Distribution and chemical association of trace elements in incinerator residues and mining waste from a leaching perspective
This work is dedicated to the brave, innocent, young children students who were martyred in a terrorist attack in 2014 at The Army Public School, Peshawar, Pakistan.
Distribution and chemical association of trace elements in incinerator residues and mining waste from a leaching perspective
Abstract

Incineration is a mainstream strategy for solid waste management in Sweden and all over the world. Improved knowledge and understanding about the distribution of trace elements (in ashes) during incineration, and how trace element partitioning respond to the changes in waste composition, are important in terms of combustion process optimization and plant efficiency. Moreover, determination of chemical association of trace elements in ashes are vital for avoiding environmental concerns and to promote possible reuse. In this study, partitioning of trace elements in ashes during incineration as function of input waste fuel and incineration technology was investigated. Further, chemical association of trace elements in resulting ashes was studied. An evaluation was also performed about feasibility of metal extraction from sulfidic mining waste and flotation tailings. Moreover, green liquor dreg (GLD) was tested with respect to stabilization of metals within the sulfidic mining waste.

Findings showed that the total input of trace elements and chlorine affects the partitioning and increasing chlorine in the input waste caused increase in transfer of trace elements to fly ash especially for lead and zinc. Vaporization, condensation on fly ash particles and adsorption mechanisms play an important role for metal distribution. Firing mixed waste, especially biofuel mix, in grate or fluidized (CFB) boilers caused increased transfer into fly ash for almost all trace elements particularly lead and zinc. Possible reasons might be either an increased input concentration of respective element in the waste fuel, or a change in volatilization behavior due to the addition of certain waste fractions. Chemical association study for fly ashes indicated that overall, Cd, Pb, Zn, Cu and Sb are presenting major risk in most of the fly ashes, while in bottom ashes, most of elements are associated with stable fraction. Further, fuel type affects the association of elements in ashes. Chemical leaching of mining waste materials showed that sulfuric acid (under different conditions) is the best reagent to recover zinc and copper from sulfidic mining waste and also copper from flotation tailings. GLD indicates potential for metal stabilization in mining waste by reducing the metal mobility. Extraction methods could be applied to treat mining waste in order to meet the regulatory level at a specific mining site. Similarly stabilization/solidification methods might be applied after leaching for recovery of metals.

Keywords: trace elements, partitioning, fly ash, bottom ash, speciation, association, risk assessment, wood waste, incineration, mining waste

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List of papers

This thesis is based on the following papers.

Paper 1

Paper 2

Paper 3

Paper 4

Paper 5

Paper 6

Note: All published papers have been printed with Elsevier permission
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABA</td>
<td>Acid Base Accounting</td>
</tr>
<tr>
<td>APC</td>
<td>Air Pollution Control</td>
</tr>
<tr>
<td>ARD</td>
<td>Acid Rock Drainage</td>
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<td>ASTM</td>
<td>American Society For Testing and Materials</td>
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<tr>
<td>BA</td>
<td>Bottom Ash</td>
</tr>
<tr>
<td>BCR</td>
<td>Community Bureau of Reference</td>
</tr>
<tr>
<td>BFB</td>
<td>Bubbling Fluidized Bed</td>
</tr>
<tr>
<td>CCA</td>
<td>Chromated Copper Arsenate</td>
</tr>
<tr>
<td>CFB</td>
<td>Circulating Fluidized Bed</td>
</tr>
<tr>
<td>CBi and CFi</td>
<td>Mass Concentration of Trace Element $i$ in the Bottom Ash and Fly Ash, respectively</td>
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<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
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<tr>
<td>DIP</td>
<td>De-Inking Pulp</td>
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<tr>
<td>ESP</td>
<td>Electrostatic Precipitator</td>
</tr>
<tr>
<td>GLD</td>
<td>Green Liquor Dreg</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma-Atomic Emission Spectroscopy</td>
</tr>
<tr>
<td>ICP-QMS/SFMS</td>
<td>Inductively Coupled Plasma, Quadrupole Mass Spectrometry/Sector Field Mass Spectrometry</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Emission Spectroscopy</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>L/S</td>
<td>Liquid Solid ratio</td>
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<tr>
<td>LOI</td>
<td>Loss On Ignition</td>
</tr>
<tr>
<td>MB</td>
<td>Mass Burn</td>
</tr>
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<td>MSW</td>
<td>Municipal Solid Waste</td>
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<td>MB and MF</td>
<td>Mass of Bottom and Fly ash</td>
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<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
</tr>
<tr>
<td>RAC</td>
<td>Risk Assessment Code</td>
</tr>
<tr>
<td>RFi</td>
<td>Transfer of Trace Element to Fly Ash</td>
</tr>
<tr>
<td>RWW</td>
<td>Recovered Waste Wood</td>
</tr>
<tr>
<td>SEPA</td>
<td>Swedish Environmental Protection Agency</td>
</tr>
<tr>
<td>SP</td>
<td>Swedish Testing and Research Institute</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TTAB</td>
<td>Tetradecyl Trimethyl Ammonium Bromide</td>
</tr>
<tr>
<td>Vw</td>
<td>Virgin Wood</td>
</tr>
<tr>
<td>WTE</td>
<td>Waste To Energy</td>
</tr>
<tr>
<td>XAS</td>
<td>X-Ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>$X_i$</td>
<td>Weighted Average Concentration of Trace Element $i$ in Fly and Bottom ash</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.</td>
<td>INTRODUCTION</td>
</tr>
<tr>
<td>1.1.</td>
<td>Waste to energy in Sweden</td>
</tr>
<tr>
<td>1.2.</td>
<td>Types of waste fuel/recovered waste fuel/wooden fuel</td>
</tr>
<tr>
<td>1.3.</td>
<td>Incineration technologies</td>
</tr>
<tr>
<td>1.4.</td>
<td>Ash production</td>
</tr>
<tr>
<td>1.5.</td>
<td>Trace element partitioning in ashes during incineration</td>
</tr>
<tr>
<td>1.6.</td>
<td>Leaching characteristics of ashes</td>
</tr>
<tr>
<td>1.7.</td>
<td>Mining waste</td>
</tr>
<tr>
<td>1.8.</td>
<td>Green Liquor Dreg (GLD)</td>
</tr>
<tr>
<td>2.</td>
<td>AIMS OF THESIS</td>
</tr>
<tr>
<td>3.</td>
<td>MATERIALS AND METHODS</td>
</tr>
<tr>
<td>3.1.</td>
<td>Sampling of waste fuels used for incineration</td>
</tr>
<tr>
<td>3.2.</td>
<td>Sampling and storage of ashes</td>
</tr>
<tr>
<td>3.3.</td>
<td>Sampling of mine waste materials and site description</td>
</tr>
<tr>
<td>3.4.</td>
<td>Analytical methods</td>
</tr>
<tr>
<td>3.5.</td>
<td>Leaching procedure for waste materials</td>
</tr>
<tr>
<td>3.6.</td>
<td>Mathematical expressions</td>
</tr>
<tr>
<td>3.7.</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>4.</td>
<td>RESULTS AND DISCUSSION</td>
</tr>
<tr>
<td>4.1.</td>
<td>Trace element partitioning in ashes as function of fuel composition 39</td>
</tr>
<tr>
<td>4.2.</td>
<td>Partitioning and leaching characteristics of trace elements in ashes 45</td>
</tr>
<tr>
<td>4.3.</td>
<td>Chemical association of trace elements in fly ashes</td>
</tr>
<tr>
<td>4.4.</td>
<td>Chemical association of trace elements in bottom ashes</td>
</tr>
<tr>
<td>4.5.</td>
<td>Sulfidic mining waste: chemical leaching and stabilization</td>
</tr>
<tr>
<td>4.6.</td>
<td>Extraction of copper from flotation tailings by chemical leaching... 70</td>
</tr>
<tr>
<td>5.</td>
<td>CONCLUSIONS/IMPLICATIONS</td>
</tr>
<tr>
<td>6.</td>
<td>FUTURE DIRECTIONS</td>
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<tr>
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1. INTRODUCTION

Sweden is widely considered a waste to energy (WTE) success story. Incineration is a mainstream strategy for solid waste management in Sweden and all over the world due to limited landfill space and associated risks to air, water and soil [1]. In 2006-2007, there were 2,000 waste incineration plants in Asia, 460 in Europe (32 in Sweden) and 100 in North America [2-4]. The existence of trace elements, alkali metals, chlorine and sulfur in the waste pose a challenge during waste incineration with respect to operational problems and environmental concerns. Further, resulting by-products of incineration process (bottom/fly ash, air pollution control (APC) residues) might contain high concentration of hazardous trace elements such as Cd, Pb and As with increased level of chlorides and soluble salts which might pose a threat to human health and environment if landfilled/or utilized [5-6]. These ashes must be handled in ways which ensure that there are no negative impacts on the environment or human health. Therefore, improved knowledge and understanding about the formation of ashes, distribution of trace elements in ashes during incineration, and how trace element partitioning respond to the changes in input waste composition are important in terms of combustion process optimization and plant efficiency. Moreover, for suitable management strategy or reuse of hazardous fly ash/bottom ashes, it is crucial to understand the mechanism controlling the mobility of trace elements in ashes.

1.1. Waste to energy in Sweden

Waste to energy is a well established source of energy in Sweden. Over two million tons of household waste is processed by waste to energy plants in Sweden each year [7]. These combustion plants incinerate a substantial quantity of industrial waste as well. Biomass and biomass derived waste materials also reflects a sustainable energy source having substantial potential for replacing conventional fossil fuels. Because of concern for global warming and other environmental and political aspects, energy generating companies in Sweden use biomass and waste materials in an increasing proportion as a replacement of fossil fuels for heat/power production. The amount of waste going into landfills is continuously
decreasing while energy recovery is increasing [Figure 1-2]. Waste incineration delivers heat equivalent to the needs of 810,000 homes, about 20% of all the district heating produced, in Sweden [7]. It also offers electricity corresponding to the requirements of almost 250,000 homes [7]. International assessments
show that Sweden is one of the global leaders in recovering energy from waste [Figure 3].

![Figure 3. Comparison of waste management methods between different countries [9-11]](image)

1.2. Types of waste fuel/recovered waste fuel/wooden fuel

Various waste fuels or wood based fuels are being incinerated in Swedish waste to energy plants. Some of them include household, industrial, mixed waste, recovered waste wood, wood fuel (wood chips) and mixed wooden waste (including peat, bark and wood chips). Some of these fuels will be described in this section.

1.2.1. Municipal Solid Waste (MSW)

About 48 % of household waste is treated through incineration in Sweden [12]. Household waste is a very heterogeneous fuel comprising many individual waste fractions with different physical and chemical characteristics. Composition of the different fractions fluctuate between sub-urban and downtown areas, regions of lower income and educational characteristics [13]. Each Swedish resident produces around 480 kg of household waste/year of which the major fraction (48 %) is organic waste (mainly food waste) [8, 12]. Other fractions include 24 % packaging (including chlorinated plastics (PVC source)), 8 % newspaper, 7 % garden waste and others (including 4 % combustible waste) [8, 14]. High concentration of inorganic/organic chlorine (from NaCl, PVC) is present in the waste [13].
1.2.2. Industrial waste

Resource extraction (mining) and manufacturing industry (pulp and paper, wood and wood products) are two main industrial sectors that produced around 73 million tons of industrial waste in 2002 [14]. Around 40% of the industrial waste (excluding mining waste) is treated through incineration in Sweden [14]. Major individual fractions in Swedish industrial waste (that are incinerated) are pulp, paper and paper products, wood and wood products, chemicals, rubbers and plastic goods, waste from textile, clothing and fur industry products. Other fractions of industrial waste (that are either recycled or landfilled) include mixed metals, steel and metal works, soil and stone goods [14].

1.2.3. Recovered Waste Wood (RWW)

Around 75% of recovered waste wood (from construction and demolition) are treated through incineration [14]. According to Krook et al. [15] the most significant sources contributing to trace element contamination in RWW are surface-treated wood, industrial preservative-treated wood, plastics and galvanized fastening systems, with surface-treated wood being the key source of zinc and lead. Impregnated wood, a part of RWW is usually processed under pressure with aqueous solutions containing salts of Cu, Cr, or As etc. to protect the wood from fungi and microbial attack. One of the most common formulations is Chromated Copper Arsenate (CCA) in which arsenic and copper acts as biocides while chromium acts as a fixing agent to bind the metals to the wood [16]. Because of durable fixation, significant amounts of CCA remains in the wood for many years, thus efficiently preventing microbial attacks, but unfortunately, challenging the end-of-life disposal when the impregnated wood goes into the waste stream. In Sweden, RWW is incinerated in specially licensed energy recovery plants [14].

1.2.4. De-Inking Pulp (DIP) sludge

DIP sludge is a waste stream from the pulp and paper industry containing printing inks (black and colored pigments), fillers and coating pigments, fibers, fiber fines, and adhesive components [17]. Levels of trace elements are generally low in DIP sludge and > 55% of the solids (removed by flotation) are inorganic compounds [18]. The inorganic compounds are primarily fillers and coating pigments such as clay and calcium carbonate whereas the proportion of cellulosic fiber is small. The heating value of dry substance (DIP) depends on ash content and is 4.7-8.6 GJ/ton of dry
substance [17]. Copper content of DIP sludge is mainly due to the use of blue pigments for printing inks which contains phthalocyanino-compounds [18]. Sweden is also one of the leading biofuel users in the European Union. These fuels include peat, bark, forest residues and wood waste etc.

1.3. **Incineration technologies**

Mass Burn (MB) technique is the most common practice being utilized for combustion of waste however, Fluidized Bed Combustion (FBC) has emerged as an alternative through recent decades. Both incineration methods have been described and explained by others [19] and are hence only described briefly here.

1.3.1. **Mass burn incinerator**

In a Mass Burn (MB) incinerator, the fuel is fed onto a moving or tilting grate, and surplus air is blown to attain efficient combustion. The incineration temperature is generally above 1000 °C [19]. MB combustion has the benefits of being a simple, robust and comprehensively applied practice for waste incineration and there is only a minimal requirement for pre-sorting (shredding) and size reduction of the waste material.

1.3.2. **Fluidized bed incinerator**

Incineration in a fluidized bed boiler is carried out in a bed consisting of inert material (typically quartz or olivine sand). The inert material (sand) efficiently distributes the heat to the water tubes, making it possible to maintain a low incineration temperature, i.e. about 850 °C [19]. Generation of nitrogen oxides (NO$_x$) is reduced since oxidation of nitrogen in the air is decreased. Variety of fuels/waste fuels with dissimilar properties, such as moisture content and heating value have less influence on the incineration than in a MB incinerator. However, the FBC method needs a pre-sorting and size reduction of the waste.

1.4. **Ash production**

Bottom ash is the major ash fraction formed during incineration of MSW [20]. It generally contains metal pieces, sand and glassy slag lumps, minerals with high melting points, and is collected at the bottom of the incineration chambers [20]. Small ash particles that follow the flue gas are collected in the flue gas treatment system and is known as fly ash [20]. Formation of bottom ash generally ranges from 250-420 kg/ton of feed waste, without including the grate siftings (5 kg/ton) and boiler ash (2-12 kg/ton) [20]. Fly
ash and APC residues are often considered together to have a unique output from incineration plants. Fly ash production during waste incineration ranges from 10-30 kg/ton of feed waste [20]. Table 1 and Table 2 show typical composition of MSWI fly and bottom ashes from different countries expressed as oxides.

**Table 1. Compositions of different MSWI fly ashes (FA) (as oxides wt %)**

<table>
<thead>
<tr>
<th>Reference</th>
<th>[21]</th>
<th>[22]</th>
<th>[23]</th>
<th>[24]</th>
<th>[25]</th>
<th>[26]</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>19</td>
<td>11.5</td>
<td>19.4</td>
<td>13.6</td>
<td>18.5</td>
<td>20.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13</td>
<td>5.8</td>
<td>10.1</td>
<td>1</td>
<td>7.4</td>
<td>5.8</td>
</tr>
<tr>
<td>CaO</td>
<td>24</td>
<td>29.3</td>
<td>19.7</td>
<td>45.4</td>
<td>37.5</td>
<td>35.8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2</td>
<td>1.3</td>
<td>1.8</td>
<td>3.9</td>
<td>2.3</td>
<td>3.2</td>
</tr>
<tr>
<td>MgO</td>
<td>3</td>
<td>3</td>
<td>2.8</td>
<td>3.2</td>
<td>2.8</td>
<td>2.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>4</td>
<td>7</td>
<td>8.1</td>
<td>3.9</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>6</td>
<td>8.7</td>
<td>8.9</td>
<td>4.2</td>
<td>2.9</td>
<td>3.7</td>
</tr>
</tbody>
</table>

MSWI: Municipal solid waste incineration

**Table 2. Compositions of different MSWI bottom ashes (BA) (as oxides wt %)**

<table>
<thead>
<tr>
<th>Reference</th>
<th>[27]</th>
<th>[28]</th>
<th>[29]</th>
<th>[3]</th>
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<th>[25]</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>27.8</td>
<td>29.4</td>
<td>12</td>
<td>5.4</td>
<td>13.4</td>
<td>46.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10</td>
<td>18</td>
<td>8.1</td>
<td>3.1</td>
<td>1.2</td>
<td>6.8</td>
</tr>
<tr>
<td>CaO</td>
<td>26</td>
<td>27.2</td>
<td>14</td>
<td>42.5</td>
<td>50.3</td>
<td>26.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4</td>
<td>13.3</td>
<td>1.2</td>
<td>1.7</td>
<td>9</td>
<td>4.7</td>
</tr>
<tr>
<td>MgO</td>
<td>3.3</td>
<td>1.6</td>
<td>2.6</td>
<td>1.9</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.8</td>
<td>0.9</td>
<td>7.4</td>
<td>4.3</td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.3</td>
<td>3.6</td>
<td>17.2</td>
<td>4.8</td>
<td>12.6</td>
<td>4.6</td>
</tr>
</tbody>
</table>

MSWI: Municipal solid waste incineration

1.5. **Trace element partitioning in ashes during incineration**

Several studies have reported on the investigation of influential parameters such as waste chlorine content, combustion temperature, incineration technology, flue gas treatment system and feed moisture content for partitioning of trace elements during incineration [30-35]. Volatility of trace elements and presence of chlorine in the waste are two of the key parameters responsible for the formation of metallic chlorides. During incineration, generally highly volatile mercury and cadmium are found completely in the flue gas or fly ash and elements with medium volatility like lead and zinc are distributed equally among fly and bottom ash and/or more to fly ash while elements having low vapor pressure and high boiling point like copper...
and iron mainly stay in the bottom ash [34]. In an unsorted MSW, plastics (PVC) and food (NaCl) waste can add significant amounts of organic and inorganic chlorine, respectively, which will affect the distribution of trace elements [31].

Zhang et al. [36] studied the impact of temperature and moisture content on trace element partitioning to fly ash during MSW incineration. They observed that zinc and copper compounds transferred from chlorides to oxides with decrease in temperature and increase in moisture content while lead and cadmium distribution was not affected as much by temperature. In another study [16], different waste fractions (salt, shoes and PVC) were incinerated with normal waste fuel (MSW) and their impact on trace element partitioning during waste incineration was studied. Firing of chlorine rich waste such as PVC, salt and even shoes were found to enhance the volatilization rate of lead and an increased recovery was witnessed in fly ash and aerosol fractions. Further, organically bound chlorine was vaporized as HCl(g) whereas inorganically bound chlorine was recovered in bottom ash as alkali metal chlorides indicating that it was a critical element for metal partitioning as well as creating corrosion and deposition problems [16]. Similarly, Astrup et al. [37] investigated trace element partitioning by adding individual waste fractions such as CCA impregnated wood, household batteries, shoes and salt (NaCl) in MSW and concluded that added waste materials significantly changed the emissions in fly ash, particularly for As, Cd, Cr and Sb.

Morf et al. [38] studied trace elements partitioning as a function of input variations in a MSW incinerator and observed that increasing metal content in the waste decreased the transfer to flue gas for copper and lead while for

Figure 4. Visual observation of sampled fly and bottom ash (recovered waste wood) at the Nynäshamn facility

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Morf et al. [38] studied trace elements partitioning as a function of input variations in a MSW incinerator and observed that increasing metal content in the waste decreased the transfer to flue gas for copper and lead while for
zinc it increased. Several studies have mentioned that an increase in feed chlorine content enhance the fraction of trace elements distribution to fly ash and flue gases, mainly because of the formation and thermo-chemical stability of volatile trace element chlorides [33, 39, 40]. Type of chlorine bonding has also been reported to affect the fate of trace elements during incineration [41]. Wang et al. [42] showed that organic chlorine (PVC, C₂Cl₄) contributed more to the transfer of trace elements to gas phase compared to inorganic chlorine (NaCl, KCl). Generally, MSW has been the focus of studies regarding partitioning and distribution characteristics of trace elements during waste incineration. Limited work is reported about other types of fuels such as wood/mixed wooden fuel e.g. RWW, virgin wood or mixed wood waste including peat, bark and wood chips. Table 3 to Table 6 show the range of trace elements and chloride content in ashes for MSW incineration in various countries.

**Table 3.** Trace elements found in MSWI fly ashes (FA) (mg/kg dw)

<table>
<thead>
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<th>[44]</th>
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<tr>
<td>As</td>
<td>31-95</td>
<td>15-751</td>
<td>N/A</td>
<td>93</td>
<td>N/A</td>
</tr>
<tr>
<td>Cd</td>
<td>250-450</td>
<td>5-2,211</td>
<td>25.5</td>
<td>470</td>
<td>95</td>
</tr>
<tr>
<td>Zn</td>
<td>19,000-41,000</td>
<td>2,800-4,386</td>
<td>25,800</td>
<td>6,288</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>140-530</td>
<td>21-1,901</td>
<td>118</td>
<td>863</td>
<td>72</td>
</tr>
<tr>
<td>Cu</td>
<td>860-1,400</td>
<td>187-2,381</td>
<td>313</td>
<td>1,300</td>
<td>570</td>
</tr>
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<td>Pb</td>
<td>7,400-19,000</td>
<td>200-2,600</td>
<td>1,496</td>
<td>10,900</td>
<td>2,000</td>
</tr>
<tr>
<td>Ni</td>
<td>95-240</td>
<td>10-1,970</td>
<td>60.8</td>
<td>124</td>
<td>22</td>
</tr>
<tr>
<td>Co</td>
<td>29-69</td>
<td>2.3-1,671</td>
<td>N/A</td>
<td>N/A</td>
<td>14</td>
</tr>
<tr>
<td>Hg</td>
<td>0.8-7</td>
<td>0.9-73</td>
<td>52</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A: not available, MSWI: municipal solid waste incineration

**Table 4.** Trace elements found in MSWI bottom ashes (BA) (mg/kg dw)

<table>
<thead>
<tr>
<th>Reference</th>
<th>[43]</th>
<th>[44]</th>
<th>[47]</th>
<th>[29]</th>
<th>[48]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>19-80</td>
<td>1.3-45</td>
<td>209-227</td>
<td>138</td>
<td>13</td>
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<tr>
<td>Cd</td>
<td>1.4-40</td>
<td>0.3-61</td>
<td>6.8-7.8</td>
<td>6.5</td>
<td>3</td>
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<tr>
<td>Zn</td>
<td>1,800-6,200</td>
<td>200-12,400</td>
<td>4,261-4,535</td>
<td>1,922</td>
<td>600</td>
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<tr>
<td>Cr</td>
<td>230-600</td>
<td>13-1,400</td>
<td>323-439</td>
<td>252</td>
<td>900</td>
</tr>
<tr>
<td>Cu</td>
<td>900-4,800</td>
<td>80-10,700</td>
<td>4,139-4,474</td>
<td>314</td>
<td>500</td>
</tr>
<tr>
<td>Pb</td>
<td>1,300-5,400</td>
<td>98-6,500</td>
<td>2,474-2,807</td>
<td>347</td>
<td>2,700</td>
</tr>
<tr>
<td>Ni</td>
<td>60-190</td>
<td>9-430</td>
<td>216-242</td>
<td>48</td>
<td>180</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;10-40</td>
<td>22-706</td>
<td>49.6-53.1</td>
<td>21</td>
<td>N/A</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.01-3</td>
<td>0.003-2</td>
<td>N/A</td>
<td>N/A</td>
<td>2.6</td>
</tr>
</tbody>
</table>

N/A: not available, MSWI: municipal solid waste incineration

Trace Elements in Ashes and Mining waste
Table 5. Chloride content in MSWI fly ashes (FA) (mg/kg dw)

<table>
<thead>
<tr>
<th>Reference</th>
<th>[24]</th>
<th>[43]</th>
<th>[49]</th>
<th>[51]</th>
<th>[52]</th>
<th>[53]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>5,749</td>
<td>45,000 -</td>
<td>19,000 -</td>
<td>131,000</td>
<td>83,800</td>
<td>157,200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100,000</td>
<td>210,000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MSWI: municipal solid waste incineration

Table 6. Chloride content in MSWI bottom ashes (BA) (mg/kg dw)

<table>
<thead>
<tr>
<th>Reference</th>
<th>[24]</th>
<th>[29]</th>
<th>[30]</th>
<th>[48]</th>
<th>[54]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>2,876</td>
<td>149,500</td>
<td>201,100</td>
<td>2,300</td>
<td>1,760</td>
</tr>
</tbody>
</table>

1.6. Leaching characteristics of ashes

Utilization or management of incineration residues are often limited by high concentration of trace elements and chlorides. Fly ash consists of very fine particles which provide sufficient specific surface area for enrichment of toxic trace elements (during incineration) such as Pb, Cu, Zn, Cr, As and Cd [55]. Trace elements such as lead and cadmium can easily leach out from fly ash and cause contamination of soil and ground water, posing a great risk to human health and environment. Trace elements in bottom ash are far less mobile than in fly ash, but since bottom ash constitutes about 85-90% of the incineration residues [56], the total amounts of potentially toxic trace elements in bottom ash are also considerable. Therefore, for a suitable management strategy or reuse of hazardous ashes, it is crucial to understand the mechanism controlling the mobility of trace elements. Chemical association of trace elements in ashes significantly affects their release and migration behavior as well as their bio-toxicity [57]. Consequently, it is crucial to determine chemical association of trace elements in the ashes, since it will provide useful information for selecting the appropriate management strategy and/or knowledge for their possible reuse.

Leaching tests are common to assess risk and select proper management and disposal strategies for residues [58]. A standard leaching procedure (EN 12457-3) is generally employed to check whether the ashes are inert and meet the criteria to be landfilled or not [59]. The details of this method are reported in the next section [section 3.5.1].

Generally, the sequential extraction procedure proposed by Tessier and Campbell [60] as well as European Community Bureau of Reference (BCR), are used to investigate the bonding strength of trace elements between various phases and potential mobility under different physiochemical and environmental conditions [60-62]. The method proposed by Tessier and
Campbell [60] has reached great international recognition and vast application in soil and geological research. It must, however, be noted that the results of the sequential extraction does not reflect a certain discrete mineral phase but rather various chemical conditions during which elements can be mobilized. Leached elements during different steps in the sequential extraction are thus “operationally defined”. The “exchangeable fraction” is instantly available during neutral conditions, the “carbonate fraction” is potentially available during acidic conditions, organic matter and sulfides are available during “oxidizing conditions” and Fe-Mn oxides are potentially available during “reducing conditions”, while the “residual fraction” is stable and unavailable [6, 57, 60].

MSWI ashes has often been the focus for chemical association studies and limited work (in comparison to MSWI ashes) is reported about association of trace elements in wood/mixed wood fuel incineration ashes such as virgin wood, RWW or mixed wood fuels including peat, bark and wood chips. Since these fractions are part of the waste fuel mix being used for heat and energy production in Sweden as well as other countries, determination of chemical association or grouping of trace elements in different fractions of these ashes is also important.

1.7. Mining waste

Mining activities are well known for their deleterious impact on the environment such as occupation/degradation of large areas of land, disposal of enormous volumes of solid waste and formation of acid rock drainage (ARD). There are several abandoned mines contaminated with metals in Sweden. According to Swedish Environmental Protection Agency (SEPA) [63], around 600 historic mining sites require remediation in Sweden, 30 of which are considered to be of great risk for the environment and public health, while 100 of them are of concern and pose substantial risk for human health and have ecological implications, whereas the remainder of them presents comparatively low risk [63]. The total cost for remediation of known historic mining sites are estimated to be around $US 300-450 million [63]. There are 13 active mines in Sweden out of which 10 are sulfide ore mines [64]. Currently, in Sweden, total production of mining waste (tailings and waste rocks) is 80-100 million tons per year, in which a large proportion (59 million tons) comes from sulfide ore mines [65]. Over the years, 700 million tons of tailings and waste rock from sulfide ores have been deposited in Sweden and it continues to increase [63]. Oxidized sulfidic
mining waste often contains high concentrations of Zn, Pb, Cu, As and Cd [66]. Since these metals are not degradable and persistently present in the environment, proper treatments are therefore required.

Similarly, flotation tailings are another sort of mining waste that can also impose environmental implications if not properly managed. In Poland, industrial waste constitutes about 90% of the total produced waste, of which 80% comes from mining, power industries and the metallurgical sector [67]. Flotation tailings makes up the highest percentage of the waste produced during mineral exploitation in Poland [67]. All of the waste produced during copper extraction is deposited by Polish copper mining industry [67]. Disposal of the flotation tailings, which usually consist of sand, mud, pyrite, residual metal sulfides and reagents, might cause ecological implications with time if the tailings pond is not properly managed [66].

Heavy metals such as Cu, Zn, Cd, Cr, Pb and Ni become more soluble and mobile when flotation tailings are exposed to natural weathering and percolation. Once these metals are leached, they would not only potentially damage the stream and ground water but also the soil environment [66].

These mining waste materials can cause environmental problems while on the other hand, present a significant metal resource. There might be a possibility that extraction methods can be combined with stabilization methods to treat mining waste in order to recover metals as well as decrease the negative environmental impact.

1.8. Green Liquor dreg (GLD)

Sweden is an active country with mining activities and a large amount (59 million tons annually) of reactive sulfide mining tailings are generated [68]. Focus has been therefore on management of tailings and special attention is being paid to monitoring of polluted sites, development of new reliable approaches for tailings remediation and prediction of environmental fate of the contaminants and particularly heavy metals. One method used in Sweden, is to add lime, to tackle ARD produced during oxidation of sulfide bearing minerals, however, it is expensive and also generates more waste. Many other low cost alkaline material like cement kiln dust, red mud and sodium bicarbonate have been tested to neutralize mine waste [69-71]. Utilizing alternative industrial waste materials such as GLD and fly ash to mitigate the negative impacts of ARD would solve two waste problems simultaneously. GLD is a by-product produced by the paper and pulp industry from sulfate pulping process. In Sweden, about 200,000 tons of
GLD is produced annually [72]. Moreover, several millions tons have also been stored over time in industrial landfills. Typically GLD is comprised of sodium carbonate, sodium hydroxide, calcium carbonate, unburned carbon, sulfide and metals [73]. It normally possess a high pH and a fine clayey texture. In a few previous studies, GLD has been reported to be an affective alkaline material for stabilization of tailings through reduction of ARD, while at the same time being inexpensive and practical [68-73].
2. AIMS OF THESIS

The study was conducted to improve the understanding about trace element distribution during incineration and association in fly and bottom ashes as well as valorization of mining waste materials. Specific aims are:

- Partitioning of trace elements to ashes (fly and bottom) during incineration as a function of different waste fuel and incineration technology.

- Leaching characteristics of selected trace elements in ashes with water.

- Chemical association of trace elements in waste incineration fly and bottom ashes as a function of different waste fuels.

- Evaluating the possibility of metal extraction from mining waste (sulfidic waste rock and flotation tailings) through chemical leaching.
3. MATERIALS AND METHODS

3.1. Sampling of waste fuels used for incineration

Sampling of waste fuels for analysis is a complex procedure due to the uncertainty of being able to guarantee a representative sample from a relatively heterogeneous mixture. A sample can be used if sampling has been performed correctly in a demonstrative manner, however, with the reservation that it only represents one particular body of waste and its unique composition at the time of sampling. Heterogeneity is a major cause of sampling error [74] while other reported sampling errors include fundamental errors caused by inherent variability (variation in particle size and density), segmentation and grouping of particles, periodic and spatial variations. The complexity of sampling is considerably affected by pretreatment (crushing, segregation) of waste fuel before it was incinerated. For further information about sampling errors and related theories the reader is referred to Gy [74].

3.1.1. Sampling at grate facilities

Incoming waste fuel usually goes untreated into the boiler for incineration at grate facilities. Fuel analysis was not performed as a part of this study; data was instead collected partly from the facilities and partly from previous studies [75-76]. These studies [75-76] were conducted at the same plants using same fuel/waste fuel with identical proportions during the same time period. At grate facilities, waste fuel sampling was performed by using the segmentation method based on CEN/TS15442 [77]. A schematic overview of the segmentation process is shown in Figure 5. This method involves thorough mixing of waste before collecting 5-7 tons of sample. The collected sample is then crushed and mixed twice to reduce the large pieces to a few centimeters in size. The mixed waste fuel sample is then spread on a clean surface (10x10 m²) and split into two halves, one half is removed and the other is spread again in the same manner and the process is repeated until the thickness of waste fuel layer is 20 cm. This layer is then divided into small squares of about one square meter and from every square one sample is collected with a spade to get a total of 30 kg to ensure a possible representative sample [77].
3.1.2. Sampling at fluidized bed facilities
Waste fuel sampling at the fluidized bed facilities was comparatively easy since waste was pre-treated (shredded and mixed) before being introduced into the incineration process. A hatch (where the fuel was fed to the fluidized bed boiler) was used for sampling directly from the falling stream of waste [76]. The sample was taken by repeatedly inserting a spade in the falling fuel stream until an amount of about 30 kg was collected.

3.2. Sampling and storage of ashes
An amount of 1 kg for each ash was sampled by staff members on all facilities at four different occasions (during two days) to have a representative sample. Sample jars were filled to the rim and closed with tight lids to minimize contact with air to avoid further oxidation and carbonation. The four sub-samples of ashes were thoroughly mixed to get a possibly homogenized sample and one part (100 g) was taken out for total content analysis. During the sampling period, operation was stable and used the normal fuel mixture at all facilities. Summary of the investigated facilities is reported in Table 7. Flue gas treatment systems and fly ash sampling locations are described in Table 8. All bottom ash samples were...
collected from the ash pit after water quenching. Dry samples were collected; however, some wet samples (due to ash quenching) were dried at 40 °C, and course ashes were crushed down to < 4 mm to get homogenous and manageable samples.

### 3.3. Sampling of mining waste and site description

#### 3.3.1. Sulfidic mining waste (Ljusnarsberg, Sweden)

Sulfidic mining waste material used in this study was sampled from an old copper and lead mining site, called Ljusnarsberg, situated in the middle of a town called Kopparberg, in the mid of Sweden. Ljusnarsberg mine field was discovered in 1624 and the latest mining period ceased in 1975 [78]. Until the 19th century, the main focus of mining was copper and secondary iron ore, however, from the middle of the 19th century and onwards sphalerite (ZnS) and galena (PbS) ores were also produced [78]. Major source of economic mineralization was a more or less complex mixture of chalcopyrite/sphalerite/galena/pyrrhotite/pyrite/magnetite in various types of Ca/Mg/Fe skarns and silicified metavolcanics without carbonates. Waste rock remaining at the site was heavily oxidized and is covered with secondary precipitates. The estimated mining waste deposits are around 300,000 m³ of waste rock on 120,000 m² [78]. Material for this study was retrieved from one part of the mining site [Figure 1, Paper 5] containing highly oxidized material deposited during the mid-16th century. In this area the thickness of the mining waste is, on average, 4 m. A wheel loader was used to excavate around 100 tons of material from this section. This material was thoroughly sieved and mixed using a drum sieve machine in order to obtain a homogenized fraction < 13 mm (around 10 tons).

#### 3.3.2. Flotation tailings (Rudna, Poland)

Rudna is a copper mine in Legnica-Glogow Copper Basin- which is the major copper industry in Poland and one of the world’s biggest copper extraction sites. It is situated in south western part of Poland in Lower Silesia Province around 100 km north-west from Wroclaw [67]. Tailings were sampled fresh directly at the Rudna concentrator, during the day they were produced. Flotation tailings used in this study are deposited in the Zelazny Most dam which is the largest industrial landfill (1,325 ha, 700 Mm³) under operation in Europe [79-80]. The tailings are neutral or slightly alkaline (pH 7.5-7.8) consisting mainly of silicates and carbonates [79].
3.4. Analytical methods

3.4.1. Characterization of waste fuel used for incineration
Waste fuel characterization was performed at Swedish Testing and Research Institute (SP) [75]. Trace element (As, Sb, Cd, Cu, Zn, Pb, Cr) content was determined by Mod. ASTM D 3683 method for waste fuel analysis. This method involves combustion of waste material (6 g) to ash at 500 °C for 2 h which is then dissolved by mineral acids (HF/HNO₃/HCl digestion) and individual elements are determined by atomic absorption spectrometry [81]. Total sulfur and chlorine were quantified by CEN/TS 15289 method [82]. In this method, 1 g of sample in pellet form is kept in a metal crucible or a quartz glass and is combusted in 30 bar oxygen atmosphere. The acidic gas components are transferred into an absorption solution followed by ion chromatography for detection of sulfate and chloride (CEN/TS 15289) [82]. Trace element content of used waste fuels is reported in Table 2 of Paper 1.

3.4.2. Total concentrations of elements in ashes
For analysis of ashes, samples were sent to an external laboratory, ALS Scandinavia AB. Trace elements in ashes were analyzed by acid digestion of 0.2 g of ash sample according to ASTM D3683 (HF/HNO₃/HCl digestion) [81]. Analyses were accomplished as per EPA methods 200.7 using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and 200.8 using Inductively Coupled Plasma, Quadrupole Mass Spectrometry/Sector Field Mass Spectrometry (ICP-QMS/SFMS) (Method 200.7) [83]. Chlorine concentration was quantified by X-Ray Fluorescence (XRF). Other basic elements were determined by ASTM D3682 where alkaline fusion is performed using lithium metaborate (LiBO₂).

3.4.3. Chemical and mineralogical composition of mining waste
Total elemental content of the sulfidic mining waste (Ljusnarsberg) was determined by acid digestion (HNO₃). For analysis of trace elements, digestion was performed in a closed microwave oven (Mars V, CEM, USA) using 10 ml of concentrated HNO₃ (Merck, Germany) to 0.5 g of mining waste. Other major constituents were determined through alkaline fusion using lithium metaborate (LiBO₂) by an external laboratory. All analyses were performed according to EPA methods 200.7 using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and 200.8 using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Agilent, 4500, USA) (Method 200.7) [83]. Mineral identification of material was
performed by X-Ray Diffraction (STADI P, STOE, Germany). Moisture content of the material was determined by heating the sample at 105 °C for 24 h.

For characterization of the flotation tailings from the Rudna mine, a tailing sample was submitted to an external laboratory for chemical analysis using a combination of alkaline fusion and acid digestion. Trace elements such as Cu, Zn, Pb, Ag, Cd, Co, Mo and Ni were analyzed using four acid (HCl, HClO₄, HNO₃, HF) digestion and ICP-MS. Other elements such as Al, Fe, Ca, Mg, Na, K, and Cr were analyzed using ICP-AES after lithium metaborate fusion. Tailings were also analyzed for acid-base properties using acid-base-accounting (ABA) including parameters like paste pH, total sulfur, sulfide sulfur, sulfate sulfur and neutralization potential. Grain size distribution and mineralogical composition of the tailings was provided by the Polish mining company (KGHM Polska Miedź).

3.4.4. Characterization of green liquor dreg (GLD)
GLD used in this study was sampled from a local paper and pulp industry (Billerud Korsnäs AB, Frövi, Sweden) and its basic properties are reported in Table 1 of Paper 5. Total content of major elements in GLD were analyzed through alkaline fusion and ICP-MS, while trace elements were determined by use of acid digestion and ICP-MS. Total organic carbon was calculated from loss on ignition (LOI₁₀₀₀°C), while total inorganic carbon was determined by method SS-EN 13137 mod [84]. Buffering capacity (mmol H⁺/g dw) of GLD was determined through titration of sample down to pH 4 for 10 days. Percentage of CaO (%) was analyzed through standard test method ASTM C25 for analysis of free CaO (ASTM C25) [85]. The carbonate content was determined by wet combustion with a non-oxidizing acid in a closed and evacuated system. The pH of GLD was analyzed by using pH electrode that was calibrated using pH 4 and pH 7 standards.
3.5.  Leaching procedure for waste materials

3.5.1.  Standard leaching procedure for ashes and analysis of leachates
Samples were subjected to leaching according to a standard leaching procedure (EN 12457-3) [59]. This method is used to assess whether the criteria for disposal at landfill are met or not. According to this method, ashes are initially leached with ultra-pure water at liquid solid ratio (L/S) 2 for 6 h with shaking at 30 ± 2 r/min in an end-over-end fashion at room temperature. Phase separation is done by centrifugation at 20,000 g (11,417 rpm) for 30 min (Avanti J-20 XPI, Beckman Coulter, USA) and filtration using 0.40 µm polycarbonate filters (style 3120, Nalgene, USA). During the second stage, fresh ultra-pure water is added to the already leached ash sample and is shaken again at L/S 8 for 18 h resulting in a cumulative L/S of 10 [59]. Ash leachates samples were analyzed for electrical conductivity (CDM 210, Radiometer Analytical, France) and pH according to Swedish standards.

Chloride was analyzed using capillary zone electrophoresis. Prior to analysis, ash leachates were filtered (0.40 µm polycarbonate filter). The buffer consisted of 5 mM chromate at pH 8 and 0.5 mM tetradecyl trimethyl ammonium bromide (TTAB) was used to reverse the electro osmotic flow. Hydrostatic injection was done at 10 mbar for 30 sec.

Dissolved organic carbon (DOC) was determined using a Total Organic Carbon analyzer (TOC-VWP, Shimadzu, Copenhagen), where CO₂ formation was detected by infrared IR. All leachates were analyzed for trace elements by ICP-MS (4500, Agilent, USA) using ¹⁰³Rh as internal standard.

3.5.2.  Sequential extraction procedure for ashes
A modified four-step sequential leaching procedure by Tessier and Campbell [60], modified by Karlsson et al. [86], was employed to fractionate the trace elements into exchangeable, acid soluble, reducible, oxidizable and residual fractions. Details of each step are reported in Table 9. After each leaching step, leachates were centrifuged (Beckman Coulter, Avanti J-20 XPI, USA) at 20,000 g (11,417 rpm) for 30 min. Residual fraction was calculated as the difference between total digestion and the sum of the first four fractions. All leachates were analyzed for elements using ICP-MS (4500, Agilent, USA) using ¹⁰³Rh as internal standard.
3.5.3. Extraction procedure for mining waste materials
To determine the chemical association of trace elements in sulfidic mining waste from Ljusnarsberg mining site, a Tessier and Campbell sequential extraction scheme similar to that of ashes was used [60, 86]. Details of the extraction scheme is reported in Table 9.

For flotation tailings from the Rudna site a parallel extraction method was employed. The details are reported in Table 3 of Paper 6.

3.5.4. Leaching experiments to determine the impact of temperature, liquid/solid ratio and reagent concentration on metal leaching from mining waste
To measure the impact of different parameters on leaching of Zn, Cu and Pb from sulfidic mining waste and copper from flotation tailings, experiments were conducted using the leaching temperatures 25 °C, 45 °C, 65 °C and 85 °C (using water bath), extractant concentration of 0.01 M, 0.1 M and 1 M and liquid-solid ratios 5, 10 and 20. As leaching reagents, de-ionized (DI) water, reagent grade sulfuric acid (Merck, Germany), sodium hydroxide (VWR Chemicals AnalR® NORMAPUR®, Belgium) and sodium bicarbonate (Merck, Germany) were used without further purification. Generally 10 g of mining waste was mixed with extracting solution in a 250 ml centrifugation tube (Nalgene, USA). After 6 h of extraction time with intermittent shaking, samples were centrifuged (Beckman Coulter, Avanti J-20 XPI, USA) at 20,000 g (11,417 rpm) for 20 min to separate the extractants from suspension. The metal concentration of the final extractant was analyzed using ICP-MS (4500, Agilent, USA).

3.5.5. Leaching experiments for impact of GLD on metal stabilization
An additional set of experiments were conducted for 10 days to study the impact of GLD addition on metal (Zn, Cu, Pb) mobility from leached mining waste (sulfidic). Basic properties of used GLD are reported in Table 1 of Paper 5. A proportion of 10 % of GLD addition in mining waste was selected.

In this study, four systems were leached with 20 g of mining waste. Two systems were initially leached for metal recovery according to the method stated above (section 3.5.4) using water, and two other systems were leached using sulfuric acid (0.1 M). After leaching, one of each system was stabilized using GLD (2 g) and leached with water. All four systems were leached at L/S 10 for 24 h with shaking at 30±2 rpm in an end-over-end fashion. After 24 h of leaching phase separation was done by centrifugation.
at 20,000 g (11,417 rpm) for 20 min followed by filtration using 0.40 µm polycarbonate filters. All the leachate was removed from the systems and the metal concentration was analyzed using ICP-MS. After that, fresh DI water was added to already leached mine waste in all four systems, and shaken again for another 24 h. The DI water was changed after every 24 h, and this procedure was repeated for 10 days. All leachates samples (10 days leaching) were analyzed for metal concentration by ICP-MS, electrical conductivity (sensION+ EC7, HACH, USA) and pH (pH meter 744, Metrohm, USA) according to Swedish standard methods.

3.6. Mathematical expressions

3.6.1. Weighted average concentration of an element in fly and bottom ash

\[ \text{Weighted avg concentration } X_i = \frac{C_{Bi} M_B + C_{Fi} M_F}{(M_B + M_F)} \]

where, \( X_i \) is the weighted average concentration of a trace element \( i \) in fly and bottom ash, \( C_{Bi} \) and \( C_{Fi} \) (mg/kg dw) are the mass concentration of trace element \( i \) in the bottom ash and fly ash respectively, and \( M_B \) and \( M_F \) (ton/day) are the mass of bottom and fly ash produced.

3.6.2. Transfer of a trace element in fly ash during incineration [87]

\[ \text{Transfer of trace element to fly ash } = R_{Fi} = \frac{FC_{Fi}}{BC_{Bi} + FC_{Fi}} \]

where, \( F \) and \( B \) (%) are the dry mass percentage of fly ash and bottom ash in the incineration residues, respectively, and \( C_{Fi} \) and \( C_{Bi} \) (mg/kg dw) are the mass concentrations of trace element \( i \) in the fly ash and bottom ash respectively. It was assumed that input waste fuel matches the mass balance of fly and bottom ash, since no flue gas measurement was made.


\[ RAC = \frac{F1 + F2}{\text{Total concentration}} \times 100\% \]
RAC uses the active fractions (F1: ion exchangeable, F2: acid soluble) of the total content and grades the risk in fly ash from low to very high risk class [6].

3.7. **Principal Component Analysis**

Principal Component Analysis (PCA) is an interdependence technique in which all variables are simultaneously analyzed as a single set in a data matrix X. The original variables are transformed into new uncorrelated (orthogonal) variables called principal components (PCs). These components are used to describe the relevant information contained in the original observations. The dataset used in PCA is taken from the sequential leaching of the ashes (concentrations (mg/kg dw) in different fractions). Seven trace elements have been considered for evaluating the impact of fuel type on chemical association in ashes [Paper 3-4]. PCA was performed on both fly ash (13 samples) and bottom ash (13 samples), separately. Each trace element is contained in five fractions from sequential extraction data. The matrix [35 variables (7 elements and 5 different fractions) and 13 ash samples] was imported into the chemometric software The Unscrambler (Camo ASA, Norway) [88]. All variables were transformed into their logarithmic form and were auto scaled prior to the calculations. The results were validated through leave-one-out cross validation.
Table 7. Summary of plants investigated in current study

<table>
<thead>
<tr>
<th>Facility</th>
<th>Capacity (t/d)</th>
<th>Boiler</th>
<th>Bottom ash (t/d)</th>
<th>Fly ash (t/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kiruna</td>
<td>240</td>
<td>Grate</td>
<td>65</td>
<td>6</td>
</tr>
<tr>
<td>Liddköping</td>
<td>288</td>
<td>BFB</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>Umeå</td>
<td>480</td>
<td>Grate</td>
<td>60</td>
<td>12</td>
</tr>
<tr>
<td>Händelö P14</td>
<td>600</td>
<td>CFB</td>
<td>54</td>
<td>50</td>
</tr>
<tr>
<td>Sundsvall</td>
<td>144</td>
<td>CFB</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Högdalen</td>
<td>750-800</td>
<td>CFB</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Söderenergi</td>
<td>672</td>
<td>Grate</td>
<td>48</td>
<td>13</td>
</tr>
<tr>
<td>Nynäshamn</td>
<td>168</td>
<td>BFB</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Händelö P13</td>
<td>360</td>
<td>CFB</td>
<td>13</td>
<td>24</td>
</tr>
<tr>
<td>Eskilstuna</td>
<td>NA</td>
<td>BFB</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>Munksund</td>
<td>NA</td>
<td>CFB</td>
<td>5.5</td>
<td>10</td>
</tr>
<tr>
<td>Braviken</td>
<td>NA</td>
<td>Grate</td>
<td>71</td>
<td>35</td>
</tr>
<tr>
<td>Mälarenergi</td>
<td>1,000-1,200</td>
<td>CFB</td>
<td>13</td>
<td>42</td>
</tr>
</tbody>
</table>

BFB: bubbling fluidized bed. CFB: circulating fluidized bed. t/d: tons/day.
Table 8. Information about fuel and fly ash sampling locations for all facilities

<table>
<thead>
<tr>
<th>Facility</th>
<th>Waste Fuel</th>
<th>Fly ash sampling location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kiruna</td>
<td>Household (100)</td>
<td>ESP</td>
</tr>
<tr>
<td>Lidköping</td>
<td>Household + Industrial (70:30)</td>
<td>Bag filter</td>
</tr>
<tr>
<td>Umeå</td>
<td>Household + Industrial (60:40)</td>
<td>Bag filter</td>
</tr>
<tr>
<td>Händelö P14</td>
<td>Household + Industrial (50:50)</td>
<td>ESP + Bag filter</td>
</tr>
<tr>
<td>Sundsvall</td>
<td>Household + Industrial + Wood shavings (40:40:20)</td>
<td>Bag filter</td>
</tr>
<tr>
<td>Högdalen</td>
<td>Industrial waste (100)</td>
<td>Bag filter</td>
</tr>
<tr>
<td>Söderenergi</td>
<td>Industrial + Fuel pellets (60:40)</td>
<td>ESP</td>
</tr>
<tr>
<td>Nynäshamn</td>
<td>RWW (100)</td>
<td>Bag filter</td>
</tr>
<tr>
<td>Händelö P13</td>
<td>Wood chips (100)</td>
<td>ESP</td>
</tr>
<tr>
<td>Eskilstuna</td>
<td>Tree branches + Bark + Wood shavings + Willow</td>
<td>ESP</td>
</tr>
<tr>
<td>Munksund</td>
<td>Bark + Wood chips (70:30)</td>
<td>ESP</td>
</tr>
<tr>
<td>Braviken</td>
<td>DIP sludge + Bark + RWW (51:33:16)</td>
<td>ESP</td>
</tr>
</tbody>
</table>

RWW: recovered waste wood. ESP: electrostatic precipitator. t/d: tons/day, DIP: de-inking pulp
Table 9. Sequential extraction procedure for ashes [60, 86]

<table>
<thead>
<tr>
<th>Step</th>
<th>Target phase</th>
<th>Procedure and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Ion-exchangeable</td>
<td>20 ml 1 M NH₄Ac at pH 7, adjusted with NH₃, 1 h at 25 °C</td>
</tr>
<tr>
<td>F2</td>
<td>Acid soluble</td>
<td>20 ml 1 M NH₄Ac at pH 5, adjusted with HAc, 5 h at 90 °C</td>
</tr>
<tr>
<td>F3</td>
<td>Reducible</td>
<td>20 ml 0.043 M NH₂OH-HCl in 25 % HAc, 5 h at 90 °C</td>
</tr>
<tr>
<td>F4</td>
<td>Oxidizable</td>
<td>20 ml 0.02 M HNO₃ + 30 % H₂O₂ (3:5 v/v) at pH 2 adjusted with HNO₃, 3 h at 85 °C. Addition of 7.0 ml 3.2 M NH₄Ac in 20 % HNO₃ and 10.5 ml MQ water</td>
</tr>
<tr>
<td>R</td>
<td>Residual</td>
<td>Difference between total digestion and sum of four fractions (F1 to F4)</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSION

In paper 1, six Swedish incineration facilities have been investigated for impact of waste fuel (total content of trace elements, chlorine content) and incineration technology (type of boiler, combustion temperature) on partitioning behavior of trace elements during incineration. Facilities included were Umeå, Söderenergi, Nynäshamn, Händelö P13, Händelö P14, and Sundsvall.

In paper 2, thirteen Swedish incineration facilities are discussed with respect to impact of waste fuels and incineration technologies on partitioning and leaching behavior (with water) of trace elements in fly and bottom ashes.

In paper 3, chemical association and mobility of trace elements is discussed in fly ashes from 13 incineration facilities.

In paper 4, chemical association and mobility of trace elements is discussed in bottom ashes from 13 incineration facilities.

In paper 5, the leaching behavior of Zn, Cu and Pb from sulfidic mining waste (Ljusnarsberg) followed by immobilization of metals using green liquor dreg (GLD) is studied.

In paper 6, an evaluation is made about possible copper recovery through chemical leaching from flotation tailings sampled from a Cu-Pb mine (Rudna) in Poland.
4.1. Trace element partitioning in ashes as function of fuel composition (Paper 1)

Partitioning characteristics of trace elements during incineration were investigated as a function of input waste fuel, feed chlorine content, incineration temperature, and incineration technology. Six waste to energy facilities treating various waste fuels (household, industrial, recovered waste wood (RWW), virgin wood and mixed waste) were considered including two equipped with grate fired boiler and four with fluidized bed boilers [Table 1-2, Paper 1]. This study focuses on the concentration of trace elements in the waste fuel and their distribution in the incineration fly and bottom ash with respect to fuel composition.

Results from chemical characterization of waste materials showed that for all waste fuels Zn, Cu, Pb and Cr were the dominating trace elements [Table 1, Paper 1]. Trace elements followed the decreasing order in household waste as Zn > Cu > Pb, in recovered waste wood Zn > Cr > Cu, in virgin wood Zn > Cu > Cr, while in mixed waste (household/industrial) it is Cu > Zn > Pb. RWW contained higher concentrations of all trace elements compared to virgin wood (wood chips) that might be due to surface treatment or wood treatment using Cu, Cr and As (CCA impregnation) [15, 16, 32]. Household waste from Umeå contained high concentration of As, Cd, Zn, Pb, Cl and S in comparison to household waste from Sundsvall [Table 1, Paper 1]. With respect to chlorine and sulfur, mixed waste (industrial/fuel pellets) at Söderenergi contains highest chlorine (2.14 %) and sulfur (0.99 %) contents while virgin wood at P13 contains the lowest chlorine (0.005 %) and sulfur (0.002 %) concentrations [Table 1, Paper 1]. Household waste from Umeå had almost 3 times more chlorine and double sulfur content than household waste from Sundsvall [Table 1, Paper 1]. It might be attributed to the heterogeneous nature of household waste since its composition varies with location and time [13].

Increased chlorine in the fuel feed decreased the trace element transfer to bottom ash during incineration by forming metal chlorides that are highly volatile [31-34]. Household waste (Umeå) and mixed waste including industrial waste and fuel pellets (Söderenergi) were treated in grate boilers. Results indicated that with an increase of chlorine from 1 % at Umeå to 2 % at Söderenergi, highly volatile (mercury, cadmium) and medium volatile (Pb, Zn, As) elements showed an increased distribution to fly ash
The primary reason for an increased partition to fly ash could be the formation and vaporization of metal chlorides owing to high chlorine content in input waste at Söderenergi. Further, organic chlorine effect has been reported as dominant compared to inorganic chlorine on partitioning of trace elements during incineration [42]. Söderenergi facility is using fuel pellets and since fuel pellet production is achieved by increasing the organic content of fuel through removing the inorganic content and moisture, it might be speculated that Söderenergi waste fuel (industrial and fuel pellets) contained high content of organic chlorine. Since, organically bound chlorine prefers to be released as HCl(g) and reacts more willingly with trace elements [32], hence a large proportion of elements such as lead will be distributed to fly ash. Another reason for high transfer of elements to fly ash might be longer residence time for fuel (1,200-1,800 sec) on the grate in the case of Söderenergi facility because trace elements in fuel will be exposed to incineration conditions for a longer time so equilibrium for phases could be reached for trace elements.

Similarly, firing of RWW (Nynäshamn) in a fluidized boiler (BFB) caused increased transfer to fly ash for arsenic and chromium compared to firing virgin wood (P13) (CFB) probably also (in addition to chlorine impact) due to increased input of these elements in the input waste wood [Figure 6]. Waste fuel characterization showed that recovered waste wood contained the highest zinc concentration (3,300 mg/kg dw) of all discussed waste materials [Table 1, Paper 1]. An increased feed metal content favors high transfer rate of zinc to fly ash but not for Cu, Cd and Pb [38]. This is true for RWW incineration in this case because total input of zinc is higher in Nynäshamn input waste, so most of it partitioned to fly ash.

Another case is treatment of household waste (Sundsvall) and mixed waste including household/industrial waste (P14), in CFB. Waste fuel at P14 had higher contents of Zn, Pb, Cl and S compared to household waste from Sundsvall [Table 1, Paper 1]. Zinc distribution in fly ash increased from 52 % to almost 77 %, with an increase of Cl content from 0.33 % at Sundsvall to 0.66 % at the P14 facility. Low volatile elements Cr, Ni and Co also showed an increased partitioning to fly ash for mixed household/industrial waste at the P14 facility [Figure 6].

A very high correlation coefficient (r² 0.9) was found between chlorine in waste fuel and its transfer to fly ash indicating the possibility of excessive
volatilization and chloride formation mechanisms during incineration [Figure 7].

Volatile trace elements generally increases with furnace temperature due to vapor pressure increase. Shi et al. [89] showed decreasing order of volatility and vaporization rate as Cd > Pb > Zn > Cu during MSW incineration. In this study, only zinc and cadmium concentrations showed an increase in transfer to fly ash with incineration temperature. The enrichment of these trace elements in fly ash at high temperatures was possibly due to vaporization and entrainment processes.

Household waste was treated in both types of boilers. Moving from a grate (Umeå) to a CFB (Sundsvall) facility for household waste treatment, distribution of arsenic, lead and low volatiles (Cu, Cr, Ni, Co) to fly ash increased while transfer of zinc and antimony decreased [Figure 6]. Similarly moving from a grate (Söderenergi) to a CFB (P14) facility for mixed waste incineration showed that the transfer to fly ash increased for low volatiles, lead and zinc showed a slight increase while arsenic transfer decreased. The variance in distribution behavior might be due to the difference in waste composition as well as type of boiler and operational parameters.

Production of fly ash was almost double the production of bottom ash for Nynäshamn and P13 boilers [Table 2, Paper 1]. For grate boilers, the produced amounts of bottom ash were almost 4-5 times higher than the produced amounts of fly ash. The difference might be partly due to high combustion efficiency and high turbulence in the fluidized boilers. Uneven distribution of fuel in grate furnaces can also cause uneven combustion and increase unburned content and decrease grate boiler efficiency. Further, input fuel is pre-treated (sizing, shredding) in fluidized boilers and this might also enhance the transfer to fly ash since slightly more uniform and smaller composition of fuel would go into the incinerator.

Overall, mercury and cadmium were partitioned mostly in the fly ash in all cases during incineration, most probably because of vaporization, condensation on fly ash particles and adsorption mechanisms [31]. Around 2/3 of lead was transferred to fly ash while As, Zn and Sb showed high variations, with most of antimony and zinc distributing to fly ash. Arsenic showed a mixed behavior [Figure 6].

Low volatiles stayed in the bottom ash for grate facilities but showed surprisingly high transfer to fly ash for fluidized bed incinerators especially
in cases where recovered waste wood was used as fuel. The raw particulate matter carried over from the furnace and even clean flue gas dust has been reported [20] to contain considerable concentrations (100-1,200 μg/g) of low volatiles e.g. Cr. A likely reason could be solid particle entrainment to fly ash for fluidized boilers [20].

Waste fuel chlorine content and incineration temperature are very crucial factors affecting the partitioning of trace elements and corrosion of equipment [16, 32]. Increased chlorine in the fuel feed decreased the trace element transfer to bottom ash by forming metal chlorides that are highly volatile. Temperature has a significant impact especially on elements with low boiling points [Figure 6, Paper 1]. Zinc and cadmium concentrations increased in fly ash with increased combustion temperature [Figure 6, Paper 1].

An increased input concentration of certain trace elements, like zinc when firing recovered waste wood and chlorine while firing industrial waste or mixed waste, caused increased concentration in fly ash. Such trace elements might also boost the deposition and corrosion problems [16, 32]. So it is suggested to keep input metal and chlorine concentrations as low as possible. Waste fuel pretreatment (e.g. waste segregation), therefore, should be a mandatory step, in order to either reduce the total input of such elements or keep chlorine to a minimum level in the incoming waste.
Figure 6. Effect of input chlorine concentration on metal partitioning to fly ash for different boilers. Umeå (household), Söderenergi (industrial), P13 (wood chips), Nynäshamn (waste wood), P14 (mixed waste), Sundsvall (household)
Figure 7. Chlorine in fly ash as a function of input concentration
4.2. Partitioning and water leaching characteristics of trace elements in ashes (Paper 2)

Effect of input waste fuels (virgin/waste wood, mixed biofuel (peat, bark, wood chips) industrial, household, mixed waste fuel) and incineration technologies on partitioning and leaching behavior of trace elements was investigated. This study involved 13 facilities including 4 grate fired and 9 fluidized boilers. Summary of the plants investigated in this study are reported in Table 1 of Paper 2. Facilities with the same combustion system (boiler type) treating different waste fuels are combined [Figure 8] to explain how input waste fuels affects the partitioning of trace elements to fly ash.

Results [Figure 8a] showed that for household waste incineration in a grate boiler (Kiruna), most proportion of the studied trace elements such as Pb, Zn, Cu and Cr stayed in the bottom ash. Only cadmium and antimony showed high transfer to fly ash.

For incineration of mixed waste (household/industrial) in a grate boiler (Umeå), partitioning to fly ash increased for Pb, Zn, Sb and Cr, while for copper it decreased [Figure 8a]. Arm et al. [75] have reported an average of 1.5 % chlorine in the incoming waste fuel at Umeå facility, which could be one of the reason responsible for increased volatilization (compared to Kiruna facility) and metal chloride formation during incineration. Similarly, treating mixed waste including fuel pellets at Söderenergi facility in a grate boiler, further increase in transfer of As, Pb, Zn and Sb to fly ash was observed [Figure 8a].

Highest transfer to fly ash in grate boilers was observed for the incineration of waste containing biofuel (Braviken). Increased transfer for As, Cu, Cr and Zn was noted [Figure 8a]. Waste fuel characterization in a previous study [77] at the same facility showed high concentrations of zinc (950 mg/kg dw) and copper (230 mg/kg dw) in the sludge which is making up a major part (51 %) of the fuel mixture. Recovered waste wood that makes up about 16 % of this waste fuel [Table 8] also often contains high concentration of these elements. In Sweden, the most important sources contributing to contamination of recovered waste wood are impregnated wood, copper-chromium-arsenic (CCA), industrial preserved wood, plastics and galvanized fastening system [15]. Surface-treated wood is considered a major source of Pb, Zn, Cr and As [15, 16, 32]. Therefore, an increased
loading (input concentrations) of these elements might have caused high transfer of these elements to the fly ash.

For pure industrial waste incineration [Figure 8b] in a CFB (Högdalen), > 50 % of all trace elements (Pb, Zn, Cd, As, Cr, Sb) distributed to the fly ash except copper. For mixed waste (household + industrial) incineration in another CFB (P14), > 75 % of Pb, Zn and Sb partitioned to fly ash [Figure 8b]. Addition of household waste can cause an increased input of organic and inorganic chlorine which can trigger the transfer of trace elements to fly ash [16].

For mixed biofuel (peat, bark, waste wood) incineration in a CFB (Mälarenergi), > 75 % of all trace elements partitioned to the fly ash [Figure 8c]. Firing mixed wood waste including virgin wood and bark in a CFB (Munksund) showed a slight decrease (compared to mixed biofuel at Mälarenergi) in transfer to fly ash for As, Zn, Cu and Cr. Overall, for biofuel incineration in CFB (Munksund), most of the trace elements were distributed to the fly ash.

For virgin wood incineration in a BFB (Eskilstuna), most of the trace elements found their way to the fly ash [Figure 8d], especially Pb, Sb, Zn and Cd. Lind et al. [90] investigated the vaporization of trace elements such as Zn, Cd, Pb and Cu during the incineration of forest waste and observed that the major fractions of all these elements were enriched on fly ash particles.

For RWW incineration (Nynäshamn) as shown in Figure 8d, distribution to fly ash for Cr, Zn and As clearly increased (compared to virgin wood incineration). The reason might be an increased input concentration of these elements originating from CCA impregnated wood as reported by Blomqvist and Jones [70] at the same facility (Nynäshamn).

Though the composition of the residues has been shown to vary substantially with time as a function of process conditions and input waste composition. However, from our results and previous research about partitioning characteristics, one or more of following reasons could be given for an increased transfer of elements to fly ash:

1. An elevated input concentration of certain trace elements triggered an increased concentration in the resulting ash, e.g. Cr, As, Zn and Cu from CCA wood or Zn, Pb, Cu and Cl from household/industrial waste.
Figure 8. Impact of input waste fuel/boiler type on distribution of trace elements to fly ash (Hus: household, Ind: industrial, F: fuel, dip: deinking pulp)
(2) Mixing certain fractions in the incoming waste might change the partitioning or volatilization behavior of elements, also reported by Pedersen et al. [16].

(3) High combustion efficiency due to pre-treatment of waste fuel in fluidized bed boilers.

Resulting fly and bottom ashes from thirteen facilities were leached with water according to a standard leaching procedure, described in section 3.5.1 [59]. Leaching results of fly and bottom ashes are shown in Figure 4-5, respectively, in Paper 2. Results indicated that there were significant differences between samples with respect to leaching. Amounts of leachable trace elements from fly ashes [Figure 4] were generally low with leaching below 1% of the total content except for some samples such as Lidköping (household + industrial) fly ash. This ash leached 43% Pb, 10% Cu and considerable amount of Zn as well which means that significant amounts of these elements were present as water soluble phases. Water soluble compounds of these elements are likely to be chlorides, bromides, sulfates such as CuCl$_2$, PbBr$_2$, ZnSO$_4$ and PbClOH (slightly soluble in water) [91, 92].

Leaching results of the fly ashes [Figure 4, Paper 2] showed that the release of lead exceeded the regulatory limit of disposal in all fly ashes. Zinc in 7 samples while copper in 6 out of 13 fly ash samples respectively, leached more than the set limit of disposal. Excessive leaching of chromium was also observed in 7 fly ash samples. Similarly arsenic exceeded the regulatory limit of disposal in 4 out of 13 samples. Leached amount of antimony exceeded the regulatory limit only in one sample from Sundsvall facility, which was treating household/industrial mixed waste. In most cases, cadmium leaching was well below the detection limit. Cadmium leaching exceeds the limit of disposal at only one facility using household waste (Kiruna).

Trace elements in fly ash behave in three different ways to water leaching. Some elements are easily leached and in high concentrations e.g. lead and copper from Lidköping (household/industrial mix) and molybdenum from Söderenergi ash (industrial / fuel pellets mix). Most probably such elements were deposited on the surface of ash particles and easily leached species are washed away on contact with water [91, 93].
Secondly, some elements might have existed in the center of ash particles or enclosed inside the particles [94], they were leached moderately and slowly only after surface deposited elements were washed away. Possible example from the current study can be antimony and lead release from Sundsvall fly ash, because higher amount of antimony and lead was leached out at L/S 8 compared to at L/S 2. Another category is elements that are insoluble and found below detection limit. For example cadmium in many ashes was below the detection limit [Figure 4, Paper 2].

Correlation between total and leached concentrations (with water) in fly ash was calculated for copper $(r^2 0.6-0.7)$ and lead $(r^2 0.2-0.3)$. For other elements no significant correlations were found. Average amounts of trace elements leached with water from the fly ashes followed the decreasing order Pb > Cu > Cr > As > Zn > Mo > Sb. Leaching behavior of trace elements is different in various waste fuel ashes. Further, ash matrix and total concentration in the ash are critical factors affecting the leaching of trace elements.

In the case of bottom ashes [Figure 5, Paper 2], all four ashes that exceeded the regulatory limit of disposal for copper are from incineration of household and/or industrial waste, while lead exceeded limit in five ashes including three household and/or industrial and two virgin wood bottom ashes. Similarly, chromium surpassed the limit in six ashes including two household/industrial, three RWW containing waste fuels and one mixed wooden fuel bottom ash. Antimony exceeded the limit in four household and/or industrial waste and in one RWW bottom ash.

Nynäshamn (RWW), Högdalen (industrial waste) and Umeå (household/industrial) bottom ashes are the most contaminated with respect to number of trace elements leaching more than the regulatory limit. Leaching of As, Cr and Sb in Nynäshamn (RWW) bottom ash while Pb, Sb and Cu leaching in Högdalen (industrial waste), and leaching of Pb, Cu and Zn in Umeå (household/industrial) waste bottom ash surpassed the regulatory level.

Water soluble forms of trace elements in ashes were low with a few exceptions. Ash matrix and total concentration in ash seems to play a vital role in the leaching of some trace elements with water. For disposal criteria, leached amounts of Pb, Zn and Cr exceeded regulatory limit in 84 %, 61
% and 53 % of the fly ash samples, respectively, so all these fly ashes must be treated before being landfilled or re-utilized.

Exposing fly ashes to water removed > 87 % (based on average value) of total chlorine at L/S 10 [Figure 6, Paper 2], indicating the importance of water washing process for incineration residues before any other treatment. Astrup et al. [37] reported that affinity between chlorine and cations follows the decreasing order of H > Na/K > Pb > other trace elements. Thus, formations of highly water extractable alkali chlorides (NaCl, KCl) and CaCl₂ are much more likely during incineration, resulting in the removal of a large proportion of available chlorine. With respect to landfill criteria chlorine leaching (L/S 10) from ash should be less than 0.8 % [95]. In this study chlorine leaching in 61 % of the fly ash samples exceeded this set limit [Figure 6, Paper 2].

For bottom ashes only Umeå ash (household/industrial) showed a removal of 45 % of total chlorine at L/S 10 [Figure 6, Paper 2]. For most facilities using biofuel for incineration, leached chlorine concentration was well below the limit for disposal. The leaching of chlorine is availability controlled and is independent of pH because Cl⁻ offers rapid and complete dissolution at all pH values [42].

Further, none of the ash exceeded the limit for disposal with respect to leaching of dissolved organic carbon (DOC) [Figure 7, Paper 2]. Leaching results showed that comparatively higher DOC amounts were leached from bottom ash compared to fly ash. Low release of DOC from fluidized bed boiler bottom ash might be due to lower total carbon content, since generally incomplete combustion leads to a higher total carbon content for grate boilers [96].
4.3. Chemical association of trace elements in fly ashes (Paper 3)

Migration of trace elements from waste incineration fly ash is problematic during utilization/landfilling. In this work, the chemical association and potential mobility of trace elements in fly ashes originating from incineration of different fuels (virgin wood, recovered waste wood (RWW), mixed wooden fuel/waste, household, industrial and mixed waste) was investigated. Information summary of the plants including the location of fly ash sampling are reported in Table 1 and Table 2 of Paper 3.

Chemical characterization showed that all fly ashes were dominated by Zn, Cu and Pb with respect to trace elements and the average total concentrations in 13 fly ashes followed the decreasing sequence Zn > Cu > Pb > Sb > Cr > As > Cd. Highest variation in concentration was shown by Cd, Cu and Sb with the range 6-380 mg/kg dw, 74-16,400 mg/kg dw and 2.6-1,870 mg/kg dw respectively. Further, high concentrations of zinc 1,290-26,900 mg/kg dw and lead 118-7,460 mg/kg dw were also present in most of the fly ashes (especially those using household/industrial waste materials). High concentrations of Zn, Cu and Pb in fly ashes might be attributed to the increased total input from MSW and other waste materials [16]. Also due to the formation and vaporization of volatile metal chlorides e.g. ZnCl₂ and PbCl₂ during waste incineration, by the reaction of trace elements with incoming organic/inorganic chlorine from plastic waste and food residues respectively. These chlorides are quite volatile and could also easily be adsorbed on fly ash particles resulting in high concentrations in the fly ash [40]. To summarize, heterogeneity of waste materials, varying collection processes, incinerator type and air pollution control systems all affect the final distribution of trace elements thus causing the large variation in concentration.

Chemical association of trace elements in fly ashes are important when it comes to landfilling/utilization and it was determined by a modified sequential extraction scheme as reported in Table 9. Results of the sequential extraction of the fly ashes are presented in Figure 9-10. In Figure 9, a detailed chemical association of trace elements in each fraction for fly ash from facilities treating household, industrial or mixed waste is presented, while in Figure 10, chemical association is presented for wooden/mixed wooden fuel fly ashes.
**Arsenic**

In 10 of 13 analyzed fly ash samples residual (R) fraction was the dominating fraction for arsenic and the proportion varies from 44-93 % [Figures 9-10]. In other cases e.g. in mixed wood fuel and virgin wood fly ash at Mälarenergi and P13, respectively, exchangeable (F1) and acid soluble (F2) were the dominating phases, accommodating most of the arsenic. Arsenic in fly ash has been reported to be present in substantial amounts in the silicate matrix and an alumino-silicate matrix which is why it was not expected to be released [97]. It might be the reason for its increased presence in R fraction. The presence of arsenic in F1 or F2 in a few fly ashes might be due to the existence of calcium arsenate (Ca₃(AsO₄)₂·XH₂O) and As₂O₃, as reported by Lundholm et al. [98]. It was reported that arsenic forms arsenates with e.g. Cu, Cr, Ca, Mg, Na and K in both fly ash as well as in bottom ash [90]. There is a possibility that arsenates (Ca₃(AsO₄)₂·XH₂O) are present in a few fly ash samples and decreasing pH to 7 or 5 in F1 or F2 fractions might have increased the solubility of Ca₃(AsO₄)₂. As₂O₃ is also readily soluble so some proportion of arsenic might have, therefore, been extracted in these fractions.

**Antimony**

In most of the fly ashes, each fraction accommodated an even proportion of antimony. In 6 samples (Högdalen, Sundsvall, Lidköping, Munksund, P13 and Mälarenergi), the R fraction was the dominating phase, probably antimony contained in the silicate matrix. F1 and F2 were the next dominating phases for antimony. The lowest percentage was extracted in reducible (F3). Only in Braviken fly ash (mixed biofuel) oxidizable fraction (F4) forms about 48 % of extracted antimony.

**Lead**

In five samples, R was the dominating phase ranging from 51 to 80 % and these fly ashes originated from virgin wood (P13, Eskilstuna) and mixed wooden fuel/waste (Mälarenergi, Munksund, Braviken) incineration. Similarly in other 6 of 13 samples, F2 was the dominating phase with a range 36-60 % and these ashes originated from incineration of household/or industrial, mixed waste and RWW (Nynäshamn). Zhu et al. [99] utilized a combination of synchrotron microprobe, sequential chemical extraction and multivariate statistical analysis to investigate association of trace elements in single particles of MSWI Air Pollution Control (APC) residues. It was reported that most lead was present as chloride in APC residues and
its existence in F2 fraction was also observed during sequential extraction procedure. Presence of lead in the R fraction in the case of mixed wood incineration fly ash might be due to reaction of lead with silicates or alumino-silicates in fly ash. Lind et al. [100] investigated behavior of different trace elements during incineration of forest residues and found that lead was enriched entirely on coarser particles indicating the conversion of gas phase species to particle due to certain chemical reactions. They reported lead might have reacted with SiO₂ both in the bed as well as in fly ash. Cerussite (PbCO₃) also dissolved during this step. Lowest proportion of lead was leached in F4.

**Copper**
F1 fraction was the dominating phase for copper in 6 out of 13 fly ash samples with the proportion ranging from 52 to 82% and these ashes originated from incineration of household or mixed waste [Figure 9]. Recently, Lassesson et al. [101] investigated two Swedish MSWI fly ashes by using X-ray Absorption Spectroscopy (XAS). They reported that one fly ash contained highly soluble compounds such as sulfate, chlorides and hydroxides. Fly ash in our study might also have contained the similar sort of compounds since all fly ash samples with F1 fraction as dominating phase contained high chlorine concentrations, as reported in Table 4 of Paper 3. There is also a possibility that a complex was formed between NH₃ and copper during the F1 step, as some solutions turned dark blue during extraction. So these scenarios might be the reason for a high copper presence in the exchangeable fraction. Other 4 of 13 samples (P13, Braviken, Mälarenergi, P14) have residual fraction as the dominating phase (range 40-61%) and these facilities were treating mixed wood fuel or mixed waste for incineration [Figures 9-10]. In Nynäshamn fly ash (using RWW) most copper (56%) was found to be associated to the F4 fraction. The remainder of the samples had almost uniform distribution of copper in various fractions.

**Chromium**
For all fly ash samples, most chromium existed in the R fraction as shown in Figures 9-10. Large amount of chromium has been reported to be incorporated in the stable spinel matrix and hence will only leach after the glass phase and Fe-Mn oxides have been dissolved [102].
**Cadmium**

Highest concentration of cadmium is present in F1, for about 9 of 13 analyzed samples and its proportion ranges from 53 to 92% [Figure 9-10]. Lowest proportion was extracted in the F2 and F3 fractions. Only for one fly ash sample at Nynäshamn (using RWW) most of the cadmium was accommodated in the R fraction. Feng et al. [102] explained high extractability of cadmium in the F1 fraction due to surface absorptive ability of cadmium during incineration of waste; therefore it showed high release potential. Huang et al. [103] also reported remarkable mobility of cadmium in MSWI fly ash.

**Zinc**

In case of zinc there was no particular correlation found between fuel type and distribution in various fractions. Mostly a uniform distribution of zinc was observed in all fractions. However, in 11 (Kiruna, Lidköping, Umeå, Sundsvall, P14, Högdalen, Söderenergi, Eskilstuna, Nynäshamn, P13, and Mälarenergi) of 13 analyzed fly ash samples, active fractions i.e. (F1+F2) made up > 45% of extracted zinc as shown in Figures 9-10. In the other two ashes F1+F2 accommodated < 40% of zinc. It has been reported that zinc is present primarily as chlorides and also as Zn$_2$SiO$_4$ and ZnAl$_2$O$_4$ in fly ash [104, 105]. Chlorides are readily available in F1 phase, and in R fraction zinc might be present in the mineral forms.

Trace elements in the F1 and F2 fractions have been reported to be potentially bio-available during environmental conditions [1], while the reducible and oxidizable fractions are reported to have a lower potential bio-availability and residual fraction is generally stable [106].

In this study the decreasing order of trace elements in bio-available/potentially bio-available or stable fractions was given as:

- bio-available (F1+F2): Cd > Zn > Cu ≈ Sb > Pb > As > Cr
- potentially bio-available (F3+F4): Pb > Cu > Zn ≈ Sb ≈ Cr > As > Cd
- residual fraction (R): Cr > As > Pb > Sb > Cu > Zn > Cd

So mainly Cd, Cu, Sb, Pb and Zn were present in the forms that are easily available since high amounts of cadmium (73% based on average values) in 10 samples, copper (63% based on average values) in 6 samples and antimony (31% based on average values) in 9 of 13 fly ash samples existed in F1 fraction, respectively. Similarly, considerable amounts of lead (48% based on average values) in 7 samples and antimony (21% based on average values) in 9 of 13 fly ash samples existed in F1 fraction, respectively.
values) in 9 of 13 samples were present in acid soluble fraction. For zinc, both F1 and F2 fractions accounted for about 50% of total concentration with few exceptions. On the other hand Cr, As and part of Pb were mostly present in the R fraction.

Principal Component Analysis (PCA) performed on the sequential extraction data of the fly ashes indicates that the association of trace elements in fly ash is affected by fuel type, as shown in Figure 4 of Paper 3. Moreover, risk assessment code (RAC) results showed that almost every fly ash sample presented potential risk to the environment. Cd, Zn, Cu and Sb presented major risk in most of the fly ash samples, while Pb posed medium to high risk in a few samples. Arsenic and chromium were present mostly in low risk class [Figure 5, Paper 3]
**Figure 9.** Association of trace elements in fly ash originating from incineration of household, industrial and mixed waste materials by sequential extraction. (F1: ion exchangeable, F2: acid soluble, F3: reducible, F4: oxidizable, R: residual)
Figure 10. Association of trace elements in fly ash originating from incineration of waste/virgin wood and mixed wood waste/fuel by sequential extraction. (F1: ion exchangeable, F2: acid soluble, F3: reducible, F4: oxidizable, R: residual)
4.4. Chemical association of trace elements in bottom ashes (Paper 4)

In this work, thirteen different Swedish solid waste (virgin wood, recovered waste wood (RWW), mixed wood waste (peat, bark, wood chips), household, industrial, and mixed waste) incineration bottom ashes were investigated with respect to chemical characteristics and chemical association of trace elements.

Chemical characterization of bottom ashes showed that all bottom ashes were dominated by the presence of Cu, Zn, Pb and Cr with respect to trace elements. The average total content of trace elements in 13 bottom ashes followed the decreasing order Cu > Zn > Pb > Cr > Ni > Sb > As. The trace element content in the bottom ashes ranged from 6-104 mg/kg dw As, 0.5-321 mg/kg dw Sb, 12-2,750 mg/kg dw Pb, 395-14,800 mg/kg dw Zn, 36-17,300 mg/kg dw Cu and 43-806 mg/kg dw Cr. High variation in concentrations between the facilities might be attributed to the variety of input waste fuels treated (occurrence and distribution of trace elements, chlorine content), volatilization potential of trace elements and different furnace operation parameters during incineration (temperature, air/fuel ratio, mixing conditions) [1]. On average, the content of trace elements (Zn, Cu and Pb) in household/industrial or mixed waste bottom ashes were higher compared to wood/mixed wood fuel ashes.

Average total content of major trace elements such as Zn, Pb, Cu and Cr were found to be higher in grate boiler bottom ash (treating household/industrial) in comparison to fluidized boilers bottom ash (treating household/industrial). On the other hand, high total contents of Sb, As and Ni were found in fluidized boiler ash as compared to grate bottom ashes, both treating household/industrial waste. Possible reason might be the lack of pre-treatment of input waste fuel entering into grate incinerators which might decrease combustion efficiency and caused staying of major trace elements in the bottom ash. Further, grate furnaces also use household waste (that contains high concentration of these elements) to a much higher degree compared to fluidized boilers. Also fluidized boilers have natural dilution of the ash from the bed material. Type of waste fuel or wood waste greatly impacts the total inventory of trace elements [16].

MSWI bottom ash has often been the focus of chemical association studies and limited work is reported (compared to MSW) about association of trace
elements in wood/mixed wood fuel incineration bottom ash such as virgin wood, RWW or mixed wood fuels including peat, bark and wood chips. Since these fractions are part of waste fuels being used for heat and electricity production in Sweden, determination of chemical association or grouping of trace elements in different fractions of these bottom ashes is also important. Results of trace element association from this study are reported in Figure 11-12. In Figure 11, a detailed chemical association of trace elements in each fraction for bottom ash from facilities treating household, industrial or mixed waste is presented. In Figure 12, chemical association for wooden/ mixed wood fuel (RWW, virgin wood and mixed wood fuel including peat, bark and wood chips) incineration bottom ashes is presented.

**Arsenic**
In 9 of 13 analyzed bottom ashes, residual (R) was the dominating fraction for arsenic with its proportion ranging from 43-89 %. In the other 4 samples, ion-exchangeable (F1) and acid soluble (F2) were the dominating fractions [Figures 11-12]. In this study, generally, in bottom ashes originating from incineration of household, industrial or mixed waste, most of the arsenic existed in the R fraction. For RWW (Nynäshamn) and mixed wood waste (Mälarenergi) incineration bottom ashes, 46 % and 57 % of arsenic existed in F1, respectively. Chandler et al. [38] speculated that the major part of arsenic might be contained in inorganic parts of the input waste that could not be incinerated and thus would be retained in the bottom ash. Arsenic might be present in substantial amounts in the silicate or alumino-silicate matrix and hence not easily leached, so, it might be the reason for its increased presence in the R fraction [62].

**Antimony**
For antimony, the R fraction was the dominating phase for 12 of 13 analyzed samples with the range 52-95 %. Antimony was probably contained in the silicate matrix. In one sample (P13) mobile fractions F1 and F2 accommodated a major part (54 %) of antimony. Antimony leaching from 31 Swedish ashes was investigated by Bäckström [107]. Aluminium and sulfate were identified as important species through multivariate and geochemical calculations and it was reported that ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂*26H₂O) might govern the antimony leaching [107]. However, recently Cornelis et al. [108] reported that in addition to
ettringite, leaching of antimony in bottom ash is also governed by romeite (composition of calcium antimonates) precipitation.

**Lead**

Residual (R) fraction was again the leading phase in 12 of the 13 samples with its proportion ranging from 54 to 98%. In one sample, F2 was the dominating phase for lead with its share 59%. In a few samples e.g. Söderenergi (mixed waste) and Braviken (mixed wood waste), F2 and reducible (F3) fractions also contained a significant amount of lead. There was no particular correlation found between chemical association and waste fuel used. In RWW, lead probably originates from surface-treatments (pigments) and might be lead oxides or lead chromates [37], while in household or industrial waste it could originate from use of lead stabilizers which are the most common stabilizers in PVC applications [37].

**Copper**

In 9 of 13 bottom ash samples, most of the copper was bound to the R fraction (R), ranging from 58 to 94%, while in the other 4 samples, large amounts of copper were associated with the organic bound fraction (F4) ranging from 39 to 56% [Figure 11-12]. Sequential extraction results showed that in bottom ash from Lidköping, P14, Söderenergi (household/or industrial waste) and Braviken (mixed wood waste), > 38% copper resides in the F4 fraction. Copper has earlier been reported to have high affinity for strong organic ligands [101]. Meima et al. [110] found that copper leaching from fresh bottom ash and 1.5 year old MSWI bottom ash was mainly controlled by the presence of strong organic ligands and that in the absence of DOC, predicted leaching of copper would be lowered by a factor of 2-3. Many other studies have also mentioned an interaction between copper and organic matter in the bottom ash and that dissolved organic matter facilitates copper leaching [111, 112]. In this study, there was no correlation found between copper associated with the F4 fraction and copper leachability with water; there was, however, a correlation coefficient (r) of 0.4 between copper leaching (standard leaching) and DOC leaching. Dissolved organic matter, therefore, might play an important role in leaching of copper from bottom ash [112]. To summarize, copper seems to be strongly bound to both, solid organic matter (F4) and dissolved organic matter. Further research is needed to establish the relationship between solid organic matter and dissolved organic matter.
Chromium
Most chromium was found in R fraction. In all analyzed samples, residual was the dominating phase ranging from 72 to 97 %. Trace elements in the residual fraction has previously been reported to be strongly associated with the silicate and aluminate matrix and were very difficult to leach out [1].

Zinc
For zinc, the R fraction was the dominating phase for 9 of 13 samples ranging from 42 to 84 %. In the other 4 samples (Umeå, Söderenergi, Braviken, Högdalén) the labile fractions F1 and F2 dominated. More specifically the F2 was the major phase for zinc in most of the other 4 samples.

In two samples (Braviken and Umeå), in addition to F1 and F2, fraction F3 also contained considerable amount of zinc. Sequential extraction results showed that zinc was quite mobile in bottom ash from a few facilities treating industrial waste (Högdalén) or mixed waste (Umeå, Söderenergi) and mixed wood waste (Braviken), since > 40 % of the zinc is present in the labile fractions (F1, F2) in these ashes.

Nickel
For bottom ashes from 6 facilities [Figure 11] including Kiruna, Lidköping, P14, Umeå, Sundsvall and Söderenergi (all are treating household and/or industrial waste), R fraction was again the dominating fraction for nickel ranging from 65 to 92 %. For bottom ash from Nynäshamn (RWW) and Eskilstuna (wood chips) 59 % and 55 % of nickel was present in F4, respectively, while for bottom ash from P13 (wood chips), Mälarenenergi and Munksund (mixed wood waste/fuel) 33 %, 36 % and 32 % of nickel, respectively, was present in F4, the oxidizable fraction [Figure 12].

Based on 13 bottom ash samples investigated in this study, the decreasing order of trace elements based on average values in fractions are arranged as:

- bio-available (F1+F2): As > Zn > Sb > Cu ≈ Ni ≈ Pb > Cr
- potentially bio-available (F3+F4): Ni > Cu > Zn ≈ As > Pb > Sb ≈ Cr
- residual fraction (R): Cr > Pb ≈ Sb > Cu ≈ Zn > As > Ni

These sequences are based on percentage values from sequential extraction data. According to the sequential extraction results in this study, high amounts of arsenic (57 % based on average values) in 5 samples (mostly in waste/virgin wood and mixed wood waste/fuel), and zinc (49 % based on
average values) in 4 of 13 samples (mostly household/or industrial) are found in the fractions that are easily available i.e. F1 and F2 [Figures 11-12]. Further, 48% of copper (based on average values) in 4 of 13 samples is bound to F4 fraction. In these samples dissolved organic matter might play an important role in leaching of bottom ash [104] through the formation of complex with trace elements e.g. Cu-DOC complex during utilization/landfilling of bottom ashes.

Overall, amounts of unstable trace elements in wooden/mixed wooden fuel incineration bottom ashes were lower [Table 6-7, Paper 4]. Further, none of the bottom ash exceeded the regulatory limit of disposal with respect to DOC leaching, however; chlorine in two and sulfate in three household/industrial bottom ashes exceeded the regulatory limit for disposal, while there was one bottom ash (household) where both chlorine and sulfate exceeded the disposal limit.

LOI (550 °C) values were higher for bottom ashes from grate facilities than any of the ashes from fluidized boilers [Table 8, Paper 4] indicating presence of organic matter (probably due to no pre-treatment of the waste fuel at grate facilities).
Figure 11. Association of trace elements in bottom ash originating from incineration of household, industrial and mixed waste materials by sequential extraction. (F1: ion exchangeable, F2: acid soluble, F3: reducible, F4: oxidizable, R: residual)
Figure 12. Association of trace elements in bottom ash originating from incineration of waste/virgin wood and mixed wood waste/fuel by sequential extraction. (F1: ion exchangeable, F2: acid soluble, F3: reducible, F4: oxidizable, R: residual)
4.5. **Sulfidic mining waste: chemical leaching and stabilization (Paper 5)**

In this work, an assessment was made about the feasibility of sulfidic mining waste washing to extract Zn, Cu and Pb using various chemical extractants. Impact of extractant concentration, leaching temperature and liquid solid ratio (L/S), on metal extraction was evaluated. Further, green liquor dreg (GLD) was tested with respect to stabilization of metals in sulfidic mining waste after washing.

Results of the chemical characterization of mining waste are reported in Table 3 of Paper 5. Sample pH is quite low (2.87). Generally, an increase in pH and organic matter content reduce the metal mobility and extractability [113]. According to the chemical analysis of the mining waste samples, high concentrations of Zn, Cu, Pb and Cd were detected, posing significant risk for humane health and the environment [Table 3, Paper 5]. Further, high concentrations of iron and manganese are also present, which are not considered toxic [66], but might also significantly deteriorate quality of groundwater. In previous studies [114, 115], the acid producing potential of the mining waste from this mining site (Ljusnarsberg) was found to be 41.7 kg CaCO₃/t and 73 kg CaCO₃/t for surface acidity and total acidity, respectively.

Moreover, results from ocular inspection of all mining waste dumps and chemical analysis of 123 selected samples from the Ljusnarsberg mining site indicated that the carbonate content was very low [Table 5, Paper 5] and that the sulfidic minerals were dominating over skarn minerals followed by almost equal amounts of fine grained silicate rock, micas and magnetite [78]. It is also apparent that chalcopyrite (CuFeS₂) was dominating over both sphalerite (ZnS) and galena (PbS) while sphalerite was slightly more abundant than galena [Table 5, Paper 5]. Distribution between pyrite (FeS) and pyrrhotite (FeS₂), on the other hand, seemed to be equal. When comparing the concentrations of Cd, Cu, Pb and Zn in the waste rock with the adjusted health based reference concentrations, it was apparent that lead was found in concentrations exceeding values with possible negative health effects [78] (20 % of the examined samples exceed the adjusted value of 5,000 mg/kg dw for lead).
Sequential extraction of the mining waste sample indicated that lead was much more easily leached than the other trace elements with around 10% in F1 (exchangeable), 25% in F2 (acid soluble) and 21% in F3 (reducible), as reported in Table 7 of Paper 5. Similar findings for lead association in mining waste were also reported by Zagury et al. [116]. This indicates that lead is present as fairly soluble salts in the mining waste in addition to the fractions probably included within the HFO. Anglesite (PbSO4) was the only solid phase containing lead that was suggested by the geochemical calculations performed by Sartz et al. [117], but the possibility of the presence of occluded discrete minerals of carbonates cannot be excluded due to the results from the sequential extractions. Other trace elements (Cu, Zn and Cd) are mainly found in F4 (oxidizable) indicating the possible presence of discrete sulfide minerals within the mining waste.

Results from the chemical leaching experiments are presented in Figures 2-4 of Paper 5. Of all the tested reagents, sulfuric acid was the most effective extractant by leaching around 75% zinc and 45% of total copper at 1 M, L/S 20 and 85 °C, while lead was not much mobilized due to anglesite (PbSO4) formation during leaching. Leaching results with sulfuric acid are shown in Tables 10-12. Temperature impact on leaching of elements from sulfidic mining waste is reported in Table 10. It can be seen that leaching efficiencies for zinc (27% to 75%) and copper (11% to 45%) increased with temperature, while lead leachability was not much affected by temperature (1.2% to 2.5%). An increase in temperature generally improves the molecular movement or decreases the diffusional resistance, which might result in an increased leaching rate and therefore, an increased recovery [110]. Increase in sphalerite and chalcopyrite dissolution in sulfuric acid with temperature have been reported earlier [119, 120]. Even at 25 °C, in this study, around 26% of the total zinc was leached using 1 M H2SO4 at L/S 20; however, for copper extraction higher temperature was required. This is because of slow dissolution kinetics of chalcopyrite in sulfate media due to passivation of the mineral surface [119]. Effect of acid concentration on metal leaching is shown in Table 11. It can be noted that the extracted amounts of zinc and copper increased with concentration up to 1 M, while lead did not show any significant mobility with increased concentration. Similarly, leached amounts of zinc and copper increased with increased L/S, while lead was not much affected by changing L/S, as shown in Table 12.
Results of metal stabilization experiments using GLD are presented in Figure 13. Alkaline capacity of GLD increased the pH of the extracted mining waste and hence reduced the metal leachability. An addition of 10% GLD was sufficient to reduce the Pb, Zn and Cu leaching by a factor of 27, 14 and 7, respectively (based on average values of 10 days leaching). As described earlier in the text, lead was found in high concentrations with possible negative health effects. It can be seen in Figure 13 that GLD addition has significantly changed (reduced) the mobility of lead from the mining waste. Decreased leaching of trace metals in GLD amended system (compared to the reference, mining waste) is strongly connected to pH and hence, almost quantitative removal (> 99%) was found for Pb, Cu and Zn in the amended system. Addition of GLD increased the pH of the mining waste from 2.87 to 6.8 on the 1st day.

Table 10. Impact of leaching temperature on metal extraction using 1 M sulfuric acid from Ljusnarsberg mining waste at L/S 20

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Zn extraction (%)</th>
<th>Cu extraction (%)</th>
<th>Pb extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>27</td>
<td>11</td>
<td>1</td>
</tr>
<tr>
<td>45</td>
<td>42</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>65</td>
<td>57</td>
<td>39</td>
<td>2</td>
</tr>
<tr>
<td>85</td>
<td>75</td>
<td>45</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 11. Impact of sulfuric acid concentration on metal extraction from Ljusnarsberg mining waste at 85 °C and L/S 20

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Zn extraction (%)</th>
<th>Cu extraction (%)</th>
<th>Pb extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 M</td>
<td>13</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>0.1 M</td>
<td>67</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>1 M</td>
<td>75</td>
<td>45</td>
<td>2</td>
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</tbody>
</table>

Table 12. Impact of L/S ratio on metal extraction using 1 M sulfuric acid from Ljusnarsberg mining waste at 85 °C

<table>
<thead>
<tr>
<th>L/S</th>
<th>Zn extraction (%)</th>
<th>Cu extraction (%)</th>
<th>Pb extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>66</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>68</td>
<td>37</td>
<td>1</td>
</tr>
<tr>
<td>20</td>
<td>75</td>
<td>45</td>
<td>2</td>
</tr>
</tbody>
</table>
With addition of fresh water to the GLD + mining waste, final pH increased to 8.2 after 10 days. In a previous study by Sartz et al. [117] about mining waste stabilization at the Ljusnarsberg mining site, it was observed that GLD addition reduced the leaching of trace elements and the major mechanisms behind the reduction were sorption and carbonate precipitation. Similarly in another recent investigation about application of GLD to prevent formation of acid mine drainage, Mäkitalo et al. [73] reported that leaching of lead was inhibited by addition of GLD above pH 6, since it tends to precipitate as carbonates and that GLD might also act as an alternative to traditional silt based sealing layers because of comparatively low hydraulic conductivity and high water retention capacity [73]. Therefore, due to the strongly alkaline nature and high liming effect, GLD, seems to be an attractive option for treating and preventing acid rock drainage (ARD), and reducing the migration of toxic elements from the acidic mining waste.

Stabilization/solidification methods have been applied for treatment of mining waste since most of the metals are contained in the stable residual fraction [113]. Since immobilization treatments are not a permanent solution, therefore, extraction methods might be applied to at least reduce the metal concentrations. However, extraction methods have their own concerns such as large equipment and space, utilization of hazardous and expensive chemicals, difficulty in treating materials containing high organic matter/clay content and a proper treatment of washing effluent. Extraction methods might be applied to treat mining waste in order to meet the regulatory level at a certain mining site. Similarly stabilization/solidification methods might be applied after extraction for recovery of metals.
Figure 13. Impact of GLD addition on metal mobility in sulfidic mining waste (Ljusnarsberg mining waste) extracted with water for metal recovery at L/S 10. MW: mining waste
4.6. Extraction of copper from flotation tailings by chemical leaching (Paper 6)

Leaching of copper from flotation tailings from Rudna copper mine in Poland was investigated using various acid and alkaline extractants. Leaching temperature, extractant concentrations and liquid to solid (L/S) ratio were varied to evaluate their impact on copper release. This study was conducted to check the feasibility of copper recovery from the flotation tailings from the Rudna concentrator.

Results of chemical analysis and acid base accounting of flotation tailings are reported in Table 1 and Table 2 of Paper 6, respectively. Chemical analysis showed that the total concentration of copper is 2,450 mg/kg dw, lead (451 mg/kg dw), zinc (79 mg/kg dw), and pH is circumneutral (7.4). Acid base accounting [Table 2, Paper 6] of the tailings indicates the presence of sulfides, however; its content is low and the tailings are clearly not acid forming. Net neutralization potential based on total sulfur and sulfide sulfur were found to be 129 kg CaCO₃/ton and 142 kg CaCO₃/ton, respectively. Flotation tailings from the Rudna concentrator consists mainly sandstone and trace elements such as copper that exists as chalcocite (Cu₂S), bornite (Cu₃FeS₄), chalcopyrite (CuFeS₂), covellite (CuS), lead in galena (PbS), while zinc and nickel both occurs as sulfides and silicates.

<table>
<thead>
<tr>
<th>Table 13. Impact of leaching temperature and sulfuric acid concentration on copper extraction (%) from the Rudna flotation tailings (L/S 5)</th>
</tr>
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<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>0.01 M</td>
</tr>
<tr>
<td>0.1 M</td>
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<td>1 M</td>
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</table>

<table>
<thead>
<tr>
<th>Table 14. Impact of sulfuric acid concentration and L/S ratio on copper extraction (%) from the Rudna flotation tailings at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>0.01 M</td>
</tr>
<tr>
<td>0.1 M</td>
</tr>
<tr>
<td>1 M</td>
</tr>
</tbody>
</table>

Determination of the chemical association of copper in the tailings showed that around 50 % of the copper was released due to increased ionic strength (pH 7) and was not affected by lowered pH (pH 5 and low pH during the
reducing step). However, during oxidizing conditions, a significant additional amount of copper was released, indicating that copper is most likely associated to an oxidizable phase as well (for instance a sulfide). For other elements, most of the magnesium, calcium and iron as well as trace elements such as Zn, As, Ag, Cd and Pb were found in the reducible phase.

Results of chemical leaching experiments using sulfuric acid, and the impacts of extractants concentration, leaching temperature and L/S are presented in Table 13 and Table 14. When H$_2$SO$_4$ was used as leaching reagent, the extracted amounts of copper increased with concentration up to 1 M, with a similar trend observed for NaOH and NaHCO$_3$. Of all the tested extractants 1 M H$_2$SO$_4$ proved to be the most effective media with leaching 86 % of the total copper at 1 M, L/S 20 and 65 °C. Even at 25 °C, around 75 % of copper was leached using 1 M H$_2$SO$_4$ at L/S 20. Using alkaline reagents (NaOH, NaHCO$_3$) with different concentrations, in this study, not much copper was extracted. A maximum of 3 % of the copper content was leached using NaHCO$_3$ (1 M), at 85 °C, while only 2.2 % of copper was leached using NaOH (1 M) at 85 °C.

Leaching temperature is a key thermodynamic factor. Varying the leaching temperature from 25 °C to 85 °C while using 0.01 M H$_2$SO$_4$ at L/S 5, copper extraction surprisingly decreased from 8 % to 1 %. Similarly, using 0.1 M H$_2$SO$_4$ at L/S 5, copper extraction decreased from 51 % at 25 °C to 4 % at 85 °C. Decrease in copper leaching at high temperatures in case of 0.01 M H$_2$SO$_4$ and 0.1 M H$_2$SO$_4$ might be due to Jarosite (K, Na, H$_3$O)$_2$SO$_4$ precipitation which is favored when ferric iron is present as well as the precipitation process itself is favored by higher temperatures [120-122]. Jarosite might have formed a secondary surface over the copper mineral and hence will lower the leaching of metals from the tailings. With 1 M H$_2$SO$_4$ at L/S 5, copper extraction was always around 76-78 % at all tested leaching temperatures. Since lower the leaching temperature, the lower the overall recovery process cost will be. Therefore, leaching temperature of 25 °C could be suggested to be the best temperature in this study.

Impact of phase ratios (L/S) on copper extraction from the tailings was also evaluated. Sulfuric acid and alkaline reagents showed similar trends for copper extraction at different L/S ratios. Increasing L/S from 5 to 20 with 0.01 M H$_2$SO$_4$ and 0.1 M H$_2$SO$_4$ at 25 °C, the copper extraction increased from 8-45 % and 51-70 %, respectively. Higher L/S improved the surface
contact between extracting solution and particles, and hence increased the metal dissolution and extraction efficiencies. Increased extraction while increasing L/S could indicate solubility controlled leaching. With 1 M H₂SO₄ at 25 °C, copper extraction was always around 75-76 %, and there was no major impact of L/S, since at L/S 5, 76 % of the copper was already extracted. Smaller volume of leaching solution would decrease the cost of the overall metal recovery process. For NaOH and NaHCO₃, copper leaching increased with L/S, however, the extent of the increase was low.

Sulfuric acid proved to be the best reagent by extracting 76 % of total copper under the conditions of 1 M, 25 °C and L/S 5. Such high release of copper from tailings at room temperature and low L/S indicates that overall cost for the recovery process might be economical. These findings show that the flotation tailings pond presents a valuable source of secondary raw material for copper extraction and that it should be valorized rather than deposited.
5. CONCLUSIONS/IMPLICATIONS

Following conclusions/implications/suggestions can be drawn from the performed work

- Swedish waste fuels for incineration and resulting fly/bottom ashes are dominated by the presence of Zn, Cu and Pb with respect to trace elements.
- Fuel containing high chlorine content caused high transfer of trace elements to fly ash especially zinc and lead.
- Total input of trace elements (e.g. Zn, Pb) and chlorine content should be as low as possible since high contents of Cl enhances the vaporization of trace elements and high input concentrations of chlorine as well as Zn and Pb in the waste are critical with respect to deposition problems. At grate boilers, it might be possible through waste fuel pre-treatment (e.g. sizing, shredding).
- Variety of input fuel/waste fuel, and boiler type impacted the distribution of trace elements in ashes during incineration. Fluidized boilers generally accommodated most part of the trace elements in the fly ash.
- Vaporization, condensation on fly ash particles and adsorption mechanisms play an important role in metal distribution during incineration process.
- One or more of the following parameters could be responsible for increased transfer of element to fly ash, (1) Increased input concentration of respective element in the waste fuel, (2) A change in volatilization behavior due to the addition of certain waste fractions, (3) High combustion efficiency due to pre-treatment of waste fuel in fluidized bed boilers.
- Water washing of incinerator residues is an efficient pre-treatment step with respect to chlorine removal, since most of the total chlorine in fly ashes (≥ 87%) was leached out at L/S 10.
- Chemical association of trace elements in fly/bottom ashes are affected by fuel type being treated.
- Sequential extraction results indicated that in fly ashes from incineration of household, industrial or mixed waste, Cd, Cu, Pb and Zn pose a risk to the environment, while in the case of bottom ashes, although residual fraction was the predominant chemical association, considerable amounts of trace elements had the potential to leach out and might cause environmental problems when reused if no pre-treatment is conducted.
- Leaching experiments of sulfidic mining waste showed that sulfuric acid was the most effective extractant by leaching around 75% zinc and 45% of total copper at 1 M, L/S 20 and 85°C. Leaching temperature and extractant.
concentration has a positive impact on zinc and copper extraction from waste. GLD can be utilized to reduce the mobility of toxic elements in extracted mining waste; since 10% addition of GLD to mining waste reduced the mobility of Pb, Zn and Cu by a factor of 27, 14 and 7, respectively.

Extraction methods might be applied to treat mining waste in order to meet the regulatory level at a specific mining site. Similarly, stabilization/solidification methods might be applied after leaching for recovery of metals.

- Leaching experiments for copper extraction from tailings (Rudna mine) showed that sulfuric acid was the most effective extractant by leaching 86% of total copper with 1 M H₂SO₄ at L/S 20 and 65 °C. Temperature and extractant concentration significantly impacted the copper release from the tailings during the leaching experiments. Using H₂SO₄ (1 M), even at conditions of 25 °C and L/S 5, 76% of copper was leached from the flotation tailings. These findings show that the old flotation tailings pond in Rudna, Poland, signifies a vital source of secondary raw material for the extraction of copper and that it should be valorized rather than deposited.
6. FUTURE DIRECTIONS

Solid waste incineration fly ash and sulfidic mining waste are both by-products and waste materials. There can be a combination of these two waste streams. Alkaline by-products have been reported to be quite helpful when it comes to stabilization of mining waste. In this work we have fly ashes originating from incineration of various waste fuels, so, all these ashes must be tested in order to see what kind of fly ash is more effective in stabilization process of metals in the sulfidic mining waste.

With respect to metal partitioning during waste incineration, it is very important to understand the kinetic and fluid dynamics in the incinerator e.g. superficial gas velocity and ash particle size, since these factors will affect the particle terminal velocity. To explain the entire incineration process within the incinerator, the application of some conceptual model, matching real plant data is required, like the one reported by Toledo et al. [123].

Chemical leaching process for metal recovery from sulfidic mining waste can be improved through (1) Investigation of other chemicals on the lab scale to find the one with high selectivity towards most of the metals e.g. in addition to Zn and Cu, one should also be able to extract Pb (with the same reagent) from mining waste (2) Optimization of the leaching mechanism by controlling parameters such as leaching temperature, liquid solid ratio and grain size etc. For example a decreased L/S ratio would decrease usage of chemicals and hence cost will be reduced.

Further research is required in a few areas with respect to GLD application on large scale such as, its detailed characterization, handling problems on large scale due to its sticky nature and the effects of aging on GLD properties. Moreover, in Sweden, the total annual production amount of GLD is small in comparison to the amount of mining waste indicating the possible need for other materials as well.
7. ACKNOWLEDGEMENTS

First and foremost, I am grateful to the God for the good health and wellbeing that were essential to complete these years and research work. These last four years have been vital for me with respect to personal and professional development. I take this opportunity to express gratitude to all wonderful people who contributed in different ways to accomplish this work.

My supervisor, Mattias Bäckström, thank you very much for believing in me and introducing me to this research field. I appreciate all of your technical support, guidance, suggestions, encouragement and freedom you gave me to work in my own way.

My co-supervisor, Stefn Karlsson, I wish to express my sincere thanks for all useful and interesting discussions in the coffee room and in the lab about research and life. Thank you very much for always remembering the important coffee break. I will always wish to have such high energy level like you have every day.

Professor Bert Allard is gratefully acknowledged for giving me the opportunity to do my research at MTM research centre, Örebro University, Sweden.

My office mate, Viktor Sjöberg, thank you so much for all your co-ordination in providing ICP-MS data, helping with many different laboratory related problems, technical discussions and always willing to listen to issues I faced professionally.

My colleague, Lotta Sartz, thank you very much for help with data production about ashes.

My colleague, Anna Grandin, thanks a lot for discussions about the professional future and encouragement.

Head of department, Peter Johansson, I appreciate all administrative work that I needed to complete my research work. Thank you so much for quick responses to my emails and help regarding economical issues.

Educational and research administrator, Ingela Fransson, thank you very much for co-ordination with course work and ISP related matters.

There are a few people I would like to mention in the MTM corridor who contributed in making my stay more pleasant and wonderful. Especially Christine Schönlaud, Ulrika Ericsson, Jorden Stubleski, Monika Lam, Samira Salihovic, Jenna Davies, Ingrid Ericson Jogsten, Anna Kärrman, Magnus Engwall, Anna Ogar, Faisal Ahmad Khan, Solomon Asnake, Filip Bjurlid, Kjell Hope, Dawei Geng, Maria Larsson, Kristina Åhlgren.

My Father: Khushi Muhammad: Thank you for all your Love, support and assistance. I miss you.

My Mom: Sarwat Ara: Love u and appreciate all your love, prayers and backing.
My partner: Anjali Bajwa: Thanks a lot for your professional, personal support and being always there to listen to my formatting issues.
My Siblings: Faheem, Saima: You both are great, and I love u
My close friends: Fawad Sehgal, Usman Rehman (chodry), Waqar Ahmad (buja), Saqib Ali (tully), Mahmood Ahmed (bhai sahb), Omer Malik (buddy), Raja Usman (goli), Ahsan Farooq (Chira), Mehboob Nawaz (no comments), Manpreet Kaur, Gurshad Garry, Sana Noor & Ruhaani (love u), Priyanka Banerjee: Thank you all
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