THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Metals in MSWI fly ash

- problems or opportunities?

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Fly ash from municipal solid waste combustion. Photo: Pär Meiling

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Abstract

Incineration of municipal solid waste is a commonly used management method to take care of our waste. However, the residues produced are a problem. They often contain large amounts of potentially toxic metal compounds and soluble salts, which can cause harm to the environment and human health if released from the ash. These ashes are therefore usually classified as hazardous materials and are deposited in specialized landfills. However, as society strives towards more sustainable material cycles, a larger fraction of the materials today classified as waste will, in the near future, be recycled. Since the ashes produced from waste incineration contain significant amounts of metals, they represent a possible source of these metals. Recovery of metals from waste combustion residues would thus give an opportunity to turn a waste into a valuable resource. This thesis focuses on the leaching and recovery of minor metals, such as Cu and Zn, and proposes a recovery procedure for Cu. The leaching of metal compounds from the ash is a very important step in the recovery process and several factors, such as leaching time, pH, leaching agent used and the liquid-to-solid ratio (L/S), affect the leaching properties. In some cases more or less all Cu was leached from the ash. Recovery of metals from ash leachates can be done using solvent extraction, and the results obtained showed that about 90% of the Cu in the leachates could be selectively recovered.

The ash matrix itself is highly affected by leaching, which generally increases the specific surface area and changes the particle size distribution. In landfill leaching tests the release of many ions from pre-leached ash was lower than that measured for the original ash, indicating an opportunity to utilize the resulting ash as well.

Keywords: MSW ash, leaching, metals, Cu, solvent extraction, speciation, NH_3NO_4, water, HNO_3, pH

List of publications

This thesis is mainly based on the work reported in the following papers:

I

K. Karlfeldt, B.-M. Steenari, *Assessment of metal mobility in MSW incineration ashes using water as the reagent,* (2007) Fuel, 86, 1983-1993

II

K. Karlfeldt Fedje, S. Rauch, P. Cho, B.-M. Steenari, *Element associations in ash from waste combustion in fluidized bed*, (2010) Waste management, in press

III

Karin Karlfeldt Fedje, Christian Ekberg, Gunnar Skarnemark, Britt-Marie Steenari, *Removal of hazardous metals from MSW fly ash - An evaluation of ash leaching methods,* (2010) Journal of Hazardous Materials, 173, 310-317

IV

Karin Karlfeldt Fedje, Christian Ekberg, Gunnar Skarnemark, Britt-Marie Steenari, *Recovery of Cu from MSW fly ash leachates using solvent extraction,* Submitted to the Journal of Hazardous Materials

V

K. Karlfeldt Fedje, K. Norén and B-M. Steenari, *Recovery of Cu and Zn from MSWI fly ash – influence of ash properties and metal speciation,* in manuscript

Statement of contribution

Karin Karlfeldt Fedje is responsible for the authoring and most of the laboratory work in all papers with the support of the supervisors and co-authors. However, in paper II, the LA-ICP-MS experiments and analyses were performed by Dr. Sebastien Rauch and, in paper V, the XAS experiments and analyses were done by Associate Professor Britt-Marie Steenari and Dr. Katarina Norén.

Related publications not included in the thesis

a) Speciation of Cu compounds in ashes from MSW incineration

Karlfeldt, Karin; Lundin, Lisa; Clausén, Maria; Steenari, Britt-Marie

Swedish-Finnish Flame Days 2005, ISBN/ISSN: 91-7178-185-4

b) Tvättad aska första steg mot återvinning.

Karlfeldt, Karin: *Avfall och Miljö*, 2007, (5) pp. 28.

c) Addition of kaolin as a potassium sorbent in the combustion of wood fuel - effects on leaching of metals from the resulting fly ash.

Karlfeldt, Karin; Steenari, Britt-Marie: *4th Biennial Meeting of the Scandinavian-Nordic Section of the Combustion Institute hosted by Åbo Akademi, November 5-6 2007*

d) Addition of kaolin as potassium sorbent in the combustion of wood fuel - effects on fly ash properties

Steenari, B-M., Karlfeldt Fedje, K., (2010) Fuel, Article in press

e) Incineration of Municipal Solid Waste - Possibilities and Challenges

Karlfeldt, Karin

Proposal to the ENERGY FORUM BEST STUDENT PAPER AWARDS COMPETITION, at the Energy - Climate - Technology (ECT) Conference in Bergen, 17 - 18 April, 2008

f) CAMPUS GREENING AT CHALMERS UNIVERSITY OF TECHNOLOGY,

Karlfeldt, Karin; Kjällstrand, Jennica, Presented at the *5th EMSU Conference, Environmental Management for Sustainable Universities. Barcelona, Spain, 15-17 October 2008*

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1. Introduction

Waste that is created in households and small enterprises is generally managed through recycling of materials, incineration or landfilling. While landfilling is the most commonly used management method, incineration is increasing both in Sweden and in other countries in Europe [1, 2]. This leads to the production of significant amounts of ashes which, in turn, must be handled in ways that ensure that there are no negative effects on the environment or human health. Today this mainly means landfilling in appropriate landfilling sites. However, as society strives towards more sustainable material cycles, a larger fraction of the materials currently classified as waste will be recycled in the near future. Since the ashes produced from waste incineration contain significant amounts of metal compounds they represent a possible source of metals. Recovery of metals from waste combustion residues would thus give an opportunity to turn waste into a valuable resource. This thesis has focused on the minor and trace metals in ashes from municipal solid waste incineration (MSWI) in order to contribute to a better knowledge of their chemical context, their leaching properties and potential methods of recovery to answer the question: “Metals in MSWI fly ash- problems or opportunities?”

2. Aim of the thesis

The aim of this work was to contribute with new knowledge and a better understanding of the binding and leaching of metals in MSWI fly ash. The recovery and recycling of Cu from MSWI fly ash has also been studied with the aim to stimulate the utilization of ash.

This thesis is based on five publications. The first paper, Paper I, focuses on how variations in leaching parameters, such as liquid-to-solid-ratio (L/S), influence the amounts of metal ions detected in a leachate created from water leaching of cyclone ash from a fluidised bed boiler. The second paper, Paper II, describes an investigation of associations between major and minor elements in single cyclone ash particles. The third paper, Paper III, discusses leaching from a fluidised bed combustion filter ash using both water and other leaching agents. Paper IV discusses the development and evaluation of a selective solvent extraction method for the recovery of Cu from MSW filter ash. The last paper, Paper V, focuses on elucidating reasons for differences in the leachability of Cu and Zn in filter ashes from different waste incineration techniques.

3. Background

Solid waste generated by households is an important part of what is called municipal solid waste (MSW). However, depending on national waste management systems, the definition of MSW differs between countries [1]. The Swedish definition includes hazardous waste and yard waste in addition to normal mixed waste from households. It also includes waste similar to MSW in its composition, from offices, retail shops and schools [3]. The composition of MSW varies from place to place and over time in the same area. Naturally, cultural factors, such as the lifestyle of the population, its relative standards of living, general consumer patterns and the level of technological advancement in the specific country also influence what is included in MSW [4]. Some indications of the compositions of municipal solid waste streams in different areas are given in Table 3.1.

Table 3.1. General composition of MSW in EU-22, Sweden, the USA and the Philippines displayed as w%. [4-7]. Hazardous waste is not included.

Kind of waste	EU-22	Sweden	USA	Philippines
Organic waste incl. yard waste	7 – 52	45-55	23	45
Paper and wood	9 – 44	20-29	43	20
Plastic	2 – 15	9-11	11	23
Glass	2 – 12	1-3	6	1
Metal	2 – 8	2-4	8	4
Others	7 – 63	7-15	10	6

Approximately 4 700 000 tonnes, more than 500 kg/capita, of MSW was generated in Sweden in 2008 [2]. This is an increase of more than 100 kg/capita since 1995 [1]. A similar increase in amounts of MSW has been observed in the countries included in EU-27: from 474kg/capita in 1995 to 517kg/capita in 2006 [1, 8]. The statistics available for the USA are somewhat older, but show a similar development: an increase in MSW from 450kg/capita in 1960 to 760kg/capita in 1999 [4]. As the definition of MSW differs between countries, the numbers given here are not exactly comparable. The trend of increased waste production is evident, however.

Figure 3.1 shows statistics on the percentages of solid waste that go to recovery, incineration and landfill in the countries in EU-27 [8]. Clearly, these countries make different choices about how to deal with waste management. Sweden has one of the highest fractions of waste that is incinerated (about 15%), whereas the average is about 5%. Other examples of differences in waste management are Japan, incinerating more than 70% of the solid waste, and the USA, where more than 84% of the solid waste is landfilled [4]. The waste volumes in the statistics used by Kloek and Blumenthal include waste from households (7%) as well as waste from industries and businesses [8]. Other statistics on the management of MSW in Sweden show that almost 50% of the MSW was incinerated in 2008 [2]. Unfortunately it has not been possible to find corresponding statistics for other countries due to different definitions of and regulations for MSW.

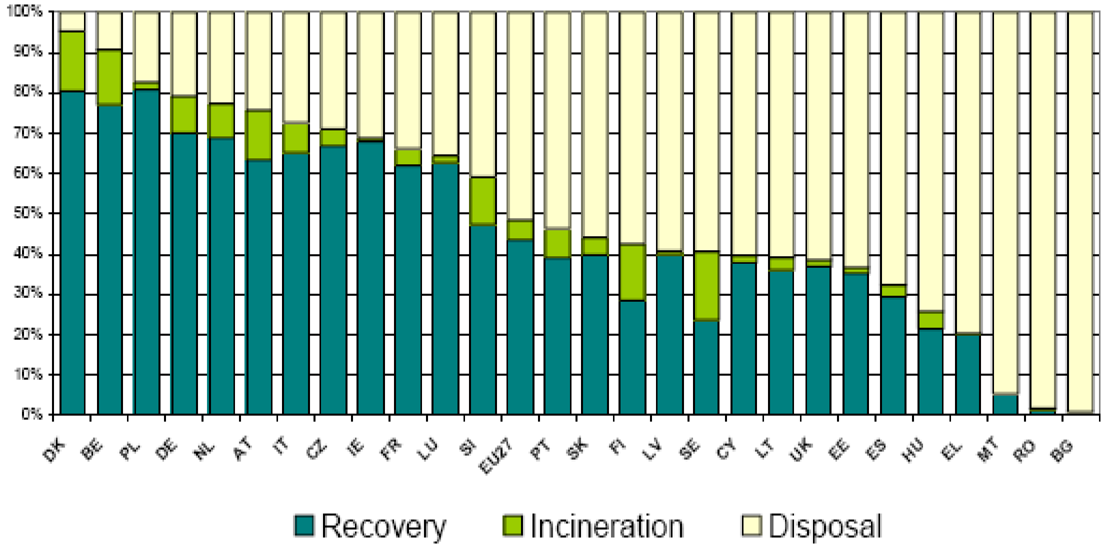


Figure 3.1. Types of waste treatment in 2006 in EU-27 [8]. Reprinted with the permission of © European Communities, 1995 – 2009.

Landfilling is a common treatment method for municipal waste but its use has decreased strongly in EU-27 during the last decade (~60% landfilled in 1995 compared to ~40% in 2006) [1]. In Sweden, only 5% of the MSW was landfilled in 2006 as compared to 35% in 1995 [1, 2]. This decrease is mainly due to new legislation stating that material recovery and incineration should be favoured over landfilling [3, 9]. Incineration offers some significant advantages over landfilling, such as a volume reduction of up to 90%, a mass reduction of up to 75% and recovery of the energy content in the waste, in addition to destruction of micro organisms and toxic organic compounds [4, 10].

Combustible waste is defined as waste that is combustible without any heat supply after the incineration process has started [11]. This generally corresponds to a heating value of at least 6-8 MJ/kg waste [5, 12]. According to calculations made by Reimann for 97 waste-to-energy plants in Europe in 2006, the average heating value for MSW is about 10 MJ/kg [13]. A similar value is obtained for the US [4]. Thus, the energy content in MSW is significant, even though it is lower than that of other commercial fuels (Table 3.2).

Table 3.2. Technical data for some fuels [1][13], [2][14], [3][15], [4][16] and [5][17].

Fuel	Average heating value, MJ/kg	CO_2-factor, g/MJ fossil fuel
MSW	10[1]	25[2]
Bio fuel	18[3]	0*
Coal	27[4]	93[5]
Natural gas	40[4]	57[5]
Crude oil	40[4,+]	74-78[5]

*The carbon dioxide emissions from bio fuels are presupposed to be a part of the natural ecological cycle. ⁺Approximate value, δ=900kg/m^3

According to calculations made by the Swedish Waste Management Association, MSW is composed of 85 percent biomass and 15 percent fossil fuel [14]. On the basis of these numbers, the average CO_2 emissions from MSW incineration are 25g/MJ fossil fuel (Table 3.2). This is much lower than for several other commercial fuels and favourable, since increased emissions of carbon dioxide to the atmosphere are assumed to strongly affect the world´s climate.

One reason why such a high percentage of MSW goes to incineration in Sweden compared to the situation in other countries in Europe and worldwide is that the heat produced can be effectively utilised in the widely spread district heating system. A similarly extensive district heating system is not present in many other countries. In 2006 about 20% of the total energy demand for district heating in Sweden was supplied by heat from waste incineration [18]. There were 29 incineration plants for MSW and industrial waste in use in Sweden in 2008 and more waste combustion facilities are presently being designed and constructed [2]. All of these combustion facilities are designed for energy recovery through the production of hot water for the district heating net and in some cases also for electricity production. Approximately 4.6 Mtonnes of waste, of which half was MSW, was incinerated with energy recovery in Sweden in 2008, giving 14 TWh, which corresponds to the annual electricity demand of almost 250 000 average sized houses and heating of more than 800 000 detached houses [2].

Combustion techniques

The type of combustion unit most commonly used for combustion of waste uses the mass burn (MB) technique, but fluidised bed combustion (FBC) has become an alternative during recent decades. These incineration techniques have been described in great detail by others and are therefore described only briefly here. More thorough information can be found in [4, 19].

Mass burn combustors

In a mass burn (MB) combustor, the fuel is fed on a moving or tilting grate, through which air in excess is blown to achieve efficient combustion. The combustion temperature is usually above 1000°C. MB combustion has the advantages that it is a simple, robust and thoroughly tested technique for waste incineration and that there is only a minimal need for pre-sorting and size reduction of the waste.

Fluidised bed combustors

The combustion in a fluidised bed boiler is carried out in a bed of inert material, usually quartz sand. The sand effectively distributes the heat to the water tubes, which makes it possible to maintain a low combustion temperature, i.e. about 850°C. The formation of nitrogen oxides (NO_x) is thus minimised since oxidation of the nitrogen in the air supplied for combustion is decreased. Variations in fuel properties, such as moisture content and heating value, have less influence on the combustion than in MB combustors. However, the fluidised bed combustion technique requires a size reduction and pre-sorting of the waste. A schematic picture of a bubbling fluidised bed (BFB) combustor is shown in Figure 3.2.

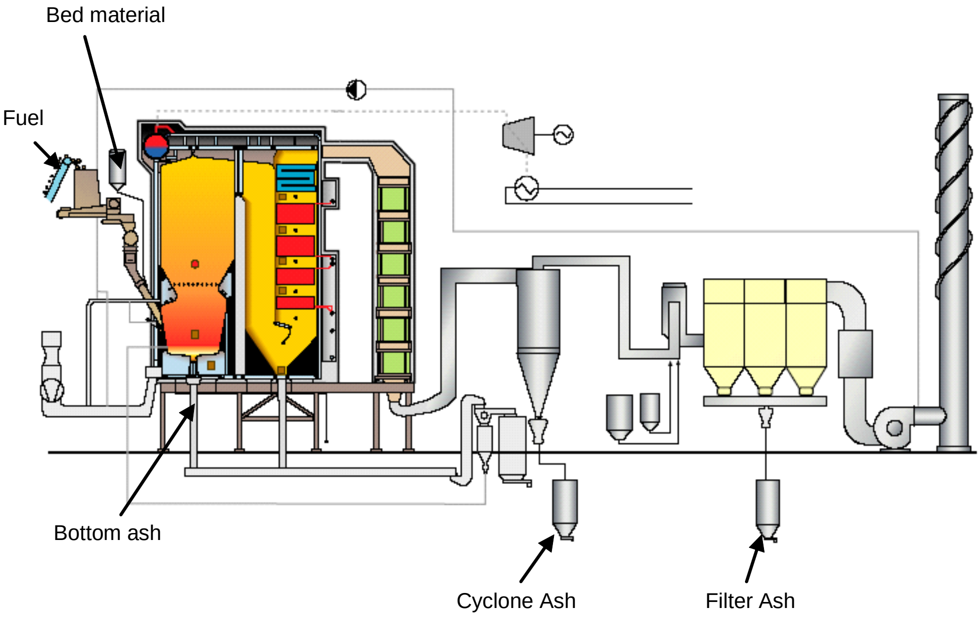


Figure 3.2. Schematic picture of a bubbling fluidised bed combustor. Printed with the permission of [20].

Ash from MSW incineration

Bottom ash is the major ash fraction produced from incineration of MSW [19]. It consists of minerals with high melting points, metal pieces, sand and glassy slag lumps and is, as the name suggests, collected at the bottom of the combustion chambers. The ash particles that are small enough to follow the flue gas are collected in the flue gas cleaning devices, and this ash flow is called fly ash. A summary of composition data for a large number of MSW fired combustion units is shown in Table 3.3 [19]. These data show that the fly ash is generally enriched in certain metals (As, Cd, Hg, Pb, Sb and Zn). These metals are all volatile as such or in the form of volatile metal chlorides. The content of chlorine (mainly chloride) in an average fly ash is in the order of 10w%, which illustrates the importance of chlorine in the formation of the fly ash (Table 3.3). Bottom ash may contain significant amounts of some potentially toxic metals, such as Cr, Cu, Ni and Pb. However, as seen in Table 3.3, there are broad composition ranges for both bottom ash and fly ash, which indicates the complex processes involved in the combustion and large variations between combustion sites and fuels.

Table 3.3. Contents of major and minor components in bottom and fly ashes from MSW combustion from various incineration techniques and countries [19]. All amounts are present as mg/kg ash.

Element	Bottom ash	Fly ash
Al	22000–73000	49000–90000
Ca	370–123000	74000–130000
Fe	4100–150000	12000–44000
K	750–16000	22000–62000
Mg	400–26000	11000–19000
Na	2800–42000	15000–57000
Si	91000–308000	95000–210000
Cl	800–4200	29000–210000
S	1000–5000	11000–45000
As	0.1–190	37–320
Ba	400–3000	330–3100
Cd	0.3–70	50–450
Cr	23–3200	140–1100
Cu	190–8200	600–3200
Hg	0.02–8	0.7–30
Mn	80–2400	800–1900
Mo	2–280	15–150
Ni	7–4200	60–260
Pb	100–13700	5300–26000
Sb	10–430	260–1100
V	20–120	29–150
Zn	610–7800	9000–70000

A great amount of research work has been done to show the metal partitioning in combustion, i.e. how the metals are distributed in bottom ash and fly ash. As discussed, chloride forming elements, such as Cd and Pb, are generally enriched in fly ash, whereas oxide forming elements, such as Al and Si, remain in the bottom ash. The partitioning of metals in different ash flows is the final result of a large number of physical and chemical processes occurring inside the combustion unit. The extent of volatilization of metal compounds depends not only on the temperature but also on the gas composition. Thermodynamic equilibrium calculations and measurements show that high concentrations of chlorine compounds such as HCl and a reducing atmosphere increase the volatility of metals (especially Cd, Pb, Cu and Zn) while the presence of sulphur can reduce the volatility [21-26]. The enrichment of these elements in the fly ash is due to condensation of their volatile compounds onto small particles already present in the flue gas. The gaseous metal species may also condense directly when the flue gas is cooled and form condensation kernels for other volatile species. Both processes lead to an inverse proportionality between the particle diameter and the concentration of metals in ash particles. Data that show such proportionality have been reported by several groups [21, 26-28]. However, published data on the distribution of elements also show differences between ash samples. Lead is generally enriched in small particles regardless of the fuel and incineration technique used, whereas the distribution of As and Cd is somewhat less predictable [29-32].

Depending on whether the metal compound condensed on a fly ash particle or formed the kernel of a new particle, the metal in question will end up either on the fly ash particle surface or be enclosed inside a particle. Using synchrotron based X-ray fluorescence spectroscopy, Camerani-Pinzani and co-workers found that some metals, e.g. Cd and Pb, were mainly present inside fly ash particles, while Zn was present both in the particle interior and on the surfaces [33]. In the work of Fujimori and co-workers on industrial waste incineration fly ash Cd, Cu, Mo and Zn were found to be enriched on particle surfaces as acid soluble compounds, while Co, Mn, Ni and Pb were found both inside the particles and on the surfaces [34]. In work done by Ramesh and Kosinsky, the amounts of Cd and Pb were found to decrease on the surfaces and increase towards the centre of a simulated waste ash pellet during solidification (1000ºC-25 ºC) [35]. The mechanism suggested was that Cd and Pb occupy the oxygen vacancies in mullite ($3Al_2O_{3*}2SiO_2$) or form stable compounds with the aluminosilicate matrix. However, the role of volatilisation was not studied. An increased understanding of the mechanisms affecting these distributions of metal compounds would be very valuable since they are important for the ash properties. One example is the release of metal ions from ash to a leachate where the location of the metal compound is important for the result. Encapsulation of metal species inside particles probably significantly decreases their leachability.

Data are available that indicate that the ash matrix may influence the distribution of volatile metals and lead to significant variations in metal concentration over the ash particle [36, 37]. Calcium and Fe have been indicated to be associated with metals such as Cd, Cr, Pb and Zn in MSW ash particles, and Cd, Cu and Pb were found to be enriched in biomass ash particles rich in quartz [37-40]. The affinity of certain volatile metal species for certain minerals has been investigated with the aim of using the minerals as sorbents for toxic metals and metal species that otherwise cause fouling and corrosion [41-45]. Limestone, silica, alumina, bauxite and various aluminium silicates, such as kaolin, have been suggested and studied. Kaolin has been shown to absorb K, Na and Zn [44, 46, 47] and to adsorb Cd, Cu, Pb and Sb and thereby decrease their volatility [43, 45, 48].

The discussion above indicates that although trace elements are generally enriched on, or in, small particles, the properties of the individual metals, as well as parameters specific to each incineration situation, are important for the mechanisms by which the trace metal species are distributed on ash particles. In addition, MSW is a very heterogeneous fuel since the composition of the waste can vary considerably. A recently published work on MSW fuel characterisation shows that its content of non-metals, such as C, H and N, varies little on an annual basis, whereas the concentrations of Na, K and Cl, as well as trace elements, such as Cu, Pb and Zn, show larger variations [49].

Methods to decrease metal species leaching from ash

There has been an extensive amount of work done in developing methods to decrease the release of metal compounds from deposited ash. One option would be to actually remove the metals from the ash, which can be done by magnetic or eddy current separation if the metal is present in metallic form. Magnetic recovery of iron alloys is used for MSWI bottom ashes but is usually not used for fly ashes [19, 50].

Thermal treatment of MSWI ash, e.g. vitrification, melting or sintering, has been suggested as a method to encapsulate metal species in the ash matrix. The result is a more stable and volume reduced ash product, where the remaining metals have been bound into the matrix of oxides and silicates, thus making them less available for leaching [10, 24, 28]. However, depending on the parameters used during the heat treatment, part of the metals forming volatile compounds can be released from the ash. As much as 100% of the Cd, Cu and Pb initially present in ash, as well as 50% of the Zn, has been reported to evaporate at temperatures around 1000°C [51]. A review of thermal treatment processes for MSWI ash concluded that the release of volatile metals, e.g. Cd, Pb and Zn, increased in a reducing environment compared to an oxidizing environment because of a reduction to metallic forms that are more volatile than the oxides present in an oxidizing environment [24]. The presence of HCl also increases volatilization due to a formation of volatile metal chlorides. Results of heat treatment experiments have shown that less than 5 % of the initial amounts of each metal (Cd, Hg, Pb and Zn) remain in the ash after treatment in a reducing atmosphere. After heat treatment with an addition of HCl, less than 2% of the studied metals remained in the ash, whereas heating in an oxidizing environment led to much higher retaining of the metals [24]. A disadvantage of thermal treatment is the high energy consumption, which makes the process costly [10, 24]. In addition, it generates a metal laden flue gas that must be cleaned and this cleaning, in turn generating a new particulate waste with high metal concentrations. Thermal treatment of MSWI ash is used at several plants in Japan, but it is not common in commercial plants in Europe and the USA [24].

One common way to solidify/stabilize ash is to mix it with cement and water, which results in agglomeration of the material. Solidification has been shown to give a decrease in leaching of metals and sulphates, but the chlorides are almost as easily released from the solidified ash as from untreated ash [10, 52].

Carbonation of moistened MSWI ash has been found to decrease the leaching of some metals, although it has been reported to give enhanced leaching in the case of other metals. Several groups have reported decreased leaching of Cu, Pb and Zn and an increased leachability of Cr [53-56]. The effects of carbonation on the mobility of Cd are less certain since both a decrease and an increase in leaching after carbonation have been reported [55, 56]. The decreased leaching of metal compounds is probably due to formation of calcite ($CaCO_3$), which buffers and keeps an alkaline pH in the ash but the carbonation and leaching mechanisms are not totally understood [53]. Calcite in an aqueous environment is involved in a dynamic dissolution and re-precipitation process, which means that the surface of the calcite crystals is continuously reproduced. Co-precipitation of other metal carbonates on calcite, as well as an incorporation of other metal ions, such as Cd^{2+} and Zn^{2+}, replacing calcium ions in the calcite structure, is known to occur [57-60]. Mixed mineral phases and solid solutions such as these generally get a lower solubility of the minor element than the corresponding pure minerals [61, 62]. Sorption of metal ions onto other mineral surfaces, such as Al and Fe (hydr)oxides, is also common and will further decrease the leaching of a number of metal ions, e.g. Pb, Cd, Zn and Cu, from ash [10, 55, 63]. Such processes, in addition to the pH buffering effect of calcite and the formation of ash particle aggregates induced by the carbonation reactions, lead to retaining of the metal ions in the solid phase.

If the aggregation and stabilization by adding water to the ash does not sufficiently decrease the leaching of metal ions, an addition of chemical reagents such as phosphates or sulphides can be used to transform the soluble metal ions to insoluble or less soluble forms and thus immobilise them in the ash aggregates [19, 64-66].

A disadvantage of solidification/stabilisation is that, as the metals are still present in the ash after treatment, there is a risk that they can be released in a long term perspective. Removal of the toxic species from the ash would therefore make the quality of the ash better.

A very common way to release metals from ash is through wet treatment, i.e. leaching. Metals forming readily soluble compounds such as NaCl or KCl are released from ash more or less independently of pH, whereas the solubility of many other metal compounds from ash is strongly affected by pH. As MSWI ash is alkaline, a leaching with water or slightly acidic water generally results in a high pH of the leachates and a low release of metal compounds [34, 64, 67-71]. Many metals form soluble cations at low pH but amphoteric metals such as Cu, Pb and Zn not only form cations at acidic pH but also form soluble hydroxides at alkaline pH; they are therefore released both at low and high pH (Figure 3.3) [10, 19]. Another leaching pattern can be identified for metals forming oxyanions at low pH. Typical examples are Cr and Mo (Figure 3.3). Metals with this behaviour are strong Lewis acids, e.g. strong electron acceptors, and react with the oxygen in water to form complexes such as $[CrO_4]^{2-}$ och $[MnO_4]^{-}$. It is generally possible to identify pH regions where the leaching of specific metals is at minimum or maximum based on such equilibrium considerations as given in Figure 3.3.

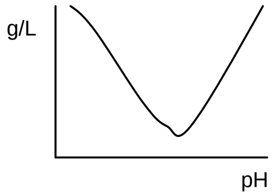
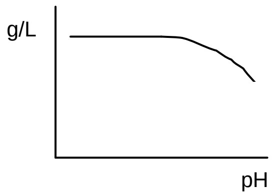
Species	**Metals**	**Leachability vs. pH**
Cation-forming and non-amphoteric elements Leaching is approximately constant at pH > 8	Ca	
Amphoteric elements Minimum leaching around pH 7	Al, Cd, Co, Cu, Ni, Pb, Zn	
Oxyanion-forming elements Leaching decreses at pH > 10	As, B, Cr, Mn, Mo, Sb, V	

Figure 3.3. The influence of pH on the leaching of certain metals from MSWI ashes. Based on [10, 19].

However, the release of metals in real ash-water systems is not only affected by pH but also includes competitions between several chemical equilibria. The most important factors, except for pH, that influence the leaching rates are: the ash particle size, the mineralogy of the ash, the chemical speciation of the metals, the red-ox potential in the ash-leachate mixture, the liquid-to-solid-ratio (L/S) and the presence of complex forming ligands in the leaching liquid (Figure 3.4) [10, 19, 50, 72, 73]. Complex formation generally increases the leached amounts while sorption processes lead to a decreased release. Mineralogical changes in the ash matrix, such as carbonation, as well as red-ox reactions, can lead to both increased and decreased leaching. An example is the reduction of Cr(VI) to Cr(III), which results in lower release of Cr as Cr(III) species are less soluble than Cr(VI) [74].

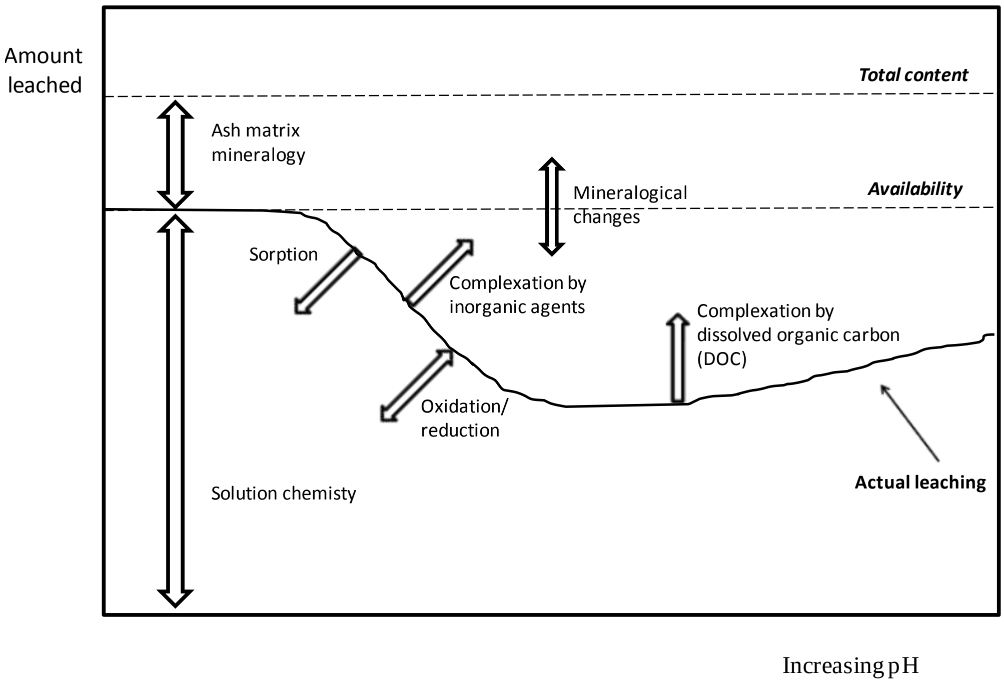


Figure 3.4. Chemical processes increasing or decreasing the release of metal compounds. Based on [75].

Enhanced leaching to release metal compounds from ash can be carried out using different leaching agents. The probably most widespread leaching method is acidic leaching using strong mineral acids, as many metal compounds have high solubility at low pH (Figure 3.3) [76-80]. Several groups have used such acids in their experiments on MSWI ash (HCl, HNO_3 and H_2SO_4 at $pH \leq 4$) and shown variable, but in most cases significant, release of Cu (7-100%), Pb (30-60%) and Zn (22-80%) [66, 81, 82]. The variability in the results of leaching may be caused by variations in ash properties, i.e. the ashes came from different combustors with differences in fuel composition and combustion parameters. A disadvantage of methods that employ acid leaching is that the alkalinity of the ash leads to a large consumption of acid.

Leaching media based on complex forming ligands, such as ethylene diamine tetraacetate (EDTA), nitrilo triacetic acid (NTA) and diethylene triamine pentaacetate (DTPA), have been used to reduce the impact of hazardous metals in MSWI ash by removing these metals as cations bound to the ligands. Treatment with EDTA or DTPA resulted in a removal of 20–50% of Cr, 40-95% of Cu and 40–100% of Zn [81, 83]. The removal of Pb was successful (60–100%) with the use of EDTA and DTPA but not as effective using NTA (<10 % of Pb removed), possibly due to a formation and re-adsorption of $Pb(NTA)_2^{4-}$ [66, 81, 84]. Organic acids are also known to form complexes with many metal ions. The release of Cu from MSWI bottom ash due to a formation of organo-copper complexes has been noted earlier, and the dissolved organic matter (DOM) has especially been shown to bind Cu in solution [85, 86]. Organic acid leaching generally result in a lower release of metal compounds compared to inorganic acid leaching [82, 83].

Another possible ash cleaning method that is also based on a treatment in aqueous media is electrodialytic remediation, which has been used to remove Zn (66%), Cd (78%), Cu (34%) and Pb (26%) from fly ash. The stability of the remaining ash is stated to be significantly improved by the treatment [87].

As discussed above, the leaching of metal compounds from ash is highly influenced by several physical and chemical factors such as pH, L/S and availability of ligands. However, the most important factor is probably the speciation of the metals, i.e. the chemical association forms or compounds of the metals present in the ash. Thus knowledge of the metal speciation in ash is needed. There are different methods that can be used to examine the speciation of metals in solid materials, such as theoretical equilibrium modelling [76], sequential extraction [88-90] and spectroscopic techniques such as X-ray absorption spectroscopy (XAS) and X-ray photoelectron (XPS) spectroscopy [36, 91-93].

Using sequential extraction methods is probably the most common way to examine the chemical association forms of metals in soil and sediment samples and granular waste such as ash. However, problems have been reported that are associated with these methods. It has been noted, for example, that different speciation results are obtained when different sequential extraction protocols are used [94-96]. On the other hand, the spectroscopic methods generally require expensive and advanced instruments, which is why their use has this far been limited. However, XAS methods have advantages over sequential extraction methods, such as a limited need of sample preparation, element specific analysis and low detection limits. Analysis of Cd (<100 ppm) in ash using XAS has been reported [36, 39]. Chemical characterization of Cd in MSW ash using XAS shows that Cd is mainly present as

$CdSO_4$, CdO and $CdCl_2$ [36]. Copper has been suggested to be present mainly as CuO, $Cu(OH)_2$ and $CuSO_4 \cdot XH_2O$ [97-99]. $CuCl_2$ is usually present in low amounts, but $CuCl_2$ has been shown to be enriched on the surfaces of filter ash particles [99]. This is suggested to be due to condensation of $CuCl_2$ on the ash particles when the temperature in the flue gas channel decreases. Zinc was found to be present mainly as oxidic minerals, such as silicates and oxides, in a study by Steenari and Norén, whereas $ZnCl_2$, $Zn(OH)_2 \cdot 2ZnCO_3 \cdot XH_2O$, $ZnSO_4 \cdot 7H_2O$ and $ZnCl_2$ were identified as the major Zn compounds in a study by Yu and co-workers [100, 101]. The differences in speciation may be due to the different incineration techniques used.

Utilization of MSWI ash

Filter ash from MSW incineration is generally not used because of the high content of potentially toxic metals and soluble chlorides, while bottom ash has been tested as construction materials in roads [102, 103]. In a study by Ferreira and co-workers, possible applications for MSWI fly ash such as construction materials and soil amendment were identified and discussed [104]. The acceptance of using MSWI fly ash is generally limited, and the most important environmental risk is leaching of metal compounds and chlorides from the ash in the resulting product. Nevertheless, fly ashes mixed with sewage sludge have been used as a part of the liner in the closure of landfills [105]. Swedish regulations controlling the use of waste in constructions were recently changed, which can affect the further utilization of MSWI ash [106].

As discussed earlier, minimization of the toxic species in ash would make the quality of the ash better, which could lead to new fields of application. Recycling specific components in fly ash is generally not done today because it is expensive, but the von Roll company has shown that it is possible to extract Zn from MSWI filter ash and run a profitable plant [107, 108]. Zinc is won by acid leaching and solvent extraction followed by electrolysis. Attempts have also been made to recover metals (e.g. V, Ga. Ge and Al) from oil and coal ashes [109]. As an example, coal fly ash was sintered in the presence of CaO to decompose the silicate phases in the ash. The resulting ash was then treated with H_2SO_4 and resulted in the release of 85% Al. The leachate was thereafter purified from impurities through solvent extraction, and pure alumina (>99%) was finally recovered [110]. Jung and co-workers reported CO_2 bubbling during water leaching of melted fly ash to enhance the release of Cl, Na, K and Ca. This resulted in an ash fraction with a higher relative content of valuable metals such as Cu, Pb and Zn, which can be used for metal recovery in nonferrous smelting processes [111].

Production of copper

Copper is mainly present as $CuFeS_2$ and Cu_5FeS_4 in ores, and the content of Cu in the ores generally varies between 0.5-2% [112]. The most common way to produce copper metal is through thermal treatment, and production of pure Cu is thus a highly energy demanding process [112]. Thermal treatment includes smelting, conversion of the copper mineral into Cu metal and electrolysis to achieve pure Cu metal. However, due to the low amount of Cu in the ores, smelting cannot be done economically without enrichment of Cu. This is usually done through selective froth floatation. The raw material is crushed (10-100µm), wetted and mixed with special reagents such as xanthates (ROC(=S)SR'). Those reagents react with the Cu minerals thus making the surfaces of the Cu minerals hydrophobic. This enhances floatation of the Cu minerals when bubbling air is forced through the mixture. Non-copper minerals are not attached to those reagents, which results in a separation and enrichment of Cu minerals (~30% Cu) [112]. Another way to produce pure Cu is through hydrometallurgical processes, i.e. leaching. Production of Cu using hydrometallurgical processes has been limited but has increased markedly in recent decades [112, 113]. Dilute sulphuric acid is by far the most commercially used leaching agent, and the copper can be recovered from the produced leachate through solvent extraction followed by electrolysis [112-114]. The highly refined Cu metal achieved after electrolysis can be used for electronic and mechanical use and typically contains less than 20 ppm of impurities [112]. Alternatively, the product could be a copper salt such as $CuSO_4$. Annually, two million tonnes of Cu are recovered through hydrometallurgical processes, which corresponds to nearly 20% of the global production of Cu [113, 115]. An advantage in using leaching compared to thermal treatment is that the Cu ore can be leached directly without enrichment and the acid used for leaching can be recyled [112, 116]. Recovery of Cu through solvent extraction is discussed in detail in the following section.

Solvent extraction of Cu

Solvent extraction is widely used to separate metal ions in solutions. The method is based on the distribution of species between two immiscible phases, generally a water phase and an organic phase. The metal species of interest is usually present in the water phase and is transferred to the organic phase using an extractant dissolved in the organic phase. The distribution of the metal between the two immiscible liquids can be described by the distribution ratio (D_M) of the metal species between the phases and is defined as

$$D_M = \frac{[M]_{t,org}}{[M]_{t,aq}} \qquad \text{[eq. 1]}$$

where $[M]_{t,org}$ and $[M]_{t,\ aq}$ refer to the total amounts of all speciess containing the metal M in the organic phase and in the water phase. As seen in eq. 1, the higher the D value, the higher the concentration of the metal species in the organic phase compared to the water phase. The D value depends on several factors, such as the pH of the water phase and the concentration of the extractant in the organic phase.

The metal of interest is usually present in the water phase together with other metal species. Therefore it is not only a high D ratio for the metal of interest that is important but also a good separation from other metals. This means that the extractant should have high selectivity for the metal of interest and transfer it to the organic phase, while leaving the other metal species in the water phase.

The separation factor ($SF_{o/a}$) between two metal species (m_1 and m_2) is defined as

$$SF_{m1/m2} = \frac{D_{m1}}{D_{m2}} \qquad \text{[eq. 2]}$$

where D_{m1} and D_{m2} refer to the distribution ratios between the phases for the metal species.

However, the distribution between the organic phase and the water phase of the metal species of interest is often not high enough after one extraction step. Series of extraction steps are thus often used in real solvent extraction processes (Figure 3.5).

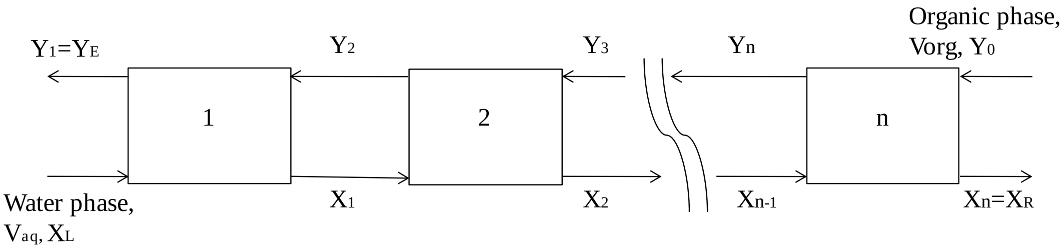


Figure 3.5. Solvent extraction process using counter-current flows in n steps. Y_0 refers to the initial amount of Cu in the organic phase, while Y_E refers to the amount in the loaded organic phase. X_L refers to the initial amount of Cu in the water phase and X_R refers to the amount of Cu after n extraction steps.

In the first step (box 1 in Figure 3.5) the solution containing the concentration X_L of the metal of interest (for simplicity, hereafter referred to as Cu) is mixed with the organic phase containing the extractant from step no 2 (box 2 in Figure 3.5). The concentration of Cu decreases in the water phase in each step and, after n extraction steps, the concentration of Cu remaining in the water phase, e.g. the raffinate, equals X_R. The decrease of Cu in the water phase, e.g. X_L-X_R, theoretically equals the increase of Cu in the organic phase, e.g. Y_E-Y_0, if equal volumes of organic and water phases are used.

If a certain number of steps (n) are applied in the extraction process, the fraction of the Cu still in the water phase (φ_n) can be calculated using

$$\varphi_n = \frac{P-1}{P^{n+1}-1} \qquad \text{[eq. 3]}$$

where P refers to the extraction factor, which is defined as

$$P = D * \frac{O}{A} \qquad \text{[eq. 4]}$$

As follows from this equation, if equivalent volumes of organic and water phases are used, i.e. O/A=1, in each step, the distribution factor, D, can be used instead of P.

After the extraction of Cu, the loaded organic phase (Y_E) is mixed with another water solution in a process called stripping. The water solution usually contains sulphuric acid and H^+ replaces the Cu^{2+} in the extractants in the organic phase. The reason will be discussed further later in the thesis. After stripping, the amount of Cu in the organic phase is theoretically 0 (Y_0) and the extractant is again available for forming new complexes with Cu. The organic phase can thus be used several times, which means there is a low consumption of chemicals. The stripping solution can also be used several times as the Cu is removed from the acid during electrolysis, which is usually used to achieve pure Cu metal from the stripping solution [112, 116, 117]. Both extraction and stripping reagents are recycled in commercial plants for Cu recovery. It is common that an extraction process consists of two extraction steps and one stripping step, but the combination chosen depends on the chemistry involved in each unique case [118].

Extraction reagents used in this work

Several extractants are available and they can be divided into different classes depending on the complex types formed with the metal species. The present work used acidic chelating extractants releasing H^+ during extraction and forming neutral complexes with Cu^{2+}.

Oxime extractants

The extraction reaction between an oxime extractant reagent and Cu^{2+} can schematically be described as

$$Cu^{2+}_{(aq)} + 2HA_{(org)} \rightarrow CuA_{2(org)} + 2H^{+}_{(aq)} \qquad \text{[eq. 5]}$$

where HA refers to the protonated organic extractant and the subscript (org) refers to complex in the organic phase. During stripping the reversed reaction takes place in which the extractant returns to the protonated form and Cu^{2+} is released. Chelating extractants such as aldoximes or ketoximes (Figure 3.6) react according to this equation.

Oximes in general and especially aldoximes are known to form very stable Cu complexes, and oximes are therefore among the most commonly used reagents for Cu extraction [113, 116, 119, 120]. The stability of those Cu complexes could be related to the very good fit for Cu in the $N_2O_2^{2-}$ cavity (Figure 3.7) [120, 121]. Addition of a substituent with H-bond accepting properties, such as Cl or NO_2, to the Q positions will lead to increased stability of the complex, while addition of a bulky substituent such as CH_3 seems to decrease stability (Figure 3.7) [122]. This is due in the first case to the formation of further stabilizing H-bonds between the substituent in the Q position and the hydrogen while, in the latter, the strength of the H-bonds is decreased probably owing to steric hinders and distortion of the CuN_2O_2 unit from planarity (Figure 3.7b) [122].

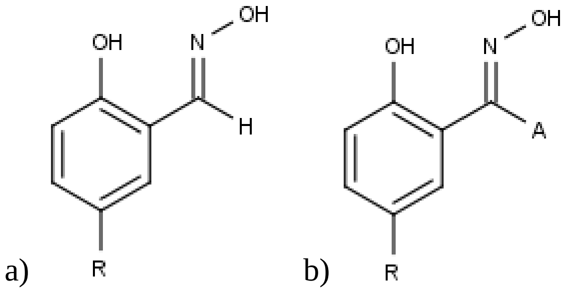


Figure 3.6. General molecular structures of oximes a) aldoxime and b) ketoxime (A= CH_3 or C_6H_5) used commercially for Cu recovery. R=C_9H_{12} or $C_{12}H_{25}$ in both cases.

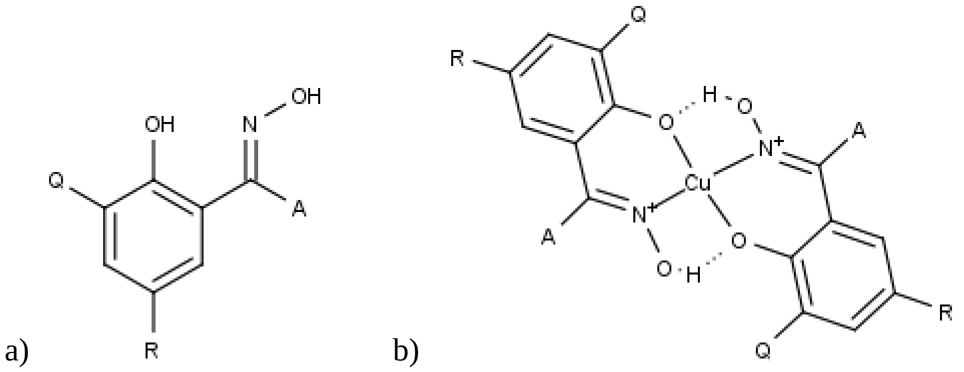


Figure 3.7. Schematic structures with possible substitution in the third (Q) position of a) oxime and b) the corresponding metal-extractant complex. (A= H, CH_3 or C_6H_5) Based on [122].

Because of the symmetry of the metal complex it is possible that substitution in the A position would lead to similar effects. Unpublished quantum mechanical equilibrium calculations made by Ylmén and Panas show that the addition of a bulky substituent in the A position also leads to distortion of the CuN_2O_2 unit (Table 3.5) [123]. This is a plausible explanation for why aldoximes form stronger complexes with Cu than ketoximes, and substitution of various groups could be used to customize the strength of the reagent.

Table 3.5. Calculated inter atomic distances in the CuN_2O_2 unit as results of different groups in the A position [123].

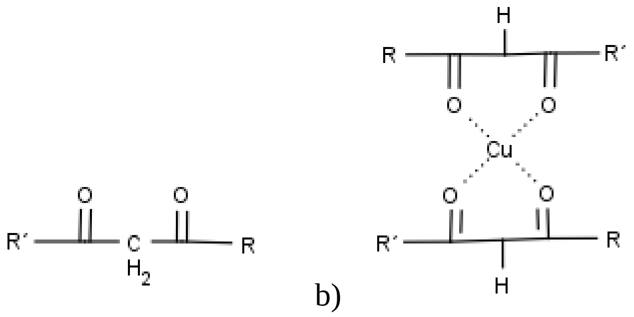
Extractant	Group in A position	Distance N-Cu in complex [Å]	Distance O-Cu in complex [Å]
aldoxime	H	1.985	1.966
ketoxime	CH_3	2.004	1.945
ketoxime	C_3H_7	2.011	1.950

The stability of many Cu-aldoximes complexes in an acidic environment is very high, resulting in the need of acid concentrations of ~2.3M H_2SO_4 to effectively strip Cu from the organic phase. This is not compatible with typical electrolytes in commercial electrolysis winning tanks (1.5-2M H_2SO_4) and pure aldoximes are thus generally not used as extractants in the organic phase [113, 116, 119]. Instead, blends of aldoximes and ketoximes are used as extractants, or modifiers can be added to the organic phase [113]. Modifiers are usually compounds such as tridecanol or highly branched esters that decrease the possibilities for Cu-extractant complex formation by blocking the active sites of the extractants [113, 119, 124]. Modified reagents in many cases increase the so called crud formation [113, 116, 119]. Crud is a emulsion found in the interface between organic and water phases and is mainly formed from solids in the leach solution, e.g. species in water phase that precipitate during mixing, and organic degradation precipitates [114, 118]. In addition, entrainment of aqueous solution into the organic phase can result in transfer of impurities such as Cl^- or NH_3 to the electrolyte [113, 114, 116, 119]. Increased degradation of modified reagents compared to non modified reagents has also been reported [113, 116, 119]. However, unmodified reagents are also chemically degraded with time (several months) and aldoximes are generally less stable than ketoximes in acidic environments [116, 119].

In this work one aldoxime extractant, LIX 860N-I, and one ketoxime, LIX 84, were included (Table 3.4).

ß-ketone extractants

As mentioned earlier, sulphuric acid solutions are the most common media for commercial Cu extraction, but the use of ammonical leach solutions is also common practice. Ketoximes can be used for such solutions as well, but ß-ketones (Figure 3.8) are also often used [116, 125].



a) b)

Figure 3.8. Schematic structure of a) ß-ketone and b) the corresponding Cu complex.

The simplified reaction for Cu extraction using ß-ketone in an ammonia solution can be written as

$$Cu(NH_3)_n{}^{2+}{}_{(aq)} + 2RH_{(org)} \rightarrow CuR_{2(org)} + 2NH_4{}^{+}{}_{(aq)} + (n\text{-}2)NH_{3(aq)} \qquad [eq.\ 6]$$

where n usually equals 4. As seen from eq. 6, high amounts of free ammonia will decrease the extraction of Cu. Fortunately, concentrations as high as 7M NH_3 are needed to strongly decrease the extraction efficiency of ß-ketones. This concentration is higher than those in the leaching solutions usually used for Cu leaching from ores [114]. Another risk of ammonia leaching is the transfer of ammonia to the organic phase during extraction, as discussed earlier. However, the ß-ketones usually transfer only small amounts of ammonia. As seen in Table 3.4 a ß-ketone named LIX 54-100 (active component 1-phenyl-1,3-decanedione), previously named LIX54 [114, 125, 126] was used in this work. Its viscosity is low compared to that of e.g. oximes, and thus higher reagent concentrations can be used in the organic phase. High transfer of Cu to the organic phase (~30g/L; ~500mmol/L) is therefore achieved even though the distribution between the organic and water phases is low [114, 125]. The stripping of Cu from ß-ketones is easy using H_2SO_4 solutions directly suitable for electrowininng [114, 125]. The selectivity (SF) for Cu over other metal ions such as Fe and Zn is moderate and the leaching pH (8.5-10) in ammonia leaching must thus be chosen such that only minor amounts of compounds of other metal are leached from the ore. In this way pure Cu electrolytes can be achieved [127]. A problem using LIX 54-100 in ammonia solutions is the risk of ketimine (ß-ketone+NH_3) formation, which degrades the active component [125, 127]. Newer reagents with modified ß-ketone structures sterically hindering ketimine formation, such as XI-N54 or XI-57, have been shown to be more resistant to degradation [125, 127].

Phosphinic acid extractants

The fourth extraction reagent used in this work is a phosphinic acid (Cyanex 272) reacting with Cu according to

$$Cu^{2+}_{(aq)} + 2(HA)_{2(org)} \rightarrow CuA_2(HA)_{2(org)} + 2H^+_{(aq)} \qquad \text{[eq. 7]}$$

where $(HA)_2$ refers to the protonated organic extractant dimer [116, 128]. Their extraction mechanism is reminiscent of those of the oximes with release of 2 H^+ but, in addition, two neutral acid molecules stabilize the complex and the extractant is usually present as dimer in organic diluents [127]. Bis(2,4,4-trimethylpentyl) phosphinic acid is one of the commercially most often used acids for extraction of Co over Ni but, depending on pH, other metal ions such as Cu, Zn and Fe can also be effectively extracted [21, 116, 129-131]. Figure 3.9 shows the schematic structures of phosphinic acid, the dimer and the corresponding Cu-extractant complex. Bis(2,4,4-trimethylpentyl) phosphinic acid is not very selective for Cu, probably due to disfavouring of planar Cu arrangements because of the bulky substituents on the phosphorous atoms [127].

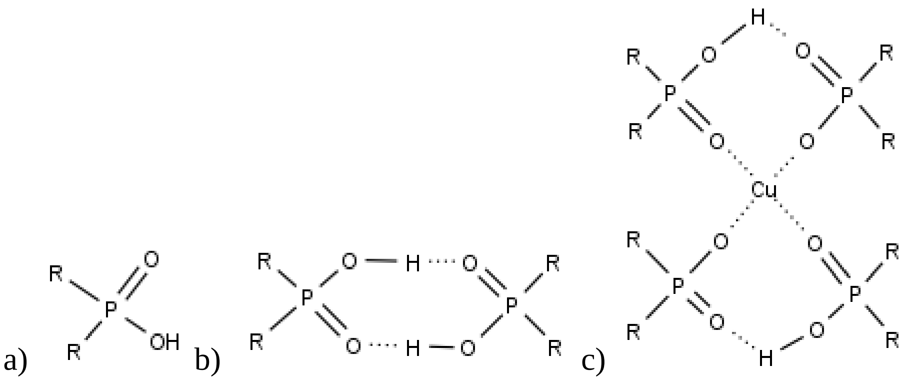


Figure 3.9. Schematic structure of a) phosphinic acid, b) the dimer and c) the corresponding Cu complex. Note that 2 H^+ are released. R=C_8H_{17} in bis(2,4,4-trimethylpentyl) phosphinic acid, the active component in LIX 272 and Cyanex 272. Based on [127].

Based on the considerations above a number of extractants typical for the four groups were chosen for the experimental work on solvent extraction of Cu from MSWI fly ash leachates. The chosen extractants are presented in Table 3.4. In summary, there is no general best choice of extraction reagent or number of extraction and stripping steps; the choices must be based on the demands on e.g. product purity and concentration differences between the target metal and other metals in the leachate in each specific situation. Thus, the optimal recovery process must be investigated and developed in each unique case [118].

Table 3.4. Relative properties of the organic reagents used for Cu^{2+} extraction in this work. Based on [113, 114, 116, 129, 132].

Property	**LIX 860N-I**	**LIX 84**	**LIX 54-100**	**Cyanex 272**
Active extractant molecule	Aldoxime	Ketoxime	ß-ketone	Phosphinic acid
$D_{o/a}$	Very high	Moderate	Low	Low
$SF_{Cu/m}$	Very high	Very high	Moderate	Low
Stability	Good	Good	Good, but risk for ketimine formation	Good
Stripping*	Moderate	Good	Very good	Very good
Costs	Expensive	Expensive	Moderate	Moderate

*A good grade refers to fast stripping kinetics and a low concentration of the acid needed.

4. Experimental

Several analytical techniques have been used in this work, such as x-ray diffraction spectrometry (XRD), scanning electron spectroscopy (SEM) and inductively coupled plasma optic emission spectroscopy (ICP-OES). However, as these are standard techniques, they are not described here. Detailed information on their use can be found in the articles and elsewhere, for instance in [93, 133-135].

Ash samples

This work included fly ash samples from fluidised bed combustion and grate fired combustion units mainly incinerating MSW. Details on the ash samples are given in Table 4.1.

Table 4.1. Details on the MSWI ash samples used in this work.

Ash	**A**	**B**	**C**	**D**	
Boiler type	BFB	BFB	BFB	BFB	
Ash collection device/ ash type	cyclone	cyclone	cyclone	cyclone	
Addition to combustion chamber	NH_3	NH_3+$NaHCO_3$	NH_3	No addition	
Annotation in papers	A in I	B in I: 2 in II	C in I: 1 in II	3 in II	
Ash	**1**	**2**	**3**	**4**	**5**
Boiler type	BFB	BFB	BFB	MB	MB
Ash collection device/ ash type	textile filter	textile filter	textile filter	textile filter	electric precipitator filter
Comments on flue gas treatment	CaO	$Ca(OH)_2$	$Ca(OH)_2$	$CaCO_3$	No addition
Annotation in papers	1 in IV and V	2 in IV and V	1 in III: 3 in IV and V	4 in IV and V	5 in IV and V

Ashes A-D all come from the cyclones of 20 MW BFB boilers. The combustion temperature was about 850ºC and in this boiler the cyclone is placed after a section containing heat transfer surfaces, which means that the temperature has decreased to about 150ºC. When the cyclone ashes were produced, ammonia (NH_3) was added to the combustion zone for reduction of nitrogen oxides, except in the case of ash D. For ash B the ammonia was treated with sodium bicarbonate ($NaHCO_3$) with the aim of also binding HCl and SO_2. Ashes 2 and 3 came from the textile filters in the same boilers as the cyclone ashes, while ash 1 came from the textile filter in another BFB boiler. Ash 4 was a filter ash from the textile filter in a MB combustor, and ash 5 was collected from an electric precipitator filter. Total contents of major and minor elements in all ash samples are given in Tables 4.2 and 4.3.

Table 4.2. Total content of major and trace elements in the cyclone ashes A-D. Major elements are given as g/kg dry ash and minor elements are given as mg/kg dry ash.

Major elements	**Ash A**	**Ash B**	**Ash C**	**Ash D**	**Minor elements**	**Ash A**	**Ash B**	**Ash C**	**Ash D**
Al	105	105	130	125	As	40	50	30	40
Ca	130	120	130	135	Ba	1900	3000	2700	4400
Fe	30	30	40	40	Cd	10	10	10	10
K	20	20	20	20	Co	50	20	30	30
Mg	15	15	15	20	Cr	490	630	550	410
Na	30	40	30	25	Cu	3800	3800	5900	7300
P	10	10	10	10	Hg	<1	<1	<1	<1
S	10	10	10	10	Mn	2100	1800	2500	1800
Si	180	195	180	180	Mo	20	10	10	30
Ti	10	10	10	15	Ni	160	160	220	210
					Pb	1300	1100	1500	1500
					Sn	70	70	120	190
					Sr	360	370	400	380
					V	50	60	50	60
					Zn	6300	5900	9000	9600

Table 4.3. Total content of major and trace elements in the filter ashes 1-5. Major elements are given as g/kg dry ash and minor elements are given as mg/kg dry ash.

Major elements	**Ash 1**	**Ash 2**	**Ash 3**	**Ash 4**	**Ash 5**	**Minor elements**	**Ash 1**	**Ash 2**	**Ash 3**	**Ash 4**	**Ash 5**
Al	20	15	20	25	30	As	50	30	80	110	1100
Ca	315	410	360	210	120	Ba	1300	440	770	1000	1100
Fe	10	5.5	5.6	9	24	Cd	60	30	90	210	370
K	15	10	25	50	70	Co	20	10	20	50	20
Mg	9.5	8.5	10	9.5	12	Cr	380	150	190	470	920
Na	20	15	30	50	80	Cu	7800	3090	5400	1500	2500
P	3	3	4	4.5	6	Hg	1	3	3	10	1
S	30	15	10	40	75	Mn	690	400	570	820	840
Si	30	25	35	45	70	Mo	10	20	10	20	40
Ti	<1	2	2	6	10	Ni	90	30	30	40	80
Cl	190	120	200*	150	110	Pb	4000	2600	5700	4800	11000
						Sb	460	160	-	1600	2300
						Se	<1	2	-	2	10
						Sn	250	150	20	750	2000
						Sr	280	290	500	300	290
						V	10	20	10	20	50
						Zn	5500	3300	5800	25600	55100

*approximate value from [136]

5. Summary and discussion of results in Papers I-V

Characterization of ash

As shown in Table 4.1 the amounts of several elements, such as Ca, Ti, Si, Cd and Pb, differ between the two groups of ash samples. Titanium and Si, mainly forming oxides with low volatility, are generally present in higher amounts in the cyclone ashes, while Cd and Pb are more abundant in the filter ashes. This is probably due to the formation of volatile chlorides. However, there are also differences between the filter ashes where for instance the addition of various Ca compounds to the flue gas channels is reflected in the concentrations of Ca. Elements As, Cd and Zn are present in higher amounts in the ashes from MB combustion (4 and 5) than in the FB ashes, which has to do with variations in the waste composition and differences in the incineration techniques used.

Even though fly ashes from MSWI are very heterogeneous materials, the XRD analyses generally showed the same major crystalline compounds in both cyclone and filter ash (Tables 5.1 and 5.2). The amounts of amorphous material are low, especially in the filter ashes. Quartz, NaCl, $CaCO_3$ and $CaSO_4$ were indentified in all ashes, as were Al_xCa_y oxides and silicates. Similar results have been obtained in other studies for MSWI fly ash [70, 71, 74, 137, 138]. Alkali metal chlorides, i.e. NaCl and KCl, were generally major compounds in the filter ashes whereas non-volatile compounds such as SiO_2 (quartz) and silicates were less common.

Table 5.1. Crystalline compounds identified in the original cyclone ash samples A-D (Papers I and II).

Mineral	Ash A	Ash B	Ash C	Ash D
NaCl	Major	Major	Minor	Trace
KCl		Trace	Trace	Trace
CaO		Trace	Minor	
$CaCO_3$	Major	Major	Minor	Major
$CaSO_4$	Minor	Minor	Minor	Minor
$Ca_3Al_2O_6$	Minor	Minor	Minor	Trace
SiO_2	Major	Major	Major	Major
$Ca_2Al_2SiO_7$	Major	Major	Major	Major
$(Na,Ca)AlSi_3O_8$	Minor	Minor	Minor	Major
$KAlSi_3O_8$		Minor	Minor	Major
Al	Major	Major	Major	Major
Fe_2O_3		Minor	Trace	Minor
Fe_3O_4		Minor		Minor
$MgFe_2O_4$				Minor

Table 5.2. Crystalline compounds identified in the original filter ash samples 1-5 (Paper V).

Mineral	Ash 1	Ash 2	Ash 3	Ash 4	Ash 5
NaCl	Major	Minor	Major	Major	Major
KCl		Trace	Major	Minor	Minor
$KCaCl_3$			Trace		
$Ca(OH)_2$	Major	Major	Major		Trace
CaClOH	Major	Minor	Major		
$CaCO_3$	Minor	Minor	Major	Major	Minor
$CaSO_4$	Major	Minor	Trace	Trace	Minor
$Ca_3Al_2O_6$	Minor	Minor	Trace	Minor	Trace
$Ca_3Al_2(OH)_{12}$				Trace	
SiO_2	Trace	Trace	Trace	Minor	Trace

The acid neutralising capacity of ash 3 was measured and a value of 10 mmol H^+/g dry ash was obtained (Figure 5.1). The main part of the acid was consumed within 30 minutes. This indicates that most of the alkaline compounds, such as $CaCO_3$ and $Ca(OH)_2$, identified in the XRD analysis are easily available. Two minor buffering regions can be identified and are probably a result of the carbonate system with $pKa_1=6.4$ and $pKa_2=10.3$ [139]. van Herck and co-workers reported a similar acid neutralising capacity (<12 mmol H^+/g ash) for a MSWI filter ash [76]. In another project, acid neutralising capacities of 7.0 mmol H^+/g ash for ash 1, 2.2 H^+/g ash for its corresponding cyclone ash and 2.7 mmol H^+/g ash for ash 5 were obtained [138]. Ash 4 was found to have an acid neutralising capacity of 1.1 mmol H^+/g ash [140]. In the same work, a filter ash from the same plant that produced ashes 2 and 3 showed an acid neutral capacity of 16.3 mmol H^+/g ash, while the corresponding value for the cyclone ash was 1.6 mmol H^+/g ash [140].

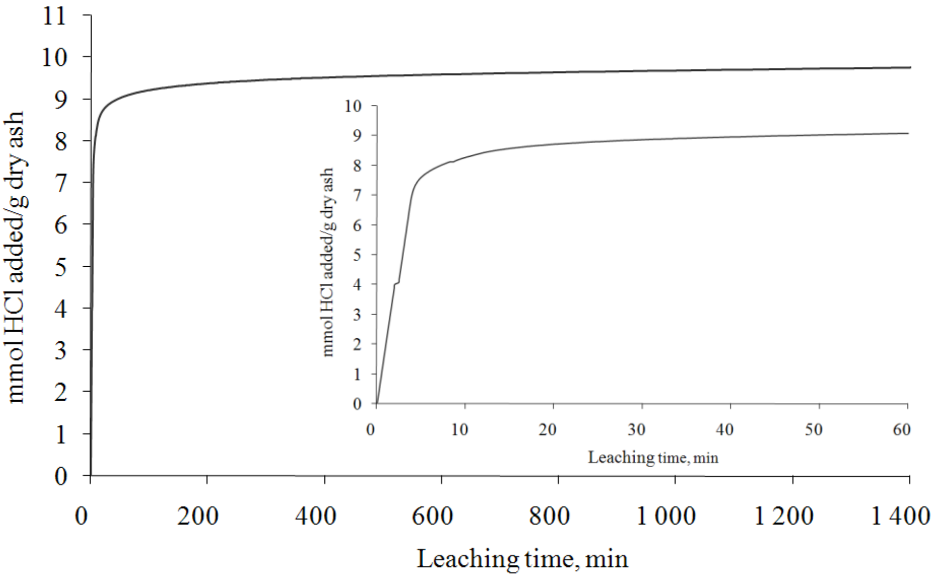


Figure 5.1. Acid comsumption rate/g dry ash during the pH-static experiments at pH 7. Magnification of the first hour is inset (Paper III).

The particle size distributions were measured in the original filter ashes 3 and 5 to investigate whether there were any differences between ashes from different incineration techniques. The data showed that the major part (>70%) of the particles were in the size fraction between 5 and 70µm (maximum around 20 µm) for ash 3, while ash 5 had a broader particle size distribution of 50-950µm (maximum around 340µm) (Figure 5.2). After a few minutes of leaching in water with ultra sonic treatment, the particle size distributions in both ashes were displaced towards smaller sizes, suggesting that the larger particles consist of agglomerated small particles. The fraction of larger particles in ash 3 also increased, however, indicating that agglomeration of particles can occur during leaching. This phenomenon was also observed in some experiments for the cyclone ashes where the average particle sizes increased with leaching (Paper I). It should be noted that only particles smaller than

118 µm could be measured in the laser diffraction device used for the cyclone ashes, and unfortunately no information about larger particles can be given.

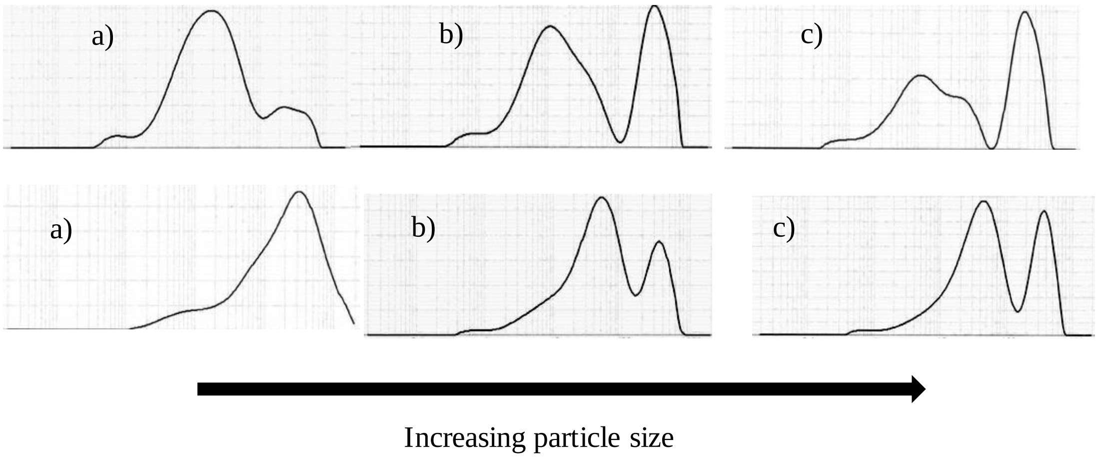


Figure 5.2. Particle size distribution (1-1000µm) for original filter ash 3 (a-c) and 5 (d-f) printed in logarithmic scale. The maximum at the Y scale corresponds to about 5 volume% of the total ash amount used in each experiment. a) ash 3, original, b) and c) ash 3, treated with US, 12kHz and 24kHz, d) ash 5, original e) and f) ash 5, treated with US, 12kHz and 24kHz (Paper V)

These results indicate that, even though the MB ash initially contained larger particles as compared to the BFB ash, the particle size distributions in the ashes after some leaching become more similar.

Distribution of metals

As discussed earlier, the distribution of metals on fly ash particles is to some extent dependent on the size of the particles. Trace metals are generally enriched on smaller particles. When studying the composition of different particle size fractions of ash D (a cyclone ash from a BFB combustor), the results for trace metals showed this expected trend with increasing metal concentration as the particle size decreased (Table 5.3 and Figure 5.3). The distribution of major elements was less predictable. Calcium, Mg and Fe were enriched on smaller particles while K showed the opposite trend and Na was more evenly distributed. Potassium and Na often occur as volatile chlorides and were therefore expected to be enriched on small particles. However, the presence of those elements in feldspar minerals in large particles probably covers the effect of chloride enrichment in small particles (Table 5.1). The SEM analyses indicated the presence of particle aggregates in the larger size fractions of ash D, which probably further explains the lack of enrichment of Na and K in small particle fractions obtained by sieving (Figure 5.4). The different particle size fractions were also analysed by XRD, and a comparison of peak heights showed that the amounts of NaCl and KCl increased with decreasing particle size. The amounts of $CaCO_3$, $CaSO_4$, $Ca_2Al_2SiO_7$ and Fe_2O_3 also increased with decreasing particle size, while the content of SiO_2 and Al metal decreased. Quartz is a remnant from the bed sand, where <1% of the particles are originally smaller than 500 μm, explaining this result. The metallic Al is probably a residue from aluminium foil or other aluminium objects in the fuel.

Table 5.3. Elemental composition of different particle size fractions of ash D. The amounts are given in g/kg dry ash for major elements and in mg/kg dry ash for minor and trace elements. (Paper II)

	$d_p > 180\mu m$	$d_p < 180\mu m$	$d_p < 125\mu m$	$d_p < 90\mu m$	$d_p < 63\mu m$	$d_p < 45\mu m$	$d_p < 32\ \mu m$
Major elements							
Ca	90	100	140	150	170	180	180
Fe	15	15	15	20	20	30	35
K	20	20	20	15	15	10	15
Mg	10	10	15	15	15	20	20
Na	20	25	20	20	25	20	25
Trace elements							
Cd	15	20	20	20	30	30	40
Cr	260	300	320	320	420	410	460
Cu	5800	5800	6900	8900	10500	10900	14600
Mn	1400	1600	1800	2200	2500	2200	2400
Pb	1300	1200	1400	1800	2500	2700	4000
Zn	6800	5000	7500	10300	13600	15100	20200

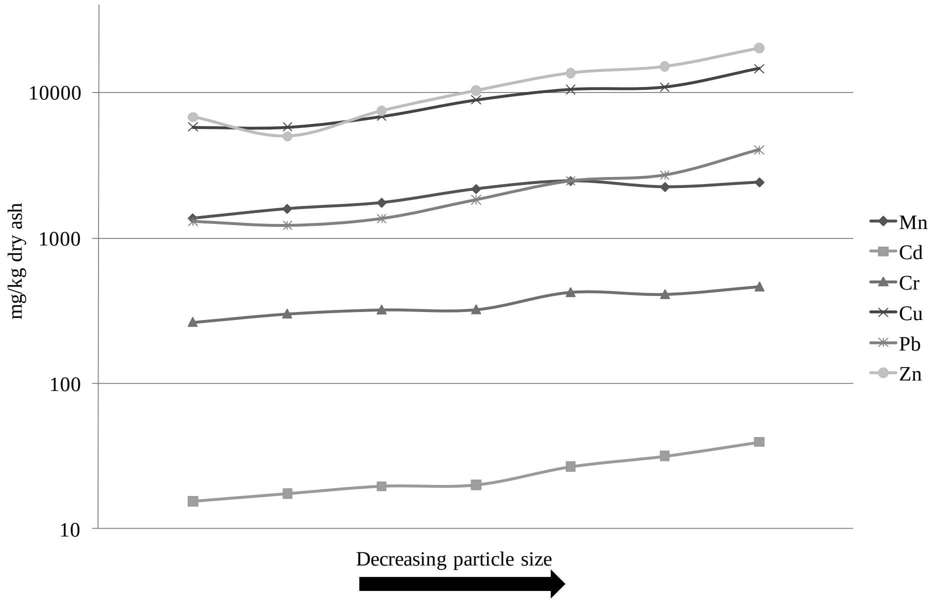


Figure 5.3. Elemental composition of different particle size fractions of ash D. The amounts are given in mg/kg dry ash and the particle sizes are decreasing from >180µm to <32 µm (Paper II).

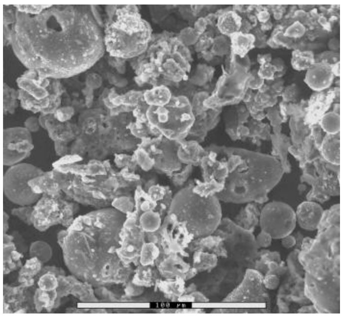


Figure 5.4. SEM image, 500x magnification, of the size fraction with particles >180 µm in ash D. The bar corresponds to 100 µm (Paper II).

Even though many groups have found an enrichment of trace metal compounds in the smallest particle sizes [21, 26-28, 141], published results show variations. Gilardoni and co-workers studied MSWI filter ash particles of sizes <100 µm and found that the majority of the particles were smaller than 1 µm. However, these small particles correspond to a minor part of the total mass of ash [142]. They further found that Fe and Zn were present in ~30-80% of all the particles smaller than 20 µm, with a distribution that was rather independent of particles size, whereas Cu was generally less abundant (occurring in less than 20% of the particles) but was concentrated to particles around 1.5 µm and 3-15 µm. Arsenic, Pb, Cu, Zn and Mo have been shown to be enriched in particles <2.5 µm compared to particles >65 µm in coal fly ash [143, 144]. Enrichment in small particle sizes was also found for Ba, Ni, Cr, V and P while the abundance of Y, Sr, Ti, Rb, K, Zr, Ca, Mg, Mn and Fe did not vary with particle size.

The distribution of metals on different particle sizes in the larger particle size fraction, such as sizes from 10μm to 1mm, is not often discussed in the literature. Liao and co-workers investigated cyclone ash particle sizes from <10μm to >850μm from biomass gasification and found that Cu, Ti, Cr, Pb and Ni were enriched in 50-125 μm particles, while no trends were found for As, Cd, Co, Ba, Mo or V [145]. It was shown in the same investigation that the major elements, Fe, Mg, Mn, Na, P, Ca and K, were enriched in the size fraction 74-180μm. However, the amounts of Cu, Ti, Cr and Ni increased in particles >400 μm, and Mg, Na, Ca and K increased in particles >850 μm. No distribution trends connected to particle size were found for Al. The increase of metals in small particles is suggested to be due a condensation of volatile metal compounds such as $PbCl_2$ due to the large surface area of small particles [145]. No explanation for the enrichment in the larger particles was given. However, a speculative explanation of the relative increase in abundance of metals (Cu, Ti, Cr, Ni) in large ash particles may be the presence of small pieces of metals and alloys. The same explanation may apply to the results obtained by Thipse and co-workers in an investigation of MSWI filter ash, where they found increased amounts of Fe, Ni and Cr with increasing particle size in 0-1200 μm particles while the amounts of Al and Si decreased with increasing particle size [146]. The amounts of Pb and Hg increased with increasing particle size up to 300 μm but decreased in larger particles.

In summary, the studies discussed above and other published results do not give clear trends for the distribution of metals in ash particles of different sizes. However, the most common trend seems to be enrichment of many trace metals in small particles, while differences depending on properties during incineration as well as variations in fuel are reasons for other distribution patterns. In addition, the ash matrix itself can have an influence on the abundance of metals in ashes, as has been found for ashes from various fuels [38, 147]. It has not been completely verified whether the ash matrix is important for the distribution of metal compounds in MSWI ashes as well. For this reason, the correlations and associations (co-occurrence of major and minor elements in minor rich particles) between major (Al, Ca, Cl, Fe, K, Na, Si and Ti) and minor (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Sr, V and Zn) elements were studied (Paper II). Associations between several minor elements (As, Cd, Co, Cu, Ni and Sr) and major elements, i.e. Ca and Fe, were observed, whereas real correlations were found only for the pairs Cd-Mg, Fe-Ni and Sr-Ca. The importance of Ca compounds such as $CaCO_3$ as hosts for trace metal compounds in ash has been reported earlier [39, 40, 148, 149]. In contrast, neither correlations nor associations between Cr, Pb, Ti and Zn and major elements were found. This indicates that the latter metals, or the species of these metals carried by the flue gas, primarily bind to available particles by a random process regardless of the particle matrix composition, whereas the binding of the former group of metals includes an affinity effect, i.e. that As, Cd, Co, Cu, Ni and Sr bind to available particles with a higher affinity for specific particle matrix types. It is also possible that the metals were already present in the particles, i.e. the association is a result from co-existence in the waste. This is probably the reason for the correlation between Ni and Fe, which is likely to be rest fractions from stainless steel. However, in general, the reasons for affinity or a lack of affinity are presently not clear and it should be noted that associations and correlations were mainly found in ash C. For ash B the addition of Na in the combustion zone led to a large enrichment in Na species, which covered possible association effects since Na was found on the surfaces of all the particles studied. Problems with water soluble chlorides hiding correlations between elements have been reported earlier [142]. When studying MSWI filter ash particles smaller than 10 μm, Zn was found to correlate only with Na in the original ash, while positive correlations between Zn and Na as well as between Zn and Fe were observed after washing in water. In addition, Zn gave negative correlations with Ca, Al and Si, and Pb was negatively correlated with Si and Al in the washed ash. Thus the results of Gilardoni and co-workers suggest that Zn and Pb would not be present in silicate or aluminate forms. A negative correlation after washing away the water soluble alkali salts was also found between Cu and Ca [142].

Element analysis with an energy dispersive X-ray (EDX) detector in a scanning electron microscope was also used to study possible correlations between major elements in ashes B and C (Paper II). The most significant correlation was found for the pair Al and Si. This was expected because of the presence of aluminium silicates. In spherical particles, Na and Cl showed a high correlation suggesting that NaCl was adsorbed on particles present in the flue gas and that local eutectic melts may cause the particles to become spherical. In addition, it was found that a high content of Al and Si was generally coupled to a low content of Ca.

It is not possible on the basis of the results discussed above to determine whether volatile metal compounds (As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Sr, V and Zn) adsorb directly onto special minerals in the particle surfaces or whether the metal species react with the components in the ash matrix after condensation. It is also possible that the particle and the metal species are remnants from the fuel and have been present in the same structure throughout the combustion process. The ash formation probably includes all processes discussed above. To be able to understand these processes and their effects on the chemistry of minor and trace metals further, investigations of the speciation, i.e. the chemical forms of minor metals, are needed. Speciation of Cu in ashes 3 and 5 using XAS data showed that CuO and/or $Cu(OH)_2$, $CuSO_4 \cdot H_2O$ and metallic Cu were the suggested dominating species in ash 3, while CuO and/or $CuSiO_3 \cdot H_2O$ in addition to metallic Cu seem to be the major Cu components in ash 5 (Paper V). The most probable speciation for Zn in ash 3 is as silicate or hydroxide in addition to $ZnCl_2 \cdot 1.33H_2O$. The data for ash 5 were less specific but indicated that Zn is bound as $ZnCl_2 \cdot 1.33H_2O$ and in oxidic forms such as ZnO, $Zn(OH)_2$, Zn silicate, Zn aluminate and/or Zn-containing spinel phases such as franklinite ($(Fe,Mn,Zn)(Fe,Mn)_2O_4$). The absence of Zn-Zn distances in the data indicates that Zn has replaced other ions in a variety of compounds. These results suggest that especially the leaching of Cu from these ashes may differ due to the presence of more soluble compounds in ash 3 compared to ash 5. This will be further discussed later in the thesis.

Information about the speciation of metals can also be obtained from sequential extraction methods. The commonly applied sequential extraction method that was originally developed by Tessier and co-workers in 1979 was intended to be used to study how various environmental conditions influence the stability of metals in soil and sediment samples [89]. However, this method has also been widely used for other materials like ashes [40, 67, 76, 88, 90, 150, 151].

The sequential extraction results obtained in this study showed that Cu was harder bound in cyclone ash than in filter ash (Figure 5.5). Similar results were obtained for all metals studied (As, Co, Cr, Ni, Pb, Zn) and the water soluble fraction was generally <1% for most elements in both cyclone and filter ash (Paper I). The only exception was Pb, which occurred in significant amounts of water soluble forms (>40%) in the filter ash. A high release of Pb and Zn from MSWI fly ash in the first steps (water soluble and exchangeable) using sequential extraction has been reported earlier and has been suggested to be due to the release of Ca compounds such as $CaCO_3$, to which Pb and Zn are suggested to be adsorbed [40, 150]. Associations between Ca and metals such as As and Cu were found in our LA-ICP-MS studies of cyclone ashes B and C (Paper II), while Pb and Zn did not correlate to any of the major elements studied. It therefore not seems likely that the release of Ca compounds is the reason for the release patterns of Pb and Zn found here. However, correlations between Pb and Zn and Ca in the filter ash cannot be ruled out. The release of Pb and Zn could also be controlled by their hydroxides as suggested in another study [76].

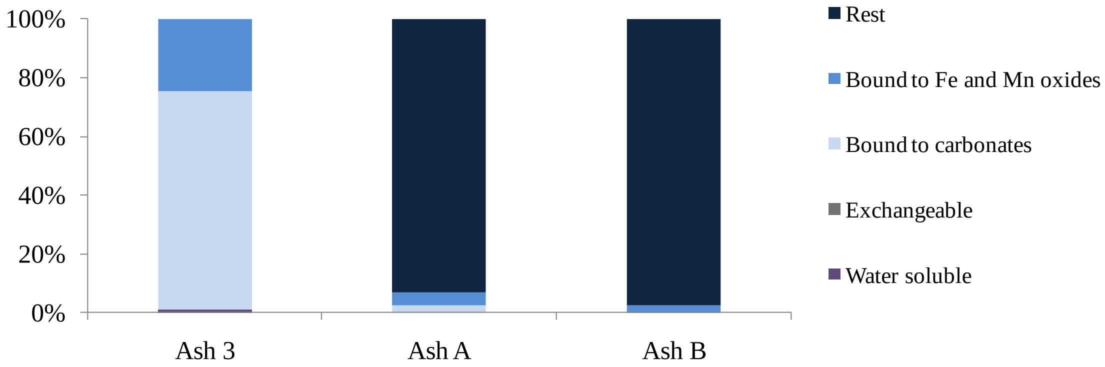


Figure 5.5. Results of sequential extraction for Cu from ash 3, ash A and ash B.

Even though sequential extraction protocols are generally easier to apply than are X-ray spectroscopic methods, such as EXAFS, they are associated with some problems because of possible reactions taking place during the different extraction steps. The results obtained from different sequential extraction methods applied to sediments and soils have given significantly different suggestions about the distribution of metals between fractions [94, 96, 152]. This lack of consistency between results may be caused by heterogeneity in sample materials but can also be due to effects caused by different leaching parameters, such as the leaching time and the L/S ratio used. As an example, the leaching times used to identify water soluble and exchangeable ions in ashes vary from 10 minutes to 16 hours between the investigations [67, 69, 90, 153-155]. Other factors affecting the amounts of metal ions detected in leachates are sorption processes. Adsorption of metal ions from a water phase onto minerals has been extensively investigated and numerous publications exist on this matter. Aluminum and iron (hydr)oxides as well as amorphous aluminosilicates are common phases in ash and to which a number of metal ions, e.g. Pb, Cd, Zn and Cu, can sorb [10, 55, 63]. Calcite and feldspars, other common minerals in ash, have also been pointed out as surfaces providing adsorption sites for metal ions [156, 157]. In addition, fly ash itself has been suggested as being adsorbent for metal ions from water [158-160]. It is important to take these effects into account when sequential extraction methods are used to determine the chemical association forms of metals in ash or soil samples. Clearly, the amount of a metal detected in a specific fraction does not conclusively describe the speciation, and the amount in each fraction can be an underestimation as well as an overestimation due to precipitation and other reactions.

Leaching

Water as leaching agent

As seen from the sequential extraction analysis, the fraction of water soluble metal compounds was generally low in the ashes studied, which has also been reported in several earlier investigations [34, 64, 67-70, 161]. However, as discussed earlier, variations in leaching parameters, such as the contact time, have been found to influence the amounts of metal ions detected in the leachates. For this reason, the leaching of metals (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb and Zn) in water from cyclone ash was studied in more detail (Paper I). It was found that variations in leaching parameters (leaching time, L/S ratio and grinding prior leaching) significantly influenced the release patterns. The release of As, Cd, Ni, Sb and Se was so low (<1mg/kg dry ash) that no trends could be shown. For the other metals, a longer leaching time generally resulted in lower amounts of metal ions detected in the leachate, as illustrated by Zn in Figure 5.6. This is probably due to precipitation of e.g. metal hydroxides as the pH in all leachates varied between 9 and 11 [76, 162].

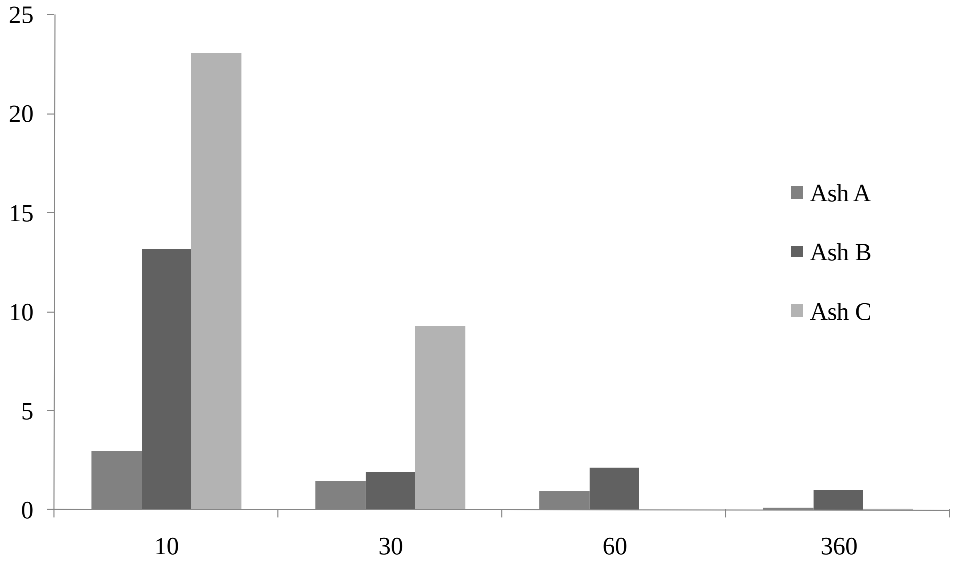


Figure 5.6. Effect of leaching time on the amount of Zn detected in the leachate from ground ashes A-C at an L/S ratio of 10. The amounts released are present as mg Zn/kg dry ash and leaching times are in minutes (Paper I).

An increased L/S ratio generally led to higher amounts of metals detected in the water for ashes A and B, whereas many metals in ash C showed the opposite trend. Increased leaching with an increased L/S ratio has been reported by others [68, 70, 111] and the solubility equilibrium for the metal compounds present in the ash is probably the limiting factor. As indicated above, the results obtained for ash C suggested different chemical characteristics compared to the other ashes studied, with a negative correlation between L/S ratio and release of several metals, such as Cu, Pb and Zn. This is exemplified by Zn in Figure 5.7. A negative correlation between the L/S ratio and Zn leaching has been reported earlier, while in the same study the leaching of Cu increased with L/S and Pb was not affected [161]. The decrease in release with increasing L/S could be due to the precipitation of secondary compounds formed from metal ions and anions released from ash compounds that were not released at lower L/S ratios. In a recent study, Guyonnet and co-workers compared different leaching standards and their relation to time (<19 months) and L/S ratio (<4) for MSWI ash in order to identify whether the L/S ratio could be used to predict the release of non-reactive constituents such as Ca, K and Na and reactive constituents (Cr and Al) [163]. They found that non-reactive constituents are released quickly more or less independently of L/S ratio while the releases of reactive constituents are influenced by reactions and kinetics rather than the L/S ratio. The importance of the reduction-oxidation process between Al and Cr on leachability from ash as well as rapid release of Ca, K and Na have also been reported by others [74, 136]. Similar conclusions were also drawn by Mizutami and co-workers, who studied the release of Pb, Cd, Cu and Zn from several MSWI fly ashes [73]. They found that the release trends in metal compounds as a function of L/S differed between ashes and explained this by referring to the different ash matrix composition in the ashes studied [73].

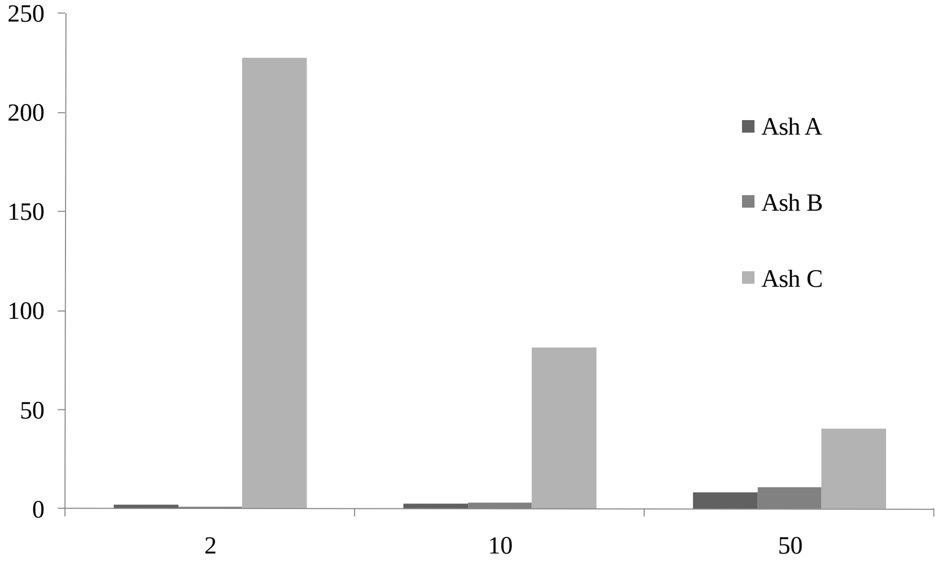


Figure 5.7. Effect of L/S ratio on the amount of Zn detected in the water from ash C with a leaching time of 10 minutes. All amounts are present as mg Zn released/kg dry ash (Paper I).

Rapid releases of soluble salts, such as NaCl, from a fly ash can also affect the leaching of minor metal compounds since the release of major ash matrix compounds results in an increased porosity [70]. Thus, encapsulated metal compounds can be exposed to the leaching agent through the new pores. With the aim of enhancing leaching by exposing as much as possible of the ash surface to the leaching agent, the cyclone ash samples were ground before leaching (Paper I). However, when some leaching tests were done without grinding the ash before leaching, it was found that the amounts released in some cases increased significantly compared to the first set of experiments. This was generally a phenomenon found for metals in ash C while the release of metals in ashes A and B was not affected to any great extent. The largest effects of grinding on release were found for Zn and Pb (Figure 5.8).

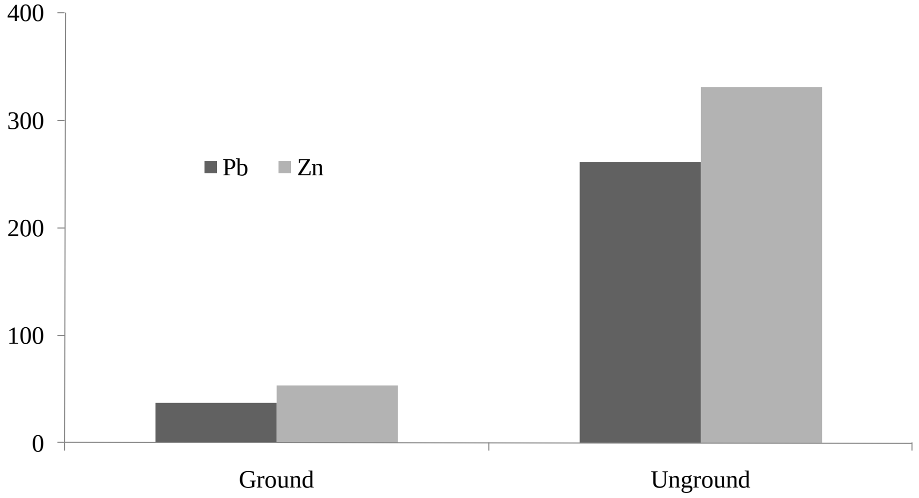


Figure 5.8. Effect of grinding on the amount of Pb and Zn detected in the water leachate from ash C with L/S=10 and 10 minutes of leaching time. All amounts are present as mg Pb and Zn released/kg dry ash (Paper I).

It is clear that grinding may have a strong influence on the amounts of water soluble compounds of metals detected in ash leachates, but its effect depends on both the ash matrix and the element of interest. No general conclusions can thus be drawn from the results about whether or not cyclone ashes from MSW combustion should be ground before leaching. However, the results indicate that grinding may lead to an underestimation of the water soluble amounts of metals. As discussed earlier and reported in paper I, particle size distribution analyses of unground original and leached ash samples showed that agglomeration of ash particles in ashes A and B occurred, whereas this was not found for ash C. However, when ash C was first ground and then leached, both agglomeration and particle disintegration were observed (Figure 5.9). The lack of agglomeration of particles in leached unground ash C probably contributes to the higher release of some metals from this ash sample.

Leaching of unground ashes A and B lead to agglomeration and probably encapsulation of metal compounds that otherwise would have been possible to leach.

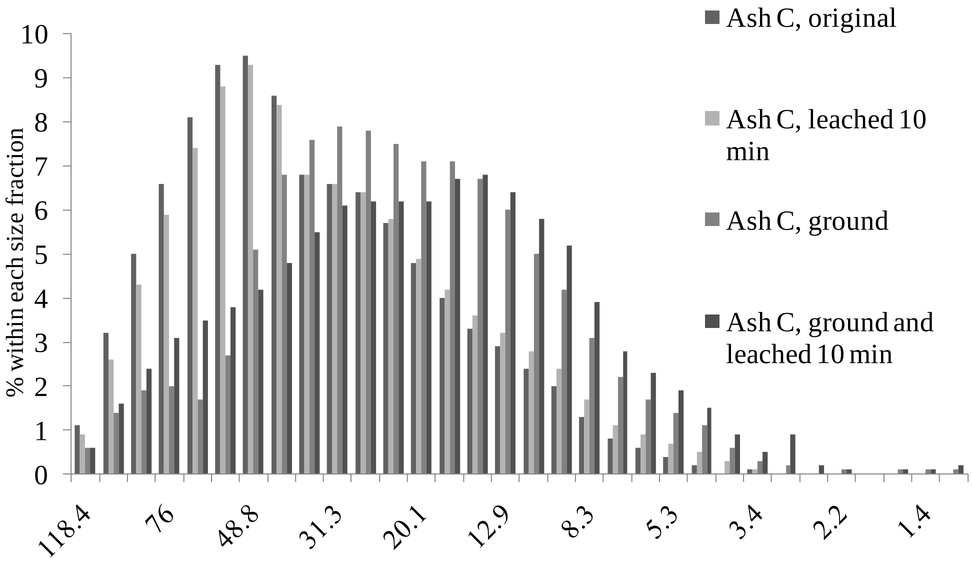


Figure 5.9. Particle size distributions for ash C in original, ground and leached (10 minutes, L/>>10) ash samples. Particle sizes are in µm (Paper I).

From the results and discussion above, it can be concluded that the release of metal compounds in water is affected by variations in leaching parameters. In addition, the ash matrix influences the amounts released. Adsorption processes and precipitation of secondarily formed compounds are most likely to be the reasons for this. The release of minor and trace elements clearly depends on the release of major ash components and the total chemical equilibrium formed in the leachate. This influences the possibilities for the minor and trace elements to react and form water soluble complexes or to precipitate. Other important factors that affect leaching are the chemical form of the trace metal and whether it is present on the surface or inside the particle. In the LA-ICP-MS analysis in this work (Paper II) it was found that the presence of different metal compounds on fly ash particles is mainly a random process. It could not be concluded whether the metals are adsorbed onto the particle surface or whether they react with it. However, neither Pb nor Zn showed any association with major components, which indicates that they are weakly adsorbed to the particle surfaces. That would explain their relatively high leachability in water.

Minor metals (Cu, Mn, Pb and Zn) in filter ash (ash 3) also showed a low release (maximum 3%) in water with the exception of Pb (>10% water soluble) (Table 5.4). This is lower than the fraction released in the first step of the sequential extraction (>40% water soluble). The reasons for the different results can be the longer leaching time and higher L/S used in these experiments, suggesting that adsorption or precipitation of e.g. $PbSO_4$ can take place. Earlier work on this ash showed that the amount of SO_4 detected decreased after 30 minutes, which suggests that 10 minutes of leaching (used in the sequential extraction) may be too short to effectively precipitate Pb as $PbSO_4$. Comparing the release of Pb with leaching results from other waste ashes, it seems that a high pH is more important than the L/S ratio (Table 5.4). This is probably due to a formation of soluble hydroxy-ions. The PHREEQC calculations (Paper III) suggest that, at a pH above 12, formation of soluble $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ is promoted, while lower pH promotes formation of the less soluble $Pb(OH)_2$.

Table 5.4. Release of selected major and minor elements in water after leaching ash 3 compared to results reported in the literature. All results are presented as % leached of total amount (Paper III).

L/S: leaching time	end pH	Al	Ca	Fe	K	Mg	Na	Si	Cu	Mn	Pb	Zn	Ash
50; 24 h	12.4	<4	31	<1	100	<1	71	4	<1	<1	14	3	Ash 3
20; 3 h	9.1	nd	18	nd	83	8	92	nd	2	4	<1	14	Industrial waste fly ash [34]
100; 3 h	10.5	3	21	-	71	-	55	-	1	-	2	1	MSW fly ash [69]
100; 1 h	10.8	18	63	10	65	12	53	nd	<1	-	1	<1	MSW fly ash [71]

nd- not detected
- not measured

When the pH was decreased to 7 the release of Pb decreased significantly (1%) whereas leaching of other metals (Mn and Zn) increased to about 20% (Paper III). The release of Cd and Mo was also high (>97%). General leaching patterns of MSWI residues in relation to pH indicate that Mo is released in increasing amounts at pH levels below 7, while Pb and Zn are amphoteric elements with minimum leaching at neutral pH (Figure 3.3). This is in agreement with the release of Pb found in this work (Paper III), and PHREEQC modelling suggests that carbonate is a solubility controlling solid at pH 7. As Zn also shows amphoteric leaching, the release is expected to be low at pH 7. The higher release found here (Table 5.4) is probably due to the speciation of Zn in ash 3. In this filter ash, Zn is present in oxidic Zn minerals such as ZnO and Zn_2SiO_4, both of which are soluble in dilute acid solutions [100, 164, 165].

As expected, elements present as chlorides such as Na and K are released in high amounts in all studied leachates, including water, indicating that this release is mainly availability controlled (Tables 5.4-5.8). Calcium is also released in high amounts but the release generally increased with decreasing pH, which is mainly due to the dissolution of calcium carbonate (pKa1=6.4 and pKa2=10.3), one of the main components of this kind of ash (Table 5.2). This is in agreement with earlier reported results [136, 163].

Leaching for metal recovery

Acidic leaching

As shown in Table 5.5 and Figure 5.10, the pH is a very important factor in controlling the release of metals from ash 3. Generally, an acidic pH resulted in a significant increase in the release of both major and minor metal compounds compared to the results for alkaline pH. In some cases, the formation of secondary compounds was observed. When using a leaching liquid based on H_2SO_4 the concentration of Ca and Pb in the leachate is controlled by the solubility equilibrium for the corresponding sulphates. Since their solubilities are low the apparent release of Ca and Pb is low (Table 5.5 and Figure 5.10). This is important if the ash is to be utilised, as the toxic Pb is present in the resulting ash instead of being removed from it. Otherwise, Pb was generally the minor metal that was most easily released of those studied (Paper III). The release of Cu, Mn and Zn was high (>70%) for the low pH solutions while it was <1% for the solutions with an end pH above 11 (Table 5.5).

Table 5.5. Fraction of major and minor ash components released from ash 3 after 24 hours of leaching using strong mineral acids compared with other results reported in the literature for similar ashes. All results are given as % released of total amount in the dry ash (Paper III).

Leaching agent	**end pH**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Na**	**Si**	**Cu**	**Mn**	**Pb**	**Zn**	**Ref**
1 M HCl L/S 5	11.7	< 4	30	< 1	64	< 1	44	4	< 1	< 1	23	< 1	
3 M HCl L/S 5	< 0	76	63	63	86	64	58	44	100	71	100	77	
1 M HNO_3 L/S 5	11.8	< 4	40	< 1	84	< 1	53	1	< 1	< 1	23	< 1	
3 M HNO_3 L/S 5	< 0	67	61	48	82	58	55	36	100	66	96	72	
1.5 M H_2SO_4 L/S 10	0.4	60	2	81	100	82	67	58	100	98	5	100	
0.2 M acidic process water L/S 5	12.0	< 1	19	< 1	92	< 1	53	< 1	<1	<1	1	< 1	
HCl	~9	<1	50-90	1-5	-	30	-	-	<1	-	<1	1-5	[81]
HCl	~4	30-40	80-95	1-5	-	40-50	-	-	20-70	-	55-60	60-80	[81]
H_2SO_4	9	-	-	-	-	-	-	-	<1	-	2	4	[66]
H_2SO_4	1.5	-	-	-	-	-	-	-	7	-	30	22	[66]

- not measured

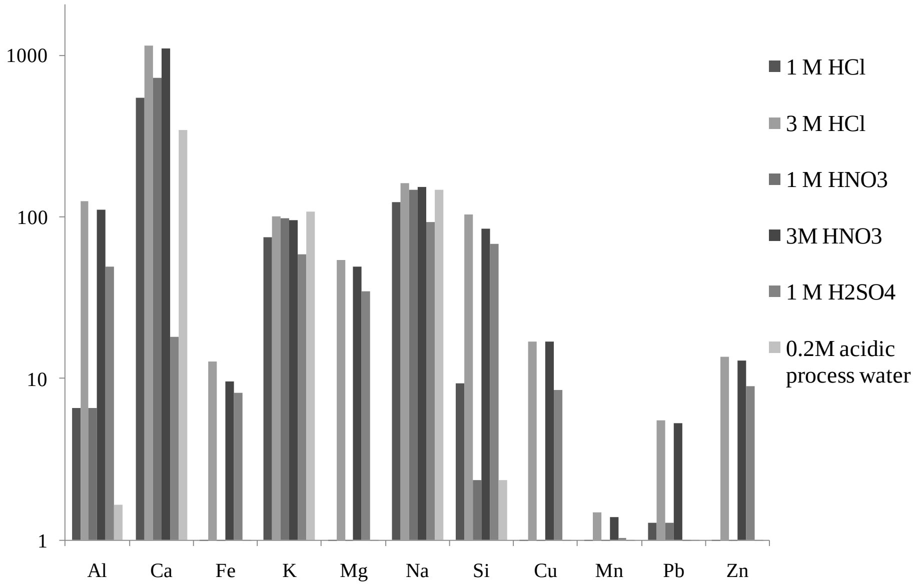


Figure 5.10. Concentrations of major and minor components in leachates from ash 3 after acidic leaching. All amounts are presented as mmol/L. No bar means that the measured concentration is <1mmol/L.

The release of minor metals (Cu, Mn, Pb and Zn) from ash 3 at an end pH of about 0 was not very different from that obtained with an end pH of 3 (Tables 5.5 and 5.6 and Figures 5.10 and 5.11). However, the release of the major elements Al, Fe and Si decreased significantly when the end pH was increased from 0 to 3. PHREEQC modelling suggested that solubility controlling phases can be various (hydr)oxides such as $Al(OH)_3$ and FeOOH. These results suggest that acid leaching of ash with the aim of maximising the removal of minor, hazardous metal compounds could be done at an optimum pH where the release of major ash forming elements is decreased. This is important as it minimises the consumption of acid for leaching. In addition, less of the ash matrix is dissolved, which is good if the ash is to be used as e.g. filling material. The relative release of metal compounds at pH 3 is comparable for all filter ash samples (Table 5.6). No difference could be seen between ashes from different incineration techniques (ashes 1-3 BFB and ashes 4-5 MB). Aluminium is an exception, with a higher fractional release from MB ashes, 4 and 5, compared to BFB ashes, 1-3. This may be due to the presence of Al in different compounds in the original ashes, but this could not be verified with the XRD data (Table 5.2). It should be noted that the comparably high end pH reached for ash 2 decreased the leaching of several metals including Cu, indicating that a pH of 5 is too high to achieve effective leaching. The leaching of Cu from ash 5 is also lower compared to the other ashes, despite the low pH (Table 5.6 and Figure 5.11). This is probably due to the presence of less soluble Cu compounds in this ash than in ash 3, as discussed earlier.

Table 5.6. Fraction of total amounts of major and minor ash components released from ashes 1-5 after 24 hours of leaching using HNO_3 at an initial pH of 2.2. All results are presented as % of total amounts (Papers IV and V).

	Ash 1	**Ash 2**	**Ash 3**	**Ash 4**	**Ash 5**
End pH	3.2	4.9	3.2	3.0	2.5
Element					
Al	29	<1	9	46	65
Ca[1]	58	62	59	79	50
Cu	95	42	>100	>100	58
Fe	3	<1	<1	9	26
K[1]	>100	>100	>100	>100	>100
Mg	100	>100	>100	>100	>100
Mn	65	76	74	103	78
Na[1]	98	74	76	>100	>100
Pb	93	76	>100	>100	76
Si	1	<1	<1	1	2
Zn	71	60	77	>100	68

[1] Semi quantitative

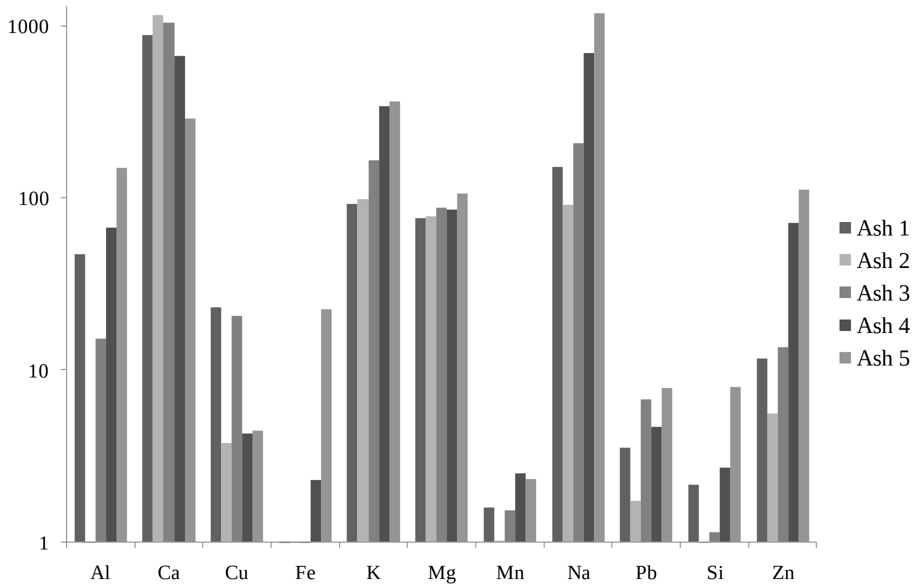


Figure 5.11. Concentrations of major and minor components in leachates from ashes 1-5 after acidic leaching for 24 hours using HNO_3 at an initial pH of 2.2. All amounts are presented as mmol/L. Ca, K and Na are semi quantitative. No bar means that the measured concentration is <1 mmol/L.

Organic acids and special complex forming agents

Some organic acids were tested as leaching agents for metal compounds in ash 3 (Paper III). The aim was to use the complex forming properties of these acids. However, with the amounts of acid used in these tests, the only metals released in significant amounts were Ca, K, Na and Pb (Table 5.7). The low release is probably due to the fact that the alkalinity of the ash samples resulted in a high pH in the leachates. Equilibrium calculations using PHREEQC for the cases of acetate and formate indicated that complexes are preferably formed with Ca over other ions. The only test where Cu was released in significant amounts was that in which the 1M lactic acid solution was used (Table 5.7). According to our PHREEQC calculations, lactate mainly formed complexes with Ca in this case as well, but the formation of lactate complexes with Cu and Pb was favoured over complex formation with Mn and Zn, which may explain those results. The release of Cu from MSWI bottom ash due to the formation of organo-copper complexes has been reported before, and especially dissolved organic matter (DOM) from the ash has been shown to be important as the ligand [85, 86].

Table 5.7. Fraction of major and minor ash components released from ash 3 after 24 hours of leaching with various leaching agents using L/S=5. All results are given as % released of total amount in the dry ash (Paper III).

Leaching agent	**end pH**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Na**	**Si**	**Cu**	**Mn**	**Pb**	**Zn**
Organic acids												
0.1 M formic acid	12.3	< 4	19	< 1	83	< 1	54	3	< 1	< 1	25	< 1
0.1 M acetic acid	12.2	< 4	17	< 1	70	< 1	52	2	< 1	< 1	32	< 1
0.1 M lactic acid	12.3	< 4	17	< 1	69	< 1	50	2	2	< 1	30	< 1
1 M lactic acid	12.0	< 4	37	< 1	100	< 1	66	< 1	23	< 1	43	1
0.5 M oxalic acid	11.6	< 4	31	< 1	100	< 1	53	1	1	< 1	1	< 1
Special complex forming agents												
0.1 M EDTA without pH adjustment	12.3	< 4	19	< 1	82	< 1	35	2	< 1	< 1	34	1
0.1 M EDTA with pH adjustment	8.2	< 4	65	< 1	97	40	40	5	100	25	94	40
0.1 M NH_4Cl	12.2	< 4	19	< 1	83	< 1	54	2	< 1	< 1	27	< 1
0.1 M NH_4NO_3	12.0	< 4	21	< 1	89	< 1	53	2	< 1	< 1	23	< 1
3 M NH_4NO_3	8.3	< 4	53	< 1	77	16	41	4	100	< 1	1	29

The use of EDTA as an effective complexing agent and the dependence of the optimal binding properties for various metals on pH are well known [166]. The results of using EDTA solutions with various end pH in ash leaching tests showed that the complex formation with Cu ions was favoured by a pH of 8. Without the pH adjustment, less than 1% was released from the ash. The effect of pH was similar for the other metals. With an optimised pH it is possible that EDTA could be used for removal of Cu, Pb and Zn from ash. Our PHREEQC modelling showed that, in the EDTA solution with the higher pH, EDTA mainly formed complexes with Ca. This fraction decreased with decreasing pH, thus favouring complex formation with other ions (Table 5.8). Other published data on the use of EDTA for metal leaching from MSWI fly ash indicate significant removal of Cu (60-70%), Pb (70-90%) and Zn (50-100%), in agreement with the results of the present work [66, 81]. The pH (~4-9) did not affect the leaching very much but an acidic environment generally enhanced leaching somewhat [81].

The solutions with low concentrations of NH_4Cl and NH_4NO_3 did not release any significant amounts of metals except Ca, K, Na and Pb, as discussed earlier (Table 5.7). However when the concentration of NH_4NO_3 was increased, the pH decreased due to the release of H^+ from $NH4^+$. Ammine formation is favoured between pH 8 and 10, where the ammonium-ammonia buffering system is most effective. As Pb does not form ammine complexes, the release of Pb decreased and the slightly alkaline pH probably also contributed to the low leaching (Table 5.7). The release of Cu was high due to the formation of stable copper ammine complexes such as $[Cu(NH_3)_4]^{2+}$ [139]. The stability of such complexes in the leachate was also confirmed by PHREEQC calculations. Formation of stable complexes in ammonium solutions from different Cu sources such as soil and ores is well known [167-169]. In this stronger ammonium solution, Zn was released in a significant amount which, according to PHREEQC modelling, is also due to ammine complex formation.

The amounts of metal species released from ash 3 and four other filter ashes (1, 2, 4 and 5) in ammonium nitrate leaching were compared. Similar patterns were found with a high fractional release of Cu, but variations between ash samples were observed. The percentage of Cu released varied between 57% and 100% (Table 5.8 and Figure 5.12). Zinc is also expected to form soluble ammine complex ions and was in fact released from all ashes in significant amounts, but with different yields: from 24% to 79%. Another example is the leaching of Ca, which was lower from ash samples 4 and 5 than from the other ash samples. This is probably due to differences in incineration technique and flue gas cleaning methods used.

Table 5.8. Amounts of selected metals leached from ashes 1-5 using 3M NH_4NO_3 after 24 hours of leaching. All results are given as % released of total amount in the dry ash (Papers IV and V).

Element	Ash 1	Ash 2	Ash 3	Ash 4	Ash 5
Al	<1	<1	<1	<1	<1
Ca[1]	49	45	65	11	16
Fe	<1	<1	<1	<1	<1
K[1]	>100	>100	>100	>100	>100
Mg	12	2	6	28	36
Na[1]	90	46	68	>100	>100
Si	<1	<1	<1	<1	<1
Cu	98	73	>100	81	57
Mn	<1	<1	<1	1	0
Pb	<1	<1	<1	<1	<1
Zn	40	24	45	79	44

[1] Semi quantitative

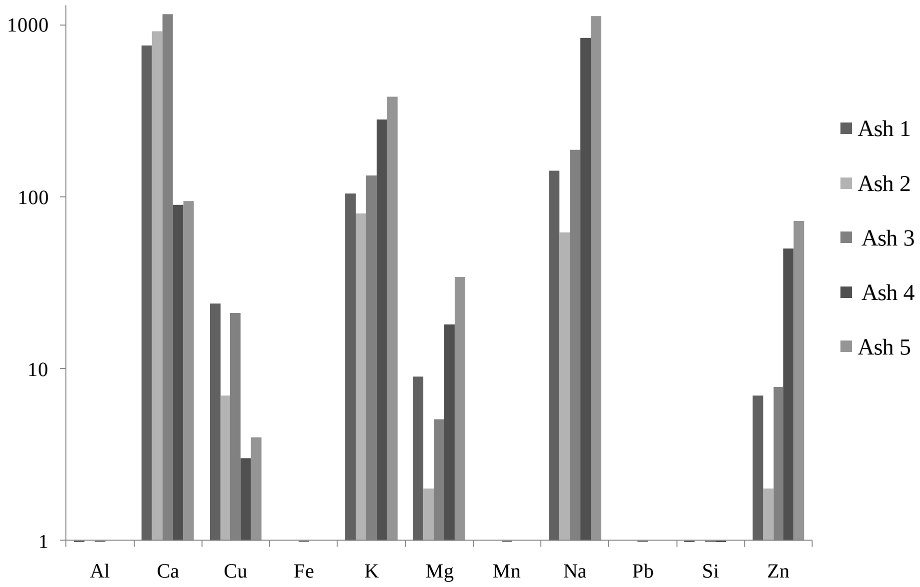


Figure 5.12. Concentrations of major and minor components in leachates from ashes 1-5 after leaching for 24 hours using 3M NH_4NO_3. All amounts are presented as mmol/L. Ca, K and Na are semi quantitative. No bar means that the measured concentration is <1 mmol/L.

An advantage of the more or less selective leaching of Cu when ammonium nitrate is used is the possibility to visually observe the effect of the leaching, as the complex formed has a characteristic blue colour. As seen in Figure 5.13, the samples in the middle and to the right correspond to ashes 1 and 3, which have the highest concentrations of Cu in the leachates (Figure 5.12). The use of ammonium nitrate as the leaching agent gives a possibility to selectively recover Cu from ash.

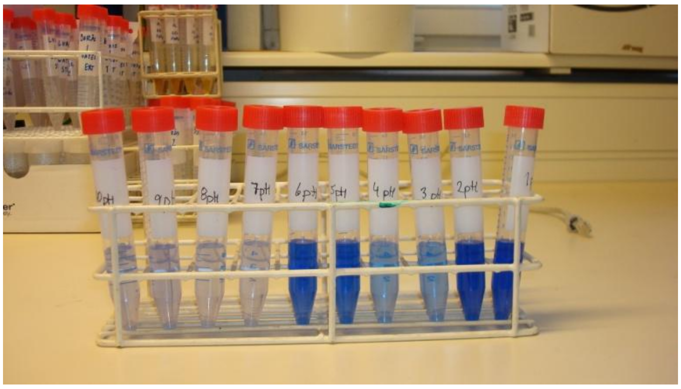


Figure 5.13. Leachates of ashes 1-5 (in duplicate) after leaching with 3M NH_4NO_3 for 24 hours.

Recovery of Cu from ash leachates

Copper can be recovered from ash leachates using solvent extraction to produce a solution from which Cu metal can be produced by electrolysis. In this thesis a method was developed for selectively recovering Cu leached from MSWI fly ash by either NH_4NO_3 or HNO_3. This section primarily discusses the solvent extraction experiments.

Ammonium nitrate leachates

As discussed earlier, the leaching of ash 3 using 3M NH_4NO_3 resulted in a high and rather selective release of Cu. This leachate was therefore used to study the possibilities to selectively extract Cu. Several extraction reagents were tested to find the best extractant for selective and efficient extraction of Cu from ash leachates, i.e. a extractant giving high D- and SF-values. Four chemically different extraction reagents (LIX 54-100, LIX 84, LIX 860N-I and Cyanex 272) were first tested on a solution containing Ca^{2+}, Cu^{2+} and Zn^{2+} in 3M NH_4NO_3. This solution was prepared to simulate the real ash leachate obtained after leaching ash 3 with 3 M NH_4NO_3 (Figure 5.12). The extraction experiments were done at two different initial pH values, 2 and 8. The higher pH value was chosen based on the pH obtained after NH_4NO_3 leaching, whereas the lower was chosen to study extraction at acidic pH. The ratio between volumes of organic phases and water phases was 1 (O/A=1), and single step extractions were used in all experiments. All reagents showed a potential to effectively extract Cu from the solution, but the best results were obtained using LIX 84 and LIX 860N-I at the lower initial pH values (Table 5.9). These extractants are both oximes which, as discussed earlier, are known to be very selective for extraction of Cu at a low pH as well. The other two reagents (LIX 54 and Cyanex 272) are less selective and form weaker complexes with Cu, which can be seen from the D values at the lower pH_{eq} in Table 5.9. Similar results have been published by others [126, 130, 131, 170-172]. Calcium was generally not extracted (Paper IV) but some reagents extracted Zn in certain pH intervals (Table 5.9).

Table 5.9. Extraction of Cu and Zn from a simulated leachate using various extraction reagents with a concentration of 37.5 w/w % in the organic phase. Volume organic phase/volume water phase (O/A) =1 (Paper IV).

	pH of water phase before extraction	pH_{eq}, pH at equilibrium	$D_{o/a}$
Cu			
LIX 54-100	8	4.2	155
LIX 84	8	7.5	247
LIX 860N-I	8	7.6	232
Cyanex 272	8	4.9	84
LIX 54-100	2.2	1.8	2
LIX 84	2.2	1.7	116
LIX 860N-I	2.2	1.8	168
Cyanex 272	3.6	1.4	<1
Zn			
LIX 54-100	8	4.2	14
LIX 84	8	7.5	<1
LIX 860N-I	8	7.6	79
Cyanex 272	8	4.9	132
LIX 54-100	2.2	1.8	<1
LIX 84	2.2	1.7	<1
LIX 860N-I	2.2	1.8	<1
Cyanex 272	3.6	1.4	101

As the oximes (LIX 84 and LIX860N-I) gave the highest D values and selective extraction of Cu compared to Zn at the lower pH, those reagents were tested on the real ash NH_4NO_3 leachates from ash 3. Both reagents gave satisfying extraction results with an initial pH of 2 (Figure 5.14). Aluminium, Ca, Co, Cr, Fe, K, Mn, Mo, Na, Ni, Pb, Sn, Si, V and Zn stayed in the water phases and all were detected in amounts <1mmol/kg in the organic phase. The pH_{eq} was 0.7 in both experiments, and the aldoxime based reagent LIX 860N-I gave a better distribution of Cu compared to the ketoxime based reagent LIX 84 ($D_{LIX860N-I}$=246 compared to D_{LIX84}=14). This was expected, as aldoximes also form stable complexes with Cu at pH<1 while ketoximes are generally most effective at pH>1.6 [116]. The relatively good extraction results obtained with LIX 84, despite the low pH, are probably due to the high concentration of reagent used compared to the amount of Cu present (about 10 times higher).

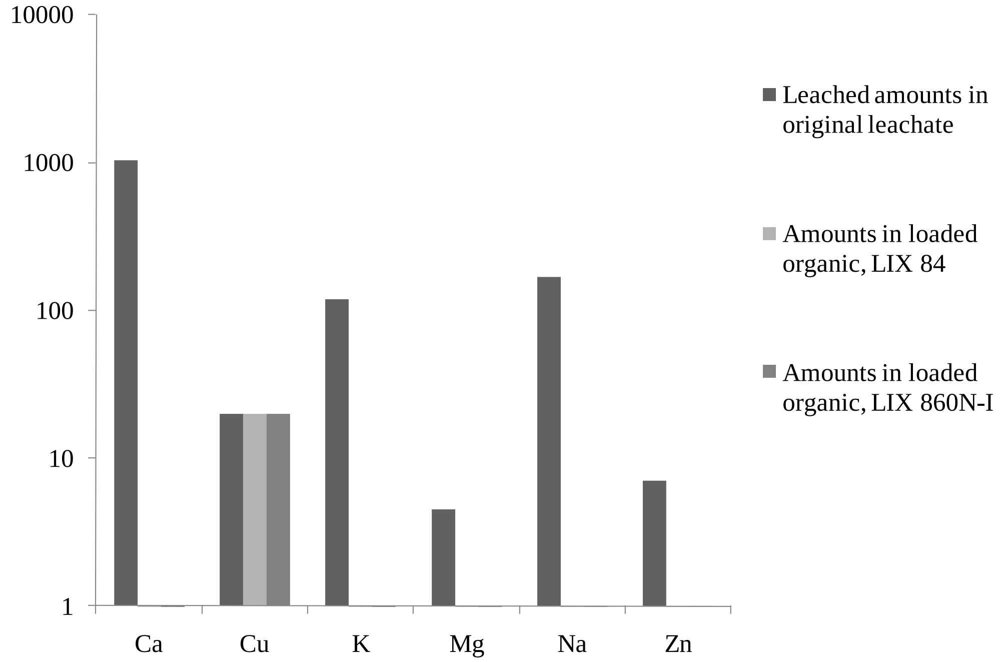


Figure 5.14. Amounts (mmol/kg) of selected elements in the original ammonium nitrate leachate from ash 3 and in the loaded organic phases (LIX 84 and LIX 860N-I, 17 w/w%) after extraction. O/A=1 (Paper IV).

2M H_2SO_4 was used to strip Cu from the LIX 860N-I loaded organic phases. About 90% of the Cu was stripped in a single step. As LIX 860N-I forms such strong complexes with Cu, this fairly concentrated acid was needed in the stripping experiments. However, this is not practical in real processes [116, 119]. This suggests that LIX 84 could be a more convenient extraction reagent, as weaker acid solutions may be used in the final Cu recovery even though the separation, i.e. the D value, using LIX 84 was inferior in the extraction step.

The proposed extraction-stripping method using ammonium nitrate and LIX 860N-I was tested on four other ashes (1, 2, 4 and 5) with satisfying results. Various amounts of Cu and other metals were leached from the ash samples, but the extraction of Cu was selective irrespective of the initial concentrations (Figure 5.15). The stripping also showed satisfying results. More than 87% of the Cu was transferred from the organic phase to the acid in a single stripping step.

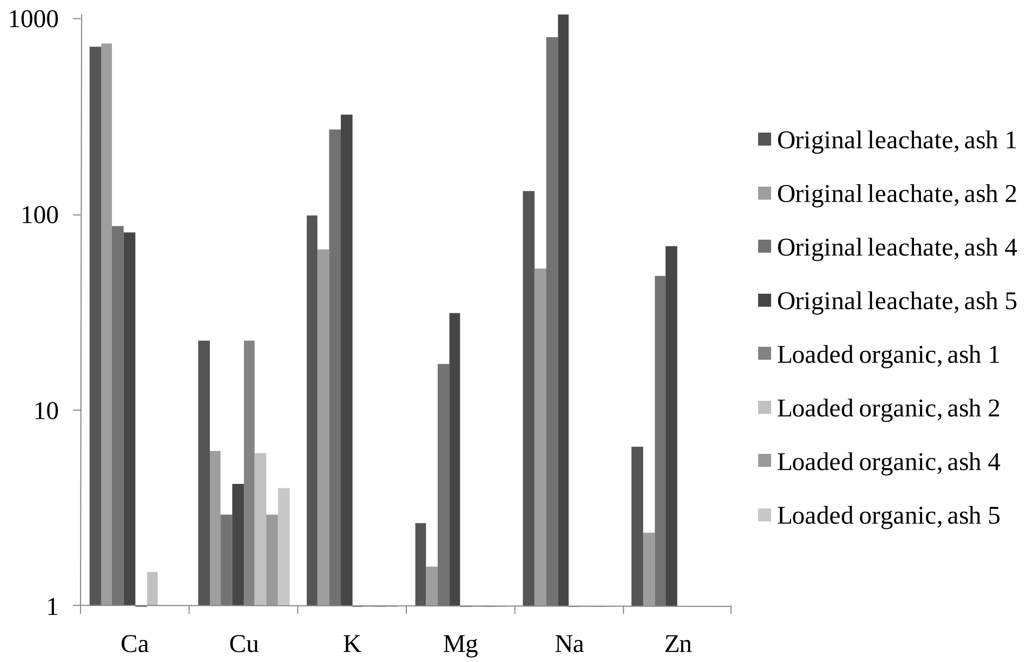


Figure 5.15. Amounts (mmol/kg) of selected elements in original ammonium nitrate leachates (ashes 1, 2, 4, and 5) and in the corresponding organic phases (LIX 860N-I, 17 w/w%) after extraction using O/A=1. The amounts of Ca, K and Na in the original leachates are semi quantitative (Paper IV).

Table 5.10 shows a summary of the copper recovery results obtained in the process based on extraction with 3M NH_4NO_3, extraction using LIX 860N-I, 17 weight% in Solvent 70 and stripping of the organic phase using 2M H_2SO_4. All volume ratios in the process steps were 1. A recovery of the leached amounts of about 90% was obtained but, according to eq. 3, a further number of extraction and stripping steps may lead to even higher recovery. The recovery of Cu compared to the total amounts in the original ashes is lower than 90% and varied between ash samples. This shows that the leaching is the most important step in a recovery process. It should be noted that it can be somewhat difficult to compare the recovery yields with the concentrations of Cu in the original ashes due to analytical uncertainties in determining low concentrations of metals in small sample volumes (generally 0.1-0.5 g of ash) [173].

Table 5.10. Summary of recovered amounts of Cu for ash samples 1-5 leached with 3M NH_4NO_3.

Ash 1	**Ash 2**	**Ash 3**	**Ash 4**	**Ash 5**
Recovered amount of total, %				
78	69	95	72	51
Recovered amount of leached, %				
89	95	95	89	89

Acidic leachates

Leaching using NH_4NO_3 (pH ~9) released significant amounts of Cu from ash but selective extraction of Cu using the reagents tested here was only obtained at acidic pH. This means that the pH of the leachate must be adjusted before extraction, which consumes chemicals. It might therefore be more practical to leach the ash at an acidic pH near the pH used for extraction. In addition, the pH in the leachate is further decreased during extraction due to the hydrogen cycle on which extraction using oximes is based. The term “hydrogen cycle” refers to the release of H^+ from the extractant during extraction and resumption of H^+ during stripping. This is beneficial if the solution is to be recycled and used for further leaching. The results of acidic leaching (end pH 2.5-5) showed that the resulting leachates were more complex compared to the NH_4NO_3 leachates (Figures 5.15 and 5.16). However, selective extraction of Cu was obtained for ashes 1-5 after adjustment of the pH to 2.2 before extraction (Figure 5.16). Some tests were also done without pH adjustment before extraction. These results showed that similar amounts of Cu were extracted, which indicates that pH adjustment to such a low pH as 2 before extraction may not be critical for the recovery efficiency (Paper IV: Tables 7 and 8).

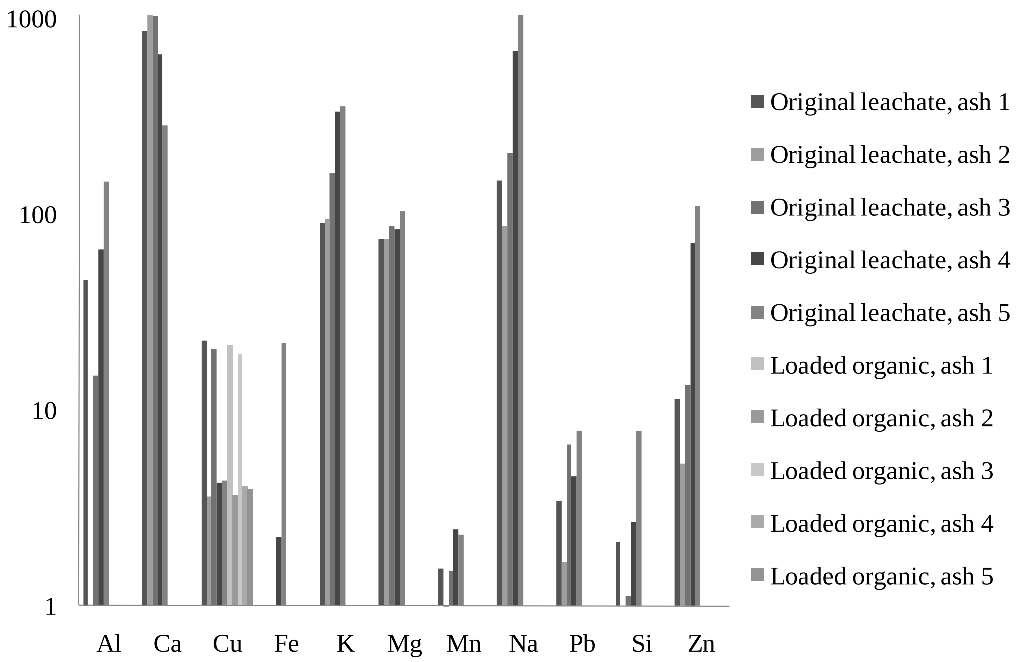


Figure 5.16. Amounts (mmol/kg) of selected elements in original leachates (ashes 1-5) using HNO3 and in the corresponding organic phases after extraction at an initial pH of 2.2. The amounts of Ca, Ka and Na are semi quantitative (Paper IV).

The stripping results were similar to the results of the NH_4NO_3 experiments, and the amounts of Cu recovered from the acidic leachates are given in Table 5.12. These amounts are comparable to the amounts recovered from the ammonium nitrate leachates (Tables 5.10 and 5.11). The amounts of Cu recovered compared to the total amounts of Cu in the ash samples are generally lower, as was also found in the ammonium nitrate experiments (Tables 5.10 and 5.11). This again points to the importance of the leaching process in obtaining an effective recovery of Cu from ash.

Table 5.11. Summary of amounts of Cu recovered in ash samples 1-5 after acid leaching and pH adjusted to 2.2±0.1 before extraction (Paper IV).

Ash 1	Ash 2	Ash 3	Ash 4	Ash 5
Recovered amount of total, %				
89	40	112	105	52
Recovered amount of leached, %				
93	96	91	91	90

In summary, the proposed leaching-extraction procedure is given as a flow sheet in Figure 5.17. It is important to note that the amounts of Cu in the leachate will vary with the ash sample and leaching media used, which will of course influence the amount of metal ions in the pregnant electrolyte.

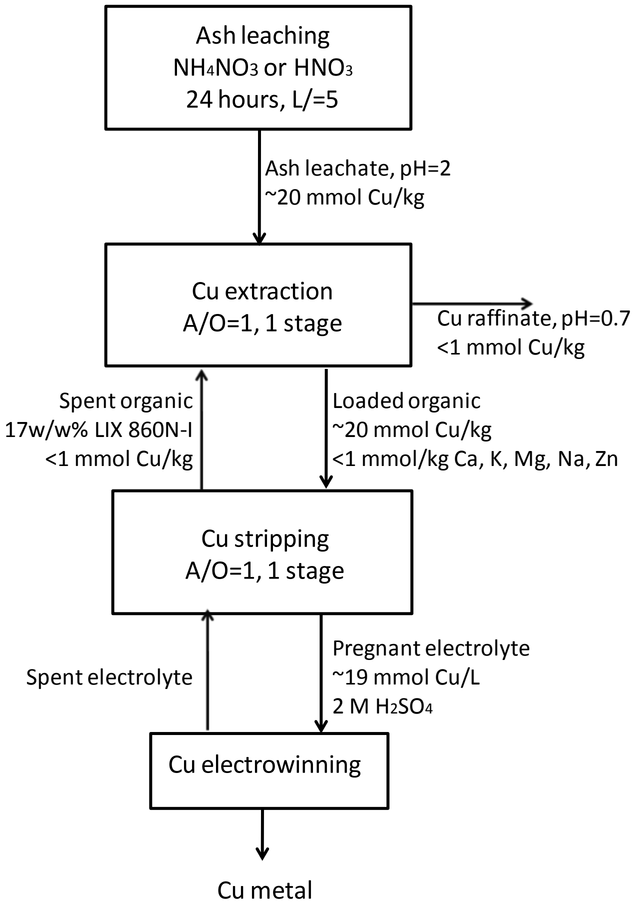


Figure 5.17. Flow sheet of the recovery method developed for Cu from ash.

A comparison of the costs for NH_4NO_3 and HNO_3 indicates that the acid is more than twice as expensive as the ammonium nitrate assuming that the “puriss” quality of the chemicals is used, 3M NH_4NO_3 or 2.5M HNO_3 and L/S=5. The leaching solution is to be recycled, however, as is done at commercial process plants for Cu recovery. Recycling of the leaching agents used in these tests has not been studied thoroughly, but initial tests show that Cu is also leached from ash with a reused NH_4NO_3 solution. The amount of Cu in the leachate was not measured, but the presence of Cu was visually identified through the characteristic blue colour of the ammine complex.

It is not possible this far to say which of the leaching agents is the better choice. However, in the longer perspective, acidic leaching may be the better choice as there is less need for pH adjustments of the leachates before extraction, which saves both time and chemicals. In addition, acidic solutions resulting from wet cleaning of flue gases might be used as a complement to stronger acid solutions in the leaching process. Such acidic water phases are also waste products that need to be neutralised before being disposed of. A utilisation option for such liquids would therefore save money. A disadvantage of acidic leaching is that a large part of the ash material is dissolved (about 60% of the weight or more) as the original ash structure is highly affected. In addition, the Cu free raffinate contains more metal ions compared to that produced in ammonium nitrate leaching, and these metal species must be taken care of in a safe way. On the other hand, the Cu free raffinate can be a source of further extraction of other metals such as Al, Mg or Zn.

Due to the high content of alkaline compounds in ash, large amounts of acid are needed to reach a sufficient low pH. Pre-washing of ash using water or slightly acidic water would decrease the amounts of acid needed for leaching by removing alkaline components. However, it was shown in the present work that pre-washing with water (L/S=50, 24 hours of leaching time) could lead to a lower release of Cu and other metals in the leaching step (Paper III: Table 5). As an example, the release of Cu using 3M NH_4NO_3 as the leaching agent decreased from a more or less complete leaching from the original ash to a release of 70% of the Cu when the ash was pre-washed with water. This is probably due to changes in the ash structure.

Changes in ash matrix during leaching and ash stability

During water leaching of the cyclone ashes (A-C), the amounts of Al metal, NaCl and $CaSO_4$ decreased, while the other major crystalline components remained almost unaffected by leaching (Paper I: Table 2). Leaching of metallic Al is suggested to be due to hydrolysis to $Al(OH)_3$ at high pH [74]. The release of NaCl is expected as it is highly soluble in water, whereas the solubility of $CaSO_4$ is much lower (0.2g/100g water) [164, 174]. However, $CaSO_4$ has been shown to react with aluminium oxides to form ettringite ($(CaO)_3(Al_2O_3)(CaSO_4)_3 \cdot 32H_2O$), amorphous or crystalline, at alkaline pH in cements [175]. This may be a reason for the results of this study, but ettringite was not identified in the leached ash samples. In addition, the formation of $CaSO_4 \cdot XH_2O$ cannot be totally ruled out.

Filter ash (ash 3) showed a similar behaviour when leached in water: release of water soluble salts such as NaCl and KCl as well as some of the Ca compounds such as CaClOH (Paper III: Table 3). When stronger leaching agents (NH_4NO_3 or HNO_3) were used, the crystalline structure was affected more and especially the release or transformation of most calcium-containing compounds should be noted (Table 5.12 and Figure 5.18). When ash 3 was leached with HNO_3 at pH<0, even more of the Ca containing compounds were released and oxides and silicates were instead identified. Thus large parts of the ash matrix are dissolved in acid leaching, which is not favourable if the ash is to be utilised. If the target pH in extraction is higher than 2, it seems to be the better choice to carry out the leaching at that pH, as the release of $CaSO_4 \cdot XH_2O$ will be lower.

Table 5.12. Crystalline compounds identified in ash samples 1-5 after leaching for 24 hours at L/S=5 a) NH_4NO_3 leaching, b) HNO_3 leaching (end pH 2) and c) HNO_3 leaching (end pH<0) (Papers III and V).

Mineral	**Ash 1**		**Ash 2**		**Ash 3**			**Ash 4**		**Ash 5**	
	a	b	a	b*	a	b	c	a	b	a	b
$CaCO_3$	Minor	Minor	Major		Major	Minor		Major	Trace	Minor	Minor
$CaSO_4$	Major	Minor	Minor					Minor		Major	
$CaSO_4 \cdot XH_2O$	Minor	Major	Trace		Minor	Major	Trace	Trace	Major	Minor	Major
$Ca_3Al_2O_6$	Minor	Minor	Minor		Minor	Minor	Major	Trace	Minor	Trace	Minor
SiO_2	Trace	Trace	Minor		Trace	Trace	Major	Trace	Minor	Trace	Minor
(Ca, Al, K) silicates							Major				

*Not analysed

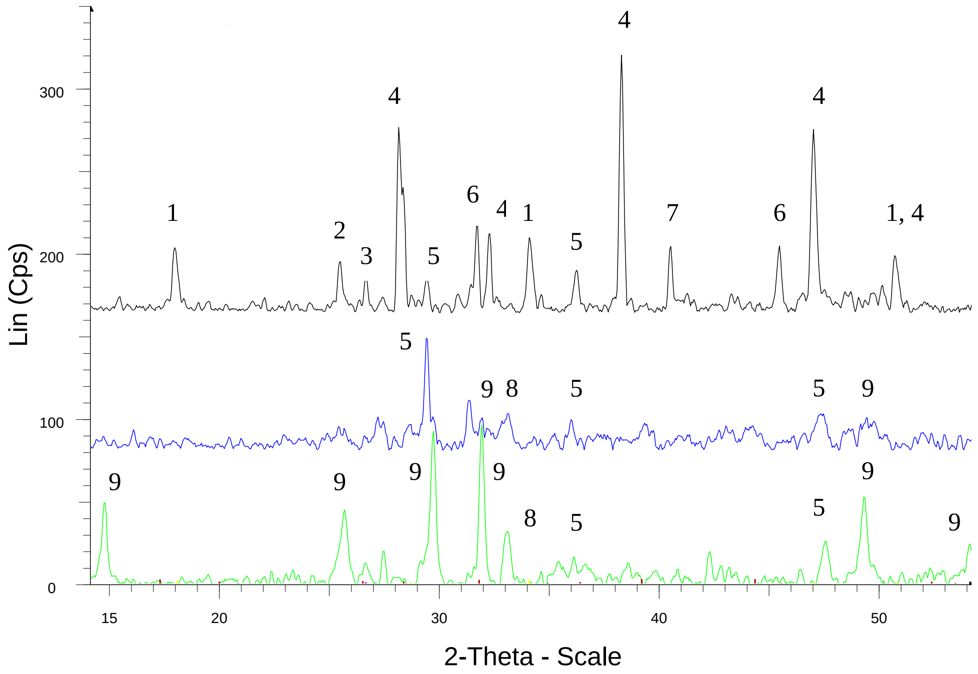


Figure 5.18. XRD patterns for original (black), NH_4NO_3 leached (blue) and HNO_3 leached (green) ash 3. The diffractrograms for the original and NH_4NO_3 leached ashes are offset along the Y-axis. 1) $Ca(OH)_2$, 2) $CaSO_4$, 3) SiO_2, 4) CaClOH, 5) $CaCO_3$, 6) NaCl, 7) KCl, 8) $Ca_3Al_2O_6$ and 9) $CaSO_4 \cdot XH_2O$.

Changes in particle sizes can influence and explain variations in the leaching step. The particle size distributions in some of the acid leached filter ashes (3 and 5) (initial pH 2) were measured and are shown in Figures 5.19 and 5.20 (Paper V). In ash 3, the average particle size was moved towards larger particles (70% between 40 and 600µm; maximum around 250 µm) (Figure 5.19). This distribution remained the same during ultra sonic treatment, indicating that those particles are rather stable. Acid leached ash 5 showed two main peaks with maxima at 35 µm and 200 µm (Figure 5.20). During ultra sonic treatment, the smaller particles remained rather unaffected while the maximum of the other peak was moved towards even larger particle sizes (maximum around 400 µm). This indicates that the larger particles agglomerate during leaching, while the smaller particles are more stable.

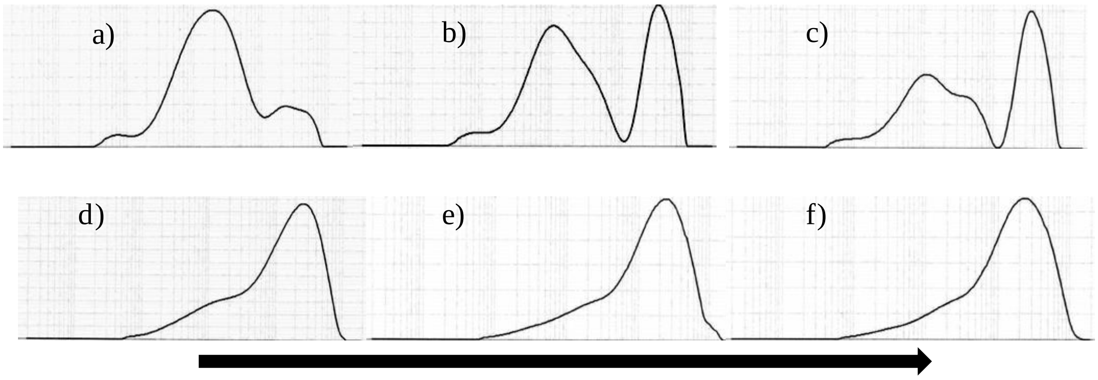


Figure 5.19. Particle size distribution (1-1000µm) for original and acid leached (HNO3, L/S=5, 24 hours, end pH 2) ash 3 printed in logarithmic scale. The maximum at the Y scale corresponds to about 5 volume% of the total ash amount used in each experiment. a) original, b) and c) original treated with US, 12kHz and 24kHz, d) acid leached ash, e) and f) acid leached ash with US, 12kHz and 24kHz

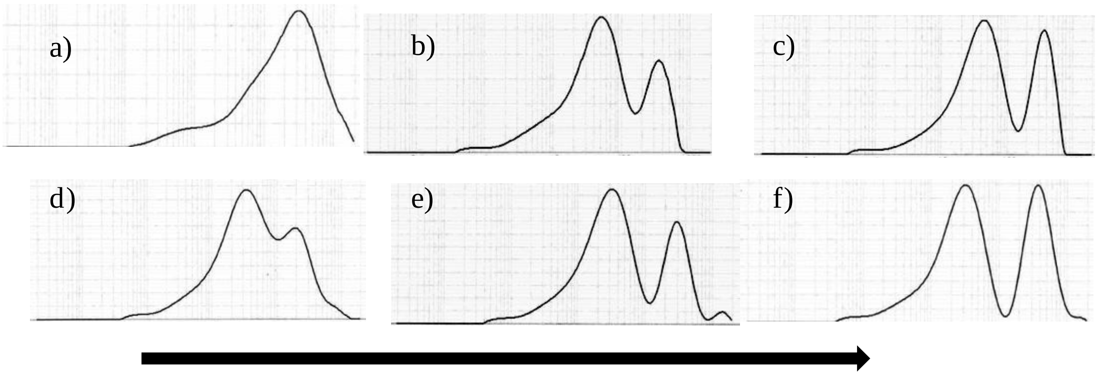


Figure 5.20. Particle size distribution (1-1000µm) for original and acid leached (HNO3, L/S=5, 24 hours, end pH 2) ash 5 printed in logarithmic scale. The maximum at the Y scale corresponds to about 5 volume% of the total ash amount used in each experiment. a) original, b) and c) original treated with US, 12kHz and 24kHz, d) acid leached ash, e) and f) acid leached ash with US, 12kHz and 24kHz

The higher amount of larger particles in the cyclone ashes compared to the filter ashes was reflected in the specific surface area measurements (Table 5.13). Leaching increased the specific surface area, and the extent of this depended on the properties of leaching media used, i.e. how effectively it could release Ca and other ash matrix elements. Similar results are reported in the literature [70]. The authors made approximate calculations comparing the relative inner surface area and the outer surface area. Before washing with water, the inner surface area was about 10 times larger than the external surface [70]. After washing, the ratio between inner and outer surface areas had increased to 70. The contact with water clearly resulted in a significant increase in porosity, probably by dissolving certain ash components and disintegrating particle aggregates.

Table 5.13. Specific surface areas of original and leached cyclone and filter ashes. The specific surface area is given in m^2/g. Cyclone ash B was leached 10 minutes, L/S=10 and filter ashes 3 and 5 were leached 24 hours, L/S=50 in water and L/S=5 in acid and NH_4NO_3 (Papers I, III and V).

Ash	Original	Water Leaching	End pH	Acidic leaching	End pH	NH_4NO_3 leaching	End pH	
A	1.2	-	-	-	-	-	-	
B	0.4	2.0	9	-	-	-	-	
C	0.8	-	-	-	-	-	-	
3	5.1	10.7	12	110 (HNO3); 20.4 (HCl)	2 (HNO3); <0 (HCl)	21.7	8	
5	3.1	-	-	26.2	2	14.2	8	
Fly ash	2.8-36.9*	-	-	-	-	-	-	[176]
Fly ash	2.2; 5.6	-	-	-	-	-	-	[81]
Cyclone ash	0.7	3.7	-	-	-	-	-	[70]

-not measured
* literature review

During leaching, the specific surface area is also affected by a formation of secondary products, crystalline or amorphous, on the particle surfaces. This effect was observed for both kind of ashes (Figures 5.21 and 5.22). The qualitative energy dispersive X-ray (EDX) analysis results obtained for the acid leached ash residues from ash 3 (Figure 5.22 d) and ash 5 suggest that these products are mainly $CaSO_4 \cdot XH_2O$, and similar results have also been suggested by others [83]. However, when using a strong acid leaching solution resulting in pH<0, the ash residue showed clean and clearly etched particle surfaces (Figure 5.22 e). This is consistent with the XRD results in Table 5.13 that show lower amounts of calcium-containing compounds after the ash matrix was attacked by the strong acid solution. The acid created pores and increased the surface area. A larger specific surface area could affect leaching of metals in two ways: first, it can increase the amounts of soluble species released since more of the ash matrix is accessed by the leaching medium. Second, it can increase adsorption of the dissolved metal ions because more mineral surfaces are available.

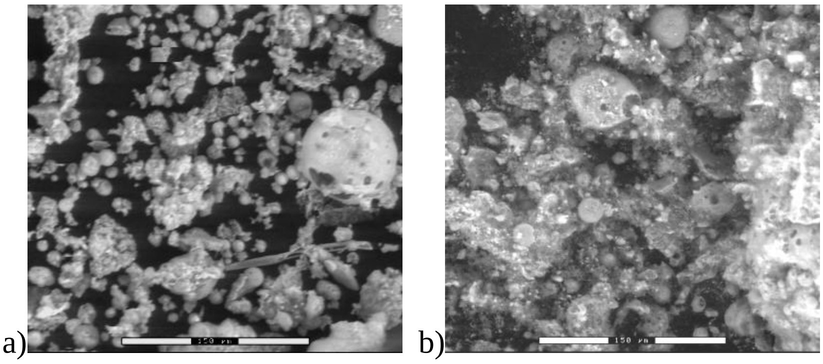


Figure 5.21. SEM images (secondary electrons) of cyclone ash B. Magnification 300 times. The bar corresponds to 100µm. a) original ash b) ground ash leached for 360 minutes in ultra pure water, L/S=10.

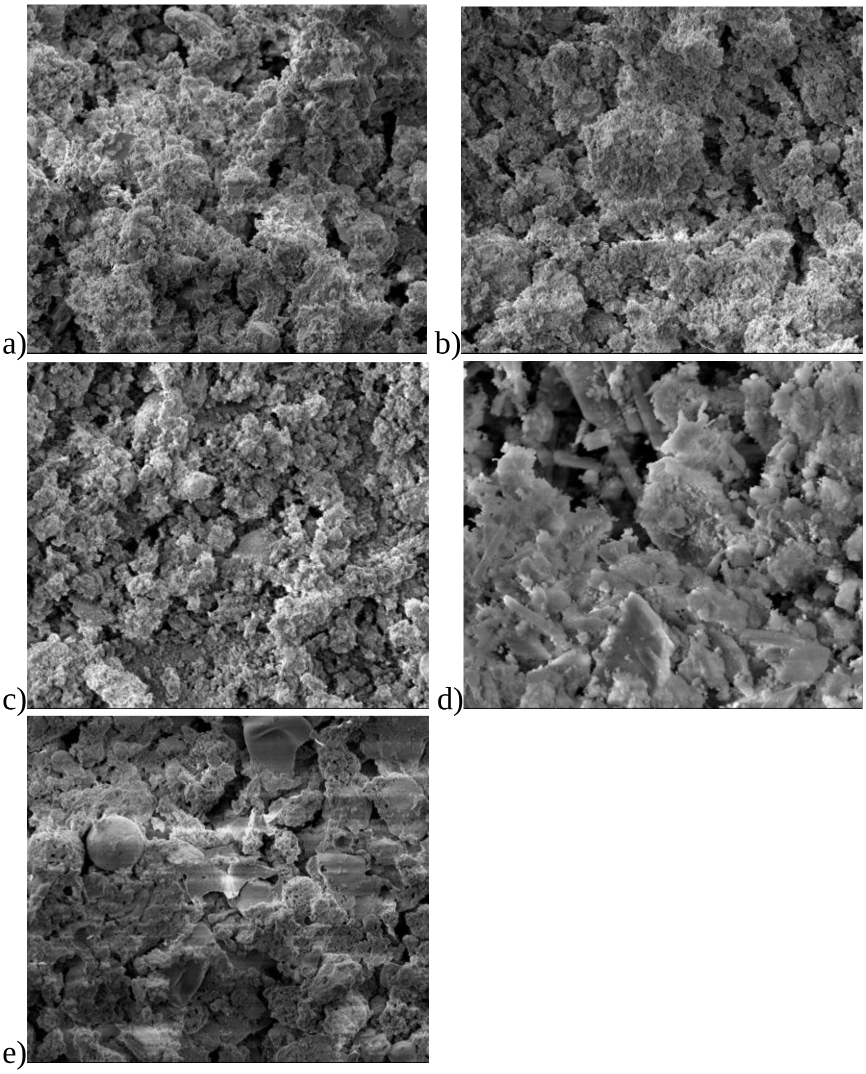


Figure 5.22. SEM images (secondary electrons) of original and leached (24 hours, L/S=5) filter ash 3. Magnification 5000 times. a) original ash a) b) ultra pure water c) 3M NH_4NO_3 d) HNO_3 (end pH 2) and e) 3M HCl (end pH<0)

Land fill leaching test for evaluation of ash stability

Various leaching tests are used to determine what kind of land fill in which an ash should be deposited in or whether it fulfils the demands for utilisation [9, 177]. The two step test using water as the leaching agent is described in the EN 12457 standard that is linked to the landfill directive [9, 178, 179]. The sample is first leached for 6 hours at L/S 2 followed by leaching for 18 hours at L/S 8. The results are given as amounts released at L/S=2 and as the accumulated release at L/S=10. When this test was used on three original filter ashes (2, 3 and 5) it was found that none of the ash samples gave results below the limit values for admittance to landfills that treat hazardous waste for all elements (Figures 5.23 and 5.24). The leaching of Cl^-, Pb and Zn generally exceeded the limits most, whereas Ni and Se were leached in amounts below 1mg/kg dry ash in all ash samples.

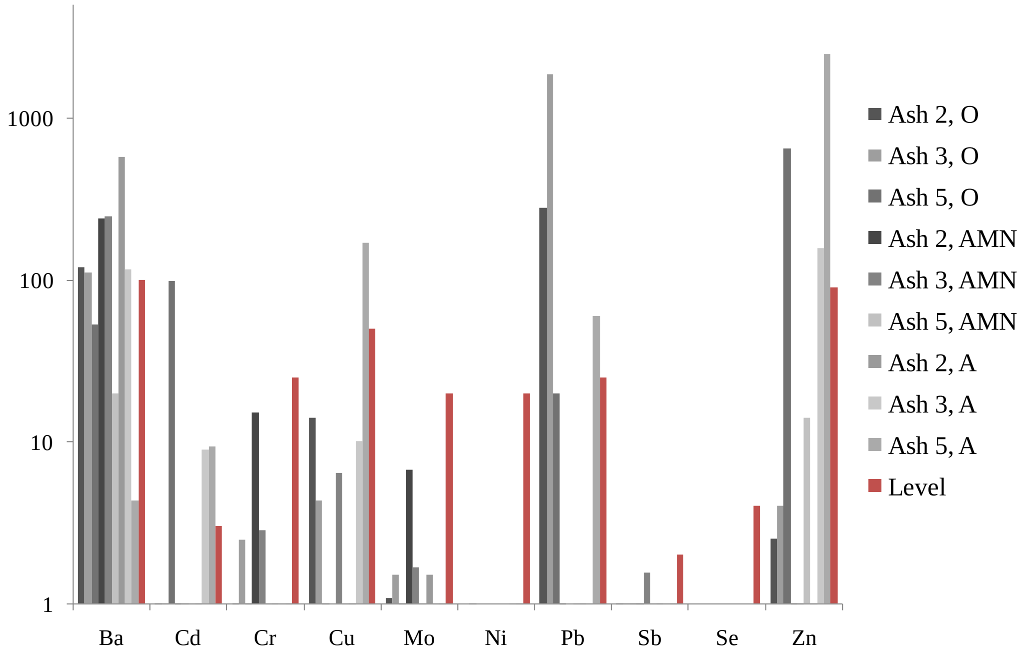


Figure 5.23. Leaching from ashes 2, 3 and 5 using the EN 12457 test, L/S=2 in original ash, ash pre-leached with NH_4NO_3 and ash pre-leached with HNO_3. The level refers to the allowed maximum amounts for a hazardous waste landfill. All amounts are present as mg/kg dry ash and no bar corresponds to an amount below 1 mg/kg dry ash. O=original ash, AMN= NH_4NO_3, A=HNO_3.

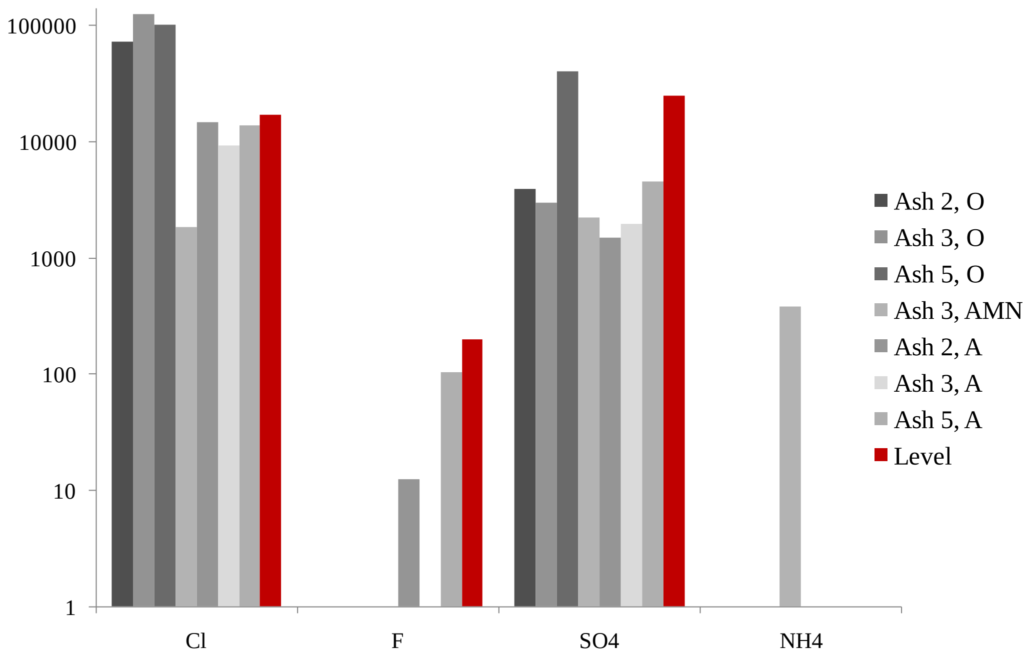


Figure 5.24. Leaching on an-ions (Cl^-, F^-, SO_4^{2-}) and $NH_4^+{}_{tot}$ from ashes 2, 3 and 5 using the EN 12457 test, L/S=2 on original ash, ash pre-leached with NH_4NO_3 and ash pre-leached with HNO_3. The level refers to the allowed maximum amounts for a hazardous waste landfill. All amounts are present as mg/kg dry ash and no bar corresponds to an amount below 1 mg/kg dry ash. $NH_4^+{}_{tot}$ was measured only in the leachates from ash 3 pre-leached with NH_4NO_3. There is no level for NH_4^+ in the leaching test. O=original ash, AMN= NH_4NO_3, A=HNO_3.

When the same ashes were pre-leached with NH_4NO_3 or HNO_3 for 24 hours, it was seen that the leaching in the two-step batch test generally decreased, especially from the ashes treated with NH_4NO_3. These ashes gave results below the leaching limit for all metals studied except Ba, where the pre-treatment in some cases increased the leachability (Figure 5.23). On the other hand, pre-treatment of the ashes using acid leads to a decreased leaching of some metals, such as Cd and Pb, while increased leaching was in some cases found for Ba, Cu and Zn. Similar trends were also found for the accumulated L/S=10 leaching, where none of the ashes totally fulfilled the leaching restrictions for a landfill for hazardous waste. It should be noted that the leaching of Cl^- from ash 3 pre-leached with NH_4NO_3 exceeded the limit for L/S=10, even though it fulfilled the limit at L/S=2, whereas the acid-leached ashes fulfilled the limits at both L/S ratios for all anions. The ashes were washed with a small amount of water after pre-leaching (L/S=0.4) to leach out species adsorbed to the surfaces during centrifugation and filtration. If this procedure had been repeated several times before the EN 12457 leaching test, it is possible that the release of Cl^- and other ions would fall below the limit.

These results indicate that some pre-treatment of the ashes is needed to make the ash comply with the limit values for landfilling, especially for the metals. Where leaching at high pH (NH_4NO_3) seems to generally decrease leaching of metal compounds, acidic pre-treatment in some cases increases leaching. This is probably due to a more general etching and destruction of the ash matrix in the acidic leaching. Thus, more metal compounds can be accessed by the water in the EN 12457 leaching test.

6. Conclusions

- MSWI fly ashes are heterogeneous materials, and the ash matrix plays an important role in how the ash will behave in various environments.

- The results obtained in the present work verified that minor and trace metal compounds are generally enriched on small particles in the fly ash. The results further suggest that minor elements such as As, Cd, Cu and Ni bind to available particles with a higher affinity for calcium and/or iron containing compounds in the ash matrix and that species of Cr, Pb, Ti and Zn mainly adsorb onto fly ash particle surfaces through a random process.

- The major compounds of Cu and Zn are not similar in the fly ash samples investigated. This was also reflected in the relative release of those metals from the ashes in different leaching media. The most probable speciation for Cu in the BFB fly ash (ash 3) is CuO and/or $Cu(OH)_2$, $CuSO_4{\cdot}H_2O$ and metallic Cu. Zn is present in this ash in oxidic minerals such as silicate and/or hydroxide in addition to chloride. The fly ash from MB combustion of MSW (ash 5) gave results that indicate that Cu occurs as $CuSiO_3{\cdot}H_2O$ and/or CuO in addition to metallic Cu. The same ash contained Zn bound in oxidic forms such as ZnO, $Zn(OH)_2$ and Zn-silicate, in addition to chloride. The absence of Zn-Zn distances in the data for ash 5 indicates that Zn replaced other ions in a variety of compounds.

- Leaching of metals involves a competition between several phenomena such as adsorption, precipitation, the presence of available anions and formation of soluble complexes. The amounts released depend on the unique parameters used in each leaching situation. In this work, this was observed as a significant dependence of leachate composition on pH, leaching time, L/S ratio, size reduction of the ash by grinding and dissolution of major ash compounds. The release of major ash compounds affects the porosity of ash as well as the formation of secondary compounds and agglomeration of ash particles, which involves the formation of new surfaces and induces co-precipitation of metal ions.

- The results obtained in this work verified that the release of metal compounds from MSWI fly ash using water as the leaching agent is generally low. Enhanced leaching of metal compounds can be achieved using strong mineral acids in high concentrations or using complex forming ligands such as EDTA. However, those leaching methods are usually non-specific and result in the release of many metals. If a selective leaching is needed, a leaching agent forming stable complexes only with certain elements must be used, such as NH_4NO_3, which forms soluble complexes with Cu^{2+}.

- Selective recovery of Cu^{2+} from MSWI filter ash after leaching using NH_4NO_3 or acid followed by extraction using solvent extraction reagents based on oximes, can be done. The best result was achieved using the LIX 860N-I reagent. The O/A ratio was equal to 1, and single steps were used in all experiments. About 90% of the Cu ions in the leachates could be selectively recovered. The leaching of the ash was identified as the limiting step, determining the yield of Cu. More work remains to optimize the proposed process for recovery of Cu from MSWI fly ash. Several parameters, such as the concentration of reagents and the O/A ratios, affect the overall result, and the influence of those parameters will be investigated in greater detail. However, the purpose of the present study was to investigate the possibilities for selective recovery of Cu from various MSWI fly ash leachates, and the results are very promising.

The focus of this work was extraction of Cu from filter ashes, but the amounts of Cu are comparable in cyclone and bottom ash. It was found in the sequential extraction experiments that Cu was harder bound in cyclone ash than in filter ash. However, the first four steps in the sequential extraction procedure used here do not include leaching at low pH [89]. This indicates that leaching using strong solutions of mineral acids resulting in low pH may also be used to leach part of the Cu from those fractions. In bottom ashes, an oxidic mineral such as CuO has been suggested to be the major compound, which indicates that significant leaching of Cu from MSWI bottom ashes is probably possible [180]. Approximate calculations assuming 1500 mg Cu/kg ash, of which 50% is released and recovered, and with an annual amount of ash of 900 000 tonnes, show that more than 500 tonnes of metallic Cu may be recovered annually from ash from waste incineration, in Sweden only. The corresponding annual amount of Cu in EU-27 would be nearly 20 000 tonnes. If the recovery efficiency could be increased to 80%, the corresponding figures would be 1000 tonnes and 30 000 tonnes of Cu recovered annually in Sweden and EU-27, respectively. The latter figure corresponds to about 0.5% of the annual amount of Cu used in Europe [181].

7. Continuation of the work

More work remains to optimise the proposed process for recovery of Cu from MSWI fly ash. The influence of several parameters, such as the leaching agent used and the concentration of reagents must be investigated in greater detail. In addition, the use of the weaker reagent LIX 84 instead of the strong LIX 860N-I should be explored, as the disadvantage of slightly less effective extraction may be compensated for by the need of less acid in the stripping step. When scaling up the process from the laboratory scale to the pilot plant scale it is also important to study the recycling of chemicals and the need for washing steps. Initial studies on recycling the ammonium nitrate solution and the extraction reagent when extracting Cu indicate that both kinds of reagents can be recycled at least two or three times. Precipitation in the raffinate and crud formation in the loaded and stripped organic phases were observed, indicating that washing steps are needed. Electrolysis of the loaded stripping solutions to achieve pure Cu metal is beyond the scope of this thesis and has therefore not yet been done. Thus, that part of a recovery scheme also needs to be optimised. As discussed earlier, recovery of Cu using solvent extraction coupled with electro winning is common practice in the mining industry and, even though ash leachates are quite different from leachates produced from normal Cu ores, much of this knowledge could be used when scaling up the process.

The leaching can be further optimised; for instance, a decreased L/S ratio would save chemicals and costs. Investigation of specific leaching agents is interesting, as this opens possibilities for the recovery of such metals as Pb or Zn for which less selective extraction reagents are available. However, initial experiments on extraction of Zn from Cu-free ash NH_4NO_3 raffinates using Cyanex 923 (a mixture of octyl and hexyl phosphine oxides) show that 90% of the Zn in the water phase was transferred to the organic phase using O/A=1 and single step extraction. Except for some extraction of Ca (1% of the amount in the Cu-free ash leachate), Zn was selectively extracted. More work has to be done on these issues in order to understand and develop the process in greater detail.

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It has been many years since I started my chemistry studies here in Gothenburg. I never believed that I would become a PhD student and graduate as a doctor of philosophy. Nevertheless, I did, and these years have been very interesting and sufficiently valuable but sometimes also difficult and challenging. I have learned a great deal, not only about chemistry but also about myself and it feels fantastic to finally be able to summarise my work in this thesis. However, this would not have been possible without the help and support of many people.

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♡

Karin Karlfeldt Fedje

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