraphs. Therefore, the sensitivity of the profitability to specific input values gives more reliable information about the actual profitability of the utilization scenarios than the calculated profitability indicators in Table 18. A sensitivity analysis was performed for both scenarios with a few of the most important inputs. Ash feed capacity, CAPEX, OPEX and landfilled ash fraction (the mass share of fine + medium fraction) were considered in this analysis. Additionally, the fertilizer value was considered for scenario 2. The results of the sensitivity analysis are presented in the following figures. The starting values were altered one at a time when other inputs were the same as in Table 18. For clarity, on the x-axis is the ratio of the input value to the initial input value in percentages. Therefore, the position of any initial value on the x-axis is 100% and when the actual value is doubled the position on the x-axis is 200% and so on. Annual return was used as a reference to visualize the sensitivity of the profitability to different inputs.

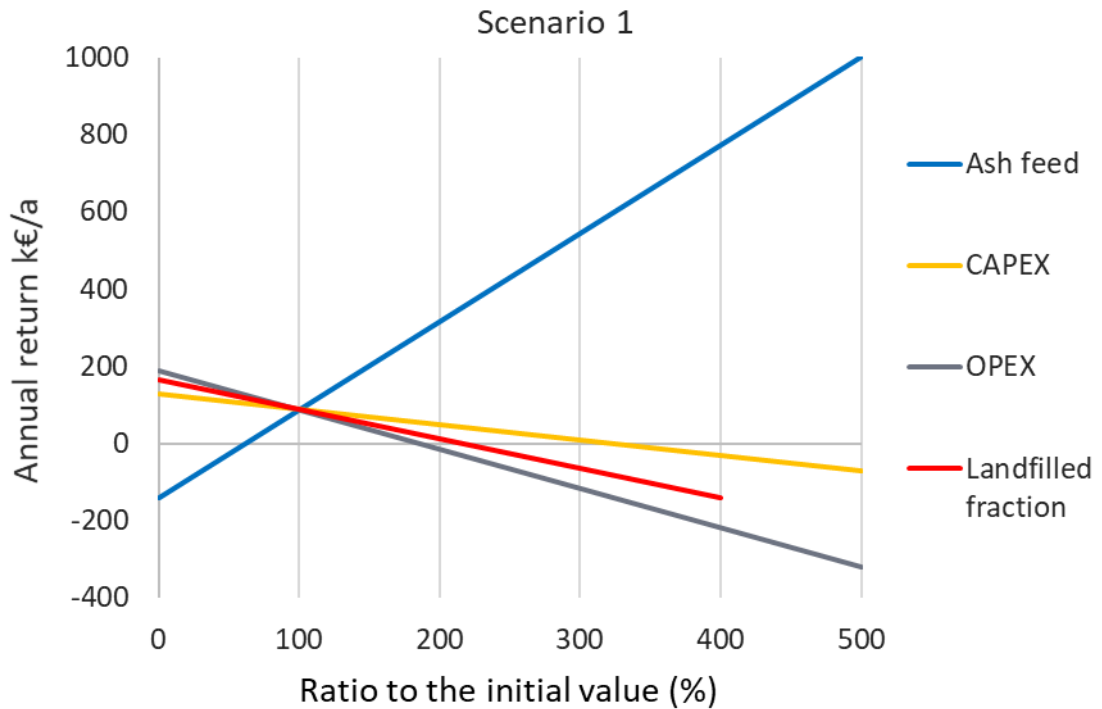


Figure 21 The sensitivity of the annual return to the various inputs in scenario 1.

Based on the data in Figure 21, the correlations of the annual return to these input values are linear. The ash feed capacity has the most significant impact on the profitability in the scenario 1 since the more ash is landfilled initially, the more savings can be achieved with air classification. The annual return becomes zero at the ash feed of 190 kg/h and is 1 M€/a at 1500 kg/h. Naturally, the CAPEX and OPEX would also increase with increasing capacity so, in practice, the rise in annual return is not as sharp as presented. Nevertheless, the capital and operational costs do not impact the profitability as much as the ash feed. In fact, at the ash feed of 300 kg/h, capital costs could be 1,35 M€ before the annual return turns negative. The payback time is then 10,6 years. The operational costs of 190 k€/a have the same effect. In Table 18, they are about 100 k€/a. Furthermore, the CAPEX and OPEX are unlikely to increase at same rate as feeding capacity when scaling up the classifier. Considering the change in OPEX from the pilot to a full-scale classifier, electricity consumption and maintenance costs will certainly increase but the employee costs will remain almost the same as no extra personnel are needed for controlling the equipment. Landfilled ash fraction was initially 25% of the ash feed and it can be 54% before scenario 1 turns unprofitable. As mentioned in Ch. 4.1.1, the controllability of the mass distribution between different size fractions was limited. Therefore, the profitability of an air classifier could be improved with better controllability.

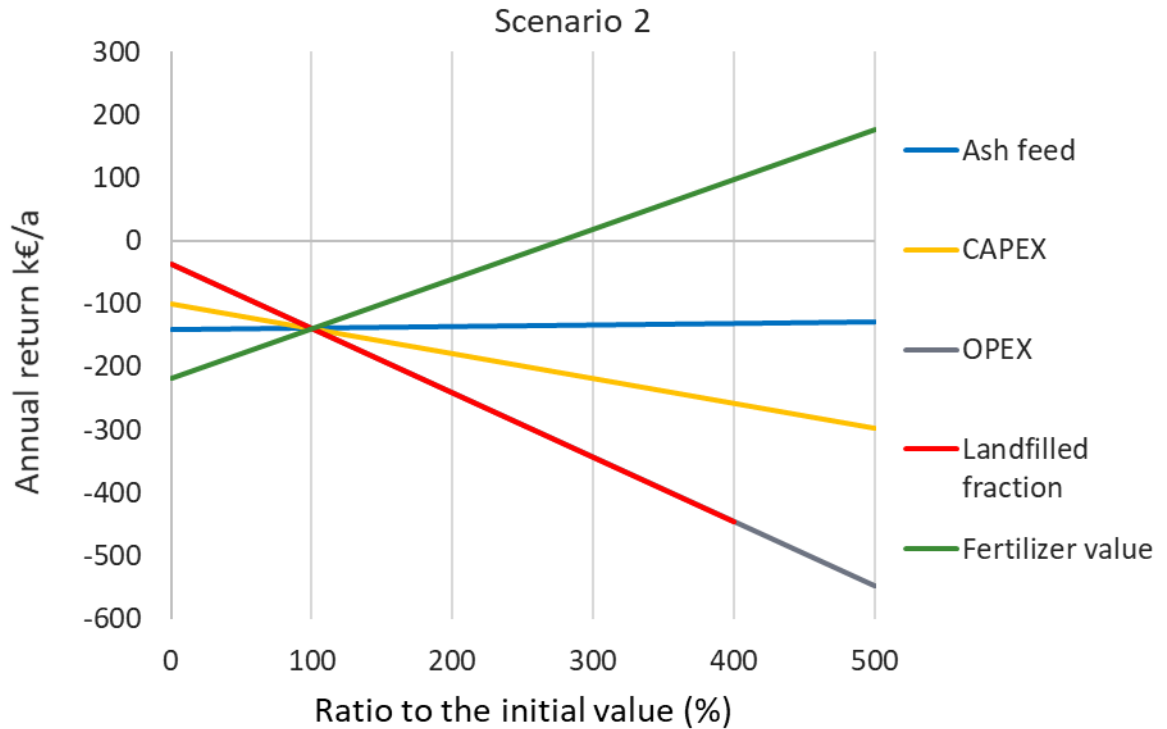


Figure 22 The sensitivity of the annual return to the various inputs in scenario 2.

Figure 22 shows that only an increase in ash fertilizer value can change the scenario 2 profitable. In Table 18, the fertilizer value was 50 €/t but it should be 140 €/t to be able to change the annual return positive. However, this is a too high a price for ash fertilizer. Ash feed does not have similar effect in scenario as in scenario 1 because the profit from ash classification is small. If the fertilizer value was at the possible level of 70 €/t, the required ash feed to change this scenario profitable would be 1250 kg/h without considering the changes in CAPEX and OPEX. The increase in the landfilled ash fraction has similarly severe effect on the profitability as the increase in OPEX. Overall, the scenario 2 needs very specific conditions to be profitable.

In summary, ash related costs make the difference between utilization scenario 1 and 2. The greater the increase in the value of the ash the more profitable the air classification becomes. If the value addition is high enough, an increase in ash feeding capacity improves also the profitability since the CAPEX and OPEX are unlikely to increase at same rate as the feed capacity. Also, the quantity of the landfilled ash fraction has a significant effect on profitability. Based on the profitability calculations presented in this chapter, an air classifier investment is profitable if ash, that is otherwise disposed of at a landfill, can be utilized. Instead, if ash classification provides the improvement in ash utilization from earth construction to fertilizing or any other utilization application providing enough additional value, it is profitable only under certain conditions.

5. CONCLUSIONS

The purpose of this research was to examine the feasibility of an air classifier in fly ash refining. The indicators defining the feasibility were the mechanical functionality of the classifier, the enrichment characteristics of elements in different ash fractions, the effect of air classification on the utilization potential of the test ashes and the profitability. These indicators were evaluated in a test run with five test ashes that originated from co-combustion of biomass and other solid fuels. The test ashes were labelled from A to E and they represented well the different co-combustion fly ashes produced in Finland. In the air classification process, feed ash was divided into three size fractions: coarse, medium and fine fraction. The basic idea was that the heavy metals enrich in the fine and medium ash fractions so the coarse fraction was more easily utilized due to the reduced heavy metal concentrations.

The experiments gave valuable information about the mechanical functionality of the air classifier. The basic operation of the classifier was satisfactory but the controllability of the mass distribution between different ash fractions was limited. The original particle size distribution of ash feed was the main parameter defining the mass distribution. Ash A had considerably larger average particle diameter than the other ashes. Therefore, the mass share of the coarse fraction of ash A was considerably higher than that of other ashes. Part of the controllability limitations were due to the air classifier design but part could probably be improved with changes in the classification air production and the ash feeding system. Better controllability of mass distribution would help to adjust the performance of the classifier to correspond to the properties of different ashes.

Particle size distribution analyses of the different ash fractions were used to evaluate the ash classification capability of the air classifier. For most of the test ashes, the classification performance was relatively good but improved significantly for ash A due to its higher average particle size. The classification performance had a clear impact on the enrichment characteristics of different elements. Heavy metal enrichment in the fine and medium fractions was considerably higher for ash A since the fine particles were more effectively separated from the coarse. However, the amount of these fractions for ash A was also much lower compared to the other ashes. Together the enrichment behaviour and the amount of the finer fractions define the reduction of heavy metals from the coarse ash fraction.

The effect of air classification on the utilization potential of the test ashes was evaluated based on the elemental composition and leachability analyses. Legislation concerning ash utilization as fertilizers limits concentrations of heavy metals, whereas the decree about ash utilization in earth construction requires leachability analyses. Air classification had

no effect on the utilization of the test ashes despite the reduced heavy metal concentrations and leachabilities in the coarse ash fraction. Most of them were already utilizable in earth construction or as fertilizer so there was no need for refining process. Ash C was initially hazardous waste due to the high leachability of a single element, molybdenum. The reduction of this leachability in the coarse fraction was not sufficient to remove the status of hazardous waste. It is worth noting that the test ashes do not represent the average ash quality of power plants A-E. The analyses for the official utilization evaluation should be made from the representative compilation samples.

Even though the air classification had no impact on the test ashes, there might be an ash that benefits from this process. Besides the technical functionality, an air classifier needs to also be profitable if such ash is found. The profitability calculations showed that an air classifier investment would be profitable if the disposal of ash at a landfill could be changed to the utilization of the coarse fraction, for example, in earth construction. If ash is already utilizable in earth construction, the air classification is profitable only in certain conditions described in more detail in Ch. 4.2.2. Overall, low availability of suitable ashes and limitations in profitability restrict the use of air classification technology in ash refinement.

It was clarified during the research that the Finnish legislation concerning ash utilization is not complete and, therefore, requires re-evaluation. The elemental composition and leachability analyses of ash C revealed some flaws in current legislation as mentioned in Ch. 4.2.1. Based on the leachability analysis, ash C was hazardous waste. On the other hand, the elemental composition analysis showed that ash C could be utilized as forest fertilizer if it was not partly originated from coal combustion. This observation leads to two possible improvements in legislation. Firstly, the same leachability analysis could be used to evaluate the utilization potential of ash both in earth construction and as a fertilizer. This requires changes mainly in the Fertilizer Product Decree [27]. The leachability analysis describes better the behavior of elements in the environment than bulk composition analysis. Not only it gives information on the behavior of heavy metals but also the mobility of nutrients. Therefore, the fertilizing effect could be also evaluated with leachability analysis. Secondly, the restrictions about the origin of ash could be entirely removed. There would be no need for limitations for the fuel, if other properties in each utilization application were precisely defined. This change would also open new possibilities for ash refining technologies when, in theory, ash from waste incineration could be used as fertilizer. Attitudes towards waste and coal ashes as environmentally hazardous substances hinder this kind of change. However, attitudes will not change if the legislation does not enable the wider utilization of these ashes.

There are some additional research that could be done with the air classifier pilot to improve the understanding of the effect of air classification on ash utilization. A more thorough research about the effects of solids loading and the other process parameters on the

classification performance and the enrichment characteristics of elements could be relatively simple to conduct. However, it requires at least new classification air fans and the results are highly uncertain. This research covered only ash utilization in earth construction and fertilizing. Therefore, one research path could be the effect of air classification on the utilization of fly ash in concrete applications. The lack of legislation concerning utilization of co-combustion and biomass ashes in these applications complicates this kind of research. A partner from cement or concrete industry would be needed to set a target for the quality of ash.

Overall, it is difficult to develop a profitable ash refinement technology since the value of the end product is low. Therefore, the utilization of fly ashes could be taken into consideration already during the planning of a new boiler, flue gas cleaning system and fuel mixture of a power plant. Fly ashes from a back pass of a boiler could be utilized differently than ashes from ESP or BHF when necessary. Alternatively, some ash classification can be achieved with ESP where the coarse fraction is collected in the first stage of ESP and finer particles with the subsequent stages as mentioned in Ch. 2.2.2. Other options are, for example, taking the quality of ash into account when planning the fuel mixture or additives injected into furnace or flue gas duct. Additional technical and economic research is needed before any changes in power plant designs can be made.

REFERENCES

- [1] S. Vassilev, D. Baxter, L. Andersen, C. Vassileva, An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification, *Fuel*, Vol. 105, 2013, pp. 40-76.
- [2] S. Vassilev, C. Vassileva, A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour, *Fuel*, Vol. 86, 2007, pp. 1490-1512.
- [3] S. Vassilev, D. Baxter, L. Andersen, C. Vassileva, An overview of the chemical composition of biomass, *Fuel*, Vol. 89, 2010, pp. 913-933.
- [4] S. Vassilev, C. Vassileva, Y. Song, W. Li, J. Feng, Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion, *Fuel*, Vol. 208, 2017, pp. 377-409.
- [5] M. Hupa, Ash-Related Issues in Fluidized-Bed Combustion of Biomasses: Recent Research Highlights, *Energy & Fuels*, Vol. 26, 2012, pp. 4-14.
- [6] S. Vassilev, C. Vassileva, D. Baxter, Trace element concentrations and associations in some biomass ashes, *Fuel*, Vol. 129, 2014, pp. 292-313.
- [7] J. Saastamoinen, Kiinteän polttoaineen palaminen ja kaasutus, in: R. Raiko, J. Saastamoinen, M. Hupa, I. Kurki-Suonio (ed.), *Poltto ja palaminen*, IRFR - Suomen kansallinen osasto, Helsinki, 2002, pp. 186-232.
- [8] B. Skrifvars, M. Hupa, Tuhka, kuonaantumisen, likaantumisen ja korroosio, in: R. Raiko, J. Saastamoinen, M. Hupa, I. Kurki-Suonio (ed.), *Poltto ja palaminen*, IRFR - Suomen kansallinen osasto, Helsinki, 2002, pp. 269-299.
- [9] S. Vassilev, D. Baxter, C. Vassileva, An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types, *Fuel*, Vol. 117, 2014, pp. 152-183.
- [10] Y. Niu, H. Tan, S. Hui, Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures, *Progress in Energy and Combustion Science*, Vol. 52, 2016, pp. 1-61.
- [11] J. Reinik, N. Irha, E. Steinnes, G. Urb, J. Jefimova, E. Piirisalu, J. Loosaar, Changes in trace element contents in ashes of oil shale fueled PF and CFB boilers during operation, *Fuel Processing Technology*, Vol. 115, 2013, pp. 174-181.
- [12] X. Querol, J. Fernández-Turiel, A. López-Soler, Trace elements in coal and their behaviour during combustion in a large power station, *Fuel*, Vol. 74, Iss. 3, 1995, pp. 331-343.

- [13] R. Meij, H. te Winkel, The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations, *Atmospheric Environment*, Vol. 41, 2007, pp. 9262-9272.
- [14] O. Dahl, H. Nurmesniemi, R. Pöykiö, G. Watkins, Comparison of the characteristics of bottom ash and fly ash from a medium-size (32 MW) municipal district heating plant incinerating forest residues and peat in a fluidized-bed boiler, *Fuel Processing Technology*, Vol. 90, 2009, pp. 871-878.
- [15] R. Pöykiö, K. Manskinen, H. Nurmesniemi, O. Dahl, Comparison of trace elements in bottom ash and fly ash from a large-sized (77 MW) multi-fuel boiler at the power plant of a fluting board mill, Finland, *Energy Exploration & Exploitation*, Vol. 29, 2011, pp. 217-234.
- [16] O. Dahl, H. Nurmesniemi, R. Pöykiö, G. Watkins, Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values, *Fuel Processing Technology*, Vol. 91, 2010, pp. 1634-1639.
- [17] S. Ryszard, T. Marzena, A. Malgorzata, Evaluation of the distribution of heavy metals and their chemical forms in ESP-fractions of fly ash, *Fuel Processing Technology*, Vol. 95, 2012, pp. 109-118.
- [18] K. Ohenoja, V. Wigren, J. Österbacka, M. Illikainen, M. Körkkö, Fly ash classification efficiency of electrostatic precipitators in fluidized bed combustion of peat, wood, and forest residues, *Journal of Environmental Management*, Vol. 206, 2018, pp. 607-614.
- [19] T. Hyppänen, R. Raiko, Leijupoltto, in: R. Raiko, J. Saastamoinen, M. Hupa, I. Kurki-Suonio (ed.), *Poltto ja palaminen*, IRFR - Suomen kansallinen osasto, Helsinki, 2002, pp. 490-521.
- [20] T. Lind, T. Vaimari, E. Kauppinen, K. Nilsson, G. Sfiris, W. Maenhaut, Ash formation mechanisms during combustion of wood in circulating fluidized beds, *Proceedings of the Combustion Institute*, Vol. 28, 2000, pp. 2287-2295.
- [21] J. Jokiniemi, E. Kauppinen, Polttoprosessien aerosolit, in: R. Raiko, J. Saastamoinen, M. Hupa, I. Kurki-Suonio (ed.), *Poltto ja palaminen*, IRFR - Suomen kansallinen osasto, Helsinki, 2002, pp. 233-268.
- [22] A. Homrich, G. Galvão, L. Abadia, M. Carvalho, The circular economy umbrella: trends and gaps on integrating pathways, *Journal of cleaner production*, Vol. 175, 2018, pp. 525-543.
- [23] M. Pohjala, Tuhkien tilastokysely 2014, *Energiateollisuus ry*, 2015, 17 p. Available: https://energia.fi/files/397/Tuhkien_tilastokysely_2014_loppuraportti.pdf.
- [24] V. Pandey, N. Singh, Impact of fly ash incorporation in soil systems, *Agriculture, Ecosystems and Environment*, Vol. 136, 2010, pp. 16-27.

- [25] Z. Yao, X. Ji, P. Sarker, J. Tang, L. Ge, M. Xia, Y. Xi, A comprehensive review on the applications of coal fly ash, *Earth-Science Reviews*, Vol. 141, 2015, pp. 105-121.
- [26] R. Husgafvel, E. Karjalainen, L. Linkosalmi, O. Dahl, Recycling industrial residue streams into a potential new symbiosis product – The case of soil amelioration granules, *Journal of Cleaner Production*, Vol. 135, 2016, pp. 90-96.
- [27] Maa- ja metsätalousministeriön asetus lannoitevalmisteista, MMMa 13.9.2011/24, 2011. Available: <http://www.finlex.fi/data/normit/37638/11024fi.pdf>.
- [28] I. Brunner, S. Zimmermann, Zingg, P. Blaser, Wood-ash recycling affects forest soil and tree fine-root chemistry and reverses soil acidification, *Plant and Soil*, Vol. 267, 2004, pp. 61-71.
- [29] K. Schiemenz, J. Kern, H. Paulsen, S. Bachmann, B. Eichler-Löbermann, Phosphorus fertilizing effects of biomass ashes, in: B. Knapp, H. Insam (ed.), *Recycling of biomass ashes*, Springer, Berlin, 2011, pp. 17-32.
- [30] S. Vassilev, D. Baxter, L. Andersen, C. Vassileva, An overview of the composition and application of biomass ash.: Part 2. Potential utilisation, technological and ecological advantages and challenges, *Fuel*, Vol. 105, 2013, pp. 19-39.
- [31] M. Izquierdo, X. Querol, Leaching behaviour of elements from coal combustion fly ash: An overview, *International Journal of Coal Geology*, Vol. 94, 2012, pp. 54-66.
- [32] Lannoitevalmistelaki, L 29.6.2006/539, 2006. Available: <http://www.finlex.fi/fi/laki/ajantasa/2006/20060539?search%5Btype%5D=pika&search%5Bpika%5D=lannoitevalmistelaki>.
- [33] J. Pesonen, T. Kuokkanen, P. Rautio, U. Lassi, Bioavailability of nutrients and harmful elements in ash fertilizers: Effect of granulation, *Biomass and Bioenergy*, Vol. 100, 2017, pp. 92-97.
- [34] M. Moilanen, A. Saarsalmi, M. Kukkola, J. Issakainen, Effects of stabilized wood ash on nutrient status and growth of Scots pine – Comparison between uplands and peatlands, *Forest Ecology and Management*, Vol. 295, 2013, pp. 136-144.
- [35] Ecolan Silva, Ecolan Oy, web page. Available (accessed 27.2.2018): <http://ecolan.fi/en/ecolan-silva-en/ecolan-silva-is-the-maker-of-your-forests-growth/>.
- [36] Naturlan metsärae, Napapiirin Energia ja Vesi Oy, web page. Available (accessed 27.2.2018): <https://www.naturlan.fi/>.
- [37] Peltotuhka, UPM-Kymmene Oyj, Hämeen Kuljetus Oy, web page. Available (accessed 27.2.2018): <http://www.peltotuhka.fi/>.

- [38] H. Mäkelä, H. Höynälä, Sivutuotteet ja uusiomateriaalit maarakenteissa - Materiaalit ja käyttökohteet, TEKES, Helsinki, 2000, 97 p.
- [39] S. Kumar, C. Patil, Estimation of resource savings due to fly ash utilization in road construction, *Resources, Conservation & Recycling*, Vol. 48, 2006, pp. 125-140.
- [40] M. Ahmaruzzaman, A review on the utilization of fly ash, *Progress in energy and combustion science*, Vol. 36, 2010, pp. 327-363.
- [41] V.G. Papadakis, S. Tsimas, Supplementary cementing materials in concrete: Part I: Efficiency and design, *Cement and Concrete Research*, Vol. 32, 2002, pp. 1525-1532.
- [42] SFS-EN 450-1, Betoniin käytettävä lentotuhka. Osa 1: Määritelmät, laatuvaatimukset ja vaatimustenmukaisuus, Finnish Standards Association, Helsinki, 2012.
- [43] C. Meyer, The greening of the concrete industry, *Cement and Concrete Composites*, Vol. 31, Iss. 8, 2009, pp. 601-605.
- [44] R. Kikuchi, Application of coal ash to environmental improvement: Transformation into zeolite, potassium fertilizer, and FGD absorbent, *Resources, Conservation and Recycling*, Vol. 27, 1999, pp. 333-346.
- [45] Regulation (EC) No 2003/2003 of the European parliament and of the council relating to fertilizers, 2003. Available: <http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=LEGISSUM:121278>.
- [46] Circular economy - Implementation of the circular economy action plan, EU, web page. Available (accessed 23.2.2018): http://ec.europa.eu/environment/circular-economy/index_en.htm.
- [47] Valtioneuvoston asetus eräiden jätteiden hyödyntämisestä maarakentamisessa, VNa 7.12.2017/843, 2017. Available: <https://www.finlex.fi/fi/laki/alkup/2017/20170843>.
- [48] Ympäristönsuojelulaki, L 27.6.2014/527, 2014. Available: <http://www.finlex.fi/fi/laki/ajantasa/2014/20140527?search%5Btype%5D=pika&search%5Bpika%5D=ymp%C3%A4rist%C3%B6nsuojelulaki>.
- [49] K. Korpijärvi, U. Mroueh, E. Merta, J. Laine-Ylijoki, H. Kivikoski, E. Järvelä, E. Wahlström, E. Mäkelä, Energiantuotannon tuhkien jalostaminen maarakennuskäyttöön, VTT Tiedotteita 2499, VTT, Helsinki, 2009, 75 p. Available: [http://www.otalib.fi/cgi-bin/thw/trip/?\\${BASE}=vttjure&\\${HTML}=wwwrecorden&\\${OOHTML}=wwwrecorden&\\${TRIPSHOW}=form=wwwabstracten&\\${FREETEXT}=R%3D61477](http://www.otalib.fi/cgi-bin/thw/trip/?${BASE}=vttjure&${HTML}=wwwrecorden&${OOHTML}=wwwrecorden&${TRIPSHOW}=form=wwwabstracten&${FREETEXT}=R%3D61477).
- [50] ST 12.2, Rakennusmateriaalin ja tuhkan radioaktiiviset aineet, Säteilyturvakeskus, 2010.

- [51] Valtioneuvoston asetus kaatopaikoista, VNa 2.5.2013/331, 2013. Available: <http://www.finlex.fi/fi/laki/alkup/2013/20130331>.
- [52] A. Hoffmann, L. Stein, Gas cyclones and swirl tubes - Principles, design and operation, 2nd ed. Springer, New York, 2008, 422 p.
- [53] J. Niskanen, M. Niskanen, Yritysrahoitus, Edita Publishing Oy, Porvoo, 2013, 460 p.
- [54] M. Haverila, E. Uusi-Rauva, I. Kouri, A. Miettinen, Teollisuustalous, Infacs Oy, Tampere, 2005, 510 p.
- [55] Valmet CYMIC and HYBEX reference list, Valmet, Unpublished document, 2018.
- [56] SFS-EN 15359, Kiinteät kierrätyspolttoaineet. Vaatimukset ja luokat, Finnish Standard Association, Helsinki, 2011.
- [57] Mastersizer 2000 user manual, Malvern Instruments, 2007.
- [58] Hydro 2000G/S user manual, Malvern Instruments, 2007.
- [59] Scirocco 2000 user manual, Malvern Instruments, 2007.
- [60] A. Ammann, Inductively coupled plasma mass spectrometry (ICP MS): a versatile tool, Journal of Mass Spectrometry, Vol. 42, 2007, pp. 419-427.
- [61] C. Novaes, M. Bezerra, E. da Silva, A. dos Santos, I. Rõmao, J. Neto, A review of multivariate designs applied to the optimization of methods based on inductively coupled plasma optical emission spectrometry (ICP OES), Microchemical journal, Vol. 128, 2016, pp. 331-346.
- [62] SFS-EN 12457-3, Jätteiden karakterisointi. Liukoisuus. Rakeisten jätemateriaalien ja lietteiden liukoisuuden laadunvalvontatesti. Osa 3, Finnish Standard Association, Helsinki, 2002.
- [63] SFS-EN 12457-2, Jätteiden karakterisointi. Liukoisuus. Rakeisten jätemateriaalien ja lietteiden liukoisuuden laadunvalvontatesti. Osa 2, Finnish Standard Association, Helsinki, 2002.
- [64] Nordpoolspot, Nordpoolgroup, web page. Available (accessed 12.6.2018): <https://www.nordpoolgroup.com/Market-data1/Dayahead/Area-Prices/FI/Yearly/?view=table>.
- [65] Sähkön hintatilastot, Energiavirasto, web page. Available (accessed 12.6.2018): <https://www.energiavirasto.fi/sahkon-hintatilastot>.
- [66] Mustankorkea - hinnasto, Mustankorkea Oy, web page. Available (accessed 15.4.2018): <https://mustankorkea.fi/neuvonta/hinnastot/suuret-kuormat-yritykset/>.

- [67] PHJ - hinnasto, Päijät-Hämeen jätehuolto Oy, web page. Available (accessed 15.4.2018): <https://www.phj.fi/jatteen-vastaanotto/hinnat/>.
- [68] Pirkanmaan Jätehuolto - hinnasto, Pirkanmaan Jätehuolto Oy, web page. Available (accessed 15.4.2018): [http://pirkanmaan-jatehuolto.fi/inet/pjoy/flow.nsf/documents/A139232C3ED6902FC22577D1003FBFBB/\\$file/Kasittelymaksut_2018.pdf](http://pirkanmaan-jatehuolto.fi/inet/pjoy/flow.nsf/documents/A139232C3ED6902FC22577D1003FBFBB/$file/Kasittelymaksut_2018.pdf).
- [69] A. Hoffmann, H. Arends, H. Sie, An experimental investigation elucidating the nature of the effect of solids loading on cyclone performance, *Filtration & Separation*, Vol. 28, 1991, pp. 188-193.
- [70] D. Boström, N. Skoglund, A. Grimm, C. Boman, M. Öhman, M. Broström, R. Backman, Ash Transformation Chemistry during Combustion of Biomass, *Energy & Fuels*, Vol. 26, 2011, pp. 85-93.