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Recovery of copper and zinc in ashes from municipal solid waste combustion

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Abstract

The amount of municipal solid waste incineration (MSWI) fly ash has increased in many parts of the world in recent years. Ashes from municipal solid waste incineration (MSWI) may be a cumbersome waste to handle since they contain significant amounts of leachable hazardous metal species and must be landfilled in special sites at high costs. Recovery of e.g. copper, zinc and lead from MSWI ashes may not only recover valuable metals that would otherwise be land filled, but also reduce the toxicity of the ash and thereby make it possible to use a less expensive landfill option or perhaps even to utilize the ash residue as a construction material.

The work presented here discusses the development and evaluation of a metal recycling process for MSWI fly ash based on acid leaching and solvent extraction. Fly ash and bottom ash from an MSWI facility was used for studying and optimization of metal leaching using different solutions (nitric acid, hydrochloric acid and sulfuric acid) and parameters (temperature, controlled pH value, leaching time, and liquid/solid ratio). It was shown that hydrochloric acid is relatively efficient in solubilizing copper (75.3 ± 3.0%), zinc (80.8 ± 5.3%) from the fly ash in less than 24 hours at 20°C. Efficient leaching of cadmium and lead (over 92% and 90% respectively) was also achieved.

After leaching, a selective solvent extraction to recover Cu using an oxime (LIX860-I) followed by a Zn extraction with phosphine oxides (Cyanex 923) were carried out sequentially. Both extraction reagents gave good yields and stripping of Cu and Zn is also possible in a single step using sulfuric acid or nitric acid respectively. The extraction of Cu was selective but a significant amount of other metals, such as Fe, were co-extracted together with Zn. It was shown that it is possible to decrease the contamination of Fe by adjusting the extraction parameters (e.g. adjusting the concentration of nitric acid solution for stripping) or by cleaning the final solution by cementation. A metal recycling process for MSWI fly ash is suggested based on the results from this study.

Keyword: Recycling, MSWI waste, acidic leaching, copper, zinc, solvent extraction, Cyanex 923, LIX860-I, waste treatment.

List of publications

This thesis is based on the work contained in the following papers:

Paper I

Jinfeng Tang, Britt-Marie Steenari, *Leaching optimization of Municipal Solid Waste Incineration Ash for the resource recovery: A case study on Cu(II), Zn(II) and Pb(II).*

Contribution: main author, most experimental work, analysis of data.

Paper II

Jinfeng Tang, Henric Lassesson, Britt-Marie Steenari, *Resource recovery from municipal solid waste ash,* Paper for the 29th International Conference on Solid Waste Technology and Management, Philadelphia, PA U.S.A. 30th March-2nd April, 2014

Contribution: main author, part of experimental work, part of analysis of data.

Paper III

Jinfeng Tang, Britt-Marie Steenari, *Selective extractions of Copper and Zinc from MSWI fly ash using LIX860N-I and Cyanex 923 – An evaluation of a metal recovery process.*

Contribution: main author, all experimental work, analysis of data.

Table of Contents

1. Introduction

The increasing amount of municipal waste generated by an increasing consumption of goods has inspired development of methods to combust the waste. This is now a widely utilized waste management method (Narayana 2009). Incineration of municipal solid waste (MSWI) gives the possibility to recover energy and reduce the waste mass by 70% as well as the waste volume by 90% (Wang, Jin et al. 2010).

Generally, municipal solid waste incineration (MSWI) produces two main types of combustion ash: bottom ashes (BA) and fly ashes (FA). Bottom ash is the major ash collected at the bottom of the combustion chambers; it contains silicates as glassy slag, metal objects, and mineral with high melting points etc. Fly ash consists of the small particles collected in the flue gas cleaning system (Sloot, International Ash Working et al. 1997).

Theoretically three parts of an ash could be used: the bulk material can be used as construction material; valuable trace metals could be recycled; potassium, calcium and phosphorous could be valorized as nutrients in soil improvement.

Both bottom ash and fly ash, especially the fly ash, contains a considerable amount of metals, salts, organic pollutants and other components, some of which are toxic which makes it necessary to investigate any suggested utilization carefully (Hjelmar 1996; Reijnders 2005; Alorro, Hiroyoshi et al. 2009). Various technologies have been investigated to utilize MSWI ashes in different countries (Lam, Ip et al. 2010), Leaching processes, followed by thermal treatments or stabilization/solidification are the common methods currently used (Mangialardi 2003). Most of the treatment methods developed aim at the use of the stabilized ash as a construction material. However, most MSWI fly ashes must be landfilled in specialized sites at high costs in order not to cause environmental pollution. The landfilling of the ashes also results in a loss of valuable metals. Therefore, the possibility of recycling the valuable metals from ashes to the material cycles as a secondary resource (Okada, Tojo et al. 2007) and removal of hazardous metals to reduce the maintenance cost for landfilling sites is an interesting option. Although many efforts have been done to process the residual waste significant quantities of metals remain in especially the fly ashes. Only one process for recovery of zinc from MSWI fly ash using acid leaching followed by solvent extraction separation and electro winning has been developed to close to commercialization (Schlumberger et al, 2007).

Objective

The aim of the work presented in this thesis is to develop sustainable processes for removal and recovery of valuable or toxic metals from municipal solid waste incineration ash. The recovery of e.g. copper and zinc and removal of other toxic metals from MSWI ashes will not only recover valuable metals that would otherwise be land filled, but also reduce the toxicity of the ash and thereby make it less cumbersome to handle. The research is primarily based on the hydrometallurgical methods: acid leaching of the ash combined with selective extraction. Firstly, the metals contained in the ashes need to be dissolved and, secondly, these metals can be separated from the other dissolved metals and recovered from solution using solvent extraction. Optimization of a leaching process for two representative MSWI fly ashes and evaluation of suitable selective extraction systems have been investigated in this project.

2. Background

2.1. Leaching

The leaching of metals from ash is strongly influenced by the type of solvent, the pH and liquid to solid ratio used as well as by the chemical compounds present in the ash. In addition, the porosity and surface morphology of the ash particles influences the transport processes that are important parts of the leaching process (Abbas, thesis).

Results obtained by using many different leaching agents for MSWI ashes have been reported in literature; one example is hydrochloric acid that has been found to be feasible to recover Cr, Cu, Pb and Zn from MSWI fly ash (Hong, Tokunaga et al. 2000). In the work by Karlfeldt Fedje and co-workers(Karlfeldt Fedje, Ekberg et al. 2010) it was observed that weak organic acids were not as effective as mineral acids as leaching agents even though they form soluble complexes with metal ions. Other complex forming chemicals for selective leaching of specific metals were also studied and the results showed that EDTA was effective for removal of Cu and Zn and that NH_4NO_3 was an interesting alternative for selective Cu leaching. The results of Fedje and co-workers illustrate the significance of the properties of the ashes since ashes from different combustion units gave significantly different copper leaching results both when using HCl and when using NH_4NO_3 as leachate. It has recently been shown that different copper speciation is an important reason for these differences (Lassesson et al, 2014).

The development of a leaching process for ash includes several considerations. As has been noted above, a suitable acid or other leaching medium must be chosen to fit the ash properties, the metal separation and purification method to be used and, not unimportantly, the economy of the process. Hydrochloric acid may be a more practical and economically feasible choice for ash leaching than for example nitric acid since many combustion units has a flue gas cleaning system that includes scrubbers for absorption of acid gases, such as HCl and SO_2, and volatile metal compounds. The scrubber liquid is a waste in itself and could be used as a cheap leachate. Sulfuric acid, on the other hand, may not be the best choice for lead removal since lead sulfate can precipitate as a secondary compound.

Since the mineral compositions of ashes differ, the pH of the leachate must be optimized for the ash type to be treated. Apart from the occurrence of the target metals in compounds of very different solubility, there is also the possible problem of secondary compound precipitation and adsorption of dissolved metals ions on mineral surfaces or on carbon/char surfaces. Adsorption (surface complex formation) of metal ions in aqueous solution on oxides, principally those of silicon, aluminum and iron, are often observed (Morel and Hering 1993), and the adsorption extent rises sharply in a narrow interval of 1 – 2 pH units from the point of zero charge, i.e. the pH where the number of positively and negatively charged surface groups of the mineral are the same. This surface complex formation may influence leaching efficiency strongly and the binding of metal ions increases with pH (Stumm, Sigg et al. 1992). Some minerals have quite low points of zero charge which means that surface complexation can influence metal leaching efficiency even in acidic conditions. The pH_{pzc} of quartz and silica gel is close to pH 2 and approximately pH 3 for feldspar (Stumm, Sigg et al. 1992). Quartz and feldspar minerals are generally more common in bottom ashes than in fly ashes but small sand particles are present in most fly ashes.

One of the fly ashes investigated in the present work (fly ash A) contains a significant fraction of activated carbon from the flue gas cleaning system. The utilization of activated carbon as adsorbent for toxic metals such as Zn, Pb, Cd and Cu and dioxins in flue gas is common. Although various parameters influence the adsorption efficiencies, e.g. type of activated carbon, particle size, presence of different salts and pH of the solution (Ferro-García, Rivera-Utrilla et al. 1990) etc., the pH of solution has been identified to be the most important (Gerçel and Gerçel 2007). It was reported from several investigations (Gabaldón, Marzal et al. 1996; Goel, Kadirvelu et al. 2005) that the adsorption of metals from solution on to activated carbon generally increases with pH. The results from (Babić, Milonjić et al. 2002) indicates the adsorption of zinc and cadmium cannot be observed at pH<4 and pH< 2.5 respectively; (Ferro-García, Rivera-Utrilla et al. 1988) reported that the adsorption of zinc, cadmium and copper at low pH is negligible in general but increases sharply in a narrow range between pH 3 to 5. Lead(II) adsorption is discussed by (Gerçel and Gerçel 2007) giving quite similar results; there is no observed adsorption at pH lower than 3 and with an increase from pH 3 to 5. This means that in the development of a fly ash leaching aiming at an optimal metal removal the effect of activated carbon in the fly ash has to be taken into account.

2.2. Solvent extraction

Solvent extraction is a purification method that utilizes the immiscibility of liquids to separate different species between two different liquid phases, usually an aqueous layer and an organic solvent layer. The transfer of species, for example metal ions, from the aqueous phase to the organic phase is aided by extraction ligands (also called extractants) forming lipophilic complexes with the target metal ions. A large number of extraction ligands have been developed and are in use in hydrometallurgical processes in industry. The chemical mechanisms by which they form metal complexes differ, but the basic principle is to transform the metal to be purified into a complex that dissolves in the organic phase which is then separated from the aqueous phase by density difference. The metal is then transferred to a new aqueous phase in a process called stripping in order to facilitate electrowinning or other methods to recover the target metal in a product form stripping.

Some of the basic parameters used in solvent extraction are presented below.

The Distribution ratio (D,) is the ratio between the total concentration of a solute in organic and aqueous phase respectively.

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \qquad (1)$$

The Separation Factor (SF) is defined as the ratio between the D-values of two solutes, A and B. SF is defined to always be larger than 1.

$$SF_{A/B} = \frac{D_A}{D_B} \qquad (2)$$

The Phase ratio (θ) is also called the phase volume ratio, which is the ratio between the volume of the organic phase and the aqueous phase.

$$\theta = \frac{V_{org}}{V_{aq}} \qquad (3)$$

The Extraction factor (P) represents the product of D value and θ.

$$P = \theta \cdot D \qquad (4)$$

The extraction percentage can be converted from the distribution ratio.

$$\%E = \frac{D}{(D+1)} \cdot 100 \qquad (5)$$

Several criteria need to be considered when assessing the extractants for industrial applications (Rydberg 2004; Flett 2005). The most important are:

- The extractant should have a high selectivity with high distribution ratios and separation factors to transfer the desired metal from the aqueous phase to the organic phase
- The extractant-diluent mixture should have good chemical stability and temperature stability
- The extractant-diluent mixture should be nontoxic, noncorrosive and inexpensive
- The extractant should be possible to regenerate for further extraction
- The complex between metal ion and extractant should not be too strong since it is necessary to be able to transfer the metal across an organic-aqueous interface for metal stripping in the final step of the process.

2.2.1. Solvent extraction using the chelating acidic extractant LIX860N-I

Acidic, chelating extractants are organic extractants that release H+ during extraction and form neutral metal chelates. These ligands often bind to the metal through two or more binding sites of atoms like oxygen, sulphur or nitrogen.

LIX860N-I used here is an aldoxime, more specifically the 5-nonylsalicylaldoxime. Oximes are generally, especially the aldoxime, known to from stable complexes with copper(II) ions, and oximes are therefore the most commonly used reagents for the copper extraction (Kordosky 1992). The extraction of a metal (M) using oxime in acidic solution can schematically be described as

$$M^{z+}_{(aq)} + zHA_{(org)} \leftrightarrow MA_{z(org)} + zH^{+}_{(aq)} \quad (6)$$

Where HA denotes the protonated organic extractant.

The formed metal complex then transfers to the organic phase since the molecular structure of the complex is lipophilic. In the extraction reaction using an acidic extractant (LIX860N-I in this work), the distribution ratio of a particular metal complex is always influenced by the pH; the availability of the free ligand for the complex is dependent on the dissociation of the organic acid, and the hydrogen ion concentration is the main parameter that affects the dissociation equilibrium. Copper was extracted using LIX860N-I in the present work, and kerosene was used as solvent.

2.2.2. Solvent extraction using solvating extractant Cyanex 923

A solvating extractant extracts an entire complex consisting of a metal ion and the ligands that are coordinated to it from the aqueous phase. Cyanex 923 is a mixture of four slightly different trialkylphosphine oxides (TRPO), as shown in table 1, has active substances very similar to TOPO (trioctylphosphine oxide) (Dziwinski and Szymanowski 1998), only slightly different in the length and/or the structure of alkyl group, which has been proven to be a good extractant for zinc and other metals (Chen, Li et al. 2011). All components in the Cyanex 923 mixture are solvating ligands.

Table 1: Chemical composition of Cyanex 923 (Dziwinski and Szymanowski 1998)

Composition	General formula	
Trioctylphosphine oxide	R3PO	14%
Dioctylmonohexylphosphine oxide	R2R'PO	42%
Dihexylmonooctylphosphone oxide	RR'2PO	31%
Trihexylphosphine oxide	R'3PO	8%

R denotes n-octyl and R' stands for n-hexyl group.

The extraction between a solvating extractant reagent, such as Cyanex 923, and metal ions can be described as (Rydberg 2004)

$$M^{z+}_{(aq)} + zX^{-}_{(aq)} + bB_{(org)} \leftrightarrow MX_zB_{b(org)} \quad (7)$$

Metal ions ($M^{z+)}$ form complexes MXz with counter ions ($X^{-)}$ in the aqueous phase. In this work X^- represents a chloride ion, which dissociates from hydrochloric acid and chloride salts. In the absence of solvating extractant B, the complexes often have very low distribution ratio due to their hydrophilic nature. During the extraction with the Cyanex 923 extractant, the water molecules are replaced by the organic molecules, forming more lipophilic complexes.

The number of extractant molecules involved in each complex has been observed to be different depending on what metal ion they bind to and on how the organic phase is composed. For cadmium, cobalt and nickel in chloride solutions two molecules per complex were observed (Reddy and Priya 2006). Lanthanides and yttrium was found to be extracted as nitric complexes by Cyanex 923 in nitric acid media and two extractant molecules per extracted nitric complex was found to be needed (Gupta, Malik et al. 2003). However, another group observed that three extractant molecules per complex was needed for the same process (Reddy, Varma et al. 1998).

A large amount of research work has been done to investigate zinc extraction in acidic chloride media, and it has been observed that the principal reactions for solvating reagents are (Cierpiszewski, Miesiąc et al. 2002)

$$H_{aq}^{+} + ZnCl_{3aq}^{-} + 3B_{org} \leftrightarrow HZnCl_3 \cdot 3B_{org} \quad (8)$$

$$ZnCl_{2aq} + 2B_{org} \leftrightarrow ZnCl_2 \cdot 2B_{org} \quad (9)$$

where B represents the solvating extractants.

Which types of zinc complexes that appears in the organic phase is influenced by the acidity and chloride ion concentration of the aqueous solution. $ZnCl_2$ is the predominant species in aqueous phase at low acidity and $ZnCl_3^-$ and $ZnCl_4^{2-}$ at higher acidity (Regel, Sastre et al. 2001), and $HZnCl_3$ was observed in organic phase when the acidity is greater than 0.1M (Tao and Yuanfu 1991). . A similar extraction mechanism as described for zinc in Eq. 8) has been also observed for iron (III) extraction(Saji, Rao et al. 1998).

In this work, Cyanex 923 was chosen to extract zinc in acidic chloride media. The advantages of using Cyanex 923 as extractant are that it is completely miscible with common organic solvents, even at low ambient temperature, and it has a low solubility with water. In addition, it does not change the pH of the aqueous phase during extraction which reduces the need for pH control or adjustment This readily available commercial extractant has been used in the recovery of nickel from aqueous phases from battery leaching in our group with quite high efficiency (Larsson, Ekberg et al. 2013). The solvent used, kerosene, contains no donor atoms and no active hydrogens, so is an inert solvent. Ionic species will have a very low tendency to enter the kerosene without an added extractant, as there is no potential for charge stabilization in the organic layer.

Metal stripping is the final step of the extraction process, where the desired metal transfers from the organic phase to an aqueous phase(Seader, Henley et al. 2011). The complex between metal ion and extractant should not be too strong since it is necessary to be able to break it to transfer the metal across an organic-aqueous interface (Flett 2005).

3. Experimental

The work presented here discusses the development and feasibility evaluation of a hydrometallurgical recycling process based on the combination of acidic leaching and selective extraction to recover Cu and a following Zn extraction. The ash samples used in the experiments were obtained from commercial combustion units. The ash samples A were fly ash and bottom ash from a grate fired boiler fired with sorted municipal solid waste and ash B was a filter ash from a bubbling fluidized bed boiler firing a similar waste. Figure 1 shows a schematic overview of the suggested process for removal and possible recovery of valuable and toxic metals from MSWI ashes.

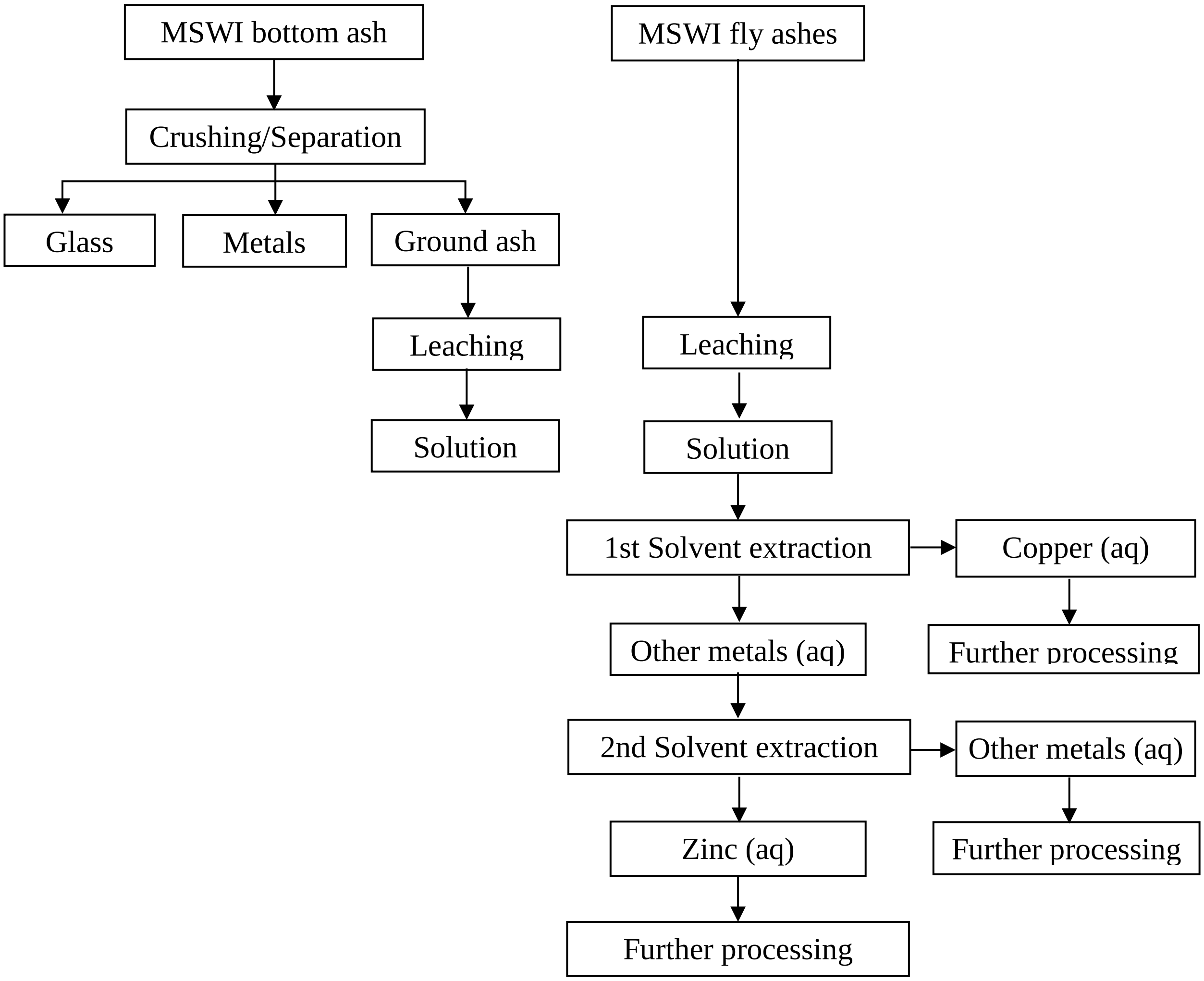


Figure 1: Schematic of the overall MSWI ash recycling process

The experiments that have been done mainly focus on the characterization of ash samples and leaching residues, the determination of the acid demand for leaching, optimization of leaching parameters and a feasibility study of the separation of copper and zinc from the leachates individually using solvent extraction methods..

3.1. Characterization of the ashes

The ash samples marked A were an electro filter fly ash and bottom ash from a grate fired boiler firing sorted municipal solid waste. The samples were collected during normal and stable operation of the combustor. The fly ash sample B is a filter ash from a bubbling fluidized bed combustor also fired with normally sorted household waste and waste from small enterprises.

Determination of total concentrations of elements in the ash samples

The concentrations of elements in the ashes were determined by ICP-OES (main elements) and ICP-MS (trace elements) after total dissolution. The dissolution of samples for ICP-OES was prepared by melting a weighed amount of ash with lithium borate and the dissolving the melt in dilute HCl, whereas the sample for ICP-MS was prepared by dissolving a weighed amount of ash in a mixture of acids including HF in a bomb. Both methods have been developed to dissolve the whole sample including silicates and are standardized. The bomb dissolution is used for preparing the solution for determination of volatile and traces metal concentrations since it prevents vapors from escaping. These analyses were done by an accredited laboratory. Since the bottom ash A was very inhomogeneous and contained lumps of slag as well as stones and metal objects a sample of approximately 10 kg was milled by the accredited laboratory before taking out a smaller sample for total content analysis. The small sample was taken by partitioning of the total sample by standardized methods.

Due to the occurrence of large slag lumps in the bottom ash a leaching procedure for recovery of metals from it was not anticipated to be successful. Therefore, the investigation was carried out on the ground ash. The particle size distribution of metals was measured in the range of 4 mm to smaller than 0.09 mm. To estimate the content of interesting metals dissolution experiments of the samples from different particle size fractions were performed using aqua regia. The aqua regia treatment did not dissolve the whole samples but minor amounts of silicates remained. Hydrochloric acid (>37%, Sigma-Aldrich) and nitric acid (65%, Sigma-Aldrich) were used to prepare the solution with a 3:1 v/v ratio. One gram of the ash sample was weighed (Sartorius research, resolution > 0.01 mg) and dissolved in 40 ml aqua regia. The solution was diluted to 100 ml with 1M HNO_3 and filtered with polypropylene syringe filters (0.45 μm). The metal contents in these solutions were determined using ICP-OES. Duplicate samples were dissolved and the ICP measurements were made in duplicates.

Mineralogy determined by X-ray powder diffraction (XRD)

Powder X-ray diffraction (XRD) was used to identify the crystalline compounds in the ash samples using a Siemens D5000 powder diffractometer with characteristic copper radiation of wavelength 1.54Å (Cu-Kα) and a scintillation detector. Measured diffraction data were compared with data for pure compounds standards (Joint Committee on Powder Diffraction Standards 2013) This method provides qualitative information about crystalline compounds in concentrations higher than 2 wt% of the sample. Amorphous material and compounds occurring as extremely small crystals cannot be identified.

X-ray absorption spectroscopy for determination of oxidations states and chemical forms of some metals

The oxidation states and in some cases the speciation of copper, iron, lead and zinc in the ash samples were investigated by Near Edge X-ray Spectrometry (XANES) measurements at the MAX-lab synchrotron, Sweden. The measurement was made at beamline I811 using a Si(111) double crystal monochromator and the second crystal is bendable for horizontal focusing. The monochromator was detuned to 30% below maximum intensity to remove higher order harmonics. The photon energy range of this beamline is 2.3 – 21 keV.

XAS data was also collected for a number of pure compounds with iron and lead in different oxidation states and used for comparison.

For a closer speciation of Cu and Zn XAS data that has been collected by our group for a large number of pure compounds were used for linear combination fitting modelling. The following standard compounds were used for zinc: Zn, ZnO, $ZnAl_2O_4$, $ZnFe_2O_4$, $Zn_5(OH)_6(CO_3)_2$, ZnS, $ZnCl_2\cdot1.3H2O$, and for copper: Cu, brass (Cu/Zn alloy), Cu_2O, CuO, $CuCrO_2$, $CuCr_2O_4$, $CuFe_2O_4$, $Cu_3(PO_4)_2$, CuCl, $CuCl_2\cdot2H_2O$, CuClOH/CuCl, $Cu_2Cl(OH)_3$, $Cu(OH)_2CuCO_3/CuCO_3$, $Cu(OH)_2$, $CuSO_4\cdot5H_2O$, $CuSiO_3\cdot H_2O$, $CuBr_2$, CuS, Cu_2S, Cu_5FeS_4/Cu_2S, CuCaOxide, CuCaPhosphate and Chrysocolla. All standard compounds were analyzed with XRD and identified as pure, i.e. < 2% impurities, with the exception of CuClOH/CuCl, $Cu(OH)_2CuCO_3/CuCO_3$, Cu_5FeS_4/Cu_2S, CuCaOxide, CuCaPhosphate and Chrysocolla. The CuClOH/CuCl was identified by XRD and XAS as CuClOH with a small fraction (≤ 7%) of CuCl. The $Cu(OH)_2CuCO_3/CuCO_3$ was identified by XRD and TGA as $Cu(OH)_2CuCO_3$ with a small fraction (~12%) of $CuCO_3$. The Cu_5FeS_4/Cu_2S was identified by XRD as Cu_5FeS_4 with a small fraction (not quantified) of Cu_2S. The CuCaOxide was identified by XRD as several mixed oxides of copper and calcium, one example being Cu_2CaO_3. The CuCaPhosphate was identified by XRD as being mainly $Ca_{21-X}Cu_X(PO_4)_{14}$, with x=1, 2 or 3. The natural copper silicate mineral Chrysocolla, with formula $(Cu,Al)_2H_2Si_2O_5(OH)_4\cdot nH_2O$, was not identifiable by XRD since it is amorphous, but was bought from a mineralogist who certified its identity.

3.2. Leaching experiments

The experiments were performed with a programmable titration instrument; Metrohm 905 Titrando titrator equipped with two titration stations making it possible to run parallel duplicate experiments. The electrode used for pH measurement was calibrated before and after the experiment using external buffer solutions in the range from pH 1 to pH 12 (Merck KGaA).

The initial volume of distilled water was chosen to approach the desired liquid to solid ratio and to create a stirrable ash slurry and partially dissolve the ash samples and. Obtaining the correct pH by adding in the total estimated amount of acid needed at the start is not feasible. This causes the pH to initially drop far below the chosen. It would then be invalid to quote the leachability of species to a specific pH value.The stirring of the leachate was kept at a rather high speed in order to reduce mass transfer resistance in the stagnant layer around the particles(Morel and Hering 1993).

For the separation of residues from leachates, a Beckman J2 -21 centrifuge with a J- 17 rotor was used with a speed of 15000 rpm for 20 minutes, the volume of centrifuge ware is 50 ml (Nalgene). The non-dissolved ash residues were collected, filtered and dried at room temperature for further investigation.

Metal concentrations in the leachates were determined by using Inductive Coupled Plasma with Optical Emission Spectrometer (ICP–OES, Thermo iCAP 6000). Totally 14 ICP-OES external standards; including aluminum, calcium, cadmium, chromium, copper, iron, potassium, magnesium, manganese, sodium, lead, silicon, titanium and zinc with concentrations of 0 ppm, 1 ppm, 5 ppm, 10 ppm and 20 ppm were prepared from ICP standards (Ultra Scientific, 1000 μg/ml, with the exception of lead which is 10 μg/ml) and approx. 1M nitric acid (65%, suprapur, Merck). The obtained leachates were diluted with 1 M nitric acid for the measurement.

Anions concentrations in the leachates were investigated by Ion Chromatography (IC, Thermo Scientific, Dionex, DX-100). External standards were prepared with concentrations of 2 μM/l, 10 μM/l and 100 μM/l.

3.2.1. The influence of acid and pH level on leaching

Leaching experiments with fly ash A were performed at pH values 2, 3, and 4 with 3 M nitric acid (65%, Sigma-Aldrich) and 3 M hydrochloric acid (>37%, Sigma-Aldrich) and for the bottom ash A with nitric acid (65%, Sigma-Aldrich). Since the presence of sulfate ions may complicate the leaching of lead due to the precipitation of lead sulphate, only some extra leaching experiments of fly ash with 1.5 M H_2SO_4 (95-97% Sigma-Aldrich) at pH 2 were done for the leaching comparison of interesting elements.

Ash B was leached using 3 M hydrochloric acid (>37%, Sigma-Aldrich) at pH 2, 3, and 4 as a reference since it represents fly ashes from a different type of combustion technique: the fluidized bed combustion.

For the separation of residues from leachates, a Beckman J2 -21 centrifuge with a J- 17 rotor was used with a speed of 15000 rpm for 20 minutes, the volume of centrifuge ware is 50 ml (Nalgene). The non-dissolved ash residues were collected and washed with pure water (MilliQ, Millipore, >18 MΩ/cm), filtered and dried at room temperature for further investigation.

Leachates were sampled and analyzed using ICP-OES, and the non-dissolved ash residues were collected and washed with pure water (MilliQ, Millipore, >18 MΩ/cm), filtered and dried at room temperature, and then sampled for the further analysis, e.g. EXAFS, XRD.

3.2.2. Investigation of leaching parameters

Investigation of leaching kinetics at different pH-levels

The kinetics of metal leaching from the Ash A fly ash was investigated in experiments with nitric acid and hydrochloric acid solutions, and fly ash B was studied using hydrochloric acid. The experiments were carried out in triplicate, at room temperature 20 ± 1 °C.

As described in section 3.2.1; the homogenized ash was first mixed with distilled water to approach the desired liquid to solid ratio and titrated for 4h, 20h and 70h at pH levels 2, 3, and 4 respectively with magnetic stirring (100 ± 20 rpm). The leachates and residues were treated as described in section 3.2.1.

Influence of the liquid to solid ratio on leaching

The influence of the liquid to solid ratio (L/S) was investigated using fly ash A with 3 M hydrochloric acid at pH values 2, 3 and 4 using L/S 5, 20 and 50 (v/w), and the experiment procedure was similar to the investigation of leaching kinetics, triplicate titrations for 4h, 20h and 70h, and the ash B was leached as a reference. The experiments and treatment were carried out as described in section 3.2.1.

Influence of temperature on metal leaching from fly ash A

The effect of temperature on the leaching efficiency was studied at room temperature (20 ± 1 °C) and at 60 ± 5 °C, in experiments where fly ash A was leached at pH 2 using 3 M hydrochloric acid (>37%, Sigma-Aldrich) and 3 M nitric acid solution (65% Sigma-Aldrich) respectively. The liquid to solid ratio was set to 20, and the leaching time was 5 hours. Triplicate tests were done for each system.

3.3. Investigation of solvent extraction separation of Cu and Zn

The aqueous phases for the extraction experiments were obtained from the leaching experiments. Leachates produced at different parameter settings were used in order to get information on how the nature of the aqueous phase influences the two extraction processes suggested: the separation of Cu with the extractant LIX860-I and the subsequent separation of Zn using Cyanex 923 as presented in figure 1.

Both extractants are commercially available and commonly used in industry. Cyanex 923 (93%, Cytec) and LIX860N-I (Cognis, Ireland) were used to prepare the organic phases with kerosene (Solvent 70, Statoil) respectively. The preparation of the aqueous phase is described briefly in each section below.

The batch experiments of solvent extraction were carried out in 3.5 ml glass vials (46 × 18 × 0.8 mm) sealed with plastic lids. Triplicates were used for each experiment system. A thermostatic shaking machine (IKA Vibrax VXR Basic) was used to mix the phases, the vibration set at 500 times per minute (vpm), the temperature was 24 ± 1°C. The phase ratio between aqueous phase and organic phase was 1, 1.5 ml of aqueous phase and organic phase was used. After phase separation, the aqueous phase was collected for the second extraction and the organic phase was stripped with acid solutions. More details on each experiment are given in sections 3.3.1 – 3.3.4.

Metal contents in the leachates before the 1st copper extraction, the aqueous phases collected after the copper and zinc extractions and the stripping were analyzed as described under 3.2(ICP–OES, Thermo iCAP 6000). The metal contents in organic phases, the distribution ratios and stripping percentages were calculated using the mass balance.

3.3.1. Influence of the hydrochloric acid concentration in the aqueous phase on the extraction

The distribution ratio dependence on the hydrochloric acid concentration in the aqueous phase was studied. The copper extractions were tested with ash B leachate, the concentration of hydrochloric acid in the aqueous phases were 0.1 M, 0.01 M and 0.001M respectively. The organic phase used was 1 M LIX860N-I diluted in Solvent 70. Ash B leachates were chosen since they had higher Cu concentrations than the leachates from Ash A.

The second set of experiments was made to study the zinc extraction. The aqueous phases were prepared with ash A leachates. The hydrochloric acid concentration is 0.01 M, 0.001 M and 0.0001M respectively. The organic phase used in the extraction was a 1M solution of Cyanex 923 in Solvent 70.

3.3.2. Investigation of the kinetics of Cu and Zn extraction

The leachates from the two fly ash samples (ash A and ash B) obtained under the leaching conditions 20 hours leaching time, pH value 2, room temperature 20 ± 1°C, liquid to solid ratio 20 and 14 v/w respectively were used as aqueous phase. Cyanex 923 and LIX860N-I diluted in Solvent 70 individually to a ligand concentration of 1 M, were used as the organic phases.

The first set of experiments was done to investigate the kinetics of copper extraction. Leachates from the f two ash samples were extracted using 1 M LIX860N-I, the extraction times were 1, 3 and 5 minutes individually, and the experiment was carried out as described in section 3.3.

The second set of experiments concerned the zinc extraction. These experiments were carried out similar to the copper extraction experiments but with the organic phase consisting of 1 M Cyanex 923 in Solvent 70.

3.3.3. The influence of extractant concentration on the extraction efficiency

The influence of extractant concentration on the zinc extraction was first investigated using a synthetic metal containing aqueous phase. This artificial solution containing zinc was kept at pH 2 by titration with a 3 M hydrochloric acid solution. NaCl was added to bring the Cl^- concentration to approx. 0.15 M. This roughly simulated the concentration found in the actual ash A leachate (20 hours leaching time, room temperature 20 ± 1°C, liquid to solid ratio 20 v/w). Organic phases were prepared with Cyanex 923 dissolved in solvent 70 using the following extractant concentrations: 0.1 M, 0.15 M, and 0.2 M.

A second set of experiments was carried out using actual ash A leachates obtained by leaching at a controlled pH of 2with hydrochloric acid at 20 ± 1°C, using a liquid/solid ratio of 20 w/v for 70 hours. Organic phases containing various amounts of Cyanex 923: 0.1 M, 0.5 M, 1 M, 1.5 M, and also undiluted extractant, 2.352 M were studied.

Due to the low content of copper in fly ash A, a third set of experiments was made to investigate the copper extraction efficiency using Ash B leachate as aqueous phase. Ash B samples were leached at pH 2 with 3 M hydrochloric acid solution for 70 hours at 20 ± 1°C, using a liquid/solid ratio of 14 w/v. Organic phases containing LIX860N-I diluted with Solvent 70 to concentrations of 0.1 M, 0.25, 0.5 M, 1 M and 1.5 M were used.

The extraction time was 5 minutes in all cases, using the procedure described in the section 3.1. The time 5 minutes was enough for equilibrium to be reached as shown by the results from the kinetics experiments described in section 4.2.

3.3.4. Development of the suggested copper and zinc recovery process including the stripping steps

As presented in figure 1, the recovery of copper and zinc as a two stage process was suggested and tested. Two 50 ml organic phases containing 1 M LIX860N-I dissolved in Solvent 70 were shaken manually with 50 ml ash A fly ash leachate and ash B leachate respectively. The leachates were the same as described in section 3.3. The contact time was 5 minutes. After phase separation, the organic phases and aqueous phases were collected. The collected aqueous phases (25 ml) were then shaken with the second extractant; Cyanex923 (25 ml, 1 M with Solvent 70) for zinc extraction. The zinc extraction was also performed with 5 minutes contact time. After the two extractions, the aqueous phases as well as original aqueous solutions were sampled (1 ml) and analysed. The organic phases loaded with metals were collected for use in the stripping processes.

Based on the results from the preliminary leaching and extraction investigations, the leachate produced from fly ash A leachated with HCl at pH 2, with leaching time 20 hours and liquid to solid ratio 20 was chosen for several reasons:

- Zinc extraction works well at low pH level from the hydrochloric acid media;
- A large fraction of the zinc was leached out at pH 2 and it was found to be unaffected by a further decrease in the pH (Karlfeldt Fedje, Ekberg et al. 2010);
- The most abundant hazardous metals, e.g. lead and cadmium are released and minimize the toxicity of ash residue;
- Copper extraction will decrease the pH value, and there is no need for a pH adjustment step.

Since the ash B had been found to be more leachable than ash A, the leachate from leaching ash B with similar leaching parameters as described above was chosen as a reference.

As mentioned in section 2.2.2, oximes are the most common reagent for copper extraction and it is also common to use sulfuric acid for stripping. For example it was found that 0.2 M sulfuric acid could efficiently recover almost all the copper ions (0.001 M) from an organic phase (Mishra and Devi 2011). Considering the composition of the metal loaded organic phase and the stripping solution used by Mishra and co-workers a sulfuric acid concentration of roughly 0.9M would be needed for the organic phases obtained in our experiments with leachates from ash B with Cu concentration of approximately 0.005 M g/l. Different concentrations of sulfuric acid (0.5 M, 1 M, and 1.5 M repectively) were prepared using concentrated stock solution (>95%, Fisher Scientific) and pure water (MilliQ, Millipore, >18MΩ/cm) for copper stripping.

To study the zinc stripping process, a special set of experiments was made since no information relevant to our application was found in literature. The organic phase (1 M Cyanex 923) with metals loaded after extraction from leachate A, was stripped using several reagents. Nitric acid (1

M, 3 M and 5M), sulfuric acid (0.5 M, 1.5 M) and hydrochloric acid (1 M and 3 M) solutions were used.

In all experiments concerning stripping of the metal containing organic phases 1.5 ml of the stripping agent was shaken with 1.5 ml loaded organic phase for 5 minutes at 20 ± 1°C. After phase separation, 1 ml of each aqueous phase was sampled, diluted with 1 M nitric acid solution (65%, suprapur, Merck), and analyzed.

4. Results and discussion

4.1.Characterization of the ashes

The concentrations of major and minor elements in the ash samples, as shown in table 2, are quite similar to those of other MSWI ashes shown in the literature (Van Herck and Vandecasteele 2001; Yu, Tian et al. 2009; Lassesson, Fedje et al. 2014).The weight losses on ignition at 550°C were 0.9% by weight for the fly ash A and 1.3% for the bottom ash A and the moisture contents 1.4% and 1.8% respectively. Fly ash B had a loss on ignition of 0.02% and a moisture content of 0.01%. The uncertainties in these values are ±10% relative. The amount of combustible material in the fly ash A was not large as described in weight but activated carbon has a large surface area per weight unit to maximize adsorption efficiency, which means that a small weight fraction might influence metal leaching.

Table 2: Concentrations of major and minor elements in the ash samples; a fraction of metals that were not possible to mill corresponding to 8.3 wt% were removed from the bottom ash A before analysis. The uncertainty of the concentration data is between 10 and 35% relative.

Major Elements g/kg dry matter	Fly ash A	Bottom ash A	Fly ash B	Minor Elements mg/kg dry matter	Fly ash A	Bottom ash A	Fly ash B
Al	36.1	38	20	As	240	68	80
Ca	180	93	360	Ba	140	1300	770
Fe	20.1	70	5.6	Cd	83	4	90
K	21.1	11	25	Co	34	33	20
Mg	18.1	12	10	Cr	450	490	190
Na	26.1	38	32	Cu	840	2700	5400
P	5	3	4	Hg	0.05	<0.05	3
S	81.5	8	7	Mn	1100	1000	570
Si	67.3	183	32.7	Mo	22	<20	10
Ti	14.1	12	1.8	Ni	220	240	30
Cl	31	3	200	Pb	3000	1400	5700
				Sb	1100	86	nd
				Se	10	<10	nd
				Sn	380	310	20
				V	70	60	10
				Zn	17100	3800	5800

The powder diffraction analysis of fly ash A indicated that it contained $CaSO_4$, SiO_2, Fe_2O_3 and probably $CaTiO_3$. The bottom ash A gave a diffractogram with many peaks that suggest many crystalline substances in low concentrations. This made the identification of compounds challenging. Probable compounds in this ash are quartz (SiO_2) and a number of silicates and feldspar minerals, KCl, $CaSO_4$, $Ca(OH)_2$, metallic Fe, FeO, Fe_2O_3, TiO_2 and $CaTiO_3$. In addition, the bottom ash contained a significant fraction of glassy slag which does not give good diffraction patterns. The crystalline components identified in fly ash B were NaCl, KCl, $KCaCl_3$, $Ca(OH)_2$, CaClOH, $CaCO_3$, $CaSO_4$, $Ca_3Al_2O_6$, SiO_2.

To further clarify the oxidation state of iron in the ashes from combustor A, X-Ray absorption spectroscopy (XAS) was used as described in Section 3.1. The results showed that iron was predominantly present in Fe(III) state and as hematite in fly ash and in an average oxidation state of 1-2 in the bottom ash. This is consistent with the powder X-ray diffraction (XRD) analysis showing Fe_2O_3, in the fly ash and a mixture of Fe metal, FeO and Fe_2O_3, in the bottom ash. The fact that iron is fully oxidized to hematite (Fe_2O_3,) already in the fly ash implies that only a small amount of the iron will be leached out due to the low solubility of hematite. Ferrous iron, as in the bottom ash, is more soluble. This was also seen in the results of the leaching experiments discussed below.

Lead X-ray Near Edge Spectrometry (XANES) data indicated that the oxidation state II was dominating for lead in fly ash A., Unfortunately the data did not allow for the types of lead compounds could not be determined.

Since it was considered interesting to know if some parts of the bottom ash could be richer is some metals than others the ground bottom ash A was sieved into different particle size fractions and the fractions were analyzed for metal contents. As presented in figure 2 most of the particles in the ground bottom ash A were in the range of 2 – 20 mm. approximately 50% by weight of the material had a particle size below 5 mm. The concentrations of a number of elements in the fractions are given in table 3 and some of the results are visualized in figures 3A-C.

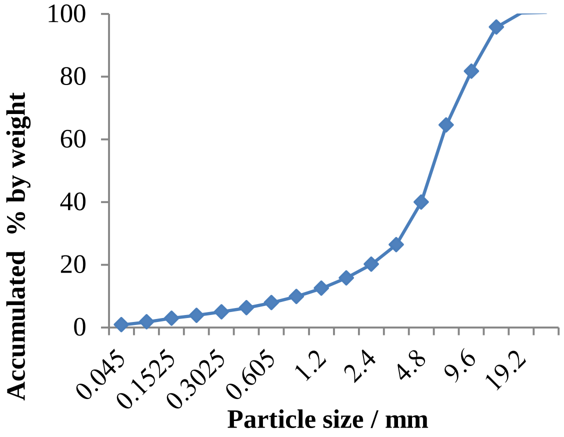


Figure 2: Particle size distribution of the ground bottom ash A used in the leaching experiments (given as accumulated wt %)

Table 3: Element content in various particle sizes of sample A bottom ash

Mesh width mm	**Al**	**Ca**	**Cu**	**Fe**	**K**	**Mn**	**Na**	**Ni**	**P**	**Pb**	**S**	**Si**	**Ti**	**Zn**
4	35100	39900	9250	248000	1090	850	6560	212	870	11	3500	53	1890	2130
2.8	14100	59100	380	168000	1650	914	7610	126	1080	79	18700	98	2250	846
2	44600	64200	96900	99800	1850	1060	10700	429	2350	159	6660	72	4280	30500
1.4	47800	72100	1750	120000	2230	1800	11500	219	1810	304	9610	87	3640	3640
1	28100	87900	14600	77900	2790	929	14800	327	3020	6580	13500	79	4270	2960
0.71	26500	87400	5180	69600	2750	1370	13800	203	2910	325	13100	104	4000	4230
0.5	29300	90700	11500	55200	2810	888	15800	347	2990	616	15800	76	3800	3020
0.355	28600	94800	3890	49200	3060	1120	17100	344	3470	733	16600	79	3540	4510
0.25	26600	94800	4820	47000	2860	1070	19500	392	3630	706	19500	145	3300	4750
0.18	28100	100000	4450	41200	3150	976	24700	310	3360	845	24600	161	3080	4680
0.125	27000	105000	3860	36100	3280	1030	34500	277	2970	659	35700	171	2600	4670
0.09	26800	106000	3770	36300	3290	1160	38700	267	2680	668	40700	168	2410	4940
<0,09	24800	112000	3460	31900	3320	1260	39400	250	2420	696	46400	175	2180	4840

Silica concentrations are low due to the fact that a large amount of broken glass accumulated in the particle sizes larger than 4 mm. The iron content decreases with decreasing particle size while the calcium content increases and the aluminum is roughly the same regardless of particle size. The concentration of copper and zinc varies widely between different particles sizes, especially for particles larger than 0.5 mm. Nickel and lead concentrations also vary but generally the contents are higher in the smaller particles than in the larger ones. Since the analyses were made on the ground bottom ash they roughly reflect the grindability of the compounds containing the metals. As an example, calcium and sulphur are present in compounds which are easy to grind. Pieces of metals and alloys, e.g. iron metal, are not particularly easy to crush which explains why they occur frequently in the larger particles. These results indicate the problem with inhomogeneity of the bottom ash which will be discussed further later in this thesis.

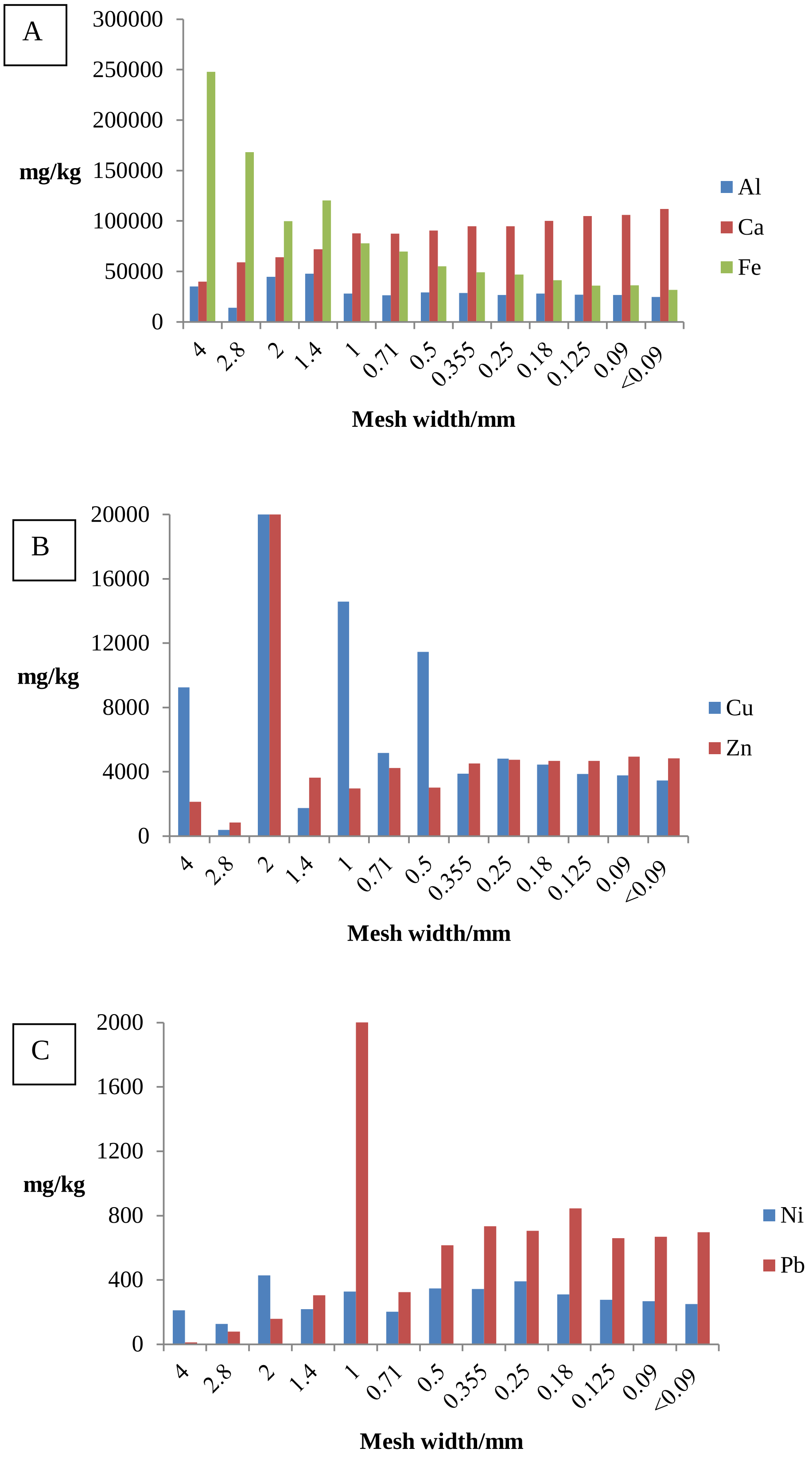


Figure 3 A-C: Concentrations of some elements in different particle sizes of ground bottom ash

Application of linear combination fitting (LCF) analysis to Cu K-edge XANES and EXAFS data gave probable speciation of copper in samples of fly ash A and fly ash B. All percentages shown in these results are atomic-percent, i.e. the number of copper atoms in a specific compound compared to the total number of copper atoms. It should be noted that the linear combination fitting method gives only semi-quantitative concentrations of compounds. The XAS Cu K-edge spectra for ash samples and relevant standard compounds are shown in figure 4, along with the LCF modelling results. It is seldom that the LCF modelling will result in the exact same best fit in both the XANES and EXAFS regions. Illustrated in figure 4 are instead approximations based on results from both regions, i.e. these are chosen to fit as well as possible in both regions.

The results indicate that copper in fly ash A exists in various oxidation states, where a mix of 5% metallic Cu, 40% CuCl and 55% $Cu_3(PO_4)_2$ explains both the XANES and EXAFS features quite well. Ash B showed a more oxidized form with primarily copper(II) species, such as sulphate, hydroxides and chlorides. This is illustrated in figure 4 with 70% $CuSO_4{\cdot}5H_2O$ and 30% CuClOH/CuCl. Due to a low copper concentration in fly ash A, the XAS spectrum was unusable at energies around and higher than 9340 eV, which made the identification of copper species harder. Additionally, the copper sulphides (Cu_2S, Cu_5FeS_4 and CuS), as well as CuCl, have quite similar XAS spectra. This means that these are hard to differentiate in the LCF, especially in lower amounts. Fly ash A contains only 840 mg Cu per kg whereas fly ash B contains 5400 mg/kg. Samples with metal concentrations lower than 1000 mg/kg commonly give rather diffuse XAS spectra at beamline I811 Maxlab due to the relatively low intensity of the beam. The same goes for the phosphate ($Cu_3(PO_4)_2$) and the silicates ($CuSiO_3{\cdot}H_2O$ and Chrysocolla). Similarities in XAS spectra from two compounds occur when the copper has the same oxidation state and approximately the same amount of neighbouring atoms with similar atomic number at similar distances, which is the case here. In this study it was seen that the XAS spectra of the phosphate ($Cu_3(PO_4)_2$) seemed to fit slightly better than the silicates and the chloride (CuCl) seemed to fit slightly better than the sulphides (Cu_2S, Cu_5FeS_4 and CuS), which is why these two were chosen in the LCF of ash A illustrated in figure 4.

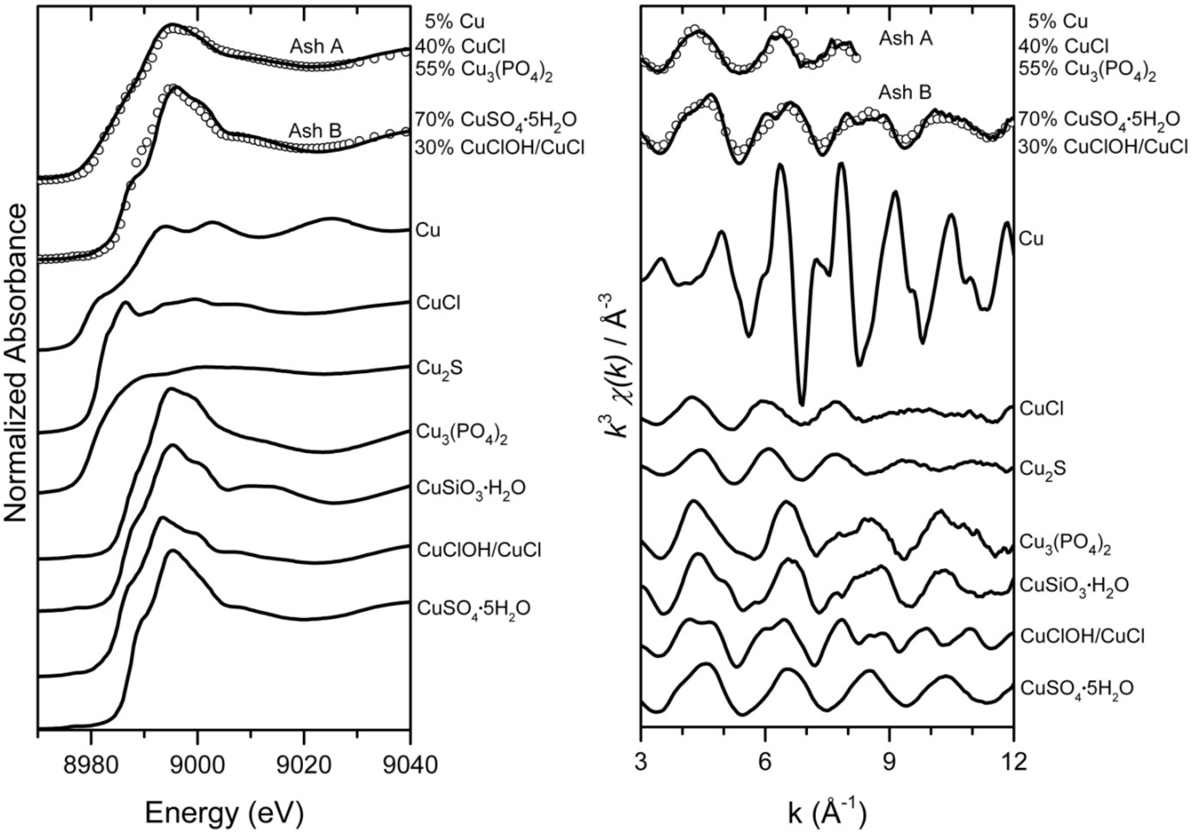


Figure 4: Cu K-edge XANES data (left) and k3-amplified EXAFS data (right) for standards and ash samples (solid lines) with results from LCF (circles).

The two Zn XAS spectra from fly ashes A and B were quite similar. Their EXAFS spectra are dominated by a Zn-O distance of 1.96 Å, with almost no signals from neighboring atoms at longer distances. The Zn-O distance fits well with e.g. $Zn(OH)_2$ and Zn_2SiO_4 but is too short to fit with e.g. ZnO, $ZnAl_2O_4$, $ZnFe_2O_4$ and $ZnSO_4$. The lack of signals from neighboring atoms beyond the first shell indicates a disordered structure or a lack of heavy neighboring atoms. A disordered structure might occur from e.g. surface adsorption, and a lack of heavy neighboring atoms might occur from e.g. hydration.

4.2. Investigation of acid leaching

4.2.1. Acid type and pH-level

One aspect of the use of acid leaching to release metal compounds from ash is that a quite large amount of acid may be needed since especially the fly ashes contains a large fraction of alkaline compounds, such as CaO, $Ca(OH)_2$ and $CaCO_3$. Thus it is necessary to estimate the amount of acid needed in a future metal recovery process. The number of acid equivalents needed to reach desired pH values for the fly ash A and fly ash B studied in this work are shown in figure 5.

The fly ash A requires 9 mmol H^+/g of hydrochloric acid to reach pH 2 which is in the same range as other types of fly ash from MSWI and biomass combustion units (Steenari and Karlfeldt Fedje 2010). The amount of acid needed is very dependent on the amount of lime used in the flue gas cleaning system. For the corresponding bottom ash 7.1 and 5.6 mmol H^+/g of ash were consumed from HCl and HNO_3 respectively. The higher consumption of hydrochloric acid when compared to nitric acid is not related to the type of acid but reflects the inhomogeneity of the bottom ash samples.

The fly ash B is more leachable and more alkaline, compared to fly ash A, 13.3 mmol H^+/g of hydrochloric acid is needed to reach pH 4 and 14.1 mmol H^+/g to obtain pH 2. The results indicate that most soluble compounds have been dissolved at pH 4 and only a small amount of extra protons is required to reach pH 2. Therefore, the pH level of a leaching process for fly ash B leaching is more flexible than that for fly ash A.

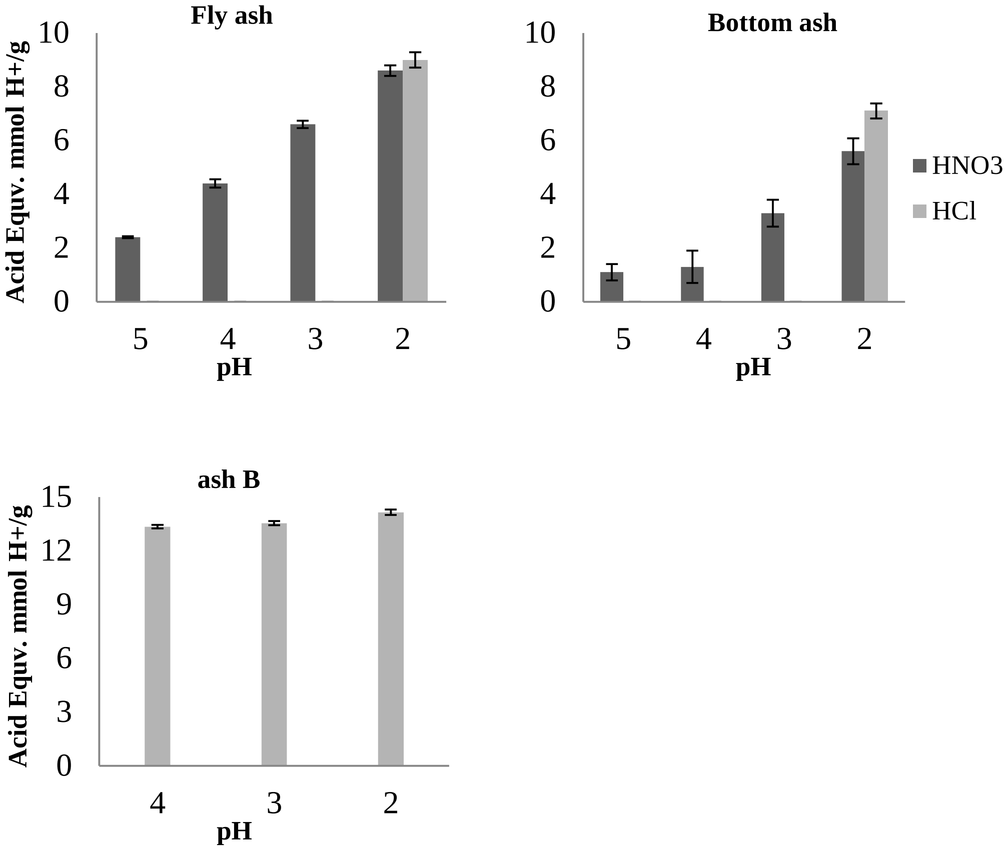


Figure 5: Quantity of acid equivalents (mmol H^+/ g of ash) used to reach the different pH-levels shown Fly ash and bottom ash from combustor A and fly ash from combustor B. 3 M nitric and hydrochloric acid solutions, the temperature was 20 ± 1 °C, leaching times 20 hours, L/S 20 for ashes A and 14 for ash B v/w, magnetic stirring 100 ± 20 rpm

The results for fly ash A and bottom ash A constant pH leaching experiments (tables 4 and 5) show that the selective leaching of interesting elements was significantly affected by the pH value in the leachates. As expected, fly ash elements mainly present as chlorides such as Na and K are released in high amounts at all pH levels studied, indicating that this release is mainly availability controlled. The fraction of alkali metals not dissolved may be bound feldspars or in glass and slag as for the bottom ash. Calcium is also released in high amounts since it is present mainly in acid soluble compounds. However, dissolving the fly ash in sulphuric acid results in a significant formation of gypsum as shown by the low fraction of calcium in solution. Depending on the goal of the ash treatment this may be desirable or not.

The results also show that Cu, Zn, Cd and Pb can be removed from the fly ash with high efficiency using hydrochloric acid leaching which is beneficial since these metals are toxic. The nitric acid systems shows less efficient leaching of Cu and Zn as well as poor leaching efficiency of Pb: only 9% could be leached even at pH 2. The sulfuric acid system has comparable leaching efficiencies of Cu, Zn and Cd as hydrochloric acid, but precipitates Pb as sulphate. This means that the leached ash will contain Pb that can be released later on which counteracts our aim to produce a detoxified ash residue.

In order to achieve the most effective leaching of Cu and Zn from both the fly ash and bottom ash from combustor A a pH-level of 2 must be kept. About 70% of the fly ash copper content and 80% of the zinc was released at this pH. The same pH level gave only 30-40% release of Cu and Zn from the bottom ash. In our work on recovery of Zn and Cu from ash leachates the recovery is done using solvent extraction methods (Rydberg 2004). It has been observed that in the separation of Zn from other dissolved metals the main obstacle is the presence of Fe since the complex forming agents used in solvent extraction bind effectively to Fe^{3+} ions (El Dessouky, El-Nadi et al. 2008). The results (table 4) show a low leachability for Fe for the present fly ash as long as the pH was kept at 3 or above. Decreasing the pH to 2 gave a release of Fe of 10-20%. Since the concentration of Fe in the fly ash is quite low this release is not a great obstacle for the solvent extraction separation of Zn. However, a pH of 2 in the bottom ash leaching liquid resulted in a significant release (about 30%) of the iron content. Since the bottom ash contains 70 g Fe per kg dry ash (as opposed to the 20 g/kg fly ash) this will give a quite high concentration, approx. 20 g/l Fe in the resulting bottom ash leachate comparing to 4 g/l in fly ash leachate.

Table 4: The fraction of major and minor fly ash elements released from fly ash A using different acids (20 ± 1 °C, 20 hours leaching time, L/S = 20 v/w, magnetic stirring 100 ± 20 rpm), all results are given in % of total amount of each metal in the dry ash. nd=not detected

	Amount of elements released (%)						
	HCl			**HNO_3**			**H_2SO_4**
	pH 2	pH 3	pH 4	pH 2	pH 3	pH 4	pH 2
Al	62.0±2.2	36.9±5.4	23.8±1.8	50.5±0.5	41.0±4.1	8.1±1.1	64.2±0.5
Ca	51.8±1.3	47.1±2.9	33.0±4.0	40.5±0.4	37.0±0.3	26.2±0.1	5.7±0.2
Cu	70.2±2.2	28.1±11.6	9.5±4.8	47.5±5.6	30.0±11.9	5.0±1.5	50.9±0.3
Fe	19.5±0.5	4.5±0.6	nd	9.5±0.6	9.0±0.1	3.4±1.6	24.5±0.7
K	97.5±2.8	87.6±3.5	85.5±2.4	82.3±0.8	74±0.2	71.2±2.5	82.7±2.9
Mn	52.2±2.9	29.1±2.2	16.4±6.2	38.0±0.5	30.5±2.8	14.9±0.1	60.5±2.2
Na	90.0±2.1	88.6±5.7	84.0±4.3	100±3.7	100±2.3	92.4±1.6	81.3±0.7
Pb	34.9 ±0.6	8.9±0.3	8.3±0.7	9.2±0.1	9.0±1.3	7.1±0.1	2.17±0.2
Si	51.5 ±1.8	20.3±6.8	7.3±4.6	51.5±0.7	39.5±4.4	9.5±0.6	50.5±1.6
Ti	nd	nd	nd	nd	nd	nd	nd
Zn	80.2±1.6	69.0±4.8	56±4.3	65±0.1	63±1.3	57±1.8	80.0±1.5
Cd	93.3±3.1	82.7±5.3	78.3±7.2				88.9±3.6

Table 5: The fraction of major and minor bottom ash A elements released using nitric acid (20 ± 1 °C, 20 hours leaching time, L/S = 20 w/v, magnetic stirring 100 ± 20 rpm), all results are given in % of total amount of each metal in the dry ash. nd=not detected

Element	**Amount released from the bottom ash (%)**	
	Nitric acid	
	pH 2	pH 4
Al	36.1±1.3	2.0±0.1
Ca	58.0±0.2	37.3±4.5
Cu	30.2±8.7	5.3±4.8
Fe	30.9±2.7	8.5±2.5
K	23.5±1.8	9.5±2.6
Mn	49.5±1.5	19.4±3.7
Na	23.5±0.3	13.2±1.0
Pb	2.4±2.0	nd
Si	18.8±0.2	3.2±0.8
Ti	nd	nd
Zn	39.0±2.5	23.7±0.5

The copper, lead and zinc is considerably more leachable from the combustor A fly ash than from the bottom ash in the pH range used, and that could be explained when studying particles from bottom ash under a microscope. It was relatively common to find metals pieces glazed in molten ash, i.e. glass. This part of the metal content is very difficult to leach out since silica glass does not dissolve readily in acid.

An interesting observation was that approx. 20% of the silicon in the bottom ash and 50% of silicon in fly ash was released at pH 2. This corresponds to about 40 g/kg and 35 g/kg of silicon in both ashes respectively that dissolved in nitric acid medium. Equilibrium speciation calculations for the bottom ash leachate using the PhreeqC software (Parkhurst 2013) and the wateq4f database (Ball and Nordstrom 2001) verified that the solution was oversaturated with respect to silica, silica gel and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$ and close to oversaturated with respect to gypsum. All leachates obtained from the bottom ash formed a brownish gel and a particulate precipitate after storing for one day. Identification of the precipitate by XRD has been attempted but the results were unclear due to its non-crystalline nature. However, the color of the gel indicates that some of the dissolved iron oxidized and precipitated as ferric hydroxide. This gel-like precipitate increases the difficulty for further metals recovery from the bottom ash leachates.

The low efficiency of leaching the target metals Cu and Zn from the bottom ash A in addition to the problems with high Fe concentration in the leachates and the risk of gel formation lead to a decision not to continue working on acid leaching of bottom ash. Probable alternatives are mentioned by two companies; a thermal waste treatment followed by a dry discharge of bottom ash is reported to recover metals such as iron, aluminum, copper by Hitachi Zosen INOVA(HitachiZosen) and a dry treatment is developed by INASHCO (Bin Hu 2009).

The results from leaching of fly ash B in hydrochloric acid are shown in table 6. In this ash the metals Cu, Cd, Pb and Zn are present in compounds that are highly acid soluble. Already at pH 4 leaching yields of 70-100% were obtained. Decreasing the pH to 2 increased the yield of Zn from 72% to 84% and the yield of Cu from 93% to 100%. However, at the same time the release of Fe increased from 11% to 41% which may be a serious drawback.

Comparing the leaching results for the two fly ashes A and B indicates that the chemical forms of Cu, Cd and Pb in these ashes are different since their solubilities are so different. For Zn the difference is not so significant. The XAS results obtained in this work verified that fly ash A contains copper compounds that are less soluble that those of fly ash B. The zinc species, on the other hand, gave rather similar SAX spectra indicating similar speciation (section 4.1).

Table 6: The fraction of major and minor elements released from ash B using hydrochloric acid (20 ± 1 °C, 20 hours leaching time, L/S = 14 v/w, magnetic stirring 100 ± 20 rpm), all results are given in % of total amount of each metal in the dry ash. nd =not detected

Element	**Amount released from the ash B (%)**		
	Hydrochloric acid		
	pH 2	pH 3	pH 4
Al	56.1±0.8	45.1±0.1	8.0±0.1
Ca	70.9±1.1	67.4±2.4	71.4±1.3
Cd	100±2.5	100±3.5	100±2.5
Cr	36.0±1.2	26.1±0.1	Nd
Cu	100±1.4	94.7±0.5	93.0±0.4
Fe	41.3±0.1	30.8±0.1	11.6±0.1
K	95.0±1.2	96.0±1.0	100±1.1
Mg	75.4±1.3	72.5±0.1	70.8±0.7
Mn	73.5±1.0	65.8±0.1	68.9±1.1
Na	68.5±0.9	69.0±0.7	67.1±0.0
Pb	86.1±1.4	84.7±1.1	85.1±0.9
Si	53.3±0.9	41.9±0.2	3.8±0.1
Ti	2.9±0.3	Nd	Nd
Zn	84.2±0.6	76.6±0.4	72.7±0.3

4.2.2. Investigation of leaching parameters for leaching of fly ash samples

Investigation of leaching kinetics

Both fly ash samples A and B were leached at pH levels 2, 3 and 4 in the pH static titrator using 3 M hydrochloric acid solution to keep the pH constant. The numbers of acid equivalents used are presented in figure 6. In the pH range of 2 to 4, these two ashes show different leaching behaviors. The acid consumption indicates that the compounds of ash B dissolve quite fast in the first 10 minutes and the equilibrium is obtained in less than 2 hours. For the ash A, it takes quite a long time to reach the equilibrium, more than 20 hours is required.

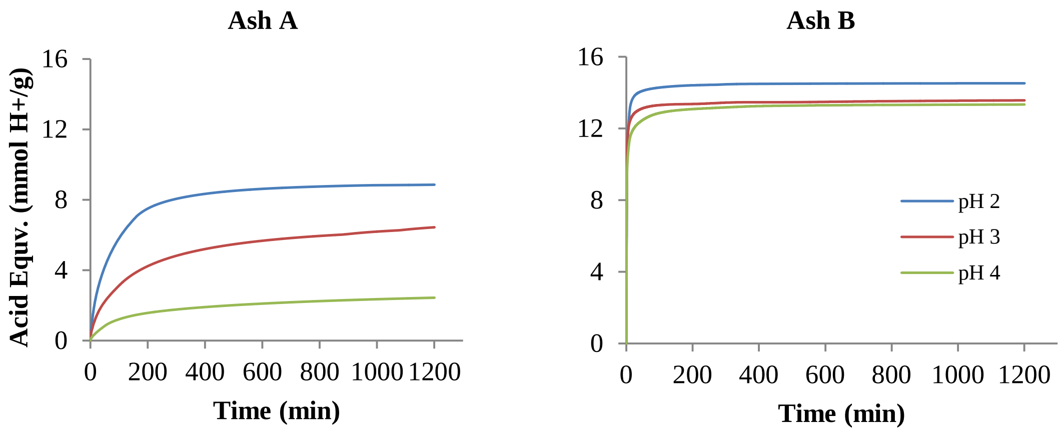
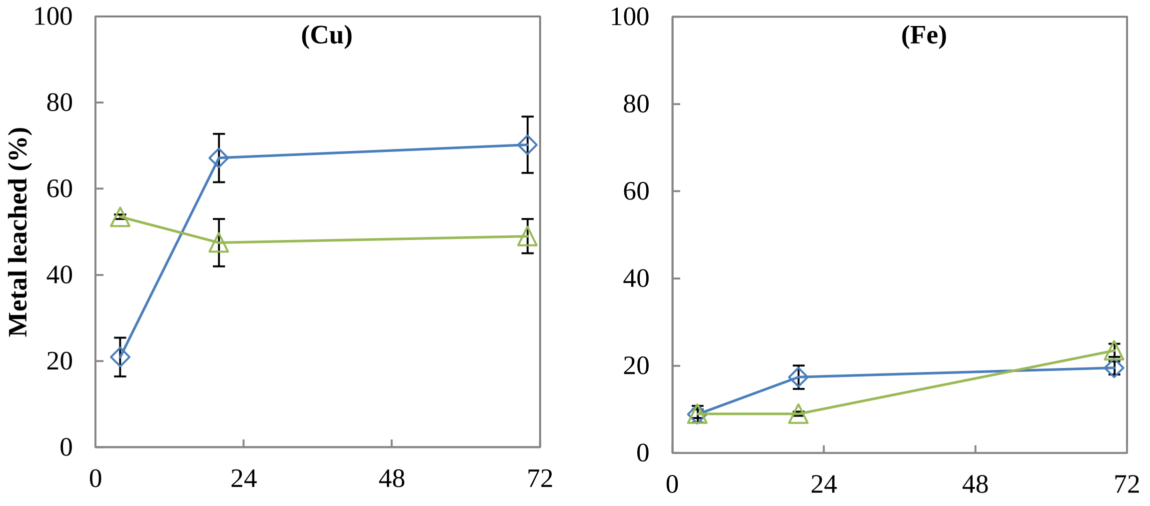


Figure 6: Acid consumption in mmol H^+/g ash as a function of time and pH for fly ash samples A and B. Hydrochloric acid (3M) was used to keep the pH-levels constant, temperature 20 ± 1 °C, 20 hours leaching time, L/S 20 for ash A and 14 for ash B (v/w), magnetic stirring 100 ± 20 rpm)

However, only the general leaching behavior for the ash matrix at pH 2 is shown in figure 6. Leaching of particular elements need to be investigated separately. The leaching kinetics for copper, zinc, iron and lead from fly ash A in HCl and HNO_3 respectively are presented in figure 7. For leaching with hydrochloric acid, the amount of all these metals released increased as the leaching time was increased but their leaching kinetics were different. The nitric acid medium gave higher leaching rates for Cu and Pb than the hydrochloric acid solution did but the total amounts of metal released were lower. This indicates that hydrochloric acid attacked Cu and Pb bearing minerals more than the nitric acid did. For Zn, the leaching kinetics were similar in both acids, the yield was, however, higher in hydrochloric acid. The higher yield of these metals in hydrochloric acid is probably due to formation of soluble chloride complexes.



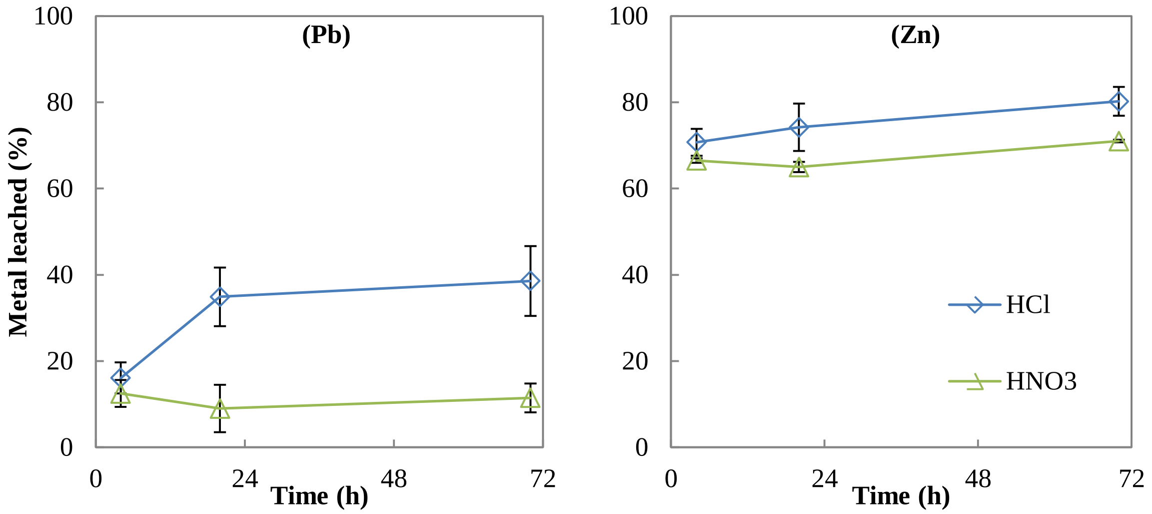


Figure 7: Copper, iron, lead and zinc leaching kinetics of fly ash A between 4 hours and 3 days (controlled pH 2, 20 ± 1 °C, L/S = 20 v/w, magnetic stirring is 100 ± 20 rpm). Standard deviation based on triplicate test.

With respect to the better leaching efficiencies for copper, zinc and lead which are probably caused by formation of soluble chloride complexes with these metals, HCl is a better choice than HNO_3 for leaching this particular ash as was discussed earlier in this thesis.

The experiments with nitric acid leaching showed a decrease in the amounts of Cu, Pb and Zn in the leachate with time. Additional tests were made to investigate if this was due to adsorption of metal ions on activated carbon particles surfaces. These leaching experiments were made at pH 4 where the adsorption should be more favored that at pH 2. The results are shown in figure 8.

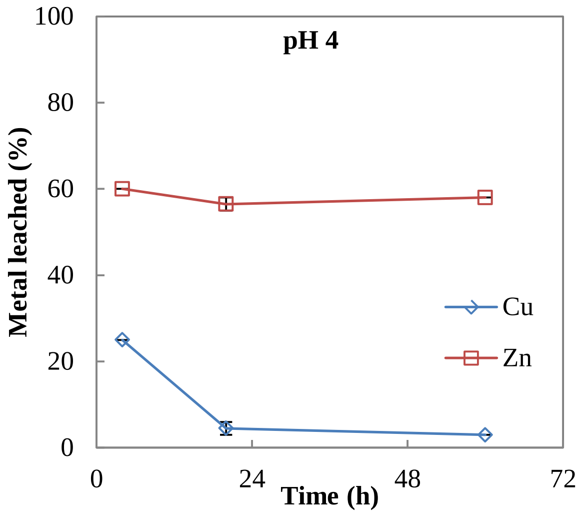


Figure 8: Leaching behavior of copper and zinc using nitric acid at pH 4 (controlled pH 4, 20 ± 1 °C, L/S = 20 v/w, and magnetic stirring 100 ± 20 rpm). Standard deviation based on the triplicate test.

It was observed that the amount of Cu and Zn present in the leachates decreased with time at pH 4. As shown in figure 8 the amount of copper in the leachate went down to almost zero whereas the amount of Zn in solution was not significantly affected. Since the content of copper and zinc ions in solution are far from the saturation and Copper has a high affinity to the types of adsorption sites present on activated carbon which makes it plausible that this is what happened here. Zinc ions are also prone to adsorb on carbon but less so than Cu^{2+} ions at these pH levels. Further work will be done to clarify the influence of adsorption in ash leaching at acid pH.

Results from leaching of metals from fly ash B in hydrochloric acid are shown in figure 9. The dissolution kinetics of copper, zinc, lead and iron components are significantly fast in this medium. The amount of copper dissolved in HCl solution at pH 2 was almost at equilibrium values in less than 2 hours. The release of lead and zinc was fast in the first hours and increased slowly with time. The fraction of Fe leached showed a maximum after a couple of hours and then decreased. This could be due to oxidation from Fe(II) to Fe(III), which can lead to precipitation of Fe(III).

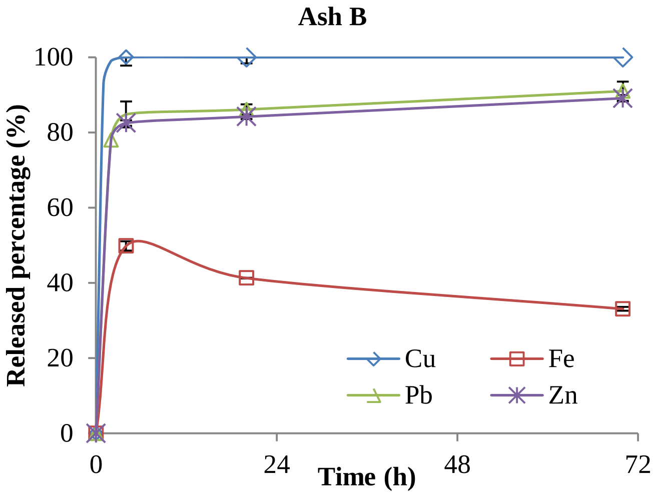


Figure 9: Ash B, Copper, zinc, lead and iron leaching kinetics between 4 hours and 3 days (controlled pH 2, 20 ± 1 °C, L/S = 14 v/w, magnetic stirring is 100 ± 20 rpm). Standard deviation based on triplicate test.

The influence of liquid to solid ratio on leaching of metals

The influence of liquid to solid ratio (v/w) on the release of metals from both fly ash A and B was investigated using a hydrochloric acid solution at constant pH levels. Figures 10 and 11 present the results that an increased L/S v/w ratio leads to different behaviour for different metals and also different leaching behaviours for the studied metals in the different ashes.

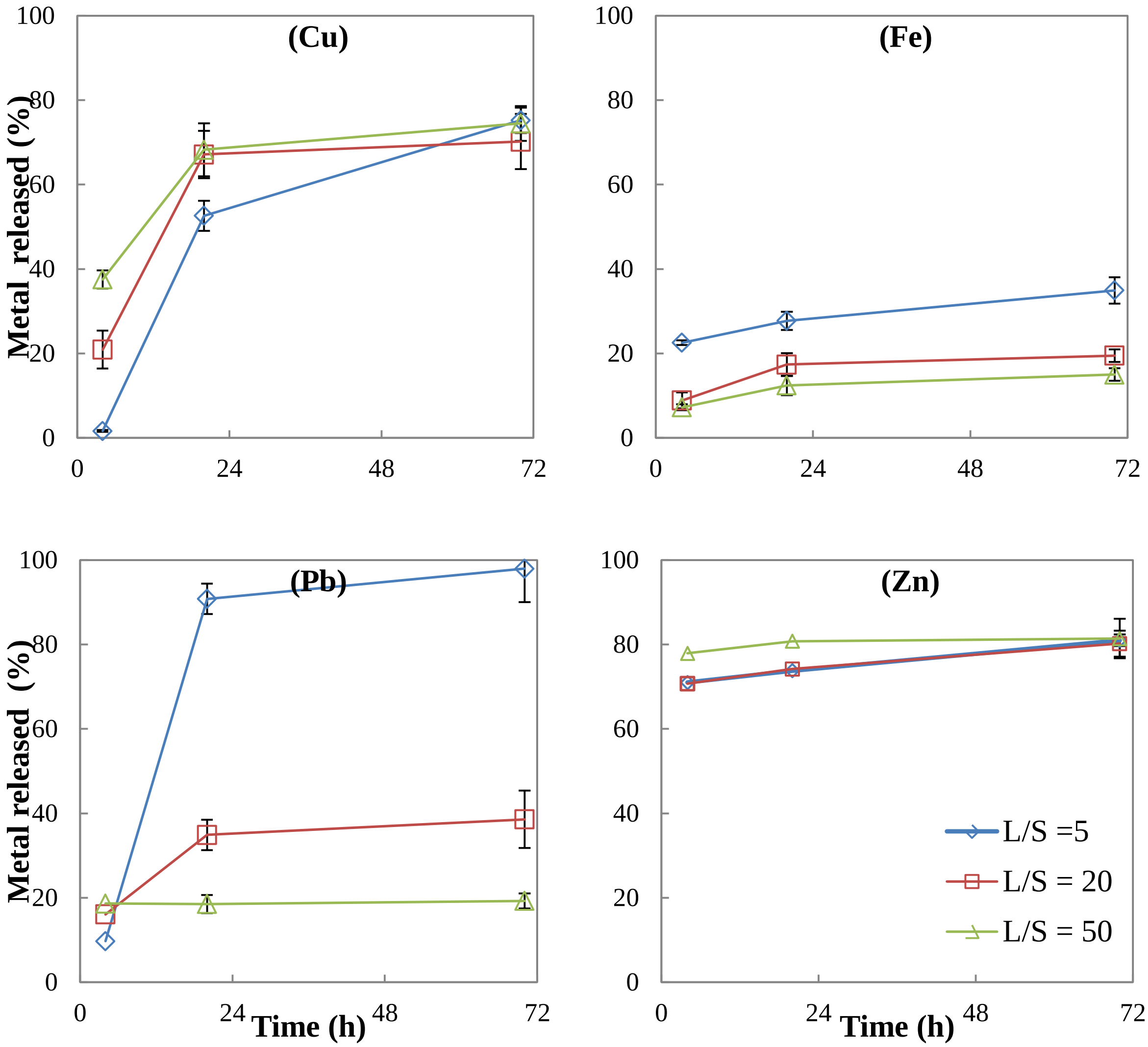


Figure 10: Leaching behavior of Cu, Fe, Pb and Zn from fly ash A at constant pH 2 in hydrochloric acid and varied L/S ratios (20 ± 1 °C, magnetic stirring 100 ± 20 rpm) (Tang, Lassesson et al. 2014).

For Cu and Zn, the increase of liquid to solid ratio (v/w) from 5 to 50 generally had a positive effect on the leaching kinetics but the total yield was similar when reaching 70 hours leaching time. Using higher L/S resulted in a decreased leaching of Fe from approximately 20% to 10%. Liu and Millero investigated the behaviour of iron(III) in acidic chloride medium and found that a high ionic strength promotes Fe(III) solubility (Liu and Millero 1999). This indicates that the observed lower iron leaching at L/S 50 than at L/S 5 can be due to the lower ionic strength.

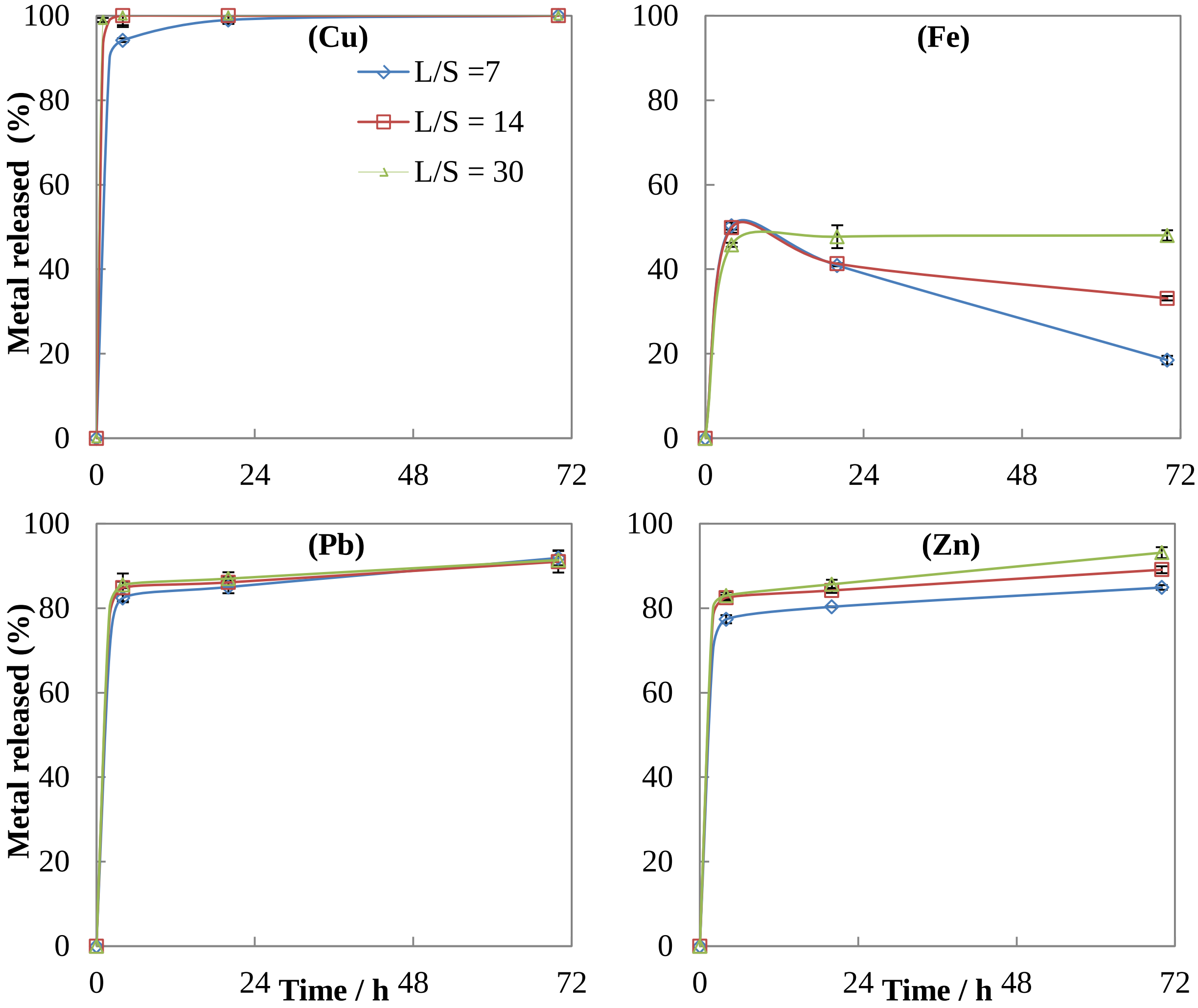


Figure 11: Ash B (a) Copper (b) iron (c) lead (d) zinc leaching behavior between 4 hours and 3 days with increasing L/S ratio, (controlled pH 2, 20 ± 1 °C, L/S = 20 v/w, magnetic stirring is 100 ± 20 rpm) all samples were measured with ICP-OES, standard deviation based on the triplicate.

For ash B an increase in liquid/solid ratio from 7 to 30 did not affect the leached amounts of Cu, Pb and Zn. However, the results for this ash indicate, as opposed to the results obtained for ash A, that iron in the leachate was oxidized and precipitated after an initial dissolution.

Since the experiments with the different fly ash samples were done in different parts of the project the liquid to solid ratios used in the experiments were not exactly the same but close enough to make them comparable (Steenari, Björefors et al. 2014).

The total released amount of Pb in fly ash A leachates decreased siginificantly from more than 90% to rougly 20% with increasing L/S ratio. To investigate the reason for the Pb behavior, ion chromatography was used to measure the concentration of sulphate ions in the leachates. The results presented in figure 12 show that an average of 27.9 ± 0.8 µM/l and 41.8 ± 1.3 µM/l of sulphate ions were determined in the liquid/solid ratio 5 and 50 solutions. The increased sulphate release is probably caused by dissolution of $CaSO_4$. It is also probable that precipitation of $PbSO_4$ is the reason for the decreased percentage of soluble Pb at higher liquid to solid ratio.

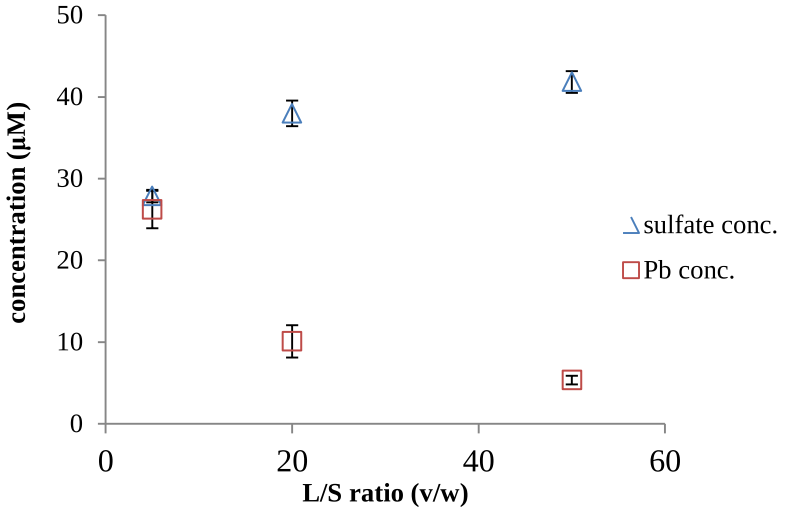


Figure 12: Sulfate and lead ion concentration in fly ash A leachate related to liquid to solid ratio (hydro chloric acid, controlled pH 2, 20 hours leaching time, 20 ± 1 °C, and magnetic stirring 100 ± 20 rpm).

Influence of temperature

The leached percentages of zinc from fly ash A are shown in figure13. Leaching at 60 ± 5 °C gives no clear improvement for the release of zinc in either nitric acid or hydrochloric acid, compared to leaching at 20 ± 1 °C. However, the solubility of iron was clearly affected giving higher release at higher temperature. Similar results have been reported for sulfuric acid leaching (Nagib and Inoue 2000). It is possible that increasing the temperature will influence the leaching kinetics due to the temperature dependence of the activation energy. This aspect will be investigated in our future work. Thus, the results ontained sofar show that room temperature is suitable for the acid leaching part of our process in order to decrease the iron contamination of the leachate and save the energy for faster kinetics.

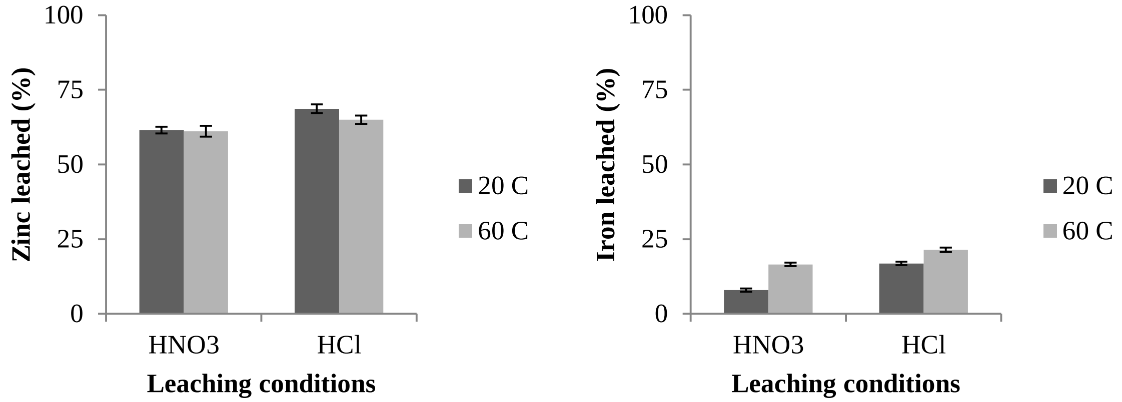


Figure 13: Released percentages of Zn from fly ash A in leaching with 3 M nitric acid and 3 M hydrochloric acid at 20 ± 1 °C and 60 ± 5 °C respectively (controlled pH 2, L/S = 18 v/w, magnetic stirring 100 ± 20 rpm) standard deviation based on a triplicate test.

4.3.Investigation of solvent extractions

The two suggested solvent extraction processes for extraction of Cu and Zn from MSWI fly ash leachates were as a first step investigated separately starting from hydrochloric acid based pH 2 leachates described in section 3.3. For clarity the leachate compositions are given in table 7 below.

Table 7: Composition of the fly ash leachates with pH 2 used as starting points for investigation of the solvent extraction steps for recovery of Cu and Zn. The standard deviation is based on triplicate tests.

Element mg/l	Leachate A	Leachate B
Al	1079.5±39.3	603.9±22.0
Ca	4556.0±121.0	12460.0±430
Cd	4.1±0.1	7.3±0.2
Cr	3.9±0.0	4.1±0.3
Cu	29.0±0.9	300.5±3.7
Fe	184.9±4.6	123.3±1.0
K	906.6±52.2	1210.0±32.2
Mg	678.4±5.2	371.8±14.0
Mn	29.1±1.6	22.5±0.3
Na	1208.0±6.8	985.6±9.7
Pb	60.5±1.0	270.8±1.1
Si	1595.0±59.8	885.7±15.6
Ti	0	0
Zn	678.3±13.4	240.8±3.5

Generally no phase ratio (volume ratio between aqueous phase and organic phase) changes were observed in the experiments. No problems with third phase formation were observed in the experiments. Both zinc and copper extraction processes gave good extraction efficiency and both the equilibrations and phase separations were shown to be fast. The aqueous phases were analyzed by ICP-OES and the metals concentrations in organic phases were calculated using mass balance for extraction and stripping. The main limiting factor for the accurate calculation of distribution ratios was the detection limit of the ICP-OES for the investigated metals (5-50 µg/l).

Influence of the hydrochloric acid concentration in the aqueous phase on the Cu and Zn extraction steps

The influence of the initial pH value of the aqueous phase on the extractions of copper and zinc using LIX860N-I and Cyanex 923 were studied using leachates of ash B and ash A fly ash individually.

The influence of acid concentration on the copper extraction step was investigated using leachates from ash B due to their high Cu concentrations. The extraction efficiency decreases with increasing HCl concentration in the investigated acid concentration range as shown in figure 14, which agrees to the extraction mechanism (Eq.6).

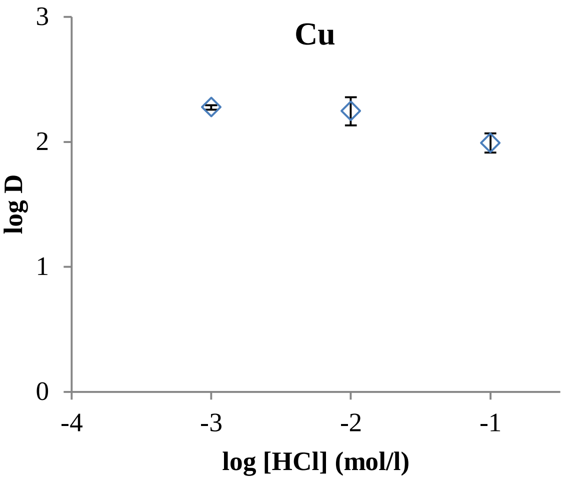


Figure 14: The effect of hydrochloric acid on the extraction of Cu using 1 M LIX860N-I. The extraction was done at 24 ± 1°C, 500vpm for 5 minutes, the phase ratio was 1. Standard deviation based on triplicate test.

Based on the reaction mechanism for the zinc extraction by Cyanex 923 (Eq.8 and 9), the equilibrium of both reaction equations will move towards formation of the zinc-ligand complex at higher hydrochloric acid concentration, thus causing more metal ions transferring to the organic phase, which means higher D value. Figure 2 shows the results of Zn extraction; the distribution ratios of zinc decreased from 72.37 (pH 2) to 28.67 (pH 4), which agrees well the reaction mechanism well.

It could be concluded from figure 15 and table 4 (section 4.2.1) that the zinc extraction should be carried out at a low pH in the investigated acid concentration range, to maximize the distributuion ratio for zinc.

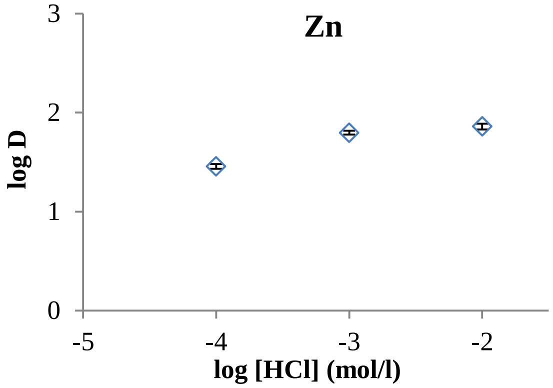


Figure 15: The influence of hydrochloric acid concentration on the extraction of zinc using 1 M Cyanex 923. The extraction was done at 24 ± 1°C, 500vpm for 5 minutes, the phase ratio was 1. Standard deviation based on triplicate test.

Kinetics of Cu extraction with 1M LIX 860-I in Solvent 70 from the HCl leachates with pH 2

The results of the Cu extraction step are shown in figure 16. The extractant LIX 860-I gave a selective extraction for Cu from the leachates from both fly ash A and B. The only metals presented in table 7 that were extracted in measurable amounts were Cu and Fe. Since the content of Cu in the aqueous phases after separation is lower than the detection limit of the ICP-OES instrument the accurate D values are far larger than 100. Small amounts of iron were also observed to be extracted with D values increase from 0.04 (1 minute) to 0.06 (3 minute) and 0.08 (5 minute) for leachate A, and decrease from 0.03 (1 minute) to 0.02 (3 minute) and 0.001 (5 minute) for leachate B. Copper could be separated from iron due to the large separation factors and it is reasonable to suggest that this separation method is feasible for industrial use.

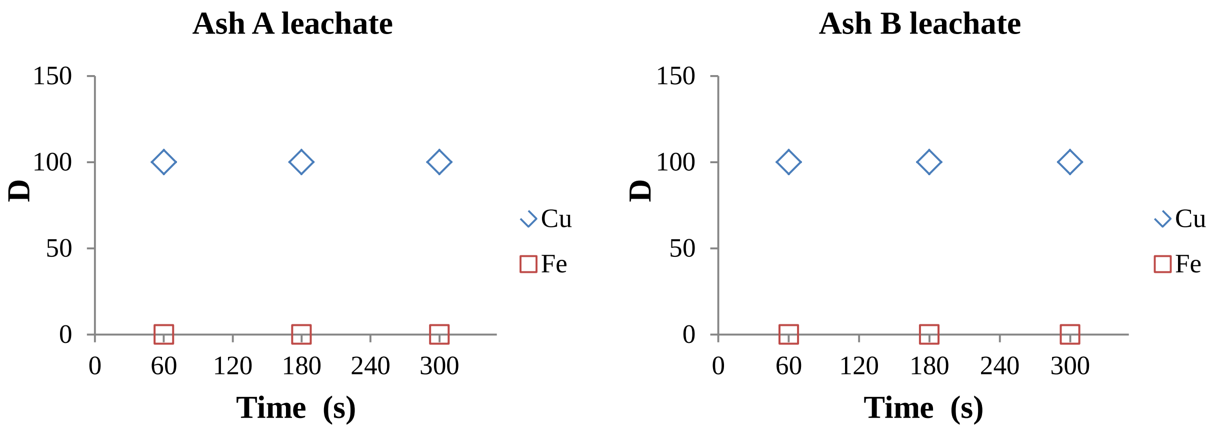
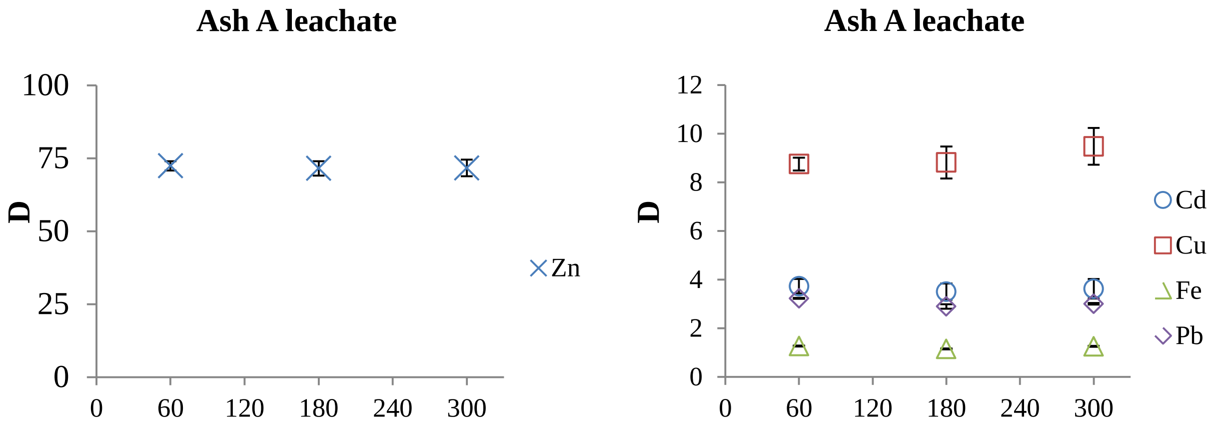


Figure 16: Kinetics of the copper extraction process using 1 M LIX860-I in solvent 70 for copper and undesired elements from two type of ash leachate. The volume ratio of the organic phase to the aqueous phase was 1.

Kinetics of Zn extraction with 1M Cyanex 923 in Solvent 70 from the HCl leachates with pH 2

The results from extraction of Zn from the fly ash A and fly ash B hydrochloric acid leachates with pH 2 (leaching parameters see previous section) using Cyanex 923 are shown in figure 17.



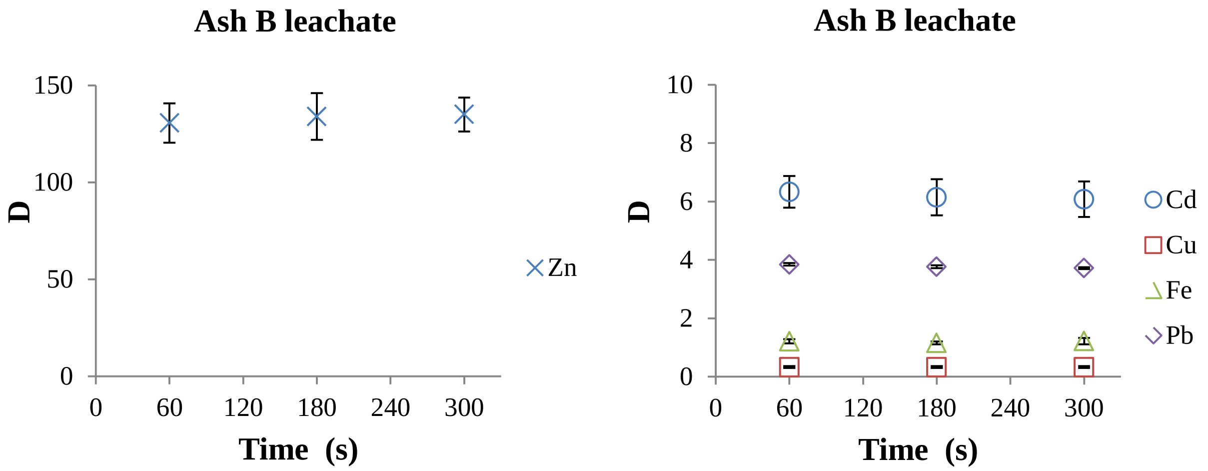


Figure 17: Kinetics of the zinc extraction process using 1 M Cyanex 923 in solvent 70 for zinc, and undesired elements from two type of ash leachate. Standard deviation based on triplicate test.

The extractant is not totally selective for Zn but extracts also Cd, Cu, Fe and Pb. The D-values for the contaminating metal ions are significantly lower than those for Zn but even so, the contaminations will have to be removed in a subsequent step. In a combined process Cu will have been removed but the other metals will remain in the aqueous phase going to the Zn extraction step. The separation factors between the extracted metals are presented in table 8. The distribution ratios are those that were obtained after 5 minutes contact time in the extraction. The separation factor is defined as $SF_{A/B} = D_A/D_B$ as was mentioned in the Background section.

Table 8: Separation factors for the zinc extraction using 1 M Cyanex 923 in solvent 70 from the two ash leachates based on HCl at pH 2 (5 minute contact time, phase ratio 1).

Extraction of ash A leachate

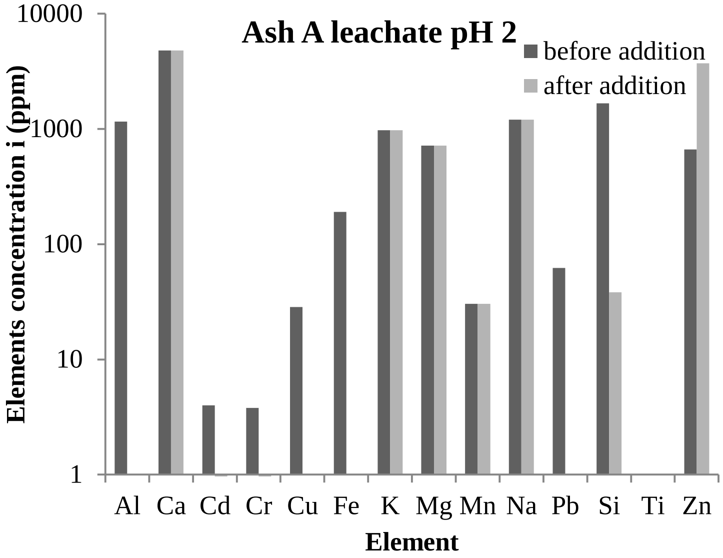
Metal A	Metal B			
	Cu	Cd	Pb	Fe
Zn	7.56 ± 0.94	19.75 ± 2.86	23.82 ± 2.26	56.90 ± 5.44
Cu		2.61 ± 0.36	3.15 ± 0.25	7.52 ± 0.61
Cd			1.21 ± 0.13	2.88 ± 0.32
Pb				2.39 ± 0.04

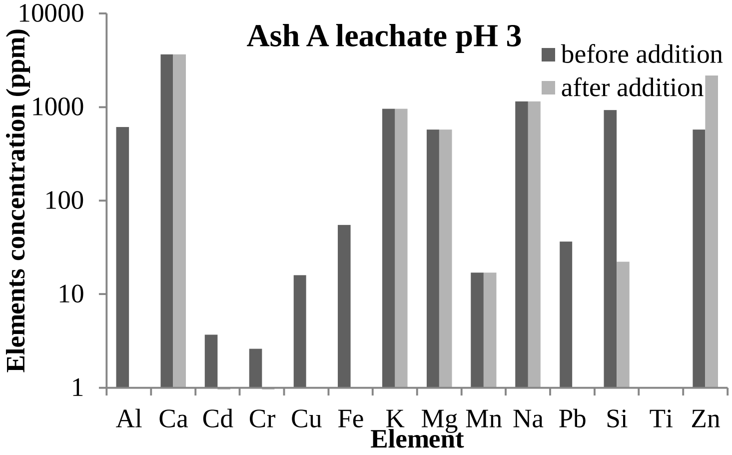
Extraction of ash B leachate

Metal A	Metal B			
	Cu	Cd	Pb	Fe
Zn	409.09 ± 45.74	22.20 ± 2.66	36.29 ± 2.38	110.66 ± 12.31
Cu		18.42 ± 2.49	11.27 ± 1.03	3.70 ± 0.47
Cd			1.63 ± 0.16	4.98 ± 0.67
Pb				3.05 ± 0.28

Reductive cementation using zinc powder to remove co-extracted metals

It is quite clear that the organic phase will contain some contaminating metals along with zinc. A secondary step for removal of these unwanted metals must be introduced if they cannot be excluded in the stripping step. One alternative is to apply a reductive cementation using zinc powder. The principle of this process is that the unwanted ions are reduced to metal by electrons provided by the less noble zinc metal. As a result the zinc dissolves as Zn^{2+}. Figure 18 shows the metals concentration before and after the addition of excess metallic zinc powder, all aluminum, cadmium, chromium, copper, iron, lead and part of the silicon precipitated from the leachate solution. The leachate (controlled pH 2) used here is used to evaluate the copper and zinc recovery process, therefore, this purification procedure can flexibly be added in to the metal recovery process either before or after the zinc extraction.





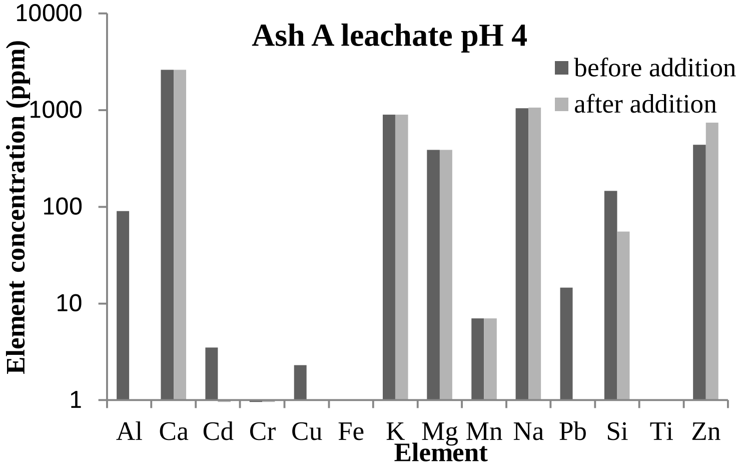


Figure 18: Element concentration in fly ash A leachate (20 ± 1 °C, 20 hours leaching time, L/S = 20 v/w, magnetic stirring 100 ± 20 rpm) before and after zinc power addition

The influence of extractant concentration on the Cu extraction efficiency

Due to the fact that the high content of copper in ash B (5400 mg/kg ash) relative to that of fly ash A (840 m/kg) gave a leachate with significantly higher Cu concentrations, the influence of LIX860N-I concentration on copper extraction was investigated using ash B leachates. The extraction results are shown in figure 19. The efficiency of extraction generally increased upon increasing the concentration of LIX860N-I. The distribution ratio of copper was 99.7 at 0.1 M LIX860N-I and increased to 242.1 at 1.5 M LIX 860N-I.

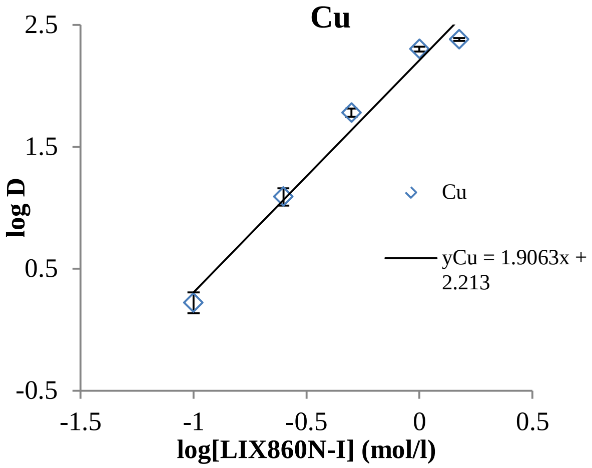


Figure 19: The influence of LIX860N-I concentration on the extraction of copper. The aqueous phases were obtained by leaching ash B for 20 hours, controlled pH value 2, at room temperature 20 ± 1°C, liquid to solid ratio 30 v/w. Organic phases containing 0.1 M, 0.25 M, 0.5 M 1 M and 1.5 M LIX860N-I in Solvent 70 The extraction was carried out at 24 ± 1°C, 500vpm for 5 minutes, the phase ratio was 1. Standard deviation based on triplicate test.

Using the slope analysis method (figure 19), a slope close to two was observed for the copper extraction. The data was correlated to the mechanisms proposed for the copper extraction(Zdravka and Madlena 2005), which confirms that the copper extracted by two molecules.

The high selectivity of LIX860N-I for Cu^{2+} in the acidic chloride solution, makes it possible to calculate the limiting amount of extractant so that the extraction can be carried out close to the loading, i.e. the maximum amount of copper in the aqueous solution, based on the extraction mechanism (equation 6), the reactions between the copper ion and extractant is described as

$$Cu_{aq}^{2+} + 2HA_{org} \leftrightarrow CuA_{2_{org}} + 2H_{aq}^{+} \qquad (11)$$

The influence of extractant concentration on the Zn extraction efficiency

Different concentrations of Cyanex 923 were used to investigate some uncertain points about the zinc extraction:

1. How the extraction is influenced by different concentrations of the extractant in the organic phase;
2. How the co-extraction of undesired elements is affected when using extractant with different concentration;
3. To study the extraction degree described in equation 6 and 7 from real ash leachates based on the theoretical extraction model.

The investigation of zinc extraction using Cyanex 923 as extractant was started with experiments using a synthetic aqueous phase with only zinc dissolved in hydrochloric acid and solution with some extra chloride (sodium chloride) added to simulate the properties of an ash leachate. The composition of the artificial solution was described in section 3.3.2.

The results from zinc extraction from the artificial solution are presented in figure 20. As expected increasing the concentration of the extractant in the organic phase lead to an increase in extraction efficiency of zinc. A slope close to two was observed for the linear equation describing the dependence of logD on log[Cyanex923] was obtained which confirms that the extraction demands two extractant molecules per Zn^{2+} ion (Equation 9). The pH values measured before and after the extraction remain at the same level, also indicating that the extraction mechanism based on equation 10 dominates the extraction at low acidity.

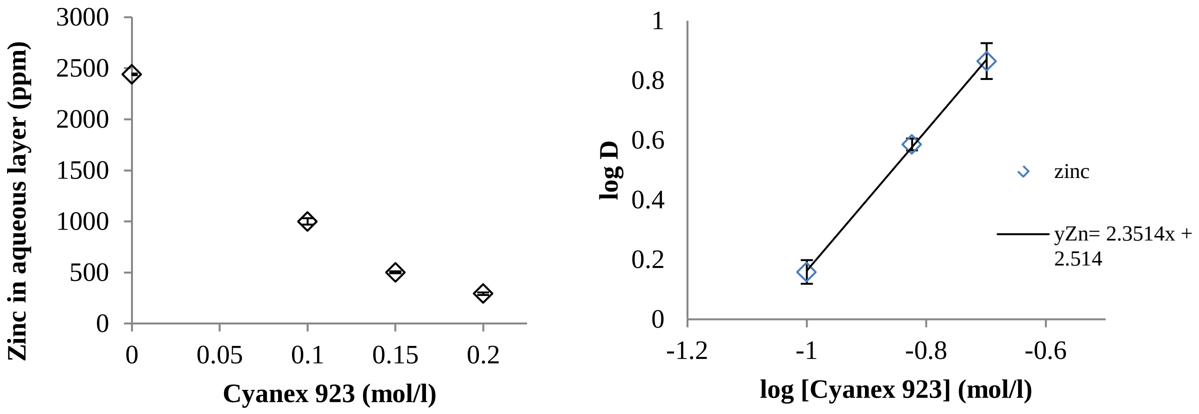


Figure 20: the influence of Cyanex923concentration on the extraction of zinc from the artificial solution. The extraction was carried out at 24 ± 1°C, 500vpm for 5 minutes, the phase ratio was 1. Standard deviation based on triplicate test.

Figure 21 presents the correlations between log[Cyanex923] and logD for extraction of Zn and other metal ions from leachates of sample A fly ash. An increase in the concentration of Cyanex 923 in the organic phase led in all cases to an increased co-extraction of Cd, Cu, Fe and Pb together with Zn. The extraction of cadmium started with a distribution ratio of 0.05 at 0.1 M Cyanex 923 in the organic phase and increased to 3.34 when the extractant concentration was increased to 1 M and to 103.1 when undiluted 2.35M Cyanex 923 was used. The distribution ratio of copper increased from 0.04 (0.1 M Cyanex 923) to 8.81 (1 M Cyanex 923), and to 127.2 when using undiluted extractant. Extraction of iron and lead also was observed using 0.1 M Cyanex 923, the distribution ratios were 0.05 and 0.06 respectively. When using undiluted extractant the D-values increased to 1.92 and 24.47. To minimize the extraction of undesired elements, i.e. preventing the co-extraction of cadmium, copper, iron and lead, a low concentration of extractant should be used. More work is needed on optimization of the extractant concentration.

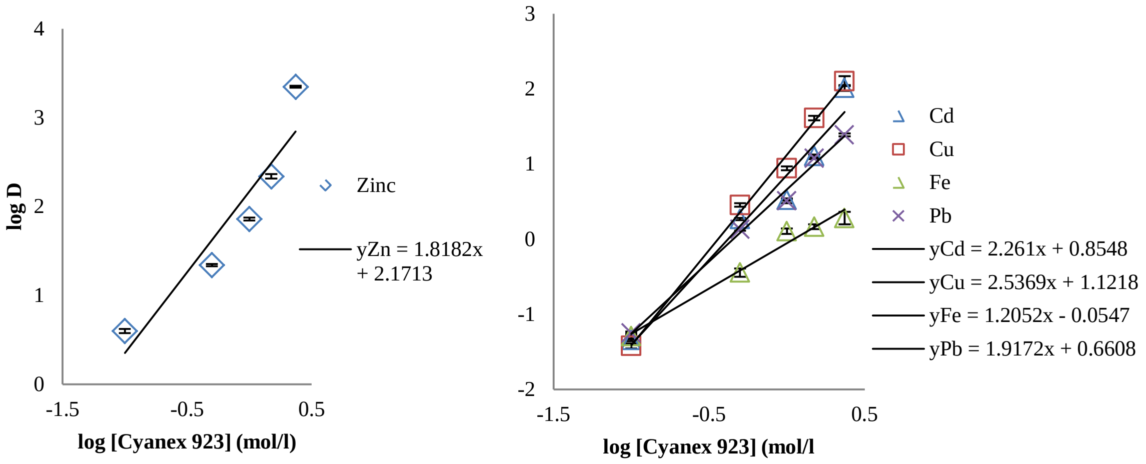


Figure 21: The influence of Cyanex 923 concentration on the extraction of zinc and co-extractions from real leachates. The aqueous phases were obtained by leaching ash A for 20 hours, controlled pH value with 2, at room temperature 20 ± 1°C, liquid to solid ratio 20 v/w. Organic phases containing 0.1 M, 0.5 M, 1 M, 1.5 M Cyanex 923 in Solvent 70 and also undiluted Cyanex 923 (2.352 M). The extraction was carried out at 24 ± 1°C, 500vpm for 5 minutes, the phase ratio was 1. Standard deviation based on triplicate test.

Based on the slope analysis for the curves in Figure 21 the extraction mechanism was confirmed (equation 10). Slight deviations in slope from two are probably due to the high extraction efficiencies when using concentrated organic phase, therefore, the accurate calculations of the distribution ratio was limited by the detection limit of ICP-OES.

4.4.Preliminary evaluation of the Cu and Zn recovery process for MSWI fly ash

The results from section 4.2 and 4.3 indicated that a general leaching of an MSWI fly ash using HCl at pH 2 followed by solvent extraction separation of Cu and Zn consecutively can be feasible. The extractants LIX860N-I and Cyanex 923 were chosen for the extraction of Cu and Zinc respectively. In this section a laboratory evaluation of the suggested process, including leaching, copper separation and zinc separation, is described.

The preliminary evaluation of the recovery process was started with the Cu extraction from leachates of ash A and ash B using LIX 860N-I. The next step was experiments of zinc extraction using Cyanex 923 with the treated aqueous phases from Cu extraction. The general procedure is shown in figure 1 and the experimental methods used are descried in section 3.3.4.

Leaching of the ash

The leachates used for this evaluation were produced from both fly ash samples A and B using the following leaching parameters:

Hydrochloric acid solution as leaching liquid

Constant pH 2 regulated by a potentiostat titrator

Leaching time 20 hours with constant stirring of the slurry

Temperature 20±1 °C

Liquid to solid ratio (volume/weight) 20 for ash A and 14 for ash B

The remaining solids were separated from the leachate by centrifugation as described in the Methods section.

Copper extraction from original leachates

Batch experiments of copper extraction were carried out at 24 ± 1°C using 1 M LIX860N-I diluted in Solvent 70 with phase ratio 1 and a contact time of 5 minutes in a sample shaker working at 500 rpm. The choice of parameters for this extraction was based on results from section 4.3; 5 minutes contact time is enough for the extraction reaching the equilibrium and organic phase with 1 M extractant concentration ensure the extraction efficiency.

The results are presented in figure 22. The extraction equilibrium was reached in a short time and the phase separation worked well. Copper and small amounts of iron (D value < 0.1) were the only metals extracted in the systems as expected.

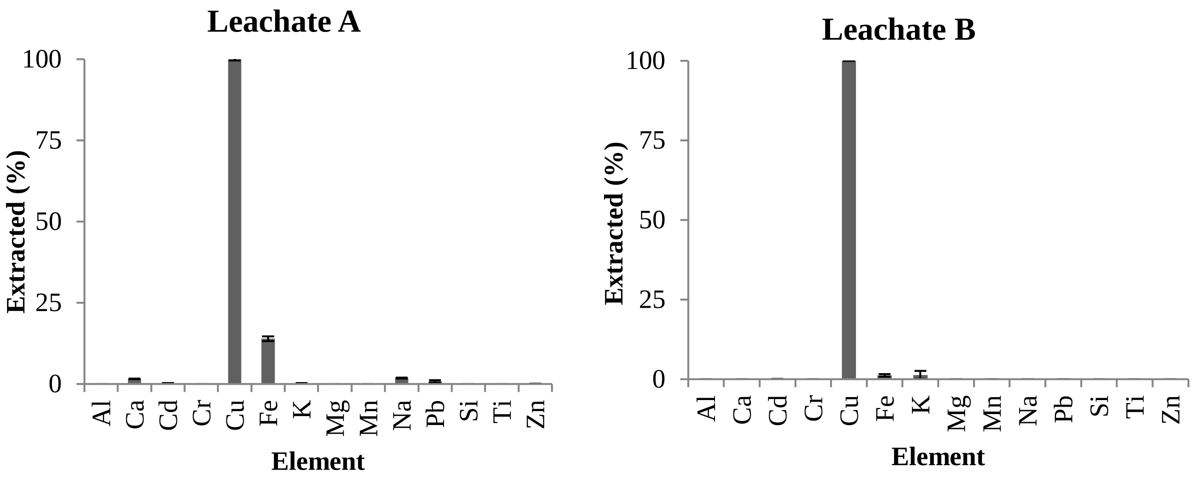


Figure 22: Results from the copper extraction process using 1 M LIX860N-I in solvent 70 at 24 ± 1°C, 500rpm for 5 minutes, phase ratio 1. Standard deviations based on triplicate tests.

Copper stripping

Different concentrations of sulfuric acid were tested to strip Cu from the copper loaded organic phase after extraction with LIX 860-I. Stripping was carried out at room temperature, 20 ± 1°C for 3 minutes using a phase ratio 1. As shown in figure 23 the percentage of Cu stripped increases with stronger acid, 85-95% of Cu was transferred to the new aqueous phase after one step stripping using 1.5M H_2SO_4 acid. Co-stripping of iron was observed for the copper loaded organic phase from ash A extraction. This may be due to the low copper content (roughly 0.028g/l in the organic phase), which favours the iron stripping by excess sulfuric acid. In contrast, copper content of the organic phase from ash B extraction is much higher, 0.3g/l.

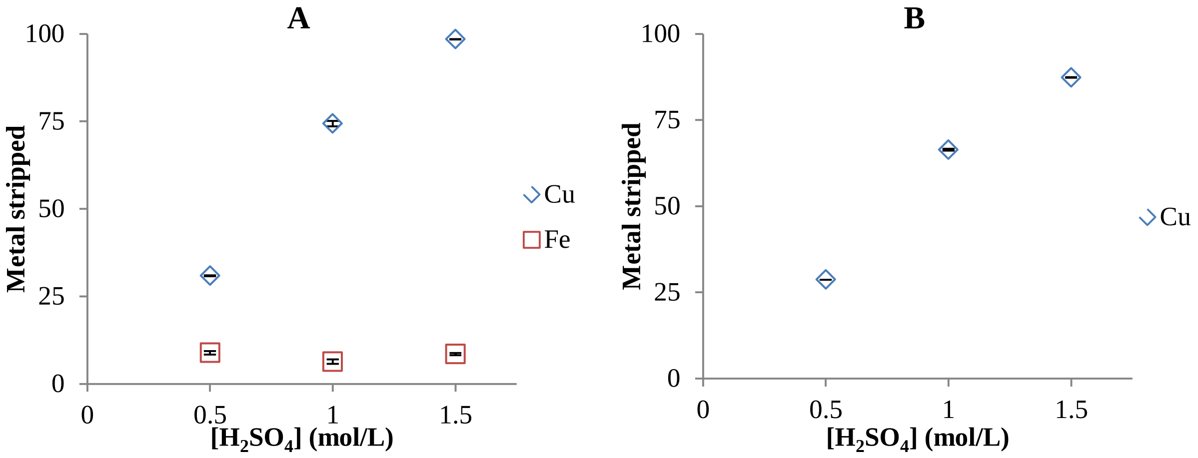


Figure 23: Results from stripping of copper and co-stripping of iron using 0.5 M, 1 M and 1.5 M sulfuric acid solutions. Organic phases containing 1 M LIX860N-I in solvent 70 were loaded with metals from copper extraction. Stripping was carried out at room temperature, 20 ± 1°C for 3 minutes using a phase ratio 1. The error bars show the standard deviation based on triplicate test.

Zinc extraction

The copper-free aqueous phases were then extracted using 1M Cyanex 923 diluted in Solvent 70 and using phase ratio 1, contact time 1 minute under constant shaking at 500 rpm in a laboratory shaker. The extractant concentration 1 M was chosen to get good extraction of Zn while keeping co-extraction of other metals on a reasonable level. As expected from earlier results undesired co-extractions, e.g. cadmium, iron and lead occurring parallel to the zinc extraction were observed (Figure 24)

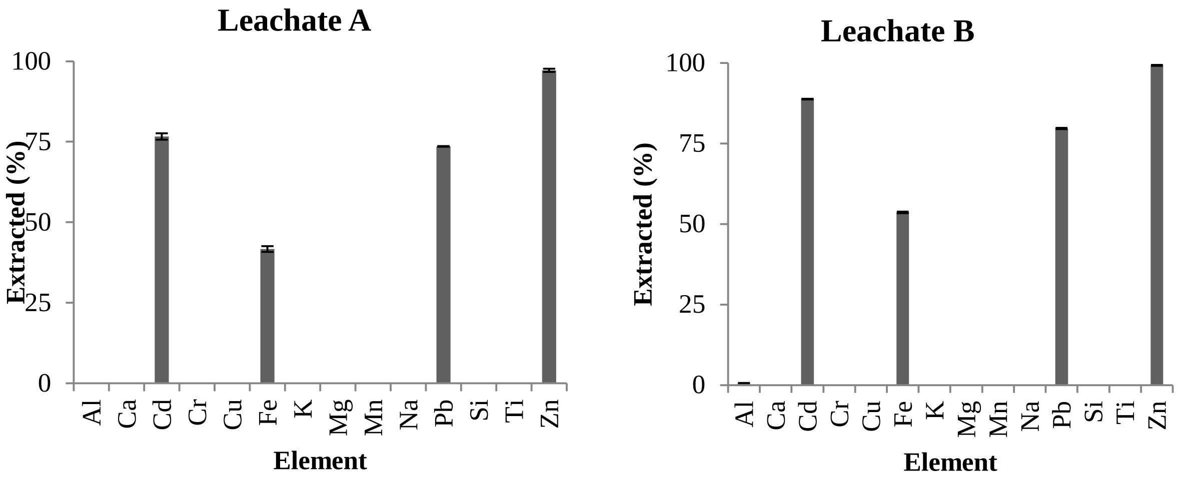


Figure 24: Zinc extraction process using 1M Cyanex 923 in solvent 70. The aqueous phases were from the 1st copper extraction. The extraction was taken at 24 ± 1°C, 500rpm for 1 minutes, the phase ratio was 1. Standard deviation based on triplicate test.

Zinc stripping

Nitric acid, hydrochloric acid and sulfuric acid solutions were studied in stripping to recover the metals in the organic phases from zinc extraction for sample A. The tests were carried out at 20 ± 1°C using a phase ratio of 1 and a contact time of 3 minutes under shaking as described earlier.

The results are shown in figure 25. Very low efficiencies were observed using hydrochloric acid: less than 1% of zinc was stripped using 3 M hydrochloric acid. Therefore, this reagent was not considered for further investigation.

Sulfuric acid solutions were shown to be effective in stripping of especially zinc and cadmium, almost complete stripping was obtained using 1.5M sulfuric acid. In addition approximately 40% of the lead and 35% of the iron was also stripped. Thus, sulfuric acid does not offer an opportunity to selectively strip zinc from the organic phase.

Nitric acid (1M) gave almost complete stripping of zinc and cadmium. With 1M nitric acid 80% of the lead, and even roughly 95% when a 3 M solution was used, was also transferred from the organic phase. However, a selective stripping that excludes most of the iron is achievable by using diluted nitric acid (1M) solution. This method made it possible to separate the iron from the zinc. Further stripping of the organic phase with sulfuric acid allowed the removal of iron, making possible the reuse of the organic phase.

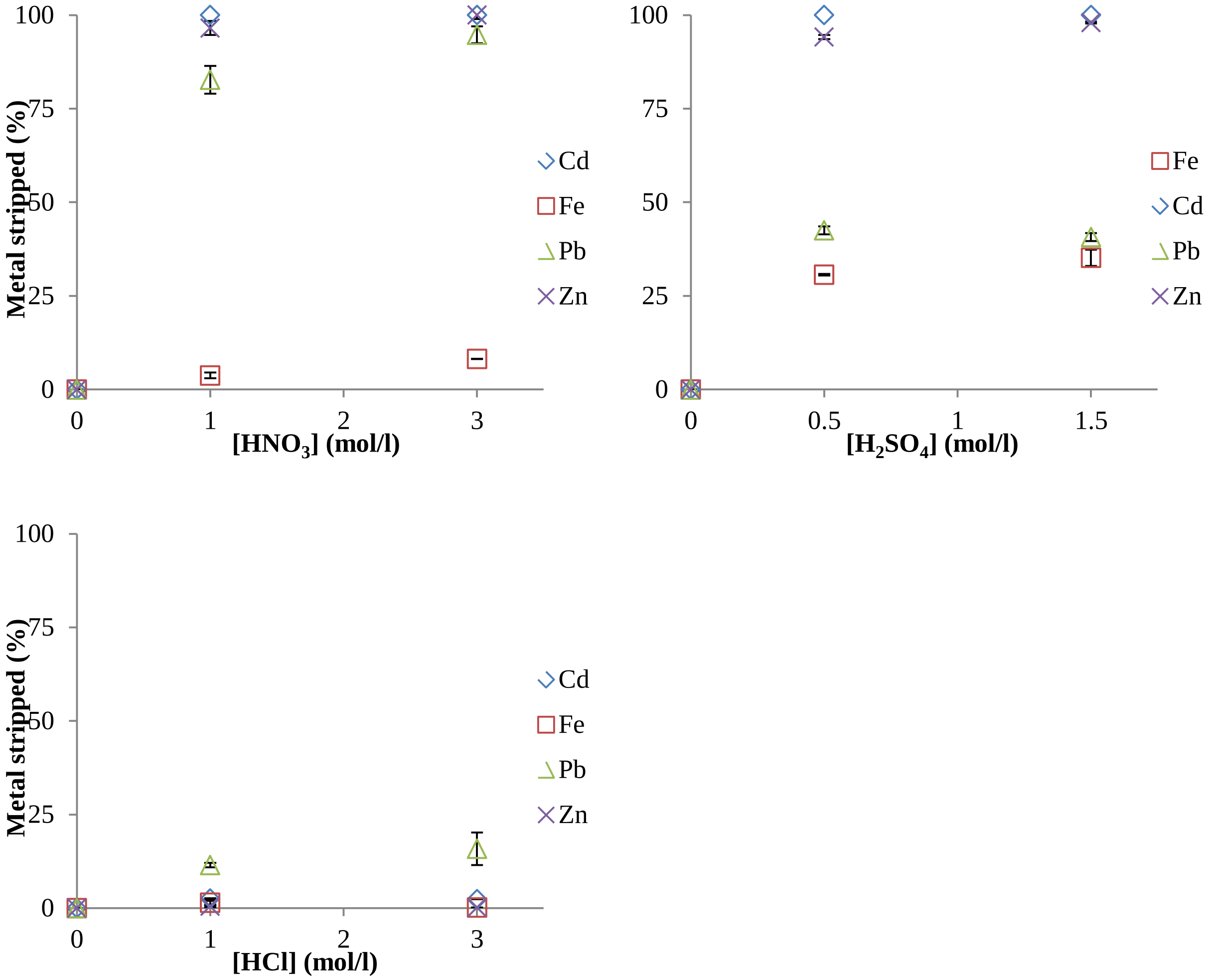


Figure 25: Results from stripping using 1 M, 3 M nitric, hydrochloric acid and 0.5 M 1.5 M sulfuric acid solutions. Organic phases containing 1 M Cyanex 923 in solvent 70 were loaded with metals from zinc extraction of Cu-free leachate A. Stripping was performed at room temperature 20 ± 1°C for 3 minutes using a phase ratio 1. The error shows the standard deviation based on triplicate test.

The possibility of selective stripping was validated using organic phase from zinc extraction of leachate B. Figure 26 shows the results for both ash samples. It is clear that it is not possible to get an aqueous solution that contains only zinc since cadmium, lead and a small amount of iron will be stripped as well. However, as has been discussed earlier in this thesis, it is possible to precipitate the contaminating metals by reductive reaction with zinc metal powder. It is probably also possible to adjust an electrolysis step to recover only Zn. In the FLUREC process used in Switzerland the zinc is recovered by electrolytical reduction directly in the organic phase after extraction (Schlumberger, Schuster et al. 2007).

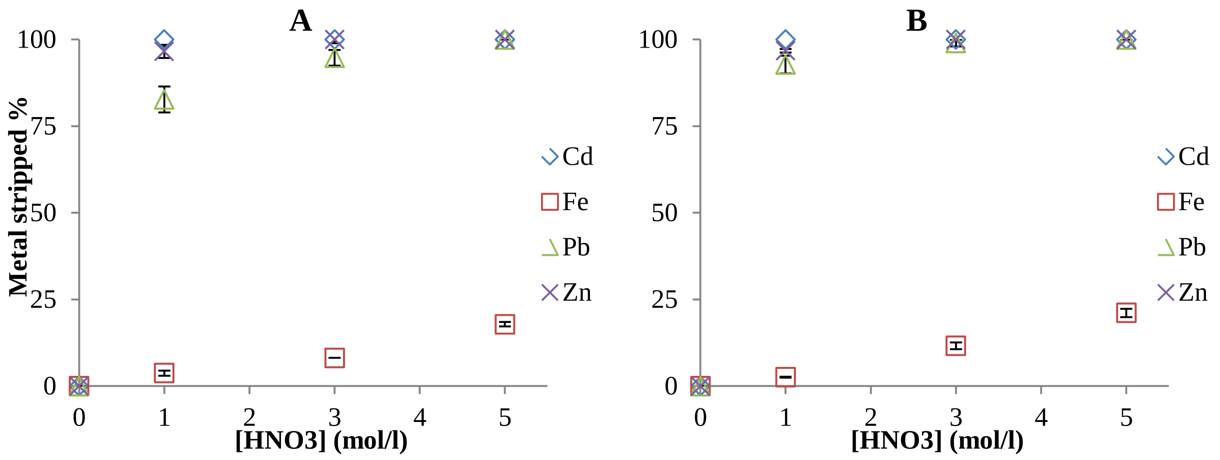


Figure 26: Stripping using 1 M, 3 M and 5 M nitric acid Organic phases containing 1 M Cyanex 923 in solvent 70 were loaded with metals from both ash A (A) and ash B (B) 2nd zinc extraction. Stripping was performed at room temperature 20 ± 1°C for 3 minutes using a phase ratio 1. The error shows the standard deviation based on triplicate test.

A summary of the overall results in a combined process for recovery of copper and zinc from MSWI fly ash is given in table 9. The copper and zinc recovery results refer to those obtained in leaching at pH 2 with hydrochloric acid, extraction of copper and zinc using 1 M LIX 860-I, Cyanex 923 respectively diluted in Solvent 70 and stripping copper and zinc from organic phases using 1.5 M sulfuric acid and 1 M nitric acid respectively. All phase volume ratios in extraction and stripping used are 1.

Table 9.1: Recovered amounts of Cu, all results given in %

	Ash A fly ash	Ash B
Leaching	70.2 ± 2.2	100.0 ± 1.4
Extraction	100	100
Stripping	98.4 ± 0.1	87.3 ± 0.1
Totally	69.1 ± 2.2	87.3 ± 1.9

Table 9.2 Recovered amounts of Zn, all results given in %

	Ash A fly ash	Ash B
Leaching	80.2 ± 1.6	84.2 ± 0.6
Extraction	97.2 ± 0.5	99.3 ± 0.2
Stripping	96.5 ± 1.9	96.8 ± 0.5
Totally	75.2 ± 2.1	80.9 ± 0.7

The total leaching-extraction procedure is described as a flow sheet in Figure 27. It is important to note that the recovery yield of Cu and Zn in the leachate will vary between different ash types depending of the ash properties and the leaching medium used. The optimization of this recycling process will be a part of the further work in this project.

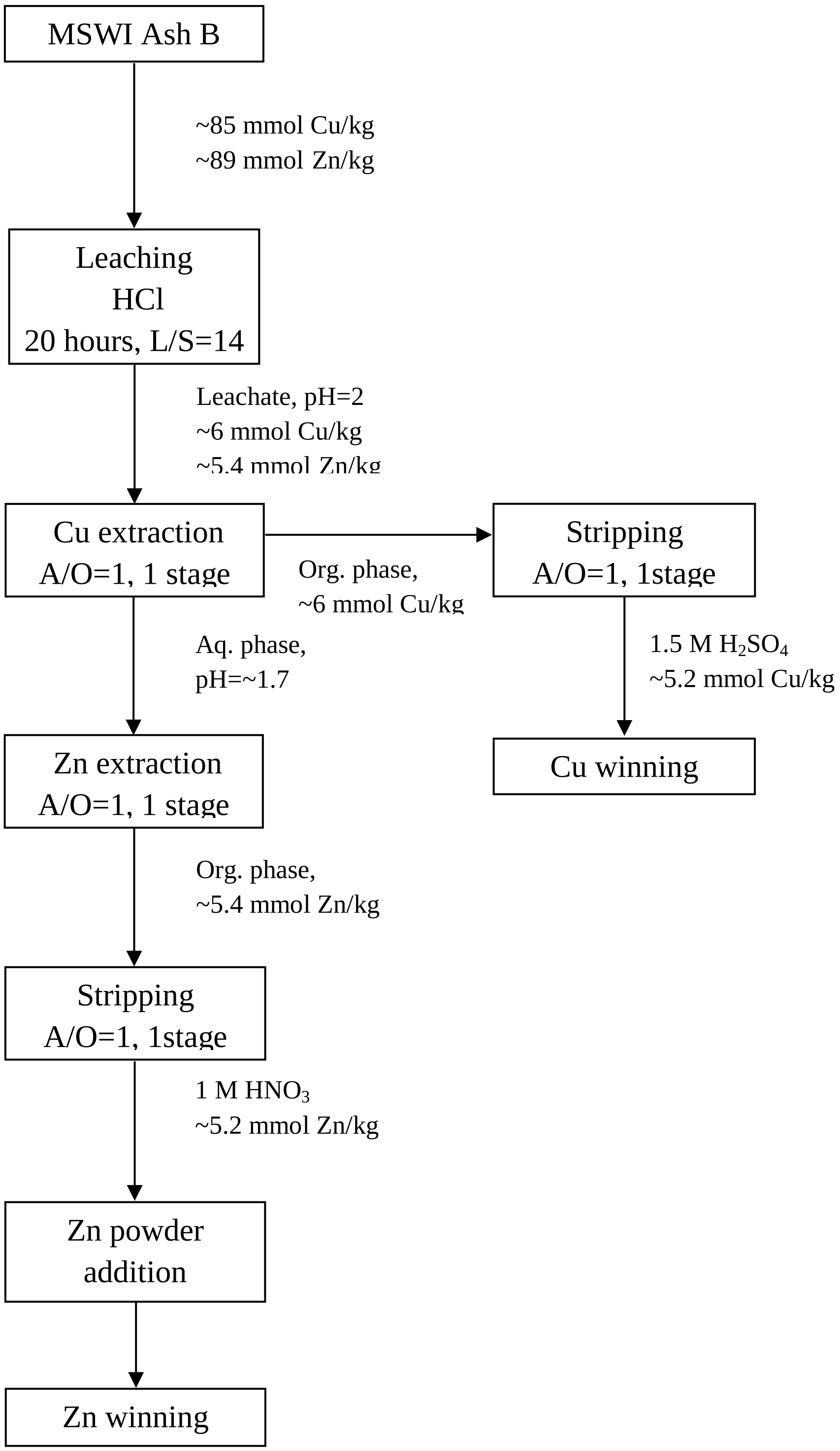


Figure 27. Flow chart of the recovery method developed for Cu and Zn from MSWI fly ash

5. Conclusions

The results of this investigation of how the release of certain metals and other ions from MSWI ashes is affected by the type of acid used, the leaching parameters, such as leachate pH, temperature, time and liquid to solid ratio showed that the leaching yield can be significantly affected by all these parameters in addition to by the chemical and physical nature of the ash matrix. The best choice of leaching process and parameters depends on the aims of the ash treatment. One set of parameters might not promote both recovery of valuable metals and removal of toxic components at the same time. These findings, that is consistent with those published by others, show very clearly that a leaching process must be adapted to the properties of the ash to be treated.

More specifically, leaching of the fly ashes from one grate fired MSW combustor and one fluidized bed combustor also firing MSW studied in this work, aimed at removal of as much as possible of the contents of Cu and Zn and as little as possible of the content of Fe. The reason for this choice was that the leachates will be used a feed for a solvent extraction separation process to recover Cu and Zn as pure metals. In the Zn recovery process Fe is a problematic contamination. A second aim was to de-toxify the ash residue as much as possible which means to remove Pb and preferably also Cd.

It was shown that parameter settings that promote all these aims can be found. In terms of efficiency and tendency to dissolve different metals in ash, the liquid to solid ratio plays a critical role: higher liquid to solid ratio leads to higher leaching efficiencies of Zn and Cu, and the amount of leached Fe, the obstacle for Zn recovery, could be lower. Lower liquid to solid ratio is an option for an effective removal or recovery of Pb from ash and the Zn and Cu leaching can still remain at a relatively high level. Based on the results, several potential methods could be used in the recycling of metals from fly ash. If recovery of copper and zinc is prioritized, the optimized leaching conditions are hydrochloric acid leachate with controlled pH value 2, up to 20 hours leaching time, room temperature, 20°C, liquid/solid ratio of 50 (v/w), to avoid the obstacle impurities of lead and iron as much as possible. If not only recovery of copper and zinc, but also removal or recovery of lead, is required, decreasing the liquid to solid ratio to 5 leads to more lead leached; very good efficiencies, greater than 95% for lead could be obtained and a significant fraction of the cadmium in the ash was removed as well.

The fly ash from the grate fired boiler contained activated carbon from the flue gas treatment system. In order to avoid re-adsorption of metal ions from acid leachates to the carbon surfaces a pH below 4 must be used.

The grate fired combustor bottom ash, which is rich in glassy slag and metal pieces, was very difficult to leach due to its matrix. The bottom ash released a large amount of Fe to the leachate and the leachate gave a gel-like precipitate in a short time making it not suitable for metal separation by solvent extraction. In addition, leaching of this ash would create problems with secondary wastes. Other, more feasible methods for metal recovery from MSWI bottom ash must be developed.

The XAS results indicate copper compounds with lower solubility in ash A (copper(I)chloride and/or sulfide along with copper(II)phosphate and/or silicate) than in ash B (copper(II) in form of chlorides, hydroxides and sulphate), which helps to explain the differences in copper yield during leaching. The similarities in zinc XAS results between the two ashes could explain why there also were no large differences in zinc yield during leaching of the two ashes.

Recovery of copper and zinc from hydrochloric acid media was performed using solvent extraction. Two commercial extractants were studied in the work, LIX860N-I was investigated for copper extraction, and a mixture of phosphine oxides (Cyanex 923) was used for zinc extraction. For the copper extraction, LIX860N-I showed high selectivity and efficiency; copper was extracted with high D value and only slight amount iron ($D < 0.1$) was co-extracted. Cyanex 923 extracted zinc effectively; however, co-extraction of copper, cadmium, iron and lead occurred. The extraction kinetics for copper and zinc, as well as the co-extractions is fast, the equilibrium was achieved within one minute.

An increase of the extractant concentration in the organic phase gave increased efficiency in copper and zinc extraction, as well as for the co-extractions. The initial pH value has only a slight influence on the copper extraction (in pH range from 1 to 3). In contrast to this, zinc extraction works better at lower pH values, whereas the distribution ratios of its co-extraction of cadmium and lead were slightly affected in studied pH range.

The extracted metals were easily stripped from the metals loaded organic phases using selected acidic solutions. Strong sulfuric acid (1.5 M) can easily recover the copper from LIX860N-I. Both nitric acid and sulfuric acid shows high efficiency on zinc stripping. An important difference is that the stripping efficiency of iron is low (< 5%) using dilute nitric acid (1 M). Therefore, separation of iron form zinc is possible during the stripping process. Alternatively a reductive cementation of the contaminating metals (Fe, Cd and Pb) by addition of Zn metal powder to the aqueous phase after stripping can be used to clean this solution before the final recovery of Zn.

A preliminary evaluation of the total recovery process of copper and zinc from the two MSWI fly ashes was done and quite good results were achieved for both metals from ash A (69% of the Cu and 75% of the Zn) and ash B (87% of the Cu and 81% of the Zn). The efficiency of the leaching step was pointed out to be the limiting factor in achieving an effective recovery.

Industrial scale separation of zinc and undesired elements can probably be possible due to the large separation factors shown by the extraction agents used. However, more work is needed on the optimization of parts of the process and on the scaling up of the total process to make it possible to evaluate it from an economic point of view.

6. Future work

The following aspects of the process will be studied in the continued work:

1. A larger range selection of ashes should be tested, for both leaching and extraction process.

2. Further clarification of the chemical mechanisms involved in both leaching and extraction is needed.

3. Expansion of the XAS database and speciation of other interesting elements, e.g. lead in original ashes and leaching residues.

4. Choice of a process sequence giving the optimum results regarding copper and zinc recovery yields, if it is possible also to maximize the removal of lead and cadmium.

5. Tests of the solvent extraction steps in the mixer-settler pilot plant for the industrial scale experiment.

6. Determination of the properties of the ash residue after leaching, especially the stability against leaching with water.

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