Tampere University

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UTILIZATION AND TREATMENT FEASIBILITY OF ASHES FROM FLUIDIZED BED BOILERS

Faculty of Engineering and
Natural Sciences
Master's Thesis
February 2020

ABSTRACT

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Master's Thesis
Tampere University
Degree Programme in Environmental and Energy Engineering
February 2020

Ash is a combustion residue from power plants which mainly consist of inorganic components as silicon, aluminum, and calcium. However, especially fly ashes are often enriched with hazardous trace elements as heavy metals and chlorides. These substances restrict the reuse and utilization of ashes which is an issue in view of circular economy. With different treatment methods, these harmful elements may be removed, or their leachability may be reduced. However, the treatment methods seem mainly to be economic unfeasible due to the low prices of bulk ash products. Sometimes, especially with fly ash from waste incineration, the treatment is essential even before the landfilling.

The aim of this thesis was to investigate ash utilization possibilities, the regulation which limits the reuse of ash, and treatment methods for different ash types. This part of the research was mainly carried out as a literature survey of the scientific articles, technical reports, statistics and regulation. The major end-uses of ash were in concrete or cement industry, road or earth construction, as fertilizer, or direct disposal including the landfill construction and the filling of old mines. In this thesis, the European Union standard of fly ash for concrete, the Finnish regulation for the ash fertilizers, and the Finnish regulation for wastes in the road or earth construction use were under consideration as a limiting regulation. In case of landfilling, the council decision of the European Union establishing criteria and procedures for the acceptance of waste at landfills was considered.

The major ash treatment technologies were divided into four classes in this research: carbonation and self-hardening, mechanical treatment, thermal treatment as well as chemical, electrochemical, and biological treatment. The variety of commercialization and techno-economic feasibility of the technologies were high. However, for the further investigation were selected acid leaching, carbonation, a commercial FLUWA process, and water washing. Cementation was considered as a dominant business as usual post-treatment method for waste incineration ashes. For the selected treatment processes, the mass and energy flows were determined with the help of technical reports. With these flows, the techno-economic analysis of the processes was executed. According to the calculations, the highest costs in the processes were input chemicals or water and effluent treatment due to the nature of the selected processes. Thus, the price of chemicals influences considerably the profitability of these processes. Within the non-process expenses, the waste tax for the landfilled ash was a significant part of the total cost. Due to this, it would be profitable to utilize as much ash as possible instead of landfilling. From the selected processes, carbonation and in some cases washing seemed to be economically feasible. Furthermore, the accelerated carbonation process could be attractive to study more due to its capability to work as a carbon capture technology.

After the process and feasibility calculations, the techno-economic analysis tool for ash utilization and treatment was implemented in Microsoft Excel. The tool provides information for the user about the utilization and treatment possibilities of ashes from different fuels. It also calculates the economic feasibility of the investment compared to the business as usual situation. With this information, the user may consider the feasibility of the ash treatment methods. At the end of this thesis, the scenario and sensitivity analysis for the calculations were performed.

Keywords: Ash, techno-economic analysis, utilization, treatment, fluidized bed boiler

The originality of this thesis has been checked using the Turnitin OriginalityCheck service.

TIIVISTELMÄ

Jere Jakonen: Leijupetikattiloiden tuhkien hyötykäytön ja käsittelyn teknistaloudellinen toteutettavuus
Diplomityö
Tampereen yliopisto
Ympäristö- ja energiatekniikan DI-tutkinto-ohjelma
Helmikuu 2020

Tuhka on palamisjäännös, jota syntyy voimalaitoksilla. Se koostuu pääosin epäorgaanisista komponenteista kuten piistä, alumiinista ja kalsiumista. Kuitenkin erityisesti lentotuhkiin rikastuu usein myös haitallisia aineita kuten raskasmetalleja ja kloridejä. Nämä aineet rajoittavat tuhkan uusiokäyttöä sekä hyödyntämistä, mikä on ongelmallista kiertotalouden näkökulmasta. Näitä haitallisia aineita voidaan kuitenkin poistaa erilaisilla käsittelymenetelmillä, tai niiden liukoisuutta voidaan pienentää. Usein tällaiset käsittelymenetelmät ovat kuitenkin taloudellisesti kannattamattomia tuhkatuotteiden alhaisen hinnan vuoksi. Joskus, erityisesti jätteenpolton lentotuhkien tapauksessa, käsittely on kuitenkin välttämätön jopa ennen kaatopaikkausta.

Tämän diplomityön tarkoituksena oli tutkia tuhkan hyödyntämismahdollisuuksia, tuhkan uudelleenkäyttöä rajoittavaa lainsäädäntöä sekä käsittelymenetelmiä erilaisille tuhkatyypeille. Näiden tutkiminen toteutettiin kirjallisuuskatsauksena hyödyntäen tieteellisiä artikkeleita, teknisiä raportteja, tilastoja sekä säädöksiä. Pääasialliset tuhkan loppukäytöt ovat betoni- ja sementtiteollisuudessa, maa- ja tierakentamisessa, lannoitteena sekä suorassa hävittämisessä, sisältäen kaatopaikkarakentamisen tai vanhojen kaivosten täyttämisen. Tässä työssä käyttöä rajoittavina säännöksinä tarkasteltiin Euroopan Unionin standardia betonissa käytettävälle lentotuhkalle, Suomen lannoitelainsäädäntöä tuhkan osalta sekä suomalaista asetusta jätteiden hyödyntämisestä maanrakentamisessa. Kaatopaikkaamisen tapauksessa tarkasteltiin Euroopan unionin neuvoston laatimia kriteerejä jätteen hyväksymisestä kaatopaikoille. Samat kriteerit pätevät myös Suomessa.

Tärkeimmät tuhkan käsittelyvaihtoehdot jaettiin neljään luokkaan tässä tutkimuksessa: karbonointiin ja itsekovetukseen, mekaanisen käsittelyyn, termiseen käsittelyyn sekä kemialliseen, elektrokemialliseen ja biologiseen käsittelyyn. Näiden teknologioiden kaupallisuusasteessa sekä teknoekonomisessa toteutettavuudessa oli suurta vaihtelua. Happoliuotus, karbonointi, kaupallinen FLUWA-prosessi ja vesipesu valittiin lähempään tarkasteluun. Sementointi valittiin mukaan vertailuksi jätteenpolton tuhkien vallitsevana jälkikäsittelymenetelmänä. Tämän jälkeen valituille käsittelyprosesseille määriteltiin massa- ja energiataseet teknisiä raportteja apuna käyttäen. Näiden taseiden avulla voitiin suorittaa teknoekonominen analyysi. Analyysistä huomattiin, että suurimmat yksittäiset kustannukset valituissa prosesseissa niiden luonteen vuoksi olivatkin prosessiin syötettävät kemikaalit sekä veden tai jäteveden käsittely. Näin ollen kemikaalien hinta vaikuttaa voimakkaasti prosessien kannattavuuteen. Prosessikustannusten ulkopuolella jätevero kaatopaikattavalle tuhkalle oli merkittävä kuluerä. Tarkastelluista prosesseista karbonointi ja joissain tapauksissa tuhkan pesu olivat taloudellisesti kannattavia. Lisäksi kiihdytetty karbonointiprosessi voisi olla kiinnostava lisätutkimuksen kohde, sillä sitä voidaan käyttää myös hiilidioksidin talteenottomenetelmänä.

Laskennan pohjalta luotiin tuhkan hyötykäytön ja käsittelyn teknoekonominen analyysityökalu Microsoft Exceliin. Työkalu tarjoaa käyttäjälle tietoa eri polttoaineiden tuhkien hyötykäyttö- ja käsittelymahdollisuuksista. Se laskee myös investoinnin taloudellisen kannattavuuden ja vertaa sitä tilanteeseen, jossa investointia ei tehdä. Näillä tiedoilla työkalun käyttäjä voi harkita tuhkankäsittelymenetelmän toteuttamiskelpoisuutta. Lopuksi laskennalle tehtiin vielä skenaario- ja herkkyystarkastelu.

Avainsanat: Tuhka, teknoekonominen analyysi, hyödyntäminen, käsittely, leijupetikattila

PREFACE

This master's thesis was made by the order of Valmet Technologies Oy in Tampere. I want to sincerely thank Marko Palonen for getting this interesting opportunity in the familiar team in which I had already worked as a trainee. I really appreciate the trust that the whole team has had on me during my career at the energy R&D projects team.

This thesis project was an interesting journey towards the graduation. From the very beginning to the completion of this whole process, there have been many stages that have taught very much. Firstly, I would like to express my gratitude to the steering group of my thesis project. Joakim Autio as a supervisor, Juha Roppo as an expert, and Teppo Riihimäki as an expert helped significantly to get this research done. Their support in everything related to ashes as well as to the project management was indispensable. Naturally, thanks for everybody who have participated in the development of this thesis in one way or another.

I want also to thank University Lecturer Henrik Tolvanen for being the responsible supervisor at Tampere University. His interest for the development of this thesis was priceless and advice solved many open questions. Furthermore, I want to thank Industry Professor Tero Joronen for his action as the second examiner.

Finally, I am grateful to my family for the support that I have had during my studies. Thanks also to all friends who have made my time in the university a lot of fun.

Tampere, 28 February 2020

Jere Jakonen

CONTENTS

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

ANC	Acid neutralization capacity
BFB	Bubbling fluidized bed
BHF	Baghouse filter
BTEX	Benzene, toluene, ethylbenzene, and xylenes
CA	Coal ash
CAPEX	Capital expenditures
CEN	European Committee for Standardization
CFB	Circulating fluidized bed
DOC	Dissolved organic carbon
DW	Demolition wood
Eco	Economizer
ESP	Electrostatic precipitator
EU	European Union
Evap	Evaporator
G/G	Grinding or granulation
HAB	Herbaceous and agricultural biomass
IRR	Internal rate of return
kWh	Kilowatt hour
L/S	Liquid to solid ratio
LOI	Loss on ignition
MIRR	Modified internal rate of return
MSW	Municipal solid waste
MWh	Megawatt hour
NPV	Net present value
OPEX	Operational expenses
PAH	Polycyclic aromatic hydrocarbon
PB	Payback period
PCB	Polychlorinated biphenyls
RDF	Refuse derived fuel
SH	Superheater
SRF	Solid recovered fuel
TDS	Total dissolved solids
TEA	Techno-economic analysis
TEX	Toluene, ethylbenzene, and xylenes
TOC	Total organic carbon
Wt%	Weight percent; mass fraction
WWB	Wood and woody biomass

d	derivative	
k	minimum required rate of return on the investment	[%]
I	initial cost of investment	[€]
m	mass	[kg]
$\dot{m}$	mass flow	[kg/h]
n	projects life	[years]
r	discount rate	[%]
t	time	
X_t	net cash flow	[€]

1. INTRODUCTION

Need for resource efficiency will increase in the future. There is not unlimited amount of virgin material for nowadays consumption, and challenges related to the climate change are going to grow. For this issue, the concept circular economy is going to respond. In the circular economy, consumption will be changed from the linear "extract-produce-use-disposal" model into the concept in which material is reused repeatedly. [1] However, the circular economy is still on the conceptual level and further research and development is needed. Nevertheless, this thesis tries to find some answers to the reuse and treatment feasibility of ashes from *fluidized bed boilers*.

In the waste framework directive of the European Union (EU), the waste utilization hierarchy has been determined. The hierarchy from the best one to the worst one is prevention, product reuse, material recycling, recovery, disposal with energy conversion, disposal other than to landfill, and landfill. [2] The first one, prevention, is the most recommended, and the last one, landfill, should be avoided. It may be concluded that when the disposal with energy conversion is preferred over the landfilling and other disposal, the amount of waste incineration will increase in the future. Thus, more complex and hazardous ashes are produced which need some treatment. Additionally, when all possible virgin material is utilized as material, the quality of waste fuel will decrease. This changes also the composition of ashes overall. Simultaneously, landfilling of ashes should be ended. Hence, this development increases the demand for different ash treatment methods.

Annually, approximately 780 million tons of coal ash and 480 million tons of biomass ash is produced [3, 4]. Furthermore, the quantity of ash from biomass combustion will likely grow in the future due to the willingness to use renewable energy sources [4][5, p. 80]. Biomass is considered as a carbon-neutral fuel, and hence it is used to cut the greenhouse gases of the energy sector. The problem are *hazardous trace elements*, usually heavy metals, which are enriched in the fly ash. [6] Therefore, technologically and economically feasible treatment methods for ashes are needed to improve the possibilities of ash reuse.

Treatment of harmful ashes causes costs for the power plant operator as well. Thus, it would be necessary to find methods either to create new value from ash or at least decrease the disposal cost. Now, it may be more expensive for the operator, depending on the location, to landfill *fly ash* from the co-combustion than utilize it for instance in cement or concrete. However, the capital expenditures of ash treatment systems are often too high for the power plant operator. [7, p. 224] In other words, the utilization of ashes is profitable but without any treatment. The International Energy Agency Bioenergy has also made the conclusion that landfilling has low costs compared with the development of new utilization technologies [8, p. 12]. Furthermore, ashes from waste incineration as well as biomass combustion have a high variety in the composition which make the utilization challenging. Additionally, the waste ash has the high content of hazardous trace elements [7, p. 226][9].

Nowadays, most of the ash from coal combustion is used in the before-mentioned concrete and cement industry. To the disposal ends up only a minor share of the produced ash. The situation is more complicated with the fuels which produce more complex ashes. However, for instance in Finland, the situation is still fair. In addition to the concrete application, other possible utilization options include road or earth construction and fertilizers. Only approximately 20% of the ashes are disposed in Finland. [10, 11] The research going on the topic of ash utilization as well as the present treatment methods are studied more in Chapter 2.

This study is restricted to the combustion of woody biomass and industrial residues as solid recovered fuel, refuse-derived fuel, and demolition wood. Coal ash is better known, and it is used as comparison. Peat is also included due to its usage in co-combustion in multifuel boilers [12, p. 127]. The study consists of three sections: a literature survey, process and economic calculations, and the techno-economic analysis tool implementation. In the end, the scenario and sensitivity analyses are executed, and results are discussed. The literature survey includes an investigation about ash formation and characterization, ash utilization possibilities and its limitations, ash treatment technologies, and the theoretical background of the process calculations and the economic evaluation. Before the techno-economic calculations, possible treatment and utilization options for different ash types are determined. Based on these possibilities, the mass and energy balance calculations of the processes are executed. These results are the foundation for the economic feasibility calculations which are applied in the techno-economic analysis tool as well.

The research questions of this thesis are the following:

- In which applications power plant ash can be utilized?
- What ash treatment technologies exist to achieve better quality or decrease the harmfulness of ashes?
- Which regulative limitations restrict ash reuse?
- Which applications and treatment methods are techno-economically the most feasible for the studied ashes?
- How can the utilization and treatment possibilities for different ashes be assessed?

The purpose of this thesis is to expand the knowledge of ash utilization and treatment. The value of this kind of information will increase in the future when the importance of resource efficiency in different industries is emphasized. Nonetheless, the knowledge is not enough to bring economic value. Hence, it is important to understand the business potential and the techno-economic feasibility of different options. On the other hand, it is necessary to be conscious for the reasons which make some processes unfeasible. Additionally, it is necessary to recognize the different economically feasible treatment possibilities before the landfilling of ash. Regulation might change the limits stricter for landfilling in the future, and thus the knowledge for the disposal of ashes, which utilization is not possible, is also essential.

2. ASH FORMATION AND UTILIZATION

In this chapter, ash formation, utilization and its limitations as well as the characterization of ashes are studied. Furthermore, treatment technologies of a different kind are introduced as well. Furthermore, this chapter represents theories for the further process calculations and techno-economic analysis. In order to understand the applications, it is necessary to understand the scientific background.

2.1 Formation of ashes in fluidized bed boilers

Ash is solid matter which is formed as a result of combustion [13]. In view of this study, it is a by-product of heat and power generation [7, p. 221]. It consists of mainly inorganic mineral elements [13]. Thermal conversions of solid fuels as well as formation of ashes in combustion are complex processes. Thus, many of mathematical models of thermal conversions are based on empirical measurements. [14, pp. 69] Even though partial reactions in the ash formation would be described well, there may still be problems on the whole process modelling [15]. This is one reason, why the utilization of some ashes is so challenging.

The composition of fuel has naturally an effect on the content of ashes. In this literature survey, the concentration is mainly on wood and woody biomass. Moreover, coal, or in some case peat, is included as comparison. Coal is often included researches related to ash reuse because its ash is better known and studied [16]. Wood belongs to the group of biomasses, but however, the term 'biomass' includes a lot of other materials and categories as well. [17, 18] Furthermore, industrial residues are included in the investigation, where appropriate. In this case, industrial residues can be considered as *solid recovered fuel* (SRF), *refuse derived fuel* (RDF) and *demolition wood* (DW). RDF is produced often from plastics or biodegradable materials and SRF from paper, wood, textiles, and plastics. Thus, the content of both fuels varies much. In addition, SRF has often a high calorific value, up to 30 MJ/kg with high hydrocarbon content. SRF, RDF, and DW are co-combusted with another main fuel, or fuels, as coal or biomass. [9, 19] Therefore, it is essential to understand the properties of the main fuel ash as well as properties of the substitutive fuel. Coal is not a homogenous group of fuels, neither. It is often divided into different types of coals, e.g. lignite, bituminous coal, anthracite and brown coal. The different coals form ashes with different compounds. [20, p. 271][21]

Furthermore, combustion conditions, the type of the burner, the possible contamination of fuel, and storage can have an influence on the ash composition. During the storing, the properties of ashes may also change. [5, p. 85] Hence, the ash-forming content in fuels varies significantly from the point of view of quantity and quality. For instance, the ash content in the wood trunk is usually less than one percent, whereas in some coals it can be more than ten percent. [20, p. 270] Vassilev et al. have stated that the ash yield for biomass is 0.1–67% while the mean value in their research article is 7.2%. According to them, woody biomass forms less ash than other forms of biomass. [13] Characteristics of ashes are described more in Section 2.2 below. Due to the variation of ash compositions, it is hard to state universally which is the best reuse application or treatment technology for the ashes. Regardless, the chemical, physical, and mineralogical properties of ashes should be defined properly to even make the utilization possible. [7, p. 221][22] Afterwards, the utilization possibilities may be categorized for every fuel and boiler [8, p. 12].

Solid fuel combustion systems can be divided into three parts: *grate combustion*, *fluidized bed combustion*, and *pulverized combustion*. All of them use different firing technologies and typical fuels which affects the composition and properties of ashes. [14, pp. 70, 72] In this thesis, concentration is on the fluidized bed combustion. From the bubbling fluidized bed boiler, the quantity of produced *bottom ash* is 5–17 weight percent, and the rest is fly ash. In some cases, the amount of bottom ash can be as high as 50–60 wt%. [23] As comparison, 10–15 wt% of produced ash is bottom ash and correspondingly 85–90% is fly ash in pulverized coal combustion [7, p. 223].

In the pulverized combustion, fly ash can be formatted in two different ways: during the vaporization of volatiles, or during nucleation and coagulation. The rest of fuel, char, forms coarser fly ash during combustion compared to the vaporization route. [14, pp. 79] In fluidized bed boilers, the ash formation is somewhat different in comparison with the pulverized combustion due to the bed material in the furnace. The formation process is described in Figure 1.

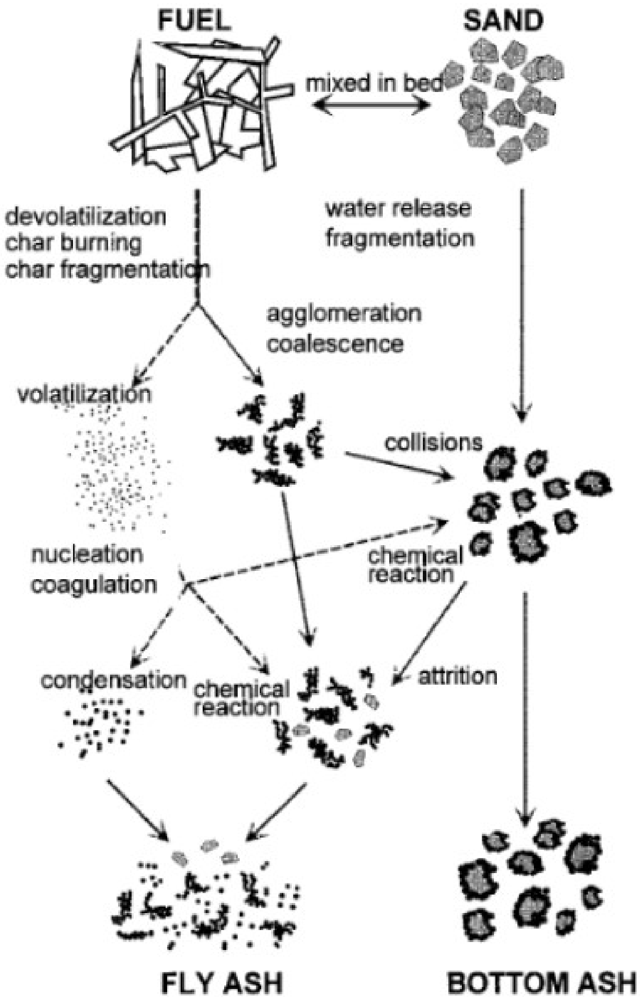

Figure 1. *Ash formation in the circulating fluidized bed boiler [15]*

In the bubbling fluidized bed (BFB) boiler, bottom ash consists of sand particles from original bed material, impurities such as soil and little stones from feedstock, and the unburnt fuel fraction. Thus, the largest component is mainly silica (SiO_2) from the sand, approximately 70–80 wt%, followed by calcium oxide (CaO), around 10–20 wt%. This kind of bottom ash is usually classified as non-hazardous waste. [23] Lind et al. noticed in their research that the bottom ash from the circulating fluidized bed (CFB) boiler was formed by the deposition of ash on the surface of sand, in this case quartz, as well as by the diffusion of the ash elements into the sand. In the porous deposit layer, there were mostly calcium (Ca) and oxygen (O) present. Correspondingly, the major elements reacting via diffusion were potassium (K), sodium (Na), and zinc (Zn). Forest residue and willow were used as a fuel in the research. On the other hand, fly ash is formed by nucleation or coagulation. The finer fraction is generated as a result of nucleation of volatized elements as potassium chloride (KCl) and potassium sulfate (K_2SO_4), whereas the coarser fly ash is formed by the coagulation of non-volatile ash species. [15]

The properties of ashes vary depending on the collection point. [7, p. 220–221] In fluidized bed boilers, there are two places where these ashes are collected. The first place is under the furnace, where the bottom ash, or sometimes called bed ash, is collected. The second collection location is in the flue gas duct, where the fly ash is captured. [14, p. 71] There can be a collection point for coarse fly ash in the cyclone of the CFB boiler as well [18].

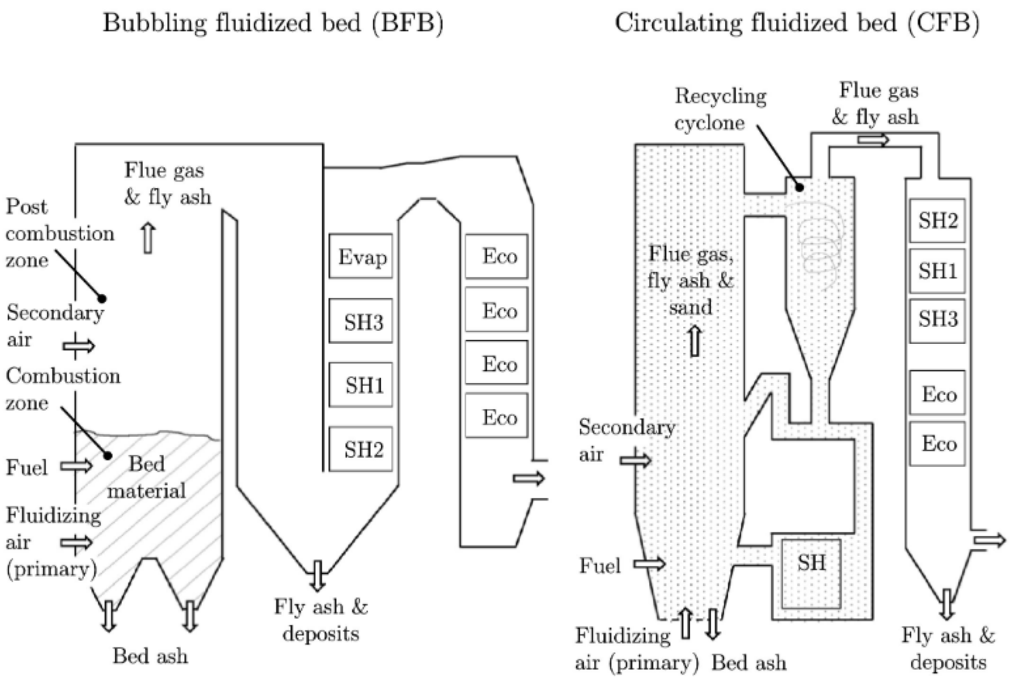

Figure 2. *Bubbling and circulating fluidized bed boilers [14, pp. 71]*

The removal locations of ashes in fluidized bed boilers can be seen in Figure 2. The abbreviations in the figure are the evaporator (Evap), the superheater (SH), and the economizer (Eco). The grain size distribution of biomass fly ash is typically a bimodal curve. The first maximum is approximately at 0.2–0.5 µm and the second one at several micrometers. The curve type is typical for the ash formation due to the two different ways of the process as mentioned before. [24] The grain size of bottom ash is greater compared with fly ash [25]. The amount of enriched trace elements is also higher in fly ash as in bottom ash [6] which makes utilization possibilities different for it. After the boiler, there might be different kind of flue gas cleaning systems as electrostatic precipitators (ESP) or baghouse filters (BHF) which collect the fine fly ash as well [18]. Furthermore, combustion additives, as limestone, may have an impact on the composition of ashes [26].

2.2 Characterization of ashes

Biomass ashes have been studied widely. Nevertheless, due to its complexity, the understanding about its characteristics is incomplete. [4] However, the composition of biomass ashes can be divided into three following parts [13]:

1. Major elements (>1% of elemental concentration)
2. Minor elements (0.1–1%)
3. Trace elements (<0.1%)

Major ash-forming components in biomass are aluminum (Al), calcium, chlorine (Cl), iron (Fe), magnesium (Mg), phosphorus (P), sulfur (S), manganese (Mn), potassium, silicon (Si), sodium, and titanium (Ti) which are commonly in an oxide form [13]. There are approximately 229 phases or minerals, mainly inorganic, identified in biomass ashes [16]. The ashes are mostly composed of amorphous non-crystalline as well as crystalline to semi-crystalline mineral components. In addition, there is some organic matter as char and organic minerals. Furthermore, some fluid matter exists as well. [4] Consequently, the ash from combustion of wood mainly consists of alkali and alkaline-earth metals, whereas silicon, aluminum and iron can be major components in coal, peat and fast-growing biomass ash. Sometimes sand or clay from treatment and transportation may increase the amount of silicon in ash. On the other hand, bedding plants have the higher content of silicon compared with perennials because it is an important element for them. The amount of nutrients (e.g. P, K) also varies during the seasons and depends on the used fertilizers. Furthermore, there are less nutrients in old plants. [20, p. 270] It is also noteworthy that the combustion conditions as well as fuel preparation have an effect on the composition of ashes [13]. Additionally, the ash-forming components are the same with coal and SRF, but the concentrations are different [9].

In view of combustion, unburnt carbon in ashes can be described with the variable *loss on ignition* (LOI). For lignite, the range of LOI of ash is 0–5%, and for subbituminous coal, it is 0–3%. Bituminous coal has the largest range of variation, 0–15%. In the research of Modolo et al., the LOI of bottom ash from biomass combustion was 2.1%. [23] Overall, the LOI as well as the calorific value of bottom ashes are often low. The situation with fly ashes varies and both very low and high LOIs occur. [7, p. 220–221] Unburnt carbon has sometimes negative effects on ash applications, for instance in concrete, so it is often an undesirable property. On the other hand, the separated carbon may have some applications e.g. as adsorbent, filler, or an option for graphite. [21]

As mentioned above, the elements which elemental concentration is more than 1% of ash are called major elements. In Figure 3 is described the variation of the major compositions of different ash types. At the corners of the triangle, there are different composition combinations. The scale on the sides describes the ratio of the combination related to the other combinations.

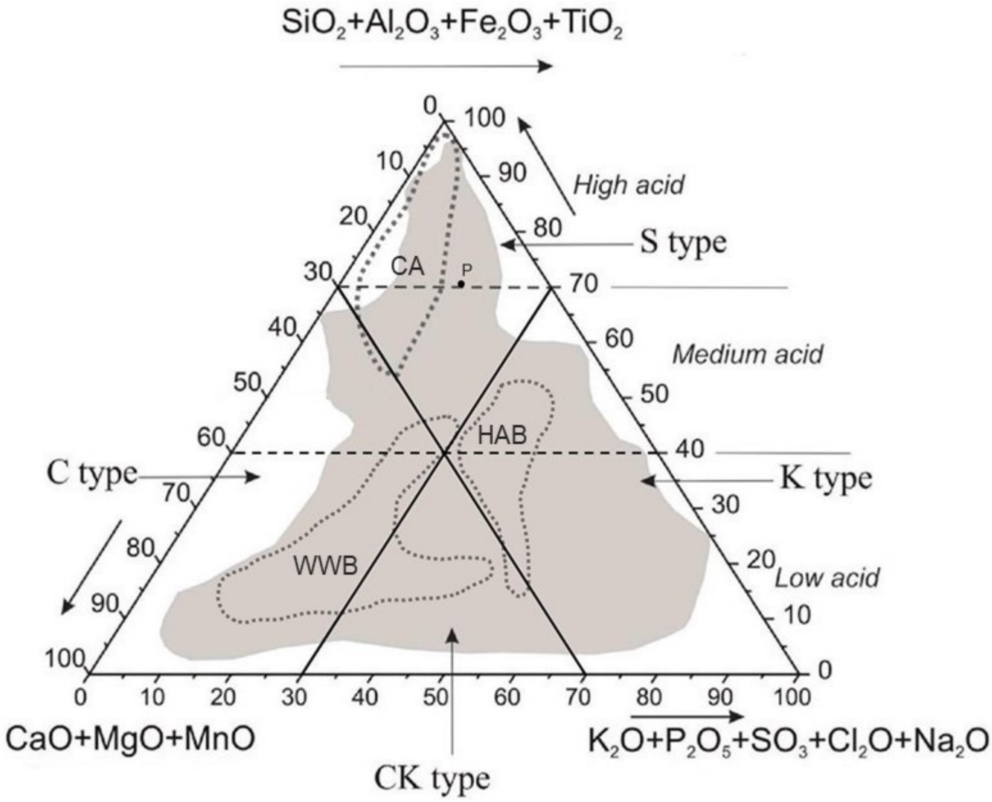

Figure 3. *Composition of different ashes, adapted from [13]*

The brown area inside the triangle is an area where biomass ashes where observed to be at. Inside the brown area, there are subareas marked with the dashed line for the ashes of the different kind. There are areas of coal (CA), wood and woody biomass (WWB), and herbaceous and agricultural (HAB) biomass. In addition, the point P is peat. These areas are the approximate zones where Vassilev et al. were located the results of different elemental analyses of ashes from multiple sources. The HAB area is described as a reference for the high potassium zone. The triangle is divided into four sections: C, K, CK, and S. Wood and woody biomass is located mainly on the C section which means that CaO, magnesium oxide (MgO), and manganese oxide (MnO) are the characteristic components of it. Correspondingly, herbaceous and agricultural biomass contains more potassium oxide (K_2O), phosphorus pentoxide (P_2O_5), sulfur trioxide (SO_3), dichloride monoxide (Cl_2O), and sodium oxide (Na_2O) so its place is on the K part. For coal, the components are SiO_2, aluminum oxide (Al_2O_3), Fe_2O_3 (iron (III) oxide), and titanium oxide (TiO_2) and the section is S. In the following Table 1, chemical compositions of ashes and the ash content from chosen fuels are described more precisely. The values are suggestive. [20, p. 270]

Table 1. *Ash content and composition of ashes from different solid fuels, wt%*

Fuel	Ash	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3	Rest	Source
Anthracite	7.4	**46.6**	**23.6**	8.1	-	7.0	1.2	0.1	0.5	6.0	6.9	[20, p. 271]
Brown coal	22.0	**42.6**	**9.7**	1.3	-	8.9	-	6.2	0.9	**15.6**	14.8	[20, p. 271]
Lignite, Greek	12.4	**32.7**	**17.3**	8.7	-	**21.2**	5.3	0.3	0.8	6.0	7.4	[22]
Peat	1.6	**31.8**	**13.1**	**11.0**		**21.1**	6.0	1.4	2.0	-	13.6	[20, p. 271]
	16.8	**20.0**	5.2	**70.0**	2.2	4.7	0.7	0.5	0.7	-	-	[20, p. 271]
Birch	0.3	0.9	-	-	3.5	**45.8**	**11.6**	8.7	**15.1**	2.6	11.8	[20, p. 271]
Birch bark	1.6	3.0	-	1.0	3.0	**60.3**	5.9	0.7	4.1	-	22.0	[20, p. 271]
DW30%	-	**53.5**	**17.2**	6.3	0.4	8.1	2.8	1.4	2.3	3.1	4.9	[27]
Pine	0.2	3.5	-	-	2.7	**41.8**	**16.1**	3.1	**15.3**	4.5	13.0	[20, p. 271]
Pine bark	1.8	**14.5**	-	3.8	2.7	**40.0**	5.1	2.1	3.4	-	28.4	[20, p. 271]
RDF	16.2	**48.1**	9.5	2.7	1.5	**18.5**	2.0	3.3	1.9	-	12.5	[19]
Spruce	0.3	1.0	-	-	2.7	**36.8**	9.8	3.2	**29.6**	4.3	12.6	[20, p. 271]
Spruce bark	3.4	**21.7**	-	1.8	2.7	**50.5**	4.2	2.8	3.5	-	12.8	[20, p. 271]
SRF	12.2	**23.9**	7.9	3.1	1.7	**31.6**	3.0	0.4	1.1	7.0	20.7	[9]
SRF2	11.1	7.5	4.3	4.5	0.8	**60.4**	1.2	0.3	0.1	-	20.9	[19]
SRF33%	-	**53.3**	**16.9**	7.6	0.5	8.1	2.5	1.2	2.1	2.4	5.4	[27]
Wood & woody biomass (mean)	4.3	**22.0**	4.57	3.24	**4.99**	**39.2**	6.4	2.0	**12.4**	4.9	-	[13]

The concentration of chlorine compounds may be high, especially with biomass or waste ashes. For instance in the table above, the chlorine content of the SRF33% sample is 0.11 wt% [27]. It is also noteworthy that components of ashes are not necessarily in oxide form [20, p. 270]. It is just common practice to describe the composition with the most common oxides due to its simplicity. As a matter of fact, ash consists mostly of more complex oxides as potassium silicate (K_2SiO_3) or calcium phosphate ($Ca_3(PO_4)_2$). [24] Nevertheless, the variation between the chemical compositions of ashes is high. Those compositions can be different between samples even when considering the same fuel. For instance, the amount of Fe_2O_3 in peat ash varies from 11.0 wt% to 70.0 wt% in the table above. This strengthens the claim, which was mentioned in Section 2.1, that it is tough to determine the best treatment method for all ashes due to the different chemical compositions.

Ash yields vary significantly from one fuel to another as well. Wood has relatively low ash content compared with peat and some coals. Moreover, the ash content in SRF and RDF fuels is clearly higher in comparison with the wood ash samples. The amount of TiO_2 in the SRF and SRF2 ash samples were also 2.5 wt% and 7.5, respectively. In the case of SRF2, the TiO_2 is mainly originated from textiles. However, the contents of SRF and RDF fuels vary much, and it is also challenging to describe their universal elemental composition. [9, 19] SRF33% means the sample in which there is 33% SRF and 67% coal. The concentration of TiO_2 in the fuel was also high, approximately 5 wt%. Correspondingly, in DW30%, there is 30% demolition wood and 70% coal in the fuel mixture. [27] In the samples, the amount of coal increases aluminum and silicon oxide concentrations in the ashes. Grammelis et al. also noticed that quantity of titanium in the lab-scale co-combustion ash samples was considerable [22]. Some TiO_2 in two samples was also observed in a research by Steenari and Lindqvist. The titanium may be from the combustion of waste board that has as a TiO_2 pigment. Nonetheless, the TiO_2 was observed to be in insoluble form and hence no problems in recycling may occur during reuse of the ash. [28]

The fluidized bed boiler is often used in multifuel combustion [12, p. 127]. There are three fly ash (FA) samples from the bubbling fluidized bed boiler represented in Figure 4. These three samples represent typical fuel mixtures that are combusted in fluidized bed boilers. The fuel mixtures of the samples are [29]:

FA1: 70% forest residues, 30% peat

FA2: 60% forest residues, 30% recycled waste, 10% sludge from the paper mill

FA3: 50% forest residues, 40% peat, 10% recycled wood waste

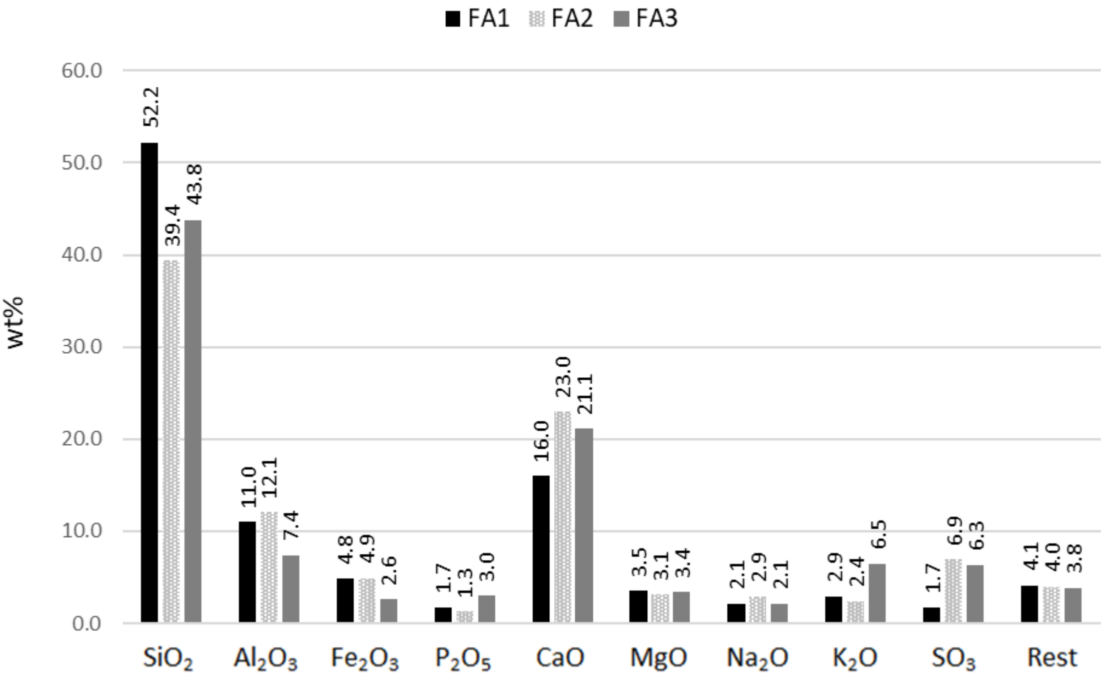

Figure 4. *Fly ash content from three Finnish multifuel BFB boilers [29]*

In comparison to Table 1, the results are on common ground. The amount of SiO_2 is higher in comparison with pure woody biomass due to peat and possible contamination from the forest residue treatment. Moreover, aluminum is originated from peat, and in case of FA2, likely from waste. The amount of CaO and K_2O are slightly low, even most of the fuel is woody biomass. In the samples FA2 and FA3, the amount of sulfur trioxide is higher than in references in Table 1. The SO_3 might also be originated from the waste.

There are always also heavy metals in biomass fuels which end up in ashes after the combustion [5, p. 83]. Additionally, contamination of feedstock can cause increased levels of heavy metals [7]. According to Karltun et al., the most common trace elements in ashes are arsenic (As), barium (Ba), boron (B), cadmium (Cd), chromium (Cr), copper (Cu), molybdenum (Mo), mercury (Hg), nickel (Ni), silver (Ag), vanadium (V), and zinc (Zn). [5, p. 84] Vassilev et al. also mentioned gold (Au), silver (Ag), beryllium (Be), rubidium (Rb), and selenium (Se) as trace elements representing in ashes [16]. However, some heavy metals, for instance Mn, Cu, and Zn, are important micronutrients for plants [30]. Cadmium is often the heavy metal which limits the usage of biomass ash [6]. The amount of hazardous trace elements is higher in finer fly ash. Many of heavy metals have low volatilization temperatures, and as a result, they end up into fly ashes during combustion. [5, p. 84][6] Furthermore, burning of demolition wood or wood treated with preservatives may have increased levels of some heavy metals as Pb and Zn in ashes. Waste wood may also contain insecticides, metals, or plastic. [5, p. 84][27]. Ściubidło and Nowak noticed also that the amount of trace elements, especially Zn, Cu, Cr, Pb, Ni, and Hg, were high in SRF ash [9].

In Table 2, typical values for the heavy metal concentrations of CFB boiler ashes are presented [31]. The fuels that are discussed are forest residues, wood, wood and peat, wood and bark as well as straw. There are also sample analysis results of ashes from two Finnish 296 MW (fly ash 4/bottom ash 1) and 246 MW (fly ash 5/bottom ash 2) BFB boilers. The boilers are located at the paper mill area. Fly ash 4 (FA4) was collected from the ESP and the fuel was 69% woodchips and bark, mostly pine, and 31% peat. Bottom ash (BA1) was collected from the outlet of the same boiler. Correspondingly, the fuels for fly ash 5 (FA5) and bottom ash 2 (BA2) were 60% bark, wood chips and sawdust, and 40% peat. The wood fuel was approximately 60% birch, 32% pine, and 8% spruce. [32]

Table 2. *Heavy metal concentrations of ashes in mg/kg, adapted from [31, 32]*

Element	Fly ash, literature	FA4	FA5	SRF33%	DW30%	Bottom ash, literature	BA1	BA2
As	1–60	14	31	10	54	0.2–3	8.5	8.1
Ba	549–588	-	-	-	-	535	-	-
Cd	6–40	3.3	3.5	6.7	9.2	0.4–0.7	0.5	<0.3
Co	2–300	-	-	26	26	0–7	-	-
Cr	40–250	74	120	**396**	**267**	>60	34	34
Cu	0–200	72	180	**1043**	**212**	15–300	23	25
Fe	3300–19500	-	-	-	-	-	-	-
Hg	0–1	0.1	0.2	0.58	1.31	<0.4	<0.04	<0.04
Mn	6000–29000	-	-	892	1005	2500–5500	-	-
Ni	20–100	33	88	90	66	40–250	13	12
Pb	40–1000	31	82	**388**	**3874**	15–60	4.6	<3.0
Ti	11	-	-	-	-	-	-	-
Zn	3280–4856	320	860	**1449**	**3604**	15–1000	430	700

There are multiple factors that impact to the amount of enriched heavy metals as mentioned before. The higher amount of enriched heavy metals in fly ash than in bottom ash can be seen in Table 2. The sample analyses FA4 and FA5 from the BFB boilers are convergent in comparison with the literature values. However, the amount of cadmium was minor in fly ashes and BA2. There was not much zinc compared to the literature values and the concentration of lead was minor in bottom ashes as well. The co-combustion of SRF or DW significantly increases the amount of Cr, Cu, Pb, and Zn. Especially, the enriched lead in case of demolition wood is extremely high. The amount is roughly 26 times the limit for ash forest fertilizers in Finland [33]. Moreover, the increased levels of polycyclic aromatic hydrocarbons (PAHs) may occur especially in fly ashes after incomplete combustion. PAHs are harmful for humans and the environment. [18] Additionally, dioxins and furans may be a problem in view of waste burning [34].

2.3 Utilization of ashes

According to Pels and Sarabér, biomass fly ash is used widely in the following applications [7, p. 222]:

1. as building materials and building products
2. as fertilizer
3. as fuels (carbon-rich fly ash).

These applications include itself many kinds of utilization forms in cement and concrete industry, road construction, landfilling, and agriculture. In agriculture, besides fertilizers, the ash usage in composting or soil stabilization are possible [8, p. 12]. Grammelis et al. introduce options to use fly ash in binders, wallboards, mineral wool production, ceramics, metallurgy, and waste water management as well [22]. In comparison, Vassilev et al. have listed the most potential biomass ash applications as follow: soil amendment and fertilization, construction materials and sorbents, and some minor usages as synthesis or production of minerals, ceramics, and other materials. [16] Voshell et al. mentioned that ash of co-combusted wood and peat may be the most feasible biomass ash in view of utilization. Other biomass ashes could be used in forest recycling, and correspondingly the possibilities for wood, bark, and wood waste ashes are forest recycling, treatment, or disposal. [6]

Table 3. *Current ash utilization, adapted from [25], the original source [8]*

Ash source	Application
Bottom ash/coarse fly ash from wood fired grate, BFB or CFB	Fertilizer, liming agent on agricultural or forest soils, additives to compost production, cement production, disposal
Fly ash from (wood fired) furnace, BFB or CFB	Cement production, brick production, construction material at landfills, concrete filler, asphalt filler, ming, soil stabilization, disposal
Bottom ash from co-firing peat and biomass in BFB or CFB	Disposal
Fly ash from co-firing peat and biomass in BFB or CFB	Fertilizer, grouting mines, soil stabilization, disposal
Bottom ashes from co-firing up to 20 wt% biomass/coal	Concrete aggregate
Fly ashes from co-firing up to 20 wt% biomass/coal	Additive in cement, concrete filler

In Table 3 above, the main applications are fertilizer or soil stabilizer and cement or concrete production. Overall, the applications seem to be similar as mentioned before. It is essential to notice that this is the current situation with practices, and the potential future applications have been listed. In Figure 5, there is statistic of ash applications presented. In case of Europe, the ashes are from coal combustion in the year 2016. In view of Finland, the ashes are from different kind of fuels in 2014. Approximately 30% of the Finnish ashes are from coal combustion and 40% from biomass combustion. Furthermore, about 10% is from multifuel boilers and 20% from waste incineration. Globally, the utilization rate of fly ashes may be relatively high, even though it depends strongly on the location. In Denmark, Italy, and the Netherlands, all the fly ash from coal combustion is further utilized. According to Gollakota et al., 45%, 38%, and 65% of the coal fly ash was utilized in China, India, and the USA, respectively. [35]

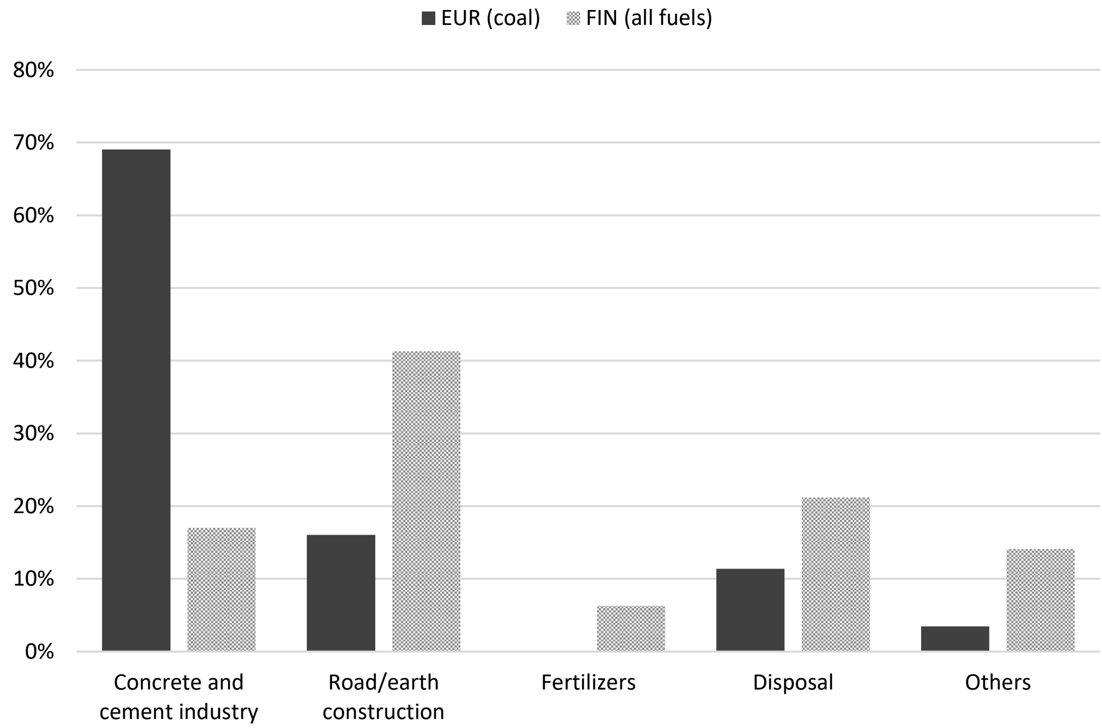

Figure 5. *Ash utilization in Europe and Finland [10, 11]*

The main application for coal ashes is in concrete and cement industry also according to the statistics in Figure 5. The share of biomass ashes decreases that kind of utilization in Finland. On the other hand, there is some fertilizer reuse, and the share of earth construction is higher. The fraction of disposed ashes is not huge with both fuels, but there are still some unused possibilities for reuse. It is noteworthy that the most of coal is combusted as pulverized [36], and hence it may be assumed that it is so in the statistics above as well. The suitable ash applications may also vary slightly compared to the fluidized bed combustion.

2.3.1 Concrete, cement, bricks, and other materials

The increase in concrete consumption has been rapid over the past 50 years due to the urbanization. Concrete production industry is a significant producer of greenhouse gases in the world. It represents globally approximately 8.6% of all anthropogenic carbon dioxide emissions, and therefore eco-friendlier concrete production alternatives are desirable. [37] Production of cement for concrete is energy intensive and thus it is the most expensive component in it. Hence, it is also profitable to replace part of the cement with fly ash. [38] Fly ash has a pozzolanic behavior and therefore it is suitable for the concrete applications. Thus, the most common application for fly ash from the coal-fired power plants is filler in concrete. Pozzolanic materials form insoluble and stable silicon and aluminum compounds with lime in the presence of water. [5, p. 83][6] This property of ash gives higher durability for the concrete. The fly ash also has several advantages compared with the conventional materials as the lower water consumption and evolution of heat, better pumpability, and improved corrosion resistance [38]. The fly ash from coal combustion is classified into two classes, C and F, depending on the concentration of calcium oxide which contribute to self-hardening properties of the concrete. When ash contains more than 70 weight percent SiO_2+Al_2O_3+Fe_2O_3, it is classified to the class F, while the ashes containing 50–70 weight percent are classified to the class C. [39] Ahmaruzzaman divided the coal ash utilization in the cement industry to three parts [38]:

1 cement replacement in Portland cement concrete

2 pozzolanic ingredient in pozzolanic cement

3 set retardant component with cement, replacing gypsum

Torgal suggests that bottom ash from coal combustion could also be used as a filler in concrete either alone or together with fly ash [40, p. 108]. Furthermore, the reuse of bottom ash from biomass combustion seems feasible, but the products should meet the targets for mechanical properties and stay below the leachability limits of hazardous trace elements [23].

Biomass complicates the situation in view of utilization. Biomass ashes can contain free CaO 2–3 wt%, K_2O 4 wt% and/or P_2O_5 3 wt% [7, p. 224]. In concrete applications, the amount of free CaO should be minor due to the formation of calcium hydroxide ($Ca(OH)_2$) which increases the volume and causes destruction of the structure [22]. Additionally, the use of biomass ashes is not attractive due to the chloride and alkali metal, e.g. potassium, content. These matters can cause for instance corrosion when leached. Furthermore, the amount of heavy metals or sometimes sulfates or loss on ignition can make the utilization impossible. [7, p. 230][16] The regulation complicates the reuse even more, and it restricts the reuse of biomass ashes in concrete [16]. The limitations of ash utilization in building products are studied in Section 2.4. However, there are also multiple studies about the usage of biomass ashes in construction materials, and the results are promising. Properties of final products have not been worse than in case of the usage of coal ash. [16] Moreover, there are some projects about the utilization of biomass ash in construction materials in Europe [25]. In view of waste ash, the usage of SRF ash has negative impact on the properties of concrete. On the other hand, the impact of demolition wood ash usage on the concrete properties was minor in the research by Sarabèr. [27]

Zhang et al. have written a review article about bricks using alternative materials and approaches. The article studies multiple researches related to the usage of coal fly ash or different biomass ashes in bricks. In case of the coal ash, it was noticed that with the samples made by the firing method, water absorption increases when the ash is used. Correspondingly, water absorption decreases when the alkaline activator is used, or the coal ash is stabilized with cement. [41] It is possible that pulverization of coal fly ash decreases the water absorption as well [41, 42]. In case of biomass ash, Zhang et al. noticed that all samples increased the water absorption and decreased compressive strength compared with the control groups without ash. The usage of biomass ashes in bricks would be able to meet the leaching behavior requirements. When considering rice husk and wood ash, the biomass ash improved the thermal performance. [41] On the other hand, fly ash bricks are lighter than the conventional ones [38]. Similar results were also in a research by Lessard et al. They concluded that it would be feasible to use biomass fly and bottom ash in dry-cast concrete products, even though the ashes had some little negative impact on the properties of the products [43].

Biomass ashes may also be utilized in porous *geopolymers*. Their advantages are low density, price, and thermal conductivity. Therefore, those materials are techno-economical feasible as thermal insulation. Furthermore, the fly ash geopolymers are fire-retardant, so there are some potential applications for the material. [44] Geopolymers are defined as alkali-activated aluminosilicates, and sometimes they are called inorganic polymers as well. [45]

Fly ash from coal combustion may also be used as lightweight aggregate. There are many applications for the aggregate, for instance the above-mentioned bricks or lightweight roofing tiles. [38] Pels and Sarabér introduced also an advanced way to utilize biomass ash concrete in artificial reefs. In the sea or ocean, the leachable alkali metals or heavy metals are not an issue, and it has not been observed that heavy metals would transfer to fauna. [7, p. 230] Carbon-rich ash, for example from pyrolysis or gasification, could also be used in production of lightweight aggregates. In addition, there are possibilities to use it as a filler in asphalt or asphalt-like products as well as in C-Fix blocks. C-Fix is a building material which consists of gravel, sand, filler, and bitumen as a binding agent. [7, p. 232]

Bottom ash from fluidized bed biomass combustion could be used as an aggregate in mortars. Modolo et al. discovered that the usage of the bottom ash had no negative impacts on the properties of the mortar. The utilization is also technically feasible. The grain size of bottom ash is suitable, but chlorides might need some treatment and control, for instance *washing*. Moreover, there may be economic potential for the mortar producers if they replace conventional processed sand with the bottom ash. [23]

The use of wood ash as a component in ceramics has also been investigated. The ash could replace conventional sand in the ceramic products. There are some changes in properties compared to the usage of the sand. Ash decreases the shrinkage and thermal conductivity, density, and compressive strength of the product. On the other hand, water absorption increases. [46] The utility of the changed property depends on the application in which the ash is used. The other materials that Vassilev et al. mention in their overview are ceramic membrane fillers for food processing, glass or glaze, overall silica based products, mineral fibers, and pharmaceutical products [16]. Other possibilities are the reuse of ashes as a raw material for synthetic basalt and fire-proof stones. [7, p. 234] The recovery of different elements and compounds from ashes is possible as well [16, 35].

2.3.2 Fertilizers and soil amendment

While plants grow, they restore nutrients from soil. After the combustion of the biomass, a lot of the nutrients end up into ashes. Consequently, it would be reasonable to recycle ashes back to soil. [7, p. 227] This is a model example of *circular bioeconomy*.

Wood ash is an interesting option as fertilizer, especially in peaty soils, where P and K are needed [5, p. 91–95][47]. Karltun et al. noticed that wood ash fertilization in mineral soils does not increase the growth of trees significantly. In mineral soils, nitrogen is the limiting component of growth, but it does not occur in ashes. Jacobson had the same result in his experimental tests that there is no increase in the growth of stems when wood ashes are used as a fertilizer in less fertile sites. By contrast, the wood ash fertilizer may increase the growth in on fertile sites. [48] However, there is no major difference in the dissolution of ash nutrients between peaty and mineral soils according to Nieminen et al. [47]. Additionally, ash works fine as pH balancer due to its basic nature [5, p. 84]. For instance, ash from clean wood pellets includes mostly Ca and Mg which form basic compounds. Biomass ashes may also contain sulfur and trace elements which are important nutrients. [7, p. 227]

As mentioned earlier, the most potential application for biomass ashes in multiple researches is usage as fertilizer or soil amendment. Biomass ash utilization as a compost additive was mentioned in literature as well. [8, p. 10] Nonetheless, knowledge of these applications is poor and further investigation is needed. For instance, necessary information about nutrients, hazardous trace elements, polluted char, the contamination of groundwater, pH and chemical balance, effects on microorganisms, extra salinity, dust emissions, ash pretreatment as well as ash swelling and obstructing of soil pores should be studied more. However, Vassilev et al. state the following concerns are the most important when considering the suitability of ashes for fertilizer usage: [16]

1. The amount of accessible or non-accessible nutrients for plants.
2. The amount of bioavailable and non-bioavailable trace elements and their impacts on the soil and plant from short-term to long-term.

The nutrient recycling is feasible especially with forest fertilization. There are all major nutrients in wood ash expect nitrogen which is released into the atmosphere with flue gases in combustion. Furthermore, the ash is usually from the local wood industry and the origin of biomass is known. In agriculture, the usage of ash fertilizers is more difficult. The ashes should be mixed with other fertilizers or manure, due to the lack of essential nutrients for arable lands.[7, p. 227][5, p. 80]

In biomass ashes, potassium is in easily leachable form and hence plants can utilize it immediately. Phosphorus is normally in an insoluble form, for instance as apatite, which can require even 20 years that it is exploitable for plants. In forests, this may be not a problem due to the long growth cycle, but the situation in agriculture is different. Fast-growing plants need phosphorus immediately, so additional phosphorus should be added to the ash fertilizers. [7, p. 227] On the other hand, the amount of released P to natural waters must be discussed when considering the usage of ash fertilizers, even though the leaching is minor in comparison with commercial fertilizers. [47] Furthermore, other useful nutrients may be in a water insoluble phases as glass, silicates, or char which makes the utilization problematic for plants [16]. By contrast, K, Na, B, and S are usually in highly soluble form [47].

The problem with some biomass ashes are enriched hazardous trace elements. The issue occurs with fine ashes and especially when semi-biomass, as wastes or demolition wood, is burned. The harmful elements as As, B, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Se, and Zn contaminate ashes, and make the reuse more difficult, particularly when these elements are in water-soluble form. The challenge is that the enrichment happens differently with every fuel and boiler. [16] However, Nieminen et al. noticed in their experimental research that heavy metals are highly insoluble form in wood and peat ash fertilizers. On the other hand, Nieminen et al. noticed also that the heavy metal and nutrient concentrations are lower in peat ash than in wood ash. [47] Huotari et al. observed that no leaching or enrichment of heavy metals to food products were reported anyway. This is an interesting finding, because in many countries, ashes are considered as waste and utilization is restricted. This is a result of concern of heavy metal leaching. It is possible that the change of pH releases insoluble heavy metals to water. On the other hand, some increase of heavy metal concentrations in berries and mushrooms after ash fertilization have still been observed as well. However, the increase was minor compared to the natural variation. In some researches, an elevated amount of Cd was found in fauna in short term. [30]

Carbon-rich ash can be used as fertilizer as well, even though carbon is not a nutrient. It is nor a contaminant, so the presence of it is insignificant from the point of view of fertilization. However, Pels and Sarabér suppose that the use as fertilizer is not the most attractive option for carbon-rich ashes. [7, p. 232–233] There may also be the large content of other non-valuable components in view of fertilization as silicon oxides. This was observed in Section 2.2 especially with coal ashes.

The reactivity of ash can sometimes be reduced with pretreatment. In that case, the ash is mixed with water and then pelletized, granulated, or spontaneously stabilized and crushed. [5, p. 85] The treatment can be useful when the fertilizers are produced. Treatment technologies are discussed more in Section 2.5.

2.3.3 Infrastructural works

Fly ash from coal combustion may be used as soil stabilizer in roadway construction due to the pozzolanic properties of the ash which are applicable at the base of the road. Additionally, fly ash is wider available in some locations compared with conventional solutions. [38] The usage of biomass fly ash in asphalt filler has been studied as well [8, p. 11]. Sarabèr concluded that the utilization of SRF and demolition wood ash from co-combustion with coal may also be feasible as asphalt filler [27]. Coal ashes may also be used as mine filling, in locations, where coal mine plants are close [38]. Or in some cases, coal bottom ash may be used in snow and ice control [25]. In Sweden, biomass fly ash is also used as construction material in landfilling [25, pp. 48].

The utilization of fly ashes in earth construction costs less than conventional options, especially when the transportation distance is short. The fly ash itself is often available for free. In the article by Ahmaruzzaman, 10–20% cost savings are mentioned, but there is no source for the number. [38] Moreover, it is not mentioned that are those savings applicable in his home country India or globally.

Bottom ashes are also commonly used in road construction, groundwork or the embankment. [7, p. 223–224] In road construction, and for example landscaping, it is important that leachable components of ashes meet regulatory limits and stay below them [7, p. 224]. In case of the bottom ash, this is not a problem due to the before-mentioned inert nature of it. By contrast, fly ashes may need some treatment because of the leachable trace elements as heavy metals. These regulatory limits will be further elaborated in Section 2.4. However, the evaluation of environmental impacts is the greatest obstacle for the wider reuse of waste materials, as well as ashes, in civil works [49].

2.3.4 Fuel or adsorbent

It is possible to replace coke or fossil carbon in metal industry with carbon-rich ash. In this application, the ash must have high quality which makes the usage unprofitable. Moreover, the amount of ash needed is high. The use of carbon-rich ash as biochar is under research as well. The ash could also be utilized as fuel due to high calorific value. [7, p. 233] In the application, carbon-rich ash can be used in a form of briquettes in barbecues and fireplaces. However, it needs an ignition fuel because the lack of volatiles makes the ignition challenging. [7, p. 234] Separated unburnt carbon from coal combustion may also be used as adsorbent, filler, or an option for graphite [7, p. 234].

In addition, there is some research executed about the adsorptive nature of biomass ashes. It could be possible use the ashes to remove harmful trace elements and compounds. The trace elements include here for instance mercury or other heavy metals and compounds of ammonia (NH_3), nitrogen oxides (NO_x), phosphates (PO_4), and sulfur oxides (SO_x). These could be removed for instance from wastewater or gas emissions. [16, 38] In case of desulfurization, the formula is [38]:

$$Ca(OH)_2 + SO_3 \rightarrow CaSO_4 + H_2O, \tag{1}$$

so it could work with biomass fly ash which has high CaO content. In case of mercury and NO_x recovery and organic matter, unburnt carbon is in a key role via adsorption. This property could be used in dye removal in textile industry, for instance. For phosphate recovery, calcite ($CaCO_3$) is in a key role. Furthermore, it is possible to produce zeolites via synthesis from coal ash. They can be used in wastewater treatment. [28]

2.4 Limitations of ash utilization

There are many regulative limitations which restrict the wider utilization of ashes. Furthermore, the regulation and standards vary around the world which makes the situation even more complex. [25, 38] Barriers may also be technical, economical, or institutional, and lack of knowledge or information make the reuse of ashes more difficult [38]. In the European Union, the commission has determined the categorization list for different wastes. In the list, fly ash from co-combustion containing hazardous substances is defined as hazardous waste. Otherwise, the rest of ashes in view of this thesis are categorized as waste. [50] The leaching limits are presented in the following Table 4. The limits are based on the leaching test standard EN 12457-2. The liquid-to-solid (L/S) ratios are 10 l/kg, when the particle size is under 4 mm as it is with ashes. Furthermore, leaching limits can be regulated tighter by the European Union's member state. [51] It should be noticed that these numbers are not comparable with the limits in Table 2 and Table 7 due to the different measurement unit. Those tables have absolute concentration limits and in the following table, the leaching limits are presented.

Table 4. *Leaching limits for landfilling in the EU, L/S=10, mg/kg dry substance [51]*

Element	Inert waste	Non-hazardous waste	Hazardous waste	Reference [52]
As	0.5	2	25	0.12
Ba	20	100	300	2.26
Cd	0.04	1	5	0.01
Cr, total	0.5	10	70	**3.35**
Cu	2	50	100	1.42
Hg	0.01	0.2	2	0.0
Mo	0.5	10	30	**1.53**
Ni	0.4	10	40	0.1
Pb	0.5	10	50	**234**
Sb	0.06	0.7	5	0.02
Se	0.1	0.5	7	0.07
Zn	4	50	200	**44.1**
Chloride	800	15,000	25,000	**33,200**
Fluoride	10	150	500	10.0
Sulfate	1,000[1]	20,000	50,000	**17,000**
Phenol index	1	-	-	-
DOC[2]	500	800	1,000	16.6
TDS[3]	4,000	60,000	100,000	-

[1] If the waste does not meet this value, it may still be considered as complying with the acceptance criteria if the leaching does not exceed 6,000 mg/kg. The value may be determined either by a batch leaching test or by a percolation test under conditions approaching local equilibrium.

[2] If the waste does not meet the limits at its own pH value, it can be tested at pH 7.5–8.

[3] The values for TDS can be used alternatively to the values for sulphate and chloride.

In Table 4, DOC is dissolved organic carbon, and TDS is total dissolved solids. The reference sample is fly ash from bubbling fluidized bed combustion of recycled wood.

There, the amount of Cr, Mo, Zn, and sulfates exceed the limits of inert waste. However, the more significant observation is that the concentration of Pb and chlorides classify the ash as hazardous waste. There are other relevant limitations to ashes in the same regulation as well. They are presented in Table 5.

Table 5. *Other relevant limitations [51]*

Parameter	Inert waste	Non-hazardous waste	Hazardous waste
TOC	30,000 mg/kg[1]	5%[2]	6%[3,4]
PAH	Limits set by the state	-	-
pH	-	min. 6.0	-
ANC	-	Must be evaluated	-
LOI	-	-	10%[3]
BTEX	6 mg/kg	-	-
PCB	1 mg/kg	-	-
Mineral oil	500 mg/kg	-	-

[1] In the case of soils, a higher limit value may be admitted by the competent authority, provided the DOC value of 500 mg/kg is achieved at L/S = 10 l/kg, either at the soil's own pH or at a pH value between 7.5 and 8.0.

[2] If this value is not achieved, a higher limit value maybe admitted by the competent authority, provided that the DOC value of 800 mg/kg is achieved at L/S = 10 l/kg, either at the material's own pH or at a pH value between 7.5 and 8.0.

[3] Either LOI or TOC must be used.

[4] If this value is not achieved, a higher limit value maybe admitted by the competent authority, provided that the DOC value of 1,000 mg/kg is achieved at L/S = 10 l/kg, either at the material's own pH or at a pH value between 7.5 and 8.0.

In the table above, TOC is total organic carbon, PAH is polycyclic aromatic hydrocarbon, ANC is acid neutralization capacity, LOI is loss on ignition, BTEX is benzene, toluene, ethylbenzene and xylenes, and PCB is polychlorinated biphenyls. In case of waste incineration, it is also possible that the ash forms hydrogen when stored due to unoxidized aluminum. This causes an explosion risk which can restrict the usage of the ash. However, for clean biomasses this risk is negligible. [49]

Nearly all of fly ash from pulverized coal combustion meets the targets of the European Standard 450 “Fly ash for concrete” by European Committee for Standardization (CEN) [7, p. 224]. The limit values for measurement results are introduced in Appendix A. In addition to the limit values, the proportion of ash from coal is not allowed to be less than 60%, or in case of green wood less than 50%. The share of coal can be calculated with the formula which is introduced in Appendix A as well. Furthermore, when using virtually ash free liquid and gaseous fuels, their share of the net calorific value should not be more than 40%. Nevertheless, those liquid and gaseous fuels can be used as a start fuel. [53] However, the regulation is only made for coal ashes with some allowance of mixing it with other fuels [49]. Furthermore, if cement is produced, the European standard EN 197 “cement composition” should be satisfied. Correspondingly, there is a standard EN 13005 for the properties of lightweight aggregates.

As mentioned before, when ashes are used in infrastructural works, they must meet the limits for leachable hazardous elements. The Finnish limits are presented in Table 6. It is essential to notice that the maximum thickness of the waste layer is 1.5 m for roads, fields, and the base of industry and warehouse buildings. Similarly, the maximum thickness is 5.0 m for the embankment and 0.2 m for the calculative thickness of the ash aggregate road. Moreover, the structure of the road or field is covered when there is more than 10 cm uncontaminated natural soil or grave material on top. For the embankment, the similar requirement is 50 cm of uncontaminated material. Correspondingly, the structure is paved, when there is an asphalt layer with the maximal dead volume of 5%, or when the maximal absorption of rainwater to the structure is 5% with the layer made of some other material.

Table 6. *Maximum leachability and concentration of harmful substances in earth construction applications in Finland, mg/kg, LS = 10 l/kg [54]*

Element	Road		Field		Embankment	The base of industry and warehouse buildings	Ash aggregate road
	Covered[2]	Paved[3]	Covered[4]	Paved	Covered		
As	1	2	0.5	1.5	0.5	2	2
Ba	40	100	20	60	20	100	80
Cd	0.04	0.06	0.04	0.06	0.04	0.06	0.06
Cr	2	10	0.5	5	1	10	5
Cu	10	10	2	10	10	10	10
Hg	0.03	0.03	0.01	0.03	0.03	0.03	0.03
Mo	1.5	6	0.5	6	1	6	2
Ni	2	2	0.4	1.2	1.2	2	2
Pb	0.5	2	0.5	2	0.5	2	1
Sb	0.7	0.7	0.3	0.7	0.7	0.7	0.7
Se	1	1	0.4	1	1	1	1
Zn	15	15	4	12	15	15	15
V	2	3	2	3	2	3	3
Chloride[1]	3,200	11,000	800	2,400	1,800	11,000	4,700
Fluoride[1]	50	150	10	50	30	150	100
Sulfate[1]	5,900	18,000	1,200	10,000	3,400	18,000	6,500
DOC	500	500	500	500	500	500	500
Concentration (mg/kg dry substance)							
Benzene	0.2	0.2	0.02	0.2	0.06	0.02	0.2
TEX	25	25	25	25	25	10	25
Naphthalene	5	5	5	5	5	5	5
PAHs	30	30	30	30	30	30	30
Phenolic compounds	10	10	5	10	10	10	10

[1]These values are not applied, if all the following applies: construction is located less than 500 meters from the sea, the leaching water flows to the sea, and there are no domestic water wells.

[2] If the thickness of the construction is maximal 0.5 m, the limits for Ba, V, chloride, and sulfate are 80; 3; 3,600; and 6,000 mg/kg, respectively.

[3] If the thickness of the construction is maximal 0.5 m, the limits for chloride and sulfate are 14,000 and 20,000 mg/kg, respectively.

[4] If the thickness of the construction is maximal 0.5 m, the limit for antimony is 0.4.

In the table above, TEX means toluene, ethylbenzene, and xylenes. The limits in Table 6 are between inert waste and non-hazardous waste limits which were presented before in Table 5. In case of an ash aggregate road, the amount of ash may not be above 30 wt%. Radioactivity properties of wood and peat ashes must also obey the limits by Radiation and Nuclear Safety Authority. [54] For other properties, the European standards EN 13282 “Hydraulic road binders” and EN 14227 “Hydraulically bound mixtures” should be applied as well.

The biomass ash fertilizers do not often meet the strict requirements of regulations and calculation methods. Nevertheless, it is necessary to create clear regulatory requirements for ash applications, and therefore the revision of European Fertilizers Regulation is under development. [8, p. 12–13] After the execution, it is possible to evaluate wider utilization and treatment processes for ashes. [49] In Finnish regulation, there are maximum limits for the hazardous elements in fertilizers as As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn as well as minimum limits for Ca, P, and K. The limits for agricultural or forestry usage are different. The ash may be originated from combustion of wood, peat, agricultural biomass, or animal waste. Untreated wood waste is accepted as well. [33]

Table 7. *Heavy metal concentration limits of fertilizers in Finland in mg/kg [33]*

Element	Forest fertilizers	Other fertilizers
As	40	25
Cd	25	1.5[2]
Cr	300	300
Cu	700	600
Hg	1.0	1.0
Ni	150	100
Pb	150	100
Zn	4500[1]	1500

[1] This value can be exceeded in case of lack of zinc in the soil, maximum is then 6000 mg/kg

[2] This value can be exceeded in case of ash or ash fertilizer usage in landscaping, farming or gardening, maximum is then 2.5 mg/kg.

From Table 7 and the literature values above, it can be noticed that the most problematic elements in ash fertilizer utilization are As, Cd, and especially Pb in case of biomass ash. There are also minimum limits for nutrients in the decree. There must be at least 2.0 wt% potassium and phosphorous summed up and at least 6.0 wt% calcium. Moreover, the major and minor nutrients must be informed, if the amount is more than 0.3% of dry substance. In case of other than forest fertilizers, the neutralization capacity (Ca) should be more than 10%. [33]

2.5 Treatment technologies

Due to the restrictions of utilization that were discussed in Section 2.4, different technologies for ash treatment shall be studied. With the treatment technologies, the quality of ashes may be improved, and thus it is possible to expand their reuse field. Nevertheless, the greatest challenge is the economic feasibility of the ash treatment processes. The level of post-treatment of ashes depends on the product that is made. According to Pels and Sarabèr, bulk products have not so high economic margins that it would be profitable to treat ash e.g. thermally or wash it. [7, p. 223] Voshell et al. mention that there is a hierarchy for the recommended treatment. The hierarchy [6] is adapted from the report of the Swedish Ash Programme [49, p. 67]:

1. no treatment
2. minimal treatment, e.g. aging or separation
3. more extensive treatment which improves the profitability of the product
4. intensive and expensive treatment processes; only if necessary

In other words, the intense processing of ashes is scarcely profitable. This means that recognition of the right application for every ash is very important. For that reason, the careful characterization of ashes is essential. In this chapter, a couple of commercial processes are introduced as well.

2.5.1 Carbonation and self-hardening

Self-hardening is a process, where ash hardens as a result of water addition. It is a simple and inexpensive method for ash stabilization. [28] Therefore, it is also a useful phenomenon in ash granulation. There occur several chemical reactions during self-hardening as hydroxide formation [28]

$$CaO + H_2O \rightarrow Ca(OH)_2, \tag{2}$$

a reaction of the *carbonation*

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O, \tag{3}$$

formation of gypsum

$$CaSO_4 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O, \tag{4}$$

and formation of ettringite

$$Ca_3Al_2O_6 + 3CaSO_4{\cdot}2H_2O + 26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O \tag{5}$$

Carbonation makes the product more brittle compared to the hydrated one. On the other hand, it lowers the solubility and thus extend the effective time of liming. It has also been noticed that the carbonation lowers the leachability of metals from ashes. [28] Hence, it can also be used before ash washing to avoid the leaching of heavy metals to wash water. Correspondingly, the stabilization of ash can be used as a pretreatment to immobilize hazardous elements before disposal. In a research by Atanes at al., sodium carbonate was used instead of carbon dioxide with promising results in accelerated carbonation. [55] By contrast, Lee and Bae noticed that the addition of $NaHCO_3$ accelerates the carbonation process more than the addition of Na_2CO_3 or NaOH. In their research, the additive was added with water to fly ash in the presence of carbon dioxide. [26] As mentioned in Section 2.1, storing changes the composition of ashes. It reacts with moisture and carbon dioxide from air and forms hydroxides, carbonates, bicarbonates, and other minerals [5, p. 85], so the reactions are similar with those above. This can be used as a treatment method as well.

Illikainen et al. and Ohenoja et al. have investigated the effect of different elements in ashes on the compressive strength of ash products. In both researches, wood and peat ashes form fluidized bed combustion were the research subject. Ohenoja et al. had also partially sludge from paper production as fuel in some samples. It still does not explain the differences. [56, 57] The impacts of the elements, which were total and reactive CaO, Al_2O_3, and SiO_2 as well as SO_3, are put in Table 8 together. The noteworthy detail is that the research group of both investigations is the same, so the results should be comparable. In addition to the table below, the content of free CaO does not have an improving effect on the self-hardening properties of ash. [56, 57]

Table 8. *Effect of reactive elements on compressive strength of ash products [56, 57]*

Component	Illikainen et al.	Ohenoja et al.
total CaO	improved compressive strength with higher concentration	no correlation
reactive CaO	improved compressive strength with higher concentration	optimal concentration 30%
total Al_2O_3	no clear correlation, even though some better results with higher concentrations	no correlation
reactive Al_2O_3	improved compressive strength with higher concentration	optimal concentration 3.5%
total SiO_2	decreased compressive strength with higher concentration	no clear correlation, optimal concentration around 25%, worse results with higher concentrations
reactive SiO_2	no clear correlation, even though some better results with higher concentrations	improved compressive strength with higher concentration
SO_3	improved compressive strength with higher concentration	no correlation, but a good result with a high sulfur sample

UPM has developed a technology with Specialty Minerals to recycle ash from the power plant. The ash is used in the paper production as calcium carbonate in the Schongau paper mill. The recycled ash can replace around one third of conventionally, and energy-intensively, produced calcium carbonate. [58] A company from the UK, called Carbon8 systems, has developed an accelerated carbonation technology for ash treatment. In the process, the ash is treated with carbon dioxide. The purpose is to avoid landfilling and get the ash reused, for instance as building material. The technology can be classified as carbon capture as well. [59]

2.5.2 Mechanical treatment

Grinding is a possible treatment method for bottom ash and coarse fly ash when finer particle size is needed. Furthermore, sometimes it may be useful to separate fractions of ash. The separation may enrich or concentrate wanted elements onto different fractions. Voshell et al. mention also air classification, flotation, and even triboelectrostatic or magnetic separation as possible options. Dry separation methods are a good alternative when reactivity is not wanted to be changed. In comparison, wet methods as flotation, can be used to remove unburnt carbon. [6]

One of the dry methods is before-mentioned air classification [6]. It seems that in combustion trace elements concentrate on finer ash fractions due to volatilization mentioned earlier [60]. Furthermore, calcium, sulfates, and chlorides are concentrated on finer fractions. Correspondingly, silica and aluminum are enriched to the coarser fraction. Thus, with dry separation it may be possible to catch enough heavy metals into fine ash fractions and utilize the coarser part of the material. [61] Mechanically, this kind of equipment is robust and simple and hence an interesting alternative. However, the grain size of coarse fraction may be too big. Therefore, it possibly needs also grinding before reuse [29].

Granulation decreases the solubility of ash compared to self-hardening and powdering [47]. It may also decrease the reactivity of ash [5, p. 85]. Thus, the ash fertilizer might only slightly increase the pH value of soil compared with the untreated ash product [30]. Moreover, the granulation decreases the dusting problem during fertilization [28].

2.5.3 Chemical, electrochemical, and biological treatment

Chemical treatment may be a good option in case of removal of heavy metals [62]. Especially, precipitation is a commonly used process to remove undesirable elements [63, p. 142]. In view of biomass, for instance, cadmium is often a limiting trace element of utilization. Other undesirable components, as chlorides, sulfates, or alkalis can be removed with chemical treatment as well. Disadvantages of this technology are the high consumption of water or chemicals, high cost, and residuals, e.g. chemical waste. [6]

One simple and inexpensive treatment option is washing of ash with water. In this process, salts, as chlorides, are dissolved in water, and thus the properties of the ash will improve in view of utilization or disposal. It is possible that some heavy metals are dissolved in water as well [55]. In a research by Mazzella et al., the disposal classification was improved only in case of chlorides, sulfates, and selenium, when the ash was treated by water. In case of heavy metals, it might be possible to remove molybdenum with water. [64] The residue water is an issue, and it must be treated further. [52] On the other hand, as mentioned previously, this technology may be economically unfeasible, even though the technological feasibility is good.

Inorganic or organic acid may be utilized in heavy metal removal. However, Karlfeldt Fedje at al. concluded that organic acids are not effective leaching agents [65]. The feasibility of the leaching process depends on the type of ash and acid. Alkaline leachates as sodium hydroxide (NaOH), NH_3, or sodium carbonate (Na_2CO_3) can also be utilized. Divalent metals react with hydroxides and form $Me(OH)_2$. Chelating agents may also be used, but it is not often utilized due to the high cost and difficulty of metal recovery from the chelated compound. [62] In addition to hydroxide precipitation, sulfides or carbonates can be used similarly for the removal of heavy metals [63, p. 144–146].

Electrochemical methods have also been researched. In the technologies, electrolysis is combined with an assisting agent for heavy metal, especially Cd and Pb, removal. [62] As mentioned before, these are one of the problematic trace elements in ashes, so this technology to remove them is an attractive option. Furthermore, bioleaching is an alternative method for heavy metals removal. In the technology, bacteria or fungi are utilized to remove hazardous trace elements. [62] Ion exchange can be applied to remove the undesirable trace elements from the effluent as well [66].

The *FLUWA process* is an example of the commercial ash treatment process. It is popular especially in Switzerland. In the process, ash is washed with the acidic scrubber liquid. Heavy metals are then extracted from ash. It is also possible to recover metals, especially zinc, from this effluent. The recover process is called FLUREC, and there is one operating plant in Switzerland. [67] By contrast, a Norwegian company NOAH treats ashes chemically without the recovery of metals. In their process, the ashes form gypsum which capture all the metals to inert form, and thus they will not dissolve in the environment. The ash is then disposed. [68]

Furthermore, Fortum has built an ash refinery for ashes from municipal solid waste incineration in Pori, Finland. In the refinery, ash is washed with sea water and waste acids. Then the dirty liquid will be cleaned, and finally the salty water flows back to the sea. Heavy metals will be absorbed to the ash, and it will be disposed. Hence, they avoid the *cementation* of ash of municipal solid waste (MSW) incineration before landfilling. [69, 70] In the cementation, the leachability of heavy metals and soluble salts, especially chlorides, is decreased before landfilling. It is one of the most common pretreatment technologies for the landfilling of waste ash. [71, 72] It is slightly unclear, how Fortum is going to refine the ashes, if they are still disposed. In Sweden, the company called Ragn-Sells has developed a similar concept. The high chlorine and heavy metal content restrict the disposal of the MSW ash without any pretreatment. The difference compared to Fortum's method is that the salts, KCl, calcium chloride ($CaCl_2$), sodium chloride (NaCl), and NH_3, are recovered from the water and utilized further, for instance as road salt. Heavy metals are also precipitated from the water and landfilled in this process after stabilization. [73]

2.5.4 Thermal treatment

Thermal treatment methods require a lot of input energy, so they are usually avoided. The possible processes are sintering, vitrification, and ash melting. The methods are mainly studied for municipal solid waste ashes and hence they are not in the scope of this study. [6] Volatilization of metals, sometimes with the assisting agent, is the major target in the thermal treatment [62]. On the other hand, the sintering just decreases the leachability of heavy metals due to the change of composition of ash. The result is a stable residue with non-leachable heavy metals. The leachability of sulfates seems also to reduce after thermal treatment, but there is no change with chlorides. [65]

2.6 Process calculations of the treatment methods

In this kind of techno-economic assessment, the mass and energy balances must be calculated first. For the economic evaluation, operational costs, investment costs as well as savings or revenues must be determined. All these above are dependent of the selected process under consideration. [74] In the mass flow analysis, the mass flow rates are calculated. In the general form, the law of conservation of mass is [75, p. 217]:

$$\frac{dm_{system}}{dt} = \sum_{in} \dot{m}_{in} - \sum_{out} \dot{m}_{out} \,, \tag{6}$$

where *dm* denotes the derivative of mass, *dt* means the derivative of time, and $\dot{m}$ denotes mass flow. The processes in this study are assumed to be steady state systems. In other words, the mass balances do not vary with time. In that case, the mass flow rates are equal in the inlet and outlet of the system, and the formula can be written as [75, p. 218]:

$$\sum_{in} \dot{m}_{in} = \sum_{out} \dot{m}_{out} \tag{7}$$

The equation means that the sum of mass flows entering the control volume equals the mass flows leaving the control volume [75, p. 218]. This form can be applied for every part of the system under consideration in this thesis. Energy in the treatment systems is often electricity. The consumption of electricity is usually given in a form of kilowatt hours per ash ton (kWh/t_{ash}) in the reports. [67, 76, 77] So, the amount of consumed electricity is got with multiplying this kind of value by the amount of ash tons.

2.7 Economic feasibility of the treatment methods

The economic feasibility of the selected treatment processes is also calculated. For the financial analysis, capital and operational expenditures as well as possible savings and revenues should be assessed [74]. After that, the profitability of the investment can be calculated. Firstly, the rough assessment of the profitability is calculated with the *payback method*. The payback method can be expressed as [78, p. 162]

$$Payback\ period = \frac{Total\ investment}{Net\ annual\ cash\ flow}. \tag{8}$$

The payback method tells how many years it takes for the net cash flow to match the initial cash outlay which is usually the investment. The method is very simple and gives some guidelines for the investment profitability, but it has a couple of disadvantages. It ignores the time-value of money as well as the cash flows after the *payback period* (PB). On the other hand, the payback period is not the best assessment method for investment profitability. [78, p. 163] Therefore, another method should be applied. In this thesis, the *net present value* method is used. The net present value method can be formulated as [78, p. 95]

$$NPV = \sum_{t=1}^{n} \frac{X_t}{(1+k)^t} - I \tag{9}$$

where X_t denotes the net cash flow at the end of the year *t*, *k* means the minimum required rate on the investment, *n* denotes the investment time, and I is the investment value. The annual cash flows are discounted to the present year with this method. Simply, if the net present value is positive, the investment is profitable with the interest rate required. [78, p. 94] Discounted cash flows may also be utilized in the *discounted payback period* method. Compared to the ordinary payback period, it considers the time-value of the money. [78, p. 162–163]

It is useful to calculate the *internal rate of return* (IRR) as well. The indicator gives the yield of the investment, or it thus it may be used as help when considering the economic feasibility of the investment. The IRR is formulated [78, p. 158]

$$\sum_{t=0}^{n} \frac{X_t}{(1+r)^t} = 0. \tag{10}$$

Here, solving the discount rate *r* gives the rate when the NPV is zero. When the IRR is higher than the minimum required rate on the investment *k*, the project is profitable. [78,

p. 158] The *modified internal rate of return* may be applied when the same reinvestment assumption at the cost of capital as in the NPV is wanted. In the MIRR calculation, cash flows generated by the project are reinvested at the cost of capital. In the IRR, the cash flows are reinvested to the internal rate of return of the project. There the sum of the terminal values of the net cash flows of the project is compared with the initial investment. With this present value interest factor, the interest rate may be determined. The interest factor from the MIRR calculation is lower than from the IRR, especially with the very profitable projects. [78, p. 176–182]

Nevertheless, the net present value is sensitive to price changes. Hence, some sensitivity analysis is needed. By changing the different inputs, the change of the NPV can be observed. However, the sensitivity analysis does not evaluate the risk and it needs to be assessed by the decision-maker. The other option for risk management is a scenario analysis. There one of the key variables is changed at a time. The analysis often seeks the worst and the best scenario which determine the range for the possible results. [78, p. 288–291]

3. MATERIALS AND METHODS

In this chapter, the selection method of the treatment for different ashes and utilization is described. It is noteworthy to state that regulative limitations as well as the properties of ashes restrict the ash reuse. To meet these limitations, some treatment technologies may be applied. In addition, the calculation methods for the mass and energy flows of the treatment processes, which are based on the theory in Section 2.6, are described. For the economic feasibility analysis, the methodology of cost calculations is introduced as well. Finally, the implementation of the techno-economic analysis tool is presented.

3.1 Method for ash treatment technology selection

In this section, the method for the creation of the possible utilization and treatment chains, which are presented in Section 4.1, is described. This information will be applied to the techno-economic analysis tool as well as to the selection of the suitable treatment processes later in this study. Firstly, some typical characteristics which often restrict the reuse of ashes are investigated. In case of heavy metals, low means that no removal treatment of trace elements is needed. Correspondingly, ash with moderate heavy metals needs some treatment before utilization, and ashes with high heavy metals are classified as hazardous waste without any treatment. Thus, the purpose of the treatment in that case is rather to get the classification from the hazardous waste to inert or non-hazardous waste. In Table 9, typical properties of fly ashes from different fuels are presented. The table is based on Table 1 and Table 2 which are presented in the theory part of this thesis.

Table 9. *Properties of typical fly ashes in this categorization*

Fly ash	Composition	Heavy metals	Chlorides	Sulfates
Typical coal	High Si and Al	Low to moderate	Low	Moderate
Typical peat	High Si, Al, and Fe	Low to moderate	Low	Moderate
Typical SRF or RDF	High variation of composition	High	High	Moderate
Typical wood	High Ca and K	Moderate	Low to moderate	Low

The composition and the regulative limitations determine in which applications ash can be used. The regulative limitation sources and the main limitations of concrete, fertilizer, and road or earth construction utilization as well as disposal are listed in Table 10. In this thesis, the limitations are used for restricting the utilization possibilities. Researches about other reuse options for certain ashes have also been carried out, but without any legal changes they cannot be commercially utilized. Due to the economic focus of this thesis, those applications, for instance geopolymers, are leaved aside.

Table 10. *Regulative limitations of ash utilization and disposal*

Utilization	Regulative limitation	Limitations	Possible ashes
Concrete	EN 450-1:2012 "Fly ash for concrete. Part 1: Definition, specifications and conformity criteria”	Property and composition requirements are described in Appendix A. [53]	Coal, wood
Disposal	Council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC	Leachability limits of harmful elements [51]	Coal, wood, peat, SRF/RDF
Fertilizer	Maa- ja metsätalousministeriön asetus lannoitevalmisteista, 24/11	Concentration limits of heavy metals, minimum concentrations of Ca and P+K [33]	Wood
Road or earth construction	Valtioneuvoston asetus eräiden jätteiden hyödyntämisestä maarakentamisessa, 843/2017	Leachability and concentration limits of harmful elements [54]	Coal, wood, peat, SRF/RDF

To reach these limits, the harmful elements needs possibly to be stabilized or separated. For this, different treatment methods can be applied. Disposal and road or earth construction have leachability limits, so either separation or stabilization of harmful elements can be utilized. With concentration limits as in concrete or fertilizer regulation, separation is needed. Here, the term road or earth construction means for example the base of roads or noise banks. Sometimes ash is also utilized as a construction material in the landfills or in the filling of old mines.

Table 11. *Treatment technologies and their effects on ash quality [6, 72]*

Treatment technology	Effect
Air classification	Separation of heavy metals, does not reduce the reactivity properties of ash: can be used before cement usage
Carbonation	Reduction of leachability of heavy metals
Cementation	Reduction of leachability of harmful elements before disposal
Chemical or electrochemical treatment	Separation or stabilization of heavy metals
Grinding or granulation	Changes the grain size of ash
Metal recovery	Recovery of separated valuable metals, requires high heavy metal content
Thermal treatment	Separation of volatile heavy metals, it is used rarely due to the high energy consumption. Changes the properties of ash and stabilizes the leachability of heavy metals as well.
Washing	Removal of salts, especially chlorides and sulfates

Treatment methods are introduced in Table 11. The most interesting separation methods are washing and the chemical precipitation of trace elements. They can be applied for ashes with high heavy metal and salt contents which are the most complicated issues in ash utilization. After the removal of heavy metals and hazardous salts, the ash can be further reused. The issue is the wastewater effluent which must be treated as well. Moreover, the chemicals in use may be expensive and thus the economic feasibility is not certain. After the separation of heavy metals, ash utilization possibilities are wider compared with the stabilization. Additionally, air classification may be a good option due to its simplicity, but its separation rate is not so good compared to the chemical treatment.

Accelerated carbonation is an interesting option for the stabilization of harmful elements. There heavy metals are trapped into the treated ash and it may be disposed with higher classification or, in the best case, utilized. The advantage of this technology is simplicity and low costs compared to thermal treatment, but the reuse possibilities are restricted.

In addition to the previous processes, metal recovery may be feasible with extremely high metal content. Therefore, it is only applied with waste ashes. Cementation should be avoided due to the big carbon footprint of cement production [38]. It also restricts the ash reuse. Additionally, it increases the volume of waste, and the ash may release harmful elements after the treatment. Nonetheless, the technology is used due to easy implementation and relatively low costs. [72]

The results of suitable utilization and treatment methods are introduced as flow charts in Section 4.1. The example of the flow chart is presented in Figure 6.

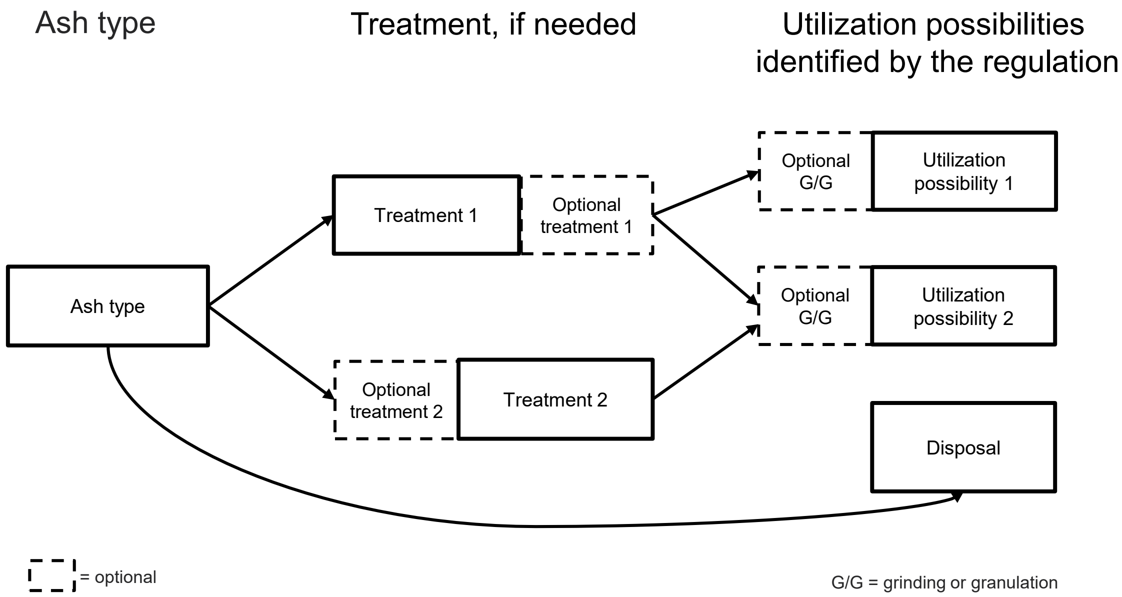

Figure 6. *An example of the flow chart*

In the figure, the ash type is on the left side. The utilization possibilities which are recognized by the regulation and are possible in view of the properties of the ash, have been collected to the right side. Furthermore, the treatment methods which are suitable before this certain utilization are presented in the middle. With this information, the chains from the different type of ashes to possible utilization via the treatment is got.

3.2 Description of the selected treatment processes

For the more detailed calculation, the processes which are presented in Section 3.1, are picked up. In the calculations, the concentration is now on the wet ash treatment processes. Thermal treatment methods are excluded due to their high energy consumption. Furthermore, in case of air classification, the cost information from the previously done master’s thesis is utilized. Metal recovery and grinding or granulation are not methods for the improvement of ash quality or composition and thus excluded as well. Hence, the processes under consideration include *acid leaching*, carbonation and washing. Additionally, the FLUWA process represents a commercial ash treatment technology. On the other hand, cementation is considered as a business as usual method for fly ash from waste incineration.

Firstly, the acid leaching is described in Figure 7. Ash is fed to the reactor with acid and possible water. The process may form the precipitate which must be removed. The process creates also an effluent stream which must be treated further. [6] The treated ash with the decreased level of harmful elements may be utilized or disposed afterwards.

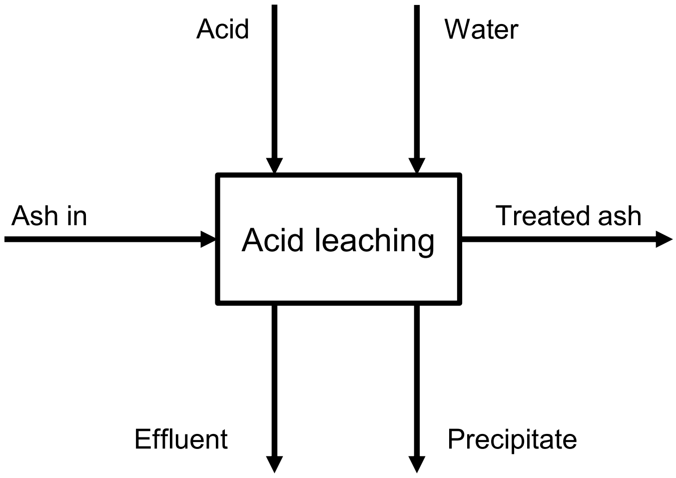

Figure 7. *Acid leaching process*

Secondly, the accelerated carbonation method is one of the processes under consideration. The acceleration may be achieved with an additive which speeds up the carbonation process [26]. Additionally, the process needs CO_2 and water. The carbon dioxide may be originated from industrial processes. [76] The carbonation process is illustrated in Figure 8. The treated ash may be utilized with decreased leaching levels of harmful elements or it may be disposed. Depending on the amount of water, there may be an effluent flow form the process as well.

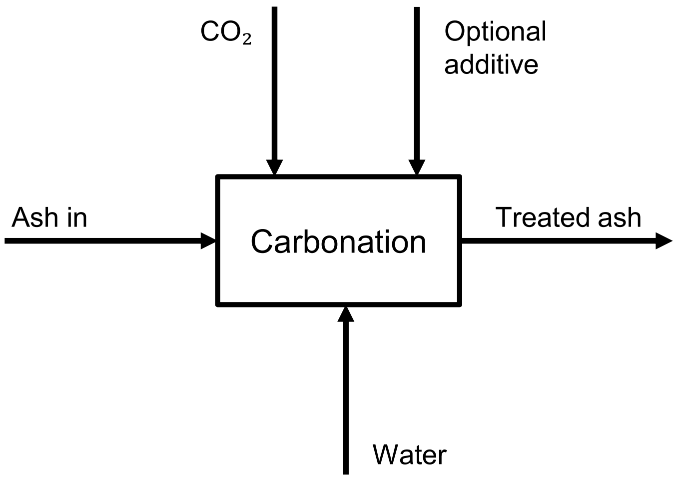

Figure 8. *Carbonation process*

Cementation is considered as a business as usual treatment method for the ash from waste incineration. There the hazardous ash is mixed with the cement and water. The stabilization decreases the leachability of harmful elements and the ash may be disposed. [72] In Figure 9, the process is described.

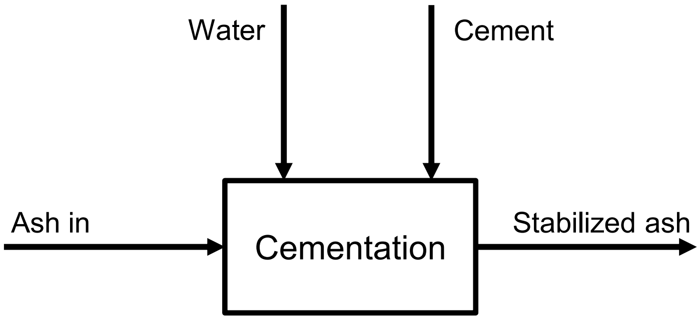

Figure 9. *Cementation process*

One of the commercial processes, FLUWA, is under consideration as well. In the process, ash is washed with acidic scrubber liquid. The acidic washing removes e.g. chlorides, sulfides and heavy metals from the ash. With the addition of CaO or NaOH, metal hydroxides, especially zinc hydroxide, may be recovered. Liquids with harmful elements may be treated as well. The process is used for treatment of ash from the waste incineration in Switzerland. [67] The process is described in Figure 10. In the process, the input water as well as the output water are purified with the ion exchange technology.

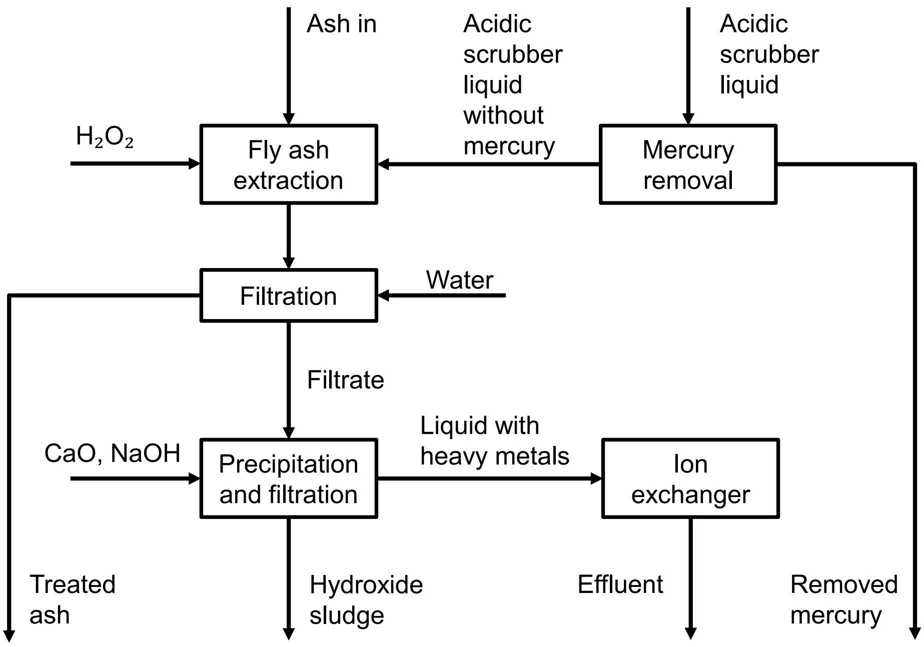

Figure 10. *FLUWA process [67, p. 11]*

Washing is a process in which ash is extracted with high amount of water. Thus, the process creates high amount of effluent which must be treated as well. The water decreases the levels of different salts, especially chlorides and sulfates. In some cases, the release of heavy metals is also possible. [55] The process is straightforward, and its flow chart presented in Figure 11.

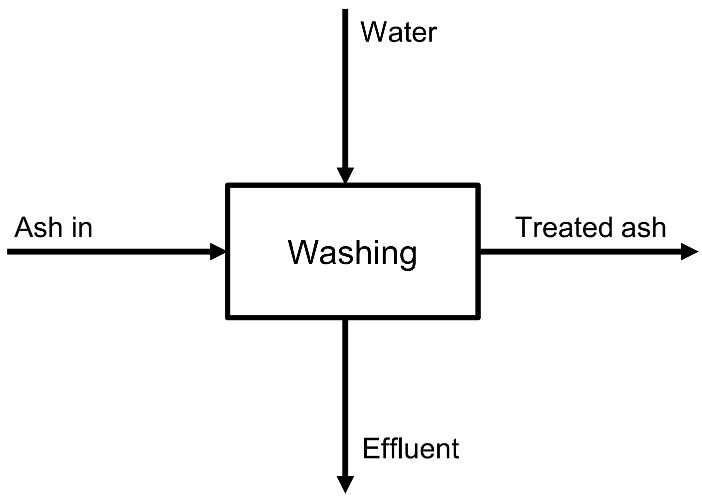

Figure 11. *Washing process*

Overall, all these processes are used in different purposes. Consequently, the processes have their different advantages and disadvantages. In the following section, mass and energy balances for these processes are determined. Those are essential for the economic feasibility analysis of the processes.

3.3 Mass and energy balances

In this section, the mass and energy flows for the processes under consideration are defined. These are necessary for the analysis of economic as well as technical analysis. The first treatment method is acid leaching. The equations 11–14 apply to the acid leaching process. In this thesis, the amount of ash input is approximately the same as is the amount of the treated ash, and hence

$$\dot{m}_{ash\ in} = \dot{m}_{treated\ ash}. \tag{11}$$

According to a report written by International Solid Waste Association, the acid extraction process by NOAH AS uses 0.9 m^3 water per ash ton. After the assumption that water density is 1000 kg/m^3, the equation is

$$\dot{m}_{water\ in} = 0.9\dot{m}_{ash\ in}. \tag{12}$$

However, they use gypsum solidification in the process, so they use the huge amount of waste sulfuric acid as well as limestone slurry [77, Appendix A]. This combination forms the gypsum which captures some heavy metals. In this calculation, the focus is on the simple acid leaching process, so it is reasonable to use the acid consumption of Fortum's ash treatment plant. There the computational consumption of 100% acid is [70, p. 20]

$$\dot{m}_{acid} = 0.444\dot{m}_{ash\ in}. \tag{13}$$

When the assumption is that there is no precipitate in this case, and the mass flows of input ash and treated as is equal, the mass flow of effluent may be formulated as

$$\dot{m}_{effluent} = \dot{m}_{acid} + \dot{m}_{water\ in}. \tag{14}$$

The next process is an accelerated carbonation. Now, the equations 15–18 may be applied to the carbonation process. According to the report of SINTEF, NOAH's carbonation process uses 75 kg of CO_2 per ton fly ash [76, p. 9]. Hence, it may be formulated as

$$\dot{m}_{CO2} = 0.075\dot{m}_{ash\ in}. \tag{15}$$

The same NOAH's report says that water consumption corresponds to 18–19 wt% of the treated ash [76, p. 9]. Hence, the formulation is

$$\dot{m}_{water\ in} = 0.185\dot{m}_{treated\ ash}. \tag{16}$$

In this case, the additive is $NaHCO_3$. As Lee and Bae noticed, the addition of sodium bicarbonate accelerates the carbonation process. According to them, the suitable amount of this additive in the process is 1 wt%. The higher amount of the chemical did not accelerate the phenomenon further. [26] The mathematical expression is

$$\dot{m}_{additive} = 0.01\dot{m}_{ash\ in}. \quad (17)$$

NOAH's carbonation process has no additives, but in this thesis, it is considered as an option. There is no water effluent in NOAH's process, neither. [76, p. 9] So, the equation with all the mass flows may be formulated as

$$\dot{m}_{treated\ ash} = \dot{m}_{ash\ in} + \dot{m}_{CO2} + \dot{m}_{water\ in} + \dot{m}_{additive}. \quad (18)$$

The mass flows of the next process, cementation, are presented with the equations 19–21. According to Fortum, all Finnish air pollution control ash from waste incineration was stabilized with cement before landfilling. The amount of created ash was 45,000 t/a, and the consumption of cement was 16,350 t/a. [69] Thus, it can be concluded that

$$\dot{m}_{ash\ in} = 2.75\dot{m}_{cement}. \quad (19)$$

According to an environmental impact assessment by YTV, the mass of treated ash is approximately 1.5 compared to the input ash [79]. Simultaneously, due to the principle of mass conservation:

$$\dot{m}_{treated\ ash} = \dot{m}_{ash\ in} + \dot{m}_{cement} + \dot{m}_{water\ in} \quad (20)$$

This means that the amount of water is

$$\dot{m}_{water\ in} = 0.55\dot{m}_{cement}. \quad (21)$$

In a report of the FLUWA process, the following mass flows are presented. The process uses acidic scrubber liquid for the washing of ash, and hence it is a combined washing and acid extraction process in a way. The mass flows have been collected into Table 12. The flows are originally for the plant of ash treatment capacity 7,400 t/a or 925 kg/h. This means that the running time in the year is 8000 h. [67] With this information, the flows may be converted from the per hour unit to t/a. A liter of liquid is approximately one kilogram.

Table 12. *Mass flows of the FLUWA process [67]*

Point	Flow	Unit	Flow (t/a)	Input/output	$\dot{m}_x/\dot{m}_{ash\ in}$
Ash in	925	kg/h	7,400	input	1
Acidic scrubber liquid without mercury	3237.5	l/h	25,900	input	3.5
Treated ash	661.375	kg/h	5,291	output	0.715
Filtrate	3593.625	l/h	28,749	-	3.885
CaO/NaOH	90.9275	kg/h	727.42	input	0.0983
Heavy metal hydroxide sludge	90.9275	kg/h	727.42	output	0.0983
Liquid with heavy metals	3593.625	l/h	28,749	output	3.885

The mass flows are converted to tons per year unit. There is also information, if the flow is input or output in a view of the whole process. Lastly, the relation between incoming ash flow and the flow under consideration is calculated.

The last process under consideration in this thesis is washing. The equations for the process are 22–24. Here, due to simplicity the assumption is that the mass flow of the input ash equals the mass flow of the treated ash:

$$\dot{\mathrm{m}}_{ash\ in} = \dot{\mathrm{m}}_{treated\ ash} \tag{22}$$

Consequently, as simplification the amount of water into the process is the same as the amount of effluent coming out from the system.

$$\dot{\mathrm{m}}_{water\ in} = \dot{\mathrm{m}}_{effluent} \tag{23}$$

L/S is typically 3–4:1 in ash washing processes [67, 77], so 4:1 is chosen in this case as well. Thus, the relation can be formulated as

$$\dot{\mathrm{m}}_{water\ in} = 4\dot{\mathrm{m}}_{ash\ in}. \tag{24}$$

In addition to the mass flows, the electricity consumption must be determined. In this thesis, electricity consumption is assumed to be linearly dependent with the incoming ash mass flow. In cementation, the reliability of the amount of electricity consumption is a question mark. Nevertheless, even the uncertainty of the consumption is high, the impact of it seems to be relatively low to the operational expenses. The electricity consumptions are presented in Table 13.

Table 13. *Electricity consumption of the treatment methods*

Treatment method	Electricity consumption (kWh/t_{ash})	Source	Reliability
Acid leaching	13	[77, Appendix A]	Literature reference
Carbonation	6	[76, p. 9]	Literature reference
Cementation	10	-	Approximation
FLUWA	146	[67, p. 18]	Literature reference
Washing	31	[77, p. Appendix A]	Literature reference

The electricity consumption of FLUWA is high in comparison with other processes. The FLUWA process has multiple stages as well as the effluent treatment in this consumption number which might explain the difference. Otherwise, the numbers seem to be the same order of magnitude.

3.4 Economic feasibility analysis

In the table below, the approximations of capital expenditures (CAPEX) are introduced. The uncertainty is high with these numbers due to the little number of investment cost information available. According to Satakunnan Kansa, a Finnish newspaper, the investment cost of Fortum’s ash treatment plant is 17 million euros [80]. With the maximum capacity 45,000 t/a [70, p. 17] this equals around CAPEX 377 €/$t_{ash}a^{-1}$. The estimation of the capital expenditures for the FLUWA process is similar in this thesis. The other processes are more subprocesses than the whole systems compared to FLUWA which mean lower capital costs. The approximations of CAPEX of the processes under consideration are presented in Table 14.

Table 14. *Capital expenditures of the processes*

Treatment method	CAPEX (€/$t_{ash}a^{-1}$)
Acid leaching	225
Carbonation	200
FLUWA	405
Washing	175

In case of cementation, the CAPEX is not in the table due to its nature as a business as usual method in this research. The assumption is that it is the present treatment method, and the other ones are alternatives for it. On the other hand, operational expenses (OPEX) are the costs which are caused by the operation of the plant. In Table 15, there are the mass flow related costs described. The chemical prices have been taken from Appendix A of the phosphorous recovery article by Egle et al. [81, Appendix A]. Water in, effluent treatment, and precipitate costs are rough approximations.

Table 15. *Mass flow related costs*

	Input		Output	
Treatment method	Chemicals (€/t)	Water in (€/t)	Effluent (€/t)	Precipitate (€/t)
Acid leaching	150 (H_2SO_4)	0	30	-
Carbonation	0 (CO_2) 240 ($NaHCO_3$)	5	-	-
Cementation	70 (Cement)	5	-	-
FLUWA	140 ($Ca(OH)_2$)	15	30	30
Washing	-	0	15	-

In case of the acid-ash effluent, the costs of effluent treatment are assumed to be 30 €/t. The treatment of the washing effluent is lighter so there the cost is 15 €/t. In water washing, extracted elements are mainly salts. Consequently, acid leaches heavy metals. In both washing and acid leaching, the input water may be pumped from the near lake or river, so the price for water is assumed to be 0 euros. Then again in cementation and carbonation, the water should be cleaner, so there are costs 5 €/t assumed. Additionally, the mercury must be removed from the scrubber water via ion exchange in the FLUWA process which is assumed to cost 15 €/t. In FLUWA, the treatment cost of heavy metal sludge is 30 €/t. In this thesis, acid leaching does not form the precipitate, even though it happens after the acid-base reaction in reality. The maintenance and personal costs are also a part of process expenses. These costs are collected into Table 16.

Table 16. *Maintenance cost and the amount of personal*

Treatment method	Maintenance (€/t_{ash})	Employees (person/t_{ash})
Acid leaching	5	3 / 20,000 t_{ash}
Carbonation	2.5	3 / 20,000 t_{ash}
Cementation	1.11	5 / 45,000 t_{ash}
FLUWA	10	3 / 7,400 t_{ash}
Washing	2.5	3 / 20,00 t_{ash}

The FLUWA process has the highest maintenance cost due to the multistage process. All the expenses in the table above are rough approximations, again. As a reference, Fortum has said that their ash refinery, with the capacity of 45,000 t/a, employs 8 people [82]. The costs which are not dependent on the process itself are presented in Table 17. These numbers are highly dependent on the country in which the treatment plant works. Now, the prices are at the Finnish level.

Table 17. *Costs which are not dependent on processes*

Cost	Amount	Unit
Electricity	80	€/MWh
Employees	50,000	€/employee
Transportation	15	€/t_{ash}
Waste tax	70	€/t_{ash}

After the determination of the CAPEX and the process OPEX for processes, the saving potential of the investment is determined. There, the present cost of ash treatment must be defined. Then, the economic indicators of the investment, which are presented in Section 2.7, are calculated. In the calculation, the net cash flow is replaced with net cash savings, but the principle is otherwise the same. This logic is utilized in the techno-economic analysis tool.

3.5 Techno-economic analysis tool implementation

The techno-economic analysis (TEA) tool is created by Microsoft Excel. In the TEA tool, the user can choose a fuel from the list of coal, peat, wood, and SRF/RDF. The choice edits the options list of the ash treatment. After the selection of the treatment method, the information box tells the effect of the treatment to the user. Together the selection of fuel and treatment determines possible utilizations and thus the limiting regulation of the application. Concentration or leaching limits may be reviewed under the drop-down rows. Additionally, the user defines the amount of treated ash under consideration as well as the present treatment cost. The quantity of the ash may be between 0 and 100,000 t/a, and the range for the present treatment cost is 0–1,000 €/t. With the amount of ash, the tool calculates the expenditures of operations, the waste tax, and the transportation cost of ash. Furthermore, the tool gives an approximation of capital expenditures. After these steps, the tool has a comparison between the calculated expenditures and the user-defined treatment cost. This calculation creates financial ratios and a cash flow figure of the investment for the user. This information should help the user to decide if it is more profitable to operate with ash business as usual, or could it be reasonable to invest in the treatment process.

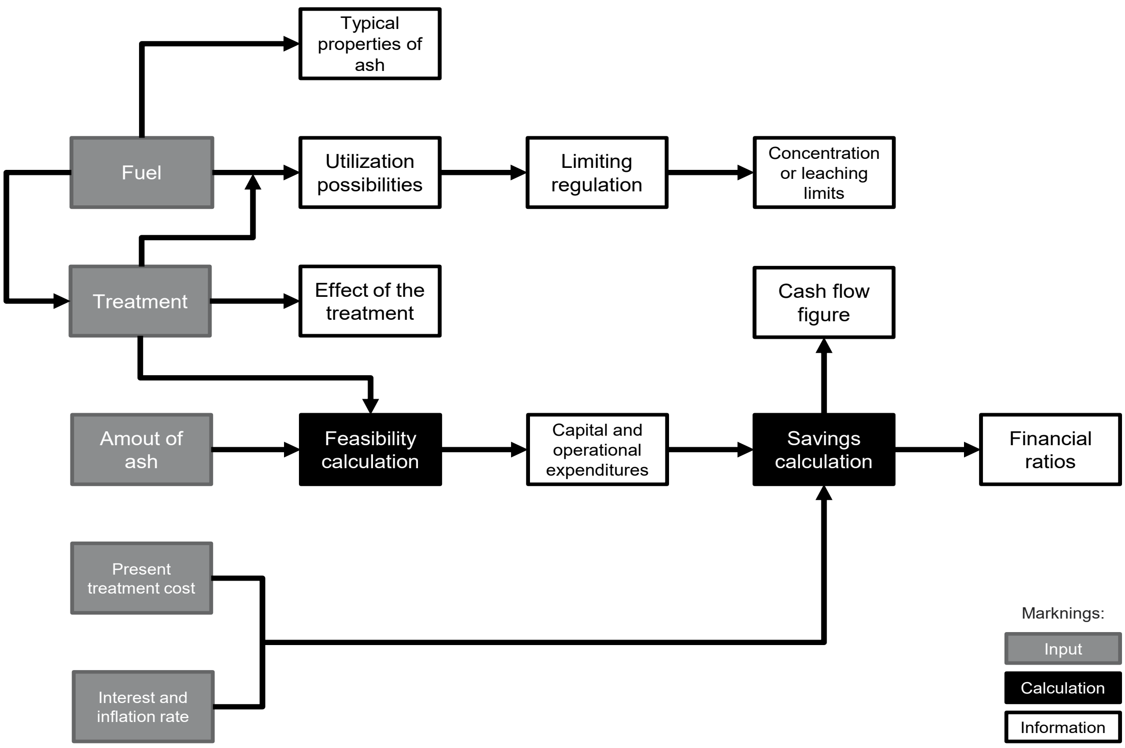

Figure 12. *Functional logic of the TEA tool*

In Figure 12, grey boxes illustrate the input values or choices. The black boxes are the calculations which cannot be seen by the user. Consequently, the white boxes represent the information that is shown to the user. The arrows describe the flow of information and its direction. Figure 13 represents the user interface of the tool. The user can select the fuel and the treatment method, and their basic information are represented. This information includes typical fuel properties, utilization possibilities, the effect of the treatment, and the limiting regulation of utilization. The logic for the selection of shown basic information was introduced in Section 3.1. The possible fuel, ash treatment, and utilization combinations are treated further in Section 4.1.

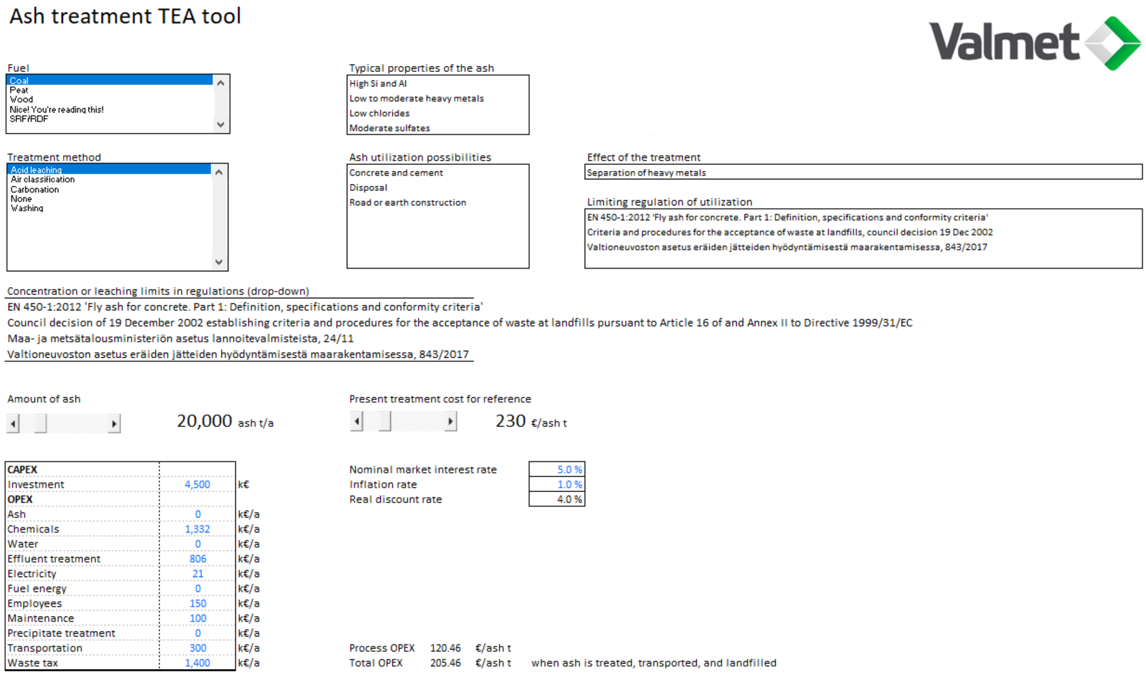

Figure 13. *The first part of the ash treatment TEA tool*

After these, the size of the treatment plant and the price of the present ash treatment may be selected. The first one has an impact on capital and operational expenditures. The price of the present treatment cost influences the savings calculations and hence to the profitability of the investment. Additionally, the nominal interest rate as well as inflation rate may be selected. The input number values are colored as blue.

		Year															
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
CAPEX	Investment	-4,500	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
OPEX	Ash		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Chemicals		-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332	-1,332
	Water		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Effluent treatment		-806	-806	-806	-806	-806	-806	-806	-806	-806	-806	-806	-806	-806	-806	-806
	Electricity		-21	-21	-21	-21	-21	-21	-21	-21	-21	-21	-21	-21	-21	-21	-21
	Fuel energy		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Employees		-150	-150	-150	-150	-150	-150	-150	-150	-150	-150	-150	-150	-150	-150	-150
	Maintenance		-100	-100	-100	-100	-100	-100	-100	-100	-100	-100	-100	-100	-100	-100	-100
	Precipitate treatment		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Transportation		-300	-300	-300	-300	-300	-300	-300	-300	-300	-300	-300	-300	-300	-300	-300
	Waste tax		-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400	-1,400
Total expenses of the investment	One year nominal expenses	-4,500	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109	-4,109
	Cumulative nominal expenses	-4,500	-8,609	-12,718	-16,828	-20,937	-25,046	-29,155	-33,264	-37,374	-41,483	-45,592	-49,701	-53,810	-57,920	-62,029	-66,138
	Discounted one year expenses	-4,500	-3,953	-3,802	-3,657	-3,518	-3,384	-3,255	-3,131	-3,012	-2,897	-2,787	-2,680	-2,578	-2,480	-2,386	-2,295
	Cumulative discounted expenses	-4,500	-8,453	-12,255	-15,912	-19,430	-22,814	-26,069	-29,200	-32,211	-35,108	-37,895	-40,576	-43,154	-45,634	-48,020	-50,314
Present treatment costs	Nominal present treatment cost	0	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600	-4,600
	Cumulative nominal present treatment cost	0	-4,600	-9,200	-13,800	-18,400	-23,000	-27,600	-32,200	-36,800	-41,400	-46,000	-50,600	-55,200	-59,800	-64,400	-69,000
	Discounted present treatment cost, one year	0	-4,425	-4,256	-4,094	-3,938	-3,788	-3,644	-3,505	-3,371	-3,243	-3,119	-3,001	-2,886	-2,776	-2,671	-2,569
	Cumul. discounted present treatment cost	0	-4,425	-8,681	-12,775	-16,713	-20,501	-24,145	-27,650	-31,021	-34,264	-37,384	-40,384	-43,271	-46,047	-48,718	-51,287
Savings	One year nominal savings	-4,500	491	491	491	491	491	491	491	491	491	491	491	491	491	491	491
	Cumulative nominal savings	-4,500	-4,009	-3,518	-3,028	-2,537	-2,046	-1,555	-1,064	-574	-83	408	899	1,390	1,880	2,371	2,862
	Discounted one year savings	-4,500	472	454	437	420	404	389	374	360	346	333	320	308	296	285	274
	Cumulative discounted savings	-4,500	-4,028	-3,574	-3,137	-2,717	-2,313	-1,924	-1,550	-1,190	-844	-511	-191	117	413	698	972
	MIRR - discount rate(%)		-89.1	-52.8	-30.2	-17.5	-10.0	-5.3	-2.1	0.0	1.6	2.7	3.6	4.2	4.7	5.0	5.3
	Nominal payback period	9.17															
	Discounted payback period													11.62			

Figure 14. *Economic feasibility calculations of the TEA tool*

In Figure 14, the operational and capital costs of the ash treatment are presented year by year. The different expenses are specified in different rows in the table. Both total expenses of the investment and the present treatment cost are presented in their own sections below the cost specification. Furthermore, the result of savings calculation is represented. With this information, the financial indicators may be determined.

Indicators		5 years	10 years	15 years	
	Net present value	-2,313	-511	972	k€
	Nominal payback period	9.17	9.17	9.17	years
	Discounted payback period	11.62	11.62	11.62	years
	IRR	-17.3	1.6	6.9	%
	MIRR, reinvest at discount rate	-10.0	2.7	5.3	%

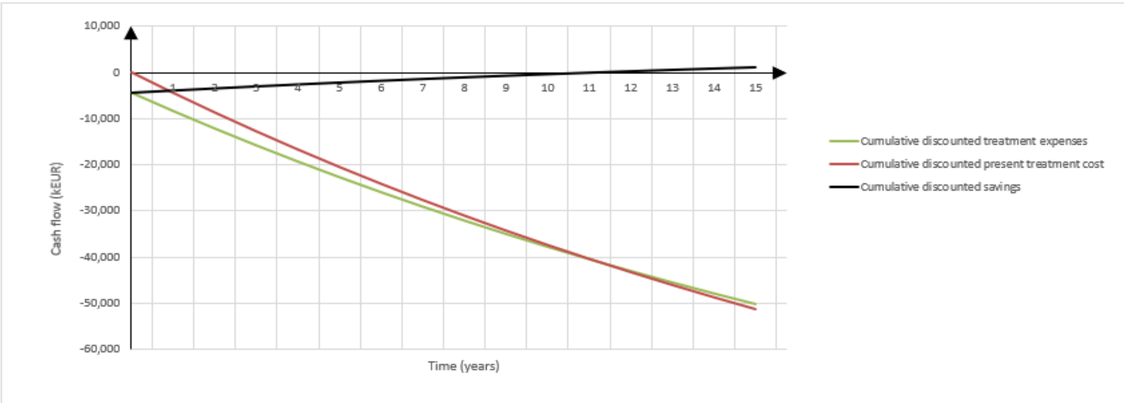

Figure 15. *Economic indicators of the TEA tool*

These indicators are at the upper edge in Figure 15. Indicators include the net present value (NPV), nominal and discounted payback periods, the internal rate or return (IRR) as well as the modified internal rate of return (MIRR). Below, there is also a cash flow figure. In the figure, there are three different curves. The red one represents the cumulative discounted present treatment cost. This is the business as usual cost when ash is treated by an outsider with the determined present treatment cost. The green line below represents the capital and operational costs of the investment. The black curve is the savings if the investment is executed.

3.6 Scenario and sensitivity analysis

In the scenario analysis, the change of the total OPEX is investigated, when some part of the total cost varies. Acid leaching, carbonation, cementation, FLUWA and washing are still under consideration. The calculations are made in a similar way as before. Furthermore, the ash treatment plant size is still 20,000 t/a. The TEA tool is utilized for the calculation. There are the scenario 0 and 4 other scenarios which are studied:

- Scenario 0: Nothing changes, the OPEX is as calculated in the thesis
- Scenario 1: The price of input chemicals doubles compared to the scenario 0
- Scenario 2: The price of the effluent treatment doubles compared to the scenario 0
- Scenario 3: The price of transportation doubles compared to the scenario 0
- Scenario 4: The waste tax increases from 70 €/t to 100 €/t

It is reasonable to investigate the scenarios in which different treatment methods are more attractive options compared with the present situation. The scenario 4 answers for that question. The aim with the scenarios 1–3 is to figure out, how strongly the processes react to the change of the prices described above. The sensitivity of the OPEX to the changes works naturally vice versa. The sensitivity tells, if these chemical, effluent treatment, or transportation prices decrease, how much the total OPEX of the processes lower as a result.

Lastly, the treatment cost calculations of different treatment processes are compared with multiple reference prices. These treatment costs are the scenario zeros of the processes presented earlier in this thesis. This gives the sensitivity of the NPV from the techno-economic calculation for this reference price. The referent price in this case means the present ash treatment cost which is set to 230 €/t as previously in the thesis. With this comparison, net present values, nominal payback periods, and discounted payback periods are calculated for the profitable processes, excluding the cementation which is the business as usual process.

4. RESULTS AND DISCUSSION

Firstly, the major treatment options for different ash types are proposed. The options are based on the selection method in Section 3.1. Furthermore, all results from the technical and economic process calculations, which have been presented in Chapter 3, are discussed in this chapter. The significance of the results is considered as well. These results are utilized in the creation of the techno-economic analysis tool.

4.1 Treatment method and utilization options

Multiple ash types, treatment methods, and applications were presented in the literature survey of this thesis. A lot of different applications have been investigated, but standards or regulation do not recognize all these utilization possibilities. In the following figures, ashes have been classified by the typical properties of the certain ash as described in Section 3.1. Possible ash applications depend on the limitations in the selected regulation and standards. Consequently, suitable treatment methods depend on the type of limitations. There are composition requirements for concrete and fertilizer applications, and the concentrations of harmful elements are limited [33, 53]. In case of concrete, it must also meet demands of the fly ash concrete standard. On the other hand, in road and earth construction as well as in disposal, the leachability of harmful elements is restricted [54].

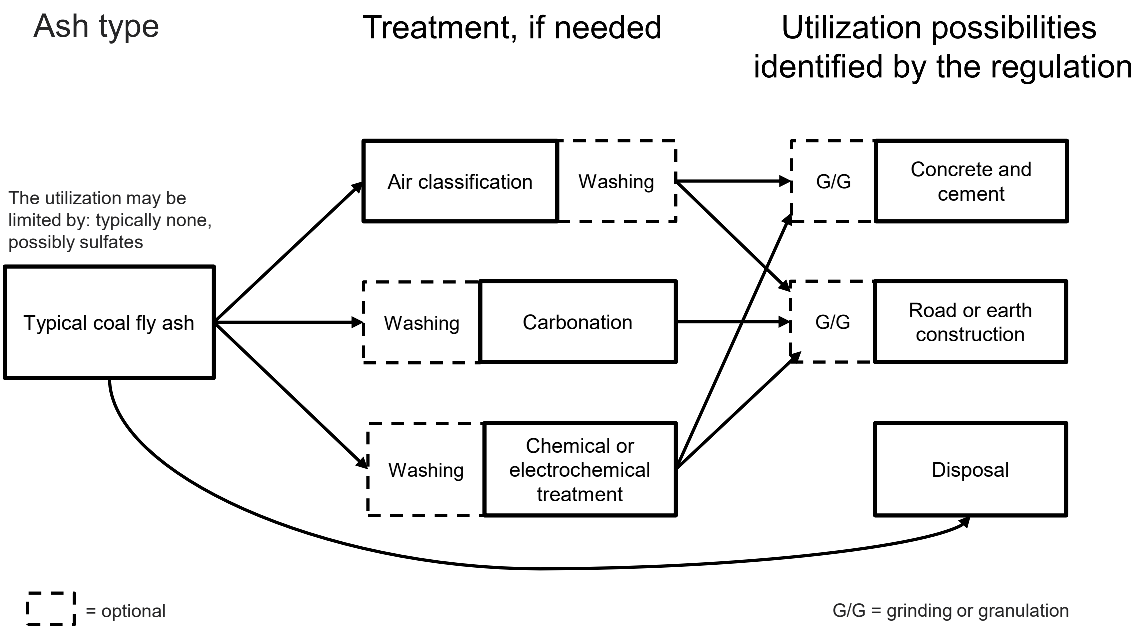

Figure 16. *Treatment methods and utilization of coal fly ash*

Coal ashes often meet the regulatory limits for utilization, and no treatment is possibly needed as can be seen in Figure 16. The need for treatment depends strongly on the composition of coal. However, the content of sulfates may be high, and thus it might to restrict the utilization. In the figure, the dashed line means an optional treatment choice. In Europe, the most common application statistically for coal ash is concrete as seen in Figure 5 [10]. With air classification or chemical treatment, heavy metal concentration can be reduced [60, 62]. In addition, carbonation may decrease the leachability of harmful elements which limits the use of ashes in road and earth construction [28, 54]. In fluidized bed combustion, grinding may also be a treatment option when considering especially bottom ash due to its greater grain size [25, 29]. Fertilizer use of the bottom ash is not often feasible due to lower Ca, P, and K composition compared to wood fly ash, for instance. [5, 23] Disposal is also possible to landfills or old mines, but in case of relatively clean ashes, it is a lost utilization opportunity. Washing can be applied before chemical treating or after a dry-separation method, air classification [6]. With washing, the chloride content may be reduced. In case of carbonation, washing may be utilized before or after the treatment. If the washing is after the carbonation, heavy metals leach less to the washing water [28]. Additionally, before utilization, the ash may be granulated or grinded (G/G) [6].

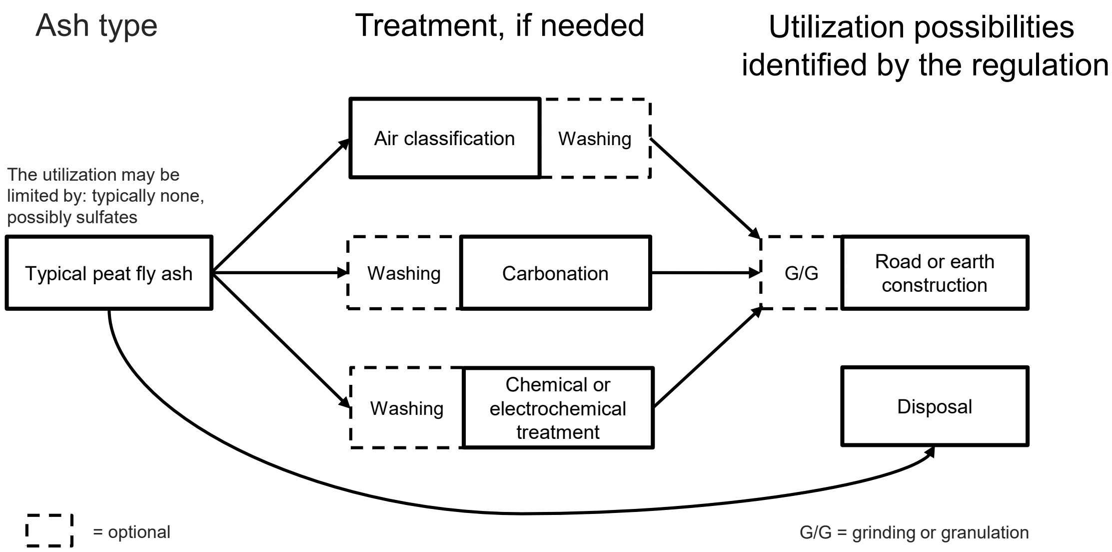

Figure 17. *Treatment methods and utilization of peat fly ash*

Peat is commonly burnt in co-combustion and, and hence practically, the utilization of its ash alone is not often a relevant subject [12, p. 127]. Its content is usually similar with coal ash [20, p. 271] and thus are the applications as well as can be seen in Figure 17. However, the European standard EN 450 “Fly ash for concrete” does not recognize the use of peat ash in concrete, so it is excluded [53]. Need for treatment depends also on the composition of peat ash which varies significantly [12, p. 127]. The effects of the treatment methods above are the same as in the case of coal ash.

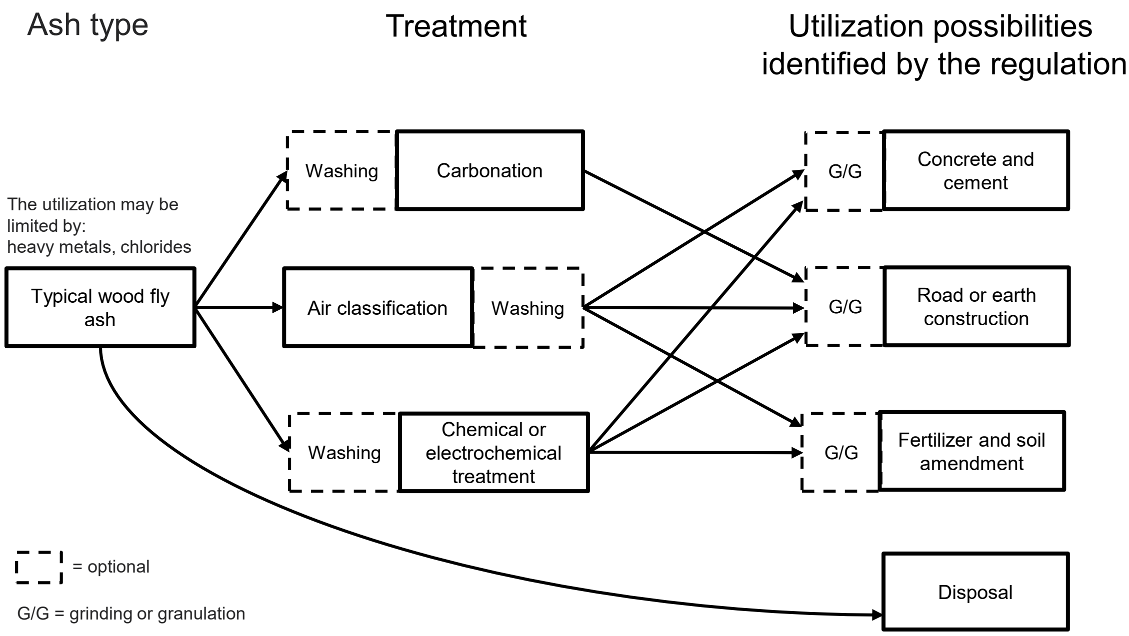

Figure 18. *Treatment methods and utilization of wood fly ash*

In Figure 18, treatment methods and applications for wood ashes are presented. As a difference compared to the previous ones, there are now fertilizer and soil amendment application as an option. The features of wood ash are proper for fertilizer usage due to the high calcium and potassium content and its basic nature. Therefore, the wood ash can be used as pH balancer in peaty, acidic, soils. [5, p. 84] With suitable air classification and chemical treatment, it is possible to utilize wood ash in all the options, if the requirements are fulfilled. On the other hand, the properties of wood fly ash may not be as good as coal fly ash in concrete due to lower silicon and aluminum content. Furthermore, as above with the other ashes, carbonation may be used to stabilize heavy metals in ashes. Thus, the leachability of heavy metals is decreased, and further utilization is possible. Due to the usage of carbon dioxide, the carbonation may be considered as a carbon capture method as well. Sometimes the self-hardening is used as pretreatment before disposal [55]. In that case, the ash is washed and then stored temporary until the phenomenon has been happened. In addition, the chemical or electrochemical treatment may be utilized to reduce the heavy metal content of ash. Consequently, the washing may be utilized for the reduction of high chloride content.

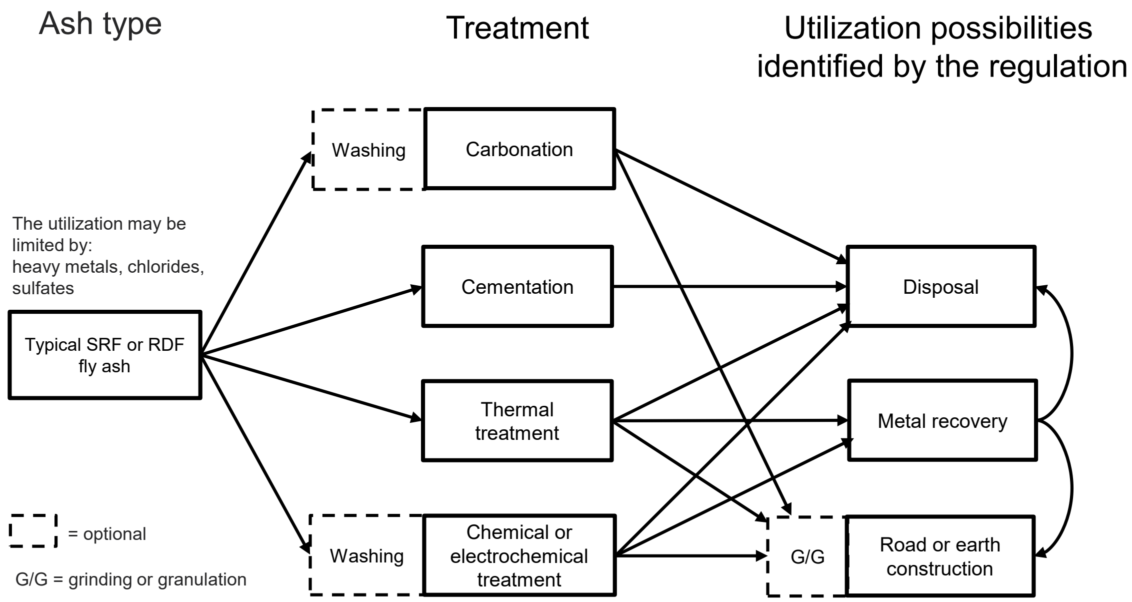

Figure 19. *Treatment methods and utilization of SRF or RDF fly ash*

The last ash type is typical SRF or RDF ash. In this case, heavy metal and chloride contents are high, and the amount of sulfate is moderate. The composition of the fuel varies significantly which makes the assessment of utilization possibilities challenging. [9] The ash is often classified as hazardous waste due to its high chloride and heavy metal content, and some treatment is needed to avoid the high disposal costs of the hazardous matter. For getting the ash from the hazardous class to non-hazardous or inert class, carbonation, thermal, or chemical treatment may be used. Additionally, from ash with high metal content, some metals could be recovered [62]. This is possible especially with MSW incineration ashes, but in SRF and RDF the levels are lower, and the feasibility is uncertain. If the leachability of heavy metals is strongly decreased, and other harmful elements are removed, SRF and RDF ashes may be used in road or earth construction as well [54]. This is a potential application, especially when the major component of the ash is silicon or aluminum. This kind of utilization is also possible after the thermal treatment as sintering and vitrification. Cementation is currently one of the major treatment methods before disposal for waste ashes. It stabilizes the leaching elements of ash and thus it may be landfilled. [71]

4.2 Mass and energy flows of the treatment methods

In this section, the mass and energy flows of the selected treatment methods are presented. The mass and energy flows are scaled to the plant which size is 20,000 t_{ash}/a. These different process flows have been collected from the calculation into Table 18. As described in Chapter 3, acid leaching reduces the heavy metal content of the ash. Carbonation decrease the leachability of heavy metals. Cementation is mainly used for ash from the waste incineration to prevent of leachability of any harmful elements. FLUWA is also used for the waste ash at the moment. Consequently, washing is a process for the reduction of salts, especially harmful sulfates and chlorides. Acid leaching, carbonation, and washing are possible treatment methods for all types of ash mentioned before.

Table 18. *Mass and energy flows of the processes under consideration*

Treatment method	Chemicals (t/a)	Water in (t/a)	Effluent (t/a)	Precipitate (t/a)	Treated ash (t/a)	Electricity (MWh/a)
Acid leaching	8,880 (H_2SO_4)	18,000	26,880	0	20,000	260
Carbonation	1,500 (CO_2) 200 ($NaHCO_3$)	4,892	0	0	26,592	120
Cementation	7,273 (Cement)	4,000	0	0	31,273	200
FLUWA	1,966 ($Ca(OH)_2$)	70,000	77,700	1,966	14,300	2,920
Washing	0	80,000	80,000	0	20,000	620

As seen in the table above, water or effluent flows may be high in the treatment processes. This naturally has an impact on the economic feasibility of the treatment method. In the following section, those feasibilities of the processes are investigated. The errors and reliability of the process calculations were considered in Section 3.4 previously. The electricity consumption is extremely high in the FLUWA process. As comparison, Fortum's ash treatment plant consumes 5,000 MWh electricity per year with the annual capacity of 45,000 tons. This value includes also all lighting in the area, so this consumption is not only for the process. [70, p. 29] Still, compared to Fortum's process, the electricity consumption of FLUWA process is high.

4.3 Economic feasibilities

In this section, the profitability of the processes is studied. Here, the plants are scaled to the plant which size is 20,000 t_{ash}/a as well. Total capital expenditures are presented in Figure 20. In addition, there are capital expenditures per ash ton if the CAPEX is allocated nominally for 15 years.

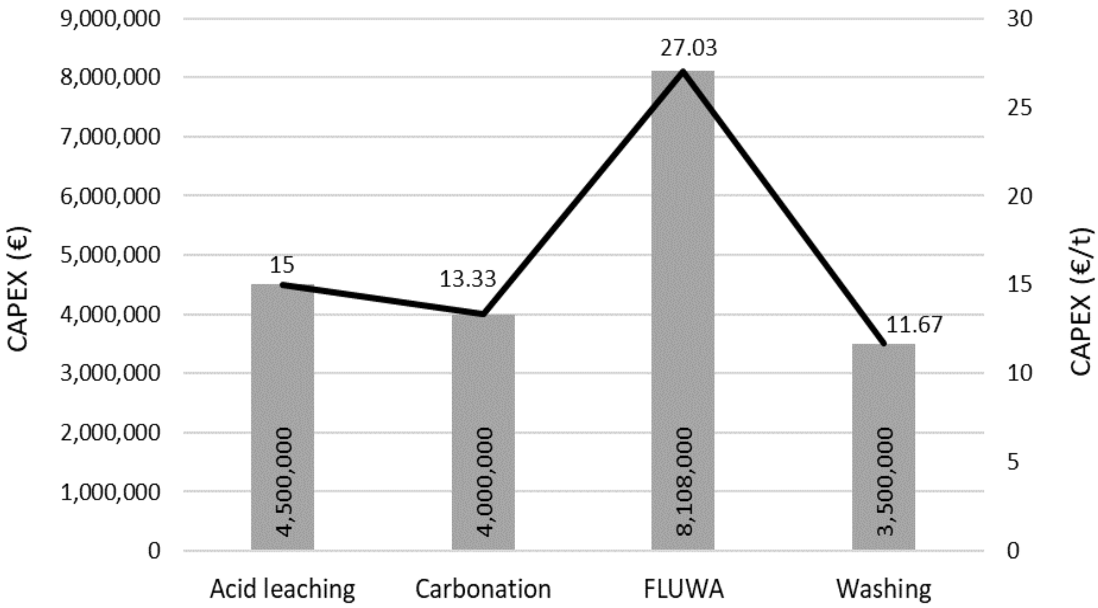

Figure 20. *Capital expenditures of the selected processes*

As mentioned before, these capital expenditures are rough approximations due to the lack of data available. Cementation is considered as the business as usual situation, so the assumption is that no new investment for the process is needed. Therefore, there is no CAPEX for it. However, the operational expenses of the cementation process are considered as a reference. The FLUWA process has the highest capital cost due to its complexity and acid leaching, carbonation, and washing are between 3,500,000 and

4,500,000 euros. Next, the total costs related to mass and energy flows are presented in Figure 21. The unit is a thousand euros per year (k€/a), and the plant size is still the same.

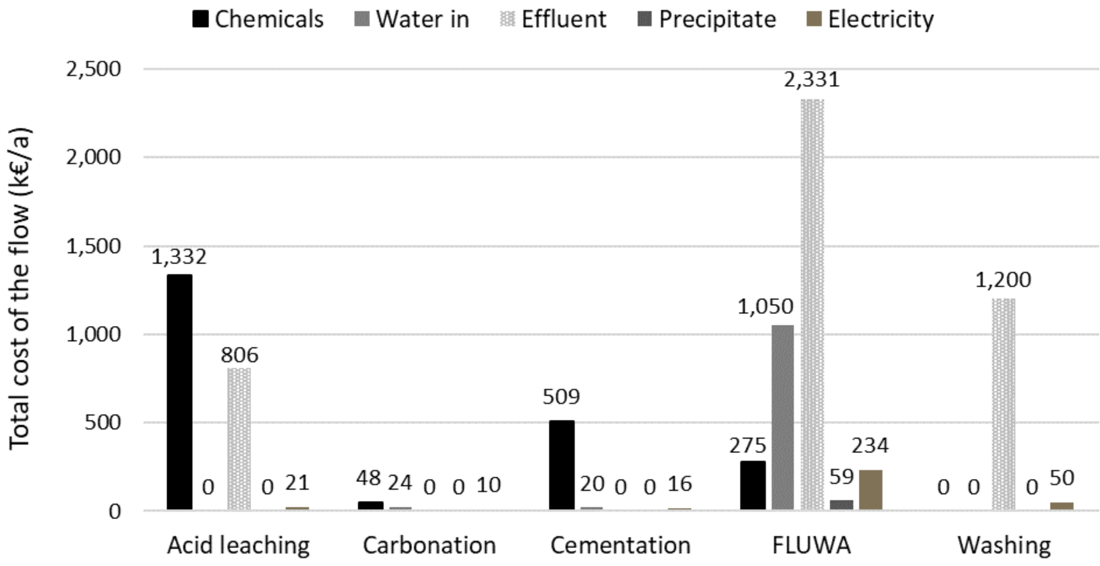

Figure 21. *The total costs of related to the mass and energy flows*

The most remarkable observation from the figure above is that the most expensive part of the processes is related to input chemicals or effluent treatment. In the effluent treatment, the cost of chemicals is also significant. This means that the most important variable in case of profitability of these treatment methods is the price of chemicals. From this point of view, NOAH's and Fortum's acid extraction processes in which waste acids are utilized are clever. They may get a fee of treating the waste acids and at the same time have an opportunity to get rid of hazardous ashes with low costs. However, the treatment of effluent in processes of this kind is in an important role and may be more expensive than in other processes. This is a result of mixing two hazardous streams, MSW incineration ash and waste acids. Next, the other operational expenses are represented in Figure 22.

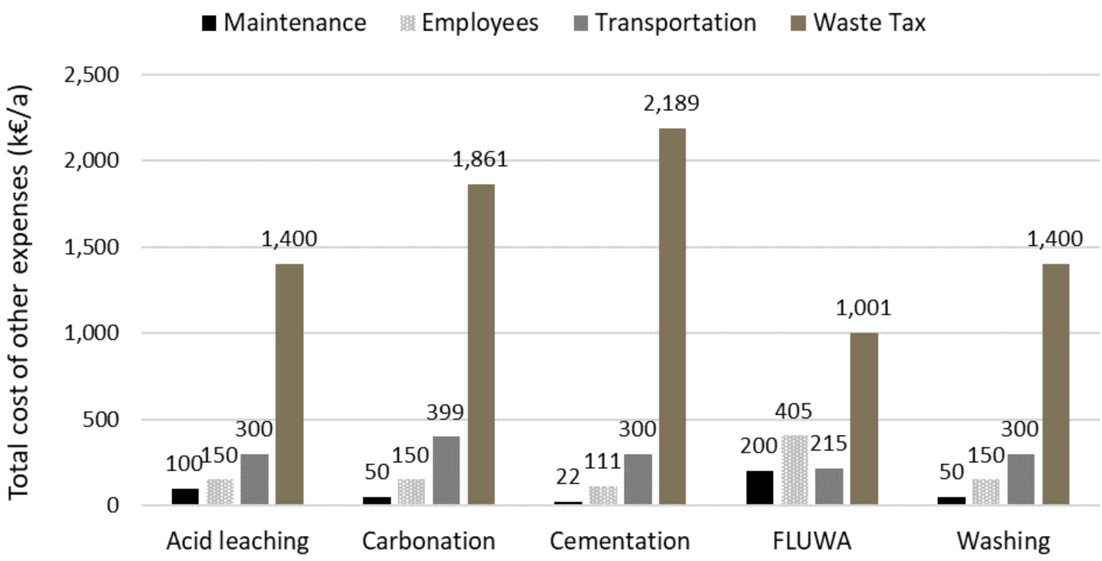

Figure 22. *Total costs of other operational expenses*

In the figure above, there are no notable surprises. The maintenance costs are rough estimates due to the lack of data available, again. It is the same is with the number of employees. However, as said in Section 3.4, their significance to the total operational expenses is minor. For other processes than cementation, the transportation is a one-way truck carriage for treated ash. Cementation is assumed to happen at the landfill, so the transportation is calculated with the mass flow of untreated ash. The transportation cost seems also to be relatively small part of the whole cost structure as well. On the other hand, the waste tax is a noteworthy expense item. Hence, it would be possible to have savings with avoiding the waste tax. The tax is paid from the landfilled masses. Due to this, the amount of waste tax from cementation is higher than from other processes. In the cementation, the mass of the treated ash-cement mix is approximately 1.5 times higher compared with the untreated ash [79]. The FLUWA process with multiple stages is more complex in comparison with the other processes, so it has higher maintenance cost as well as employee cost. The significance of these numbers for the total process OPEX is low apart from the waste tax.

In Figure 23, the summary of the total expenses is presented. The process OPEX denotes the sum of all process expenses without transportation and waste tax. The second column represents the sum of the process OPEX and CAPEX which is allocated for 15 years. The sum describes all the costs related to the treatment system without transportation or waste tax. In the total OPEX number, the process OPEX, transportation, and landfilling are included. However, in these last numbers, the CAPEX is not involved in. The plant size is still the 20,000 t/a.

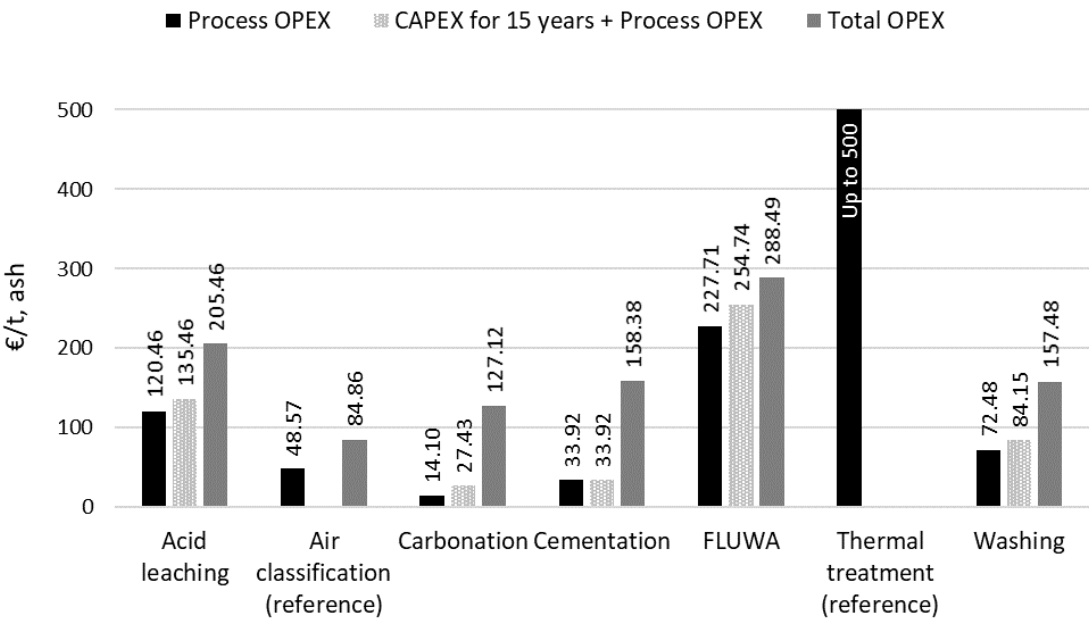

Figure 23. *The sum of total expenses for the processes*

Air classification as well as thermal treatment have been taken from literature references for the comparison [83, p. 67][84, p. 52]. In the book "Treatment Methods for Waste to Be Landfilled" by Ole Hjlemar, some treatment costs of demonstrated ash treatment technologies have been introduced. Compared with the numbers in the book, the FLUWA process has the similar treatment cost as in the calculations of this thesis. In the book, the treatment cost for the FLUWA process is defined as 150–250 €/t_{ash}. The cementation-based stabilization by Ragn-Sells is also comparable with the price of 90–146 €/t_{ash} for the treatment and disposal. In the total OPEX of the cementation, there is also the transportation of untreated ash in the table above. Without it, the price of treatment and disposal would be 143.38 €/t_{ash} which is inside the proposed range. This means that for the waste incineration ash, that is the reference level price of the business as usual. If the cementation is wanted to be avoided, the treatment cost of the new process must be below this. The carbonation price for fly ash is about 69–93 €/t_{ash}. Without the extra chemical stabilization and effluent treatment, the price is at the lower end. With avoidance of the lime addition, the treatment cost is also approximately 4 euros per ton lower according to the book. [84, p. 46–54] Compared to the calculations in this thesis, the cost is still higher. In the calculations of the carbonation treatment in this thesis, there is no lime addition, effluent treatment cost, or extra chemical stabilization. Furthermore, the carbon dioxide of the process is assumed to be free, for instance from the flue gas of the nearby power plant. Due to these, it makes sense that the actual process OPEX is relatively low. However, this does not explain the difference between the calculations and the reference.

The washing treatment cost is comparable with the FERROX process in which washing and ferrous sulfate are utilized for the precipitation of heavy metals as iron oxides. The cost estimation including the investment cost is 65 €/t_{ash} according to the report by International Solid Waste Association. Their price is lower even they have a chemical stabilization in the process as well. However, the difference is not huge, and the costs stand on the same ground. [77, Appendix A] In case of acid leaching, the process OPEX seems to be reasonable as well. The treatment cost of the process is probably between washing and FLUWA, and the executed calculations indicate that as well. As comparison, the treatment cost of NOAH's acid extraction process is 50 €/t_{ash} [77, Appendix A]. This is a result of utilization of waste acids. With this kind of combined waste acid and ash disposal process, it is possible to reduce the treatment cost significantly. This may be a key for the profitability of the processes.

In Figure 24, there are nominal and discounted payback periods represented. The present treatment cost is defined as 230 €/t. The cost is relatively high, but it is modelling the functioning of the TEA tool well. On the other hand, in many cases, only one of the following processes of acid leaching, carbonation, or washing is not enough to achieve the leaching or concentration limits of utilization or landfilling. This means that multiple stages are often needed. In the saving calculations, the ash is in any case landfilled after the treatment. In other words, the total OPEX is compared with the given present treatment cost. The discount rate for the calculation is 4.0%. The cementation is not in the figure due to lack of capital expenditures in this thesis. Therefore, it cannot have a payback period.

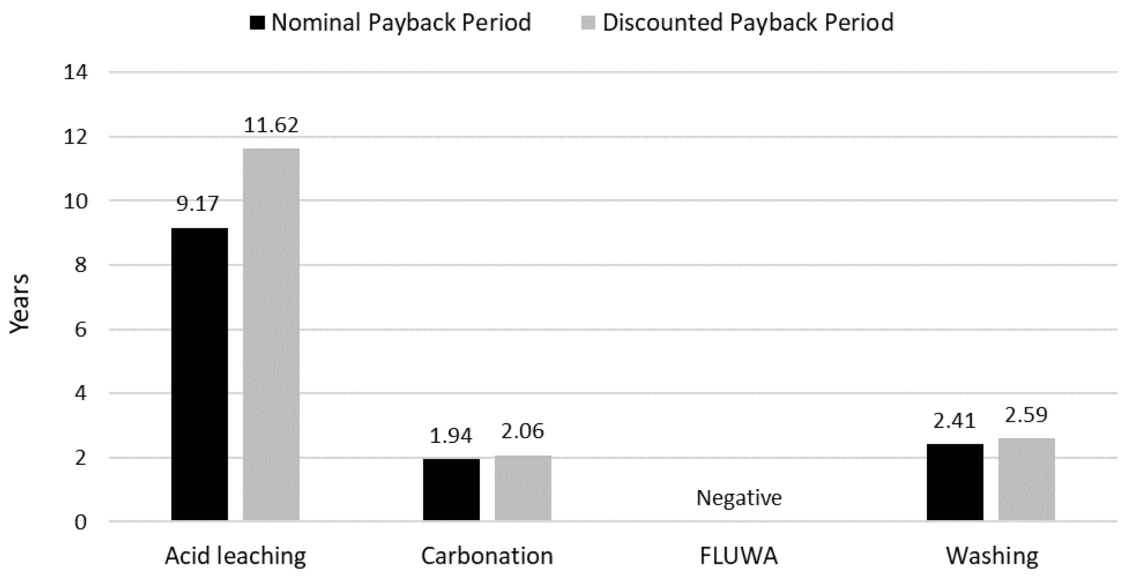

Figure 24. *Payback periods of the processes compared to the present treatment cost of 230 €/t*

The figure above shows that the investment to the FULWA process is not profitable, if the present treatment cost is 230 €/t_{ash} or less. On the other hand, carbonation and washing seem to have relatively short payback periods. Thus, carbonation is an interesting option in view of economic feasibility. If the technical feasibility achieves the fair level, the carbonation method should be noticed, when the investments for the ash treatment are considered. Washing is a robust technology for the reduction of salts, but it rarely works alone due to its limited ability to remove heavy metals. This means that there must often be another stage, as acid leaching, and then the profitability is not so well anymore in comparison with the pure washing process.

The net present values of acid leaching, carbonation, and washing for 15 years are presented in Figure 25. These curves underline the same fact as earlier: carbonation and washing seem to be very profitable processes with the comparison price 230 €/t. Acid leaching is profitable as well, but the NPV curve is significantly lower compared with the other processes.

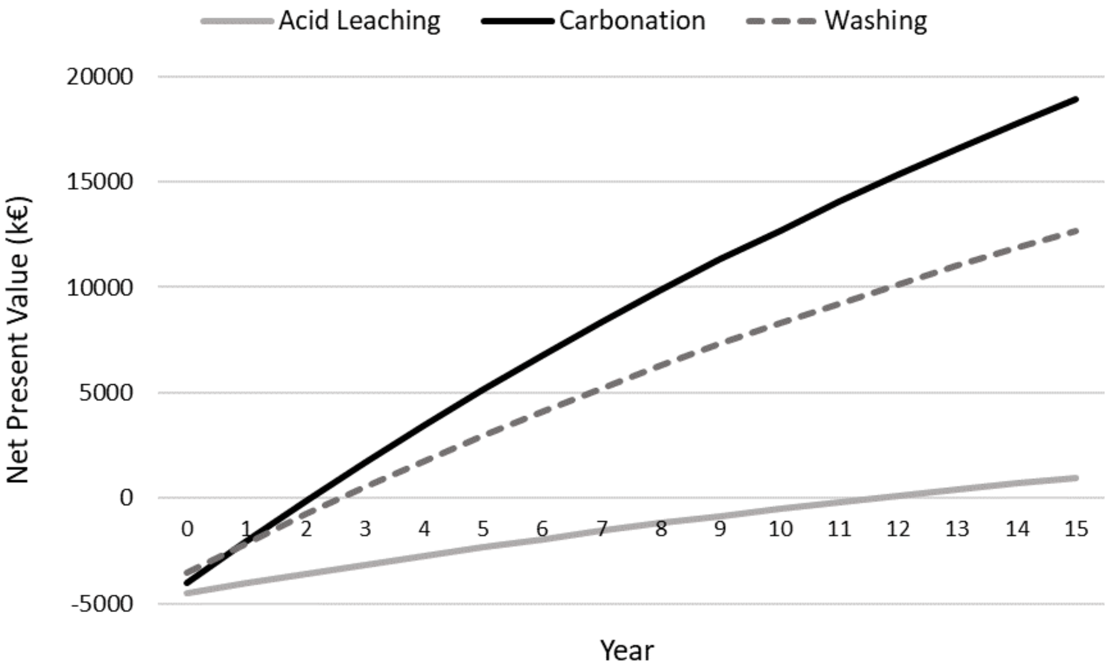

Figure 25. *Net present values of the selected processes*

In following Table 19, the internal rates of returns as well as modified internal rates of returns for the processes are presented. The FLUWA process was unprofitable with these inputs so there were no results for IRR and MIRR, neither.

Table 19. *IRRs and MIRRs of the processes*

Treatment	IRR, 15 years (%)	MIRR, 15 years (%)
Acid leaching	6.89	5.32
Carbonation	51.26	16.80
Washing	41.21	15.13

The IRRs and MIRRs give the same result as the economic indicators earlier. Washing and carbonation have high both modified and the conventional internal rates of returns. The processes are overwhelming profitable according to these numbers. However, the avoidance of the reference price 230 €/t_{ash} with washing only may not be reality. The MIRR values of the processes are closer to each other compared to the IRRs. It is typical for the MIRR to delineate the better profits compared with the IRR. In the MIRR, cash flows are reinvested at the cost of capital. Here, washing and carbonation stays below the value of 20%. For acid leaching, the change is not huge compared to the IRR.

As mentioned in the introduction of Section 2.5, Saraber and Pels concluded that the ash treatment with washing is not profitable. According to the calculation, this is true, if the benefit of the treatment is less than 84 euros which is the process OPEX and capital expenditures combined. For instance, if the target is to avoid the waste tax 70 €/t, the investment is unprofitable. In other words, the achieved saving is minor in comparison with the investment and process costs. In Table 20, some scenarios about the present treatment prices for the power plant operator are represented. Potential savings, which may be realized via the treatment process investment, and their origin are presented as well.

Table 20. *Potential savings compared to the present treatment price*

Ash and utilization	Present treatment price ($€/t_{ash}$)	Potential savings
Clean ash, landfilled by the power plant operator	85	70 €/t, Waste tax
Clean ash, landfilled by the outsider	100	**85** €/t, Waste tax, gross margin
Clean ash, utilized in the road basement by the outsider	30	15 €/t, Gross margin
Semi-hazardous ash treated and landfilled by the outsider	150	**135** €/t, Treatment cost, gross margin, waste tax
Semi-hazardous ash treated and utilized by the outsider	80	65 €/t, Treatment cost, gross margin
Hazardous ash treated and landfilled by the outsider	250	**165** €/t, Treatment cost, gross margin

Potential savings are assumed to be either 70 €/t waste tax, 15 €/t gross margin of the outsider, or the treatment cost which include the upkeep of the hazardous waste landfill and some treatment for the incoming ash. In case of semi-hazardous ash, the treatment cost is 50 €/t and for the hazardous ash, it is 80 €/t. The transportation cost is 15 €/t, which cannot be saved.

With these assumptions, the treatment cannot ever be profitable if the CAPEX and the process OPEX are together more than 165 $€/t_{ash}$. This is also close to the price of the cementation that has been presented earlier. In many cases, the price should be less than 100 euros. In this case, *only carbonation and occasionally washing are economically feasible solutions after the calculations of this thesis.* According to the reference, the air classification achieves this level as well. In Figure 26, the treatment costs are compared with the potential savings. In the figure, the acid leaching is on the feasible side as well. Consequently, the washing is on the unfeasible side. However, their profitability depends on the realization of the savings. Furthermore, the cost of thermal treatment is up to 500 €/t_{ash}, so it is the most expensive option. According to Hjelmar et al., the cost range for thermal treatment is 100–500 €/t_{ash}. However, Voshell et al. concluded that the energy consumption is extremely high which makes the 100 €/t_{ash} doubtfully low. VTT Technical Research Centre of Finland has also calculated that the melting process would cost approximately 200–300 €/t_{ash} according to Yle, the national Finnish Broadcast company [85]. Therefore, the cost range for the thermal treatment is chosen to be 200–500 €/t_{ash} in this thesis. However, the savings potential is high as well. In case of acid leaching, carbonation, and air classification the potential savings are higher than the treatment costs. The dashed line denotes the situation in which the potential savings equals the treatment cost.

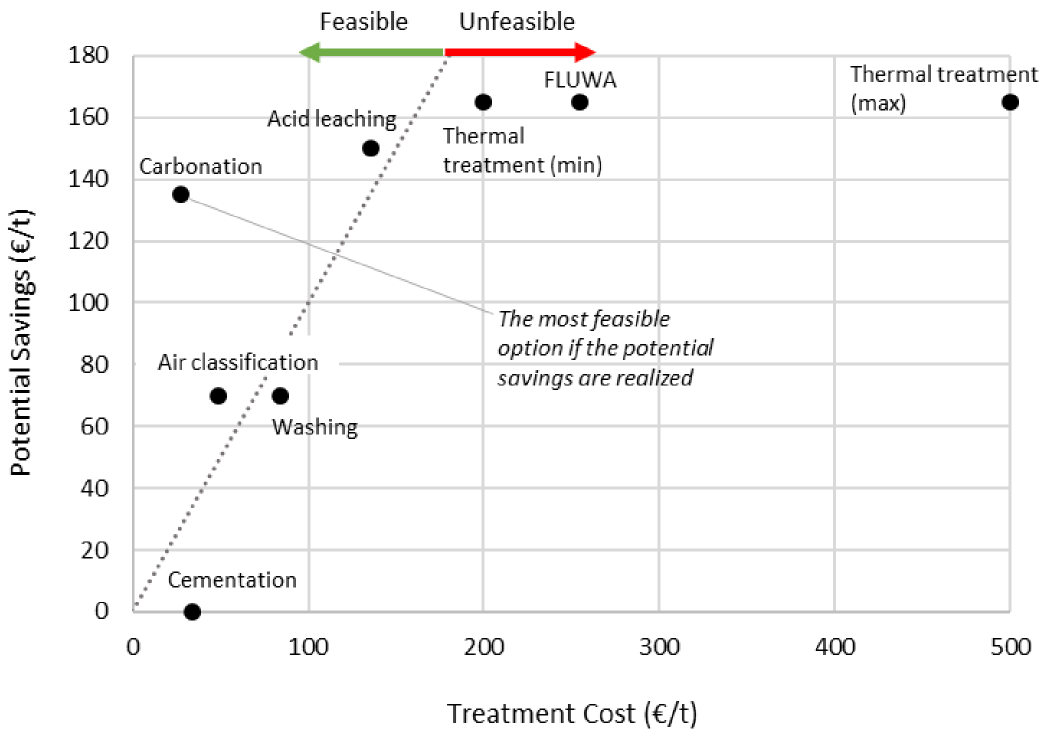

Figure 26. *Potential savings compared to the treatment cost*

Treatment costs include the CAPEX allocated for 15 years as well as the process OPEX in the figure above. Possible transportation or disposal is not included in the treatment cost. For washing and air classification, the possible saving is to avoid the waste tax, 70 €/t. With carbonation and acid leaching, savings are the waste tax and some treatment fee. The FLUWA process as well as thermal treatment savings are a result of avoiding the treatment cost of hazardous ashes. With these two processes, the assumption is that the ashes are in any case landfilled or otherwise disposed, and thus the waste tax is also paid after the treatment. This decreases the potential savings. With these assumptions, the carbonation seems to be the most feasible option. However, the feasibility is highly dependent on the functionality of the technology as well. For instance, the carbonation is a semi-dry version without any effluent flow in this thesis. The semi-dry process might have technological challenges in reality. However, if the carbonation works ideally, and the potential savings are realized, it is an inexpensive ash treatment method for reduction of leachability of harmful elements.

Overall, it may be concluded that there are two options in which the ash treatment may be economically feasible. The first is to avoid the waste tax with the relatively clean ash. This means that with a light treatment, the ash may be utilized outside the landfill. The waste tax is one of the main factors which affect the profitability of ash treatment. If the waste tax is high, it would be possibly profitable to treat ashes before utilization as well. Another way to make the treatment profitable is to avoid the treatment fee by an outsider. This is a possible situation with waste incineration ashes which treatment costs may be high. The treatment and disposal may be relatively expensive in the hazardous landfills due to its special structural requirements and limits for pollutants [70]. Ash must meet the regulated leachability limits of the landfilling of the hazardous waste as well. Sometimes the ashes from waste combustion must be even treated before the disposal. In this situation, it may be profitable by the ash producer to invest in their own treatment process. However, the case-by-case discretion must be done, and the profitability of the treatment processes is also highly dependent of the present treatment cost. There is no universal answer to all kinds of ash treatment questions.

4.4 Scenario and sensitivity analysis

In this section, the operational expenses of the processes are investigated when the costs vary. The method is presented in Section 3.6. The treatment costs of the scenario 0 are represented in Figure 23. The scenario 0 represent the situation, where nothing changes, and the costs are as calculated in this thesis earlier. The processes of acid leaching, carbonation, cementation, FLUWA, and washing are studied. In the scenario 1, the price of the input chemicals is doubled compared to the scenario 0. The total expenses after the rise in prices are presented in Figure 27. Inside the bars, the relative increase of the prices compared to the scenario 0 are presented.

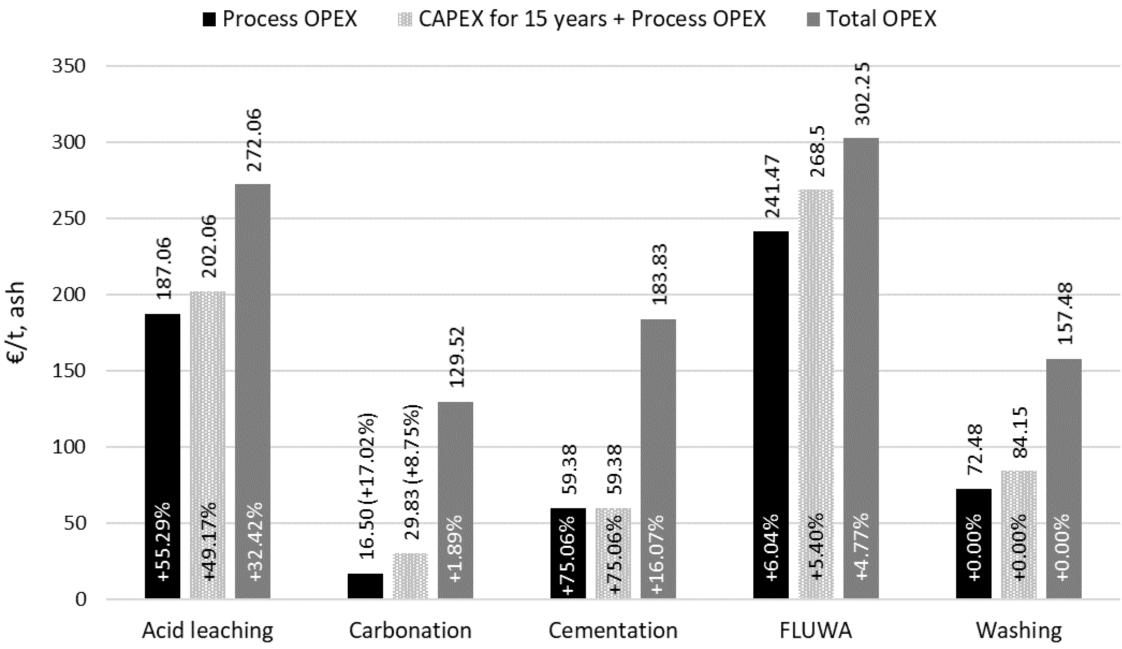

Figure 27. *Total expenses if the chemical cost doubles*

The process OPEX of the acid leaching is approximately 1.5 times higher compared to the original process OPEX, 120.46 €/t. As seen in the figure, the acid leaching is very sensitive to the variation of the chemicals cost. This means also that the process expenses decrease sharply if the chemical cost decreases. For the carbonation, the change of costs is not significant, and especially for the total OPEX, it is only 1.89%. Cementation suffers much in view of process profitability. The cement is assumed to be a chemical in this calculation, so it explains the high rise in the process expenses. The FLUWA process has multiple stages, and the increase of the chemical prices has not a significant role in the process OPEX. Its water treatment is also executed with the ion exchange instead of the chemical treatment, so the consumption of chemicals is not high. In the washing process itself, there is no chemical consumption. However, the rise of chemical costs would affect also the washing process via the possible chemical water or effluent treatment. In this calculation, the effluent treatment is assumed to be an independent subprocess. In the following scenario 2, the price of the effluent treatment doubles compared to the scenario 0. The total expenses after the rise are introduced in Figure 28.

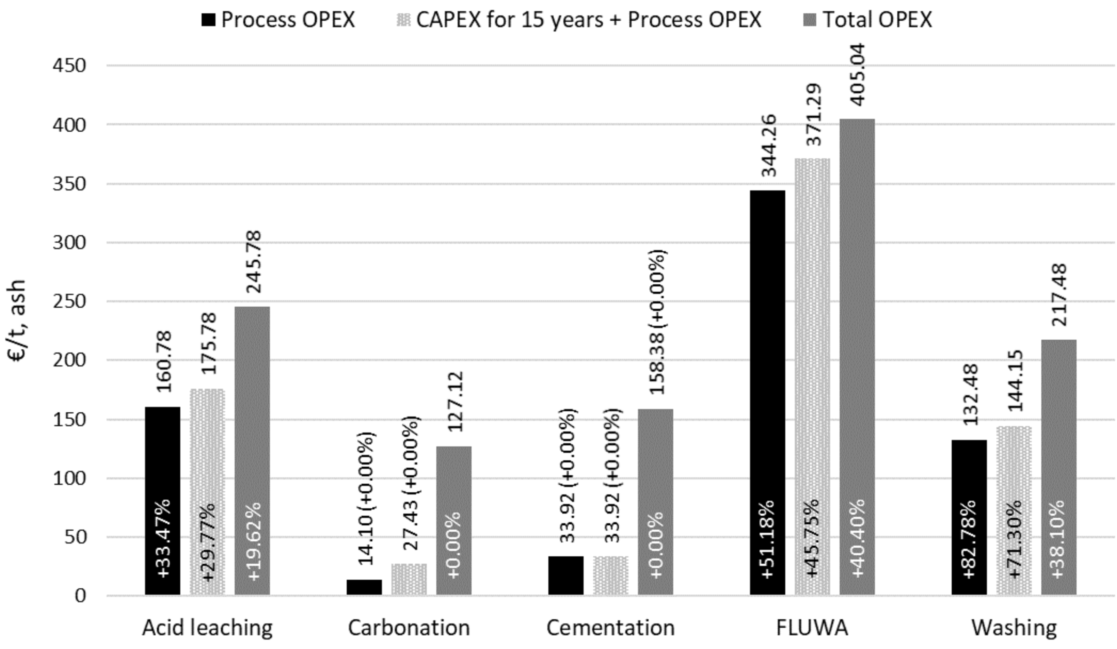

Figure 28. *Total expenses if the effluent treatment cost doubles*

As seen in the figure above, acid leaching reacts strongly to the price change again. The increase is not so radical as in the previous scenario but still significant. There is not effluent in the carbonation process of this thesis, but it is possible to have a wet carbonation process with the effluent flow as well. The cementation has the same situation as the carbonation. In the FLUWA process as well as in the washing, the rise of the effluent treatment cost has a noteworthy influence on the operation cost of the ash treatment. This is due to the high L/S ratio in the processes which means high amount of effluent. In other words, the amount of water is high compared with the amount of ash in the process.

In the scenario 3, the price of transportation doubles compared to the scenario 0. The transportation is picked up to this sensitivity analysis because it is usually the highest cost in a group of maintenance, employees, and transportation according to Figure 22. It may be concluded that the effect of a price change of maintenance or personnel would be minor in comparison with the price change of the transportation. In addition, a scenario 4 is investigated. In the scenario, the waste tax increases from 70 €/t to 100 €/t. In Figure 29, these both results of the scenarios are presented. Compared to the scenario 1 and 2, there are only total operative expenses represented. The process operational expenses do not vary after the change of transportation cost or waste tax. Hence, the total OPEX is only investigated, due to it includes the transportation and waste tax.

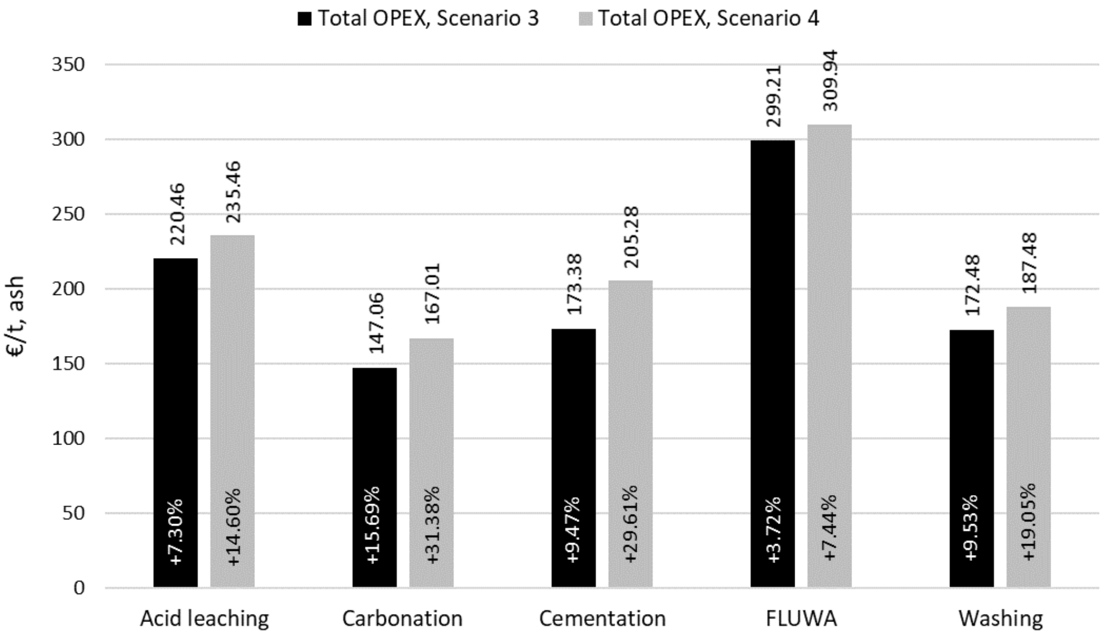

Figure 29. *Total operational expenses after the rise of transportation cost or waste tax*

The doubling of the transportation cost has minor impact on the total OPEX compared with the other scenarios studied previously. The change in case of carbonation is +15.69%, but otherwise it stays below 10%. This is due to the low process cost of carbonation, and thus the share of the transportation cost is higher in the total cost. However, the increase in price in euros is moderate 20 €/t_{ash}. The rise of the waste tax from 70 €/t to 100 €/t has more significant impact on the total OPEX. The increase is the sharpest with carbonation and cementation which expenses rise 31.38% and 29.61%, respectively. In both treatment methods, the share of the waste tax is important which means they are sensitive for its changes. On the other hand, the FLUWA process decreases the mass of landfilled material compared to the situation in which ash is landfilled directly. In other words, the output ash cake from the process has less mass compared to the ash coming into the process. It is noteworthy to notice that the increase of waste tax makes landfilling more expensive as well. The rise of the direct landfilling cost would be approximately 43% in this scenario. This may change the profitability of ash treatment from economical unfeasible to feasible. Especially, with the methods in which the mass of landfilled ash is decreased, this may be reality.

After the sensitivity analysis of the process expenses, the sensitivity analysis of the reference price, also known as the present treatment cost, is investigated. The process expenses are investigated as in this thesis earlier, but the present treatment cost is varied. With the comparison of the reference price and the expenses of the process, the net present value, the nominal payback period as well as the discounted payback period in different situations are calculated. In Figure 30, the sensitivity of the net present value of the acid leaching process is represented. The plant size is 20,000 tons ash per year, and the interest rate is 4%.

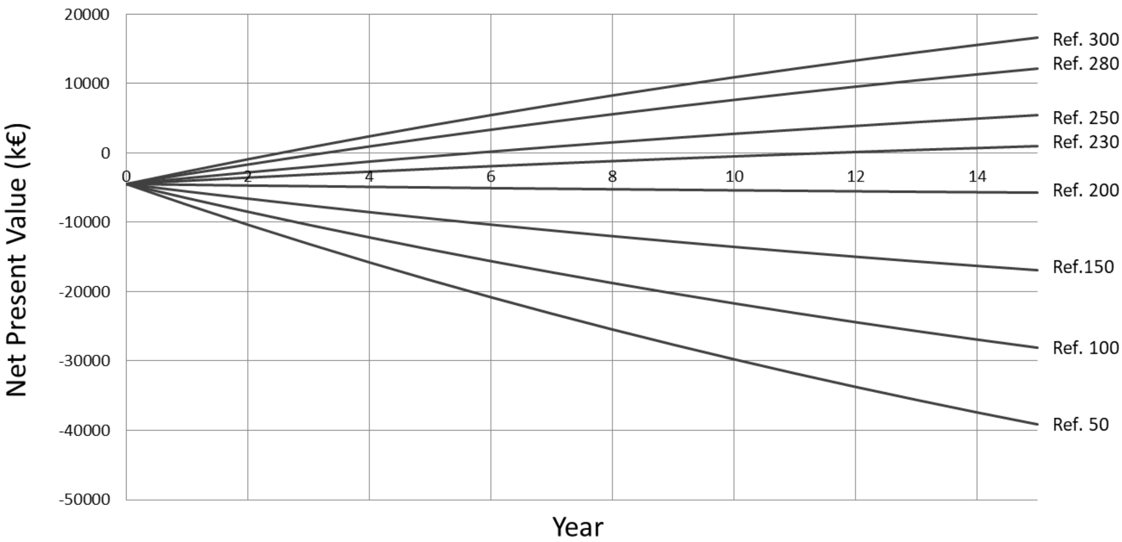

Figure 30. *Sensitivity of the NPV of the acid leaching process to the reference cost*

The first time, when the net present value is positive after 15 years, is with the reference price of 230 €/t_{ash}. However, the value of the NPV is not significant there. With the reference price of 250 €/t_{ash}, the investment seems to already be quite profitable. Therefore, it can be concluded that the profitability limit is somewhere there between these numbers. To put it another way, if it is possible to avoid the treatment cost of 230–250 €/ton ash, the investment is profitable in 15 years. It is noteworthy to notice that if the ash may be utilized instead of landfilling after the processing, the profitability of the process is better. In that case, from the reference prices may be removed the part of the waste tax, 70 €/t. Hence, the NPV of the investment is positive in 15 years, if the treatment fee 160–180 €/t_{ash} is avoided, and the ash is utilized instead of landfilled. However, this calculation takes only a stand on the question if it is better to pay for an outsider for ash treatment or is it more profitable to invest in their own system. In Figure 31, the nominal payback periods and discounted payback periods of the acid leaching process are presented. With the reference costs of 50, 100, 150, and 200, the payback periods were negative, so they are excluded from the figure.

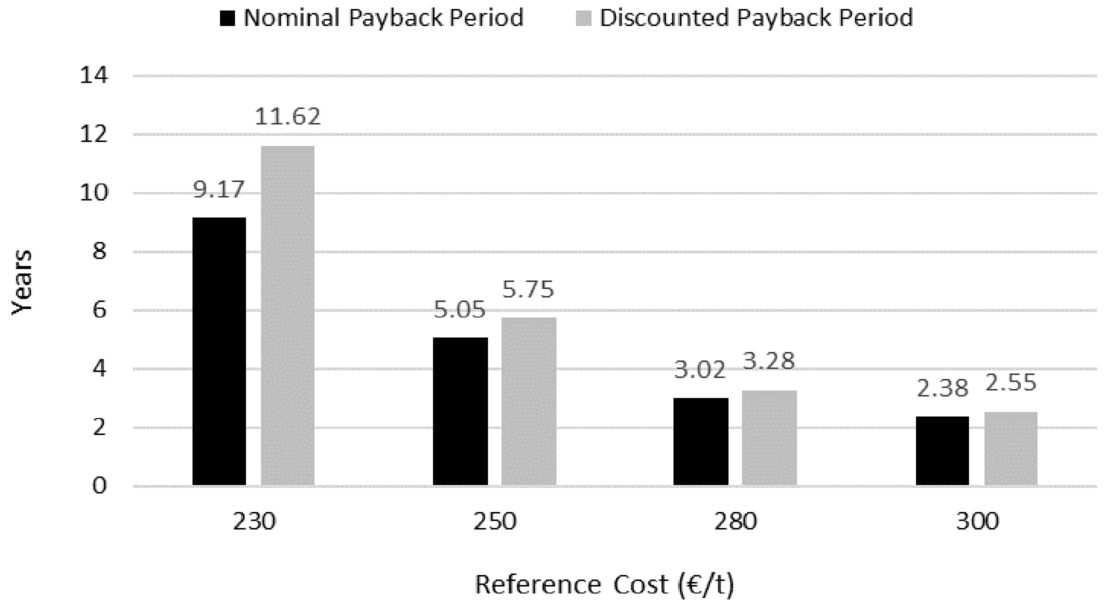

Figure 31. *Sensitivity of the nominal and discounted PB of the acid leaching process to the reference cost*

As seen in the figure above, the payback periods decrease strongly if the reference cost increases. The Figure 31 gives the information of a same kind as the previous one. The investment may be economical feasible in the period of 15 years, if it is possible to avoid the present treatment cost of 230–250 €/t_{ash}. The higher end of the reference cost is not relevant with the other ashes than fly ash from waste incineration. In Figure 32, the sensitivity of the net present value of the carbonation process is represented. The plant size is 20,000 tons of treated ash annually and the interest rate 4%, again.

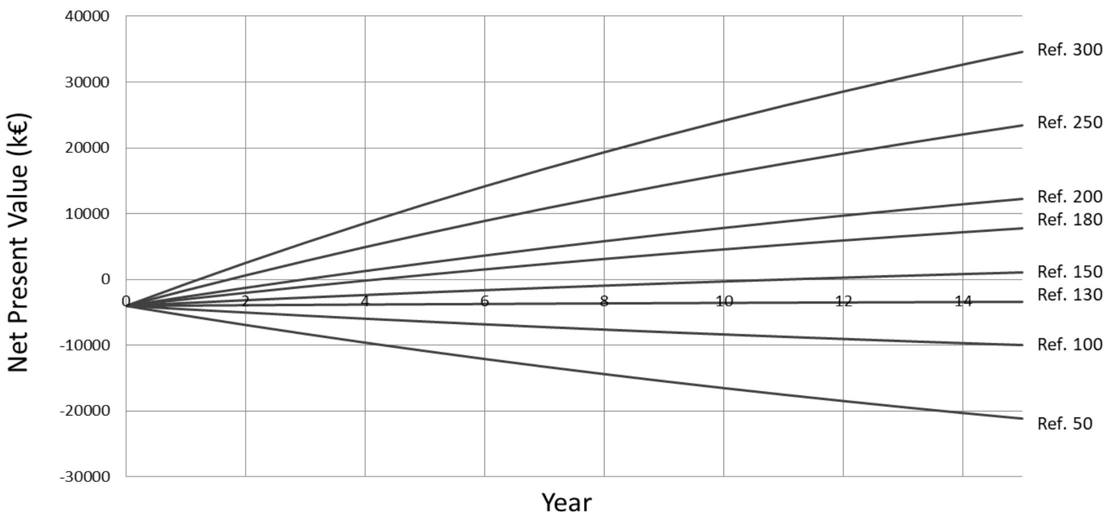

Figure 32. *Sensitivity of the NPV of the carbonation process to the reference cost*

Here, the first time when the reference curve ends up onto the positive side of the NPV after 15 years, is with the reference cost of 150 €/t_{ash}. However, the NPV is barely positive, and hence the break-even point is somewhere between the reference prices of 150 and 180 €/ton ash. The profitability seems to be better even with the lower reference price compared to the acid leaching which makes it an attractive investment option. In Figure 33, the nominal payback periods and discounted payback periods of the carbonation process are presented. With the reference costs of 50 and 100, the payback periods were negative, so they are excluded from the figure. The nominal payback period was 69.39 years with the reference price of 130 €/t_{ash}, so it was excluded as well.

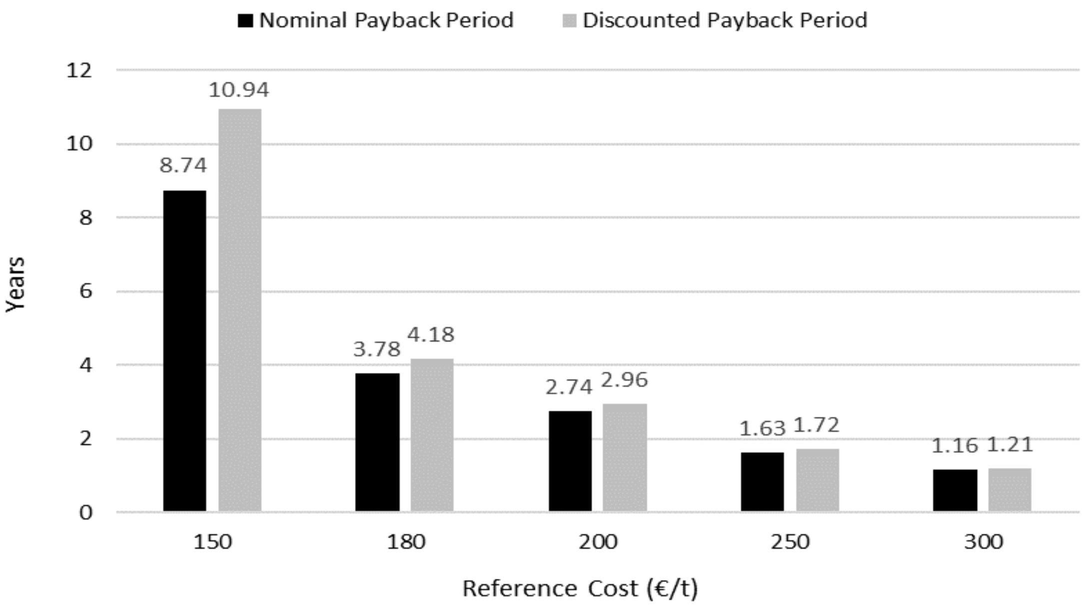

Figure 33. *Sensitivity of the nominal and discounted PB of the carbonation process to the reference cost*

The payback periods are shorter than in case of the acid leaching. Especially with lower reference costs, the payback periods are significantly shorter. Again, the payback periods shorten sharply if the reference cost increases. In Figure 34, sensitivity of the net present value of the washing process is represented. The plant size is still 20,000 t_{ash}/a, and the interest rate is 4%.

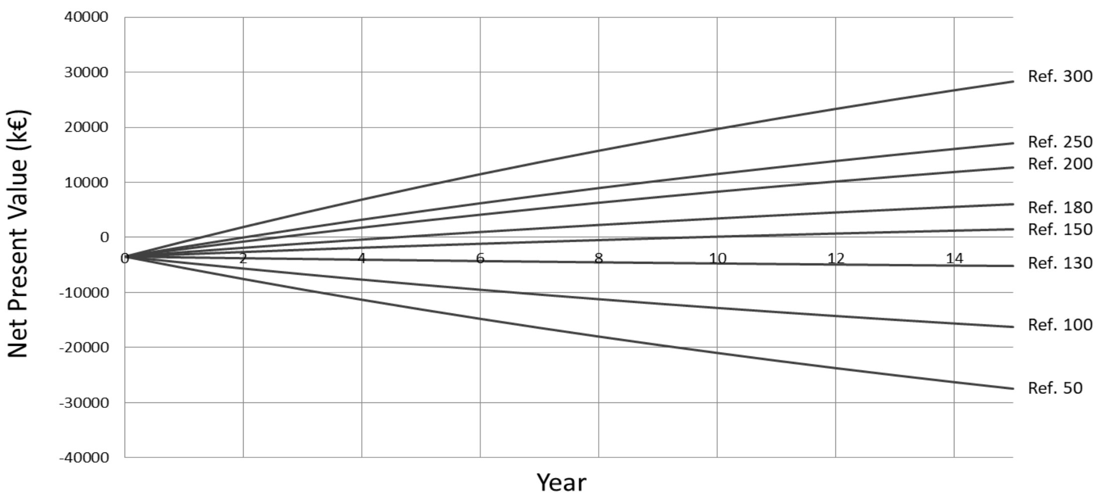

Figure 34. *Sensitivity of the NPV of the washing process to the reference cost*

Similarly, as in the carbonation process, the NPV is positive for the first time with the reference price 150 €/t_{ash}. However, the NPV is not noteworthy above the zero, again. Thus, the profitability level is somewhere between the reference price 150 and 180 €/t_{ash}. In Figure 35, the nominal payback periods and discounted payback periods of the carbonation process are presented. With the reference costs of 50 and 100, the payback periods were negative, and hence they are again excluded.

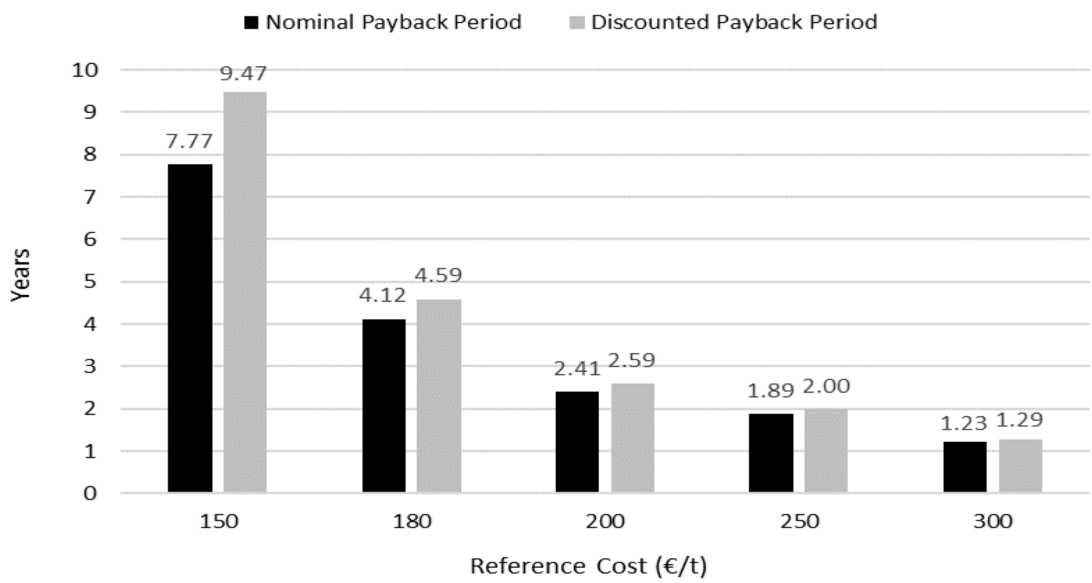

Figure 35. *Sensitivity of the nominal and discounted PB of the washing process to the reference cost*

The payback periods look similar to the results from the carbonation. However, the payback period is shorter with the low reference cost. This is due to the lower capital expenditures compared to the carbonation. Still, the saving potential is higher with the carbonation, and it seems to catch up the washing with the reference cost between 150–180 €/t_{ash}.

4.5 Overall discussion

The amount of waste incineration will likely increase in the future due to the coal phase out and the better utilization of other solid fuels like wood. Furthermore, the quality of waste fuel becomes worse due to the extremely high recycling rate of materials as plastics. This is a challenge in view of ash treatment due to the variation of fuels. There will be more components of a different kind in ashes, and they are more harmful compared to ashes from conventional fuels like wood or coal. The properties of ashes will vary more as well, and it may be difficult to appoint some clear application for ashes, especially for fly ash. Nowadays, the major components mainly determine the utilization, but if the variation is high, even the evaluation of feasibility is challenging.

Politics influences strongly the economic feasibility of the ash treatment. Regulation, prohibitions, or financial support may change the operational field, and thus make the treatment profitable or necessary. For instance, the EU is working hardly on the circular economy theme [1] which may accelerate the utilization of ashes. The other good example is Switzerland. There, the prohibition of landfilling of municipal solid waste took effect in the early 2000's. This has made the waste-to-energy solutions become a dominating technology for the waste management and has developed the different technologies for the ash treatment, for instance the FLUWA process. [86, p. 3] In this operational environment, the higher operational expenses of the ash treatment, as 200 €/ton, are acceptable due to the obligatory treatment of ashes. The treatment of fly ash as well as the recovery of heavy metals from fly ash must be implemented in Switzerland by 2021 [86]. Germany has made the similar decisions related to the sludge incineration ashes. There, wastewater treatment plants must have implemented processes for phosphorous recovery, including the sludge incineration ash, by 2029. [87] Overall, the regulation should be comprehensive and clear in any case. The limits for different hazardous elements as well as requirements for different properties should be determined precisely. After the determination, it is possible to use ash in new commercial applications.

In this thesis, the main purpose was to extend the knowledge about the techno-economic feasibility of ashes, especially fly ashes. Additionally, the original plan was to find a potential technology which could be further investigated. However, this did not happen due to the economic challenges of the processes. Therefore, the plan changed to the implementation of the TEA tool. After the change of plans, the creation of the tool was successfully executed. In the tool, there are still a couple of disadvantages. It scales the treatment plants linearly which means that the economies of scale are not considered.

Thus, operational expenses per ash ton are the same with small and huge plants. There is also some uncertainty in the partial cost of the processes. This is mainly a result of the insufficient techno-economic data of the processes available. Many of the treatment technologies are under the development which means that the data is not public. The greatest approximation is in the capital expenditures, due to the lack of data available as well. However, the thesis answer to the determined research questions well. The literature survey gives information about utilization and treatment possibilities and the regulation in the area of the EU. The chapters of materials and methods as well as results and discussion study the techno-economic feasibility of the treatment methods and try to answer the question how the ash utilization and treatment possibilities may be assessed. Results in this thesis are similar in comparison with the literature references, even though some differences were found. The main contributions of this thesis are

- the creation of the methodology for the selection of proper treatment and utilization options for different ashes
- the techno-economic feasibility analysis of multiple ash treatment methods
- the conclusion that in the investigated treatment processes, the most significant expenses are the chemical price, the effluent or water treatment as well as the waste tax in case of the landfilled ashes
- the conclusion that the carbonation as a treatment method is the most profitable if the technological feasibility is at a proper level
- the TEA tool implementation

However, the most common way to study treatment technologies is to write a technical report which collects data from the existing treatment plants. In reports of this kind, there are mainly just total process expenses presented. This means that there is not any analysis of the cost structure of treatment methods. Occasionally, there is not any information about the treatment cost at all. This depends highly on the willingness of the developer to give this data for the researcher. From this point of view, this thesis offers a wider approach to this topic compared to these technical reports. The novelty value of this study is on this techno-economic feasibility focus.

5. CONCLUSIONS

The purpose of this thesis was to investigate the utilization and treatment possibilities for ashes, especially for fly ash. For understanding all the utilization possibilities, the compositions of different ashes had to be investigated. Ashes from different combustion processes have different major, minor, and trace elements. Some of the minor and trace elements are hazardous for the environment as well as for humans. Due to this, the utilization and disposal of fly ash is regulated and supervised. However, the utilization in a way or another is a common practice for the ash from combustion. Only a minor share of all produced ash ends up to the disposal. On the other hand, the share of waste incineration may increase in the future which means more hazardous ashes. The treatment of these ashes is often essential before the landfilling. Additionally, it seems mainly economically unfeasible to treat ashes before any kind of utilization. The price of the bulk ash products is not high, so there are not high margins, neither. Then again, there are not many commercial, highly developed, ash treatment technologies which would be profitable. However, different technologies, as acid leaching, carbonation, thermal treatment, or washing have still been demonstrated. These processes are technologically feasible and may be utilized for different kinds of issues of ashes as high chloride or heavy metal contents.

With these most developed treatment methods, the utilization and treatment possibilities were determined. For typical coal, peat, and wood ashes, the possible treatment methods before utilization are air classification, chemical or electrochemical treatment, grinding or granulation as well as washing. With these relatively clean ashes, the main saving potential is in the avoidance of the waste tax after the treatment. The waste incineration ash, as SRF or RDF ash, needs some treatment in any case and there are also more potential savings. Treatment possibilities for this ash type are carbonation, cementation, chemical or electrochemical treatment, and thermal treatment. The savings are higher if it is possible to avoid the treatment fees of an outsider and the ash is possible to landfill with the higher classification or even utilized.

Utilization possibilities of certain ashes depend on the regulation which restrict the ash reuse. In this thesis, the regulation under consideration were the EU standard of fly ash for concrete, Finnish regulation for ash fertilizer use as well as the Finnish regulation for wastes in the road or earth construction use. In case of landfilling, the European Union's council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills is considered. In the concrete standard, property and composition requirements for the fly ash are determined. The fly ash for concrete is mainly from the coal combustion due to its high aluminosilicate content. In comparison, ash in the fertilizer use is often originated from wood combustion. The wood ash has high calcium, potassium, and phosphorous contents which are useful elements in fertilizers. In the fertilizer regulation, the maximum concentration limits for hazardous elements as well as the minimum limits for Ca, K, and P are defined. Consequently, the earth and road construction regulation have maximum limits for the leachability and concentration of hazardous elements. If ash does not meet the regulatory limits of utilization, it must to be disposed. There are leaching limits for hazardous substances as well as three different classifications for the landfilled material. Thus, treatment may elevate the classification of the ash disposal. In that way, it is possible to achieve cost savings and environmental benefits due to lower leachability of heavy metals and salts, especially with waste incineration ashes. If the regulation is changed, the ash treatment may become obligatory or profitable. Hence, it is essential to recognize the barriers which make the treatments unfeasible now. On the other hand, with the better knowledge it would be possible to reduce the cost of treatment processes, and thus make the treatment profitable.

The economic feasibility calculations as well as the techno-economic analysis tool are a solution for better understanding about the processes in view of economics. Firstly, the mass and energy flows of the processes under consideration were determined. After this, the capital expenditures as well as the operational expenses were defined. With this information, the implementation of the techno-economic analysis tool was executed. The processes under consideration were acid leaching, carbonation, cementation, FLUWA, and washing. The operational expenses without transportation or landfilling of the ash for each process were calculated as 120.46, 14.10, 33.92, 227.71, and 72.48 €/t_{ash}, respectively. The highest costs in the processes were mainly input chemicals or treatment of water or effluent. This means that the operational expenses were also sensitive to the changes of these costs. From the non-process costs, the waste tax is significantly the highest one in case of the landfilled ashes. Therefore, the higher waste tax may revise the ash treatment and utilization instead of landfilling as an attractive option. The cost of the cementation treatment was around 160 €/t_{ash} according to the calculations. This cost includes also the transportation and the landfilling of the ash. If the cementation is wanted to be avoided, the treatment cost of the new process should be below this.

From another point of view, the treatment methods of carbonation and washing seemed to be profitable, when it was possible to avoid a reference cost of 150 €/t_{ash} or more. For the acid leaching, the similar break-even point was the reference price 230 €/t_{ash} or more. The reference cost represents the fee which some outsider is charging for the disposal and, if necessary, for the treatment of ash. If the ash was utilized instead of landfilled, the break-even reference costs would be 80 €/t for carbonation and washing and 160 €/t for acid leaching. In other words, if the present treatment fee is more than these numbers, it would be reasonable to consider the investment for the own treatment process. Therefore, the investment to the carbonation process is economically the most feasible option for the ash treatment due to its capability to reduce heavy metal leachability. On the other hand, washing is a robust and effective technology for salt reduction. In the ends, all this data was collected to the techno-economic analysis tool. The TEA tool may be suggested for the approximate estimation of profitability for different ash treatment methods. The tool also gives information about the utilization possibilities and limiting regulation of ash utilization. However, the case-by-case evaluation for every investment must be done.

For the better understanding about the composition of different ashes, more research is needed in the future. For instance, the concentrations of hazardous elements are swinging around the limits of utilization. Thus, it would be necessary to have deeper understanding how to control the concentration of the hazardous elements already in the boiler when the fuel composition is varying. Furthermore, there is only insufficient amount of data about the exact composition of ashes in view of treatment available. The composition is usually given in an oxide form, but there are for instance sulfates, carbonates, and hydroxides in different fractions. The reduction of the hazardousness of fly ash from fluidized bed boilers is also in a crucial role in the competitiveness against the grate boilers in waste combustion. It would be also necessary to know the effect of the post-combustion treatment of the flue gas on the ash composition. For example, an electrostatic precipitator, a baghouse filter, or additives may influence the composition of the fly ash at the collecting point. Naturally, the research on the technical feasibility of the simple and robust treatment methods is needed. Especially, carbonation seems to be a profitable treatment method, but there are some question marks on its efficiency and technological feasibility. Additionally, the knowledge about recoverable materials from ash may be a key for the economic feasibility. Due to the anxiety of the phosphorous shortage, the laws for the phosphorous recovery have been changing, for instance in the middle Europe. The nutrient may be recovered from the ash from sewage sludge combustion, and hence it should be under research as well. Overall, the regulation is different from one location to another, and it should be investigated as well.

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APPENDIX A: CONCENTRATION LIMITS IN THE EU STANDARD OF FLY ASH FOR CONCRETE

Conformity of fly ash should be continually evaluated. The properties, test methods and the minimum testing frequencies for the auto control testing by the producer are specified in the standard. In addition to the statistical conformity criteria, conformity of test results to the requirements of this document requires that it shall be verified that each test result remains within the single result limit values specified in Table 21.

Table 21. *Limit values for single measurement*

Property	Unit	Limit value
Loss on ignition (upper limit value)	% by mass	7.0 (category A) 9.0 (category B) 11.0 (category C)
Fineness (upper limit value)	% by mass	45 (category N) 13 (category S)
Fineness variation (lower and upper limit values)	% points from declared value	±15 (category N only)
Chloride (upper limit value)	% by mass	0.10
Free calcium oxide (upper limit value)	% by mass	1.6
Reactive calcium oxide (upper limit value)	% by mass	11.0
Sulphate content (upper limit value)	% by mass	3.5
Silicon dioxide + aluminum oxide + iron oxide (lower limit value)	% by mass	65
Total content of alkalis (upper limit value)	% by mass	5.5
Total phosphate (upper limit value)	% by mass	5.5
Soundness (upper limit value)	mm	11
Activity index at 28 days (lower limit value)	%	70
Activity index at 90 days (lower limit value)	%	80
Particle density variation (lower and upper limit values)	kg/m3 from declared value	±225
Initial setting time (upper limit value)	times the setting of the test cement alone	2.25
Water requirement (upper limit value)	%	97 (category S only)

The proportion of ash derived from co-combustion shall be calculated with Formula (X):

$$M = \frac{K_1 \times A_1 \times K_2 \times A_2 \ldots K_n \times A_n}{K_c \times A_c + (K_1 \times A_1 \times K_2 \times A_2 \ldots K_n \times A_n)} \qquad \text{(A1)}$$

where

M is the proportion of co-combustion ash in total fly ash, in % by mass;

A_i is the ash content of co-combustion material no. *i*, in % by mass;

n is the number of co-combustion materials being used;

A_c is the ash content of coal, in % by mass;

Ki and K_c are respectively the proportions of co-combustion material(s) and coal being fired;

and where

$(K_c + K_1 + K_2 + \cdots K_n) = 1$ and $K_c \geq 0.60$, or 0.50 if the co-combustion material consists of green wood only.

In addition, if virtually ash free liquid and gaseous fuels are used as co-combustion materials, their percentage by net calorific value shall be determined and shall not exceed 40% of the total net calorific value. Higher percentages of virtually ash free liquid and gaseous fuel may be used during the start-up process of a power plant.

Table 22. *Types of co-combustion materials*

1	Solid Bio Fuels conforming to EN14588:2010 including animal husbandry residues as defined in 4.5 and excluding waste wood as defined in 4.52, 4.132 and 4.174
2	Animal meal (meat and bone meal)
3	Municipal sewage sludge
4	Paper sludge
5	Petroleum coke
6	Virtually ash free liquid and gaseous fuels