Ammonia Hydrometallurgy and Other Innovations for Sustainable Management of Waste Incineration Fly Ash

Dissertation for the degree of Philosophie Doctor

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Abstract

Incineration serves as a viable method for managing non-recyclable waste, allowing for waste volume and weight reduction while also enabling energy recovery. However, this process inevitably gives rise to the generation of inorganic hazardous waste by-products, which necessitate appropriate management. Significant volumes of inceration hazardous by-products, which predominantly consist of fly ash, fill up specialised landfills, which have limited and valuable capacity. Consequently, the exploration of alternative approaches for reprocessing/detoxifying and recycling valuable fractions derived from ash waste becomes imperative to establish sustainable long-term waste management strategies.

Today, fly ash from all over Scandinavia is deposited on Langøya by the company NOAH AS Received fly ash is regularly chemically analyzed. This has led to a large dataset of chemical composition for different fly ashes over time. Statistical analysis of this dataset, performed as part of the work presented in this thesis, has significantly increased the understanding of fly ash as a waste product and resource.

The chemical composition of fly ash demonstrates its potential as a suitable candidate for salt recovery, metal extraction, and utilisation as raw material for Portland cement clinker. The resource potential in fly ash is elaborated in the thesis. In addition, the fine particle fraction in bottom ash from waste inceration is discussed due to its high copper content, significant volumes, and similar chemical composition to fly ash. Zinc and copper constitute the two main valuable metals in the ash, but tin, antimony, silver, and gold can represent valuable by-products in a metal recycling process.

Furthermore, the chemical variation in fly ash is studied, as knowledge of this variation is important when the waste is to be used in processes for recycling valuable products. Here, we observe different chemical compositions for fly ash from incineration plants with different combustion technologies - fluidized bed versus grate oven technology. Additionally, the chemical differences of fly ashes separated from different flue gas cleaning systems - wet and dry systems - are illuminated. The chemical variations are systematized and quantified. How the chemical composition varies over time is also presented. Here, a decrease in concentration over the past decades is shown for certain heavy metals, but a relatively stable concentration for others. Heavy metals that are heavily regulated for use in products correlate with the decrease of these metals in fly ash.

Furthermore, selective metal extraction methods through ammonia hydrometallurgy are proposed for the recovery of zinc and copper. Laboratory experiments show good selective extraction under relatively mild conditions. The average yield for copper and zinc is approximately 50% and 70%, respectively. The hypothesis for limitations in achieving higher yields is the presence of highly insoluble copper and zinc species in the fly ash. Ammonia leaching of copper from bottom ash is also demonstrated with good selective yield. It is shown that the residual material after desalination washing and ammonia leaching exhibits good leaching resistance for landfill disposal. Suggestions for further separation and processing of the ammonia solution are discussed, highlighting the advantages and disadvantages of different approaches. Parallel is drawn to well-known old technology used for various copper and zinc ores.

Zinc and copper recovery through the ammonia process is integrated into the system of other material recovery and potential comprehensive fly ash recycling processes are presented.

Combined with salt recovery, fly ash can be even better suited as a raw material for the production of Portland clinker. This can be achieved with minimal generation of new waste streams. However, several process steps can be relatively energy-intensive and investment costs may be high.

Potential methods for antimony and tin recovery are also discussed through the formation of selectively extractable sulfides - both thermal and wet processes. Relevant literature for similar systems is referenced. Potential methods for silver and gold recovery through an ammonia process under oxidative atmospheres and copper catalysis are similarly discussed. The comprehensive process presented forms a basis for further experimental studies that are necessary for validating theoretical work.

To summarize, this work has contributed to an increased understanding of the chemical composition of fly ash and how it varies. It has shown that ammonia is a favourable leaching agent for copper and zinc recovery from fly ash and bottom ash. Additionally, it has presented comprehensive process ideas that can recycle the entire fly ash with minimal generation of new waste streams.

Sammendrag

Forbrenning brukes for håndtering av brennbart ikke-gjenvinnbart avfall siden det er gunstig med avfallets volumreduksjon kombinert med energigjennvinning. Imidlertid fører forbrenning til dannelse av uorganisk farlig avfall, som krever riktig håndtering. På grunn av betydelige mengder restprodukter fra forbrenning, som hovedsakelig består av flyveaske, fylles opp verdifull kapasitet av spesialdeponier designet for å håndtere farlig avfall. Dette er ikke bærekraftig på lang sikt og nye strategier for flyveaske-håndteringer er ønsklig. Material gjennvinning fra asken og annen reprosseringer hvor restmasser ikke har farlig avfall egenskaper vil redusere trykket betraktlig på dagens deponikapsitet.

I dag deponeres flyeaske fra hele Skandinavia på Langøya av selskapet NOAH As. Mottatt flyvaske blir regelmessig kjemisk analysert og dette har over tid ført til et stort dataset av kjemisk sammensetning for ulik flyveaske. Statistisk analyse av dette datasettet har gitt betydlig økt forståelse av flyveasken som avfallsprodukt og ressurs.

Den kjemiske sammensetningen av flyveaske viser potensial for salt- og metallgjennvinning fra asken, samt for askens bruk som råstoff i produksjon av Portland-sementklinker. Ressurspotensialet i flyveaske for resikulering er attraktivt og utdypes i avhandlingen. I tilegg blir finpartikkelfrasksjonen i bunnaske blir diskutert grunnet høyt kobber gehalt, betydlige volumer og lignende kjemisk sammensetning som flyveaske. Det er sink og kobber som utgjør de to viktigste verdimetallene i asken, men tinn, antimon, sølv og gull kan representere verdifulle bi-produkter i en metall resikurlingsprosess.

Videre studeres kjemisk variasjonen i flyveaske, ettersom kjennskap til variasjonen er viktig når avfallet skal brukes i prosesser for resikulering av verdifulle produkter. Her ser vi ulik kjemisk sammensetning for flyveaske fra forbenningsanlegg med ulik forbrenningsteknologi - fluidiserende seng verus rist ovn teknologi. I tilleg belyses kjemiske forskjeller av flyveasker separert ut av ulike røykgassrense systemer – våt og tørr sytemer. De kjemiske variosjonene er sytsematisert og kvatifisert. Hvordan kjemisk sammensetning varier med tid blir også presentert. Her vises nedgang i konsentrasjon for visse tungmetaller, men relatvt stabil konsnetrasjon for andre. Tungmetaller som er sterkt regulert for bruk i produkter korerelerer med nedgang av disse metallene i flyveaske.

Videre foreslås selektive metallekstraksjonsmetoder gjennom ammoniakkhydrometallurgi for gjenvinning av sink og kobber. Laboratorieførsk viser til god selektiv ekstraksjon under relativt milde forhold. Utbyttet for kobber og sink utgør gjennomsnittlig henholdsvis 50 og 70 prosent. Hypotesen for begrensingene for høyere utbytte er megnden tungtløslige kobber og sink specierer i flyveasken. Ammoniakkluting av kobber fra bunnaske blir også demostrert med godt selektiv utbytte. Det er vist at restmaterialet etter avsaltningsvask og ammonaikkluting viser gode ulekkningsegeksaper for deponering. Forslag til vidre separasjon og videreforedling amoniakkløsningen diskuteres med fordeler og ulemper ved ulike fremgangsmåter. Her trekkes det parareller til kjent gammel teknolgi brukt for ulike kobber og sink malmer .

Sink og kobber gjennvinning gjennom ammoniakkprosess blir satt i sytem med annen materialgjennvinning og potensiell helhetlig flyve aske resikuleringsprosesser blir presentert. Kombinert med saltgjennvinninig kan flyveasken egenes endra bedre som råstoff for produksjon av Portland-klinker. Dette med minimalt generering av nye avfallstrømmer. Dog flere prosessteg kan være relativt energikrevende og investeringerkostander kan være høye.

Også potensielle fremgangsmetoder for antimon og tinn gjennvinning er diskutert via dannelse av sulfider – både en termisk og en våt prosess. Her vises det frem til litteratur for lignende systemer. Poteniselle metoder og sølv og gull gjennvinning via amoniakkprosess under oksidative atmosfere og kobber katlylastor er på samme måte diskutert. Den helhetlige prosessen presentert danner et grunnlag for videre eksperiementell studier som er nødvendig for validering av teoretisk arbeid.

Oppsummert har arbeidet bidratt med økt forståelse av kjemisk sammensetning av flyveaske og hvordan den varierer, vist at amoniakk er gunstig lutningsmiddel for kobber og sink gjennvining fra flyveaske og bunnaske og presentert helhetlige prosessideer som kan materialvinne hele flyveask med minimalt ny genering av avfallstrømmer.

Preface

I had no plan of becoming a chemist. When I started my PhD four years ago, I did not dare call myself a chemist. Even though I had a material science background, I did not have chemistry classes in high school, I did not do well in chemistry during my undergrad studies, and I did for example not have a single credit in organic chemistry (still do not have). But now, I dare call myself a chemist and I am proud of it after this journey. I may not know that much about the world of chemistry, but enough to look at the world and see how much that can be understood with the principles of chemistry. There is so much that is decided by electrons' life at the atomic scale and processes down on a molecular scale. Getting insights into this has been very pleasing.

The PhD work has been a bumpy road, and it has been difficult to find the right paths to solve difficult challenges related to fly ash management. When I started the PhD position, the topic /challenges to solve were not really defined – I was supposed to help NOAH with a vague circular economy concept. I am very thankful for having got such an open thematic for my work. I got the freedom to do what I wanted and could develop ideas by my own doing. However, it proved also to be challenging. Sometimes, you follow stupid ideas; other times things are not lined up for exploring what you have in mind.

Some of the dead ends I started working with was HCl leaching of fly ash for metal recovery and aluminium particle separation by electrostatic separation techniques. I also stopped characterising the fly ash with RAMAN, together with XRD. The ash was too heterogenous. I stopped since I could not justify the time I needed for doing fruitful work. A value of having such an open PhD is the possibility to stop work on topics that you find out might be a dead end (either for the PhD deliverables or for science in general). During the last part of my PhD, I also initiated experiments related to Sb, Sn, Ag and Au extraction from fly ash with high-pressure ammonia leaching or alkaline sulfide hydrometallurgy. However, no immediate positive result due to practical problems made me abandon the pursue of getting "proof of concept" experimental data.

Also, managing my time to either finish "PhD deliverables" or continue work on what I mean is important for solving "real scientific challenges" has been a dilemma. I must admit that it has been more "thinking" than "doing". Some writing days have passed just stirring into my computer screen and reading papers without writing a single word. Moreover, I am of the opinion that thinking has little value if concepts are not tested in the laboratory – and I wish I could have had more time for trying out ideas. Experimental work is indispensable. On the other hand, doing lab work without thinking is not fruitful either.

The PhD years have been rewarding. I am now looking forward using my acquired knowledge in new arenas. Life is a never-ending learning process; continuing on this journey will be fun!

Acknowledgment

First, I would like to thank Dag Øistein Eriksen for his supervision, as a good sparring partner, for all the good talks about chemistry and other thematics, and for the good atmosphere he spreads around him. Without him, none of this PhD work would have happened, and I am very thankful for working and getting to know Dag. I would also like to thank Ørnulf Borgan for all his help and collaboration in statistics, during the first part of my PhD. Such a pleasure to collaborate with skilled professionals. I thank Jon Petter Omtvedt for his supervision and for introducing me to the realm of nuclear chemistry. Even though my PhD did not include radioactivity, the little nuclear chemistry knowledge I acquired will be useful in the future. Niels Høymark Andersen for supervision, introducing me to RAMAN and all the good chemistry talks. Tor Bjørnstad with similar good lunch discussions. Such a pleasure to talk to people with good insight into chemistry.

To Deniz Avsar as a partner in crime the nuclear chemistry group. Looking forward to being your colleague at IFE as well. To the master students working on similar topics as me, Aslak Roalkvam Skåra, Ragnhild Dirdal and Silje Aarnes. To Leonard, Ragne, Olga, Zjelka, Hans, John-Paul and others at NUC and the guys at environmental chemistry.

Thanks to Ole Bjørn Karlsen for helping with SEM and LM imaging – he was so helpful and accommodating. To the PRICE collaboration – especially to the PhD students Önder and Pauline for fun times during gatherings. Also, extra thanks to the guys in NOAH, Haakon, Kai Erik and Morten. Thanks to all the other persons that have been who have been involved in greater or lesser extend in my PhD. And for funding from Research Council of Norway (grant number 294543).

Lastly, I would like to thank my family and Irmeline for their continuous support and love throughout this PhD period. They have been a constant source of encouragement throughout this journey. I am truly grateful for their presence in my life.

List of Papers

Paper 1. "Variation in chemical composition of MSWI fly ash and dry scrubber residues.» Nedkvitne, Eirik Nøst, Ørnulf Borgan, Dag Øistein Eriksen, and Haakon Rui. "Variation in Chemical Composition of MSWI Fly Ash and Dry Scrubber Residues." *Waste Management* 126 (May 2021): 623–31. https://doi.org/10.1016/j.wasman.2021.04.007.

Paper 2. (not peer-reviewed) "Decrease in Cr, Cd, Pb and Sn concentrations in fly ash – evidence of positive outcome of EU." Nedkvitne, Eirik Nøst, Ørnulf Borgan, Dag Øistein 6

Paper 3. Nedkvitne, Eirik Nøst, Dag Øistein Eriksen, and Jon Petter Omtvedt. "Grade and Tonnage Comparison of Anthropogenic Raw Materials and Ores for Cu, Zn, and Pb Recovery." Resources 12, no. 3 (March 2023): 33. https://doi.org/10.3390/resources12030033 .

Paper 4.a (not peer-reviewed) "Toxic and valuable metals are enriched in fine particles – characterization of water-insoluble coarse, fine, and dense particle fractions of waste incineration ashes" Nedkvitne, Eirik Nøst, Dag Øistein and Jon Petter Omtvedt

Paper 4.b (not peer-reviewed) "Hazardous waste classification assessment of separated water insoluble coarse particle fraction of MSWI fly ash based on elemental analysis according to EU framework." Nedkvitne, Eirik Nøst, Dag Øistein and Jon Petter Omtvedt

Paper 5. (submitted for publishing) Copper and Zinc recycling from MSWI fly ash with ammoniacal leaching – an alternative to the acidic route?

Paper 6. Dirdal, Ragnhild Elise, Aslak Roalkvam Skåra, Eirik Nøst Nedkvitne, Jon Petter Omtvedt, and Dag Øistein Eriksen. "Recovery of Copper and Zinc from the Ash of Incinerated Municipal Waste." *Materials Proceedings* 15, no. 1 (2023): 60. https://doi.org/10.3390/materproc2023015060

Table of Contents

1 General introduction to the doctoral thesis

The doctoral work comprises 3 peer-reviewed research papers, 3 without peer review and one peer-reviewed conference paper, that have been produced during about three years of work. These papers and reports are written assuming that the reader has a good understanding of the topic. However, the following thesis provides knowledge for better comprehending the papers. They also contextualize the research within a broader perspective and address challenges this work has been formed around.

Moreover, the thesis aims to build competence towards transitioning the process industry to handle more secondary raw materials. The introduction comprises challenges and more specific goals for the PhD thesis related to fly ash waste management, while the following chapters share findings and competence built during the process. Work that has not been incorporated into papers and reports are also presented here. Lastly, the final part comprises recommended process schemes to be studied based on my acquired experience.

2 Introduction – fly ash management today

As the global population continues to grow and industrialization expands, the amount of inorganic waste produced has risen significantly. Our current economic model, which involves extracting raw materials, manufacturing products, and disposing of them as waste, poses significant challenges for efficient waste management. While policies and frameworks like the circular economy have been proposed to reduce waste generation, the laws of thermodynamics dictate that some waste will always be produced unless energy is invested in separating and upgrading waste. One type of inorganic waste that has gained more attention is by-products from waste incineration plants.

Incineration is used as an alternative to direct landfilling for managing non-recyclable waste. The incineration plants used are referred to by different names depending on the focus of the service provided. If the main focus is energy recovery, the plant is called a waste-to-energy (WTE) plant. The heat generated by incineration can be used to produce electricity, steam for various industries, or district heating. The thermal energy present in waste is significant, with a caloric value ranging from 7-23 MJ/kg (Peter Quicker, 2000). Compared to coal, which has a caloric value of 25-35 MJ/kg, the energy potential of waste is substantial. However, the primary purpose of waste incineration is to manage waste. When this is the emphasis, the plants are called municipal solid waste incineration (MSWI) plants. The definition of municipal solid waste (MSW) varies across countries, but it generally refers to waste from households managed by local authorities. MSWI plants offer additional waste management services to energy recovery, including reducing waste volume by up to 95% and weight by 75-85%. The reduced weight makes transportation easier, while the reduced volume helps to reduce landfill fill-up rates.

Waste management through incineration offers significant advantages in terms of energy recovery and reduction in waste volume. However, it is crucial to address the challenges associated with managing the by-products generated during the incineration process and to implement proper systems for controlling flue gas emissions. Approximately 13-15% of the waste incinerated results in residual ash, including bottom ash, fly ash, boiler ash, and various residues from flue gas cleaning. **Figure 1** provides a simplified representation of where these solid waste fractions are generated in an incineration plant.

The terminology used to describe these waste fractions can vary, depending on the specific separation process and context in which the waste is mentioned. Common terms include flue gas cleaning residues (FGC residues) and air pollution control residue (APCr), but the term “fly ash”, or MSWI fly ash, is often used as a general label for solid residues resulting from flue gas cleaning. In this work, the term “fly ash” is used in a broad sense to encompass these solid flue gas cleaning residues. However, it should be noted that if a fraction is separated from specific units, this is explicitly specified.

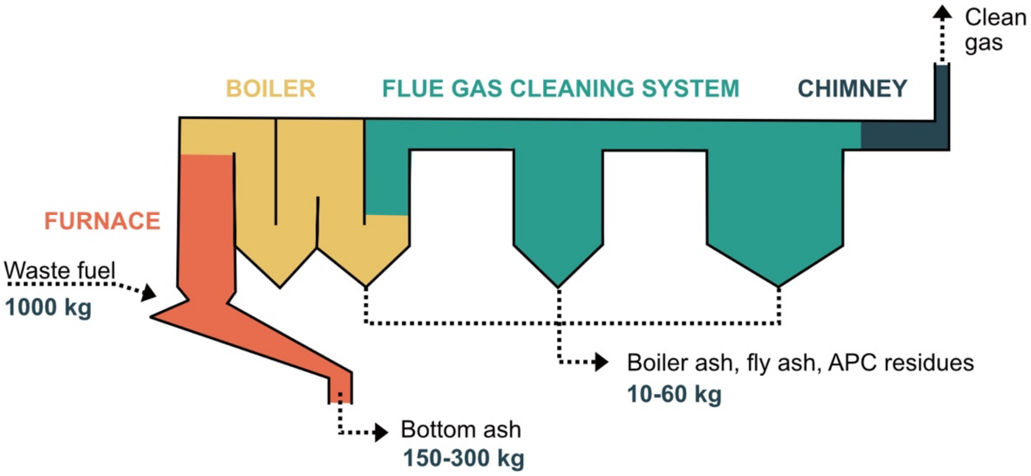


Figure 1 Simplified figure of waste incinerator. Combustion occurs in the furnace and energy recovery in the boiler with subsequent flue gas cleaning.

It is important to understand that all fly ash, regardless of specific definitions, is considered hazardous waste and requires specialized landfill disposal. It's considered hazardous due to elevated concentrations of heavy metals, soluble salts and other organic pollutants. Typically, the hazardous portion of fly ash constitutes approximately 2-4% of the total mass of waste incinerated. The total tonnages of waste resulting from incineration are huge. In the EU-27 (EU members states by 1. February 2020), around 7 million tonnes of hazardous fly ash and bottom ash were generated. When compared to other types of inorganic hazardous waste, such as chemical waste, mineral waste from construction and demolition, and hazardous soil, hazardous incineration ash comes in as the fourth largest category, according to Eurostat. For an overview of the selected hazardous waste types generated in the EU-27, is presented in **Figure 2.**

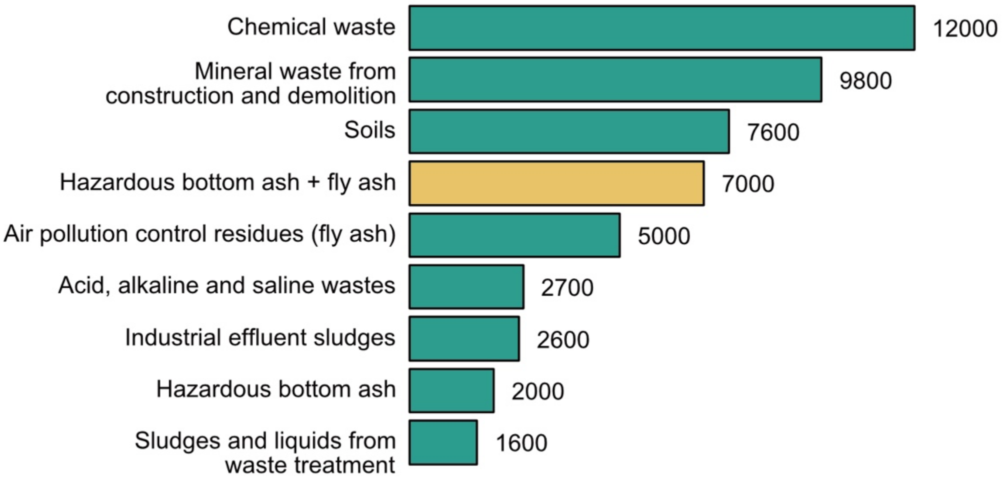


Figure 2 Hazardous waste tonnages generated in the EU. Waste incineration residues are highlighted in orange.

Another well-known hazardous waste type is red mud, which is generated during the production of alumina, the raw material for metallic aluminum. Approximately 1-1.5 tons of red mud is produced for every ton of aluminum. Aluminum is the second most commonly produced metal, surpassed only by iron. Red mud has gathered attention due to the challenges associated with managing its substantial quantities. The tonnage of fly ash generated in EU is comparable to the estimated amount of red mud resulting from Eus primary aluminum demand (see **Figure 3**).

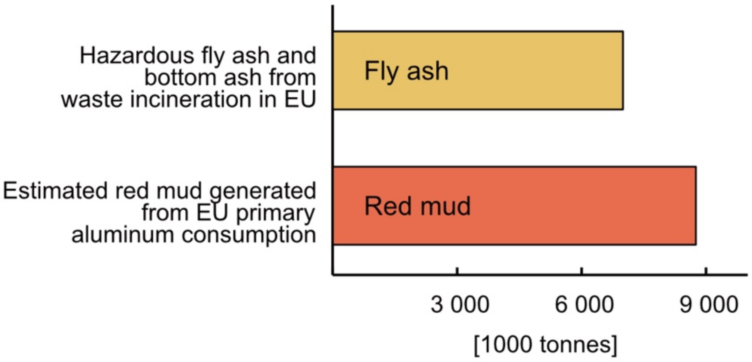


Figure 3 Tonnages of hazardous incineration waste compared to estimated amounts of red mud generated from EU primary aluminium demand. The demand for aluminium was set to 7 000 000 tonnes and 1.25 tonnes red mud generated per tonne alumiminum was used for the estimation.

The amount of fly ash generated has gradually increased in the past decades, and few indications point towards stagnation. **Figure 4** shows tonnages incinerated (with and without energy recovery) in the past decade. A small decline 2020 stems most probably from reduced economic activity during the covid pandemic.

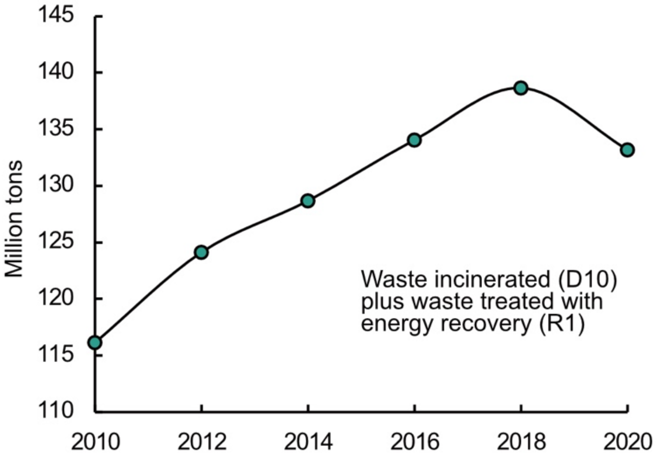


Figure 4 Waste incinerated in EU-27 from 2010 to 2020. Data is based on waste R1 and D10 classifications (Directive 2008/98/EC). This includes waste used in industrial facilities such as cement kilns and co-incineration of sewage sludge RDF from municipal waste for power production. (European Commission. Eurostat, 2011)

The potential for energy recovery from waste in Europe is currently not being fully realized, as Eurostat statistics reveal that a significant portion of treated municipal solid waste is being sent to landfills. In 2019, the average in EU-27 countries had 48% of waste being recycled or composted, 27% incinerated, and 24% directly landfilled. **Figure 5** illustrates the varying share among different countries, with Romania, Greece, Spain, and Poland being notable examples of nations with large amounts of waste going to landfills. A study conducted by Scarlat et al. (2019) estimates that around 330 new waste-to-energy plants could be developed in Europe, with 248 of these located in the EU-27. In 2016, there were 512 plants with a combined capacity of 93 million tonnes, and the newly estimated potential could contribute an additional 37-50 million tonnes through incineration.

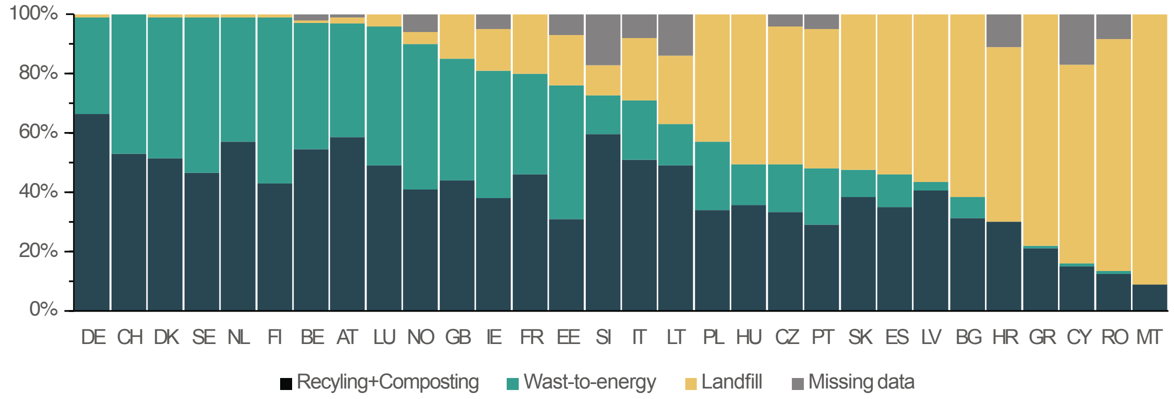


Figure 5 Share of MSW treatment by country in EU. Data is from Eurostat statistics.

In the past decade, efforts to recycle plastics, paper, and other combustible products have significantly intensified, driven by the goal of achieving a more circular economy. The increased circularity would result in reduced waste for incineration. However, despite these efforts, the success of circularity initiatives remains limited. Critics of the concept emphasize underestimated factors such as thermodynamic limitations, downgrading, the complexity of waste streams, and constraints related to material properties (Corvellec et al., 2022; Cullen, 2017). Waste incineration is expected to maintain its central role in today's economy, necessitating the implementation of sustainable methods to manage hazardous incineration waste effectively.

The current practice in Europe for managing hazardous fly ash entails depositing the waste in abandoned salt mines. These locations offer a closed and dry environment with a stable atmosphere, ideal for long-term storage (Kirrmann and Jacquinot, 1999). Germany, France, and Belgium have large salt mines that can accommodate significant quantities of fly ash. However, Scandinavian countries lack such mines and rely on other types of landfills. The largest landfill for hazardous fly ash waste is Langøya in Norway. As hazardous waste requires specific conditions and processes, not every country possesses sufficient deposition capacity. Consequently, trade of hazardous fly ash has become prevalent, with Norway and Germany emerging as the dominant importers. The amount of fly ash imported in 2021 can be ranked in decreasing order as follows: Germany (317,400t), Norway (295,200t), Austria (34,700t), Belgium (32,700t), France (13,400t), Finland (7,600t), Spain (6,600t), and Hungary (2,100t). These figures are drawn from Eurostat data, and the waste codes for fly ash, 190105, 190107, 190113, and 190209, are aggregated. **Figure 6** presents a map representing the quantity of hazardous fly ash waste being traded across Europe. The map highlights that Norway and Langøya landfill is a highly significant recipient of this waste.

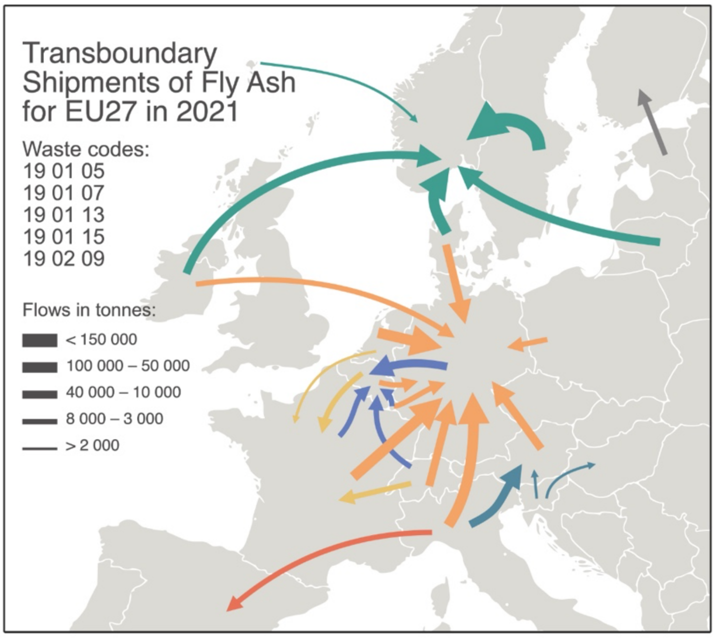


Figure 6 Transboundary shipment of fly ash in EU27 countries in 2021. Waste codes 190105, 190113, 191007, 190115 and 190209 are aggregated. (Eurostat, 2023)

Langøya landfill is situated on an island in the Oslo fjord and serves as a disposal site for hazardous inorganic waste. The site is located within an old limestone quarry. Since 1993, the quarry has been used to deposit gypsum, which is produced from spent sulfuric acid by Kronos Titan, a titan dioxide pigment producer. The limestone from the quarry is utilized to neutralize the sulfuric acid waste, thereby preventing any release of sulfuric acid into the Glomma River, thus mitigating one of that decade's main environmental concerns (Sandvik and Sverreson, 1994). **Figure 7** shows a picture of Langøya and incineration plants in Norway, Danmark and Sweden. Most incineration plants use Langøya for deposition of fly ash.

Over time, Langøya became the designated national landfill for all types of inorganic hazardous waste, including a significant proportion of fly ash resulting from waste incineration. The iron-rich gypsum present in the landfill is an effective means of immobilizing heavy metals found in the fly ash. As a result, NOAH, the operator of the landfill, started to import larger quantities of fly ash from Scandinavian countries to exploit this approach, which enabled efficient management of both fly ash and spent sulfuric acid. A simplified flowsheet is presented in **Figure 8.**

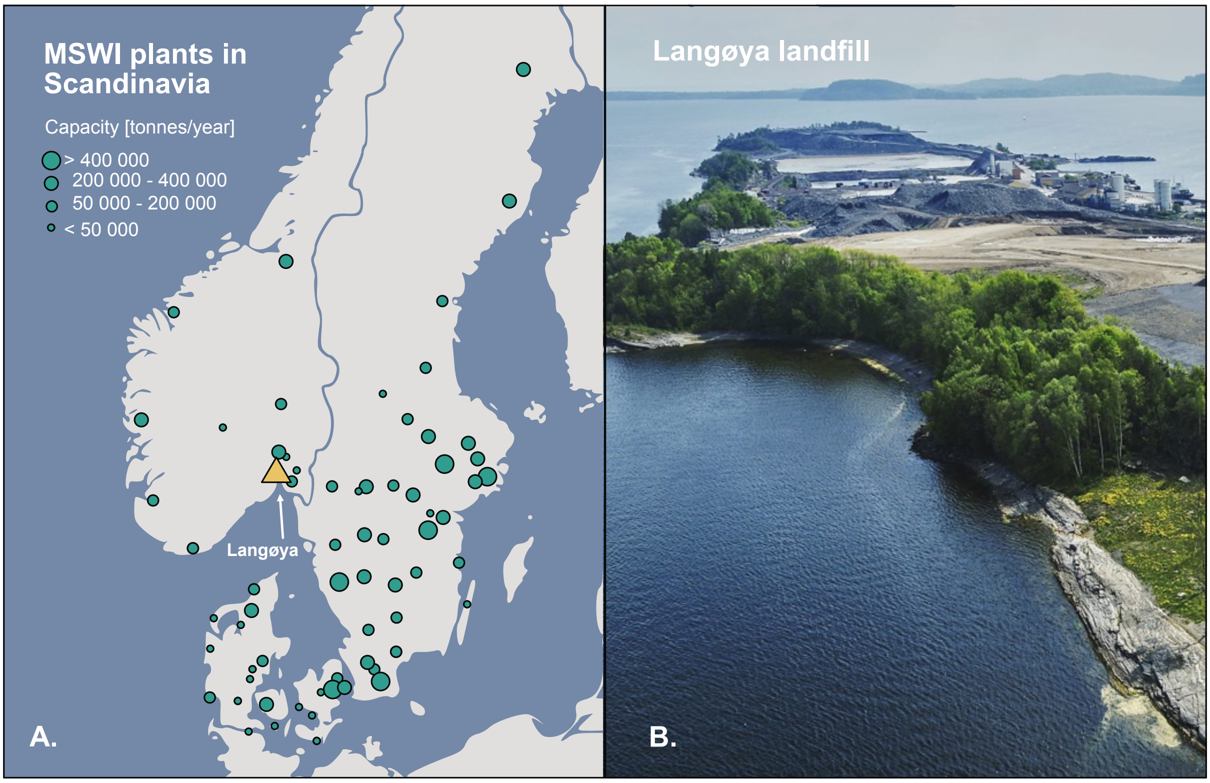


Figure 7 Lacation of MSWI plants and Langøya (A) and picture of Langøya landfill (B). Photo: Bård Gudim, NOAH AS.

Langøya landfill is gradually approaching its maximum capacity and is projected to reach full capacity by 2024 based on standard operating procedures. However, NOAH AS has received approval from Norwegian authorities to utilize innovative dewatering technology, allowing them to deposit gypsum above sea level and extend the landfill's lifespan until 2030. Langøya plays a crucial role in both the Norwegian industry and waste management sector, but with just a decade remaining, it is imperative to explore new and alternative solutions before 2030. In 2016, two reports (Frøiland et al., 2016; Jan Cramer et al., 2016) were published, highlighting potential new sites for hazardous landfill.

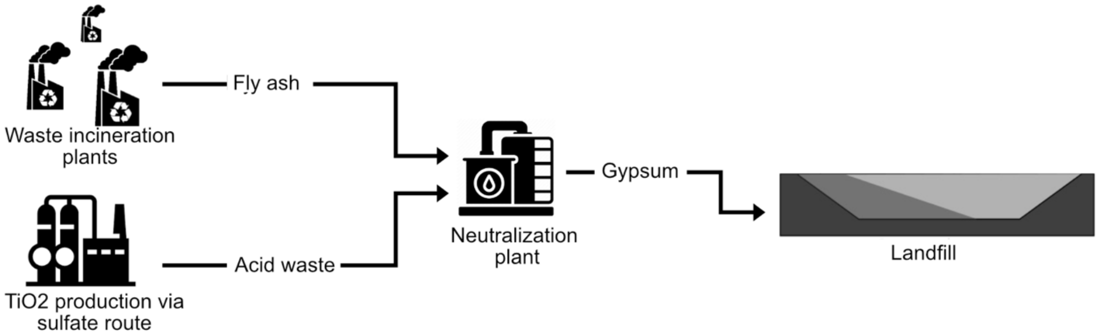


Figure 8 Simplified process scheme of hazardous waste treatment in Norway.

Although there have been identified new potential sites for managing hazardous inorganic waste, establishing new landfill sites often encounters difficulties due to local opposition. This resistance often takes the form of the "Not In My Backyard" (NIMBY) phenomenon, which is not uncommon in the context of hazardous waste landfills (Groothuis and Miller, 1994; Hermansson, 2007). However, several strategies can be employed to address and minimize

NIMBY opposition (Rasmussen, 1992). Additionally, various factors, such as geographic and geological constraints, limit the availability of suitable landfill sites. The geological structure of a landfill crater or an underground deposit must ensure the safe containment of waste while minimizing the risk of pollution or emissions. Moreover, a suitable site should be conveniently accessible for waste transportation. To address the challenges of managing inorganic hazardous waste, shifting focus towards waste processing and recycling is essential.

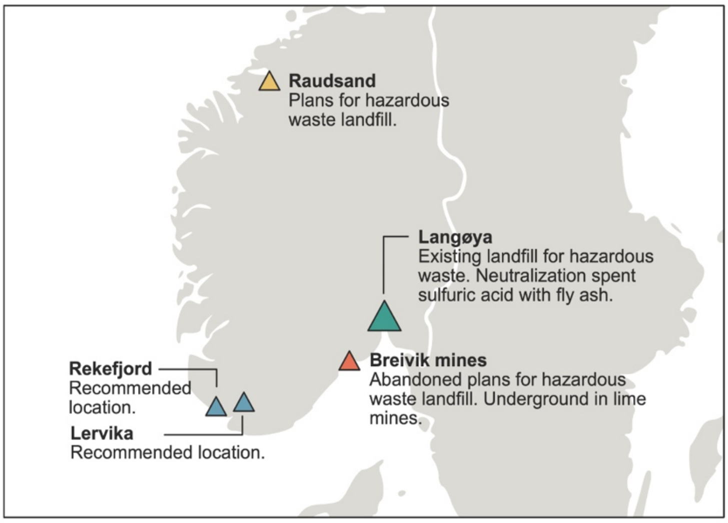


Figure 9 New hazardous landfill siting that’s been under evaluations.

Current practices of stabilizing and depositing fly ash waste offer no long-term solutions to address the scarcity of hazardous waste landfill sites. To minimize the need for specialized landfill space, it is essential to prioritize the reprocessing of the waste fraction and the recycling of waste materials. Taking action is crucial to ensure a sustainable approach to hazardous waste management. Furthermore, these recycling practices align with the need to recover critical and valuable metals that are essential for today's society. Not only does recycling valuable parts of fly ash contribute to resource conservation, but it can also be economically sustainable. Recovering valuable metals from fly ash can potentially generate revenue that can be used to fund better fly ash treatment and make it more economically viable. By embracing recycling/reprocessing practices, a more efficient, environmentally friendly, and economically viable approach to fly ash hazardous waste management may be achieved.

The aim of this work was to meet the challenges presented, by contributing with new knowledge and introducing new ideas to innovate sustainable long-term fly ash management processes. This is elaborated throughout the thesis.

To establish viable material recovery processes, a comprehensive understanding of fly ash composition and chemical variations is essential. Therefore, an extensive chemical analysis of fly ash deposited at Langøya has been conducted as part of this research. The first part of the thesis will establish the basis of variation in fly ashes based on their production methods, providing insight into how these differences can affect processing and management practices. These part supports findings presented in **Paper 1** and **Paper 2**. Also fundamentals for landfill regulations are presented which is essential to know in order to reduce fill-up rates of hazardous landfills.

The second part of the thesis will discuss the potential resources present in fly ash, as well as potential ways to recycle these values. A compositional analysis of the waste with the aim of material recovery is presented as well as possible metal recovery process routes that support experimental work presented in **Paper 3**, **Paper 4**, **Paper 5** and **Paper 6**.

Lastly, the third part will explore more holistic process schemes based on research findings. This section will present recommendations for further investigation into processes that can address some of the challenges associated with fly ash management. This part will represent my recommendations for further research that I believe can innovate current fly ash waste management.

3 Chemical variations in waste incineration ash

NOAH AS is regularly monitoring incoming fly ash for landfilling. Over the years, a large dataset of chemical compositions has been acquired that can be used for getting a better understanding of the wastes' complex characteristics. In **Paper 1**, the chemical compositional variability is analyzed with respect to different plants and plant technology. In **Paper 2** the chemical variation with respect to time is reported. In the following subchapters, more information on what affects the observed variation and the importance of such knowledge is provided.

3.1 Variations affected by waste fuel composition

The average chemical composition of fly ash, derived from the non-combustible portion of fuels utilized in incinerators, is depicted in **Figure 10A**. The non-combustible fraction is divided into bottom ash and fly ash, which are collected from the flue gas, during incineration. Bottom ash has lower levels of volatile species, while fly ash contains higher concentration of volatiles. **Figure 10B** provides an illustration of the extent of volatilization for heavy metals. However, it's important to note that the degree of volatilization can vary based on various factors, such as the type of waste being incinerated and the specific conditions within the incineration process.

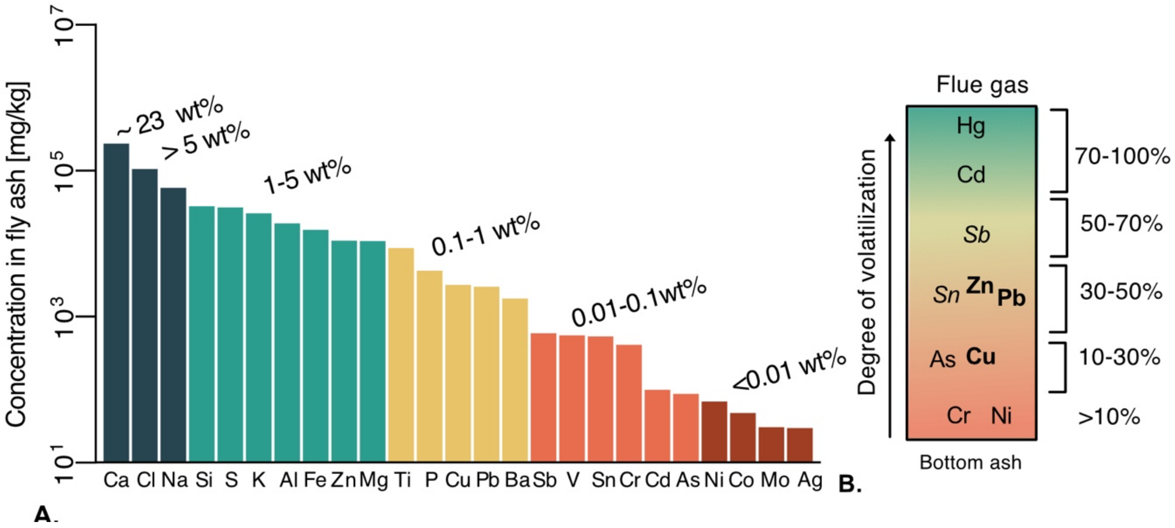


Figure 10 Average chemical composition of fly ash (A) and estimation of partitioning of metals into flue gas and bottom ash (B). The chemical data is based on Langøya data set and the partitioning by literature (Nakamura et al., 1996; Rio et al., 2007; The International Ash Working Group (IAWG), 1997).

The composition of fly ash can be affected by the variety of MSW fuels that are used, making it challenging to identify the source of unwanted (or desired) metals. Nonetheless, it is essential to acquire a comprehensive understanding of the origin of fly ash waste composition to predict its future chemical makeup. Knowledge of this kind is critical in determining waste management strategies since upstream waste management practices impact future waste characteristics.

Paper 2 provides data on changes in fly ash composition over the past ten years, which can facilitate such decision-making and clarifies that fly ash composition is dynamic with respect to time. Additionally, waste statistics, like those presented in **Table 1** provide an overview of the diverse waste types incinerated in Sweden, which may contain varying levels of heavy metals.

Table 1 Share of waste fuel origin in Swedish incinerators (Sahlin et al., 2019).

Waste category	Percentage to incineration
Imported	23%
Household	36%
Commercial	31%
Construction and renovation waste	10%

However, waste statistics only provide a general overview of the waste types incinerated and do not provide specific waste composition information. To acquire this information, compositional analyses must be performed. Sahlin et al., (2019) offers more detailed waste composition quantification, clarifying the origin of constituents in waste incineration ash. Main findings are summarized in **Figure 11**. The report contains compositional analyses of average waste composition from household waste and from construction and renovation waste. It is noteworthy that there are other waste fractions that can be co-incinerated with MSW waste, such as tires, automotive shredder residues, forestry wood waste, sewage sludge, poultry litter, and waste oils. Some of these special waste fractions have high concentrations of certain heavy metals, resulting in fly ash wastes with compositions that differ significantly from the typical MSWI incineration ash.

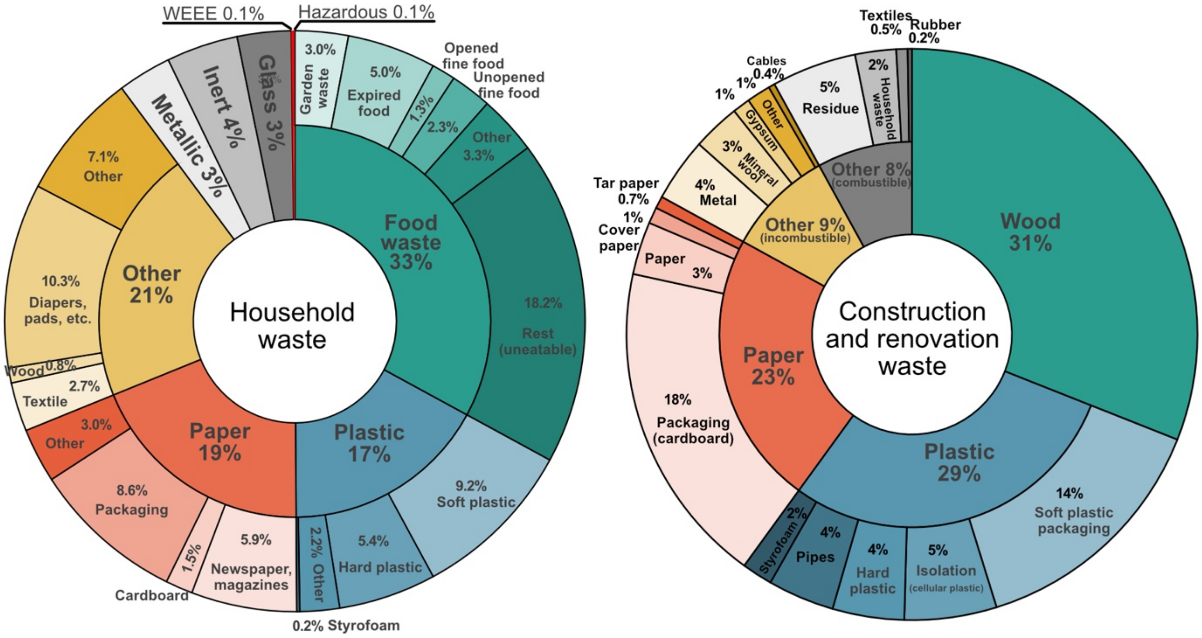


Figure 11 Composition of waste that goes in incinerators in Sweden from household waste and construction and renovation waste (Sahlin et al., 2019).

Sahlin et al., (2019) affirms that paper and plastics constitute a significant portion of the waste used as fuel in incineration. The high quantity of calcium in fly ash is mainly attributed to the most common fillers in papers and plastics (Wiesinger et al., 2021). On average, 23 wt% of fly ash constitutes calcium (Langøya dataset). This means that assuming all calcium is present as for example calcium carbonate, 57 wt% of fly ash will be calcium carbonate. Calcium carbonate is a primary filler in paper and plastic production processes and the primary source of calcium in fly ash (Blechschmidt et al., 2012; Pelzl et al., 2018; Rothon and Paynter, 2017, 2017). It is the high proton exchange capacity of calcium carbonate (and hydroxide) that is exploited in the NOAH neutralization process at Langøya landfill.

Moreover, fly ash contains various minor metals that can originate from plastic additives used to enhance specific material properties. These additives typically constitute about 23% of the total mass of plastics (Pelzl et al., 2018). Plastic additives serve various purposes, including acting as antioxidants, light stabilizers, heat stabilizers, flame retardants, and pigments. These additives ensure the plastic properties wanted in various products. However, the wide range of additives makes it challenging to fully comprehend the direct link between fly ash composition and what ends up in fly ash. To provide some insight into the origin of fly ash composition, a few examples of specific components are presented here. Heat stabilizers such as Ca-Zn compounds are used in plastics approved for food applications, while Na_2SO_4 and $BaSO_4$ serve as transparent plastic fillers. Flame retardants like $Al(OH)_3$, $Mg(OH)_2$, Sb_2O_3, zinc, and barium borates are employed, with lead carbonates often used as heat stabilisers in PVC. Zinc salts can be used as antioxidants, and ZnO acts as a white pigment. Additionally, barium, cadmium, and tin carboxylates are utilized in PVC to enhance lightfastness, particularly for outdoor plastics. These examples demonstrate the highly complex origins of fly ash compositions, contributing to the challenges involved in comprehending its chemical origins.

Efforts have been made to regulate specific harmful additives in consumer products that will end up in fly ash. **Paper 2** addresses the changing composition of fly ash over time, linked to modifications in fuel composition influenced by additive regulations in consumables. Aspects to consider important for dealing with compositional changes with time is the lifetime of products. Short-lived products that go to incineration give faster changes to fly ash chemical composition compared to long-lived products, as shown in **Figure 12**. Understanding these dynamics is crucial to comprehend the behavior of fly ash's chemical composition with time. Additionally, upstream waste management processes, such as sorting plastic, organic, or electronic waste for recycling, can impact fuel composition in MSW incinerators. Consumer behavioral changes also contribute to these factors impacting fly ash composition.

Figure 12 Conceptional illustration of waste flows of end-of-life products based on their lifetime after production.

Fillers and additives used in plastic and paper often have fine particle sizes, making them easily transported by conventional flows. This phenomenon can account for the presence of significant quantities of non-volatile elements in fly ash. Furthermore, as indicated in **Paper**

4a, heavy metals tend to be enriched in the small particle-size fraction of fly ash. These elements can be volatilized and subsequently condensed, along with smaller non-volatile particles that are carried upward with the flue gases. Considering the characteristics of fly ash, it is plausible to argue that the majority of heavy metals primarily originate from the additives in plastic and paper rather than from highly metal-enriched wastes, such as unsorted electronics. This hypothesis is also supported by compositional analyses of waste, which revealed a minimal presence of electronic waste (only 0.1% in household waste). However, it is important to note that this remains speculative.

3.2 Variations affected by incineration technology

Apart from the influence of waste fuel composition on fly ash composition, the chemical makeup of fly ash is also impacted by the incineration technology used. Various furnace technologies exhibit different partitioning between bottom ash and fly ash based on volatilization conditions. Also, distinct condensation conditions and the use of reagent additions in diverse flue gas cleaning units contribute to variations in the collected ash. These findings are demonstrated in **Paper 1**, providing insights into the effect of incineration technology on fly ash composition.

Grate-fired incinerators are commonly used for MSW incineration, but fluidized bed incineration is also prevalent. Rotary kilns are often used for hazardous waste incineration. Illustrations of the different designs are presented in **Figure 13**. The type of incineration affects the chemistry and characteristics of the residues. Different designs operate at varying temperatures, impacting mineralogy and volatilization. Partitioning between bottom ash and fly ash varies, influenced by factors like airflow and separation processes in fluidized bed reactors. Also, fluidized bed incinerators may introduce different bed materials into the residues.

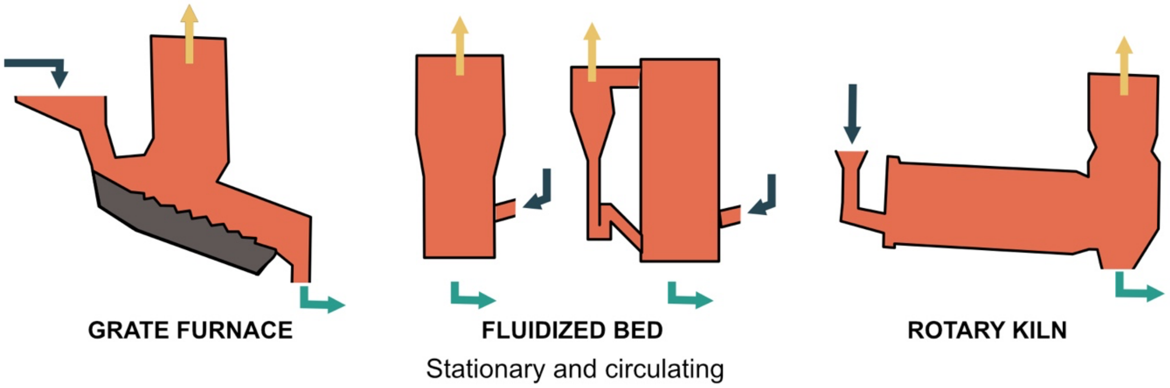


Figure 13 Different types of incinerator technologies used for MSWI.

In grate incinerators, the typical mass partitioning between bottom ash and fly ash is 1:5. However, fluidized bed incinerators often have a more equal partitioning. This results in larger proportions of refractory, non-volatile materials in fly ash, which would typically be found in bottom ash. Consequently, there is less enrichment of volatile elements observed in fly ash from fluidized bed incineration. Studies have extensively examined metal partitioning in grate incinerators (Nakamura et al., 1996; Rio et al., 2007; The International Ash Working Group (IAWG), 1997). Additionally, Lane et al. emphasized the significance of reducing and oxidizing atmospheres for metal volatilization (Lane et al., 2020b). It is worth noting that bottom ash fines may serve as a more significant source of Cu for recycling compared to fly ash.

Numerous system configurations exist for ensuring clean gas emissions to the environment, with significant variations in design. **Figure 14** shows three principal types of cleaning systems that produce different classes of fly ash: dry, semidry, and wet systems. These systems employ different reagents to neutralize acidic gases and uses either electrostatic precipitators, baghouse filters or cyclones for particle separation. In a wet system, particulate matter, including fly ash, is frequently separated prior to acid neutralization.

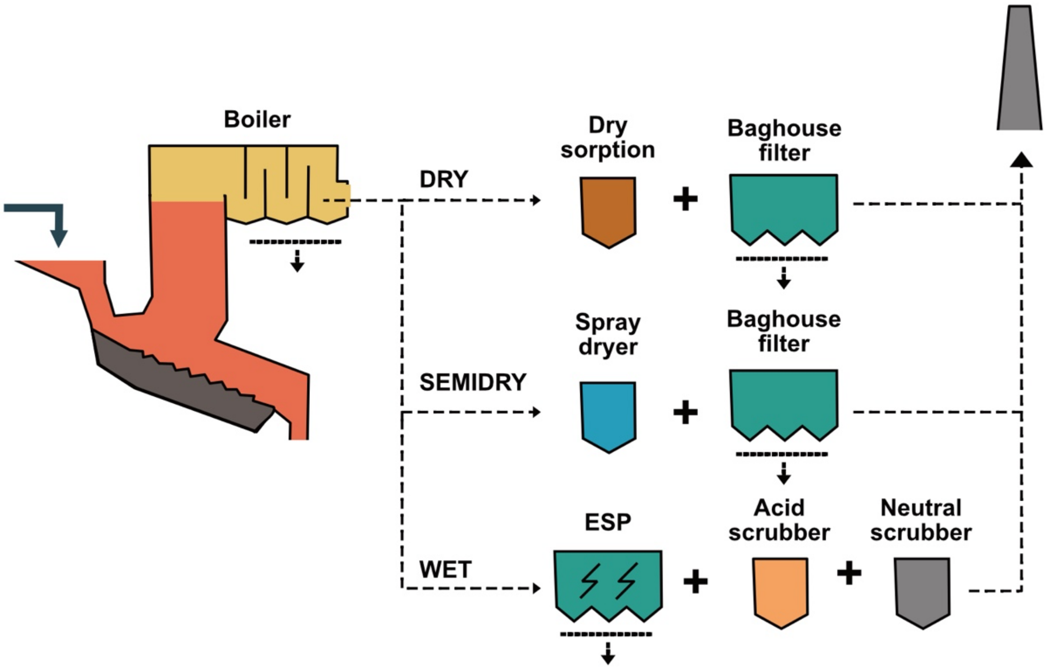


Figure 14 Examples of principal flue gas cleaning systems used for acid gas scrubbing and particular matter removal. The abbreviation ESP stands for electrostatic precipitator.

Incinerators equipped with wet scrubbers produce wastewater. Processing of this wastewater can be more expensive if the incinerators are not connected to seawater discharge, which has less stringent quality standards for treatment of wastewater intended for release in fresh water.

Acid neutralization capacity is an important characteristic of different fly ash types, with implications for processes such as those employed at Langøya, where fly ash is used to neutralize spent sulfuric acid. It is also crucial for hydrometallurgical processes reliant on acids for metal extraction, or when ash is used for neutralizing spent acid for landfills. **Figure 15** illustrates the titration curves for four residue types produced from waste incineration, demonstrating substantial variabilities in the acid-neutralization capacity across distinct ash types.

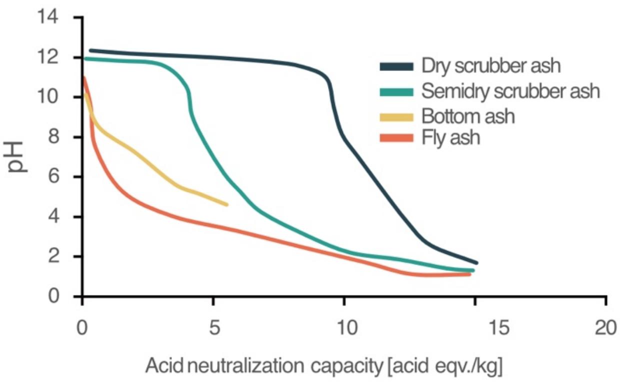


Figure 15 Acid neutralization capacity of various types for incineration wastes (Based on Christensen, 2011).

The composition of fly ash can continue to change after incineration, particularly during storage, as it remains far from equilibrium with standard conditions (Brännvall et al., 2014). This leads to a reduction in the acid-neutralization capacity, significantly reducing the leachability of Ba, Ca, Cl^-, Cr, Cu, Pb, K, and Na. In contrast, the leachability of Mg, Zn, and SO_4^{2-} increases. Typically, heavy metals such as Ba and Pb form stable sulphates and carbonates. Carbonates are created through atmospheric CO_2, while loosely bonded sulphates in the ash contribute to the production of sulphates. Chemical changes with storage of fly ash can be important to understand when designing processes such as salt extraction, as it can greatly affect the solubility of heavy metals.

Understanding the distinct characteristics of various fly ash types is essential when creating recycling processes for fly ash waste management. Each type of ash may respond differently in various processes, and consequently, developing robust processes capable of accommodating this diversity is necessary to handle wastes from different incineration systems. Some types of ashes may be good for some applications, and some ashes may be better suited for other applications.

4 Classification of waste and landfill types

Knowledge of waste management law and landfilling laws is vital when reprocessing waste, especially if the aim is to minimize the utilization of scarce hazardous waste landfill space. Waste classification of reprocessed ash is discussed in **Paper 4b**. Here, separated coarse fly ash particles are classified after desalting. Furthermore, **Paper 5** assesses the leaching properties of the residue after metal extraction experiments.

Waste Classification systems can vary from country to country but are often equal to EU recommendations. A technical note from the commission provides guidance on the classification of waste from a practical perspective (European Commission, 2018). A decision flow sheet is presented in **Figure 16**. The waste must be linked to common waste types equal to one of the waste types listed in the “Annotated list of waste”. The waste types are classified as absolute hazardous/non-hazardous or as mirror entries. Absolute entries cannot be changed. However, mirror entries can be classified as hazardous or non-hazardous if they have appropriate properties.

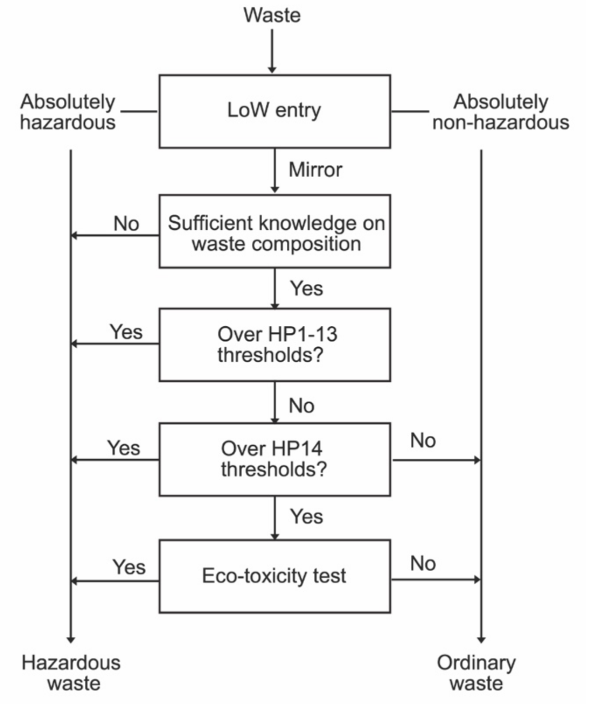


Figure 16 Classification assessment of mixed waste.

For mixed waste, the appropriate properties can be difficult to determine. Often the “summation methods” must be applied. The chemical composition of the waste is measured, and, the presence of worst-case compounds is assumed. The worst-case compound has different thresholds for obtaining hazardous properties. If the waste has potentially higher concentrations of the compounds than the thresholds, the waste is classified as hazardous. The exemption is if the waste exceeds only ecotoxic hazardous properties (HP14). This property can be prevailed by bioassays. However, these assays are often not described or defined in the laws. **Table 2** shows elemental concentration thresholds important for MSWI fly ash, assuming worst case compound presence of the element methodology.

Table 2 Elemental concentration thresholds to consider for fly ash using the summation rule. Worst-case speciation is assumed.

Element	wt%	mg/kg		Haz. Prop.
As	0,03	326	Cut-off (0.1%)	HP7
Ba	0,87	8729	Cut-off (1%)	
Cd	0,06	613	Thresholds (0.1%)	
Co	0,2	1966	Thresholds (0.25%)	
Cr	0,05	520	Thresholds (0.1%)	HP7
Cu	**0,2**	**1997**	**Thresholds (0.25%)**	**HP14**
Hg	0,07	739	Thresholds (0.1%)	
Mo	0,67	6667	Cut-off (1%)	
Ni	0,08	786	Thresholds (0.1%)	
Pb	**0,22**	**2231**	**Thresholds (0.25%)**	**HP14, HP10**
Sb	0,42	4177	Thresholds (1%)	
V	0,28	2800	Cut-off (1%)	
W	0,79	7929	Cut-off (1%)	
Zn	**0,2**	**2009**	**Thresholds (0.25%)**	**HP14**

Aside from the waste classification rules, it's necessary to determine specific guidelines and leaching potential characteristics to comply with landfill laws. Different countries have various categories of landfills, with different construction requirements. However, the classifications in the EU tend to be similar across nations. In Norway, for example, there are three landfill categories (1, 2, and 3), with different design requirements for each. The waste classification, combined with the leaching test results, determines the appropriate landfill for each waste type. The waste leaching potential is evaluated through the shaking and column leaching tests. Thresholds for metal leached through the shaking test are presented in **Table 3**.

Table 3 Leaching thresholds for different landfill categories for shaking test.

Component	Shaking leaching test [mg/kg]		
Landfill type	Inert (3)	Non-reactive haz.(2)	Haz (1)
As	0,5	2	25
Ba	20	100	300
Cd	0,04	1	5
Cr	0,5	10	70
Cu	2	50	100
Hg	0,01	0,2	2
Mo	0,5	10	30
Ni	0,4	10	40
Pb	0,5	10	50
Sb	0,06	0,7	5
Se	0,1	0,5	7
Zn	4	50	50
Chloride	800	15000	25000
Fluoride	10	150	500
Sulphate	1000	20000	50000
DOC	500	800	1000
TDS	4000	60000	100000

There is also thresholds for a column leaching test which are not shown here.

To be landfilled without pretreatment, hazardous waste must be beneath certain thresholds. If the leaching potential of the waste is lower than a particular value, it is categorized as unreactive hazardous waste and can be deposited in category 2 landfills. Similarly, if ordinary non-hazardous waste doesn't exceed specific thresholds, it can be classified as unreactive and disposed of in category 3 landfills. **Figure 17** illustrates the various pathways for landfilling waste.

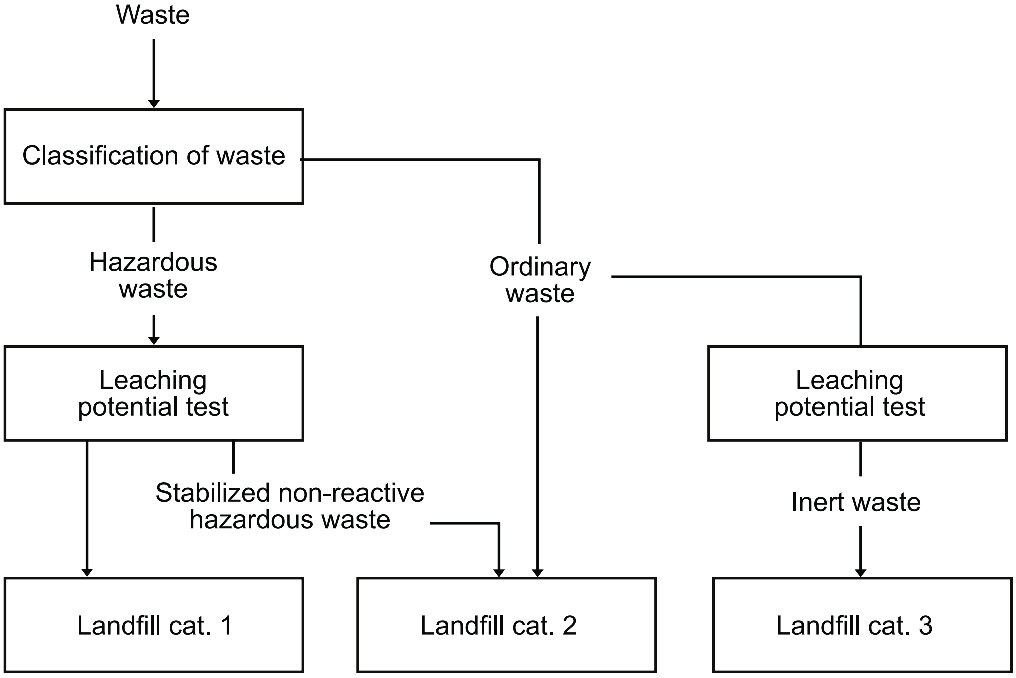


Figure 17 Waste classification for landfilling.

In summary, to comply with landfill regulations and reduce the amount of hazardous fly ash waste filling up landfill capacity, several possible measures can be taken. Firstly, by implementing better waste management practices and recycling programs, we can effectively reduce the generation or reprocessing of hazardous waste to more inert waste. New fly ash waste management technologies, as presented later in the thesis, can be methods of hazardous waste reduction combined with material recycling. This will be elaborated further.

Secondly, it is imperative to enhance stabilization technologies to classify hazardous waste as non-reactive. This classification would enable its disposal with ordinary waste in Category 2 landfills. NOAH at Langøya landfill site serves as a model here, employing filtering presses to ensure that the resulting gypsum remains within the landfill category 2 thresholds. This efficient system allows for safe landfilling above sea level, and the predicted landfill lifetime can endure until about 2028.

Third, it is crucial to increase knowledge about waste composition to ensure that species present in fly ash do not surpass hazardous properties thresholds HP1-14. Conducting ecotoxicity tests is essential in evaluating potential environmental hazards and addressing any concerns related to HP14 compositional thresholds more effectively.

Lastly, and most importantly, would be to lower the consumption of products that end up as incineration waste. Though, this is a measure beyond the scope of this thesis. However, increased knowledge of incineration ash management challenges, as this thesis addresses, can promote an understanding of more sustainable consumption of products. Nonetheless, this thesis has focused on alternative technological solutions, where recycling technologies can act as detoxification processes of fly ash.

5 Alternative fly ash management technologies

Current and future innovation in fly ash management can follow various routes, which can be categorized into six general routes based on their objectives, as introduced by Quina et al. (2018): backfilling, pre-treatment before landfilling, decontamination/detoxification, product manufacturing, practical applications, and materials recovery. In this thesis, the routes have been simplified into three main categories.

The first category is stabilization and disposal of the fly ash by backfilling in mines or deposition in landfills. This is the most common approach employed today, as seen at Langøya in Norway, salt mines in Germany, or the FLUWA process in Switzerland.

The second category is the manufacturing or recycling of bulk materials for construction purposes, such as aggregates, absorbents, clinkers, and cement blocks. In Japan, for example, about 380,000 tons of bottom ash and fly ash were recycled in cement factories in 2017 (Sakanakura, 2020), with the salt removed from the fly ash prior to use. This type of recycling can be considered as down-cycling slightly because calcium species originally come from purer fractions as absorbents in flue gas cleaning systems or as precipitated or ground calcium carbonate in paper and plastics.

The third category is the recovery of metals and chemicals, with no or limited down-cycling involved. This approach aims to recycle valuable metals, salts, or other compounds that can be extracted chemically. Often, these different management types are combined, such as salt recovery combined with landfilling or cement production, since chlorides are unwanted. Another example is metal recovery, which can serve as a detoxifying process before ash landfilling.

Another way to categorize fly ash waste management is by where processing appears. Fly ash can be processed locally, where it is generated, or centrally, where fly ash from multiple plants is processed and deposited. Local processing is ideal for reduced transport costs, but it requires a larger investment cost per material recovered. **Figure 18** visualises the three different methods, as well as combinations of these methods and management options for local or central processing.

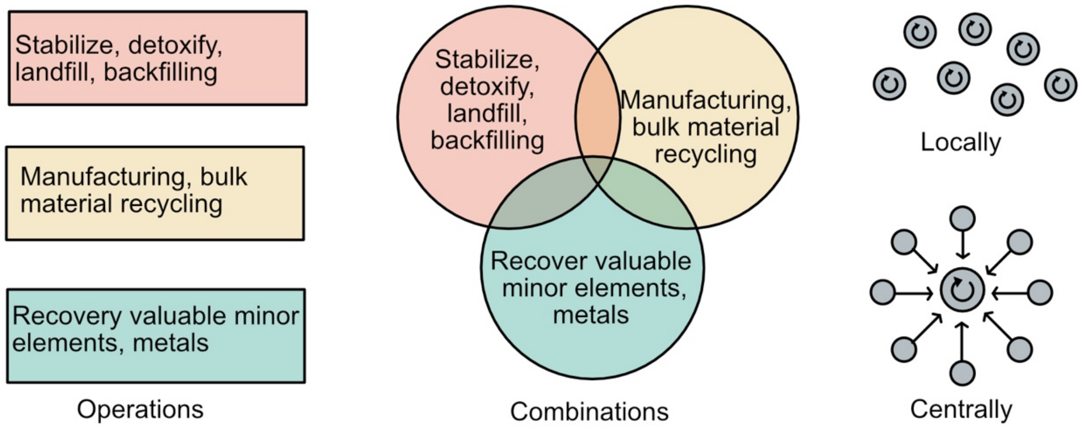


Figure 18 General approaches to fly ash processing and management.

Below follows more details on salt and metal recovery, as well as on the recycling of bulk material into clinker raw material.

5.1 Salt recycling

MSWI fly ash contains significant amounts of soluble salts such as NaCl, $CaCl_2$, and KCl. Fresh fly ash also contains metal chlorides like $PbCl_2$, K_2PbCl_4, $ZnCl_2$, $ZnKCl_3$, and $CdCl_2$ (Funatsuki et al., 2012; Struis et al., 2009). While the presence of salts in the waste is undesirable when landfilled, they can also be a potential source of recycling salt for industrial purposes. Therefore, salt recovery from fly ash serves a dual purpose - detoxification of fly ash and providing industrial chloride salts.

For mixed wastes, the leaching-characteristics threshold for chloride is 15000 and 25000 mg/kg for landfill categories 1 and 2, respectively, when tested with shaking. High chloride concentrations can facilitate the mobilization of metals in landfills due to their complexing properties. For example, the solubility of lead increases with higher chloride concentration, as lead form soluble chloride complexes (Tan et al., 1987).

Fly ash can contain between 20-40% water-soluble salts. Hence, a significant amount of salts can be easily extracted. Industrial implementation of salt recovery has gained attention, with Ragn-Sells inaugurating the first commercial plant for salt recovery in 2023. Additionally, the HALOSEP technology has been implemented at the Væsteforbrenning incineration plant for salt and zinc concentrate recovery. Tang et al. (2014) demonstrate how separation of $CaCl_2$, KCl, and NaCl technically can be achieved. The impurity level of approximately 90% was achieved using evaporation crystallization and antisolvent precipitation with ethanol. While salt recovery reduces the amount of waste that needs to be disposed of, it also leads to increased concentration of non-water-soluble metals in the ash.

The significant commercial interest in salt recovery presents opportunities for process innovations that can be easily implemented with current technology. One possibility is the implementation of wet physical separation methods during the solubilization of salts. Since fly ash is suspended in water, few additional steps are required. Enriching metal impurities into particle fractions can benefit downstream metal recycling or waste characteristics for landfilling. **Paper 4** explores the possibility of achieving this using simple bench-scale settling separation methods. The article shows that heavy metals are primarily present in fine particles/condensates, which can be separated from larger particles. **Figure 19** illustrates areas in fly ash with smaller particles and condensate surrounding larger particles prior to separation.

Additionally, dense particles can be found in fly ash (see **Figure 19**), which may be separable using physical methods. The fraction of larger particles may be more suitable for raw material manufacturing due to lower impurity concentrations. Metal-enriched fractions may also reduce the downstream cost of metal extraction processes. **Paper 4b** shows that the coarse fraction has a low Pb content, which does not classify it as hazardous other than for ecotoxicity. This allows for the performance of ecotoxicity assays to classify the waste as non-hazardous. However, further research is required to investigate the possibility of achieving better metal partitioning. In a process targeting metal recycling, a significant loss of metals would go to the metal-depleted coarse particle phase.

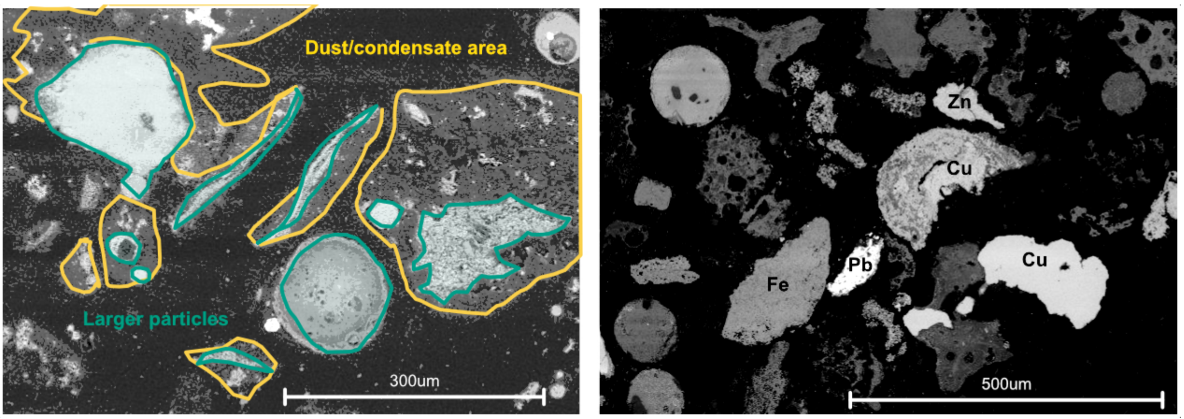


Figure 19 SEM back scattering images of fly ash marking fine particles in dust/condensation area (left). Dense metallic species found in fly ashes in SEM back scattering image (right).

As mentioned, the storage time of fly ash impacts the amount of metals solubilized during the desalination process. $PbCl_2$, for example, converts to less soluble species when exposed to air containing CO_2 (Shimaoka et al., 2002). Lead is believed to substitute calcium in ettringite and other calcium species during aging. Fly ashes are often aged before landfilling to reduce their potential for metal leaching. These considerations should be taken into account. Desalting of ash is beneficial for using ash as raw material for clinker raw material. Here, salts can jeopardize process operations and clinker quality.

5.2 Ash as raw material to Portland cement clinker

While using fly ash in clinker production is not entirely new, it is seldom practiced. As far as the author is aware, only Japan implements this on a large scale. Nonetheless, significant amount of research has been conducted on the topic (Ashraf et al., 2019; Aubert et al., 2006; Lam et al., 2011; Loginova et al., 2021; Saikia et al., 2007; Wang et al., 2022)

The Langøya dataset on fly ash composition enables us to evaluate its chemical composition for its potential as a suitable raw material for clinker production. **Figure 20** shows the major element composition of fly ash, excluding salts and minor elements, under three different categories of fly ash types. **Table 1** displays the typical composition of Portland cement, after adding gypsum to the clinker.

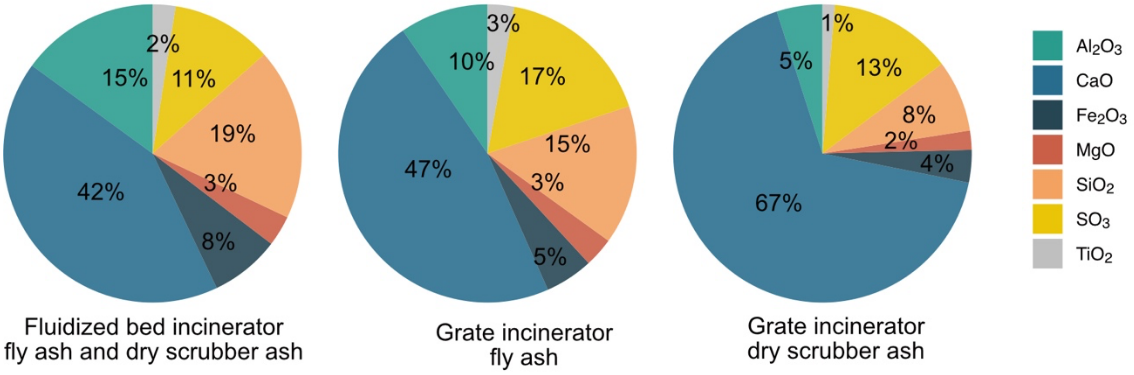


Figure 20 Composition of major elements, converted to its oxides, of fly ash (excluding salt forming elements like Na, K and Cl). Note that Ca are also present as chlorides.

A comparison between the chemical composition of fly ashes and regular Portland cement (as seen in **Table 4**) reveals slightly higher levels of iron oxide and alumina in fly ash, whereas silica concentrations are generally a bit lower. Additionally, while dry scrubber ashes exhibit higher calcium content, fly ashes and those coming from fluidized bed incinerators have slightly lower concentrations.

Table 4 Typical composition of Portland cement (Hewlett, 2003)

Parameter	Min	Max
SiO_2 (%)	19.5	22.2
Al_2O_3 (%)	4.1	6.2
Fe_2O_3(%)	2.1	3.3
Mn_2O_3(%)	0.03	0.16
P_2O_3 (%)	0.07	0.23
TiO_2 (%)	0.20	0.31
CaO (%)	63.2	66.4
MgO (%)	0.9	2.2
SO_3 (%)	2.5	3.0
CO_2 (%)	0.3	0.78
K_2O (%)	0.43	0.80
Na_2O (%)	0.13	0.24
Free lime (%)	0.9	2.1
Loss of ignition (%)	0.75	1.7
Insoluble residue (%)	0.8	1.7
Na_2O equivalent (%)	0.52	0.63

Correct calcium, silica and alumina composition is important to create the required constituents in Portland cement. **Figure 21** shows the composition of samples in the Langøya data in the CaO-SiO_2-Al_2O_3 phase diagram. Ideal Portland clinker composition is also marked.

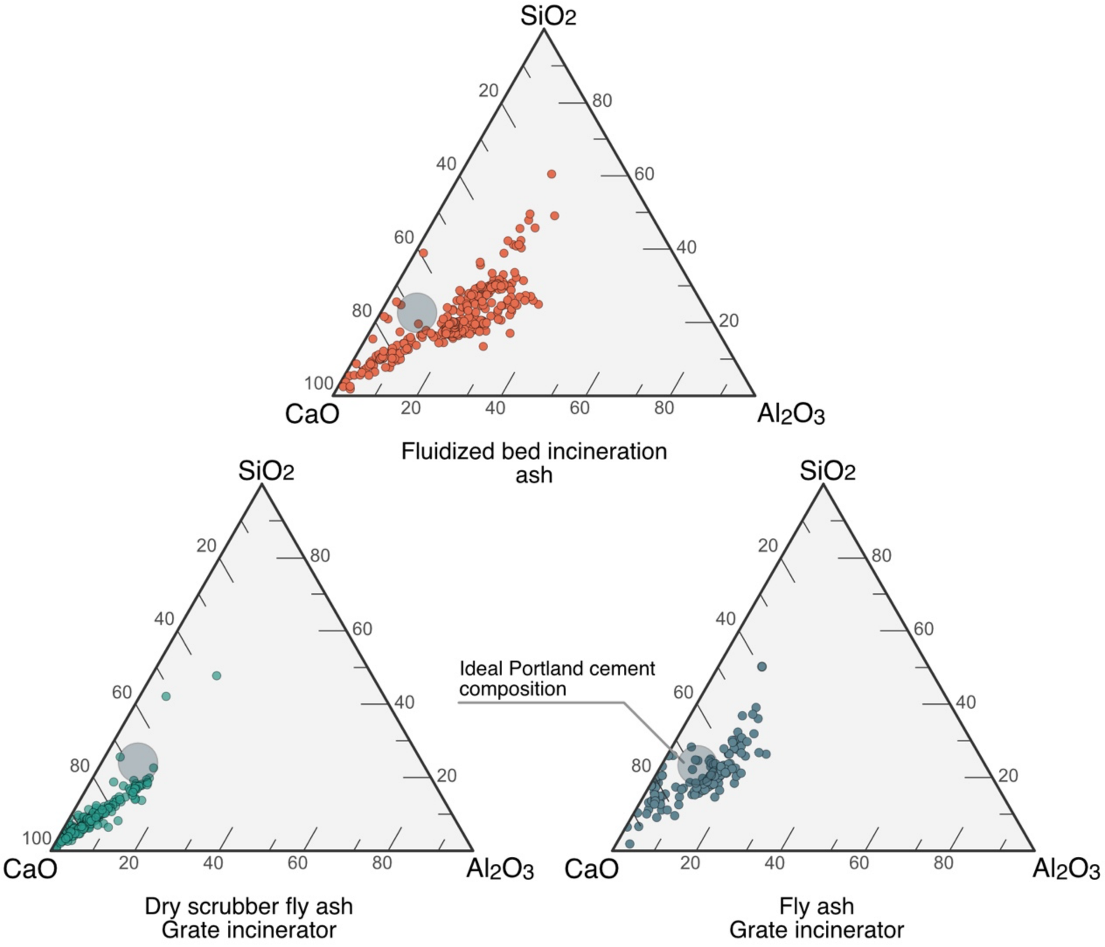


Figure 21 Fly ash composition plotted in the CaO-SiO_2-Al_2O_3 ternary phase diagram. Gray circles represent Portland clinker composition.

All fly ashes are relatively close in composition to Portland cement. Regular fly ash from grate incineration ash has the most similar ratio between CaO, Al_2O_3 and SiO_2 compared to ideal Portland cement. This indicates that little extra material is needed to create correct clinker phases using fly ash as raw material.

The ideal composition for Portland cement typically features 70% CaO, 23% SiO_2, and 7% Al_2O_3 when only these constituents are considered. With an analysis of fly ash data, it is possible to calculate the component additions required to achieve this ideal Portland cement composition with the following equations:

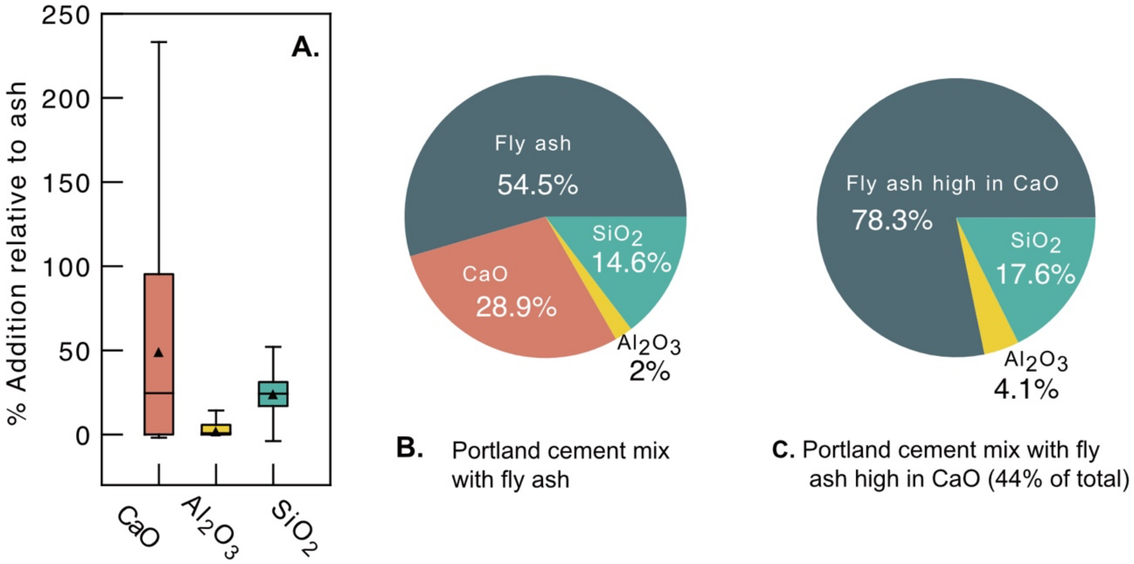
$$\mathrm{m_{FA}f^{FA}_{CaO} + m_{CaO} = f^{PC}_{CaO}(m_{FA} + m_{CaO} + m_{SiO_2} + m_{Al_2O_3})} \quad (1)$$

$$\mathrm{m_{FA}f^{FA}_{SiO_2} + m_{SiO_2} = f^{PC}_{SiO_2}(m_{FA} + m_{CaO} + m_{SiO_2} + m_{Al_2O_3})} \quad (2)$$

$$\mathrm{m_{FA}f^{FA}_{Al_2O_3} + m_{Al_2O_3} = f^{PC}_{CaO}(m_{FA} + m_{CaO} + m_{SiO_2} + m_{Al_2O_3})} \quad (3)$$

In these equations, $f^{PC}_{compound}$ represents the fraction of the compound in ideal Portland clinker composition, while $f^{FA}_{compound}$ represents the fraction of the compound in fly ash, and $m_{compound}$ represents the additional mass added.

Figure 22 displays the results when using the above equation for all samples in the Langøya dataset. According to the data, the average fly ash amount to be included in ideal Portland cement clinker would be 54.5% for all fly ashes and 78.3% for fly ashes high in CaO. However, it is essential to note that the amount of fly ash that can be used in Portland cement clinker would be much higher if the compatible ashes depleted and enriched in compounds are mixed smarter, not by adding additional raw materials to each ash sample as presented here.



B. Portland cement mix with fly ash

C. Portland cement mix with fly ash high in CaO (44% of total)

Figure 22 The average amount of addition of constituents to reach optimal Portland cement clinker composition.

Although the composition of fly ash includes appropriate levels of CaO, SiO_2, and Al_2O_3/Fe_2O_3 concentrations, there are challenges in using MSWI fly ash as a clinker raw material. Specifically, the presence of chlorides and alkalis is unwanted due to operational difficulties and a reduction in cement quality. Fly ash contains high concentrations of both. Clavier et al. (2020) emphasize the difficulties posed by the deposition of alkali/chloride/sulfur compounds in the preheater tower and the rotary kiln, as this can negatively impact normal kiln operation. These compounds must be manually removed to prevent process jeopardization or irregular clinker composition. High alkali/chloride concentrations can also lower the quality of the resulting cement product.

Chlorides can even corrode steel reinforcements but have negligible effects for concentrations below 0.4%. The standard of cement for reinforced concrete (NS-EN 206) permits a maximum concentration of only 0.1 wt% (See **Table 5**).

Table 5 The threshold for chloride in cement, according to NORCEM AS (2023)

Threshold for chloride in cement [%]	Corrosion
< 0.4*	Negligible
0.4-1.0	Possible
1.0 -2.0	Plausible
> 2.0	Sure

* Threshold according to NS-EN for reinforced concrete.

Excessive alkali concentration in cement should be avoided as it can cause swelling and volumetric expansion through the alkali-silica reaction and alkali-carbonate reaction. **Table 6** presents the critical alkali concentrations in regular Portland cement.

Table 6 Critical alkali concentrations used in cement according to NORCEM AS (NORCEM AS, 2023)

Binder	Critical alkali concentration	
	[kg Na_2O ekv. /m^3]	[wt% Na_2O ekv.]
Portland cement	0.3-7	~ 0.21-0.47

The removal of salt from fly ash before clinker production is crucial to reduce chloride and alkali concentrations. In a study by Chen et al. (2012), they successfully removed approximately 95% of chlorine from MSWI fly ash through water washing and carbonation, resulting in a treated fly ash with only 0.26 wt% Cl. Saikia et al. (2007) demonstrated that water-washed fly ash can be utilized as a raw material for clinkers. However, their process involved using high liquid/solid ratios, which may not be cost-effective.

High metal concentrations in fly ash can also impact the formation of Portland cement. In a study by Gineys et al., (2011), they investigated the thresholds for Cu, Ni, Sn, and Zn in Portland cement concerning the limit of solid solution in the cement. The study found that the thresholds for Cu, Ni, Zn, and Sn were 0.35, 0.5, 0.7, and 1 wt%, respectively. Cu affected the concentration of $3CaO \cdot SiO_2$, while Zn affected the concentration of $3CaO \cdot Al_2O_3$ formation. The average concentrations of Cu and Zn in MSWI fly ash are around these thresholds. Therefore, some extraction of Cu and Zn is necessary to avoid affecting the clinker phase composition when using fly ash as the primary raw material in clinker production. Selective extraction of Cu and Zn would be beneficial for clinker quality.

However, metal concentrations are also important for the finished product. Construction products, such as cement and cementitious materials, must meet standards for environmental quality to prevent negative impacts on the environment and public health (Van Der Sloot, 2000). This is regulated through the European Construction Products Directive (CPD) or the Drinking Water Directive (DWD). These products are assessed based on their leaching characteristics, including whether they release trace elements or organic compounds into the environment. Yang et al., (2018) showed that Portland cement with 30% washed fly ash blended did not exceed regulations in China.

The use of suitable wastes in clinker production offers a significant advantage in reducing the volume of waste requiring specialized landfill disposal. Inclusion of fly ash in cement production allows for the management of all generated fly ash due to the large quantities of cement employed in the industry. The volume of generated fly ash is reasonably compared to the typical production capacity of cement plants. In Norway, there are two major cement clinker plants, with NORCEM at Breivik producing 1,000,000 tonnes and approximately 50,000 tonnes of MSWI fly ash is generated in Norway. Langøya processes around 450,000 tonnes from Nordic countries. The incorporation of 5% of MSWI fly ash as a raw material in clinker production at Norcem Breivik could utilize all of Norway's generated MSWI fly ash, while all ash treated at Langøya would represent 45% of Breivik's production capacity. Approximately 30-40% of the ash can be removed as salts. These considerable production volumes demonstrate that accommodating fly ash in cement production can be possible without compromising the quality of Portland clinker or control of the process.

If the presence of high metal concentrations in fly ash poses a risk to the quality of cement, both mechanically and environmentally, the implementation of selective metal extraction processes could improve the suitability of the ash as a raw material for clinker production.

5.3 Metal values in waste incineration ash

The high metal concentrations in fly ash present an opportunity for metal recycling. While metals can also be a hazardous component of incineration ash that needs disposal in landfills, there is potential for the use of this ash in construction materials. The data set from Langøya provides a reliable source for estimating metal concentration in incineration ash in Scandinavia, given fly ash variation in chemical composition.

Metal enrichment

The ratio between ore grade to average elemental concentration in the earth's crust shows the degree of enrichment. The price of metals and metalloids (from here on, referred to as metals for simplicity) relates to enrichment. Higher energy consumption needed for processing lower enriched ores gives higher metal prices (Watson and Eggert, 2021). Other factors also influence the price (the ability to mineralize, the toxicity, and the physical nature of the metals), but generally, a rarer metal has a higher price than a common one. The ratio can therefore be a first indicator to determine which elements have value as a resource.

The ratio can also indicate valuable metals extraction from low-value waste streams. Secondary metal production operates in the same market as primary production. However, primary production makes up most of the volume for most metal demands. It is, therefore, primary production that dictates metal prices. **Figure 23** shows the degree of enrichment of metals and metalloids in MSWI fly ash. Data used comes from Langøya dataset and Haynes (2016).

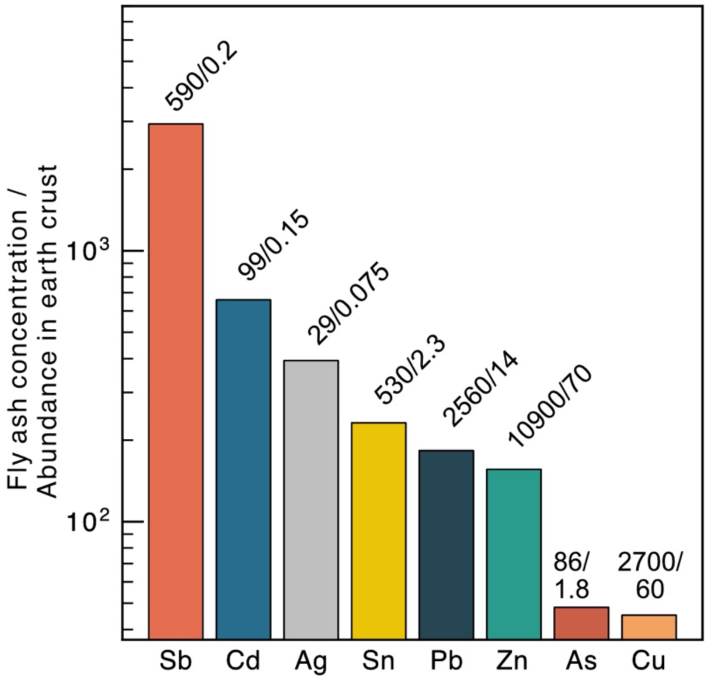


Figure 23 Enrichment factor of metals and metalloids in MSWI fly ash compared to abundance in the upper earth crust. The values used are annotated above the collumns.

In declining order, the most enriched elements found in fly ash are Sb, Cd, Ag, Sn, Pb, and Zn.

Estimation of metal values

Potential metal values in fly ash can be presented with general metal commodity prices. However, the prices can fluctuate significantly with time, and the price of metal products varies with the degree of impurity, morphology, type of metal compound etc. USGS annual report gives an overview of metal commodities where metal prices are included. **Figure 24A** shows the average metal prices from 2021 of elements enriched in fly ash. These prices can indicate what metals have the greatest value. **Figure 24B** shows metal values according to prices plotted in **Figure 24A** when assuming 100 per cent extraction and refining of the metal constituents.

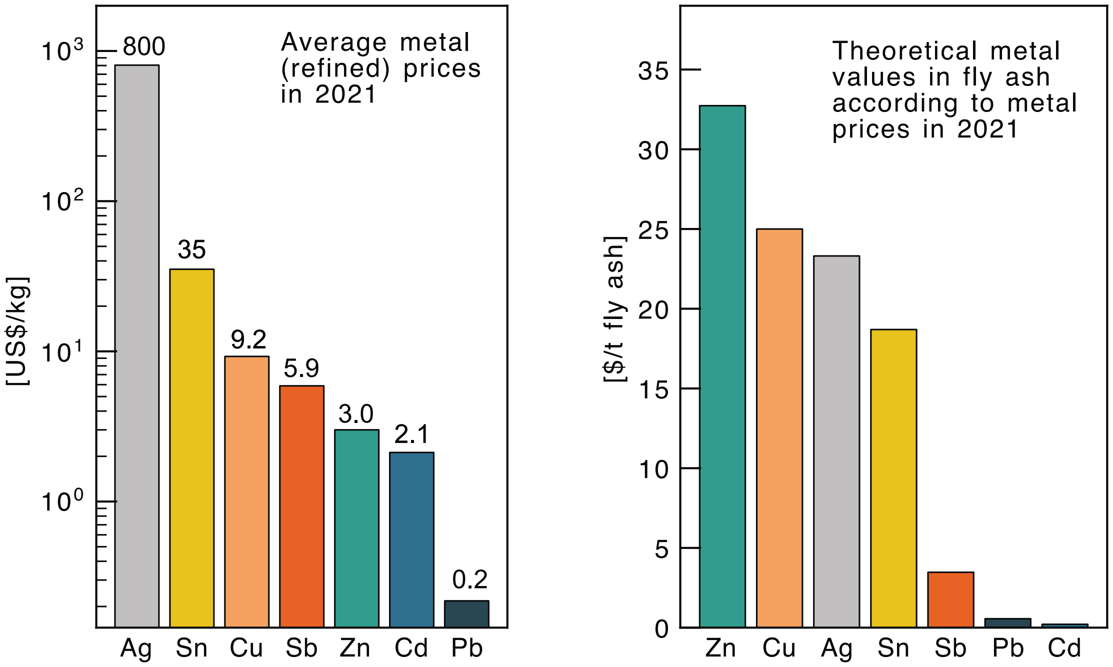


Figure 24 Metal prices according to USGS in 2021 and estimated theoretical values in fly ash.

According to the simple method used to estimate metal values in the fly ash, Zn has the greatest value, followed by Cu, Ag and Sn. Sb also has substantial value. The sum of the values is approximately 100 USD per ton of fly ash, where about 30% is from Zn and about 20% for Cu, Ag, and Sn. This is only theoretical value, but it gives a good understanding of which elements to target for recycling. According to my knowledge, Zn is the only metal targeted for recycling, together with some research on Cu extraction. However, this simple analysis shows that Cu, Ag and Sn should almost be treated similarly to Zn.

EU Critical raw materials

European countries are leading research and implementation of metal recycling from MSWI fly ash. It is the region with the highest share of MSW going to incineration compared to landfilling, and the region has high recycling goals. In addition, the European Union have profound initiatives securing critical raw materials as the EU almost exclusively depends on imports of many raw materials.

For the metals found in fly ash, Cu and Sb (and, to a certain degree, arsenic and bismuth) are important metals included in the EU's list of critical raw materials. Cu is important for the electrification of cars and renewable energy. Sb is used in various applications as flame retarding substances for plastics, paints, textiles and rubber; catalysts for PET production; in lead-antimony alloys used in batteries, ammunition, corrosion-resistant pumps and pipes, tank linings, roofing sheets, solder, cable sheaths, anti-friction bearings, etc. (Anderson, 2012).

Tonnages and similar raw materials

Recycling on a small scale can be a challenge from an economic standpoint. In **Paper 3,** focusing on ash from northern Europe, a detailed estimate of fly ash tonnages, including a fine fraction of bottom ash, is provided. The fine fraction of bottom ash demonstrates similar properties as fly ash and presents significant additional potential source of Cu. Hence, **Paper 6** mainly focuses on Cu recovery from bottom ash.

Moreover, it is important to identify other sources of metals with similar properties to fly ash that can be processed in the same way. Cu tailings, which are rich in calcium carbonate and have a high acid-exchange capacity, can be one such source. Welsh oxides can also be considered as a source of Zn derived from iron production. Additionally, sludges resulting from the runoff of old mines or industries can contain substantial amounts of Cu and Zn.

Gold and silver in MSWI ash

According to the Langøya dataset, the average Ag concentration in fly ash is 29 ppm. The dataset does not cover Au measurements, but it is assumed that almost all gold goes to the bottom ash. Moreover, several studies claim to find high concentrations of Au in the bottom ash. Muchova et al. (Muchova et al., 2009; Muchová and Rem, 2006) studied precious metals separation by physical methods from bottom ash. They claim that it was about 0.4 ppm Au and 10 ppm Ag in the bottom ash in MSWI from Amsterdam. Morf et al. (2013) studied the concentration of precious and valuable rare elements in MSW input fraction for an incineration plant in Switzerland. Au and Ag concentrations were measured at 0.4 ppm and 10 ppm, respectively.

A rough estimate gives theoretical metal prices equal to 36.8 USD Cu and 25.4 USD Au per tonne bottom ash fines, respectively. The metal concentration is assumed to equal 0.4% Cu and 0.4 ppm Au, and the metal prices used are equal to 63,500 USD per kg gold (average price in 2022 ("Gold Prices - 100 Year Historical Chart")) and 9.2 USD per kg Cu ("Mineral Commodity Summaries 2022," 2022). These metal values would be in the same order as Zn in MSWI fly ash.

The concentrations can be compared with ore grades. According to the concentrations stated above, bottom ash fines have higher Cu, Au and Ag grade than the Aitik Cu mine in Sweden. Here, the grade is 0.28% Cu, 0.2 ppm Au and 2 ppm Ag. Even though fly ashes contain precious metals, extracting them can be challenging.

5.4 Metal recovery processes

Metal extraction is one of the oldest chemical technologies and processes that has been developed and optimized throughout history. Often, as the chemistry dictates possible methods for extractions, most extraction systems have been thoroughly investigated. However, new types of raw materials occur, the accessibility of cheap chemicals or energy changes, higher standards of environmental requirements for the process and the different options must be assessed for the given time they are developed. Old technologies might not be suitable for the demands at that time they were phased out. However, the demands of today's society may differ, and the technologies might be suitable for today's situation. The essence of this is captured by Tom Frestons quote "Innovation is taking two things that already exist and putting them together in a new way."

When finding information from metal extraction technologies, the characteristics of the ore need to be taken into consideration. Some fly ash characteristics distinguish from traditional ores that need to be considered for the design of a metal extraction process. Several important aspects to consider include:

- High alkalinity (high proton exchange capacity) results from calcium species.
- The complex morphology and mineralogy.
- Challenges posed by high chloride and sodium content.
- Various combinations of enriched elements (different from common ores).

The impact of these factors on the practicality of operational methods today can be seen through various examples. For instance, halogens are undesirable impurities in hydrometallurgical Zn smelters and must be removed entirely. However, producing a Zn concentrate from fly ash that is suitable for such processes poses a significant challenge. The morphology and mineralogy of fly ash are distinct from those of ores, meaning that the conventional beneficiation methods developed for ores may be unsuitable for fly ash.

When designing a metal extraction process for fly ash, it must fulfil requirements for being a hazardous waste management process. Hence, some aspects must be highlighted:

- Minimization of the generation of new waste streams.
- Make sure the residue after metal extraction has better characteristics for landfilling or further valorization than the initial material had.

In the following pages, I discuss the selective extraction of metals and by-products in fly ash. This includes Ag, Au, Sb and Sn, in addition to Cu and Zn using ammoniacal hydrometallurgy. But first, some chemical aspects of elements relevant for fly ash are discussed.

Chemistry of valuable elements

In order to selectively extract metals, it is necessary to take advantage of the different chemical properties of the valuable substances that differ from the bulk material. Based on analysis, the important metal components in fly ash are found to be Zn, Cu, Ag, Sn, and Sb. The dominant element in the matrix is Ca, with Si, Fe, Mg, and a small amount of other elements, also present. **Figure 25** presents an overview of the elements in a periodic table after application.

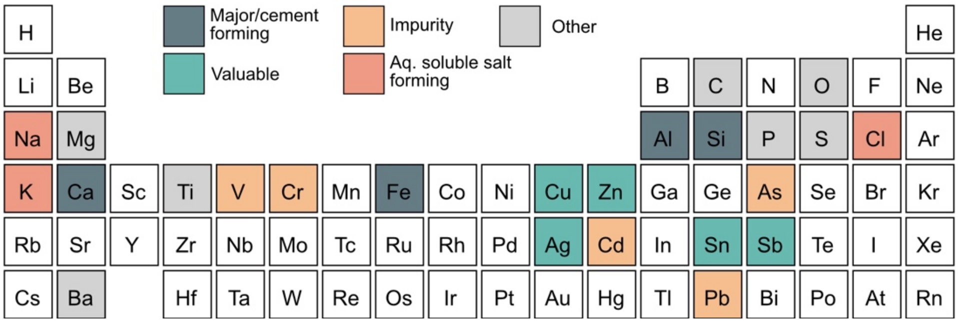


Figure 25 The Periodical Table (exlcluding heavier elements, lantanides and actenides)

The periodic table does not take into account the varying cations and anions of the elements. However, how different ions bond together can be predicted by the Hard and Soft Acid-Base (HSAB) theory. In this theory, cations are considered as Lewis acids and anions as Lewis bases. Cations and anions are categorized as either hard or soft, with soft ions bonding well with other soft ions and hard ions bonding well with other hard ions. The Railsback Periodic Table (Railsback, 2003) gives a good graphical representation of the HSAB theory (with a lot of other information as well). **Figure 26** provides a simplified version of the table that highlights the ion symbols of the elements that are important for fly ash composition in bold, and it also illustrates this concept of hard and soft ion bonding.

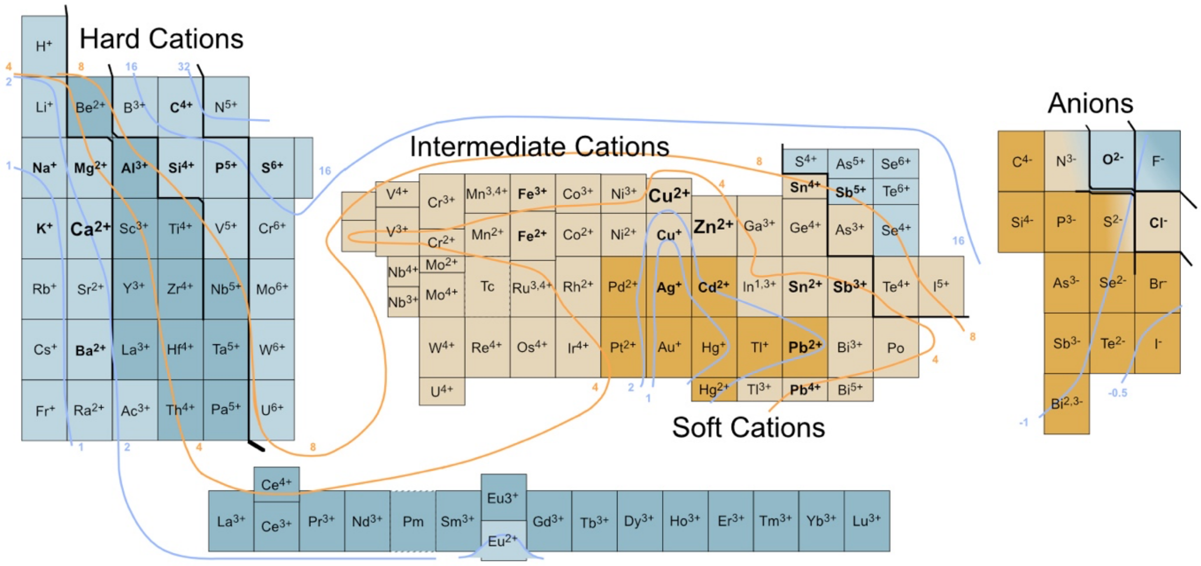


Figure 26 Simplified verison of Railsbacks periodical system illustrating HSBA theory. Symbols of ions important for the fly ash system are made bold. The lines represents the charge of the ion over its radius.

The polarizing power of cations can be predicted using the ionic potential, which is shown with lines in **Figure 27A**. This measurement is useful in predicting the stability of ions bound as oxides. **Figure 27A** displays a plot of the charge over radius of cations relevant for fly ash composition. Low ionic potentials result in soluble oxides, while medium ionic potentials produce very stable oxides. In contrast, high ionic potentials lead to the formation of oxo-complexes that are very soluble. It should be noted that the ionic potential is more reliable in predicting oxides and fluorides, but less applicable in predicting sulfides, where covalent bonds are more prevalent.

Several elements in fly ash can exist in different oxidation states, which impacts their chemical properties. The standard electrode potential is a useful measurement tool for predicting the stability of cations in certain oxidation states in aqueous solutions. **Figure 27B** illustrates the standard potential of elements in water. It should be noted that the way in which cations are bound in an aqueous solution can significantly alter their redox potential.

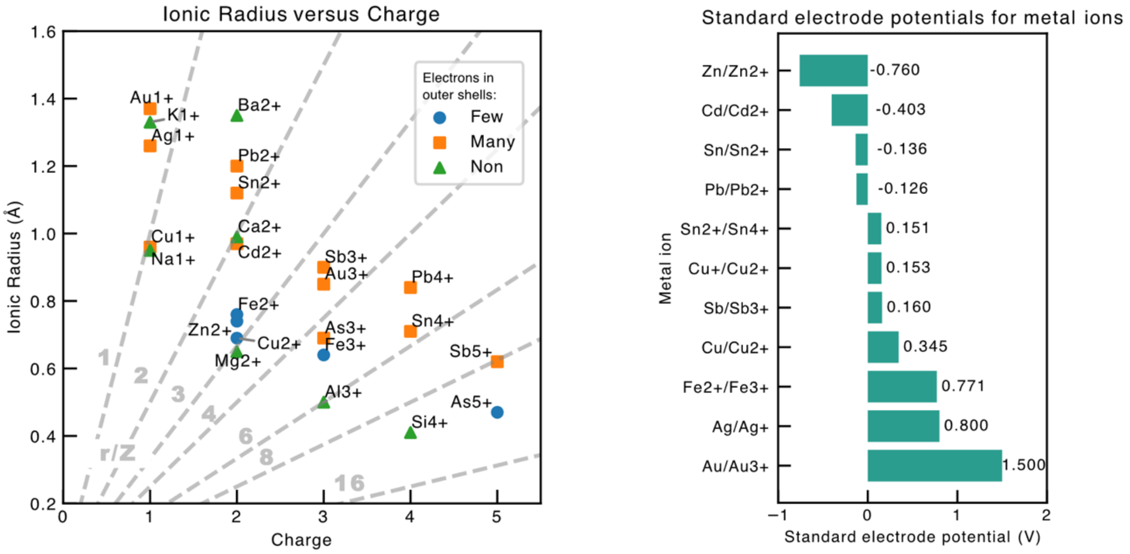


Figure 27 Left (A) charge of ions versus ion radius. Right (B) standard electrode potential.

Taking a closer look at Cu and Zn, both elements are located in the d-block of the periodic table. However, Cu is classified as a transition metal because it has partially filled d-orbitals, while Zn has a full shell of d-electrons and is therefore not considered a transition metal. Both elements have stable oxidation states of +2, but Cu can also exist as Cu^+. The divalent cations are categorized as intermediate acids in HSBA theory, whereas Cu^+ is considered soft. The intermediate character of the cations means that they can form complexes quite well with chloride and ammonia in aqueous media. The Cu^{2+} ion is smaller than Zn^{2+} and has larger polarizing power than Zn (Ionic potential: Cu = 2.89 $Å^{-1}$ while Zn = 2.70 $Å^{-1}$). This means that Cu makes more stable oxides than Zn. This is reflected in K_{sp} values for CuO 2.0 x 10^{-20} versus 4.5 x 10^{-17} for ZnO.

As Cu^{2+} possesses d-orbitals that are only partially filled, it is able to receive additional stabilization from degenerate d-electrons as described by the Ligand Field Theory. The extent of ligand-field stabilization-energy is influenced by the degree to which ligands are able to degenerate the d-orbitals. In general, increasing stabilization corresponds to the following ligand donors order: Halide donors < Oxygen donors < Nitrogen donors < Carbon donors. For instance, Cu would experience higher stability in a complex such as $Cu(NH_3)_4$ as opposed to CuO (N donors instead of O donors). This affect is exploited in ammonia hydrometallurgy presented in **Paper 5** and **Paper 6** and further down in this section It is worth noting that Ag and Au, which are in the same group as Cu, possess even higher ligand-field stabilisation-energy due to their placement in periods below Cu. Consequently, this contributes to their ability to form exceptionally stable complexes with N-donors for Ag^{1+} and Au^{3+} ions.

Fly ash is also enriched in Pb, Sn, and Sb, and to a lesser extent As. While both Pb and As can be considered impurities, Sn and Sb are valuable elements desired to be extracted. These elements exist in two cationic oxidation states - one where p-orbital electrons are removed, and one where also the s-orbital electrons are removed. For Sn and Pb, these oxidation states are 2+ and 4+, while for Sb and As, they are 3+ and 5+. Each element contains electrons in the same orbital types. The fully oxidized species tend to form more stable oxides as they possess a higher ionic potential, classifying them as hard cations. Arsenic is especially hard as it readily forms highly soluble oxo-complexes. Generally, Sn^{4+} is more stable than Sn^{2+}, and Pb^{2+} is more stable than Pb^{4+}. In nature, cassiterite (SnO_2) and galena (PbS) are considered the main ores of the two metals.

The lower oxidation states of Pb, Sb, and Sn are typically categorized as soft cations and are bound with equally soft anions, such as sulfides. Their relatively high electronegativity makes covalent bond formation more favorable. The high degree of covalency in sulfide bonds generally promotes more molecular structures, which tend to display lower thermal stability. These structures typically sublimate and melt with ease. **Figure 28** indicates how greater electronegativity promotes more covalence in in the sulfide-metal (metalloid) binding, which in turn affects their melting points. This tendency to form molecular structures with sulfides can be exploited when devising various extraction schemes.

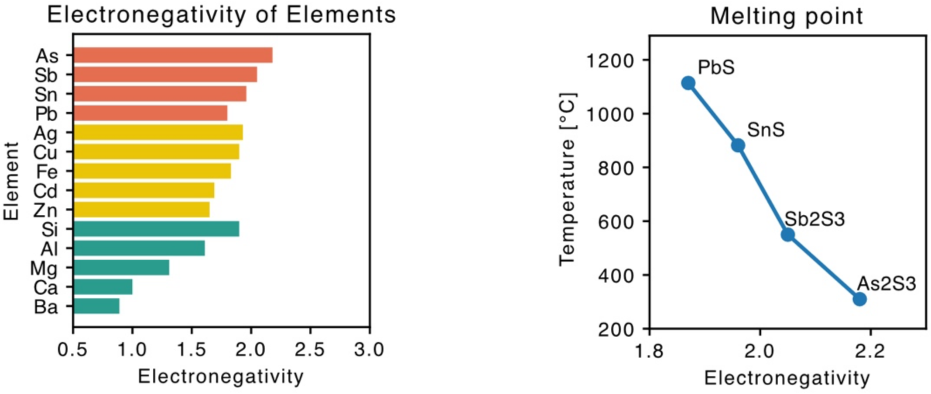


Figure 28 A (left) shows Pauling's electronegativity of selected elements. B (right) shows the electronegativity of Pb, Sn, Sb and As versus the melting point when they are bonded to sulfide.

The general chemistry of elements in fly ash is evident in the significantly different properties exhibited by valuable elements when compared to bulk materials. This implies the possibility of selective separation of valuable elements from bulk material; however, the specific binding of different species can present significant challenges in achieving successful extraction.

Existing processes

Various methods for extracting metals from MSWI have been extensively studied, yet only a limited number of the process schemes have been successfully implemented commercially or tested in pilot plants. Notably, the FLUWA FLUREC has been operating in Switzerland with Zn extraction at full scale. Also, HALOSEP processes have been operating at pilot scale in Denmark. While the former is intended for producing pure metal products, the latter separates the metal concentrate for additional processing. **Figure 29** illustrate the simplified flow sheets for FLUWA FLUREC process.

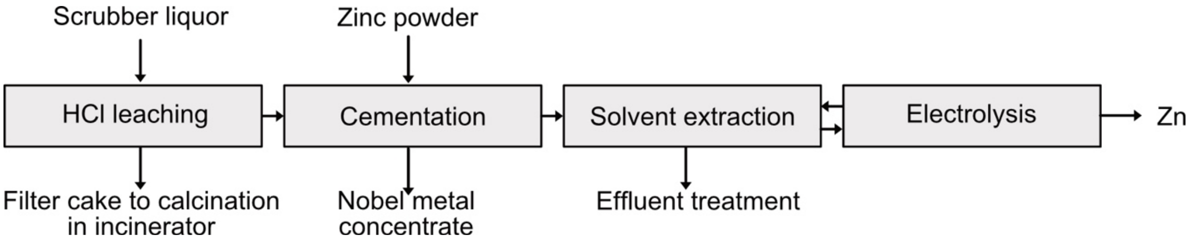


Figure 29 Simplified flowsheet of FLUWA FLUREC process.

Both processes use HCl. Chloride acts as additional stabilizing agent for Zn and Cu in the aqueous phase by complexation (chlorides complexes well intermediate soft cations Zn^{2+} and Cu^{2+}) and acids for the dissolution of oxides/carbonates/hydroxides. In order to improve extraction yields efforts to increase complexation stability with NaCl and increasing oxidation of metallic species by the addition of hydrogen peroxide have been studied (Weibel, 2017)

There exist several notable similarities between these two processes for dealing with the specifics of fly ash characteristics. Firstly, both processes are on-site at the incineration plant, which reduces transport costs. Secondly, they both employ inexpensive acid derived from the acidic scrubbers. It is crucial to avoid the utilization of costly acids as leaching agents due to the high proton exchange capacity of fly ash, which leads to acid loss. Consequently, acid-based processes tend to yield effluent with highly dissolved solids content. These dissolved solids, in turn, contribute to the formation of new waste fractions that necessitate appropriate management.

Ammonia hydrometallurgy for zinc and copper extraction

An alternative approach to metal extraction involves the implementation of selective extraction, where the lixiviant can be regenerated. In **Paper 5**, I propose the application of ammoniacal hydrometallurgy for targeted selective Zn and Cu extraction from fly ash. Various historical use of ammonia hydrometallurgy is also presented in the paper. Moreover, as the paper shows, ammonia leaching is superior to HCl in order to dissolve Cu, and close to equal in dissolution of Zn. This can be explained by the extra stability transition metal complexes get from strong field ligands such as NH_3 compared to weak field ligands like Cl^- and H_2O.

Ammoniacal hydrometallurgy showcases selectivity, and the lixiviant can be regenerated. These may be advantages that offer an alternative route to metal extraction of fly ash, given its unique characteristics. Ammonia acts as a complexing agent for transition metals. Ammonia's ability to complex certain metals at pH where general metal solubility is low allows selective extraction during leaching. Ammonia is used industrially as a complexing agent for Co, Ni, Cu. and Zn. The ammonia complexing power is utilized in many metallurgical applications. A more thorough summary can be found in **Paper 5**. The stability of ammonia complexes can be described by the stability constant. A list of stability constants for ammonia systems is presented in **Figure 30**.

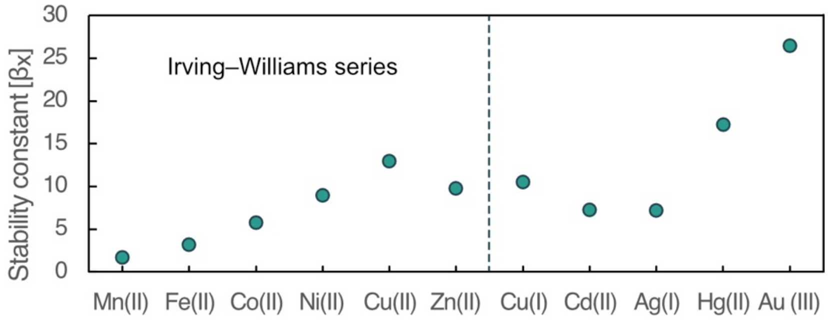


Figure 30 Stability constant of ammonia complexes (Mironov et al., 1992; Skibsted et al., 1974a).

In addition to NH_3 NH_4^+ is needed for addition of the hydronium ion to break oxide bonds. A high concentration of ammonium can compensate for low hydronium concentration, dissolving metal oxides by donating its proton. In addition, ammonia is needed for the creation of soluble metal complexes. This makes ammoniacal hydrometallurgy operate where both ammonia and ammonium co-exist in solution according to equation 4. The pK_a of ammonia is 9.25.

$$\mathrm{NH_3(aq) + H_2O \leftrightarrows NH_4^+(aq) + OH^-(aq)} \tag{4}$$

The ammonium ammonia equilibrium is shifted to the left at higher temperatures. Also, the concentration of counter ion to shift the equilibrium of equation 4. In hydrometallurgical processed the counter ion is either chloride, carbonate or sulfate. These anions affect the pKa value differently (see **Figure 31**).

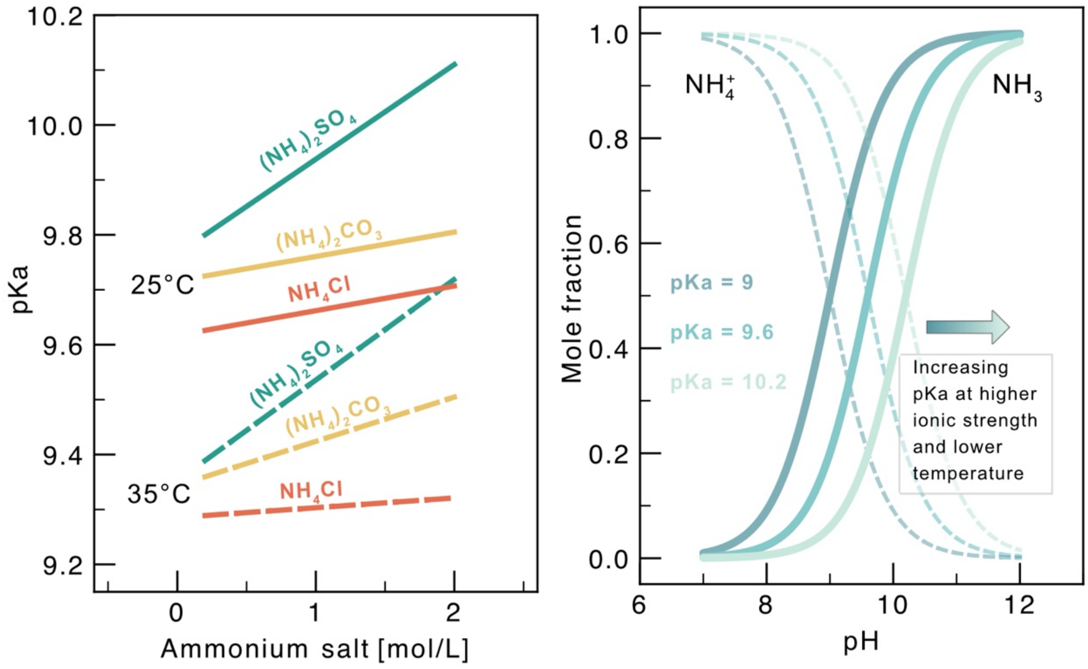


Figure 31 Left (A) counter ion and temperature effect on pKa (Velásquez-Yévenes and Ram, 2022). Right (B) illustration of ion distribution with respect to pH with differences in pKa.

Increasing effect for the counter ion to change the pKa is as following $Cl^- < CO_3^{2-} < SO_4^{2-}$. Increased pKa means less NH_3 and more NH_4^+. This is a consequence of the anion's ability to form ion pairs with ammonium. The higher ability to form ion pairs, the better the anion will shift the equilibrium of **equation (4)** to the right. Hence, increasing the pKa.

$$NH_4^+(aq) + SO_4^{2-}(aq) \leftrightarrows NH_4SO_4^-(aq) \tag{5}$$

$$NH_4^+(aq) + CO_3^{2-}(aq) \leftrightarrows NH_4CO_4^-(aq) \tag{6}$$

Ammonia is a rather expensive lixiviant compared to common lixiviants as H_2SO_4 and HCl. Therefore, recycling the lixiviant is essential. Ammonia's volatile character at high pH allows regeneration by evaporation/distillation shifting equation 7 to right. Increasing temperature is shifting equations to the right. Also, increasing pH for example with CaO would shift the equilibrium towards volatilization.

$$NH_3(aq) \leftrightarrows NH_3(g) \tag{7}$$

Deammoniazation: 100kg of ammonia requires the same energy as evaporation of 50 kg of water as the heat of vaporization is 22.7 kJ/mol for ammonia compared to 40.65 kJ/mol (Kazinczy, B. et al., 2000). So even though ammonia can be regenerated, it is somewhat energy intensive.

Ammonia hydrometallurgy for gold and silver extraction

It is proven that Au and Ag can be dissolved in ammoniacal solutions with an appropriate oxidant. Au forms complexes with ammonia. The complexation has been studied by Skibsted et al (Skibsted et al., 1974a, 1974b). However, Au's and Ag's low stability in higher oxidation states makes ideal oxidation conditions crucial. In addition to ammonia/ammonium salt, high oxygen partial pressure and an oxidative catalyst are needed to increase oxidation kinetics. Cu^{2+} can be used as catalyst.

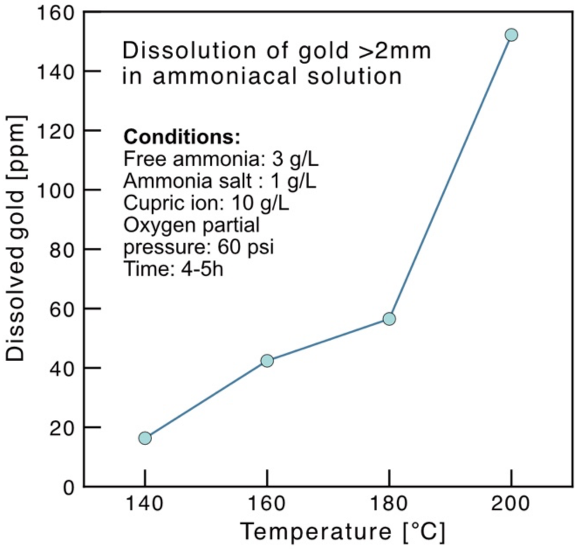


Figure 32 Au dissolution in ammonia solution at various temperatures presented in patent by Han et al. (1993)

Ammonia hydrometallurgy for Au and Ag extraction was pioneered by Han et al. **Figure 32** shows dissolution kinetics of metallic Au particles and **Table 7** summarizes the ammonia hydrometallurgy performed on sulphide ores, refractory ores, carbonaceous ores, froth flotation concentrate and industrial incinerated ash.

Table 7 Summary of parameters and results of experiments presented in patent by Han et al. (1993) named "Ammonia Extraction of Gold and Silver from Ores and other Materials."

Conditions and extraction yields	
Raw material/ore type	Sulphide ores, refractory ores, carbonaceous ores, froth flotation concentrate, industrial incinerated ash
Free ammonia conc.	3-4 M
Ammonium salt conc.	0.5 M
Type of ammonium salt	$(NH_4)_2SO_4$,$(NH_4)_2CO_3$, $NH_4CH_3CO_2$
Oxygen partial pressure	70-200 psi (4.8 - 13.8 bar)
Temperature	120-200°C
Cupric ion conc.	5-15 g/L
Leaching time	1.5-5h
Pulp density	7-25 wt%
Gold yield (in 9 examples)	88-98%
Silver yield (in 3 examples)	95-98%
Copper yield (in 2 examples)	70% and 99%

Chmielewski et al., (2009) show that Ag can be extracted efficiently together Cu, Zn, Ni and Co from lubin-shale middlings.

Alkaline sulphide hydrometallurgy for antimony and tin extraction

Alkaline sulphide hydrometallurgy can be applied to Sb, Te, As, Sn, Au, and Hg recovery. These elements make strong sulphide complexes and can selectively be extracted by leaching. Commercially, alkaline sulphide hydrometallurgy is used for Sb extraction from sulfidic ores (Anderson, 2012). However, research has been conducted on using the technology for other raw materials and for targeting the recovery of the other elements that complex well with sulphides. In particular, Corby G. Anderson et al., have contributed well on alkaline sulphide hydrometallurgy during the 1990s and 2000s.

It is preferable to obtain Sb in its 5+ oxidation state rather than 3+, (sodium thioantimonate rather than sodium thioantimonite). This is because of crystallization qualities (Anderson et al., 1994).

In relation to gold recovery, alkaline sulphide hydrometallurgy has been used to liberate gold from antimonides and telluride minerals. The leaching yields and operation conditions for alkaline-sulfide leaching is presented in **Table 8**.

Table 8 Parameters and results obtained by alkaline sulfide leaching of ores reported by C. G. Anderson and L. G. Twidwell (2008) (Anderson and Twidwell, 2008).

Leaching condition and yields	
Leaching time	6-12 hours
Percent solids	100-250 g/L

Temperature	105°C
Sulphur concentration	100 g/L
Free hydroxide	10-25 g/L
Antimony yield (5 examples)	99.4%, 100%, 95%, 89%, 95%
Tin yield (4 examples)	99.1%, 100%, 99%, 96%
Arsenic yield (3 examples)	2.0%, 100%, 60%
Gold yield (3 examples)	9.1%, 1.7%, 20%

Antimony, tin and lead extraction by reductive volatilization

Another way of selectively extracting metals is to exploit volatilization of metals with lower volatility than bulk material at elevated temperatures. It can typically be done in fluidized bed reactors or rotary furnaces with controlled atmosphere.

Sb and Sn can thermally be volatilized under a reductive atmosphere (Lane et al., 2020b, 2020a). Lane et al. showed that Sn and Sb could be volatilized from untreated fly ash in a reducing atmosphere (10:90 H_2:N_2). Recoveries ranged from 18-87% for Sn and 18-78% for Sb. Thermodynamical calculation predicts the formation of $Sb_2S_3(g)$ and SnS(g) as the soluble species. Lead is also volatilized as sulphide PbS(g) and up to 80% is removed. The amount of sulfides from decomposition sulphates may be a limiting factor for volatilization. For example, it was shown that $CaSO_4$ decomposed around 700°C.

As shown in though literature search on sulfide-based extraction technologies and experimental work on ammonia hydrometallurgy (**Paper 5** and **Paper 6**) selective extraction of valuable metals from fly ash can be possible. However, setting these technologies is industrial system for fly ash management can be challenging when aiming at minimizing generation of new waste streams and minimized use chemical and thermal energy.

6 Discussion on waste ash processing schemes

"The whole is greater than the sum of its parts." – Aristotle

In this chapter, I will introduce potential process schemes and ideas for the management of fly ash and bottom ash waste. Based on experimental research, resource evaluation, and literature; I will propose a holistic approach to handling these waste materials considering low waste generation, recycling metal valuables and reduced need for hazardous landfills. This includes experimental data on selective extraction of Cu and Zn by ammonia hydrometallurgy presented in **Paper 5** and **Paper 6**, knowledge on chemical composition of fly ash presented in **Paper 1** and **Paper 2**, resource potential as metals and cement clinker presented in **Paper 3, Chapter 5.2** and **Chapter 5.3**, literature review on selective extraction presented in **Chapter 5.4** and understandings of the fly ash waste management challenges presented in the introduction. More extensive research and analyses are needed to validate, find pitfalls and analyze cost and environmental aspects. However, the schemes presented can be valuable for further research and technology development.

6.1 Combined salt and metal recovery with clinker production

To my best effort and based on the work performed during this thesis project, I asses that combining salt recovery, and selective metal extraction with a clicker production can fulfil incineration waste management issues with deposition and exploit valuables in the ash. The composition of fly ash indicates its use in clinker production as viable. However, chlorides and alkalis jeopardize both clinker quality and cement kiln operation. Therefore, desalting is inevitable. Ammonia hydrometallurgy extracts the two most valuable metals in fly ash without the generation of new waste streams. Also, the operation removes metal and sulfates unwanted in cement. Cement kilns are a "waste-free" process where oxidation of organic toxins and metals can occur. Oxidizing metallic aluminum present is for example wanted. Managing to convert waste ash to cement would eliminate the need to use scarce special landfills for deposition. Recycling of salts, Cu and Zn can be considered upcycling processes while clinker production downcycling. The different recycling step can complement each other.

A simplified process flow scheme is presented in **Figure 33**. Bold marked inflows and outputs represent the treatment of waste or output products. Underlined italic inflows are input variables needed to produce valuable recycled products. Each operation is marked with a number, which facilitates further elaboration of the scheme in the following discussion.

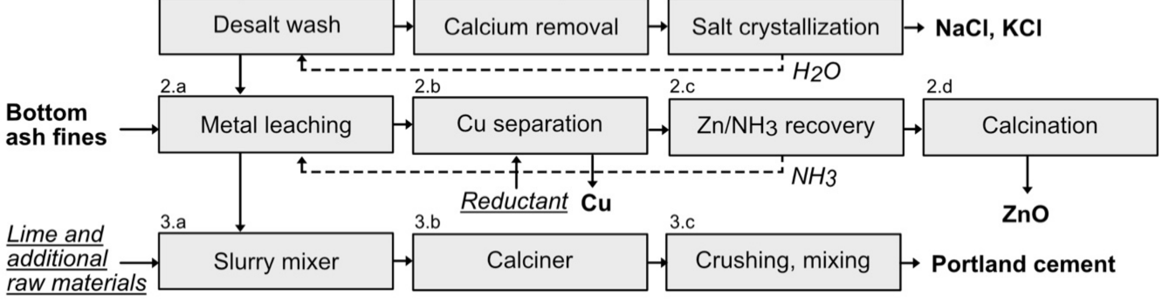


Figure 33 Proposed flow sheet for further investigations.

Alkaline and alkaline earth salts can easily be washed out with hot water (1.a). The saline solution has a high pH, which makes it possible to precipitate calcium and other impurities as carbonates. This opens two possibilities: directly process saline solution via crystallizing scheme into $CaCl_2$, NaCl or KCl, or removal of calcium and other impurities by carbonation before crystallisation of NaCl and KCl, as shown in **Figure 33** (1.b). Freshly produced ash is more likely to release soluble metal salts more easily than aged ash, where the ash is naturally carbonated by CO_2 from the atmosphere. Precipitated impurities into the solid phase via carbonation may reduce effluent treatments/waste management for the salt crystallizer process. If impurities like Pb limit the quality of $CaCO_3$, carbonation can be done during the desalting step before filtration (1.a). Alternatively, precipitate $CaCO_3$ directly into ammonia leaching step 2. from Ca removal step. An alternative to chloride crystallisation is the use of chloralkaline process of the NaCl/KCl saline solution for NaOH and Cl_2 production.

Bottom ash fines make up a large waste fraction of MSWI that is not recovered. The high content of Cu in the fine particle fraction, makes it attractive for co-processing with fly ash (2.a). However, the compositional analysis must be evaluated to decide how this would affect the composition of the waste for clinker production. Further processing of the leach solution must be evaluated. The most common method for NH_3 leaching is the cementation of Cu and other noble metals with Zn powder. Cu can further be refined with electrorefining. An alternative reductant is hydrogen gas under pressure. Zn is recovered by distillation/steam stripping of the solution. This is the most energy-intensive operation in the scheme. Solvent extraction of the leachate may be necessary to enrich the solution to reduce the energy needed for NH_3 regeneration. This may also be used if sulfate accumulate in the solution to jeopardize steam stripping.

During the ammonia carbonate leaching (2.a), sulfate will be solubilized and accumulated in the lixiviant (2.c). Eventually sulfate must be removed to regenerate ammonium carbonate lixiviant. This can be done with adding $Ca(OH)_2$ for gypsum precipitation. However, if carbonate is present this must be precipitated before sulfate is removed as Ca has a higher affinity towards carbonate than sulfate. This can consume a lot of $Ca(OH)_2$. Applying $Ca(OH)_2$ after carbonate (and ammonia) removal with stream stripping would lower slaked lime consumption. Minimising lixiviant concentration is therefore important for reduced costs. This can make up a waste fraction from the Zn/Cu production. However, carbonate/gypsum may be used in concrete and may be included in clicker production to produce cement or to fillers in plastics or paper.

$$(NH_4)_2SO_4(aq) + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O(s) + 4NH_3(aq) \qquad (8)$$

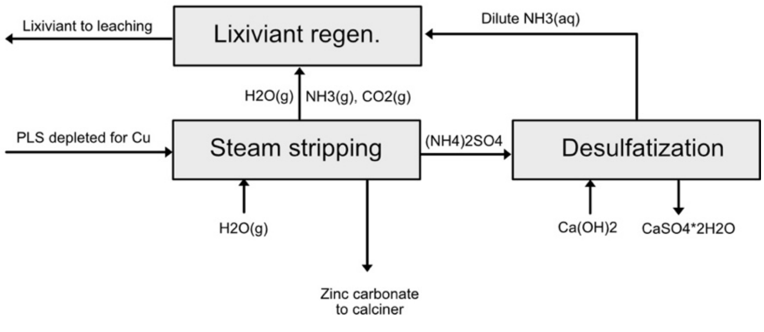


Figure 34 Simplified flow sheet for handle enrichment of sulfate in lixiviant.

It is well known that the regeneration of ammonia and the precipitation of Zn is the most critical part of the ammonia processes regarding high energy usage. If this is the case, implementing solvent extraction for co-extracting Zn and Cu and regeneration of the lixiviant may be an option. Co-extraction of ammonia to organic solvent (lixiviant loss) may be critical for such a process. Oxime types of extractants are typically used for Cu extraction in ammonia solutions and can be a natural place for investigation.

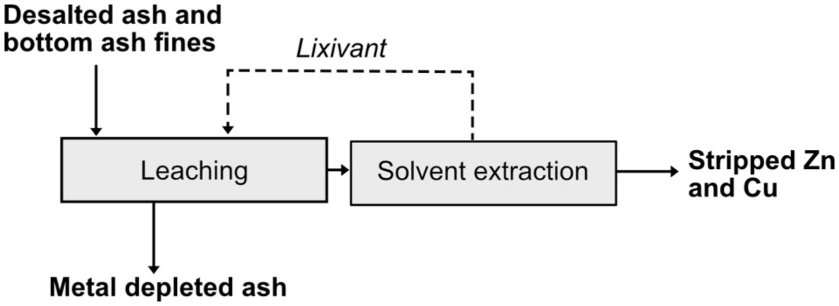


Figure 35 Simplified flow sheet using solvent extraction.

There are two principal processes for clinker production – a wet and a dry route. The wet case is most suitable as the waste is already in a slurry state from metal extraction. Entering the slurry metal extraction process reduces the need for effluent treatment from metal extraction. Additional raw material must be added to reach the optimal composition of Portland clinker composition.

The Portland cement quality is important to assess, and concrete products must be designed accordingly. High chlorine would for example not be suitable for reinforced concrete, but may have excellent properties for fundaments.

To my understanding, the process scheme concept can completely process waste incineration ash without generating large new waste streams and limits the use of substantial amounts of reagents. However, all process steps are believed to be energy intensive – salt crystallization, ammonia, regeneration and high-temperature cement kiln operations.

6.2 Concepts for by product processes

The process schemes do not exploit Ag, Sn and Sb valuables in fly ash and the potential Au in bottom ash fines. However, the potential of change in NH_3 leaching conditions may manage to leach Ag and Au. As shown by Han and Meng (1994), Ag and Au can be extracted with NH_3. Such processes need slightly different technology as higher pressures and temperatures are needed for such dissolution. In this process, it is important to maintain high cupric copper concentration in the lixiviant. Therefore, it would be better to precipitate both Cu and Zn in the stream stripping process in addition to a reductant for noble metals (ore co-extraction with solvent extraction). The lixiviant can be regenerated with high cupric concentration that can act as catalyst for the extraction of Au and Ag in the raw material. However, there are sulphate control issues as sulfate is not removed in the scheme. Reduced sulfate is important for the distillation crystallization step. $Ca(OH)_2$ addition during leaching can maybe control this.

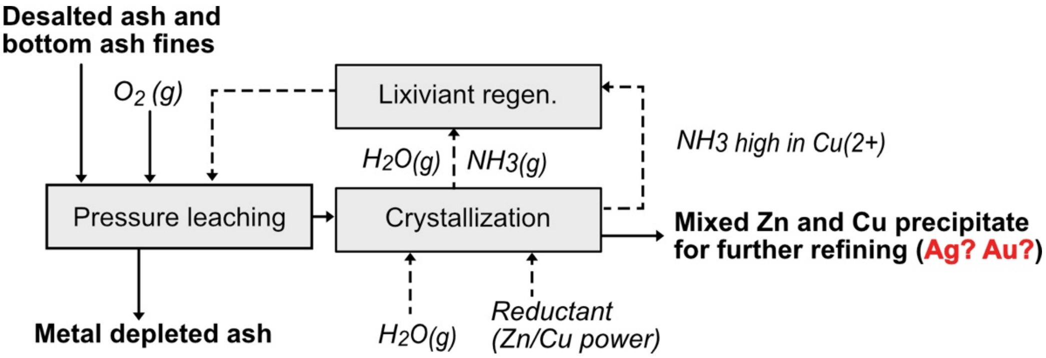


Figure 36 Flow sheet of ammonia pressure leaching maintain high Cu(2+) concentration for catalytic oxidation effects.

Sn and Sb contributes to the values in fly ash. Both thermal volatilization and alkaline hydrometallurgy can be used for selective extraction. Both processes exploit the elements' high affinity to sulfide. Alkaline hydrometallurgy creates soluble sulfide complexes in an alkaline solution.

A reductive atmosphere is needed to ensure the volatilization. Such volatilization can be implemented as the materials are planned to go into high temperature in the cement kiln. However, Sb's volatilization needs a reducing atmosphere. Co-incineration of fly ash in regular cement kiln, most Sb end up in cement clinker in valence 4+ (Wang et al., 2018). Sulfur concentration is important for Pb, Sb and Sn volatilization. Therefore, it is important to maintain sulfates after ammoniacal leaching. Solutions can be higher degree of ammonium sulfate in the lixiviant or the addition of $CaSO_4$ to the metal volatilization step. Adding $CaSO_4$ before volatilization can also be beneficial for Portland clinker composition as average MSWI is somewhat deficit on calcium (see Chapter 5.2). Unvolatilized sulfur will end up as sulfate in normal clinker production (Eriksen et al., 2001).

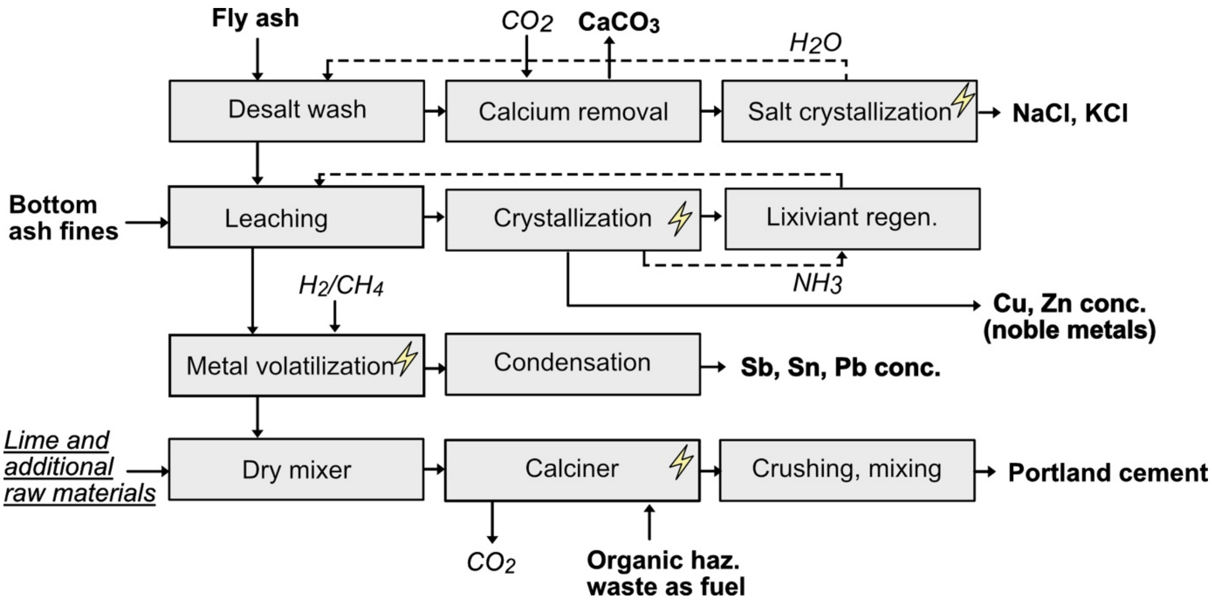


Figure 37 Hypothetical process scheme for selective metal extraction, salt recovery and cement clinker production

Cement kilns operate at high temperatures to destroy organic toxins and persistent organic pollutants (POP). This makes such a process scheme possible to treat hazardous organic waste. This can be a third waste management business strategy, in addition to managing fly ash and bottom ash fines.

The presented process schemes are rather speculative and is not tested experimentally. However, I have chosen to include it in the thesis to provide ideas or visions for improved fly ash waste management with minimal waste generation. Moreover, if such process flow schemes can be proven to work, several challenges in today's society can be solved.

- Reduced need for hazardous landfills
- Enhanced circularity and recycling of base metals like Cu and Zn
- Supply of critical elements like Sb ad Sn
- Recycling of salts and provide new raw materials for Portland cement clinker

However, even though such a process is proven to be technically and economically feasible, higher demand for energy is needed compared to today's management and there is new potential for small release of pollutants related to process chemistry operations. The large investment will need a centralized plant to take advantage of economy of scale. This will also lead to lot of transport of waste. However, this is still the case for today's situation for transporting the waste to suitable landfills. I believe that the main challenge to achieve such processes as proposed is the large investments in R&D and in a process plant that is needed.

7 Conclusions

In conclusion, this work has contributed to the knowledge that can innovate fly ash management. Foremost, the work clarifies challenges and opportunities related to fly ash management that need to be considered for process development: waste characteristics, resource potential, metal extraction, resource origin, waste minimization etc.

In more detail, through comprehensive chemical analysis, this study has provided valuable insights into the chemical composition of MSWI fly ash. The research has highlighted variations in composition across different plants and over time. This is presented in **Paper 1** and **Paper 2.** This is crucial in many aspects of fly ash management.

The research has also shed light on the metal values present in fly ash. Metal values are shown in **Paper 3** and further elaborated in **Chapter 5.3**. Elements like Sn, Sb and Ag should get more attention. Bottom ash fines should be regarded equally as resources for Zn and Cu as in fly ash.

Chemical compositional analyses have shown that fly ash main components are suitable usage of raw material in Portland clinker production with few additional raw materials for reaching optimum Portland cement clinker composition (see **Chapter 5.2.**). Such reuse leads to the final destination of fly ash waste to avoid fill-up rates of landfills and would solve significant issues related to opening new hazardous landfills. More efforts should be made to investigate if this is possible.

Experimental work has shown that ammonia leaching selectively targets Cu and Zn extraction. This can be an alternative method for metal recycling from fly ash instead of today's methods using spent HCl as lixiviants (see **Paper 5** and **Paper 6**).

This thesis has proposed ideas for a holistic fly ash management process for exploiting the entire fly ash – including synergies of combining salt recovery, metal recycling and clinker production (see **Chapter 6**). A few parts of the process are tested experimentally. Therefore, I propose a further experimental investigation of the system proposed to investigate challenges with such a process.

In summary, by enhancing our understanding of the composition of hazardous fly ash waste and proposing recycling processes that utilize the entire waste stream, this study lays the foundation for a more sustainable approach to fly ash waste management, addressing some of today’s critical waste management challenges.

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9 Appendix

9.1 SEM and LM images of fly ash

Backscattering SEM imaging revealed that substantial amounts of metallic particles could be found in my fly ash samples. As the metal particles have an average high atomic mass density, they are lit up compared to matrix particles by increased intensity of backscattered electrons. Chemical analysis by EDS in the SEM identified several dense particles like metallic copper, tin, zinc, iron, barium sulfate, iron oxides, and manganese oxides. Also SEM images reveal the variety of particle morphologies, sizes and chemistry of particles in fly ash. The following images are from ESP ashes.

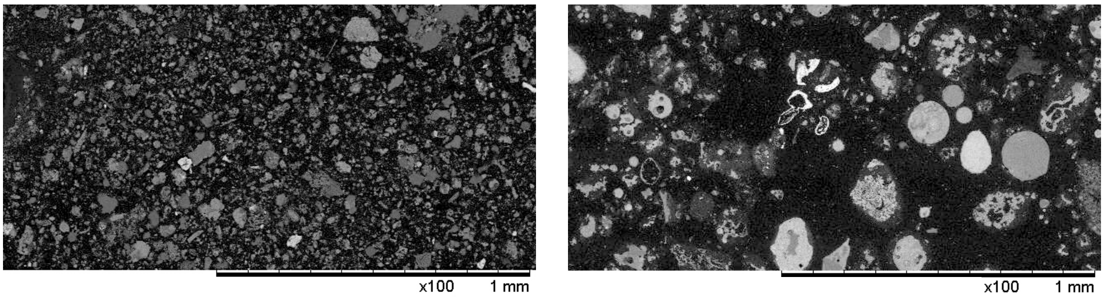


Figure A 1 SEM images of two different fly ashes illustration differences in particle size and morphology.

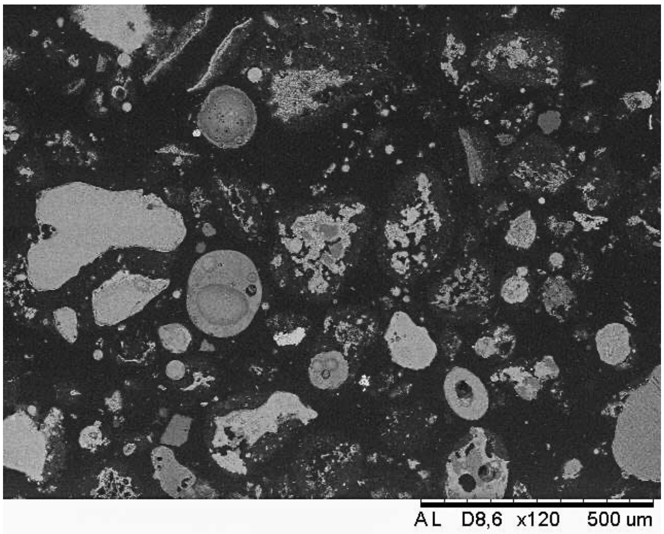


Figure A 2 SEM images of fly ashes illustration different morphology of particles.

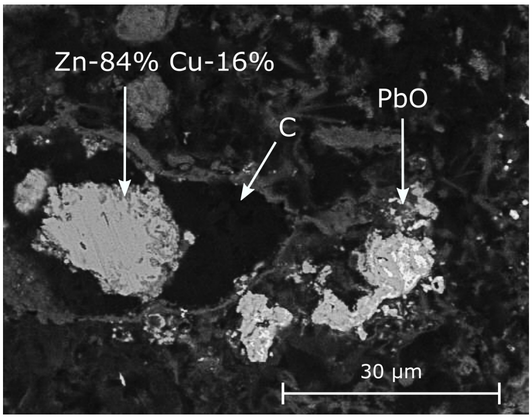
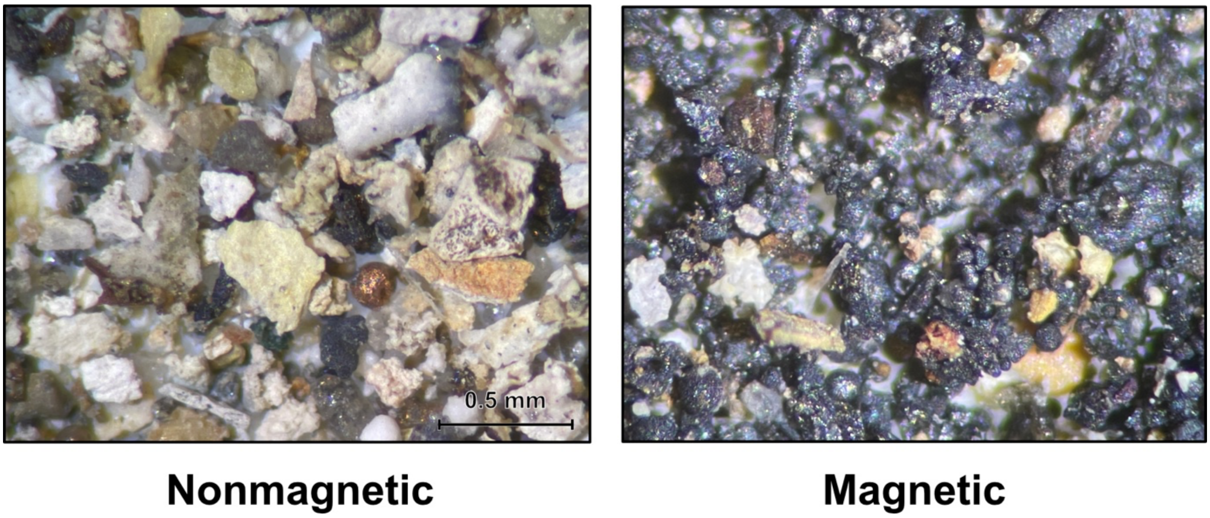


Figure A 3 SEM images of metallic and PbO particle in fly ash.



Nonmagnetic **Magnetic**

Figure A 4 LM images of non-magnetic and magnetic part of dense particles in fly ash. The image is from experiments presented in **Paper 4a.**

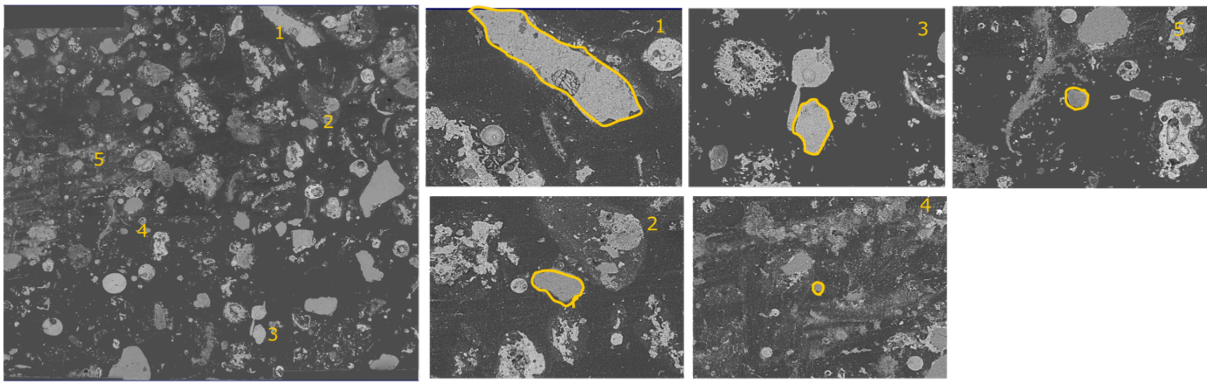


Figure A 5 BSE image of arbitrary chosen area of fly ash embedded in epoxy. Five aluminium particles with average diameter of 100 µm (max =250 µm, min 22 µm) can be observed. Minor aluminium particles might also be present.

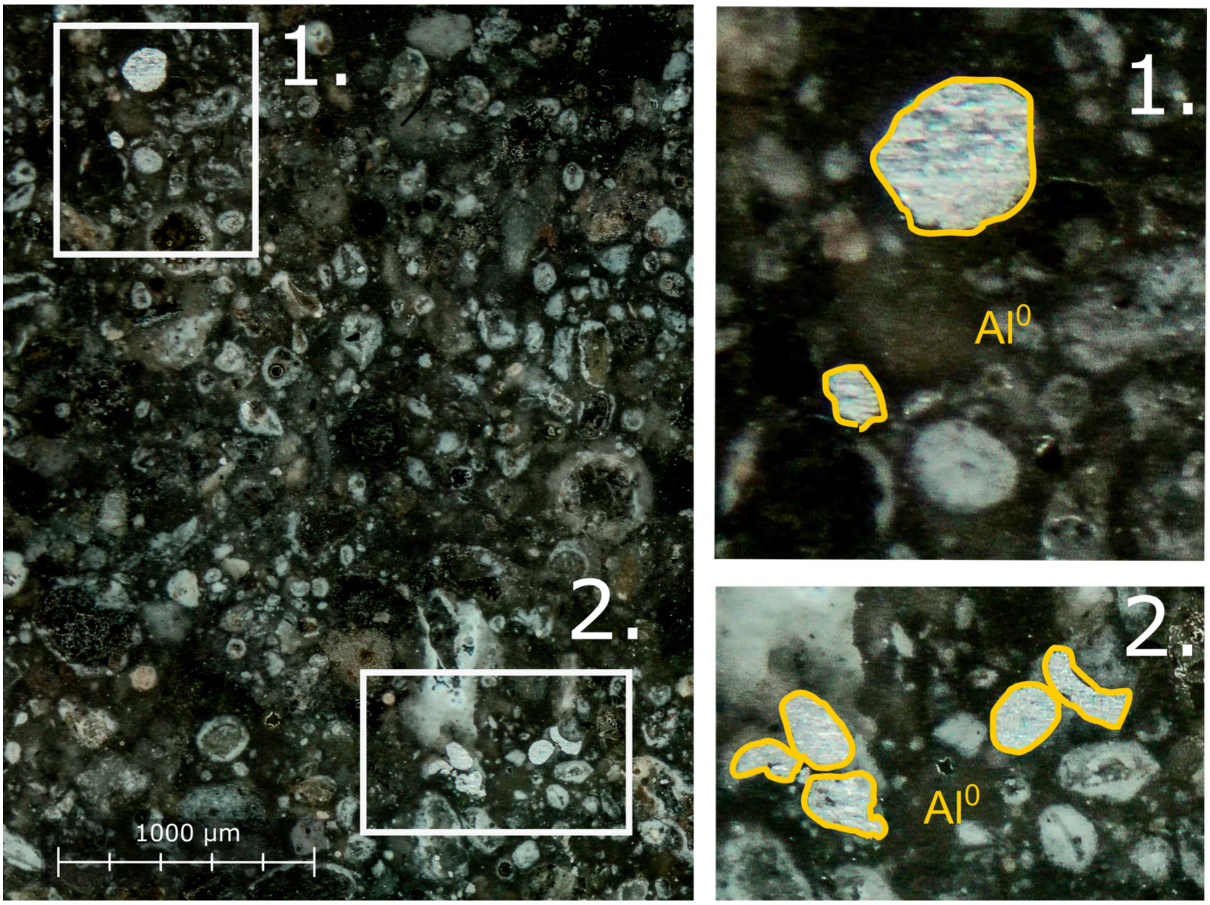


Figure A 6 Dark Field light microscopy image of arbitrary chosen area of fly ash embedded in epoxy. Seven aluminium particles with average diameter of 80 µm (max = 160 µm, min= 50 µm) can be observed. Minor aluminium particles might also be present.

10 Papers

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Variation in chemical composition of MSWI fly ash and dry scrubber residues

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ABSTRACT

Our society generates extensive amounts of municipal solid waste (MSW), which are mainly incinerated for volume reduction and energy recovery. Though, MSW incineration generates hazardous air pollution control (APC) residues that must be treated and deposited in appropriate landfills. An alternative to landfilling is material recovery, leading to regeneration of valuable products and reducing hazardous waste amounts. The chemical composition of APC residues, stemming from MSW, makes the waste attractive for metal and salt recovery, but its variation makes the development of material recovery processes challenging. This study investigates results from 895 X-ray fluorescence analyses of fly ash and dry scrubber residue samples originating from Norway and Sweden between 2006 and 2020 to explore variation in chemical composition within and between different incineration plants. The average relative standard deviation of elemental concentration in APC residue was estimated to 30% within plants. The variation in elemental concentration between grate fired incineration plants is about half of the average variation within the plants. The study also clarifies compositional differences from APC residues originating from fluidized bed incinerators and grate incinerators. Also, reported concentrations of APC residues from other countries than Sweden and Norway showed significant differences in chemical composition. The presented variations clarifies the importance of holistic approaches for waste valorization processes which can substitute stabilization processes for landfilling.

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1. Introduction

With the increase in municipal solid waste (MSW) generation and the lack of raw material availability in Europe, the importance of MSW management and material recovery is imperative. According to Eurostat, Norway and Sweden generated 739 kg and 434 kg MSW per capita in 2018, respectively. This makes Norway among the largest producers of MSW in Europe, whereas Sweden lies at the European average. MSW incineration (MSWI) has become the standard method for treating MSW with its benefit of 95% volume reduction and additional energy recovery. During the incineration process, volatile metals, halogenide compounds and persistent organic tend to mobilize into the flue gas (varying with their volatile character). Consequently, solid matter originating from the flue gas cleaning system is high in concentration of toxic pollutants and is therefore deposited in appropriate landfills.

The International Ash Working Group (IAWG) (1997) defined fly ash (FA) as collected flue gas dust prior to any sorbents and reagent injection in the flue gas cleaning system. In comparison, air pollution control (APC) residues are defined as residues originating from dry scrubbers, semi-dry scrubbers and wet scrubber systems. In this article, the definition presented by IAWG is used for designating FA, dry/semi-dry scrubber residues are referred to as DS residues, and APC residues is used as a collective term for all solid residues from air pollution cleaning systems. The term APC residues is also used to design residues that are a combination of FA and DS residues or used when there are uncertainties about the residues' origin. FA usually originates from a wet-scrubber system

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Abbreviations: APC, air pollution control residues; BFB, bubbling fluidized bed; CFB, circulating fluidized bed; DS, dry/semi-dry scrubber; EO, extreme outliers; FA, fly ash; FB, fluidized bed incinerators; FB-APC, air pollution control residues from fluidized bed incinerators; G, grate incinerators; G-DS, dry scrubber residues from grate incinerators; G-FA, fly ash from grate incinerators; IAWG, International Ash Working Group; MSW, municipal solid waste; MSWI, municipal solid waste incineration; RSD, relative standard deviation; SD, standard deviation; WS, wet scrubber; XRF, X-ray fluorescence analysis.

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where electrostatic precipitators remove all particular matter before the flue gas enters a wet scrubber. For grate incinerators, the acronyms G-FA and G-DS are used for FA and DS residues, respectively. For APC residues from fluidized bed incinerators, the acronym FB-APC is used.

Hazardous waste landfills may be potential sources of pollution. Because opening new landfills are costly and politically difficult, efforts have been made to valorize APC residues. Waste valorization and material recovery processes are good alternatives to landfilling with the benefits of reducing hazardous waste amounts and the generation of valuable products. Environmental benefits can justify the use of additional resources and costs. Quina et al., (2018) emphasize 4 different routes that promote recovery of secondary raw materials/products from APC residues: decontamination/detoxification, product manufacturing, practical application, and recovery of materials. All these routes are dependent on the characteristics of the APC residue, e.g. chemical composition, mineralogy, morphology and organic constituents. Huber et al., (2018) showed that a metal recovery process is the most environmentally friendly waste management strategy when comparing four different strategies in a life cycle analysis (LCA) study. One of the most uncertain parameters in the LCA model was the metal concentration in FA.

Hydrometallurgical methods have shown promising results for removal and recovery of toxic heavy metals. In Switzerland, Zn and Pb metal concentrate is recovered from FA with the FLUWA FLUREC process (Weibel et al., 2017). A large pilot plant is testing the HALOSEP® process operated by Stena Recycling A/S to recover salts at the Vestforbrændingen plant in Denmark (“Life HaloSep”, 2020). Both processes use spent acid scrubber liquor to leach metals from FA. The FLUWA FLUREC process uses metallic Zn cementation to remove less noble metal impurities and further liquid extraction and electrowinning for Zn recovery. HALOSEP® uses selective precipitation by regulating pH to separate heavy metals and a salt solution. Studies on Cu recovery utilizes solvent extraction and leaching with various solvents on Swedish fluidized bed (FB) incineration APC residues have also been performed (Karlfeldt Fedje et al., 2012; Tang, 2017; Tang and Steenari, 2015). Even though the methods mentioned above have demonstrated positive results for metal recovery, such processes can be sensitive to elemental compositional variations resulting in variable yields and challenging quality control. Elomaa et al., (2019) point out that Fe can be a costly impurity in their leaching study. The alkaline character of the residues can also offer challenges. The Ca concentration, as the largest constituent in APC residues, indicates the residues acid neutralization capacity, which is important for acid consumption when aiming for leaching at low pH. High acid consumption will be economically disadvantageous. However, leaching with concentrated solution may reduce costs by the lower total volume of aqueous solutions.

Removing highly soluble salts from APC residues might be the most uncomplicated process for material recovery, where residue reduction and reduced heavy metal mobility in deposited residues are gained. Here, Colangelo et al., (2012) have studied water consumption for washing out salts from APC residues. Further, utilizing APC residues for construction materials, which demands large amounts, would significantly decrease the volume needed for applicable landfills. Ca, Si, Al, and Fe phases present in APC residues make the residues applicable as raw materials in the cement industry (Quina et al., 2018). Here, chlorides are undesirable, but sulphates are acceptable (Moen, 2019).

The dynamic character and variation in APC residues’ chemical composition make the development of recycling and material recovery processes challenging. Such processes must be robust and withstand variations in chemical composition. The elemental composition varies with geographical regions and time (year and seasons) (Haberl et al., 2018; Ohbuchi et al., 2019; Wang et al., 2019). It also varies with incineration technology (Leckner and Lind, 2020), flue gas cleaning system (Jurczyk et al., 2016a, 2016b), upstream waste management system and downstream management (e.g. mixing of different APC fractions for storing and transport). Metals have different partitioning between bottom ash and APC residues. The partitioning is dependent, e.g. on strength of convective air flows, on vaporization of metals which again depends on temperature, the residence time in the incinerator and MSW composition that can catalyze vaporization reactions. Ruth, (1998) reports the enrichment factors (concentration in FA compared to the concentration in waste fuel) for selected metals: Cd 500, Sb 60, Zn 25, Pb 20 and Cu 3 for grate fired incinerators. The enrichment factors are significantly different in FB incinerators because the chemical conditions for gaseous species formation are different. Also, the total mass partitioning between APC residues and bottom ash is different. About 3–4% of incinerated waste ends up as APC residues and 15–20% as bottom ash in grate incinerators. In comparison, FB incinerators lead to about 8–9% APC residues and 6–7% bottom ash (Olofsson, 2006). According to Olofsson (2006), more APC residues are generated from FB incinerators, but the solid residues’ total mass is lower. Different scrubber designs with variations of reagents and adsorbents generate concentration variation. Activated carbon is usually added to remove organic pollutants and Hg prior to dust filters (Jurczyk et al., 2016b).

This article provides an overview of 895 X-ray fluorescence analyses (XRF) samples of DS residue and FA from plants in Norway and Sweden gathered from 2006 to 2020. Variation in chemical concentration of APC residues originating from incinerators with different combustion technologies and flue gas cleaning systems are explored and presented. Differences between FB-APC and G-APC, as well as differences between G-FA and G-DS, are quantified. The chemical concentrations are compared to residues from other countries for putting Scandinavian APC residue characteristics into a global perspective. We consider this important for clarifying variations that can affect holistic waste management and material recovery process strategies for APC residues. Understanding the variation of APC residues is key for developing robust material recovery processes that can handle variation in chemical composition.

2. Methodology

2.1. Data source

A data set of chemical analyses of MSWI APC residues performed by NOAH AS at the Langøya landfill in Norway is the basis for this study. NOAH AS has performed XRF of Swedish and Norwegian APC residues between 2006 and 2020. Samples are taken from incoming trucks to Langøya. These are considered representative of bulk APC residues and rather homogenous due to well mixing during the transfer from temporarily storage siloes to trucks for transportation. Most samples originate from yearly verification of toxic heavy metals and many from periods with intense XRF analyses for technology development. The number of samples per year does hence vary.

Table 1 gives an overview of the dataset. The data represent 127 000 tons per year of MSWI residues which is the amount of residues delivered annually from all plants considered in 2017–2020. The plants are denoted with the letters A-Z. There are 310 samples of G-DS residues (all lime-based), 165 samples of G-FA, 65 samples of G-APC residues and 355 of various FB-APC residues. Further, circulating fluidized bed (CFB) and bubbling fluidized bed (BFB) combustion technologies are differentiated, as for dry scrubber

Table 1
Overview of dataset, where FA is fly ash, DS is dry scrubber, SDS is semi dry scrubber, WS is wet scrubber filter cake.

Plant	MSWI incineration technology	Type of MSWI residue	# XRF samples	XRF sampling years	Yearly tonnage waste delivered to Langøya in the period between 2017 and 2020
A	Grate	DS	44	2006–2020	5800
B	Grate	DS	43	2005–2020	3600
C	Grate	DS	20	2007–2020	1200
D	Grate	DS	18	2006–2020	1600
E	Grate	DS	64	2006–2020	16,600
F	Grate	DS	18	2006–2020	1800
G	Grate	SDS	38	2015–2017	–
H	Grate	DS/SDS	18	2010–2020	2600
I	Grate	SDS	18	2011–2020	2700
J	Grate	DS/SDS	14	2009–2020	800
K	Grate	DS/SDS	15	2009–2020	3500
L	Grate	FA	30	2008–2020	2800
M	Grate	FA	41	2007–2020	13,700
N	Grate	FA	18	2006–2020	1400
O	Grate	FA	45	2007–2020	1900
P	Grate	FA	31	2006–2015	–
Q	Grate	SDS/FA	15	2006–2015	–
R	Grate	SDS/FA	38	2010–2020	6400
S	Grate	SDS/WS	12	2010–2020	1900
T	FB (CFB)	SDS	121	2014–2020	24,500
U	FB (CFB)	SDS	29	2015–2020	5800
V	FB (CFB)	SDS	40	2015–2020	7300
W	FB (BFB)	DS	28	2011–2020	6100
X	FB (BFB)	Unknown	72	2009–2020	8100
Y	FB (BFB)	DS	46	2007–2020	3300
Z	FB (BFB)	DS	19	2008–2020	4000

residues (DS) and semi-dry scrubber (SDS) residues. Elsewhere in this article, CFB and BFB are combined, and so are DS and SDS. Before 2017, samples were analyzed with a loose powder XRF while samples from after 2017 were analyzed with pelletized powder XRF.

2.2. Descriptive statistics

The residues from the different plants were grouped into DS from grate incinerators (Plants A-K, Table 1), FA from grate incinerators (Plants L-P, Table 1), mixed APC residues from grate incinerators (Plants Q-S, Table 1) and APC residues from FB incinerators (Plants T-Z, Table 1). Mean elemental concentration with standard deviations (SD) were calculated for each group after extreme outliers were removed. The extreme outlier criterion was: $X < Q1 - IQR \times 3$ or $X > Q3 + IQR \times 3$, where X is the elemental concentration, Q1 is the lower quartile, Q3 is the upper quartile and IQR = Q3 – Q1. The normality of the distributions of the elemental concentrations for each group was checked visually with normal probability plots and tested with the Shapiro-Wilk test. A robust principal component analysis (PCA) was performed in order to see variations between the groups in a multivariate system. The software package R 4.03 with robustPCA from the package pcaMethods (v1.64.0) was used.

2.3. Variation due to MSWI technology

The mean elemental concentrations of MSWI APC residues originating from grate incinerators were compared with those originating from FB incinerators to explore differences emerging from different combustion technologies. The distribution in G-DS, G-DS, and FB-APC concentration are presented in density plots (kernel smoothed) in the results chapter. Wilcoxon tests were also executed, shown in the Appendix. The same procedure was followed for the mean elemental concentration of G-DS, which were compared with G-FA to compare APC residues originating from different flue gas cleaning systems.

2.4. Geographical variation

The XRF data from different MSWI technologies and flue gas cleaning systems were compared with literature data to highlight the geographical variations in chemical composition. Three different sources were selected for comparison: First a comprehensive overview of FA and DS residues from 1997 illustrating time variation (The International Ash Working Group (IAWG), 1997); secondly, the comprehensive overview of heavy metals from Chinese grate incinerator and FB incinerator APC residues (Wang et al., 2019); and third, studies related to the Zn recovery process FLUWA FLUREC in Switzerland (Weibel et al., 2018, 2017). The number of samples for each source is about 40 (varying with the element), about 200 (varying with the element) and four samples, respectively.

2.5. Other variations

Variations between plants that are not subjected to geographical or principal technological characteristics were explored. These variations originate, e.g. from the number of incineration lines at a plant, from changes in fuel composition in short and longer perspectives and from different designs of flue gas cleaning system. After removing extreme outliers (same as previous criteria) from samples originating from each plant within the groups (G-FA, G-DS, and FB-APC), the average standard deviation was calculated as a measure of the variation within plants. The average standard deviation in a group was compared to an estimate of the variation between the plants in the group. The latter estimate denoted τ was obtained using a one-way random-effects ANOVA model, as explained in Appendix E. This was done in order to compare the variation of APC residues within and between plants.

Elements with a large potential for material recovery and elements with the most extensive variations in either technology, geography or time were presented for all statistical analyses. V, As, Ag, Co, Ni, and Mo had too low concentrations to be reliable for the XRF method and were therefore excluded from the analyses. The Appendix contains more comprehensive results, normal probability plots, mean elemental concentrations for the plants, estimates of the variation between the grouped plants, and statistical hypothesis testing results.

3. Results and discussion

The mean concentration, standard deviation, relative standard deviation, number of removed outliers and the number of samples for selected elements are presented in Table 2. Fig. 1 B-D presents boxplots ordered from highest to lowest elemental concentration. Regarding the highest concentrations over 10 wt%, both Ca and Cl concentrations can be found in G-FA and G-DS (B and C), while only Ca can be found in FB-APC (D). Regarding concentrations between 0.1 and 1 wt%, Na, K, S, Si, Al, and Zn are found in G-DS and G-FA while Cl, Si, Al, Na, Fe, S and K are found in FB-APC. Elemental concentrations of Cu, Zn and Pb, are between 0.01 and 0.1 wt% for FB-APC. The Cu concentrations are lower than 0.01 wt% for G-DS and G-FA. Cu and Fe have the most extreme outliers for grate incineration residues, while Si, Al and S have the most outliers from FB-APC residues (Table 2).

The PCA (Fig. 1A) shows an apparent clustering of samples from the grouped incineration technologies and explains 67.3% of the variance (47.8% for the first principal component and 19.5% for the second component). The first principal component (PC1) separates the difference between G-APC residues and FB-APC residues, and a high score is decided by the high concentrations of non-volatile elements (Cu, Fe, Al, Ba, Si, Ti, Cr and P). FA and DS scrubber residues from grate incinerators are separated into two clusters by the second principal component (PC2). High PC2 scores are decided by high concentrations of volatile elements (e.g. Sb, Cd, S, Zn, K, Sn and Pb) and relatively lower Ca and Cl concentrations. In Fig. 1 A, green colour is G-APC residues not covered by G-DS and G-FA and represent plant Q-S in Table 1. These samples are more closely linked with DS residue than FA. The FB-APC residues clustering into several groups in the PC1 direction indicates a large variation in FB residues from plant to plant. This difference comes from the different FB combustion technologies (variations of CFB and BFB) and flue gas cleaning system.

Normal probability plots for the elemental distributions in the groups G-DS, G-FA and FB-APC and the results of Shapiro-Wilks test for normality are given in Appendix B. Most elemental distributions deviate significantly from the normal distribution. The most considerable deviations from normality are found in the FB-APC group, followed by the G-DS group. Elements with the most significant deviation from normality are Al, Ba, Fe, P, S, and Si for grate incinerators. The deviations are generally high for FB-APC elemental concentration. Density plots with mean concentration marked are given for selected elements in Figs. 2 and 3 and for all elements in Appendix C. These figures show that mean concentration is a good measure of centrality for the distributions.

3.1. Variation due to MSWI technology

3.1.1. Combustion technology

FB-APC residues have significantly higher mean elemental concentrations of non-volatile metals compared to G-APC residues. Cu, Fe, Al, Ba, Si, Ti, Cr and P show higher concentration by the first principal component in Fig. 1 A. The mean elemental concentration ratios for FB-APC versus G-FA and G-DS are highest for elements in the following order: Cu (6.8 and 4.4), Fe (4.1 and 2.3), Al (4.4 and 1.8) and Ba (3.0 and 1.6). The differences are also apparent for Ti (2.9 and 1.2), Si (2.8 and 1.2) and Cr (2.1 and 0.9). In contrast, the elemental concentrations are much higher for volatile elements in G incinerators compared to FB incinerators. The mean elemental concentration ratios for G-FA and G-DS versus FB-APC are K (3.7 and 1.9), Cd (2.5 and 2.0), Na (3.2 and 1.9), Sb (2.5 and 2.0), Cl (1.7 and 2.1), Zn (2.3 and 1.6), Sn (2.0 and 1.3) and S (1.7 and 1.4). The differences are clearly seen in density plots in Fig. 2. Figures for all elements are found in attached Appendix C.

The difference between FB-APC and G-APC can be explained by the different elemental partitioning between bottom ash and APC residues. For FB combustion, a larger portion of residues ending up in the flue gas cleaning system is due to more turbulent conventions leading to higher concentrations of non-volatile elements in APC residues. Metallic Al concentrations of 4–5 wt% in Swedish CFB APC residues have been reported (Östrem, 2019). This indicates that a large portion of Al in FB-APC is in the metallic state. This can give rise to special residue properties as metallic Al has a high reduction potential. Some Si and Al may come from the bed material (sand) that end up in the flue gas.

Another key difference for the combustion technologies is the difference in chemical condition for volatilization. FB operates at lower temperatures than grate incinerators. Nonetheless, the operating temperature depends on the plant design and can vary significantly. One FB plant included in this study reports incineration temperatures around 500 °C. It is also reported that typical temperatures is 850 °C for FB incinerators compared to <1100 °C in grate incinerators (Leckner and Lind, 2020). Lower temperatures in FB incinerators result in lower up-concentration of volatiles. The vaporization kinetics and equilibrium are very dependent on temperature. Different kinetics and equilibrium below and above 750 °C have been reported (Falcoz et al., 2009; Rio et al., 2007). The low temperature in FB hinders heavy metals like Cd, Pb and Zn to be volatilized in contrast to grate incinerators which have

Table 2
Descriptive statistics of dataset. Concentrations are in mg/kg. SD is standard deviation, RSD is relative standard deviation, EO is number of extreme outliers and n is number of samples. Mean, SD and RSD is calculated from groups trimmed for EO.

		Cu	Pb	Zn	Cd	Sb	Sn	Cr	Fe	Ca	Si	Al	S	Cl	Na	K
G-FA	Mean	1200	2900	15,900	200	800	900	500	11,000	187,200	37,700	17,300	39,000	118,200	84,900	51,200
	SD	260	980	5250	50	270	200	130	3970	42,040	15,100	8730	11,790	27,100	19,260	12,530
	RSD	22%	34%	33%	25%	34%	22%	26%	36%	22%	40%	50%	30%	23%	23%	24%
	EO	8	1	0	2	2	0	0	4	1	0	0	1	1	0	0
	n	164	164	164	164	163	164	164	164	163	163	164	163	163	119	163
G-DS	Mean	770	2400	10,900	110	640	490	240	6300	288,500	15,500	6900	31,000	138,700	51,400	25,700
	SD	280	970	3900	40	280	160	130	2800	46,800	11,300	7400	13,400	43,900	19,200	8400
	RSD	36%	40%	36%	37%	44%	33%	53%	44%	16%	73%	107%	43%	32%	37%	33%
	EO	4	0	0	0	0	0	3	7	2	3	0	1	0	1	1
	n	305	305	305	305	305	305	305	305	305	305	305	305	305	164	305
FB-APC	Mean	5280	2270	6950	50	340	390	500	25,680	203,950	43,700	30,710	22,500	66,900	27,230	13,550
	SD	1670	930	1890	20	110	100	150	11,430	43,930	18,860	14,150	7590	36,370	12,310	4140
	RSD	32%	41%	27%	40%	32%	26%	30%	45%	22%	43%	46%	34%	54%	45%	31%
	EO	1	5	5	3	5	2	5	3	6	10	12	14	1	0	3
	n	355	355	355	355	355	355	355	355	355	355	355	355	355	164	355

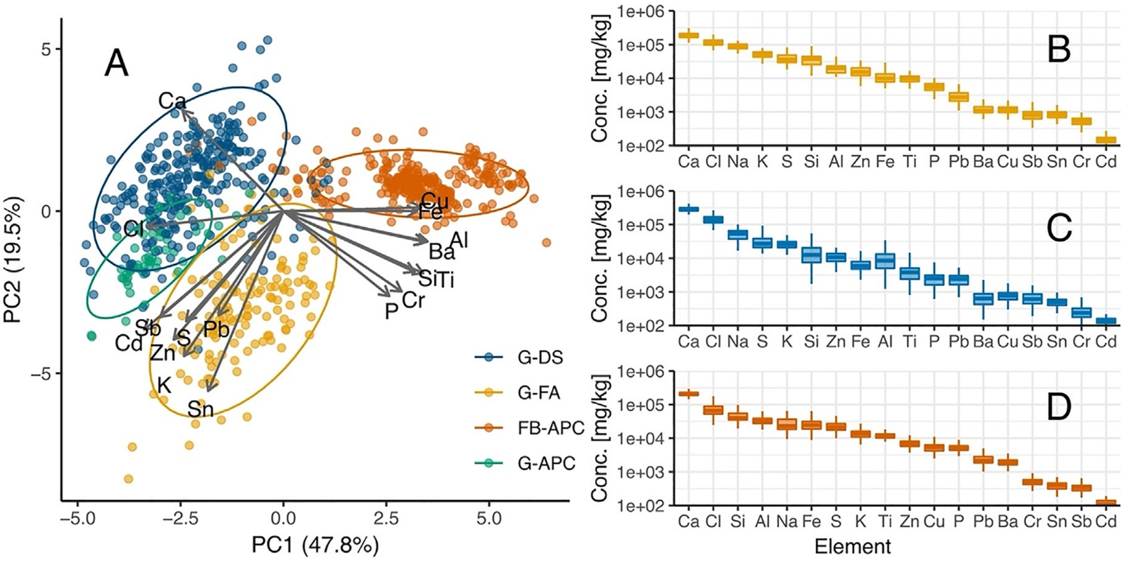

Fig. 1. A: Principal component analysis of XRF dataset. B-D: Elemental concentration ordered from highest to lowest concentration for G-FA, G-DS and FB-APC, respectively. Note logarithmic y-axis. In figure A, green are G-APC residues which are neither pure DS nor FA, but rather a mix of different APC residues. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

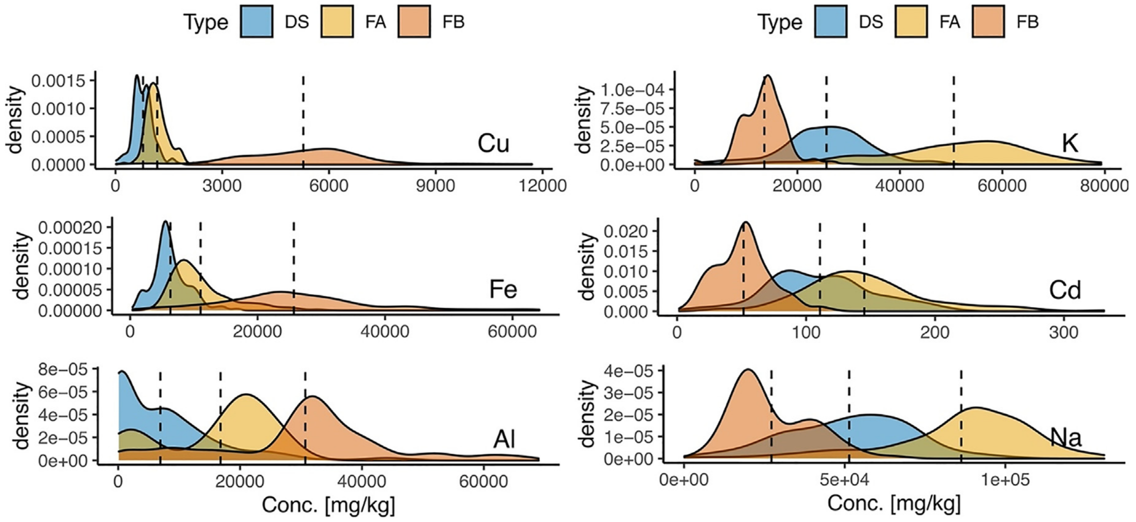

Fig. 2. Concentration distribution for elements with the highest difference between mean elemental concentration from G-APC and FB-APC, where Cu, Fe and Al are highest in FB-APC and K, Cd and Na are highest in G-APC. Stippled lines are concentration means.

higher combustion temperatures. From highest to lowest, Cd, Sb, Zn, Sn and Pb are the heavy metals with a significantly higher concentration in G-APC than FB-APC. This is the same order as elemental enrichment factor from waste to FA reported by Ruth (1998).

The alkali volatilization is very dependent on temperature (Ma et al., 2020) and alkali chlorides volatilize around 700 °C, whereas alkali carbonates and sulfates decompose around 850 °C. Char-bound alkalis also decompose significantly in the temperature range between 800 and 850 °C. The highest differences in elemental concentration between FB-APC and G-APC observed in this study are K, Cd and Na.

The high heating rate in FB incinerator retards Cl volatilization compared to the slow heating rate in grate incinerators (Liu et al., 2001; Ma et al., 2020). Experiments have also shown significantly less Cl and S volatilized at 600 °C compared to 900 °C (Watanabe et al., 2004). The difference in Cl concentration between FB-APC and G-APC reflects that lower temperature in FB incinerators does not volatilize Cl to the same extent as grate incinerators. The Cl concentration is about twice as high for G-APC compared to FB-APC.

Because of Cr's non-volatile character, a more considerable difference in concentration of FB-APC than G-APC is expected. This is, however, not observed in this study, which can indicate special Cr volatilization mechanisms in grate incinerators. Ebbinghaus (1995) show with thermodynamic modelling that Cr_2O_3 can be volatilized as $CrO_2Cl_2(g)$ with $HCl(g)$ present at typical incineration conditions.

3.1.2. Flue gas cleaning system

Only the mean elemental concentrations of Ca and Cl are higher in G-DS than in G-FA: Ca is 1.5 times higher, whereas Cl is 1.2 times higher. The lowest mean concentration ratios of G-FA versus G-DS

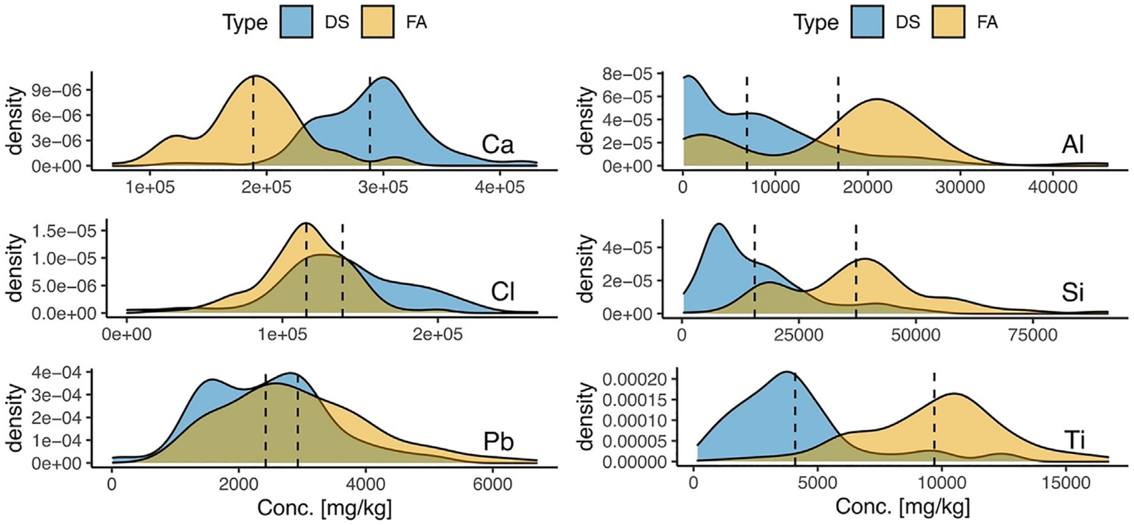

Fig. 3. Concentration distributions for elements with highest difference between mean elemental concentration from FA and DS from grate incinerators. Stippled lines are mean concentrations.

are Ca (0.6), Cl (0.9), Pb (1.2), S (1.3), Sb (1.3), Cd (1.3) and Zn (1.5). The Cu, Mg, Na, Sn, Fe, Ba and K mean concentrations of G-DS versus G-FA lie between 1.5 and 2. The highest differences are present for P, Cr, Ti, Si and Al, which lie between 2.2 and 2.4 times higher. The elements with the most considerable difference between mean elemental concentration from FA and DS from grate incinerators are presented in Fig. 3. Figures for all elements are displayed in Appendix C.

The Ca mean concentration is approximately 100 g/kg higher in DS residues compared to FA. This indicates that 10% of DS residues is added lime. The difference in Cl content illustrates the DS system's efficiency for removing HCl(g) from the flue gas. The lime addition is primarily for HCl(g) neutralization. HCl(g) is stable at low temperatures, while other gaseous species (e.g. SO_X, KCl(g), K_2SO_4 (g)) nucleates before particle filters in wet scrubber systems (Ma et al., 2020). Therefore, the concentrations of S are not higher in DS residues as regular particle filters can remove most S-based gaseous species before wet scrubbers.

The difference in elemental concentration between the two different flue gas cleaning systems can indicate which elements have the highest chance of going through a particle filter without the addition of neutralization agent, adsorbents or other reagents. This may imply that Pb, S, Sb, Cd and Zn, in that order, tend to form stable gaseous species that can penetrate regular particle filters when no reagents or neutralization agent are added for nucleation.

3.2. Geographical variations

Boxplots presenting selected elemental concentrations from this study and literature data are shown in Fig. 4. Figures for all elements considered can be found in Appendix D while the mean elemental concentrations found in literature are presented in Table 3. The Zn and Pb concentrations are approximately twice and three times higher for G-FA reported by Weibel et al. (2018, 2017) than for G-FA analyzed in this study. In Switzerland, industrial waste is commonly mixed with MSW for incineration, which results in the elevated heavy metal concertation of the generated FA (Haberl et al., 2018). he high elemental Zn concentration makes the Swizz FA more suitable for Zn recovery with, e.g. the FLUWA FLUREC process. The Swiss FA is only based on 4 different samples, which question its representativeness.

Chinese APC residues are significantly lower in heavy metals than Swedish and Norwegian APC residues. Even Cu and Cr concentrations from FB incinerators are lower than concentrations in G-FA and G-DS residues. The Chinese MSW composition differs from high-income countries where, e.g. the organic fraction is higher (Mian et al., 2017). The APC residue concentrations reported by IAWG (1997) are significantly different than the values reported in this study, in particular for heavy metals like Pb and Cd. This clarifies that the elemental concentration of APC residues changes with time due to waste fuel changes.

3.3. Other variations

The variation in chemical concentration from plant to plant and within plants can be seen in Fig. 5, where each plant's concentration distributions are presented in boxplots for selected elements. Figures for all elements can be found in Appendix E. The average relative standard deviation for the elemental concentration of G-DS plants is 28%; for G-FA plants, it is 33%, and for FB-APC plants, it is 22%. The average relative standard deviation for Ca in DS residues is about half of the other elements because Ca is added as the main element in lime-based neutralization agent in a controlled manner. The average RSD for all elemental concentrations for G-FA plants was 28%, close to RSD for all samples in the whole group (29%). The RSD for all samples in the G-DS group is 47% and is much higher than the average RSD within the plants at 33%. This indicates that there are more considerable differences between DS residues than FA residues from various plants.

The variation between plants estimated by τ (Appendix B) showed equal trends. On average, the τ estimates are 40% less than the average standard deviation for G-FA plants, while they for G-DS plants on average are 20% lower than the average standard deviation. This distinction might be explained by more considerable variations in dry/semi-dry scrubber designs compared to particular filter designs utilized before wet-scrubber systems. Also, the different reagent types may cause a larger variation for DS residues. The average τ is 40% higher than the average standard deviation per incinerator for FB-APC plants, resulting from FB technologies (e.g., CFB and BFB) and flue gas cleaning system technologies not being differentiated.

The estimate τ is obtained from a one-way random-effects ANOVA model. As seen in Appendix E, this model assumes equal

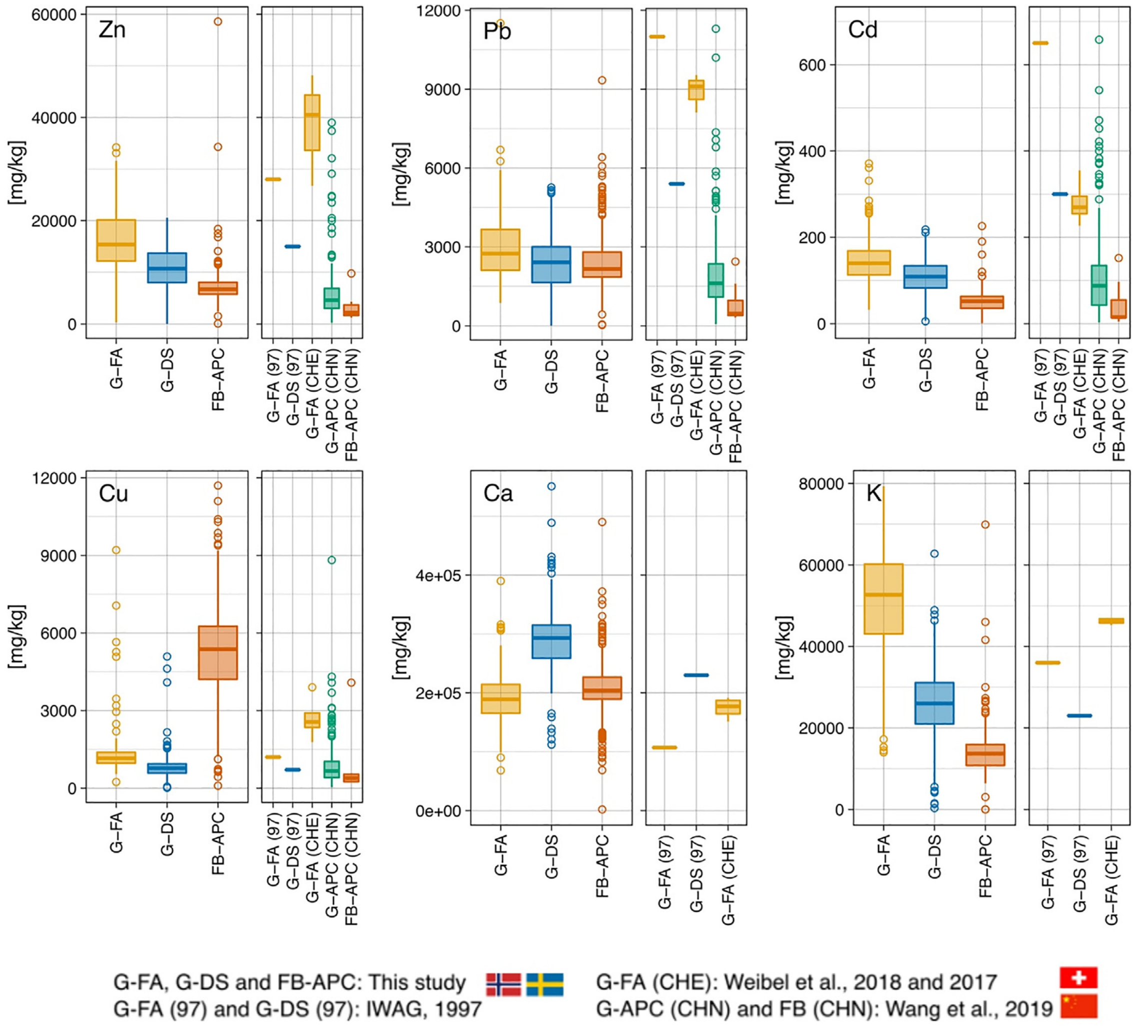

Fig. 4. Zn, Pb, Cd, Cu, Ca and K elemental concentration of APC residues from this study (left plot) and from the literature, Table 3 (right plot). G-FA, G-DS and FB-APC are represented by yellow, blue and red colours, respectively. In plots of literature data, green colour represents grate incineration APC residues. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Mean elemental concentration in mg/kg of literature data where G-FA (97) and G-DS (97) are from IAWG (1997), G-FA (CHE) is Swizz FA from Weibel et al. (2018, 2017) and G-APC (CHN) and FB (CHN) are Chinese APC residues from Wang et al. (2019).

	Cu	Pb	Zn	Cd	Sb	Sn	Cr	Fe	Ca	Si	Al	S	Cl	Na	K
G-FA (97)	1200	11,000	28,000	650	530	1400	390	25,000	107,000	160,000	71,000	26,000	74,000	31,000	36,000
G-DS (97)	710	5400	15,000	300	790	890	180	12,000	230,000	69,000	26,000	15,000	180,000	17,000	23,000
G-FA (CHE)	2699	9704	45,160	280	2699	1444	569	20,344	174,263	78,150	38,325	54,493	104,215	46,951	46,218
G-APC (CHN)	990	2004	6370	121	–	–	121	–	–	–	–	–	–	–	–
FB-APC (CHN)	718	810	3105	42	–	–	42	–	–	–	–	–	–	–	–

variances of the elemental distributions for all the grouped incineration technologies. However, this assumption is not fulfilled for most elements, as shown in Fig. 5, from the homogeneity of variance test in Appendix E and from the tests presented in Appendix B. Therefore, the exact numerical values of τ must be interpreted with care, but approximate conclusions can be drawn. Roughly, estimates show that the variation is twice as high within a grate incineration plant than between grate incineration plants – with a larger variation for DS residues than FA. In comparison, for FB-APC plants, the variation in residues are larger between plants than within the plants. Therefore, the FB-APC residues should be well differentiated with respect to different FB technologies and flue gas cleaning systems and should be further investigated. This is substantiated with the different FB-APC clustering in the PCA (Fig. 1 A).

4. Valorisation of MSWI APC residues

Zn and Cu are considered the most valuable metals in APC residues. The Zn concentrations are higher in G-FA and G-DS (1 and 1.6 g/kg, respectively) than FB-APC residues (0.7 g/kg). The mean Cu concentration is higher in FB-APC residues (0.5 g/kg) than G-

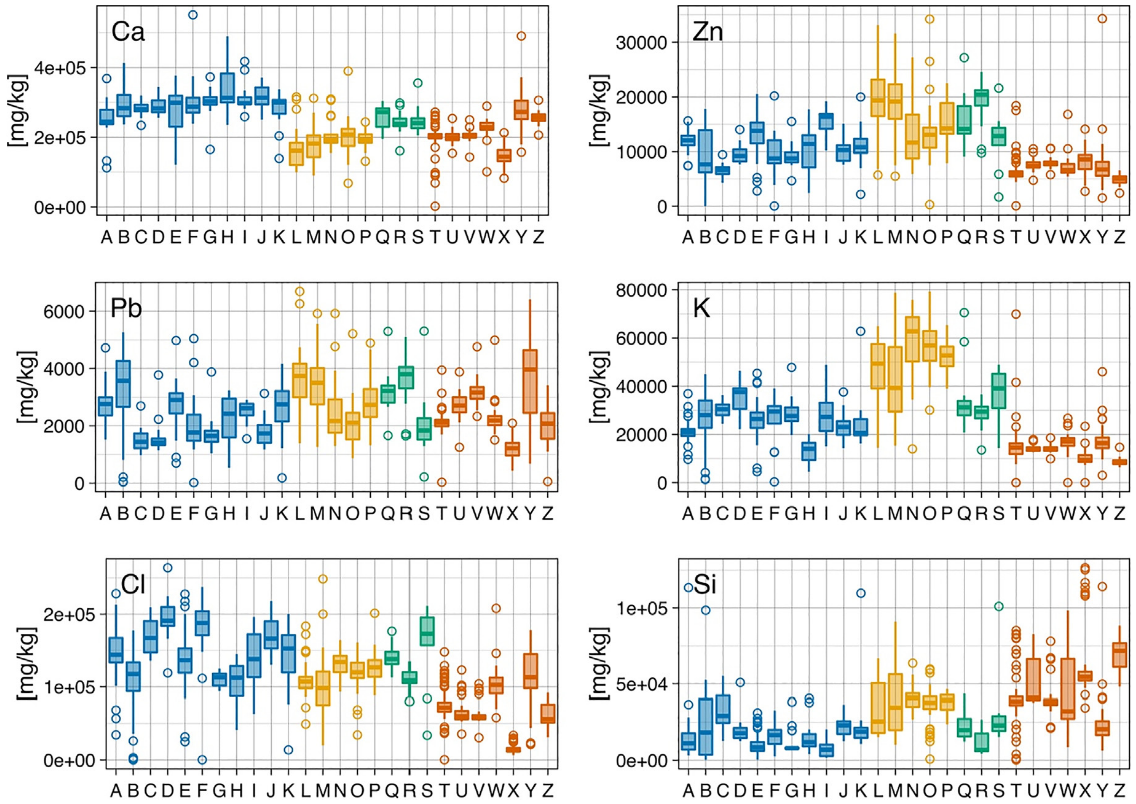

Fig. 5. Zn, Pb, Cd, Cu, Ca and K elemental concentration of APC residues from different incineration plants A-Z. G-FA, G-DS and FB-APC are represented by yellow, blue and red colours, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

DS and G-FA (average of both 0.1 g/kg). For FB-APC residues, Cu should be the target metal for recovery. However, these described metal concentrations apply to Norwegian and Swedish APC residues as a result of their MSW management systems. The variation between Scandinavian, Chinese and Swiss MSWI APC residues illustrates that metal recovery processes must be adapted to geographical location and the location's holistic waste management system.

A high acid neutralization capacity of the APC residues results from the high Ca content (G-DS 1.5 higher mean than G-FA with 28.8 wt% compared to 18.7 wt%). This results in ideal properties for neutralizing spent industrial acid, as performed at the Langøya landfill. The high Ca concentrations may also allow the residues to be processed into suitable construction materials. However, the high Ca content can be challenging in metal extraction processes as high amounts of acid must be used to reach an acid extraction regime. The mean concentrations for Cl, Na, and K are about twice as high for grate incineration APC residues than FB residues, facilitating economic salt recovery.

The variation between different APC residues is important when considering the design of a material recovery process, especially if the process shall be centralized to handle several plants' residues. Larger variation should be expected from FB-APC than from G-DS, which should be expected higher than G-FA.

It is important to emphasize that the chemical concentrations only show the potential for material recovery. The concentration of organic pollutants, inorganic speciation and mineralogy in APC residues are not specified in this study yet are necessary for understanding separation processes in material recovery processes.

5. Conclusion

This article presents representative data on chemical composition of Swedish and Norwegian MSWI APC residues from 2006 to 2020. The APC residues are categorized as G-FA, G-DS and FB-APC residues, where the variation in chemical composition is presented and quantified. These variations must be taken into account when designing material recovery processes. This study clarifies several aspects concerning differences in chemical compositions for MSWI APC residues.

First, combustion technologies give rise to significantly different APC residues. G-FA and G-DS residues have higher concentrations of volatile elements compared to FB-APC residues, typically elements with low metal or metal oxide melting temperatures. The difference is evident for K, Na, Cd, Zn, Sb and Sn. In contrast, FB-APC residues have a higher concentration of Cu, Fe, Al, Si and Cr. This is due to lower combustion temperatures and more turbulent flows in the combustion chambers, which give a more even partitioning between bottom ash and APC residues. Large variations are observed in the FB-APC and are most likely coming from the different FB combustion technologies. The characteristics of different FB-APC residues should be further investigated and differentiated.

Second, various flue gas cleaning systems also give rise to significantly different APC chemical compositions. Differences between lime-based DS residues and FA from wet scrubber systems, both from grate incinerators, are quantified. Ca and Cl concentrations are higher for DS residues, while the other elemental concentrations are higher for FA. Further, chemical compositional variations are larger for G-DS than for G-FA due to more considerable variation in DS designs than in dust filter designs for wet scrubber systems. Differences in DS and FA's chemical composition may indicate that Pb, S, Sb, Cd and Zn (in that order) tends to form stable gaseous species that can penetrate regular particle filters in wet scrubber systems.

Third, there is more considerable chemical compositional variation within MSWI plants than between MSWI plants. However, the variation between plants is significant. The variation is about twice within grate incineration plants than between grate incineration plants. The average relative standard deviation for elemental concentration within plants is 30%.

Fourth, metal recovery processes must be adapted to geographic variations, waste management systems and be robust considering chemical variation over time. The metal concentrations are significantly different for Scandinavian, Swiss and Chinese APC residues. Swiss FA is high in Zn, which is more beneficial for Zn recovery, while Chinese APC residues are low in valuable metals like Zn and Cu. The different metal concentrations of Scandinavian APC residues from 2006 to 2020 and FA reported by the IAWG (1997) illustrate the dynamic character of MSWI residues over time. Typical APC residue characteristics must be revised over time as MSW composition changes with time.

With an increased comprehension of the variation in chemical concentrations of MSWI APC residues, more insightful decisions regarding the development of material recovery processes may be taken. Hopefully, this might lead to more sustainable waste management practices for MSWI APC residues.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2021.04.007.

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Appendix

Additional figures, results and statistical hypothesis tests are presented in this Appendix. The software R 4.03 was used for all analyses. The Package *stats* version 4.0.3 was used for all statistical tests. Non-parametric methods were applied. Heatmap visualisation of p-values is presented in Figure 6.

A Continuation of tables

Table 1. Additional elements to Table 2 in article. Concentrations are in mg/kg. SD is standard deviation, RSD is relative standard deviation, EO is number of extreme outliers and n is number of samples.

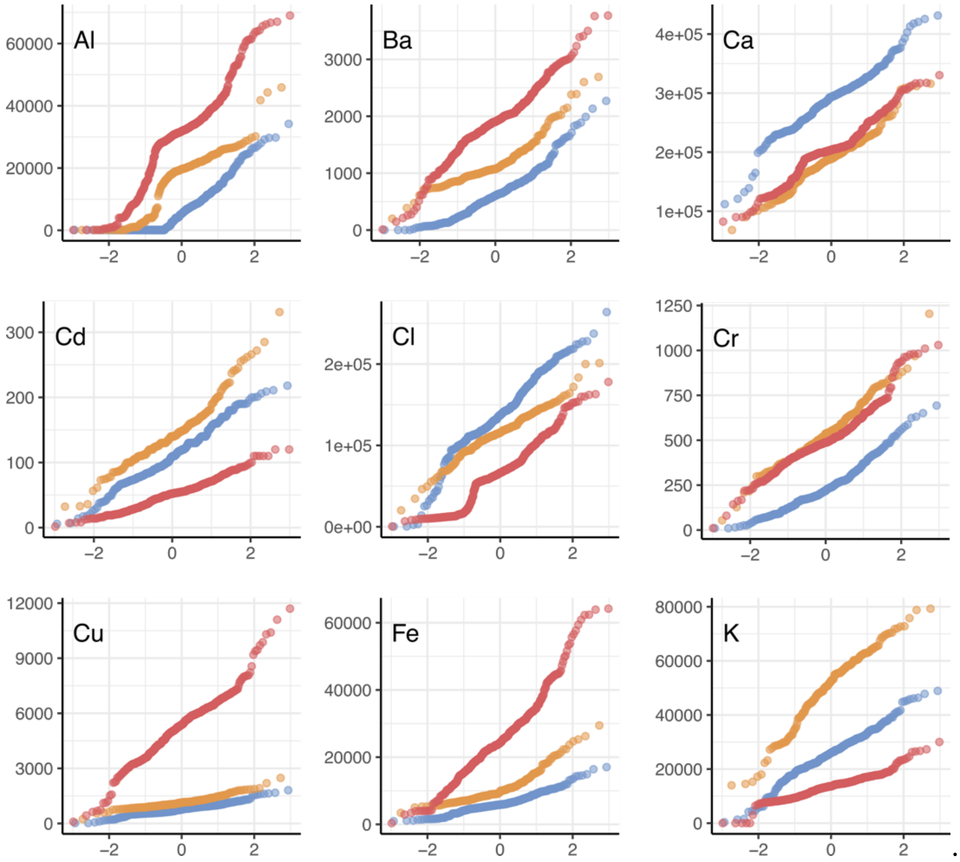
		P	Ti	Ba	Mg
G-FA	Mean	5607	9696	1193	11501
	SD	1382	2619	411	3283
	RSD	25%	27%	34%	29%
	EO	0	0	7	1
	n	163	164	164	119
G-SD	Mean	2600	4093	640	7380
	SD	1382	2619	411	3283
	RSD	53%	64%	64%	44%
	EO	2	8	7	3
	n	305	305	305	164
FB-APC	Mean	4994	11671	1895	15735
	SD	1577	2910	582	4924
	RSD	32%	25%	31%	31%
	EO	4	9	8	3
	n	355	355	355	86

B Normality and homogeneity of variance tests

Table 2. P-values for normality test (Shapiro–Wilk test)

Element	G-FA	G-DS	FB-APC
Al	3,6E-09	1,9E-16	1,8E-09
Ba	3,0E-08	1,2E-09	2,8E-05
Ca	1,2E-02	1,3E-05	3,4E-07
Cd	1,0E-04	1,3E-02	3,5E-04
Cl	4,2E-02	2,3E-05	1,5E-08
Cr	2,9E-02	7,5E-08	4,5E-09
Cu	1,7E-05	7,2E-06	1,4E-05
Fe	2,9E-10	2,5E-08	1,5E-07
K	2,9E-03	5,4E-03	4,8E-08
Mg	7,6E-01	1,0E-06	1,2E-02
Na	6,2E-06	5,1E-01	1,8E-04

P	7,7E-01	8,1E-13	1,9E-08
Pb	4,2E-04	8,2E-04	2,3E-09
S	1,2E-05	3,5E-13	1,8E-12
Sb	8,0E-04	1,0E-04	5,0E-09
Si	2,0E-04	1,1E-14	2,2E-09
Sn	1,3E-01	9,0E-05	1,5E-01
Ti	1,5E-01	1,5E-14	4,6E-10
Zn	3,3E-02	2,5E-01	1,0E-06



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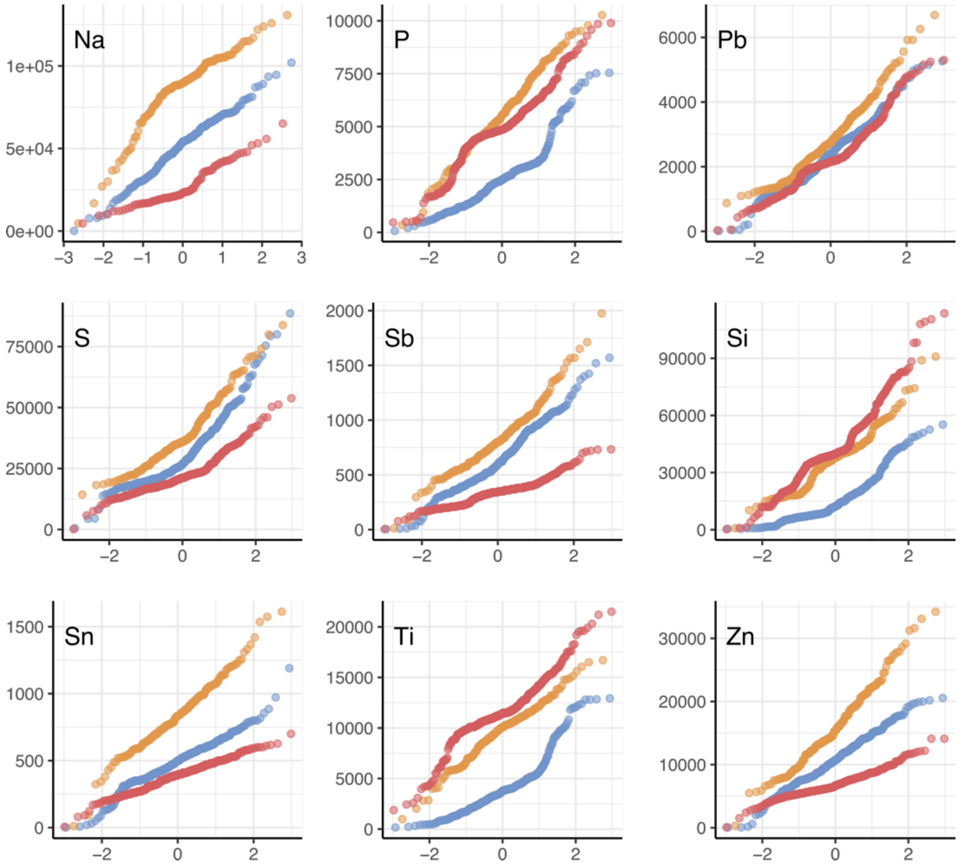


Figure 1. Normal probability plots for elemental concentration trimmed for extreme outliers for G-FA (yellow), G-DS (blue) and FB-APC (red) residues. Y-axis is elemental concentration in mg/kg and x-axis normalized quantiles.

Table 3. Flinger-Killeen test of homogeneity of variance. Null Hypothesis: All populations variances are equal. **Alternative Hypothesis:** At least two of them differ.

Element	Plants in G-DS	Plants in G-FA	Plants in FB-APC
Al	5E-13	4E-07	4E-03
Ba	4E-09	1E-03	2E-03
Ca	2E-05	3E-03	1E-08
Cd	2E-03	2E-01	6E-10
Cl	2E-04	6E-02	2E-13
Cr	3E-10	5E-01	1E-08
Cu	3E-08	3E-04	6E-06
Fe	2E-09	9E-08	1E-10
K	2E-05	1E-04	9E-07
Mg	4E-02	7E-02	2E-02
Na	9E-01	5E-03	6E-02
P	8E-21	2E-02	2E-12
Pb	1E-09	5E-01	5E-21
S	5E-10	1E-01	4E-06
Sb	2E-05	3E-02	5E-11

Si	4E-14	3E-08	3E-04
Sn	3E-05	1E-01	3E-03
Ti	5E-13	5E-02	6E-14
Zn	7E-06	7E-02	6E-11

C Mean comparisons – tests and all figures

Table 4. P-values for Wilcoxon test for pairwise mean elemental concentration comparisons of G-FA, G-DS and FB-APC.

Element	G-FA/ G-DS	G-FA/ FB-APC	FB-APC/ DS
Al	2E-24	1E-31	1E-76
Ba	2E-36	2E-36	4E-87
Ca	6E-55	3E-05	2E-74
Cd	1E-13	2E-66	4E-73
Cl	3E-11	3E-38	6E-70
Cr	3E-52	9E-03	4E-74
Cu	1E-33	2E-67	3E-103
Fe	8E-33	6E-46	5E-91
K	7E-52	7E-72	1E-72
Mg	1E-25	9E-14	2E-27
Na	8E-28	2E-30	1E-19
P	5E-45	4E-04	7E-60
Pb	2E-05	2E-10	2E-02
S	2E-11	2E-42	2E-21
Sb	5E-11	2E-62	9E-57
Si	6E-41	5E-04	4E-71
Sn	8E-45	7E-65	6E-23
Ti	3E-49	4E-13	6E-88
Zn	1E-20	5E-59	1E-46

Table 5. P-values for test of equal mean elemental concentration of plants within G-DS, G-FA and FB-APC (Kruskal Wallis-test).

Elements	Plants in G-DS	Plants in G-FA	Plants in FB-APC
Al	1,0E-20	2,3E-04	1,1E-26
Ba	5,3E-07	1,0E-02	1,9E-28
Ca	7,8E-09	4,5E-04	2,2E-46
Cd	2,6E-23	1,3E-05	5,7E-41
Cl	4,7E-24	2,2E-06	1,1E-48

Cr	2,7E-19	1,1E-11	3,7E-21
Cu	1,4E-15	7,8E-14	1,8E-27
Fe	4,5E-11	3,8E-17	7,3E-44
K	1,6E-19	8,5E-06	3,2E-30
Mg	3,9E-10	1,2E-01	9,7E-08
Na	1,6E-06	5,0E-05	8,2E-05
P	1,4E-22	2,8E-19	9,7E-34
Pb	3,3E-22	9,9E-12	3,7E-47
S	2,0E-12	5,1E-06	5,9E-16
Sb	1,6E-25	8,0E-06	6,8E-31
Si	5,1E-15	3,3E-01	6,8E-35
Sn	7,3E-17	4,2E-12	2,6E-39
Ti	1,0E-14	4,6E-13	2,6E-18
Zn	1,0E-20	1,8E-07	5,0E-24

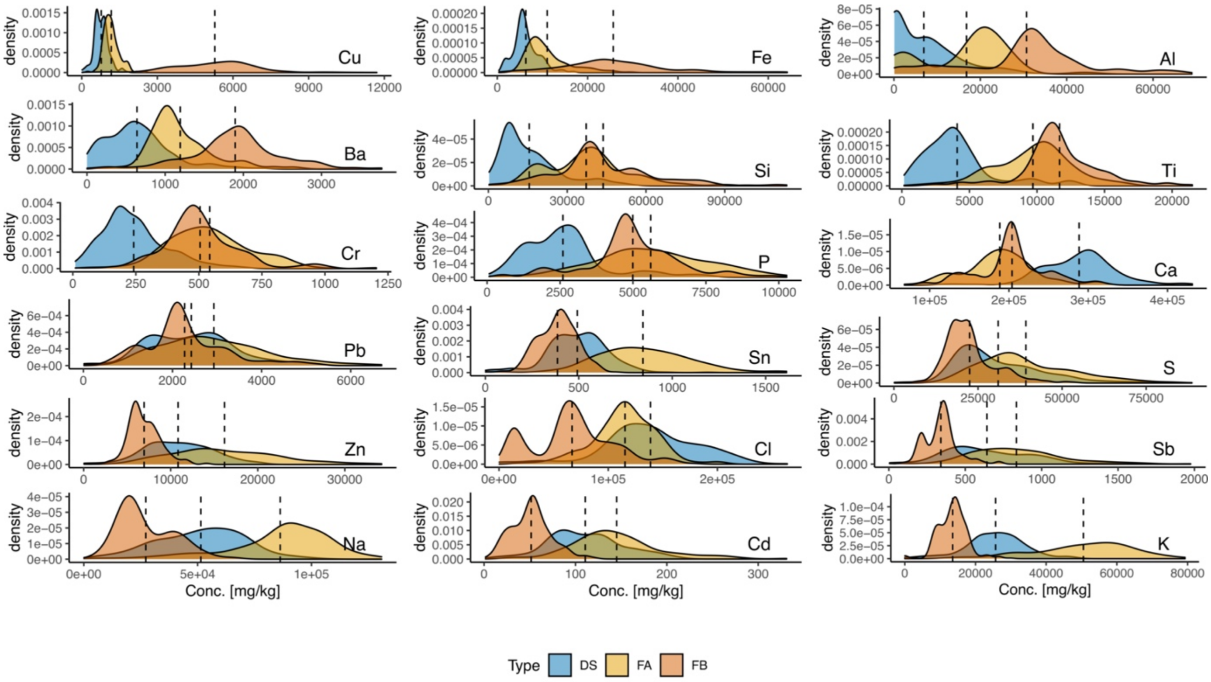


Figure 2. Density plots for G-DS, G-FA and FB-APC ordered from largest difference in mean between FB-APC and G-APC residues. Mean concentrations is marked with stippled lines.

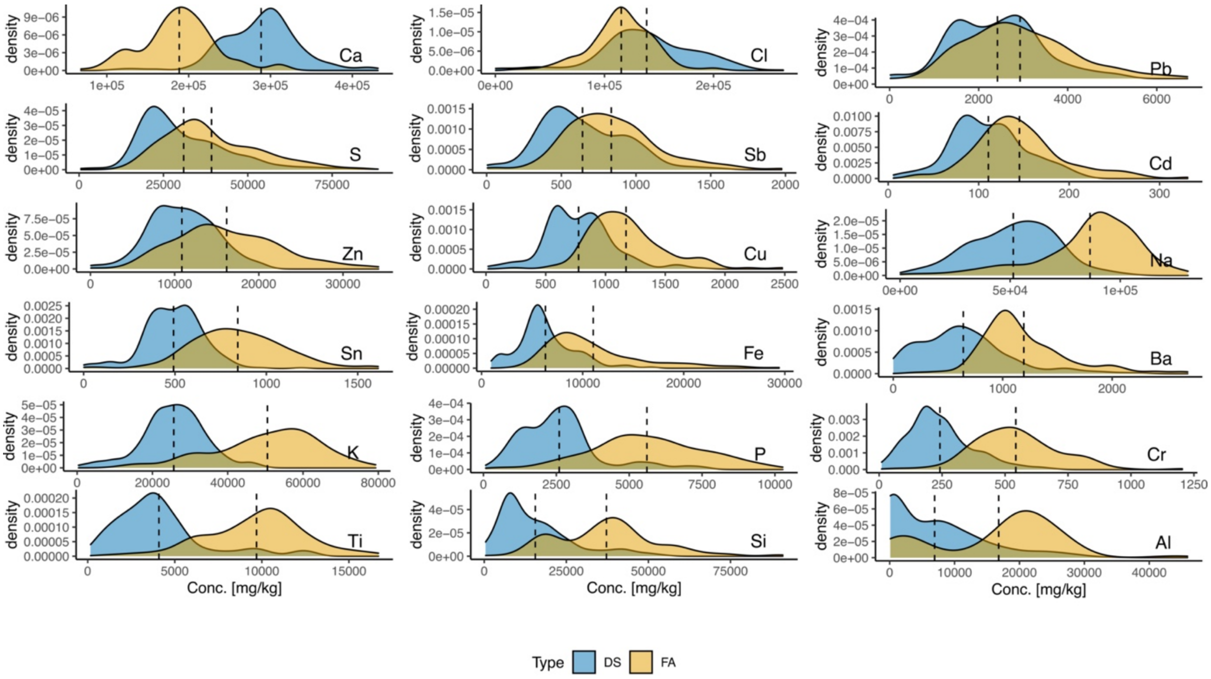
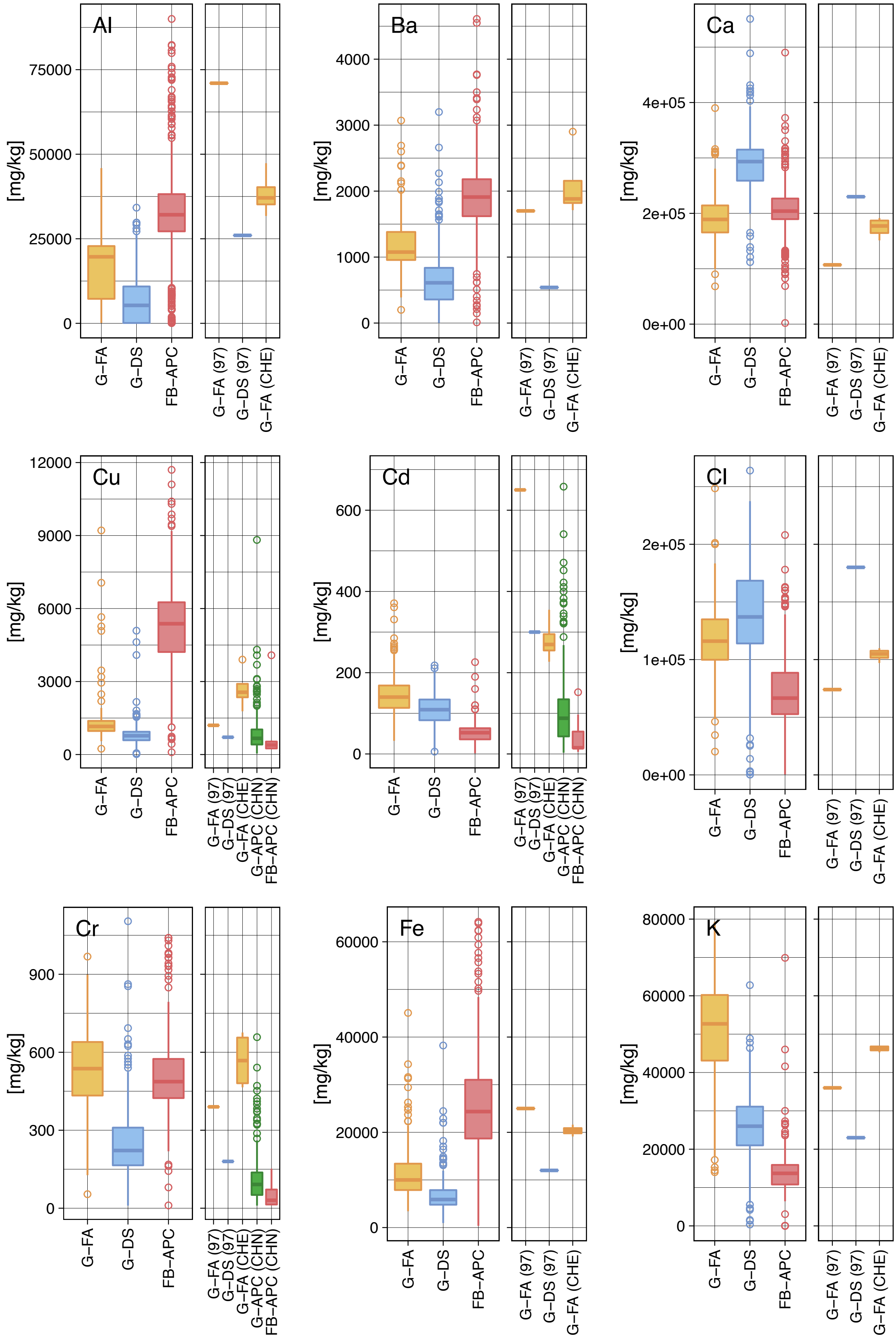


Figure 3. Density plots for G-DS and G-FA ordered from largest difference in mean between G-DS and G-FA. Mean concentrations is marked with stippled lines.

D Geographical variation – all figures



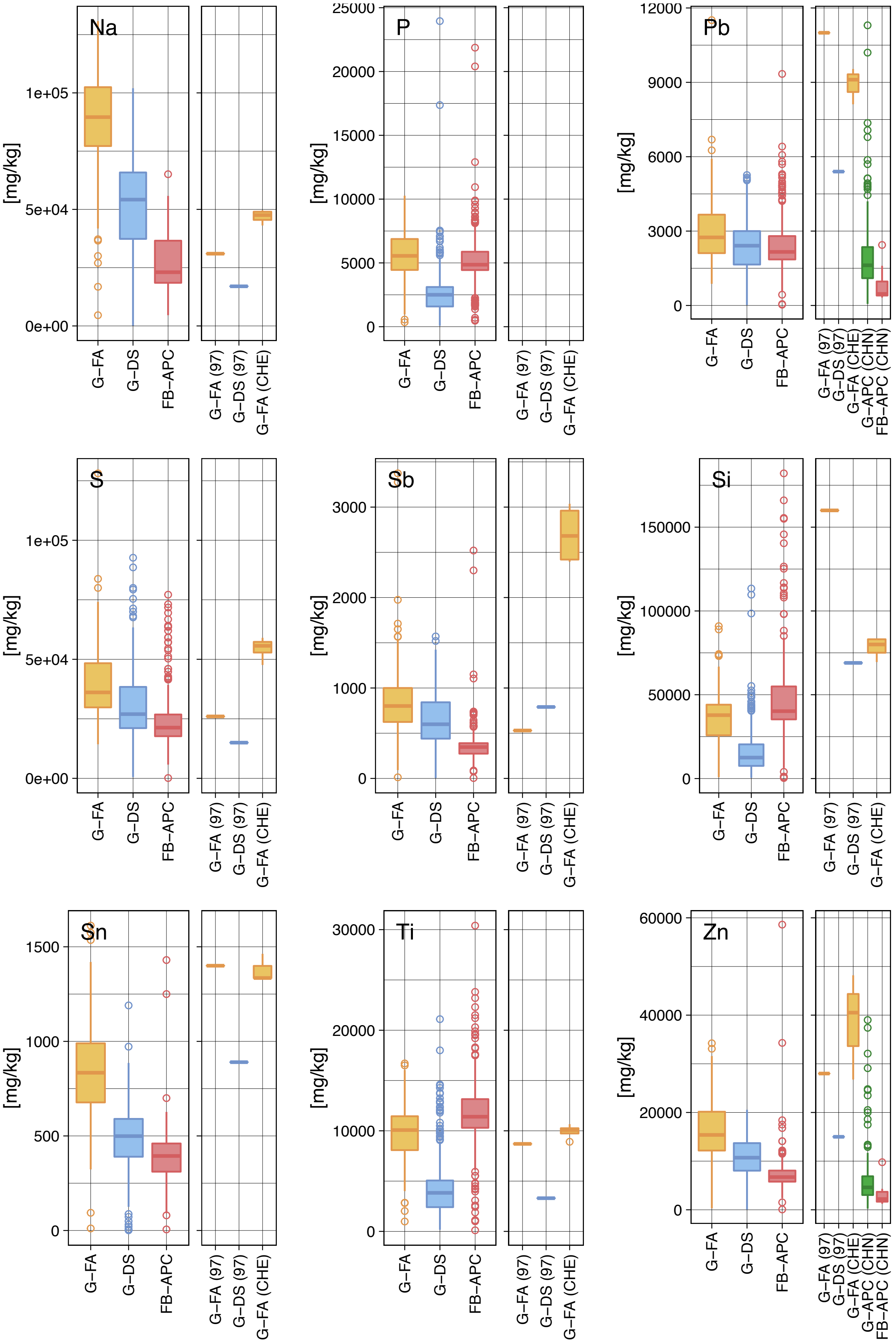


Figure 4. Elemental concentration of APC residues from this study (left plot) and from the literature, Table 3 (right plot). G-FA, G-DS and FB-APC are represented by yellow, blue and red colours, respectively. In plot of literature data, green colour represents grate incineration APC residues.

E Other variation – method, results and all figures

a. τ – measure for variation between plants

We consider a one-way random effects ANOVA model for the elemental concentrations from a group of k incineration plants. For plant number i we have a sample of n_i concentration measurements, and it is assumed that the j-th of these observations may be written as

$$X_{ij} = \mu + V_i + e_{ij}, \qquad \text{(I)}$$

where all the random variables V_i and e_{ij} are independent with mean zero. The standard deviation of the random effects V_i is a measure of the variation between the incineration plants. This standard deviation may be estimated by

$$\tau = \sqrt{\frac{\sum_{i=1}^{k} n_i(\overline{X}_i - \overline{X})^2 - (k-1)S^2}{N - \frac{\sum_{i=1}^{k} n_i^2}{N}}}\,, \qquad \text{(II)}$$

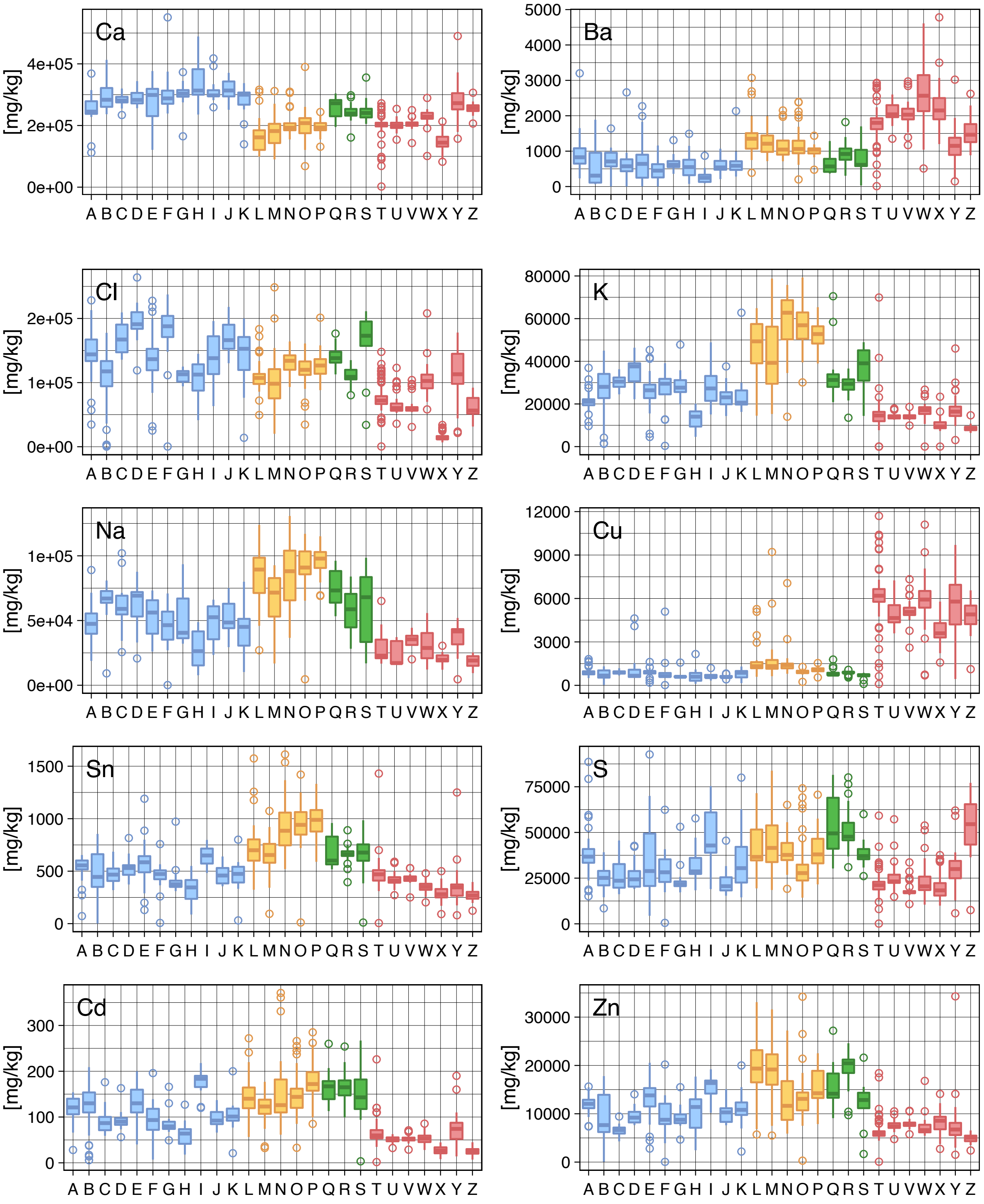
where $\overline{X}_i$ and $\overline{X}$ are the means of the observations from plant *i* and all plants, respectively, $N = \sum_{i=1}^{k} n_i$ is the total number of observations, and $S^2 = \sum_{i=1}^{k} (n_i - 1)\, SD_i^2/(N-k)$.

b. Results – τ and average standard deviations for plants

Table 6. Tau estimator and the average of standard deviations for plants within a group.

Element	G-FA τ	G-DS τ	FB-APC τ	G-FA $\overline{SD}$	G-DS $\overline{SD}$	FB-APC $\overline{SD}$
Al	4100	4600	11000	7900	4600	6700
Ba	100	130	400	360	310	400
Ca	11300	21600	45400	39000	35100	21400
Cd	20	30	20	50	30	10
Cl	11300	28000	36300	24000	32400	15100
Cr	100	90	80	130	90	120
Cu	200	120	1000	250	230	1100
Fe	4000	1400	9700	3300	2200	6700
K	6300	5000	2600	12200	6200	2400
Mg	280	2300	4900	2000	2100	3400
Na	10800	10100	8900	20200	17200	9200
P	1500	940	1400	1400	870	790
Pb	690	620	930	1000	670	580
S	6800	6800	10300	11400	10400	7100
Sb	130	190	80	260	200	80
Si	590	7000	14700	13100	7700	7800
Sn	160	80	90	210	120	70
Ti	2000	1650	1500	1900	1700	2200
Zn	3200	2400	1200	5300	2900	1400

c. *All figures*



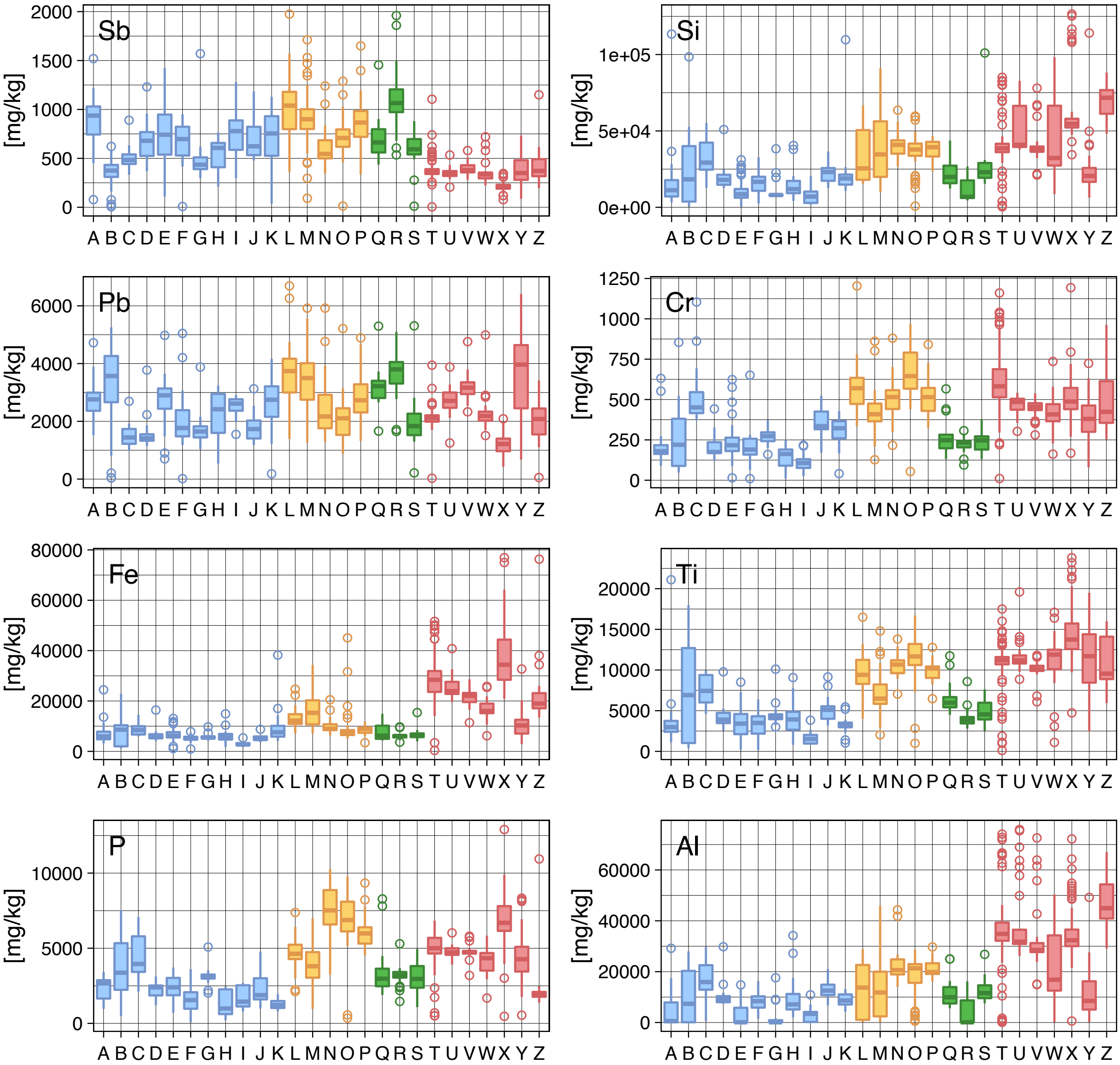


Figure 5. Boxplots of elemental concentration from each plant ordered from lowest to highest tau relative to mean of G-APC residues. Blue, yellow, green and red represent G-DS, G-FA, G-APC and FB-APC, respectively.

F Heatmap visualizations

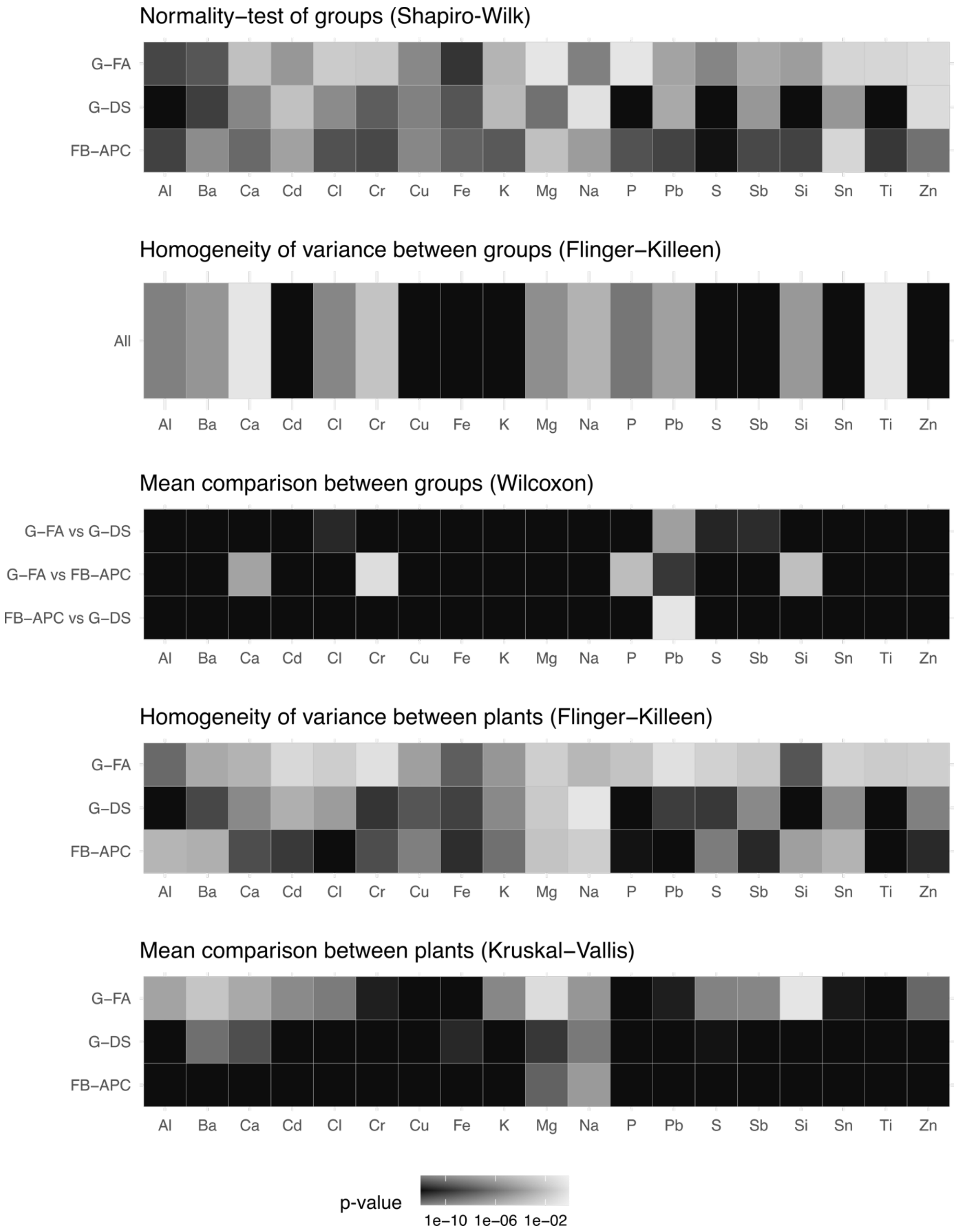


Figure 6. P-values of statistical tests presented with heat-maps.

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Article

Grade and Tonnage Comparison of Anthropogenic Raw Materials and Ores for Cu, Zn, and Pb Recovery

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Abstract: Primary metal production operates with large tonnages and takes advantage of economies of scale. Metal recycled from low-value waste streams, competing in the same global metal market as primary production, will be more competitive by also taking advantage of up-scaling. However, an overview of metal tonnages in low-value waste streams to see upscaling potential needs to be provided in the literature. In response, this study provides estimates of copper, zinc, and lead metal tonnages in waste incineration ash—A major waste stream going to landfills. Metal concentrations and tonnages are compared to tonnages and concentration grades found in ores. Copper, zinc, and lead concentration averages are about 3–5 times lower in ash compared to the worldwide average head grade of ores. Tonnages of metal in the ash generated from waste incineration in European countries bordering the Baltic and the North Sea are about 1/3 of mining metal output from Sweden, a leading mining country in the region. Therefore, incineration ash should be considered a significant potential Cu, Zn, and Pb metal source.

Keywords: MSW; MSWI; fly ash; bottom ash; copper; zinc; lead; low value waste stream; Europe; recycling; waste management

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1. Introduction

Small metal tonnages often constrain economically feasible recycling from low-value waste streams. Such recycling can be costly compared to primary metal productions, which have the advantages of economies of scale, easier transport logistics, and more homogenous raw material streams. Today, recycling is often limited to high-value metal waste streams, such as waste from electrical and electronic equipment and vehicle scrap. It is economically feasible due to the relatively easy sorting, remelting, and refining procedures. In contrast, metal recycling from low-value waste streams faces more technical challenges, similar to those facing primary metal production. Moreover, the economic benefits of large annual primary metal production tonnages often outcompete recycling from small annual tonnages of low-value waste.

Substantial amounts of anthropogenic copper, zinc, and lead are lost in waste flows going to incineration. Metals are sorted out from the waste, both before and after incineration. However, conventional physical separation methods cannot recover metals embedded in products or small-size particles [1]. Fine particle fractions go to landfills [2]. This applies to municipal solid waste incineration (MSWI) fly ash and fine particle fractions of MSWI bottom ash [3]. MSWI fly ash and MSWI bottom ash are in this paper further referred to as fly ash and bottom ash. The general term for the two is referred to as "waste ash". High concentration of heavy metals in fly ash is classified as a hazardous waste. A waste stream must be carefully treated before being deposited in special hazardous waste landfills. Hence, recycling metals from fly ash has received considerable attention for solving waste management challenges with fly ash [4], particularly since large tonnages are generated. Figure 1 shows tonnages of waste incinerated in central and northern European countries.

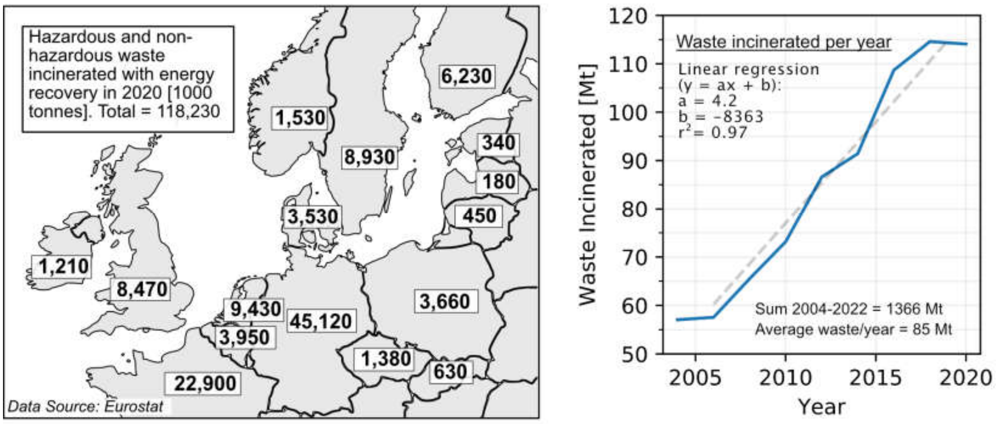

Figure 1. (**Left**): Map of northern Europe showing municipal solid waste tonnages (in thousands of tonnes) incinerated by country in 2020. (**Right**): MSW tonnages incinerated with energy recovery by year for the countries shown in the left figure. Eurostat is the source of data [5].

Today, zinc metal is recovered from one incineration plant in Switzerland using acid leaching and solvent extraction technology [6,7]. However, few other plants have implemented the technology due to high costs. One opportunity to reduce costs is processing larger ash tonnages and exploiting economies of scale at a centralized processing plant. Hence, metal recycling may be more competitive in a global metal market and contribute to meeting metal recycling goals [8]. Mapping metal tonnages in ash is essential to assessing the potential for large-scale processing. This study aims to estimate annual tonnages and concentrations of copper, zinc, and lead in waste ash, which can be compared to primary production data for comparison. This contributes to building a foundation for the qualitative assessment of an economically viable metal recycling process from waste ash competing with primary metal production.

2. Method

Waste ash copper, zinc, and lead concentrations are compared to head grades of ores rich in the same metals. Data on head grades were gathered from publicly available MDO data [9]. Fly ash concentrations are gathered from the Langøya data set (XRF of 895 ash samples) [10]. The data is available for download in supporting information. A model for estimating metal tonnages in fly ash and fines from bottom ash was built. Fines from bottom ash refer to the fine particle fraction of bottom ash. The model is based on Monte Carlo methods to consider uncertainties in input variables. Concentrations in fly ash for the tonnage estimate are based on the Langøya data set. Metal concentrations in the fines of bottom ash are assumed to be equal to those in fly ash, though literature indicates slightly higher concentrations of copper and lower concentrations of zinc [11–14]. For the metal tonnage estimates, four different cases are considered.

The first case comprises the tonnage of fly ash landfilled at Langøya annually. In 2021, 370,000 tonnes of fly ash originating from Sweden, Denmark, Norway, Ireland, and Lithuania were treated and landfilled there. Case 2 comprises fly ash as in case 1, but in addition, there are estimated amounts of fines in bottom ash originating from the same incinerators as the landfilled fly ash. The estimate is based on the ratio of fly ash to bottom ash generation from waste incineration and fractions of fines in bottom ash. The cut-off particle size for fines in bottom ash is set at 0.5 mm, as state-of-the-art physical separation methods cannot separate out smaller metallic particles than this [1]. The mass fraction of particles under 0.5 mm is derived from the average particle size distribution of bottom ash [1] (see Figure 2). This leads to a fraction making up 20% of the total bottom ash mass. Chemical selective separation methods, on the other hand, may be more appropriate than physical separation methods for metal recovery of particles larger than 0.5 mm. In addition, due to technological hindrances in treating fine particle fraction in Europe, 54 wt% of treated bottom ash went to landfills in 2018 [2]. This is considerably more than the estimated 20% derived from a 0.5 mm cut-off particle size. Tonnages for bottom ash fines in this study may therefore be an underestimation. Case 3 estimates fly ash tonnages from statistics from Eurostat [5] of waste tonnages incinerated with energy recovery from the northern European countries shown in Figure 1. Case 4 also considers estimated amounts of fines from bottom ash. The equations used for the estimates are as follows:

$$M_m = M_{FA}\, c_m \tag{1}$$

$$M_m = M_{FA}\, c_m + (f_{BA}\ / f_{FA})\, M_{FA}\, c_m \tag{2}$$

$$M_m = M_{MWS}\, f_{FA}\, c_m \tag{3}$$

$$M_m = M_{MWS}\, f_{FA}\, c_m + M_{MWS}\, f_{BA}\, f_{fines}\, c_m \tag{4}$$

Equations (1)–(4) are used for cases 1, 2, 3, and 4, respectively. M_m, M_{FA}, M_{MSW}, c_m, f_{BA}, f_{FA}, and f_{fines} stand for annual tonnage of metal, annual tonnage of fly ash, annual tonnage of municipal solid waste, concentration of metal in ash, fraction of bottom ash generated by incineration, fraction of fly ash generated by incineration, and percentage of fines in bottom ash, respectively. The input variables' descriptions and values, uncertainties (standard deviation), and references are presented in Table 1.

Table 1. Variables for the tonnage estimation model.

Variable, Symbol, [Unit]	Value	SD	Source
Cu concentration, c_{Cu}, [wt%]	0.27	0.04	Langøya data set
Zn concentration, c_{Zn}, [wt%]	1.09	0.04	Langøya data set
Pb concentration, c_{Pb}, [wt%]	0.26	0.02	Langøya data set
FA generated per MSW, f_{FA}, [%]	3.00	0.2	[15]
BA generated per MSW, f_{BA}, [%]	27.5	2	[15]
Percentage fines in BA, f_{fines}, [%]	20.00	3	[1]
MSWI fly ash at Langya, M_{FA}, [t]	350,000	–	NOAH AS [10]
MSW in northern Europe, M_{MSW}, [t]	118,200,000	–	Eurostat [5]

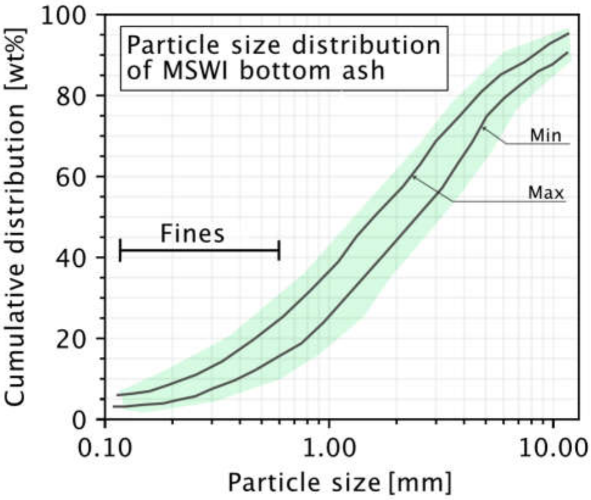

Figure 2. Typical minimum and maximum cumulative particle size distribution function of bottom ash [1], which is used to estimate tonnages of fines in bottom ash. The figure is adapted from [17], with permission from Elsevier, 2023.

Annual tonnages are compared with reference annual output tonnages from the mining industry. Sweden has one of the largest mining industries in Europe, and tonnages of mined metal outputs are used as a reference. The country has large mines for copper, zinc, and lead. Their annual metal mining outputs are 100,000 (SWE-1), 250,000 (SWE-2), and 70,000 tonnes (SWE-3) for copper, zinc, and lead, respectively [16]. In addition, the production capacities of Norwegian refineries for zinc and copper are used as tonnage comparisons. Boliden Odda (NOR-1) has a zinc production capacity of 350,000 tonnes, and Glencore Nikkelverk (NOR-2) has a production capacity of 39,000 tonnes of copper. The tonnage estimates and concentration are also compared to selected mines processing low-grade copper ores [9].

3. Results

3.1. Concentrations

Figure 3 shows boxplots of fly ash concentrations from the Langøya data set and head grade ores from mines reported in public MDO data The concentration of valuable metals is lower in fly ash compared to ore head grades. The mean copper concentration is 3.4 times lower in ash (0.27 wt%) than the average copper head ore grade (0.92 wt%), while the mean zinc concentration is 3.9 times lower (1.09 wt% compared to 4.2 wt%). The difference is even larger for lead, with a 5.3-fold lower mean concentration (0.26 wt% compared to 1.34 wt%). The median concentrations are lower than average head ore grades and concentrations in ash. This reflects the fact that portions of both raw materials have higher grades.

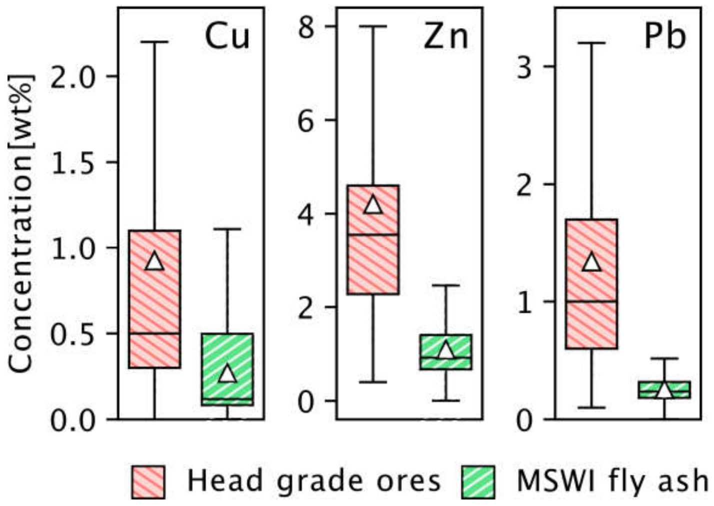

Figure 3. Boxplots of head grade ores (red) (number of mines: nCu = 219, nZn = 64, nPb = 45) and fly ash concentrations (green) (895 ash samples from 26 different plants located in Sweden and Norway). Mean concentrations are marked with a triangle. Source: 2017–2022 MDO Data Online Inc. (public data) [9] and Langøya data set [18].

The copper mean concentration of head grade ores from the MDO dataset was higher than the stated average copper ore grade, equaling 0.76%, of today's mining projects utilizing milling/flotation-based technology [19]. In addition, the global average copper ore grade is stated to be as low as 0.62% [20]. Taking this into consideration, the copper concentration in fly ash is only 2.8 and 2.3 times lower compared to the two references mentioned, respectively.

3.2. Tonnages

Annual tonnages of ash and metals in ash are presented in Table 2 with the percentages of reference tonnages. According to estimates, annual metal tonnages can be doubled by including fines from bottom ash with fly ash. This comprises case 2 compared to case 1 and case 4 compared to case 3. Uncertainties are lowest in case 1, where fly ash landfilled at Langøya is considered. Here, copper and zinc tonnages represent 1.1 ± 0.1 and 2.4 ± 0.4 percent of the production capacities of the Boliden Odda zinc refinery and the copper refinery, respectively. The highest annual ash tonnage (case 4) of 10.1 ± 1.1 million tonnes of ash is estimated to have 27,300, 110,100, and 25,800 tonnes of copper, zinc, and lead, respectively. These annual tonnages occupy large parts of the Norwegian refinery capacity (70% for copper and 31% for zinc) and are roughly equal to 1/3 of Swedish metal output from mining.

Table 2. Annual tonnage estimates of metal in incineration waste ash from four different cases. Cases 1 and 3 include only fly ash, and cases 2 and 4 include fly ash and fines in bottom ash. Cases 1 and 2 comprise ash landfilled at Langøya, while cases 2 and 3 are estimates from MSW generated from countries bordering the Baltic and North Sea. The percentage of reference tonnages from primary production is also presented.

Case	Variable	Mass Flow [t/Year]	Percentage of SWE1–3 [%] [1]	Percentage of NOR1–2 [%] [2]
Case 1: MSWI fly ash processed at Langøya	Ash	350,000	–	–
	Cu	900 ± 100	0.9 ± 0.1	2.4 ± 0.4
	Zn	3800 ± 100	1.5 ± 0.1	1.1 ± 0.1
	Pb	900 ± 100	1.3 ± 0.1	–
Case 2: Case 1 plus related bottom ash fines	Ash	995,000 ± 116,000	–	–
	Cu	2700 ± 500	2.7 ± 0.5	6.9 ± 1.3
	Zn	10,900 ± 1300	4.3 ± 0.5	3.1 ± 0.4
	Pb	2500 ± 400	3.6 ± 0.5	–
Case 3: MSWI fly ash from northern Europe	Ash	3,546,000 ± 535,000	–	–
	Cu	9600 ± 2000	9.6 ± 2.0	24.6 ± 5.2
	Zn	38,700 ± 6000	15.5 ± 2.5	11.1 ± 1.8
	Pb	9100 ± 1500	13.0 ± 2.2	–
Case 4: Case 3 plus related bottom ash fines	Ash	10,072,000 ± 1,113,000	–	–
	Cu	27,300 ± 5100	27.3 ± 5.2	70.0 ± 13.3
	Zn	110,100 ± 12,800	44.0 ± 5.3	31.4 ± 3.8
	Pb	25,800 ± 3500	36.8 ± 5.2	–

[1] SWE1 for Cu: Swedish copper mines output (100,000 t/year); SWE2 for Zn: Swedish zinc mines output (250,000 t/year); and SWE3 for Pb: Swedish lead mines output (70,000 t/year). [2] NOR1 for Cu: Glencore Nikkelverk copper production capacity (39,000 t/year); NOR2 for Zn: Boliden Odda zinc production capacity (350,000 t/year).

In 2000, about 60% of the zinc produced worldwide came from mines producing under 100,000 tonnes of zinc annually [21]. For copper, mines producing less than 50,000 tonnes of copper per year account for 16% of global production [21]. By comparing annual metal tonnage estimates from waste ash generated in northern Europe to worldwide mine sizes, waste ash can be seen as a larger zinc resource than a copper resource. Table 3 presents the head ore grades and annual production of selected operating open-pit mines that are processing low-grade copper ores. The head grades are, on average, similar to waste ash concentrations, with 0.3% compared to 0.27%. The average annual production is 63,600 tonnes of copper, which is about twice as much as the annual tonnages of copper in waste ash in northern Europe, according to the highest estimates provided in this study.

Copper and zinc concentrations vary with different types of fly ash [18]. The unequal distribution of different types of ashes landfilled at Langøya and the distribution of ash types generated in northern Europe may be a source of uncertainty in the tonnage estimate. The Langøya data set has about 20% of fly ashes coming from fluidized incinerators, where copper concentrations are higher and zinc concentrations are lower than the average. Therefore, a slight overestimation of copper (and an underestimation of zinc) may have occurred, as fluidized bed incinerators are not as common as grate incinerators. However, copper concentrations in the fines of bottom ash are, in general, higher than fly ash, and zinc is lower. That may compensate for the estimation errors and even result in overestimation.

Table 3. Selection of open-pit mines processing low-grade copper ores. Source: 2017–2022 MDO Data Online Inc. (public data) [9].

Mine	**Head Grade**	**Annual Production**
Mount Milligan Mine (CA)	0.23% Cu, 0.39 g/t Au	25,800 t Cu (2016)
Aitik Mine (SE)	0.28% Cu, 0.2 g/t Au, 2 g/t Ag	99,300 t Cu (2018)
Sierrita Mine (US)	0.23% Cu, 0.02% Mo	68,900 t Cu (2018)
Mount Polley Mine (CA)	0.38% Cu, 0.3 g/t Au, 0.9 g/t Ag	6791 t Cu (2018)
Pinto Valley Mine (US)	0.35% Cu, 0.007% Mo	58,513 t Cu (2021)
Constancia Mine (PE)	0.31% Cu, 89 g/t Mo, 0.07 g/t Au, 3.04 g/t Ag	122,178 t Cu (2018)

The cut-off particle size of 0.5 mm for defining bottom ash fines makes the tonnage estimate conservative. Considering that 54% of bottom ash fines go to landfill [2], and assuming the same copper concentration as fly ash in this fraction, the tonnage contribution from bottom ash fines would be doubled. This would result in a 1.6 times higher metal tonnage than the highest estimate presented.

Waste incineration has been ongoing for decades and large tonnages of ash have been landfilled. Subsequently, large tonnages of copper, zinc, and lead can be found in such landfills. According to Eurostat, 1366 million tonnes of waste were incinerated from 2004 to 2020 [5]. Hence, it can be estimated that on average, 6900, 26,000, and 6600 tonnes of copper, zinc, and lead have been incorporated in landfilled fly ash annually (fines in bottom ash not considered). These tonnages may be exploitable stocks for metal recovery in addition to annual waste ash flows. The accessibility of this potential resource should be further studied.

4. Discussion

Tonnages and concentration grades indicate the potential for economically feasible metal recycling. However, many other variables are essential and decisive: how easy the metals are to separate, the energy demand of extraction technology, the potential for generation of valuable by-products, the amount of generated waste that needs treatment, the ease of removing contaminants for downstream refining, transport logistics, the amount of technology development, research needed to exploit the raw materials, etc. Comparing waste ash with ores can provide qualitative considerations for using ash as a raw material for metal production. First, as in all recycling cases, environmental impacts from mining are avoided.

Metal recycling from waste ash does not need energy-consuming comminution or shredding (for example, shredding of vehicle scraps). The energy usage for comminution in mining increases as average ore grades deplete [20]. In copper mining, comminution can take up to 30–50% of the energy used to produce the final metal product [22,23]. An economic evaluation of copper extraction from copper mining tailings in Chile states that the tailing needs a grade above 0.41% to be economically viable [24]. This is another waste stream that does not require comminution. The grade is lower than the average copper concentration in fly ash originating from fluidized bed incinerators, which is 0.52% [18].

As fly ashes are classified as hazardous waste, recycling procedures can "detoxify" the ash and improve its properties for landfilling. Hence, recycling metals in waste ash can also be considered a waste management service and help reduce the fill-up rates of special hazardous waste landfills. Reduced cost by avoiding the deposition of untreated fly ash is essential for the economically feasible implementation of the zinc extraction process, FLUWA FLUREC. Economic analyses show that avoiding standard fly ash deposition makes up 61 percent of total savings [7,25]. This demonstrates the importance of the quality of processed ash for landfilling after a metal extraction process. If processed ash deteriorates regarding the metal leachability properties for landfilling, it significantly hinders achieving an economically viable process.

Transport logistics may be more challenging in waste ash processing than in primary metal production, as ash generation is distributed over larger areas. However, today's waste ash management practices, e.g., ash transported to Langøya, show this is practically feasible even without an additional material recovery process. Ash metal recycling offers opportunities for the production of by-products like salt or raw materials for clinker production [4]. A salt extraction plant is now (2023) opening in Sweden using Ash2Salt technology, demonstrating economically viable salt recovery from fly ash [26]. Thus, a metal extraction process should be able to generate valuable by-products like salt.

Metal extraction and mining are capital-intensive industries. Exploiting the economics of scale is therefore important. Zinc and copper mines have increased in size to exploit economies of scale over the past century. This is in order to compensate for increased production costs related to the depletion of ore grades [21]. The Australian copper mining industry had an average return on scale from 1969–1995 of 0.15 [27]. This demonstrates how favorable upscaling has been in the capital-intensive industry. Likewise, capital investments make up the largest share of costs in the economic analysis of implementing the FLUWA-FLUREC process [7,25]. Therefore, scaling up a metal extraction plant may be important to compensate for the large investments. To exploit large waste ash tonnages, a metal extraction process must be robust to process differences in fly ash types. The annual estimated tonnages presented in this study show that it is possible to scale up metal production from fly ash and bottom ash fines to equal sizes as typical mines operating today [21].

Technology for processing ores has been improving for centuries, and processes have been fine-tuned for low production costs. This contrasts with metal extraction from waste ash, where technology must be improved and infrastructure built. In addition, ash has some characteristics different from most common processed ores that need to be considered differently. The fine particle size and complex crystallographic composition may make selective beneficiation techniques difficult. This, in combination with the low-grade, indicates the use of a hydrometallurgical extraction route rather than a pyrometallurgical one. Waste ash has a fine particle size and a non-uniform particle size distribution. This may negatively influence the percolation properties for percolation leaching methods [28]. Pre-agglomeration may be needed. Percolation leaching is often used in large-scale mines of low-grade ores and may be interesting for large-scale processing. Waste ash also has a higher proton exchange capacity than common ores. This can be costly due to the high acid consumption of an acidic extraction route. Waste ash has different contaminants compared to common ores, e.g., the high content of halogens can be difficult to handle in zinc electrowinning plants processing ores. The special waste ash properties must be considered when developing the best possible metal recovery process.

Tonnage estimates show that large-scale operations for metal recovery from fly ash and bottom ash are possible. This will reduce investment costs per metal produced. Lower waste ash grade compared to a higher grade of mineral ores may be compensated by lack of comminution, the potential avoiding conventional hazardous waste ash treatment process, and the ability to generate secondary products (e.g., salts). More efforts should be invested in making metal recovery from waste ash a reality. Many positive indications for possible economically viable processes can be seen when comparing waste ash with ores. Furthermore, metal extraction from waste ash must be seen as a holistic process for metal recovery and the treatment of hazardous waste ash.

5. Conclusions

Considerable copper, zinc, and lead tonnages can be found in waste incineration ashes. Yearly flows have tonnages that are comparable to typical annual mine tonnage outputs. Estimates show that fly ash and bottom ash fines from countries bordering the Baltic and North Sea make up about 1/3 of Swedish mining output for copper, zinc, and lead production. However, metal concentrations in ash are lower than head grades from mines. The concentrations are about 3–5 times lower than the average head grades of worldwide ores.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/resources12030033/s1, the supporting information is consented to the Figure 3: Metal concentration comparison.

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Recovery of copper and zinc from ash from incinerated municipal waste†

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Abstract: *We have tested possible processes for using ashes from incinerators, both fly ashes and bottom ashes, and included old processes like the Schnabel process in our assessment. The possibilities for selective leaching with ammonia and ammonium carbonate are utilized as well as recycling of the ammonia. Fly ash and bottom ash may be treated similarly, but with some specific differences. Our conclusion is that recovery from incinerated municipal waste ash is an economical viable source for copper and zinc. Such a process will also reduce the amount of waste to handle and also make it more chemically stable due to the alkalinity of the residue.*

Keywords: Copper; Zinc; Ammonia-Ammonium Carbonate; AAC; Fly ash; Bottom Ash

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1. Introduction

EU's 2020 list of critical raw materials (CRM)comprises more than 40 elements and EU's CRM act sets a goal of at least 10% of each of these materials to be produced in Europe and at least 15% to be recycled. Ashes from incinerated municipal waste are known to contain critical metals such as copper and antimony, in addition to important base metals like zinc and tin. Our work has shown that the potential recovery of copper and zinc may be in the same order of magnitude as virgin ores. Such source materials are ready to be treated hydrometallurgically compared to primary production. Costly mining, grinding, milling and beneficiation operations of ores are avoided. However, the heterogeneity of the contents in municipal waste to be incinerated is great since it will vary with factors like time and consumer trends, the site where the waste is collected, and the incineration technology that is used. Municipal waste volumes in the Western world are huge. Normally municipal waste is collected and incinerated in order to reduce volumes and recover energy. This creates energy for consumption and causes reduced volumes to deposit and handle. For example, Norway's 5 million inhabitants generates annually 1.5 million tons to be incinerated. Nedkvitne et al.[1] provide an overview of the incinerated waste in Northern Europe in 2020. Also shown is the annual increase in incinerated waste. Such incineration creates two types of waste to be handled: bottom ash and fly ash, including air pollution control-residues. As the line between fly ash and APC-residue is not always very clear in the literature we will in this article use fly ash as a collective term. Both components can be divided into different types after the technology used for the incineration, but in our work we have strived for developing a robust process capable of handling all kinds of incinerated waste and we have focused on the constituents of highest values.

The content in municipal waste will vary over time and also depend on the region it is collected from. Therefore the value of what is in the waste will vary. However, the most valuable constituents are copper, zinc and lead. These metals are, on the average, so high in concentration that these ashes may not be deposited at landfills due to regulations concerning the content of toxic pollutants. Based on 895 XRF analyses of fly ash, Nedkvitne et al. (2021)[1] have shown that on the average Zn is about 10, Cu 1.2, V, Cd, and Ni 0.2 g per kg fly ash, respectively. The variations are, however, huge. The most abundant components are Ca, Cl, Na, Si, S, K, Al and Fe.In Figure 1 the average of some selected elements found in bottom ash in EU are shown. The concentration of each element is the calculated median of the data gathered, and the number of samples for each element varies between 50 and 1700. The major elements (> 10 g/kg) are shown in the left panel, while the minor elements (> 1 g/kg) are shown in the right panel. Trace elements (< 1 g/kg) are not shown in the figure.Nedkvitne et al. (2023)[2] have also shown that the content of copper and zinc in the ashes in question is at the same magnitude as low concentrated mineral ores. But compared to ore, there is no need for mining and no gangue material to take care of. All of these three metals, Cu, Zn and Pb, are found in both fly ash and bottom ash, but the two former ones are abundant while the concentration of Pb is mostly quite low.

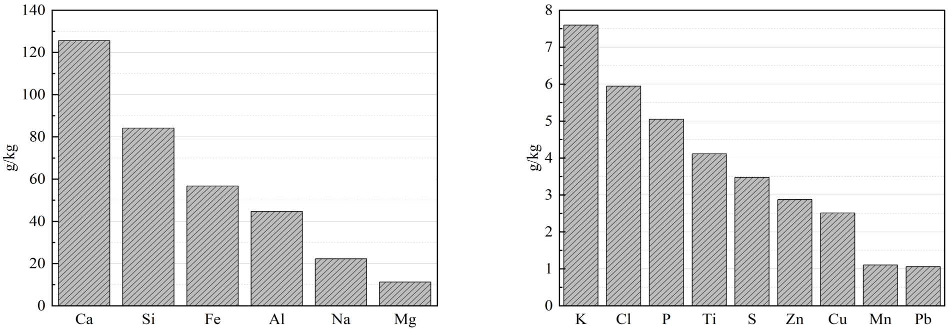

Figure 1. Overview of the average elemental composition of municipal solid waste bottom ash based on data gathered from individual member states of the European Union (EU). Left panel: Major constitutens; Right panel: Minor constituents, but with concentration > 1 g/kg. The data was made available by the Confederation of European Waste-to-Energy Plants (CEWEP)[3].

Copper and zinc are both considered to be soft Lewis acids together with nickel, cadmium, mercury, silver etc. [4] To extract Cu and Zn selectively from oxidizing incineration ashes, a soft Lewis base is needed. One type of leaching agent is appealing: Ammonia (solution). This makes the pregnant leach solution (PLS) alkaline which means that most metals with low soluble hydroxides (harder Lewis acids) will not go into solution. Both copper and zinc forms ammine complexes which will keep them in solution and increase their solubility. In addition, ammonia can be recycled by heating, so the consumption of ammonia can be kept at a minimum and alkaline solutions are usually less corrosive than acidic ones.

Ammoniacal leaching is a well known topic. A useful tool to see at which pH and redox-potential the various metals of interest are in solution and as what kind of species is the Pourbaix- or Eh-pH diagram. Meng and Han[5] provided such diagrams for both Cu and Zn. However, they only include one kind of ammonia complex for Cu(II) and one for Cu(I). Wei et al.[6], in a very comprehensive study of the leaching of copper oxide with ammoniacal solutions, claim there are five complexes, all with quite large complexing constants, β_i:

$$\beta_i = \frac{[Cu(NH_3)_i^{2+}]}{[Cu^{2+}][NH_3]^i} \qquad \text{Eq.1}$$

Here the bracket parentheses denotes activity. According to the Pourbaix-diagram provided by Meng and Han[4] the pH for leaching should be in the range 8 – 10 in order to leach both Cu(II) and Zn(II). A pure ammoniacal solution will have a pH of almost 12. To reduce the pH to the optimum interval ammonium is the preferred acid forming a buffer with ammonia. Wei et al.[5] prefer NH_4Cl but have to include the low solubility of the compound $Cu(OH)_{1.5}Cl_{0.5}$ and also other combinations of copper compounds with ammonia, chloride and hydroxide. Bingöl et al.[7] argue for the use of $(NH_4)_2CO_3$ for leaching of CuO and Rodriguez et al.[8] do the same for ZnO. Such solutions consisting of ammonia and ammonium carbonate are denoted AAC. To recover zinc by using AAC has been known since 1880 and the process is named after the inventor, Schnabel. The Schnabel process is reviewed by Harvey[9].

In Figure 2 we see the increase in dissolution rate between pure ammonia and AAC for one type of bottom ash.

We have the following reaction model for leaching with pure aqueous ammonia:

$$MO(s) + 4NH_3(aq) + H_2O \leftrightarrow M(NH_3)_4^{2+}(aq) + 2OH^- \qquad \text{R. 1}$$

Where M denotes Cu or Zn. But for AAC, we have:

$$MO(s) + 2NH_4^+ \leftrightarrow M^{2+} + 2NH_3 + H_2O \qquad \text{R.2}$$

$$M^{2+} + 4NH_3 \leftrightarrow M(NH_3)_4^{2+} \qquad \text{R.3}$$

Sum reaction: R.2+R.3:

$$MO(s) + 2NH_4^+(aq) + 2NH_3(aq) \leftrightarrow M(NH_3)_4^{2+}(aq) + H_2O \qquad \text{R.4}$$

Employing the Law of Mass Action or the principle of Le Chatelier we clearly see the advantage of AAC versus ammonia.

In addition, there are two simultaneous buffers: NH_3/NH_4^+ and CO_3^{2-}/HCO_3^-. Tests during leaching have shown quite stable pH at just below 9.8, just in the optimum pH region.

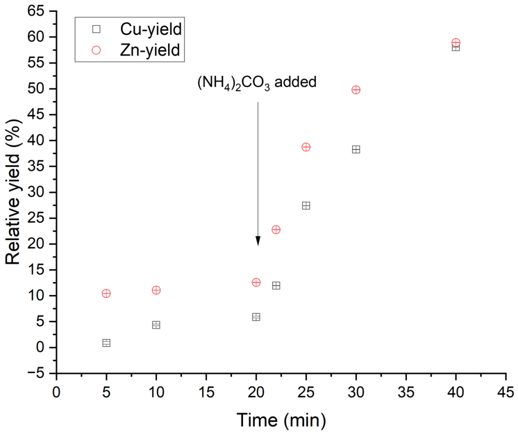

Figure 2. Experiments performed as part of this work with pure ammonia and ammonia-ammonium carbonate. Ammonium carbonate was added after 20 minutes of the leaching time had passed. (Total NH_3=4.68M, T=40°C, pulp density= 100 g/L, stirring 250 rpm, NH_3:CO_3=3:1, V=250.0 mL). Uncertainties are analytical standard deviations, not representing the average of the sample contents.

To recover the copper from the PLS a very simple sedimentation process is possible. Being the most noble element in the PLS (exception may be silver) adding elemental zinc to the solution will reduce Cu^{2+} to Cu^0. This part is also a part of the Schnabel process as reviewed by Harvey[8]. The dark blue color of the copper amine complex disappears and finely divided copper is precipitated. Since initially, there is zinc in the PLS, there will be an increase in the concentration. This process step is an option and has to be evaluated in competition with first electrolysis of copper and then for zinc and other less noble metals present. Here the purities of the metals will play a significant role in the assessment of the best economical and technical way to recover the metals. We have not yet performed this assessment.

It is also possible to force the precipitation of $Zn(OH)_2$ by heating and evaporation of NH_3. This recycles ammonia and recover the zinc. According to Meng and Han[4] the pH interval to handle this precipitation is 7 – 8, which is quite narrow. We consider the zinc-reduction process as more robust.

During incineration of municipal waste the temperature can rise to values sufficient to evaporate metals and metal oxides of Cd, Hg, Pb etc. In fly ash there may therefore be more of the toxic heavy metals than in the volatile fraction left – the bottom ash. We have also assessed other metals, e.g. Cd and Pb, but we focus on Cu and Zn in this work.

2. Materials and Methods

Since these kind of raw materials are very variable in contents it is impossible to give exact and reliable yields. We have therefore used XRF as a method of determining the concentrations of the metals and accepted that the yields of copper and zinc will be uncertain. The yields were calculated from the volumes and concentrations of the PLS relative to the concentration of the solid samples as determined by XRF. However, for our samples we have selected the procedures giving the highest yields and also being robust. Parameters tested were leaching duration, temperature, pulp density, ratio NH_3/NH_4, etc. Stirring was kept constant as long as the viscosity of the slurry was low enough to allow good mixing. When this was no longer fulfilled, the test of parameter in question (pulp density) was stopped.

2.1 Chemicals:

Ammonia as 28% aqueous solution $NH_3(aq)$ was purchased from VWR and used as such. Ammonium carbonate, $(NH_4)_2CO_3(s)$, as solid salt was also purchased from VWR and used as such. Standards for chemical analyses were provided by Teknolab AS. For dilution of samples and preparation of them 68% HNO_3 purchased from VWR was used as such. Water used was Type II water(15,0 MΩcm) purified by Milli-Q® Integral Water Purification System from Merck Millipore.

2.2 Instruments:

The analytical instruments at our disposal were MP-AES, ICP-OES, XRF and XRD. Analyses of aqueous samples were partly performed with Microwave Plasma Atomic Emission Spectroscopy (MP-AES) using Agilent 4100 MP-AES with Agilent SPS 4 autosampler or with ICP-OES using a Horiba Jobin Yvon Ultima 2 instrument. Analyses of solid samples by XRF measurements were performed by NOAH AS using a SPECTRO XEPOS 5 HE whereas XRD measurements were performed employing a Bruker D8 Discover with Bragg-Brentano geometry.

2.3 Solids, i.e. fly and bottom ashes:

Samples of fly ashes were all provided by NOAH AS, a Norwegian waste handling enterprice (en.noah.no). The samples were all washed with water to recover dissolvable chlorides, i.e. NaCl, KCl and $CaCl_2$. Thus, these ashes were depleted in chloride compared to ordinary fly ashes. The ashes were dried and used as such.

The bottom ashes were provided by four Norwegian waste handling facilities. They were sampled at a random time and are considered to be representative within the variation explained in the introduction. The ash particles are sintered and to leach them they were initially grinded in a rotor mill to a particle size of < 2mm. Tests with both coarse and grinded ashes showed a clear advantage of grinding. The yields were 2 – 3 times higher when grinded. The coarse material is leached slowly, but we do not know how long it will take before saturation. The grinded ashes reacted faster and were thus better to work with.

3. Results and discussion

To find the optimum ratio between $NH_3(aq)$ and $(NH_4)_2CO_3$ on leaching fly ash, a series of tests where the ratio was altered were performed. The results for Cu and Zn are shown in Figure 3. As is shown, both yield curves have a maximum and then decrease. The separation factor between Cu and Zn is increasing on the expense of yield. For Cu the peak is close to

$$\frac{[NH_3]}{[NH_4^+]} = 1.5$$

Not only the ratio between amine-ammonium, but also the total concentration of $[NH_3]+[NH_4^+]$ may play a role. In Figure 4 two different samples of bottom ashes are shown for three different total concentrations. The ratio between ammonia and ammonium is 1.5 in all these tests. There is an increase in yields for both Cu and Zn going from 1.56 to 3.12 M, but the increase from 3.12 to 4.68 M is almost within uncertainty. However, the figure show the great differences there might be between the bottom ashes from waste handling incinerators.

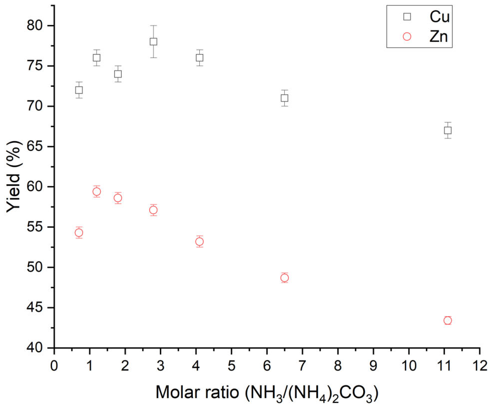

Figure 3. Tests to find the optimum ratio between NH_3(aq) and $(NH_4)_2CO_3$ on leaching fly ash. (Temperature: 25 °C, pulp density 250 g/L, leaching time: 60 min).

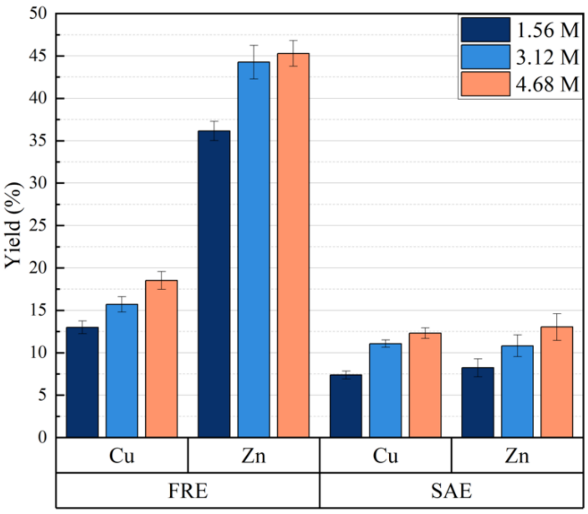

Figure 4. Effect of total ammonia concentration ($NH_3 + NH_4^+$) with regard to the yields of copper and zinc for two different types of bottom ash: FRE (left) and SAE (right). (Ambient temperature,

pulp density = 100 g/L, leaching time: 40 min, stirring speed 250 rpm). The ratio between NH_3 and NH_4^+ was 1.5 in all the tests).

Tests on the leaching of bottom ashes showed clearly that while copper yields increased with increasing temperature the yield of zinc decreased. We interpret this as the activity of $NH_3(aq)$ increases and as the Cu-complex is stronger than the Zn-complex there may be less NH_3 available for the weaker complex. Also the competition from OH^- may be increased forming colloidal $Zn(OH)_2(s)$ and $Zn(OH)_4^{2-}$.

4. Conclusion

We have clear indications that combination of fly and bottom ash may represent potential source for copper and zinc. There is a strong possibility that both materials can be leached by the same method and with the same parameters. The recommended lixiviant is ammonia-ammonium carbonate, AAC, where the molar ratio of ammonia to ammonium is 1.5 and the total ammonia + ammonium concentration is 1.6 M and a leaching time of 180 min.

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