THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Removal and Recovery of Metals from Municipal Solid Waste Incineration Ashes by a Hydrometallurgical Process

JINFENG TANG

Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

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JINFENG TANG
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Nuclear Chemistry and Industrial Materials Recycling
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1000

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Municipal solid waste incineration fly ash

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Abstract

Municipal Solid Waste Incineration (MSWI) fly ash contains significant amounts of leachable metals, and is therefore considered as hazardous waste. The increased amounts of fly ash generated cause environmental issues, management costs and accumulation of valuable metals in landfills. All these factors contribute to an increased interest in recognizing the ash as an urban mining target of metal resources. Recovery of metals, e.g. copper and zinc from fly ash, is not only beneficial for the availability of valuable metals that otherwise would be lost, but it can also decrease the amount of potentially soluble and toxic metal compounds in the ash residue, making it possible to landfill the ash at a lower cost.

A hydrometallurgical process for the recovery of copper and zinc from MSWI ash is presented in this thesis. The process consists of leaching followed by sequential solvent extraction of metals. With respect to leaching efficiency and feasibility, it was found that hydrochloric acid is the best option for recovery of copper and zinc from the fly ash. In addition, efficient leaching of cadmium and lead was also achieved.

A commercial extractant, LIX860N-I, was chosen for the copper extraction. No third phase formations or phase separation problems were observed. The copper extraction gave a good extraction yield with high selectivity. The extracted copper in organic phase can be stripped in a one stage process using a selected sulfuric acidic solution (1.5 M). Zinc extraction followed the copper extraction by extracting the raffinate using Cyanex 272, Cyanex 572 or Cyanex 923. Cyanex 923 showed the highest efficiency and no pH adjustment of the aqueous phase was needed. However, this extractant co-extracts iron, cadmium and lead with the zinc. A novel phosphorus-based extractant, Cyanex 572, is less effective, but more selective for zinc extraction compared to Cyanex 923. Selective stripping processes were suggested for zinc extraction using Cyanex 572 and Cyanex 923, respectively.

Laboratory pilot scale experiments using mixer-settler systems were carried out based on the batch experiment results. McCabe Thiele diagrams were used to model the processes with respect to the number of stages needed for conducting the extractions in mixer-settler systems. The solvent extraction process was then demonstrated in pilot size mixer settler equipment consisting of two stages for copper extraction and three stages for zinc extraction and gave a recovery of 90% of the copper and ~100% of the zinc in the leachate.

Keywords: MSWI ash, copper, zinc, leaching, solvent extraction, LIX860N-I, Cyanex 572, Cyanex 923, mixer-settler.

LIST OF PUBLICATIONS

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

Paper I:
Tang, J., Steenari, B.-M., 2016. Leaching optimization of municipal solid waste incineration ash for resource recovery: A case study of Cu, Zn, Pb and Cd. Waste Management 48, 315-322.
Contributions: main author, all experimental work

Paper II:
Tang, J., Lassesson, H., Steenari, B.-M., 2014. Resource recovery from municipal solid waste ash, The 29th International Conference on Solid Waste Technology and Management, Philadelphia, PA U.S.A., pp. 352-361.
Contributions: main author, majority of the experimental work, the X-ray absorption data treatment and analysis was done by Henric Lassesson

Paper III:
Tang, J., Steenari, B.-M., 2015. Solvent extraction separation of copper and zinc from MSWI fly ash leachates. Waste Management 44, 147-154.
Contributions: main author, all experimental work

Paper IV:
Tang, J., Ylmén, R., Petranikova, M., Ekberg, C., Steenari, B.-M., Comparative study of the application of traditional and novel extractants for the separation of metals from MSWI fly ash leachates, manuscript
Contributions: main author, all experimental work

Paper V:
Tang, J., Petranikova, M., Ekberg, C., Steenari, B.-M., 2016. Mixer-settler system for the recovery of copper and zinc from MSWI fly ash leachates: An evaluation of a hydrometallurgical process, Journal of Cleaner Production, 148, 595-605.
Contributions: main author, majority of the experimental work

Table of Contents

1. Introduction

In recent years the amount of municipal solid waste incineration (MSWI) ash produced annually has rapidly increased in the world, due to the wide use of combustion for energy recovery from MSW. The content of problematic metals, such as mercury, lead, copper, zinc, cadmium and chromium in toxic and leachable forms in the MSWI ash, especially in fly ash, creates a serious challenge for its handling and landfilling [1, 2].

Various methods of MSWI ash treatment and stabilization have been developed over the years. Thermal treatment has been suggested to evaporate the toxic metals in the fly ash or to stabilize them in a glassy matrix [3, 4]. Thermal evaporation removes the toxic metals in vapor form, with or without the use of additives such as addition of extra chlorine to form metal chlorides with lower boiling points than corresponding metals or metal oxides [5, 6]. Thermal stabilization, e.g. sintering or vitrification, aims to convert the fly ash into a ceramic or glass-type material to decrease the leachability of metals [7-12]. The problems of thermal treatment are the formation of new flows of material that have to be handled in an appropriate way, together with the associated high energy consumption [13]. Evaluation of the thermal treatment methods has shown that these are not economically feasible [14-16].

The use of additives to the ash for stabilization has also been put forward as a viable option. One of the more drastic treatment methods is to add cement and water to the fly ash to encapsulate it in a dense solid matrix. However, many other methods are based on removal of chloride and sulfate, in addition to a binding of metals in less soluble forms. The aim is to avoid the common situation that the ash does not comply with leaching limit values due to release of harmless salts. All of the stabilization methods are based on the view that most MSWI fly ash components are hazardous. Therefore, the approach has been to retain the constituent chemical compounds in the stabilized fly ash and thus stop them from being emitted by leaching. It means that the treated ash might still be hazardous to the environment, especially if the material is disintegrated [17, 18]. Even if the ash is enclosed in concrete or in a landfill, the high leachability of fly ash metal compounds can be a critical issue [19, 20].

The increased amounts of ashes generated and accumulation of valuable metals in landfills has contributed to an increased interest in recognizing the ash as an urban mining target of metal resources. The main goal of this project was to investigate and develop a process that is technically feasible in an industrial scale for the recovery of copper and zinc from MSWI ash and that gives pure metal concentrates as well as removing as much of the toxic metals from the ash as possible. The developed process should be robust enough to be able to handle considerable variations in the ash.

The aim and scope of this work was to investigate the possibility of reducing the concentrations of toxic metals in MSWI ash and to recover copper and zinc sequentially, based on a combination of leaching and selective solvent extraction.

2. Background and Theory

2.1. Municipal solid waste incineration ash

Municipal solid waste incineration (MSWI) generally 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 glassy silicate slag, metal objects, and minerals with high melting points. Fly ash consists of the small particles collected in the flue gas cleaning system of the combustion plant. [21].

Both bottom ash and fly ash, especially the fly ash, contain considerable amounts of metals, salts, organic pollutants and other components, some of which are toxic. This makes it necessary to investigate any suggested utilization carefully [22-24]. Over recent years source sorting of waste in households has improved, which has decreased the metal content in the waste, and consequently in the ashes. The combustion practices have improved and strict regulations for gaseous and particle emissions and handling of solid residues (ashes) have been implemented, but still the millions of tons of MSWI ashes produced annually are considered as troublesome waste. In the European Union almost 80 million tons of waste are combusted annually. The content of copper in the waste is lower than that of zinc, with common copper contents in MSWI fly ash of 3000-5000 mg/kg whereas a common zinc content is 10 000-30 000 mg/kg.Treatment of MSWI ash.

Since MSW combustion ashes are commonly landfilled, or used as construction materials on landfills, large quantities of metals are more or less lost [25, 26]. Reclaiming these resources at a later stage will be significantly more difficult than recovering them in a process directly subsequent to the combustion. In the ongoing transition of industrial material use from a linear to a circular model the development of such processes is ongoing [27, 28]. Schlumberger and co-workers have developed a recovery method for zinc based on acid leaching, solvent extraction and electro winning [29]. Other initiatives have been to separate metals as chlorides in a hydrocyclone [30] and to remove metals by combinations of thermal methods (for cadmium, copper and lead) and hydrochemical methods (for zinc, chromium and nickel) [31].

2.2. Characterization of ash

Many factors can influence leaching behaviors, including chemical speciation, particle size, minerals and incinerator type [32, 33]. Speciation analysis is of major importance as it provides crucial evidence on the mineral phases and chemical form of target metals present in the waste matrix, and this basic understanding at a molecular scale is essential in the management of environmental pollution [34, 35].

Techniques and methods have therefore been developed for speciation analysis. X-ray powder diffraction is used for qualitative (and in some cases quantitative) analysis of the crystalline compounds of major elements in ash. The detection limit is about 2 wt.% of each compound for mixed materials [36, 37].

Since the concentration of trace elements in fly ash is always less than 0.1 wt.%, the detection limit makes direct analytical speciation of these metals impossible with XRD. Even zinc, which generally is the most abundant trace metal in fly ash, is present in total concentrations below 2 wt.%.

Sequential extraction procedures have been used to determine the speciation, or chemical associations, of particular metals [38, 39]. However, it has also been reported that sequential extraction leads to alterations species of metal speciation during the different extraction steps. Formation of new compounds, adsorption of dissolved ions onto organic matter or minerals are typical secondary processes that can affect the results. If this occurs, the results obtained from sequential extraction do not provide an accurate account of trace metal compounds within the major matrix compounds, which have a significant influence on the experimental results. Therefore, the protocols have been extensively discussed and questioned [40-43]

Synchrotron radiation based X-ray Absorption Spectrometry (XAS) is a technique capable of identifying metal species and has been widely applied to the investigation of environmental materials, such as soils and sediments. It has also been used to elucidate the chemical speciation of metals in ash samples [44]. Extended X-ray Absorption Fine Structure (EXAFS) can be used to determine the chemical structure information, such as coordination number of the element of interest, bond distances, and the identity of neighbor atoms [45]. In addition to the investigation of the EXAFS region, the X-ray Absorption Near-Edge Structure (XANES) also provides some valuable information about the oxidation states and structure of compounds [46-48]. A combined analysis of data from XANES and EXAFS using Linear Combination Fitting (LCF) of spectra from reference compounds can be a valuable tool for identifying the compounds present in a mixture.

This has therefore been used as a method to investigate hazardous wastes and evaluate the potential use of wastes as sources of valuable elements [49-54].

So far, not many investigations of chemical speciation of copper and zinc in MSWI ash using XAS have been published, and the reported results are quite variable. The species of copper were reported to be $CuCl_2$, CuO, $Cu(OH)_2$, and a small amount of CuS was found [35]. However, it was also indicated that the predominant species were $CuCl_2 \cdot 3Cu(OH)_2$ and $CuCl$, and no pure $CuCl_2$ was found [54]. In another investigation it was found that CuO and $CuSO_4 \cdot 5H_2O$ were the main copper compounds in the fly ash [55]. Lassesson and co-worker explained the difference in copper leaching yield for two ashes by comparing the copper speciation, the one with higher solubility was copper sulfate, hydroxides and chlorides, and the another one was of less soluble copper compounds (Cu(II)phosphate/-silicate along with Cu(II)oxide and Cu(I) sulfide/-chloride) [41]. Zinc species have been reported as oxides, silicate [53, 56], or chloride, oxide and sulfide [57], while $ZnCl_2$, $3Zn(OH)_2 \cdot 2ZnCO_3 \cdot xH_2O$ and $ZnSO_4 \cdot 7H_2O$ were the major species found in another study [49].

2.3. Leaching of ash

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

- Diffusion of the solvent into the pores to reach the actual mineral/compound surfaces,
- Chemical dissolution at the mineral surface in the pore,
- Transport of dissolved ions out of the pores due to the concentration gradient between compound surface and the bulk leachate outside the ash particle,

Results obtained by using many different leaching agents for MSWI ashes have been reported in the literature; one example is hydrochloric acid that has been found to be feasible to recover chromium, copper, lead and zinc from MSWI fly ash. The efficiency of the acid treatment was dependent on final pH, and increased with an increasing hydrochloric acid concentration [58]. Chloride leaching has several advantages; metal chlorides generally have high solubilites and leaching is promoted by the formation of chloride complexes [59]. In the work of Karlfeldt Fedje and co-workers it was observed that weak organic acids were not as effective as mineral acids as leaching agents, although they form soluble complexes with metal ions [60]. Other complex forming chemicals for selective leaching of specific metals were also studied and the results showed that EDTA was effective for removal of copper and zinc and that NH_4NO_3 was an interesting alternative for selective copper leaching, due to the formation of soluble copper-ammonia complexes. 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 the leachate. It has recently been shown that different copper speciation can be an important reason for these differences [41].

The development of a leaching process for the 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 nitric acid, for example, since many combustion units have 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. Another consideration that has to be made is the possible formation and precipitation of secondary products. Sulfuric acid, for example, 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 metal 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, is often observed [61], 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 equal . This surface complex formation may influence leaching efficiency strongly and the binding of metal ions increases with pH [62]. 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 [62]. 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 as well.

One of the fly ashes investigated in this work contains a significant fraction of activated carbon from the flue gas cleaning system. The utilization of activated carbon as adsorbent for dioxins and toxic metals such as zinc, lead, cadmium and copper 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 [63] etc., the pH of the solution has been identified to be the most important [64]. It was reported from several investigations [65, 66] that the adsorption of metals from solution onto activated carbon generally increases with pH.

Results [67] indicate that the adsorption of zinc and cadmium has not be observed at pH< 4 and pH< 2.5, respectively. It has been reported [68] 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 has been discussed [64], 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 aimed at an optimal metal removal the effect of activated carbon in the fly ash has to be taken into account.

2.4. Solvent extraction

2.4.1. General

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 metals. 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.

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.

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

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

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

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

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

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

$$P = \theta \cdot D \qquad \text{(Eq. 4)}$$

The extraction percentage can be converted from the distribution ratio.

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

Several criteria need to be considered when assessing the extractants for industrial applications [69, 70]. 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.

2.4.2. LIX860N-I extractant for copper extraction

LIX860N-I, is an organic extractant that releases H^+ during extraction and forms neutral metal complexes, i.e. an acidic extractant. These ligands often bind to the metal through two or more binding sites since they contain different donor atoms incuding oxygen, sulphur or nitrogen.

LIX860N-I is an aldoxime, as shown in Fig. 1, more specifically the 5-nonylsalicylaldoxime is a typical example having OH-groups as well as a nitrogen. Oximes are generally, especially the aldoxime, known to form stable complexes with copper(II) ions, and oximes are therefore the most commonly used reagents for copper extraction [71]. The extraction of a metal (M) using oxime in acidic solution can schematically be described as:

$$M^{z+}_{(aq)} + zHA_{(org)} \leftrightarrow MA_{z(org)} + zH^{+}_{(aq)} \qquad \text{(Eq. 6)}$$

Where HA denotes the protonated organic extractant.

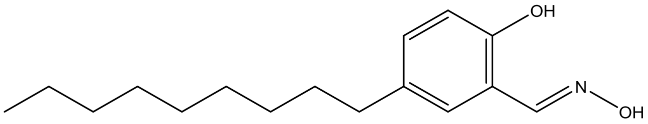

Fig. 1. Chemical structure of LIX extractant

The metal complex formed then transfers to the organic phase, since the molecular structure of the complex is lipophilic. In the extraction reaction using an acidic extractant, 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.

2.4.3. Cyanex 272, Cyanex 572 and Cyanex 923 for zinc extraction

Three commercial extractants were used in this work for zinc extraction; Cyanex 572, Cyanex 272 and Cyanex 923. Cyanex 272 and Cyanex 572 are phosphorous-based acidic extractants and Cyanex 923 is a phosphorous-based chelating extractant. The active component of Cyanex 272 is bis(2,4,4-trimethylpentyl) phosphinic acid (Fig. 2a), which has been proven effective in solvent extraction of zinc [70, 72]. The efficiency of an extraction process including Cyanex 272 as the ligand is dependent on a strict pH control.

Cyanex 923 has also been proven to be an efficient extractant for zinc [73, 74]. It is a mixture of four slightly different tri-alkyl-phosphine oxides (TRPOs). The structure of one TRPO is shown in Fig.2b.

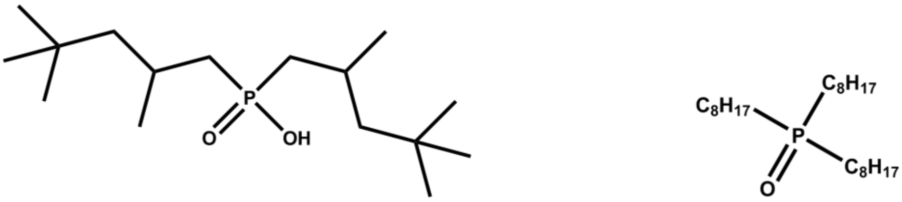

Fig. 2. Chemical structure of bis(2.4.4- trimethylpentyl) phosphinic acid, Cyanex 272 (left) and a typical TRPO (right)

Cyanex 923 has active substances very similar to TOPO (trioctylphosphine oxide) [75]. The only difference is in the length and/or the structure of the alkyl groups. This readily available commercial extractant has been used in the recovery of nickel from aqueous phases of battery leaching as well as REEs from aqueous phase of fluorescent lamp waste leaching in our group with quite high efficiency [76] [77].

Table 1. Chemical composition of Cyanex 923 [75]

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 the n-hexyl group.

All components in Cyanex 923 are solvating extractants. A general extraction using a solvating ligand is described in Eq. 7 [69]:

$$M_{aq}^{z+} + zX_{aq}^{-} + bB_{org} \leftrightarrow MX_zB_{b\ org} \qquad \text{(Eq. 7)}$$

The metal ions are thus extracted together with their counter ions, i.e. as complexes that were already formed in the leachate. In this work X$^-$ represents a chloride ion, and the number of extractant molecules (B) has been found to be two for the extraction of Zn^{2+} ions from an acidic chloride solution [78].

$$ZnCl_{2aq} + 2B_{org} \leftrightarrow ZnCl_2 \cdot 2B_{org} \qquad \text{(Eq. 8)}$$

The composition of Cyanex 572 has not been disclosed yet, but it is reported to be a mixture of phosphinic (H$_2$P(=O)OH) and phosphonic acids (HP(=O)(OH)$_2$), and it is claimed that the extractant has good phase separation and that extracted metal ions can be stripped with a low concentration of acid [79, 80]. At the moment only a handful of investigations using Cyanex 572 in the extraction of rare earth elements (REEs) are available in the literature [81-83]. No investigation of the use of this extractant for zinc extraction has been found in the literature. Eq. 9 shows the extraction mechanism for extraction of three-valent rare earth elements by this ligand [79].

$$REE_{aq}^{3+} + 3HA_{org} \leftrightarrow REEA_{3org} + 3H_{aq}^{+} \qquad \text{(Eq. 9)}$$

Where HA denotes the protonated organic extractant.

2.4.4. Effect of the diluents in solvent extraction

In solvent extraction one of the classification methods for diluents divides them into five classes, based on their abilities to form hydrogen bonds [69]. The classes can be summarized as:

I: liquids capable of forming a three-dimensional hydrogen bond network, e.g. water, poly- and amino-alcohols, .

II: liquids having hydrogen bond donor atoms (such as N, O or F) and active hydrogen atoms (H), but that do not form a three-dimensional network themselves, e.g. primary alcohols, primary and secondary amines,

III: liquids consisting of molecules with bond donor atoms, but no active hydrogen atoms, e.g. ethers, ketones, tertiary amines,

IV: liquids containing molecules with active hydrogen atoms, but no donor atom, e.g. chloroform and some other aliphatic diluents.

V: liquids with no hydrogen bond-forming capabilities and no donor atoms, e.g. hydrocarbons, carbon tetrachloride,

According to the definition water belongs to class I, and the organic diluents of the same class are miscible with water, therefore they are poor choices for a solvent extraction. The effect of diluent on solvent extraction has been described by Löfström Engdahl and co-workers. The nature of the diluent influences the attractive energy between the extracted species and the organic phase, and also the energy that is needed for cavity formation; formation of the hole in the liquid where a species can be placed. Non-polar diluents have a small cost for cavity formation [84].

2.4.5. Mixer-settler equipment and process scale up

Mixer-settler units consist of a mixing chamber and a part where the aqueous and organic phases can separate due to the density difference. Combinations of mixer settlers are used for small-scale continuous tests of solvent extraction processes, as well as in large scale industrial applications. The mixer-settlers can be arranged in many different flow schemes, such as counter-current, which gives a good phase contact. Mixer-settlers are easy to manage and they can handle quite a wide range of flow ratios. The process efficiency can be improved by adding more extraction stages at a low cost. In addition, the results based on small scale mixer-settlers can be linearly scaled up from small scale to full industrial scale [69].

The phase contact time is described in equation (10).

$$\mathrm{T} = V/(F1 + F2) \qquad \text{(Eq. 10)}$$

Where:

T- contact time

V- volume of the chamber

F1- flow rate of the aqueous phase

F2- flow rate of the organic phase

In scale up of a process a modelling of the extraction and stripping steps is made by construction of the extraction isotherm in a diagram according to the McCabe-Thiele method [85]. The so called McCabe-Thiele diagram is a graphical construction of an extraction or stripping (transfer of the extracted metal ions to a new aqueous phase) isotherm, an operation line, and the stepwise evaluation of the number of stages needed to obtain a certain separation result. The slope of the operation line is equal to the phase ratio, i.e. the volume ratio between organic phase and aqueous phase. McCabe-Thiele diagrams are widely used to describe solvent extraction processes, and specifically for modeling of the extraction and stripping sub-processes. The use of McCabe-Thiele diagrams makes it possible to calculate the number of mixer-settler stages required, or alternatively, to predict the performance at a given set of conditions [86, 87].

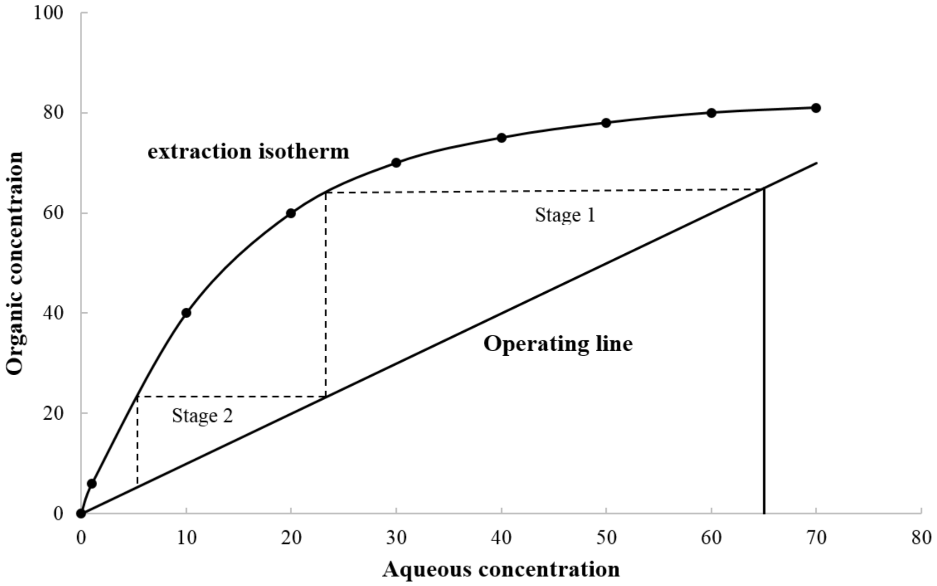

Fig. 3. Example of a McCabe-Thiele diagram

An example of a McCabe-Thiele diagram for calculation of the operating line and number of stages of a multistage processes is shown in Fig.3. The calculation is made with the assumptions that the phase ratio (θ) is constant and the equilibrium is reached in all extraction stages. The vertical line is the metal concentration of original feed. In order to calculate the number of theoretical stages. A horizontal line is drawn from the intersect point of the vertical line and operation line towards the extraction isotherm until it intersects with the isotherm. Then a vertical line is drawn until it intersects with the operating line. This procedure can be repeated until the desired metal concentration in the raffinate is reached. The number of “stages” in the figure represents the number of ideal stages, i.e. in practical work the number of mixer settler units.

3. Experimental

An overview of the experimental work carried out is presented in Fig. 4. The investigations were mainly focused on characterization of MSWI ash samples and leaching residues, evaluation of a hydrometallurgical process combing leaching and solvent extraction separation of copper and zinc for fly ash and preliminary investigations of metal contents and leachability in different particle sizes of crushed MSWI bottom ash. The results discussed in Section 4 are based on the four publications and one manuscript listed at the beginning of the thesis, as summarized below.

- Characterization of the MSWI ash and the leaching residue (Publications I and II).
- Investigation of leaching for the removal of copper, zinc and other metals in the ash in bench scale experiments (Publications I and II).
- Solvent extraction separation of copper and zinc from ash leachate (Publication III).
- Batch extraction of zinc with Cyanex 272, Cyanex 572 and Cyanex 923 (Manuscript IV).
- Evaluation of the hydrometallurgical process tested in laboratory pilot scale (Publication V).

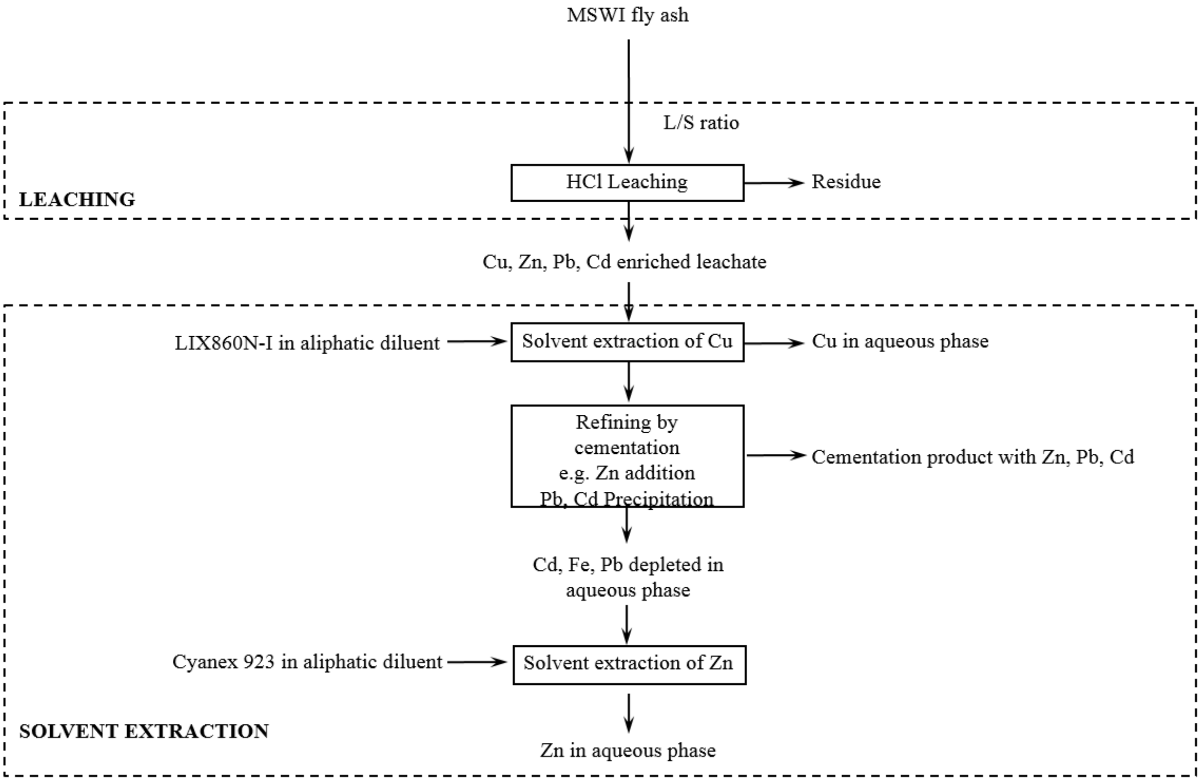

Fig. 4. A simplified flowchart for the recovery of copper and zinc from municipal solid waste incineration fly ash.

3.1. Origin of ash samples

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 fly ash sample B is a textile filter ash from a bubbling fluidized bed combustor also fired with normally sorted household waste and waste from small businesses. The samples were collected during normal and stable operation of the combustors.

In both combustors lime is injected before the filter for absorption of acid gases, i.e. HCl and SO_2 and in Combustor. Activated carbon is also injected before the filter to adsorb dioxins and volatile metals, such as mercury.

3.2.Characterization of the ash and leaching residues (Paper II)

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 sample for ICP-OES was prepared by melting a weighed amount of ash with lithium borate and 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 have been standardized. The bomb dissolution is used for preparing the solution for determination of volatile and trace 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.

Due to the occurrence of large slag lumps in the bottom ash, a leaching procedure for recovery of metals from the bottom ash in its original form was not anticipated to be successful. Therefore, the investigation was carried out on the ground ash. The particle size distribution of metals in the ground ash was measured to be 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 and 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 content in these solutions was determined using ICP-OES. Duplicate samples were dissolved and the ICP measurements were made in duplicate.

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 was compared with data for pure compounds standards [88]. 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.

XAS measurements and data evaluation

The X-ray absorption spectroscopy measurements were carried out at the beam line I811 in the Maxlab Swedish national synchrotron facility at Lund University that was operable until recently. The beam line was situated on the 700MeW ring MaxIII [89]. Zn K-edge and Cu-K-edge spectrum data were collected using a Si(111) double crystal monochromator. All Zn spectra were calibrated by assigning the first inflection point of the Zn metal K-edge to 9.959 keV. The Cu spectra were calibrated by assigning the first inflection point of the Cu metal K-edge to 8979keV.

The sample spectra were collected in fluorescence mode by a Lytle detector. Zinc or copper foil data for energy calibration were simultaneously collected in transmission mode by ionisation chambers filled with Ar. The intensity of the primary beam, I_0, was measured using ion chambers filled with N_2 to 1.1 bar. The intensity of the beam after passing the sample (I_1) and after passing the metal foil (I_2) were measured using ion chambers filled with Ar to 0.1 bar and 2 bar, respectively.

In addition to data for the ash samples, data was also collected for a number of pure zinc compounds that were considered possible to find in the ashes: Zn, ZnO, $Zn(OH)_2$, Zn_2SiO_4, $ZnAl_2O_4$, $ZnFe_2O_4$, $Zn_5(OH)_6(CO_3)_2$, ZnS, $ZnSO_4$, $ZnCl_2$, chalcophanite, hemimorphite, $ZnCO_3$ (Smithsonite), $ZnPO_4$*$4H_2O$, $ZnSO_4$*H_2O. In addition, solid state reaction products between Zn salts and oxides at temperatures corresponding to combustion conditions were included: Zn-acetate reacted with quartz at 850°C and 950°C; $ZnCl_2$ reacted with quartz at 950°C; Zn-acetate reacted with Fe_2O_3 at 900°C; Zn-acetate reacted with Al_2O_3 at 900°C.

Data was also collected for a large number of pure copper compounds: Cu, brass (Cu/Zn alloy), Cu_2O, CuO, $CuCrO_2$, $CuCr_2O_4$, $CuFe_2O_4$, $Cu_3(PO_4)_2$, CuCl, $CuCl_2 \cdot 2H_2O$, CuClOH/CuCl, $Cu_2Cl(OH)_3$, $Cu(OH)_2CuCO_3/CuCO_3$, $Cu(OH)_2$, $CuSO_4 \cdot 5H_2O$, $CuSiO_3 \cdot H_2O$, $CuBr_2$, CuS, Cu_2S, Cu_5FeS_4/Cu_2S, CuCaOxide, CuCaPhosphate and Chrysocolla. All standard compounds were analysed 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. The iron compounds used as standards were: Fe metal, FeO, Fe_3O_4, Fe_2O_3.

Data treatment and evaluation was made using the Athena software developed by Bruce Ravel [90]. The XAS data were energy calibrated and averaged, followed by pre-edge subtraction and spline removal. When necessary the data was smoothed using a standard method. Linear combinations of spectra for pure compounds were used to model the semi-quantitative speciation of Zn and Cu in the ash samples, both in the XANES region and, if the data was good enough, in the EXAFS region. A preliminary evaluation of the data with respect to the identity of and distance to neighbour atoms was made using the software EXAFSPAK. The EXAFSPAK program uses data from crystallographic database to calculate the theoretical distances between atoms.

3.3. Batch leaching experiments (Paper I)

The experiments in Paper I 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 experiments using pH 1, pH 3, pH 7, pH 9 and pH 11 buffer solutions (Merck KGaA) [91].

The leaching behavior of metals in the ashes was studied using hydrochloric, nitric, and sulfuric acid solutions. The study mainly focused on the hydrochloric acid system. Various parameters were investigated, including leaching pH value (constant 2, 3 and 4), leaching time (up to 70 h), liquid to solid ratio (up to 50 v/w), and temperature (20°C, 60°C). 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 was 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 Inductive Coupled Plasma with Optical Emission Spectrometer (ICP–OES, Thermo iCAP 6000). In total 14 ICP-OES external standards were used for calibrations, 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. These concentrations were prepared from ICP standards (Ultra Scientific, 1000 μg/mL) and approx. 1mol/L nitric acid (65%, suprapur, Merck). The obtained leachates were diluted with 1 mol/L nitric acid for the measurement.

Anion 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.

3.4.Solvent extraction, batch experiments

3.4.1. Copper extraction with LIX860N-I (Paper III)

Batch extraction of copper from hydrochloric acid-based leachates from both ash A and ash B using LIX860N-I was carried out. The influence of the contact time (1-5 min) and ligand concentration (0.1 - 1.5 mol/L LIX860N-I) (Cognis) were investigated. Stripping of the copper extracted was performed with sulfuric acid (0.5 - 1.5mol/L). The phase ratio of all batch experiments, including extraction and stripping, was 1 and was performed in glass vials. The extraction/stripping experiments were carried out in a thermostatic shaking machine with 1500 vibration per minute (vpm) under ambient temperature (20 ± 1 °C).

3.4.2. Zinc extraction with Cyanex 272, Cyanex 572 and Cyanex 923 (Papers III, IV)

The investigation of three commercial extractants for zinc extraction targeted the influence of various parameters, e.g. contact time (1-30 min), ligand concentration (0.1-2 mol/L) in organic phase, diluents (aliphatic, aromatic and long chain alcohol diluents), initial pH value in the aqueous feed (0.5-3.7) and temperature (20 - 60°C). Stripping of metal ions from organic phases based on 1 mol/L Cyanex 272, Cyanex 572 and Cyanex 923 (all from Cytec) in Solvent 70, respectively, previously contacted with feed solution, i.e. the remaining aqueous phase from copper extraction, in order to extract zinc, was carried out using hydrochloric acid, nitric acid or sulfuric acid of concentrations in the range of 0.5 - 5 mol/L and water (MilliQ, Millipore, >18MΩ/cm) as stripping agents. The stripping tests were performed for 5 min with a phase ratio of 1. The extraction/stripping experiments were carried out in a thermostatic shaking machine with 1500 vibration per minute (vpm).

The diluents tested were a kerosene (Solvent 70, Statoil); toluene, tert-butylbenzene, 1-octanol (Sigma Aldrich); and an isoalkane (Isopar L), de-aromatized kerosene Escaid 120 and heavy aromatic solvent naphta Solvesso 150 (ExxonMobil) without additional purification. The characteristics of each diluent are presented in Table 2.

Table 2. Tested diluents and their characteristics.

Diluent	Commercial name	Characteristics	Water solubility (wt. %)
Aliphatic	Solvent 70	0.5 wt.% aromatic	traces [92]
	Isopar L	< 2% aromatic	0.15 [93]
	Escaid 120	<0.01 wt.% aromatic	none [94]
Aromatic	Toluene	>99.5wt.% aromatic	0.03 [69]
	Tert-Butylbenzene	>99 wt.% aromatic	traces [95]
	Solvesso 150	>99 wt.% aromatic	traces [92]
Alcohols	1-Octanol	Long chain	0.06 [92]

3.4.3. Cementation Test (Paper V)

The reduction of metal ions by a metal with a more positive reduction potential is called cementation. In the current investigation cementation of iron, lead and cadmium by addition of zinc metal particles was used. The mixture of reduced metals precipitates on the surface of the zinc particles. The oxidized zinc will go into solution and be recovered. This type of cementation process is common in industrial zinc production for purification of the feed to electrolysis.

Cementation experiments were carried out at 20 ± 1 °C. The stirring velocity was constant at 500 rpm. The Metrohm 905 Titrando titrator was used to control the acid addition (1 mol/L HCl) for maintaining the set pH value (pH = 2). Zinc powder (99.9%, Sigma Aldrich) was added to the reaction vessel in one portion and the ratio of solid zinc to leachate was 4 g/L. Samples of the solution were taken at 120 min, centrifuged and filtered for ICP-OES analysis of metal ion concentration.

3.5.Laboratory pilot scale test leaching and extraction (Paper V)

A schematic of the pilot scale setup for metal recovery from MSWI fly ash using a combination of acidic leaching and solvent extraction in small pilot scale equipment is presented in Fig. 5. An amount of 250g MSWI fly ash A was leached with hydrochloric acid in a 5 L vessel equipped with a propeller operated at 500 rpm for 20 hours at room temperature (20 ± 1 °C). Initially the ash and distilled water was added to the vessel to create an ash slurry that was possible to stir. Acid was then added for ash leaching. The leaching experiments were carried out at a constant pH (pH 2) and with a final liquid to solid ratio (v/w) of 20 using Metrohm 905 Titrando titrator.

The feed for extraction was passed through a filtration station with glass fiber filters having 0.4 µm pores. A counter-current mixer settler system comprising two sets of chambers for copper extraction and zinc extraction individually, as shown in Fig. 5, was used. The aqueous and organic phases were pumped into the mixer by electromagnetic pumps (IWAKI). The flow rate was adjusted by metering pumps. The flow rates of aqueous feed and the organic feeds, including LIX860N-I and Cyanex 923, were determined by Eq. 10 and the bench scale experiments in section 3.4. The Aqueous feed, Raffinate I, Raffinate II, Stripping product I and Stripping product II in Fig. 5 were sampled for metal concentration analysis. Loaded organic I and Loaded organic II were collected for analysis of the stripping process. The metal concentration in those two organic phases was determined by calculation using mass balance and the concentrations in the aqueous phases.

The time needed for equilibrium to be obtained in the extractions was determined in a series of preliminary experiments. The first set of experiments was done to investigate copper extraction; the contact time was 1, 3 and 5 min individually with the organic phase to aqueous phase volume (O:A) ratio 1:1. The second set of experiments was to study the zinc extraction, which was carried out similarly to the first set.

The data needed to construct the isotherms of McCabe-Thiele diagrams for pilot scale extraction were obtained in bench scale experiments carried out with an ash leachate with pH 2 (Aqueous feed in Fig. 5) and at six phase ratios (O:A, v/v) from 6:1 to 1:6 (6:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5, 1:6). The extractants used were 0.01 mol/L LIX860N-I and 0.1 mol/L Cyanex 923, both diluted in kerosene (Solvent 70). The contact times used were based on the results from the preliminary experiments.

Copper stripping was performed using sulfuric acid solutions with different concentrations (0, 0.5, 1, 1.5, 3, and 5 mol/L, respectively) from Paper III and another work [74, 96]. The organic phase was a Loaded Organic I (Fig. 5), and stripping was carried out with an O:A ratio of 1:1.

Based on the results from Paper III [74], it was decided to investigate the influence of protons, nitrate, sulfate and chloride ions on the stripping of zinc and co-extracted metals, such as cadmium, iron and lead from the organic phase (Loaded Organic II in Fig. 5). Thus, stripping solutions based on chloride, nitrate and sulfate solutions, including salts and acids, as well as pure water (MilliQ, Millipore, >18 MΩ/cm) were used. The concentration of sulfuric acid was 5 mol/L, sodium sulfate 0.5 mol/L and other solutions 1 mol/L. The O:A ratio used here was 1 and contact time was 1 min.

Solutions of potassium chloride (1 mol/L), pure water, and sulfuric acid (5 mol/L) were further chosen for selective stripping of the zinc loaded organic phase (Loaded Organic II) with different phase ratio. The loaded organic phase was stripped for 1 min at various O:A phase ratios between 6:1 and 1:6 (6:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5 and 1:6).

The metal concentrations were measured in samples of aqueous phase, taken before and after contact with the loaded organic phase, and stripping efficiencies were calculated using the mass balances.

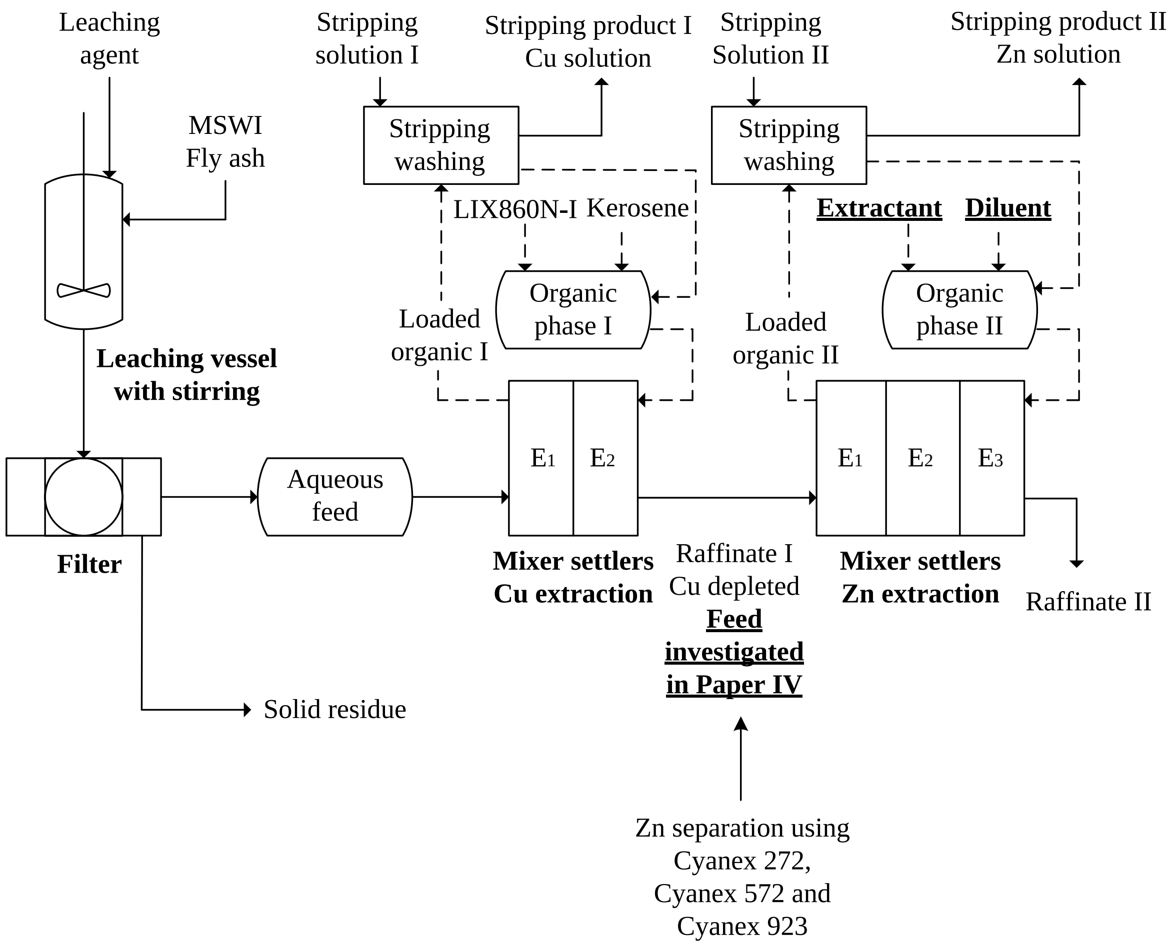

Fig. 5. Schematic flowchart of the hydrometallurgical process. The dashed lines show the flow of organic phases.

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 3, are quite similar to those of other MSWI ashes shown in the literature [41, 49, 97].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 content was 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%, respectively. The amount of combustible material in 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 even a small weight fraction might influence the metal leaching significantly.

Table 3. Concentrations of major and minor elements in bottom and fly ashes from various incineration units and countries [98]. Ash A and ash B are the ash samples used in this study, 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%, respectively. All amounts are present as mg/kg ash.

Elements	Bottom ash	Fly ash	Fly ash A	Bottom ash A	Fly ash B
Al	22000 - 73000	49000 - 90000	36100	38000	20000
Ca	370 - 123000	74000 - 130000	180000	93000	360000
Fe	4100 - 150000	12000 - 44000	20100	70000	5600
K	750 - 16000	22000 - 62000	21100	11000	25000
Mg	400 - 26000	11000 - 19000	18100	12000	10000
Na	2800 - 42000	15000 - 57000	26100	38000	32000
S	1000 - 5000	11000 - 45000	81500	8000	7000
Si	91000 - 308000	95000 - 210000	67300	183000	32700
Cl	800 - 4200	29000 - 210000	31000	3000	200000
As	0.1 - 190	37 - 320	240	68	80
Ba	400 - 3000	330 - 3100	140	1300	770
Cd	0.3 - 70	50 - 450	83	4	90
Cr	23 - 3200	140 - 1100	450	490	190
Cu	190 - 8200	600 - 3200	840	2700	5400
Hg	0.02 - 8	0.7 - 30	0.05	<0.05	3
Mn	80 - 2400	800 -1900	1100	1000	570
Mo	2 - 280	15 -150	22	<20	10
Ni	7 - 4200	800 - 1900	220	240	30
Pb	100 - 13700	5300 - 26000	3000	1400	5700
Sb	10 - 430	260 - 1100	1100	86	nd

V	20 - 12	29 - 150	70	60	10
Zn	610 - 7800	9000 - 70000	17100	3800	5800

The powder diffraction (XRD) 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, which suggests 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 3.2. 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.

Since it was considered interesting to know if some particle sizes of the ground bottom ash were richer in some metals than in others the ground bottom ash A was sieved into different particle size fractions and the fractions were analyzed for metal contents. As presented in Fig. 6, most of the particles in the ground bottom ash A were in the range of 2 – 20 mm. Approximately 40% by weight of the material had a particle size below 4 mm. The concentrations of a number of elements in the fractions are presented in Table 4 and some of the results are shown in Figures 7A-C.

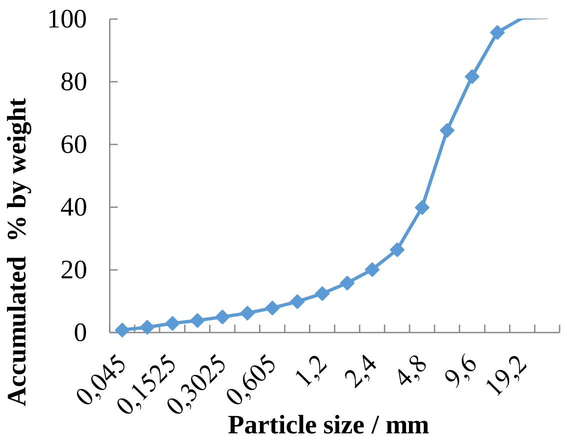

Fig. 6. Particle size distribution of the ground bottom ash A used in the leaching experiments (stated as accumulated wt.%)

Table 4. Element content in various particle sizes of sample A bottom ash (mg/kg dry 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 decreased with decreasing particle size, while the calcium content increased and the aluminum was roughly the same regardless of particle size. The concentration of copper and zinc varied widely between different particle sizes, especially for particles larger than 0.5 mm. Nickel and lead concentrations also varied but generally the contents were 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 that are easy to grind. Pieces of metals and alloys, e.g. iron metal, are not particularly easy to crush, which explains why these occur frequently in the larger particles.

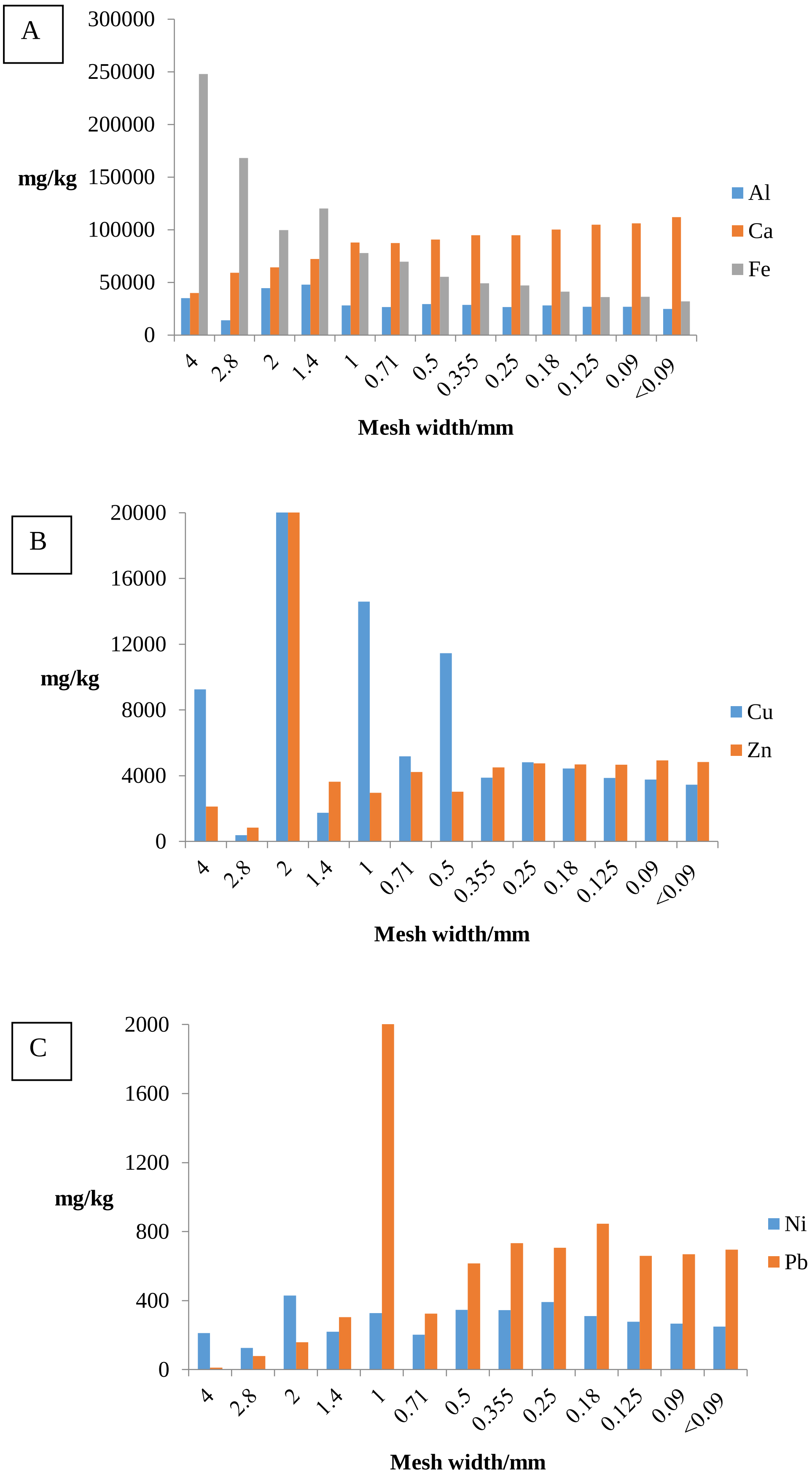

Fig. 7. Concentrations of some elements in different particle sizes of ground Bottom ash A

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 Fig 8, 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 Fig. 8 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 copper, 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 Cu(II) species, such as sulphate, hydroxides and chlorides. This is illustrated in Fig 8 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 Fig. 8.

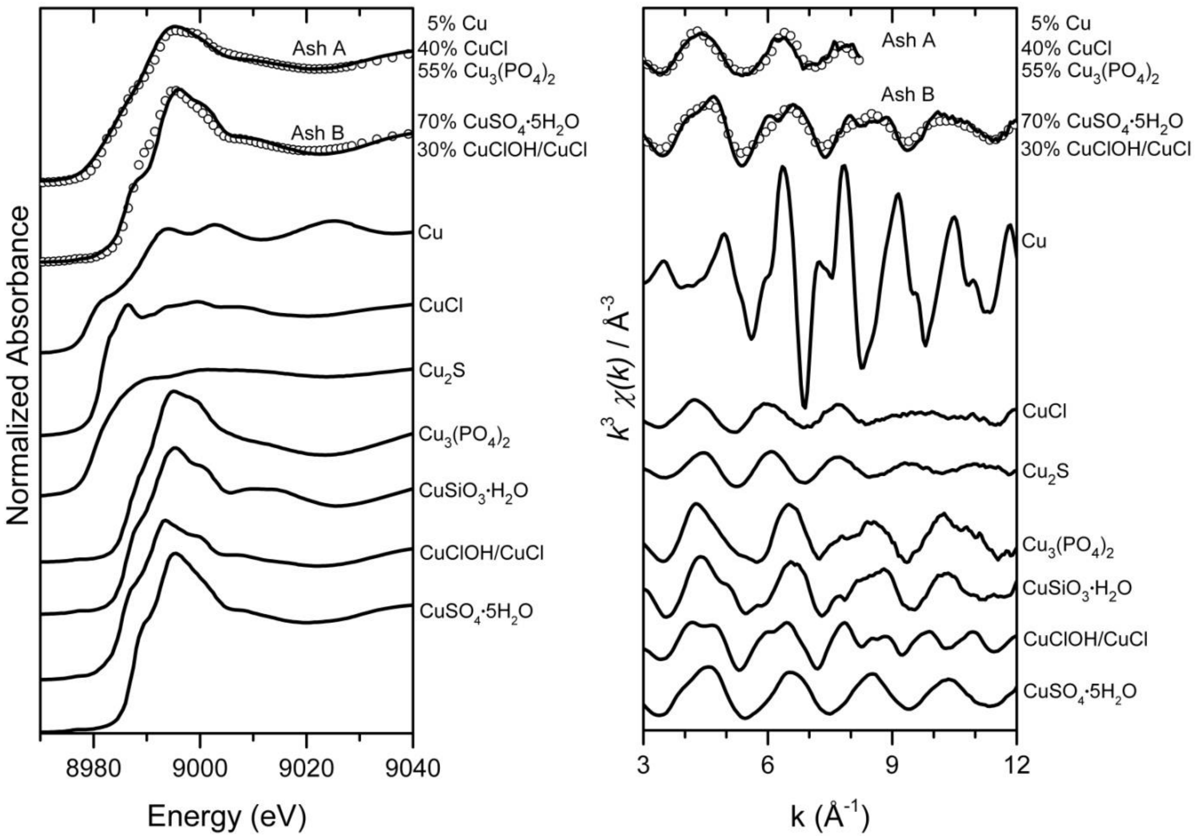

Fig. 8. Cu K-edge XANES data (left) and k3-amplified EXAFS data (right) for standards and ash samples (solid lines) with results from LCF (circles).

The two zinc 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 only weak signals from neighbouring atoms at longer distances. The Zn-O distance obtained with the EXAFSPAK software 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 neighbouring atoms beyond the first shell indicates a disordered structure or that zinc is present in species adsorbed on mineral surfaces.a surface adsorption of Zn species on mineral surfaces. The LCF modelling of the zinc XAS data for fly ash A pointed at different combined metal oxides, perhaps with some hydrate water such as in Chalcophanite $(Zn,Fe^{2+},Mn^{2+})(Mn^{4+})_3O_7 \cdot 3(H_2O)$ in combination with Zn_2SiO_4. The evaluation the XAS data for original and leached fly ashes is ongoing and a full presentation of the results will be published separately.

Lead X-ray Near Edge Spectrometry (XANES) data indicated that the oxidation state II was predominant for lead in fly ash A. Unfortunately the data was too noisy to allow for identification of the types of lead compounds present. For Ash B no lead data could be collected due to lack of beam time.

4.2.Leaching experiments

A suitable acid and pH level must be determined to fit the entire metal recovery process. One aspect of the use of acid leaching to release metal compounds from ash is that quite a large amount of acid may be needed, since the fly ash contains a large fraction of alkaline compounds such as CaO, $Ca(OH)_2$ and $CaCO_3$, especially if the flue gas treatment includes lime addition for absorption of acid. It is therefore necessary to estimate the amount of acid needed in a future metal recovery process. The number of acid equivalents needed to reach pH 2, 3, 4 and 5, and to keep the pH constant for 48 hours to ensure that equilibrium is reached are shown in Fig. 9.

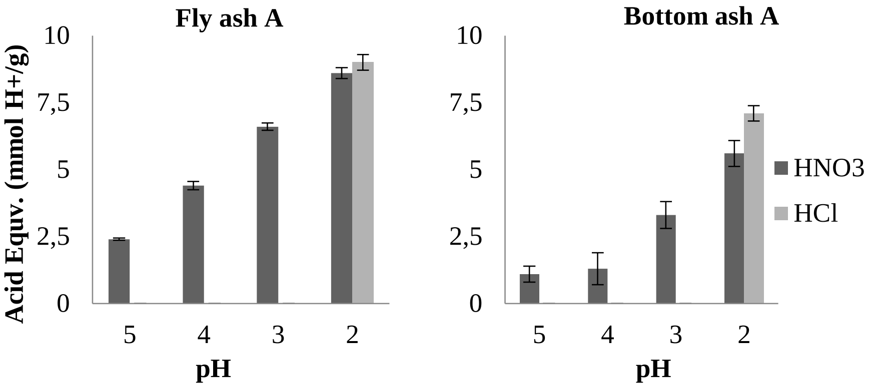

Fig. 9. Number of acid equivalents (mmol H^+/g of ash) needed to keep the pH constant at 2-5 during leaching with nitric and hydrochloric acid, respectively, for 48 hours at L/S 20.

The fly ash requires 9 mmol H+/g of ash to reach pH 2, which is in the same range as that of other types of fly ash from MSWI and biomass combustion units [99]. For the bottom ash investigated 7.1 and 5.6 mmol H+/g of ash were consumed from HCl and HNO_3, respectively. The higher consumption of hydrochloric acid compared to that of nitric acid was probably due to formation of chloride complexes with metal ions. The HCl leachates contained higher concentrations of copper, zinc and lead than the HNO_3 leachates did.

The number of acid equivalents consumed for the fly ash when leached with hydrochloric acid solution at pH 2, 3 and 4 are presented versus leaching time in Fig. 10 as an example. In the pH range of 2 to 4 the acid consumption indicates that it takes quite a long time to reach equilibrium, i.e. to consume the alkalinity of the ash; more than 20 hours is required in the present set up with continuous addition of acid. In an industrial process the leaching time could probably be shortened by adding acid in larger amounts at the beginning of the leaching.

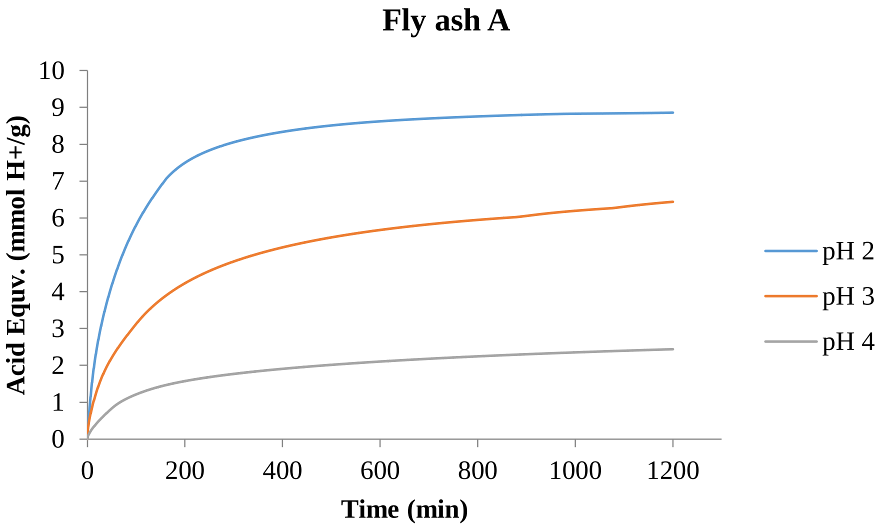

Fig. 10. Number of acid equivalents in mmol H^+/g ash consumed versus leaching time using hydrochloric acid at L/S = 20.

The results from the constant pH leaching experiments (Tables 5 and 6) show that the 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 sodium and potassium, are released in high amounts at all pH levels studied. The fraction of alkali metals not dissolved may be bound in feldspars or in glass and slag, as found for the bottom ash. Calcium is also released in high amounts as it is present mainly in acid soluble compounds. However, dissolving the fly ash in sulfuric acid resulted 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.

Copper, zinc, cadmium and lead were removed from the fly ash with high efficiency using hydrochloric acid leaching, which is beneficial since these metals are potentially toxic. The nitric acid was less efficient at releasing copper, zinc and especially lead; only 9% could be removed at pH 2. The sulfuric acid gave leaching results comparable to those of hydrochloric acid for copper, zinc and cadmium, but precipitated lead as sulfate. Thus the leached ash will contain lead that can be released later, which counteracts our aim to produce an ash residue with lower content of potentially toxic metals.

In order to achieve the most effective leaching of copper and zinc from both the fly ash and bottom ash a pH-level of 2 must be maintained. About 70% of the fly ash copper content and 80% of the zinc was released at this pH level. However, the same pH gave only 30-40% release of copper and zinc from the bottom ash. The results (Table 5) show a low leachability for Fe in the present fly ash as long as the pH is 3 or above. Decreasing the pH to 2 increased the leaching of iron by 10-20%. The relatively low leachability for iron is probably caused by iron being present as hematite (Fe_2O_3), which is less soluble than the Fe(II)-compounds present in the bottom ash as indicated by the XAS data. In fact, decreasing the pH to 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 iron per kg dry ash (as opposed to the 20 g/kg fly ash) this will give a quite high concentration, approx. 20 g/L iron in the resulting bottom ash leachate compared to 4 g/L in fly ash leachate. The presence of so much iron in the leachate may be a problem in the zinc separation since some extractants used in solvent extraction bind to iron as well as to zinc ions. This causes unnecessary consumption of chemicals in the process.

Table 5. The fraction of major and minor fly ash elements released using different acids (20 hours leaching time, L/S = 20). All results are given in % of total amount of each metal in the dry ash. nd=not detected

	Amount of elements released from the fly ash (% of the total concentration in the ash)						
	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	67.1±5.6	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	17.4±2.7	4.5±0.6	nd	9.5±0.5	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	37.5±1.2	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±6.8	8.9±0.3	8.3±0.7	9.2±0.1	9.0±1.3	7.1±0.1	2.2±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	74.2±5.5	69.0±4.8	56.1±4.3	65±1.2	63.4±1.3	56.5±1.5	80.0±1.5
Cd	93.3±3.1	82.7±5.3	78.3±7.2	77.0+2.7			88.9±3.6

Table 6. The fraction of major and minor bottom ash elements released using nitric acid (20 hours leaching time, L/S = 20). 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%**	
	HNO_3	
	pH 2	pH 4
Al	36.1±1.3	2.0±0.1
Ca	58.0±0.2	37.3±4.5
Cd	nd	nd
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

Copper, lead and zinc are considerably more leachable from the 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 metal pieces, such as copper wires, glazed with molten ash, i.e. glass or glassy slag. This part of the metal content is very difficult to leach out, which is unfortunate since this bottom ash had a higher copper concentration (2700 mg/kg) than the fly ash (840 mg/kg). It may be possible to release and recover these metallic pieces from the bottom ash with mechanical treatment and Eddy current separation, but that is outside the scope of this thesis.

An interesting observation was that approximately 20% of the silicon in the bottom ash and 50% of the silicon in the fly ash was released at pH 2. This corresponds to about 40 g/kg and 35 g/kg of silicon from the respective ashes that dissolved in the acid. Equilibrium speciation calculations for the bottom ash leachate using the PhreeqC software [100] and the wateq4f database [101] showed that the solution was oversaturated with respect to silica, silica gel and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$ and the solution was also close to saturated 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 chemical composition of the precipitate by XRD was attempted but the results were unclear due to the non-crystalline nature of the precipitate. However, the color of the gel indicates that some of the dissolved iron oxidized and precipitated as ferric hydroxide. This gel-like precipitate makes further recovery of the dissolved metals from the bottom ash by solvent extraction unfeasible.

The low efficiency of leaching of the target metals copper and zinc from the bottom ash, in addition to the problems with high iron concentration in the leachates and the risk of gel formation, lead to a decision not to continue working on acid leaching of this type of bottom ash. Possible alternatives could be the thermal waste treatment followed by a dry discharge of bottom ash to recover metals such as iron, aluminum, and copper that was developed by Hitachi Zosen INOVA [102] and the dry treatment developed by INASHCO [103].

Leaching of the fly ash also released significant amounts of aluminum, silicon and calcium, which needs to be taken into account both when designing a process for separation of specific metals from the leachate and for the final treatment of the leachate.

The time dependence for leaching of copper, cadmium, iron, lead and zinc from the fly ash in HCl and HNO_3, respectively, are presented in Fig. 11. The nitric acid gave a higher leaching rate for copper than the hydrochloric acid solution did, but the total amounts of copper, cadmium, lead and zinc released were lower. The kinetics for zinc leaching were similar in both acids, but the yield was slightly higher when using hydrochloric acid. The higher leaching yield of these metals in hydrochloric acid is probably due to the formation of soluble chloride complexes.

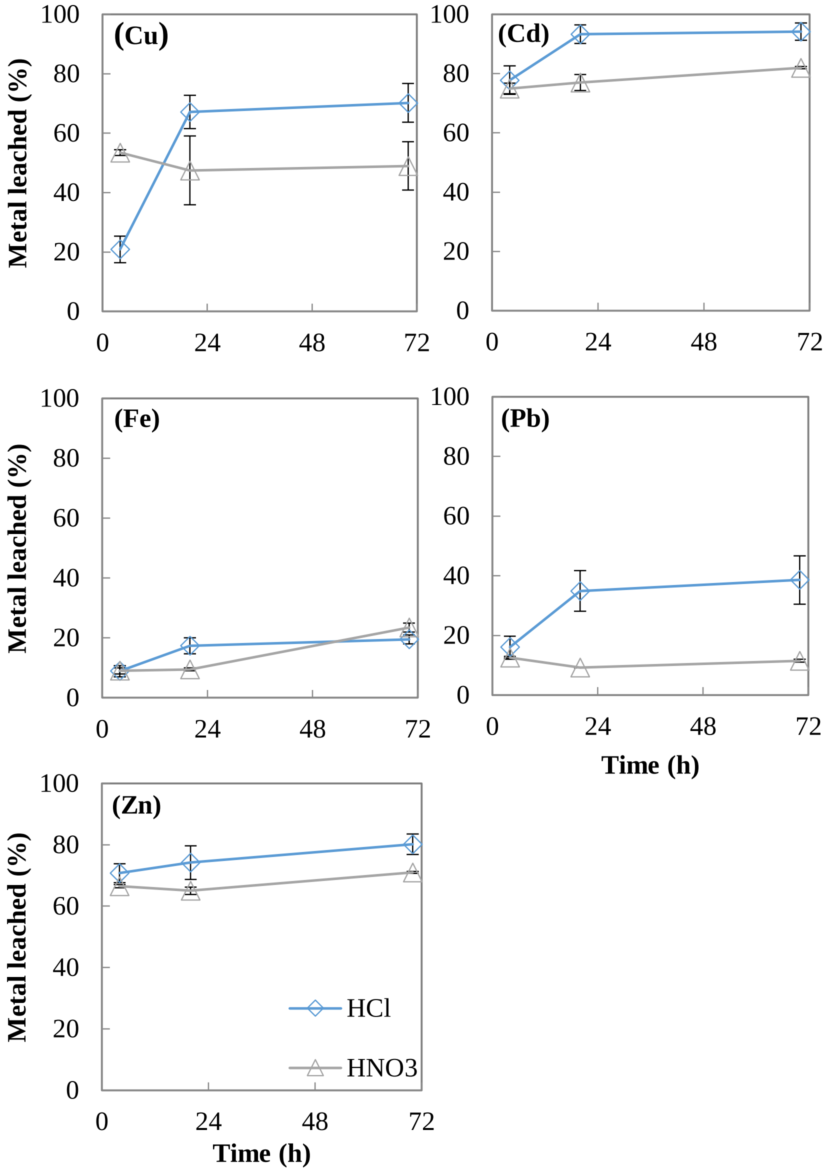

Fig. 11. Copper, cadmium, iron, lead and zinc leaching of fly ash A at L/S = 20 and pH = 2. Standard deviation based on triplicates.

Results from similar work done by other research groups have shown similar leaching yields (73% for copper, 42% for zinc, 98% for lead and 86% for cadmium) from a Chinese MSWI fly ash when using the best set of parameters, which were 5.3 mol/L HNO_3 and a liquid to solid ratio of 20 [104]; 59.4% release of lead and 77.0% of copper using 0.5 mol/L HNO_3 and a liquid-solid ratio of 20 as well [105]. When studying leaching of copper, zinc and lead from samples of MSWI fly ash at a liquid to solid ratio of 20 and different pH levels, Lui and co-workers also found that a starting pH of pH 2 gave the most efficient release of copper, zinc and lead [106]. Sulfuric acid has also been used in several investigations and found to be efficient in removing cadmium and copper, but less efficient in removing nickel and zinc [107].

In another series of similar experiments carried out with the investigated fly ash A at different pH levels using nitric acid and L/S 20 it was observed that the amount of copper present in the leachates decreased with time at pH 4. As shown in Fig. 12, the concentration of copper in the leachate dropped to almost zero. The fraction of zinc found in the leachate decreased as well, but only to a minor extent. As discussed above, copper ions are prone to sorb onto activated carbon. This fly ash contains activated carbon and this may be an underlying reason for the observed behavior. The metal ions may also adsorb on minerals, such as silicates, which are abundant in ashes. An additional effect that could remove metal ions from the leachate during a prolonged leaching is co-precipitation with oversaturated compounds.

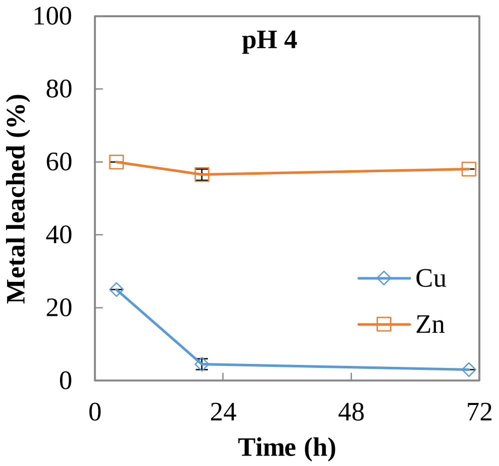

Fig. 12. Leaching of copper and zinc at pH 4 using nitric acid (L/S = 20 v/w). Standard deviation based on triplicates.

Fig. 13 shows that an increase of L/S (v/w) ratio leads to different behaviours for different metals when leaching the fly ash with hydrochloric acid. For copper, cadmium and zinc the increase of liquid to solid ratio (v/w) from 5 to 50 generally had a positive effect on the initial leaching kinetics, but the total yield was similar when reaching 70 hours leaching time. Using higher L/S resulted in a decreased leaching of iron from approximately 20% to 10%. Liu and Millero investigated the behaviour of Fe(III) in acidic chloride medium and found that a high ionic strength promotes Fe(III) solubility [104]. This effect may offer an explanation for the decrease in iron leaching at higher L/S observed in our experiments.

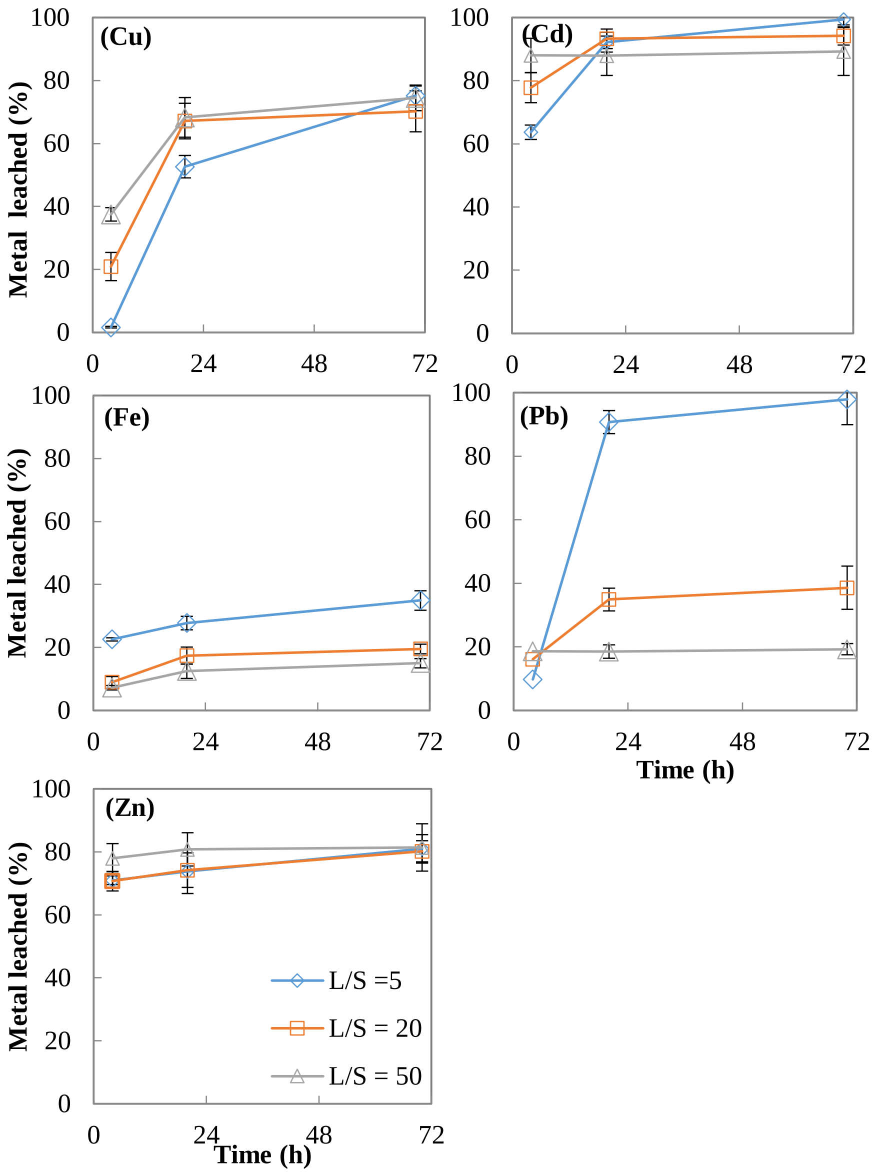

Fig. 13. Leaching of copper, cadmium, iron, lead and zinc from fly ash A at pH 2 using hydrochloric acid and different L/S ratios.

The total released amount of lead decreased significantly from more than 90% to rougly 20% with increasing L/S ratio. To investigate if precipitation of lead sulfate could be the reason for this, ion chromatography was used to measure the concentration of sulfate ions in the leachates. The results presented in Fig. 14 show that an average of 27.9 ± 0.8 μM/L and 41.8 ± 1.3 μM/L of sulfate ions were measured in the liquid/solid ratio 5 and 50 solutions. The increased sulfate release is probably caused by dissolution of $CaSO_4$. It is possible that the higher availability for sulfate ions lead to precipitation of $PbSO_4$ and that this was observed as a decreased percentage of soluble lead at higher liquid to solid ratios.

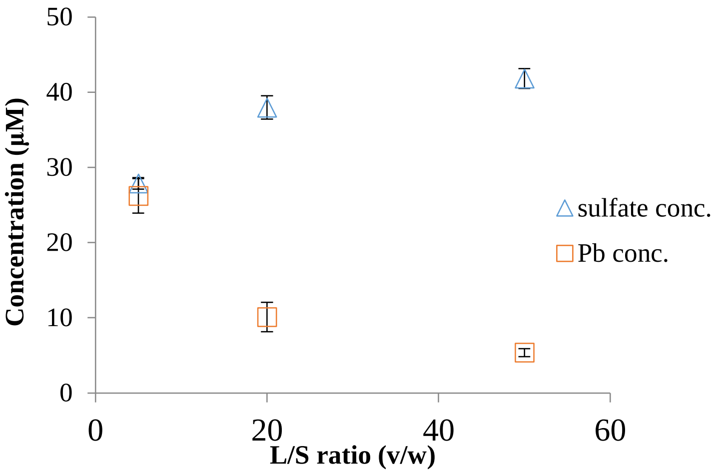

Fig. 14. Sulfate and lead ion concentrations in the hydrochloric acid pH 2 leachate versus liquid to solid ratio after 20 hours leaching time.

The effect of temperature on the leaching was briefly investigated by leaching at two temperatures. As shown in Fig. 15, leaching at 60 ± 5 °C gives no improvement of the leaching of the targeted element zinc compared to leaching at 20 ± 1 °C for either nitric acid or hydrochloric acid. However, the solubility of iron was clearly affected by temperature, giving higher release at higher temperature. Similar results have been reported for sulfuric acid leaching [105]. Thus, the results show that room temperature can be used for the acid leaching part of our process in order to decrease the energy consumption and the iron contamination in the leachate.

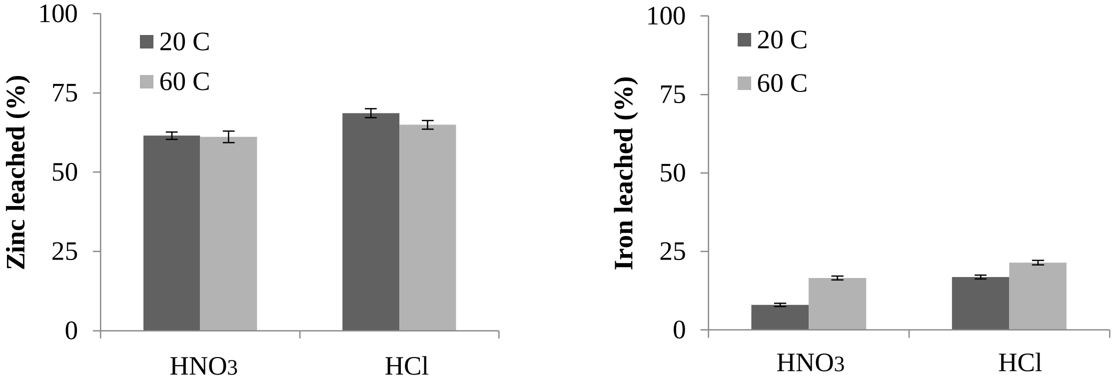

Fig. 15. Percent release of zinc and iron in nitric acid and hydrochloric acid pH 2 leachates at 20 ± 1 °C and 60 ± 5 °C, respectively, using L/S 18. Standard deviation based on triplicates.

4.3.Solvent extraction

The separation and purification of copper and zinc by solvent extraction from fly ash A and B leachates produced at pH 2 and with L/S 20 was investigated first in laboratory size experiments in order to find the best process settings. The compositions of the leachates are shown in Table 7.

Since a good extractant for the copper extraction (LIX860N-I) had been found in earlier work by Karlfeldt and co-workers [96] it was decided to use that extractant here as well. However, it was necessary to investigate the copper extraction for the specific ash leachates produced in the present work.

The second part of the development of a suitable set of solvent extraction steps for the present leachates concerned the purification of zinc. Three extractants were compared with respect to selectivity in the extraction as well as in the stripping steps. Based on the results that will be discussed more in detail in section 4.3.2, the extractant Cyanex 923 was investigated in more detail and chosen for the subsequent upscaling tests of the sequential separations of copper and zinc.

Table 7. Composition of the pH 2 fly ash leachates produced with liquid to solid ratio 20.

Element mg/l	Leachate from Ash A	Leachate from Ash B
Al	1079.5±39.3	603.9±22.0
Ca	4556±121	12460±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

4.3.1. Solvent extraction of copper with LIX860N-I

The extraction mechanism using LIX860N-I is presented in Eq. 6, and the copper extraction can be specified as

$$Cu_{aq}^{2+} + 2HA_{org} \overset{K_{ex}}{\Leftrightarrow} CuA_{2org} + 2H_{aq}^{+} \qquad \text{(Eq. 11)}$$

$$K_{ex} = \frac{[CuA_2]_{org} \cdot [H^+]_{aq}^2}{[Cu^{2+}]_{aq} \cdot [H^+]_{aq}^2} \qquad \text{(Eq. 12)}$$

$$K_{ex} = \frac{D \cdot [H^+]_{aq}^2}{[HA]_{org}^2} \qquad \text{(Eq. 13)}$$

$$\text{Where D} = \frac{[CuA_2]_{org}}{[Cu^{2+}]_{aq}} \qquad \text{(Eq. 14)}$$

Taking the logarithm of Eq.12 and rearranging:

$$\text{logD} = \text{log}K_{ex} - 2log\,\frac{[H^+]_{aq}}{[HA]_{org}} \qquad \text{(Eq. 15)}$$

The influence of LIX860N-I concentration in the organic phase on the distribution ratio for Cu extraction from leachate of ash B is shown as a graph in Fig. 16. The slope of the line shown in Fig. 16 is - 1.9 which indicates that the extraction mechanism involves 2 extractant molecules per Cu^{2+}-ion transferred.

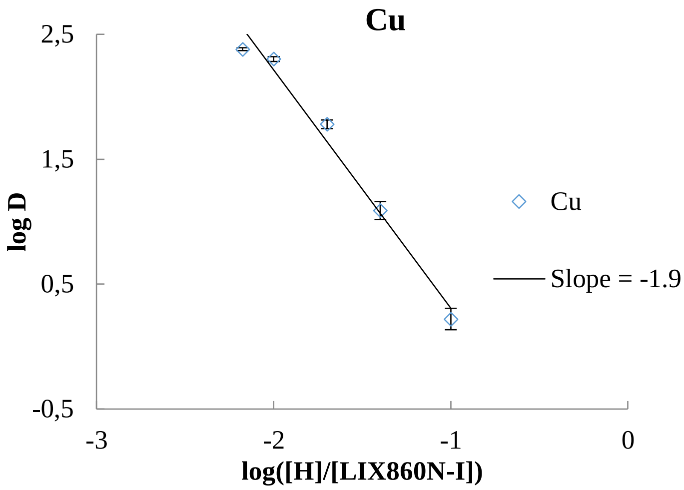

Fig. 16. The influence of LIX860N-I concentration on the extraction of Cu. Equilibrium values were plotted. Extraction was carried out at 20 ± 1°C, with a phase ratio of 1. The contact time was 5 min.

No third phase formation or other problems were observed in the extraction experiments. The D-values are very high, i.e. >100 in some cases. Similar results were obtained by Karlfeldt Fedje and co-workers when using 17% LIX 860N-I in Solvent 70 to extract Cu from a MSW combustion fly ash leachate at pH 0.7 (Karlfeldt Fedje et al, 2012) and has also been reported by others [106].

The only detected co-extraction of an undesired element was some iron extracted by the LIX860N-I. The distribution ratios for Fe extraction were in the range 0.01-0.1 under these experimental conditions. Thus, the Cu/Fe separation factors are so large, from 1200 to 2500 for extraction of the leachate from Ash A and from 3400 to 5900 for the extraction of leachate from Ash B, that it is reasonable to assume that this separation method is feasible for industrial use.

Different concentrations of sulfuric acid were used to strip copper from the Cu-loaded organic phases. As shown in Fig. 17, the percentage of copper stripped increases with increasing acid concentration, with 85-95% of copper transferred to the new aqueous phase after stripping using 1.5 mol/L H_2SO_4 acid. Co-stripping of a small fraction of iron was observed for the Cu-loaded organic phase from Ash A extraction.

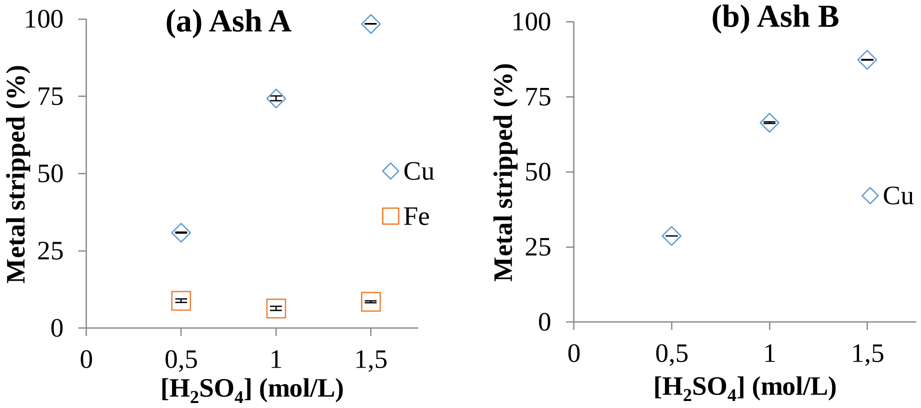

Fig. 17. Results from sulfuric acid stripping of copper from organic phases at $\theta = 1$ in extraction of (a) Ash A leachate and (b) Ash B leachate.

4.3.2. Solvent extraction of zinc with Cyanex 272, Cyanex 572 and Cyanex 923

Solvent extraction of zinc is commonly done using phosphonic and phosphinic acids, such as Cyanex 272, or trialkylphosphine oxides, such as Cyanex 923, which have been known to extract zinc effectively in industrial use. As an example, Schlumberger and co-workers have developed a method based on extraction using Cyanex 272 for the recovery of zinc from MSWI fly ash (Schlumberger et al., 2007). However, recently a new ligand, Cyanex 572, has been introduced on the market. Although originally designed for the separation of rare earth elements it was considered interesting to compare it with the well-known extractants Cyanex 272 and Cyanex 923 with regard to the ability to extract zinc in the presence of iron and other contaminants. In addition to the choice of extractant, the nature of the organic diluent used in a solvent extraction process can have a significant influence on the efficiency of the process. Therefore, the three extractants included in this part of the work were combined with a number of diluents with different chemical properties.

The extraction behavior of zinc and co-extracted metals over 30 min is shown in Fig. 18. All three systems reached equilibrium within 5 min for the extraction of zinc. The extraction of cadmium and lead in the Cyanex 923 system reached equilibrium equally fast. In contrast, it took more than 30 min to reach equilibrium for the iron extraction in all systems used here.

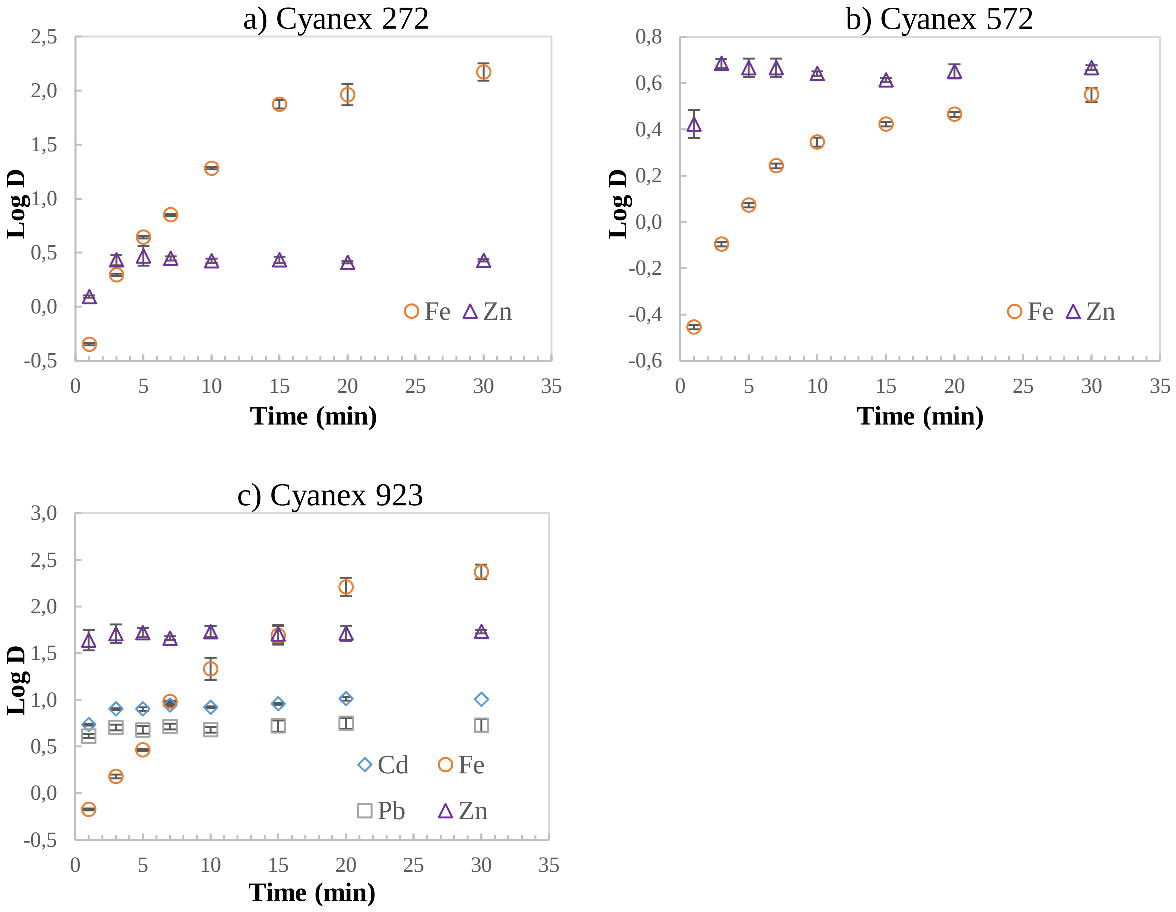

Fig. 18. Kinetics of the extraction of zinc and co-extracted metals using 1mol/L Cyanex 923 (a), 1mol/L Cyanex 572 (b) and 1mol/L Cyanex 272 (c) at ambient temperature (20 ± 1°C). The phase ratio was 1.

The results also show that Cyanex 923 is the preferred extractant for zinc under the tested conditions (log D > 1.5). However, Cyanex 923 was less selective compared to Cyanex 272 and Cyanex 572, since not only iron, which was co-extracted in all three extraction systems, but cadmium and lead were co-extracted as well. Cyanex 572 showed a higher distribution ratio for zinc in the extraction, with a logD of approximately 0.65, compared to that of Cyanex 272 (logD ~ 0.45), and a lower distribution ratio of co-extracted iron. The $\log D_{Fe}$ is 0.1 and 0.6 for Cyanex 572 and Cyanex 272, respectively, under the experimental conditions used here. Therefore, Cyanex 572 is expected to give a better separation of zinc from iron compared to Cyanex 272. To obtain a higher extraction percentage, a multi-stage mixer-settler system can be used to achieve the target, and the required number of the mixer-settler stages can be calculated with a McCabe-Thiele diagram [69, 87] as in Paper V, where a two stage mixer-settler system was set up for zinc extraction using Cyanex 923 with a result of > 99%.

The aqueous solutions used for stripping in this work, in addition to water, were hydrochloric, nitric and sulfuric acid solutions with concentrations in the range of 1 to 5 mol/L. The organic phases were prepared by contacting the 1 mol/L Cyanex 272, Cyanex 572 and Cyanex 923 in Solvent 70 with the original aqueous feed respectively for 5 min as described above.

The nature of the organic diluent used in a solvent extraction process can have a significant influence on the process. The extraction results for zinc using the three extractants in different diluents are presented in Fig. 19. The highest zinc extraction efficiencies were obtained using aliphatic diluents, Solvent 70, Escaid 120 and Isopar L, in all three systems. The aromatic diluents Toluene, Butylbenzene and Solvesso 150 gave similar extraction results as aliphatic diluents for Cyanex 923, but a 10% to 20% decrease in Cyanex 272 and Cyanex 572 systems, respectively. The use of 1-Octanol led to a significant decrease in the extraction results with all extractants compared to the other diluents. The results obtained in this work agree with those obtained in other investigations [69, 84]. One influence of the diluent is the ability of the diluent to form hydrogen bonding that can affect the solubility of extractant in the organic phase. Diluents such as octanol can form a three dimensional net structure by hydrogen bonds, resulting in low solubility of extractant and/or aggregation of extractant molecules, which causes a low D value. This was also seen in this investigation (Fig. 19). The aliphatic diluents do not form hydrogen bonds and can easily make space (form a cavity) for the metal-ligand complex. The aromatic rings have a slight electronegativity that makes weak hydrogen bonding possible and can make aromatic diluents somewhat less effective as diluents in solvent extraction. The results obtained in this work showed less effective extraction with aromatic diluents than with aliphatic diluents for the extractants Cyanex 272 and 572, but not for Cyanex 923. This shows that the chemical nature of the extractant is important as well. However, there are also other properties that may affect the result. The polarity of the diluent, for example, can affect the extraction efficiency. The solubility of the neutral complex formed by extractant and metal ion in organic phase is inversely proportional to the diluent polarity. The non-polar diluents e.g. aliphatic hydrocarbons thus generally have a high ability to dissolve complexes, leading to an high D-value. Based on the results presented in Fig.19, kerosene (Solvent 70) was selected as the diluent for other experiments in the present work.

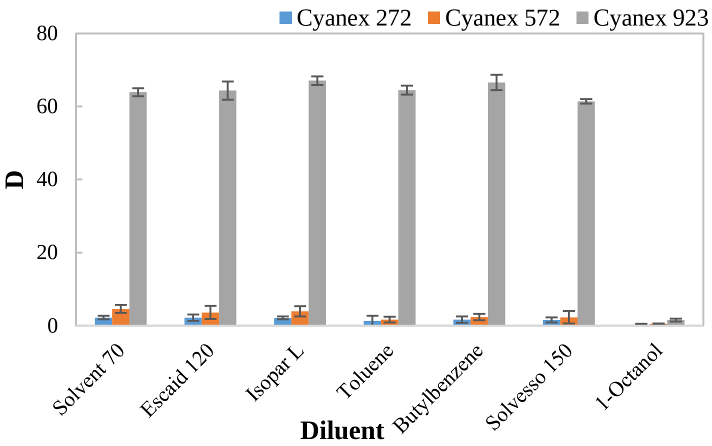

Fig. 19. D-values obtained in the extraction of zinc using 1 mol/L of those three Cyanex ligands in various diluents. Solvent 70, Escaid 120 and Isopar L are aliphatic diluents. Toluene, Butylbenzene and Solvesso 150 are aromatic diluents, and 1-Octanol is an alcohol. The contact time was 5 min with a phase ratio of 1 at 20 ± 1°C.

Extraction mechanism using Cyanex 272 and/or Cyanex 572

The extraction of zinc(II) ions from chloride solutions with Cyanex 272 and/or Cyanex 572 may be represented with equation 16 where HA represents the protonated ligand and A the de-protonated one.

$$Zn^{2+}_{(aq)} + 2HA_{(org)} \overset{K_{ex}}{\Leftrightarrow} ZnA_{2(org)} + 2H^{+}_{(aq)} \qquad \text{(Eq. 16)}$$

Where K_{ex} denotes the extraction constant.

$$K_{ex} = \frac{[ZnA_2]_{org} \cdot [H^+]^2_{aq}}{[Zn^{2+}]_{aq} \cdot [H^+]^2_{aq}} \qquad \text{(Eq. 17)}$$

$$K_{ex} = \frac{D \cdot [H^+]^2_{aq}}{[HA]^2_{org}} \qquad \text{(Eq. 18)}$$

$$\text{Where } K_{ex} = \frac{D \cdot [H^+]^2_{aq}}{[HA]^2_{org}} \qquad \text{(Eq. 19)}$$

Taking the logarithm of Eq.17 and rearranging:

$$\text{logD} = \text{log}K_{ex} - 2log\frac{[H^+]_{aq}}{[HA]_{org}} \qquad \text{(Eq. 20)}$$

Therefore, by plotting the logarithm of the distribution ratios of zinc extraction versus the logarithm of the ratio between the concentrations of protons and extractant at equilibrium, the results should be linear and the slope should equal to -2, which indicates the number of extractant molecules that are needed for binding of one zinc ion in the extracted complexes.

The influence of extractant concentration on the metal extraction results was studied in the range 0.1 to 2 mol/L. The aqueous phase was the original feed with $pH_{in} = 2$, and the pH value was measured after extraction. The plots shown in Fig. 20 of log D versus log($[H^+_{(aq)}]$/[Cyanex $272_{(org)}$] and log($[H^+_{(aq)}]$/[Cyanex $572_{(org)}$] are linear with a slope of -2 and -2.1 individually, which indicates that the results showed a good correlation with the theoretical model with two ligands per metal ion.

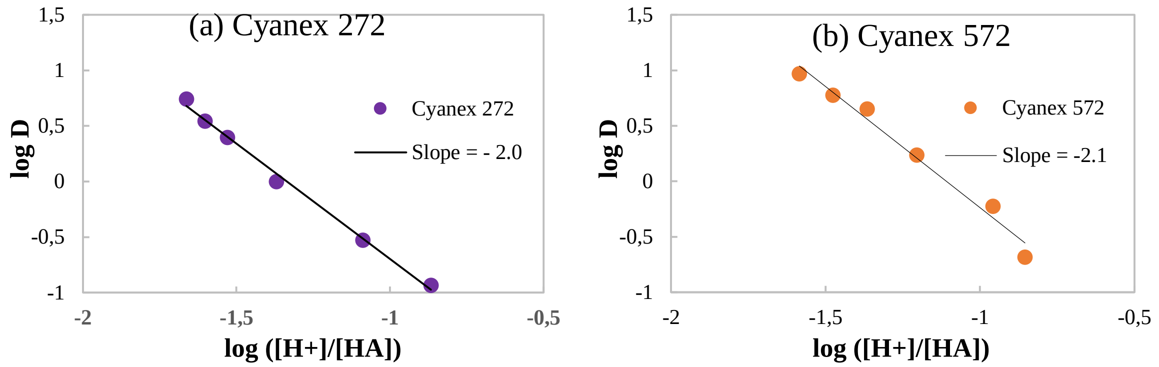

Fig. 20. Influence of extractant concentration on zinc extraction using Cyanex 272 and Cyanex 572. Plot of log D vs. equilibrium log ($[H^+]/[HA]$). a) was Cyanex 272 and b) was Cyanex 572 in Solvent 70, 0.1 mol/L – 2 mol/L. The contact time was 5 min with a phase ratio of 1 at 20 ± 1°C.

Effect of Cyanex 923 concentration

The mechanism for zinc extraction by Cyanex 923 as presented in Eq.1 and 2, follows the equation 2 where the extractant molecules are represented by B.

$$Zn_{aq} + 2Cl_{aq} + 2B_{org} \overset{K_{ex}}{\Leftrightarrow} ZnCl_2 \cdot 2B_{org} \qquad \text{(Eq. 2)}$$

The equilibrium constant, K_{ex} for the extraction process is expressed as:

$$K_{ex} = \frac{[ZnCl_2 2B]_{org}}{[Zn^{2+}]_{aq} \cdot [Cl^-]^2_{aq} \cdot B^2_{org}} \qquad \text{(Eq. 21)}$$

Where D $= \frac{[ZnCl_2 2B]_{org}}{[Zn^{2+}]_{aq}}$ (Eq. 22)

Substituting D, rearranging and taking logarithms gives,

$$logD = logK_{ex} + 2\log[Cyanex923]_{org} + 2\log[Cl]_{aq} \qquad \text{(Eq. 23)}$$

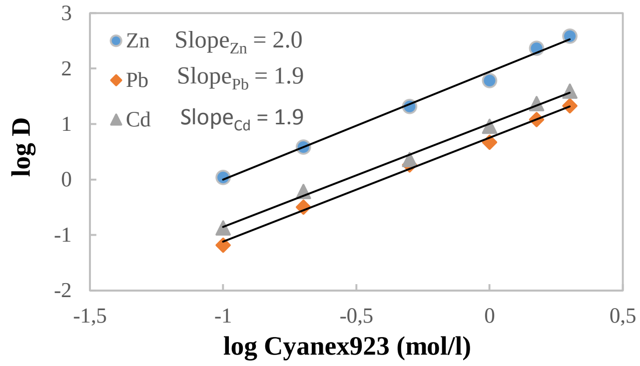

Fig. 21. Influence of extractant concentration on zinc extraction and co-extracted metals using Cyanex 923. Plot of log D vs. equilibrium log[Cyanex 923]. The extractant concentration was in the range of 0.1 - 2 mol/L in Solvent 70. The contact time was 5 min with a phase ratio of 1 at 20 ± 1°C.

An increased concentration of Cyanex 923 in the range 0.1- 2 mol/L leads to an increase in the percentage of zinc extraction, as shown in Fig.21. The number of extractant molecules involved in the extraction of one zinc ion was determined by plotting the logarithm of the Cyanex 923 concentration versus the logarithm of the distribution ratio. A slope close to two was observed from Fig. 21 for the linear equation, which confirmed that the extraction demands two extractant molecules per Zn^{2+} ion. This is in agreement with results from work by Cierpiszewski and co-workers who investigated zinc extraction in acidic chloric media [78, 107].

The three extraction systems were also studied at five different temperatures: 20 ± 1°C, 30 ± 1°C, 40 ± 1°C, 50 ± 1°C and 60 ± 1°C. Phase separation was found to be faster at higher temperature compared to at 20°C. This may be due to a change in the viscosities of the solutions with temperature [108].

As shown in Fig.22, increased distribution ratios for iron in all three extraction system were observed with the increase in temperature, and the most significant increase was seen for Cyanex 923. In contrast, the distribution ratio of zinc was less influenced by the change of temperature and those of cadmium and lead decreased with increased temperature in the range 20 to 60°C.

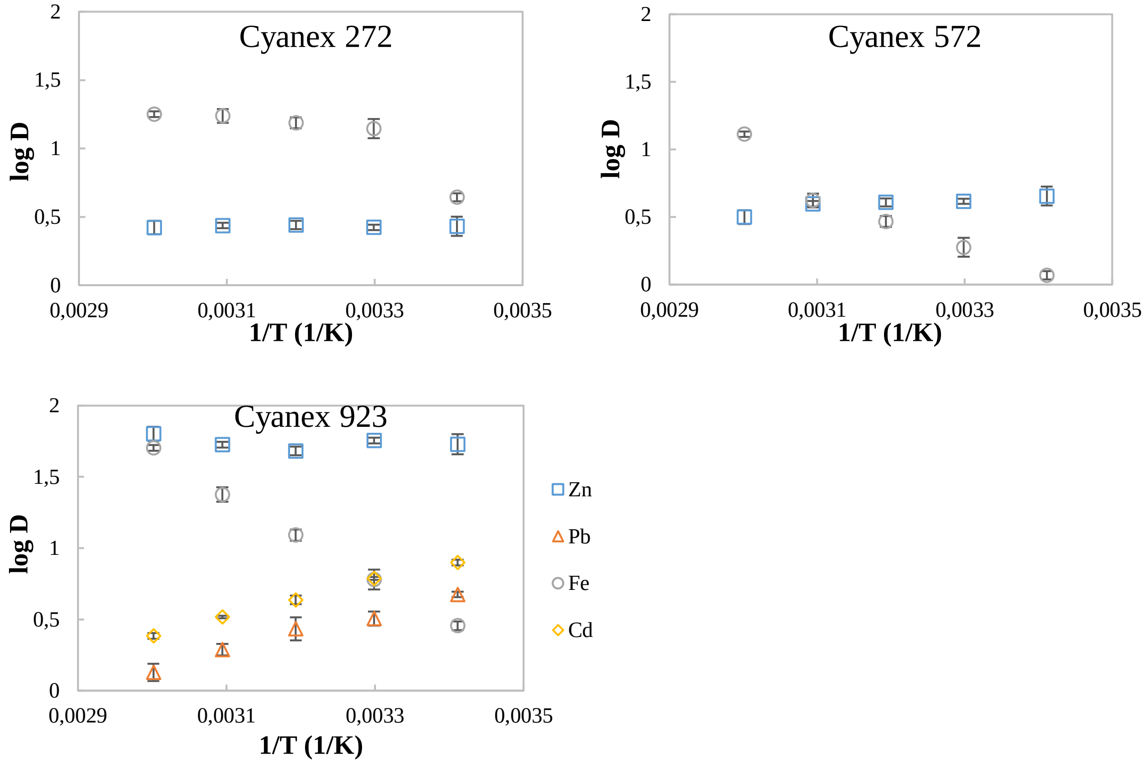

Fig. 22. Results of zinc extraction and co-extracted metals at various temperatures in the range 20 - 60°C (± 1°C). The concentration of extractant was 1 mol/L in Solvent 70, contact time was 5 min and the phase ratio was 1.

Based on the results shown in Fig.22, the increase in temperature has a negative effect on the separation of zinc from co-extracted iron in all three extraction systems, especially the one using Cyanex 923; the separation factor $SF_{Zn/Fe}$ at 20°C was 20 and decreased to 1.2 at 60°C. It is thus advised to carry out the separation at low temperature to obtain higher zinc purities. In the remaining part of this work, the experiments were conducted at room temperature, i.e. 20 ± 1°C.

The equilibrium constant K_{ex} can be calculated based on the distribution ratios and the extraction mechanism presented as Eq. 20 and 23 (Eq. 24 is the linear form of Van's Hoff's equation). By plotting the natural logarithm of the equilibrium constant Kex against the inverse of the temperature (1/T), the enthalpy (ΔH°) and entropy (ΔS°) can be determined from the slope and the intercept of the plot, respectively.

$$lnK_{ex} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad \text{(Eq. 24)}$$

Based on Eq. 11 and 14, lnK_{ex} was calculated for the zinc extraction between 293 K and 333 K, and the results are shown in Fig. 23.

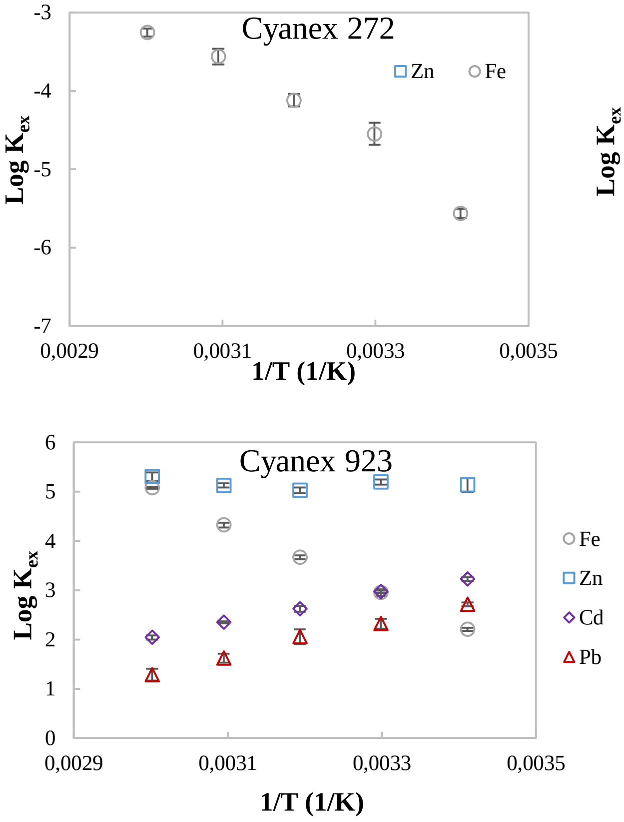

Fig.23. The effect of extraction temperature in the equilibrium constant of the extraction of iron and zinc from ash leachate using 1 mol/L Cyanex 272, Cyanex 572 and Cyanex 923 in solvent 70, respectively.

Aqueous phases with different pH values made from the original aqueous feed, as described in section 3.3, were used in the extraction with organic phases containing 1 mol/L of the three extractants diluted in Solvent 70. The pH values shown in Fig. 22 were measured after the extractions, i.e. they reflect the pH change that occurs due to the acidity of the ligands. The starting pH values were 0.5, 1.0, 1.6, 2.0, 2.6, 3.1 and 3.7, as described in section 3.4.2. Another neutralized aqueous feed was prepared with higher pH_{in} = 4.1 but a slight precipitation was noticed so no aqueous phase with starting pH above 3.7 was used. There was no pH adjustment made during the extraction since it is not technically feasible in batch experiments carried out in sealed glass vials using a shaking machine. The extraction behavior of zinc and co-extracted metals at various pH values is shown in Fig.24.

The total fraction of zinc extracted using Cyanex 272 increased with pH in the selected pH_{end} range, and the co-extraction of iron showed the same tendency. At pH_{end} = 1.7 more than 80% of the zinc and more than 70% of the iron was extracted. Cyanex 572 presents a better separation of zinc from iron since more than 90% of the zinc and less than 40% of the iron was extracted at pH_{end} =1.4. Cyanex 923 is effective for zinc extraction over the whole pH range, pH_{end} from 0.5 to 3.7. However, iron, lead and cadmium were extracted effectively as well.

Based on the results from these batch experiments the extraction pH should be chosen so that it gives a pH_{end} > 1.7 for Cyanex 272 and > 1.5 for Cyanex 572, respectively. Furthermore, the pH value in solution should be controllable during extraction using acid or alkali to achieve optimized results.

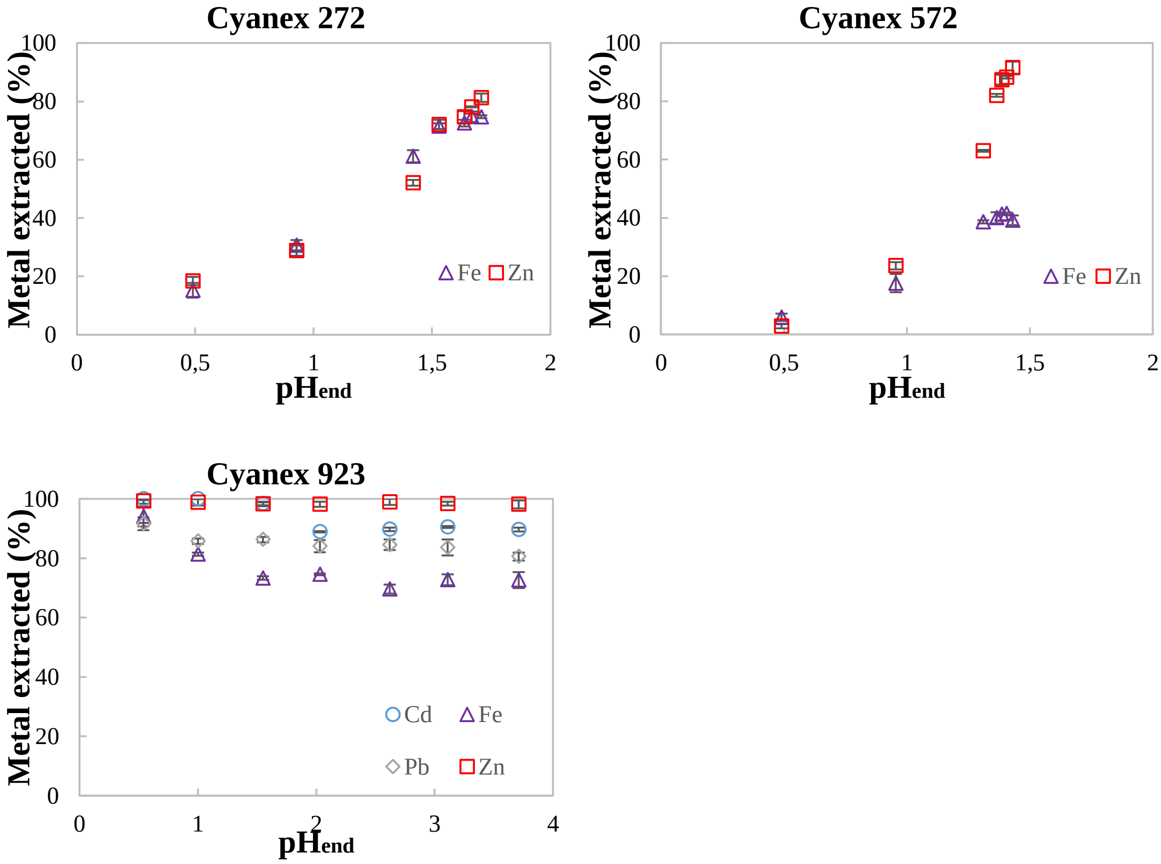

Fig. 24. Results for extraction of zinc and co-extracted metals. Extraction was performed with 1 mol/L Cyanex 272, 572 and 932 in Solvent 70 at ambient temperature contacting aqueous phases with various pH values, using a phase ratio of 1.

The results from stripping of metal ions from the organic phase based on Cyanex 272 is presented in Fig. 25, roughly 70% of the extracted zinc was stripped by hydrochloric acid of concentration > 1mol/L, and approximately 60% of the extracted iron at a concentration of hydrochloric acid > 2mol/L. In contrast, nitric acid was more selective and effective for zinc stripping, with more than 95% of the extracted zinc released to the new aqueous phase. In addition, the 1mol/L nitric acid solution did only transfer 0.3% of the iron. Thus, a rather weak nitric acid solution can be used to selectively strip zinc from the un-desired iron.

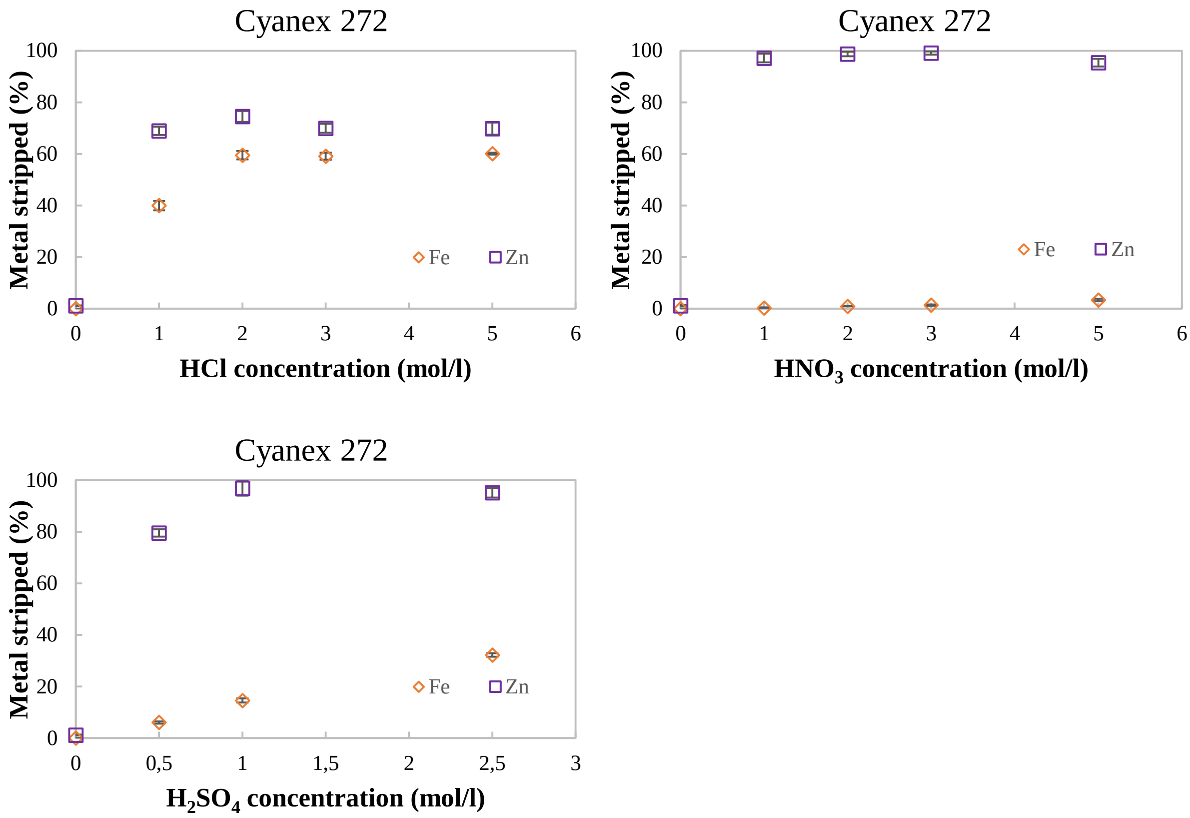

Fig. 25. Stripping results for zinc and co-extracted iron in one stage with hydrochloric, nitric and sulfuric acid solutions of various concentrations. The contact time was 5 min and the phase ratio was 1 at 20 ± 1°C.

The stripping results of zinc and co-extracted iron from Cyanex 572 organic phases by the three acids was similar to those obtained for organic phases based on Cyanex 272, as shown in Fig. 25 and 26. The extracted zinc in the organic phase can be effectively stripped using nitric and sulfuric acid solution, without stripping the iron at the same time. More than 95% and 90% of zinc, respectively, was stripped out using nitric and sulfuric acid solutions with concentrations ≥ 1 mol/L. Hydrochloric acid solutions with concentration ≥ 3 mol/L on the other hand were able to strip more than 95% of the extracted zinc and iron. The acid that should be used as a stripping agent depends also on whether the recovered zinc can be sold as a zinc sulfate solution, for example.

From the results obtained in this investigation, a flowchart showing a zinc separation process from a copper depleted MSWI fly ash leachate based on hydrochloric acid is suggested (Fig. 27) for zinc recovery using Cyanex 572. The pH of the leachate can be adjusted using sodium hydroxide to optimize the zinc extraction before or during the extraction process, and the zinc-loaded organic phase can be stripped using 1 mol/L nitric acid to recover the zinc from the organic phase after the extraction process. Only minor amounts of iron (<1%) will be co-stripped with zinc in this step. The choice of acid for the stripping step also depends on in what form the zinc is preferably recovered. If it is going to an electrolysis unit available close to the extraction plant it is probably beneficial to use sulfuric acid for the stripping, since the electrolyte in a zinc electrowinning plant is normally based on sulfuric acid.

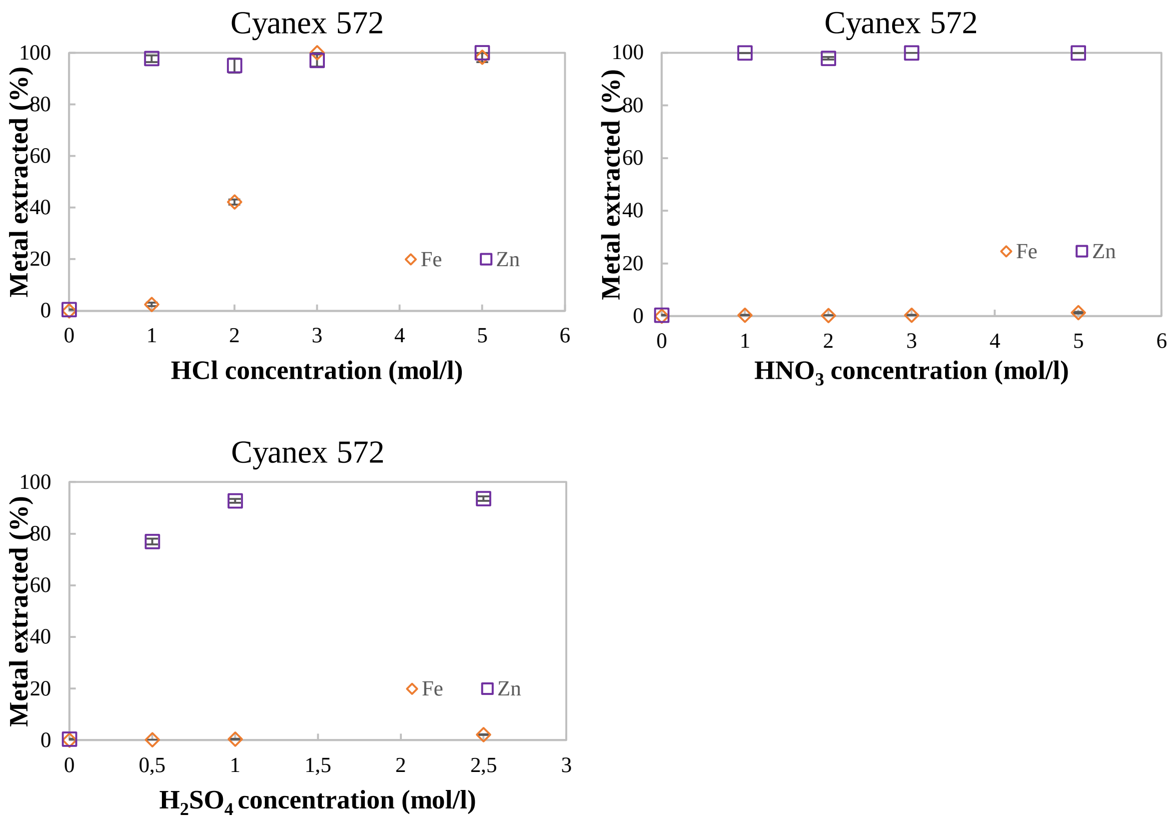

Fig. 26. Stripping results for zinc and co-extracted iron in one stage with hydrochloric, nitric and sulfuric acid solutions of various concentrations. The contact time was 5 min and the phase ratio was 1 at 20 ± 1°C.

The washing step is included to remove the remaining iron in the organic phase to make it reusable. A 3 mol/L hydrochloric acid solution can be chosen for this step due to its high stripping efficiency for iron.

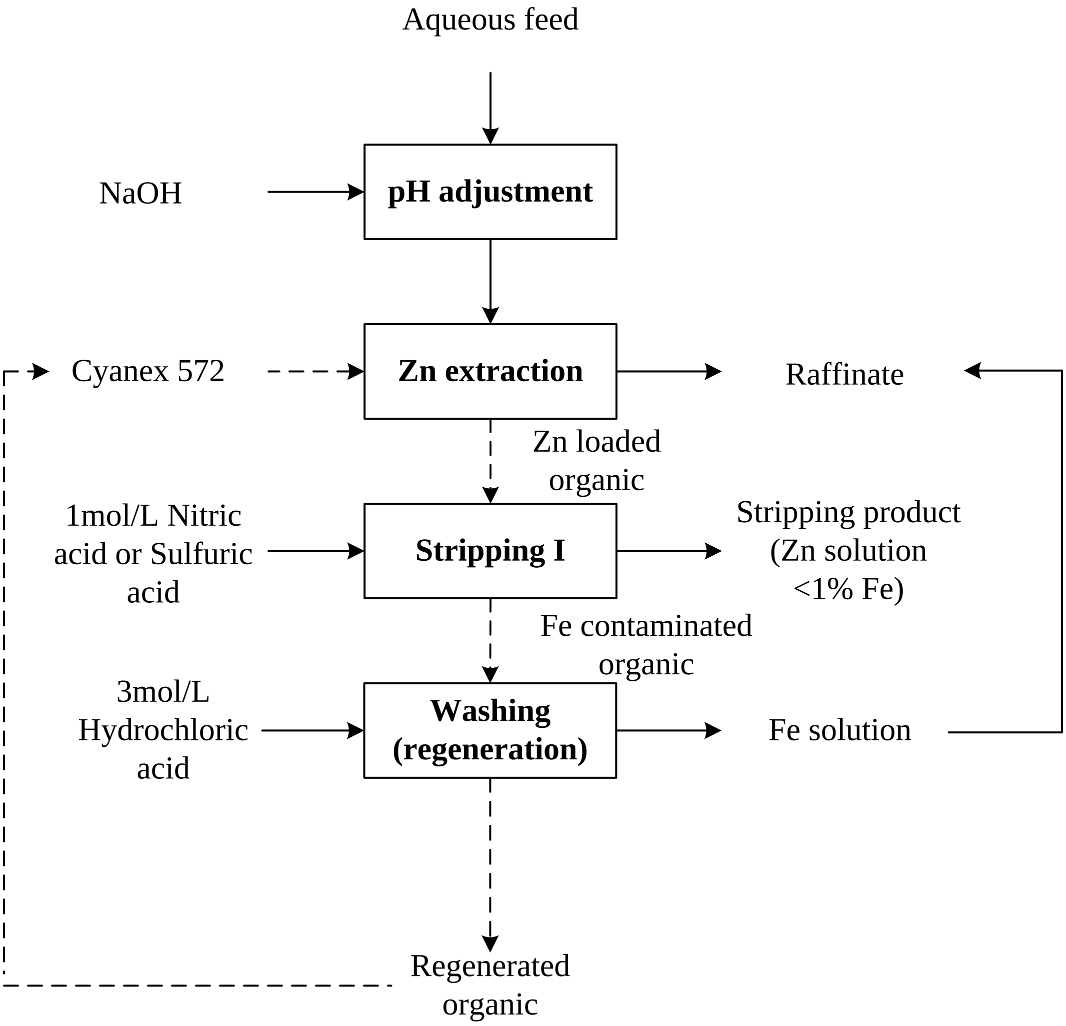

Fig. 27. Schematic of zinc recovery using Cyanex 572. The dashed lines show the flow of the organic phases. pH adjustment is suggested before or during zinc extraction.

In paper V, the selective stripping of zinc from Cyanex 923 organic phase was investigated to separate zinc from the undesired cadmium, iron and lead [109]. The results for stripping of zinc and co-extracted metals using different acids, salt solutions and pure water are presented as distribution ratios in Table 8. Zinc was stripped quite efficiently in all cases except in the chloride systems. All chloride solutions used prevented stripping; only 6.1% was transferred by the KCl solution, 5.1% by the NaCl solution and 3.6% by the HCl. This is quite as expected since the Cyanex 923 extractant binds zinc as chloride complexes. In contrast, nitrate and sulfate solutions, as well as water, gave up to 95% stripping of zinc within 1 min contact. Iron was not stripped other than in acidic conditions. An increasing acidity led to increased stripping of iron. Cadmium and lead were stripped in all experiments except for 1 mol/L HCl where cadmium had a distribution ratio of 3.6, showing that it remained in the organic phase to a large extent. Lead had a distribution ratio of 10 in 5 mol/L sulfuric acid, indicating that 5 mol/L sulfuric acid is not a suitable agent for lead stripping. In addition, the presence of sulfate ions may give precipitation of lead sulfate, which would disturb the mixer settler function.

Table 8. Distribution ratios (D) obtained for metal stripping from the organic phase from Cyanex 923 zinc extraction using various agents; O:A ratio was 1:1 and contact time was 1 min.

	D_{Cd}	D_{Fe}	D_{Pb}	D_{Zn}
Pure Water	0.11±0.01	>100	0.35±0.01	0.10±0.01
1mol/L NH_4NO_3	0.16±0.02	>100	0.74±0.02	0.10±0.01
1mol/L KCl	<0.1	>100	0.90±0.02	15±1
1mol/L NaCl	0.14±0.01	>100	1.1±0.1	18±1
1mol/L $NaNO_3$	0.35±0.01	>100	1.0±0.01	0.18±0.01
0.5mol/L Na_2SO_4	0.25±0.01	>100	0.92±±0.02	0.16±0.02
1mol/L HCl	3.6±0.1	5.9±0.3	0.97±0.02	27±2
1mol/L HNO_3	<0.1	3.3±0.1	0.24±0.01	<0.1
5mol/L H_2SO_4	<0.1	0.63±0.03	10±0.5	<0.1

A set of steps that can be used to separate zinc from the co-extracted, undesired metal ions can be suggested based on the results from Table 8. Since 1 mol/L KCl strips cadmium and lead quite efficiently, but leaves iron and zinc in the organic phase, and pure water strips zinc, those aqueous phases were chosen for the investigation of selective stripping. The stripping results using 1 mol/L KCl (with O:A ratios from 6:1 to 1:6) are presented in Fig.28. KCl was quite effective for the stripping of cadmium and lead, removing more than 95% of the cadmium and 75% of the lead from the organic phase in one stage. The best results were obtained at a phase ratio of 1:6.

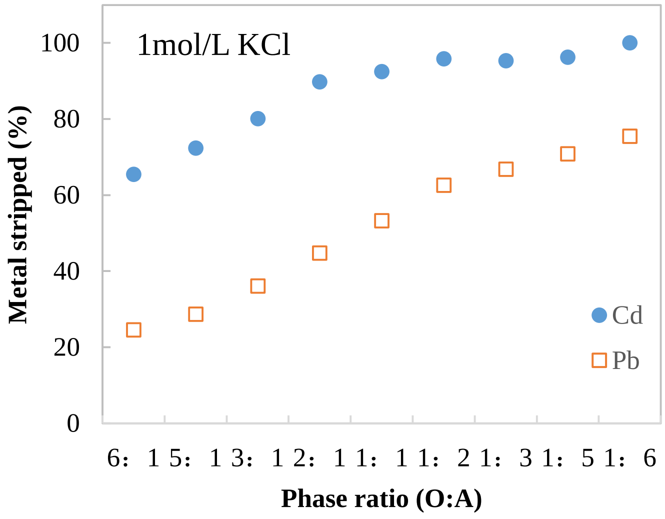

Fig. 28. Percentage of cadmium and lead stripped with 1 mol/L KCl using O:A phase ratios between 6:1 and 1:6.

Fig.29 presents the results for zinc and iron stripping using pure water, which is planned to be used after the stripping of cadmium and lead. The transfer of both zinc and iron from the organic phase to the aqueous phase increased with decreasing phase ratio (O:A) from 6:1 to 1:6, for zinc from 87% to more than 99% and for iron from 0.3% to 1.7%. The large separation factor (>1000) between zinc and iron indicates that these two elements can be separated, and due to the large separation factor at all selected phase ratios, higher phase ratio (O:A) is favored to concentrate the zinc aqueous solution.

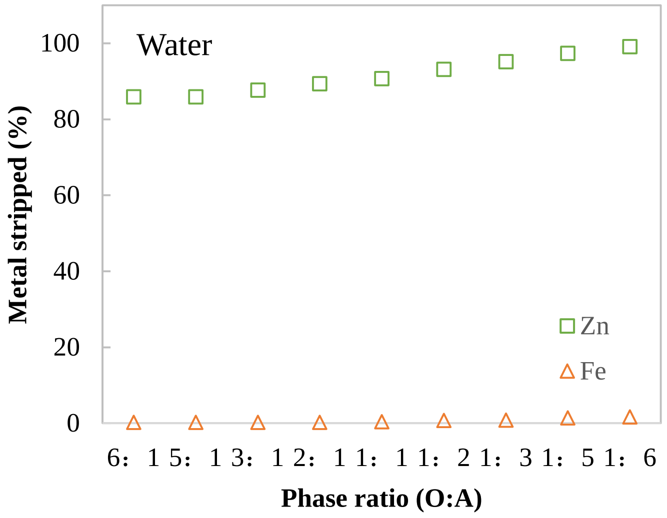

Fig. 29. Percentage of zinc stripped with pure water with O:A phase ratios between 6:1 and 1:6.

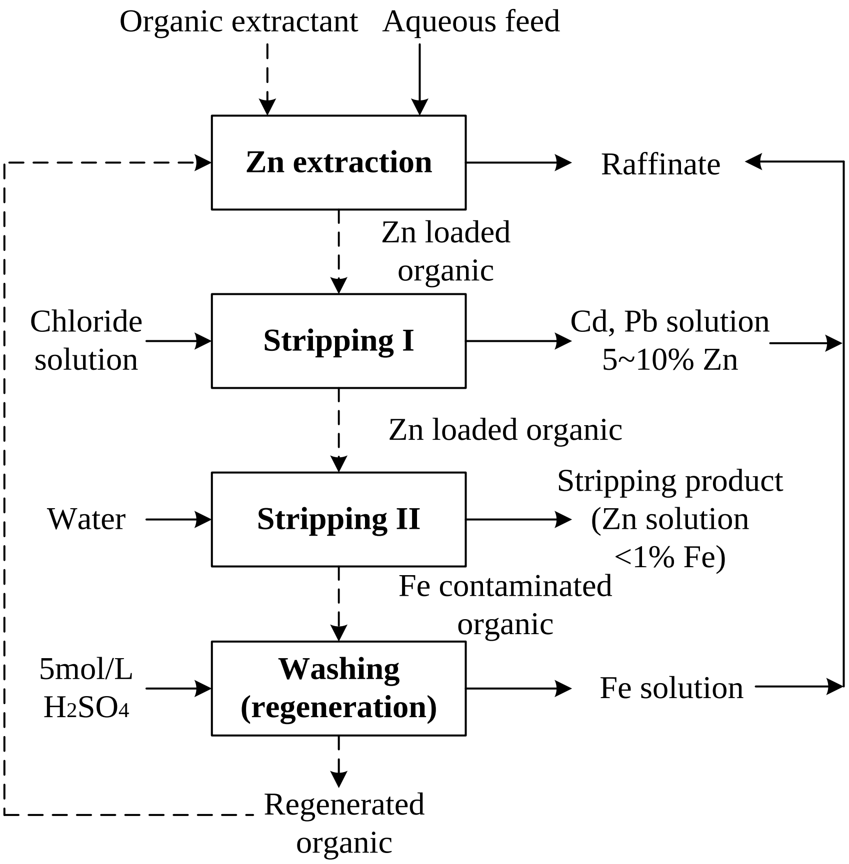

Fig. 30. Schematic of selective stripping process for the separation of zinc from impurities using Cyanex 923. The dashed lines are the organic flow.

From these results a selective stripping process is suggested, as shown in Fig.30. A chloride stripping agent, e.g. 1 mol/L KCl, can first be used to strip cadmium and lead out from the zinc-loaded organic phase (Organic phase II) with 5~10% loss of zinc. The next step would be a zinc stripping using water. Only minor amounts of iron (<1%) will be co-stripped with zinc in that step. The relatively pure zinc solution can then be adjusted to an acidic sulfuric solution for incorporating into industrial electrowinning. The washing step is used to remove the remaining metal ions in the organic phase to make it reusable for extraction. A 5 mol/L H_2SO_4 solution can be chosen for the washing due to the high stripping efficiency of the remaining iron in this solution.

4.3.3. Cementation as an alternative purification method

Cadmium, iron and lead, which will be co-extracted as undesired elements during zinc extraction, are more noble, i.e. they have more positive standard reduction potentials than zinc, as described in section 4.3.2 and in more detail by others [110]. Therefore, it is possible to precipitate those elements by reductive reaction with zinc metal using what is known as a cementation reaction. In the present work cementation was carried out by adding zinc metal powder with a ratio of zinc powder to leachate of 4 g/L. After 2 hours reaction time the pH value remained constant at 2, indicating that the solution had reached equilibrium. The results of the displacement reactions of cadmium, chromium, copper, iron and lead using zinc powder are shown in Fig. 31. The concentrations of cadmium, chromium, copper, iron and lead were lower than the detection limit after the cementation reaction.

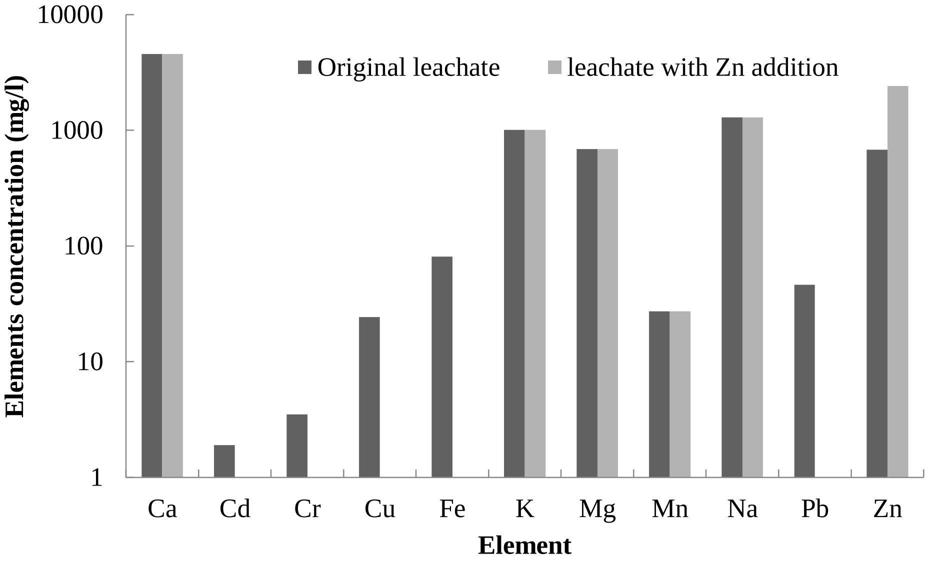

Fig. 31. Cementation test using original leachate. Zinc powder was added in one portion and stirred for 2 hours. The ratio of zinc powder to leachate was 4 g/L.

These results demonstrate that the cementation process can be used to remove all the impurities, either before or after the zinc extraction, and thus a more concentrated zinc solution can be obtained in one stage. It would be favorable to use cementation before the zinc extraction, as shown in Fig. 32, which makes it possible to use electrolysis for zinc recovery after the extraction as is done in the FLUREC process [111], or to obtain a stripping product to transform into a sulfuric acid solution.

4.3.4. Preliminary evaluation of the sequential extraction process for copper and zinc

The suggested process is presented in Fig. 32, based on the results described in earlier sections consisting of leaching with HCl at constant pH 2 with a liquid to solid ratio of 20, followed by extraction of copper using 1 mol/L LIX860N-I and a consecutive extraction of zinc from the copper-depleted aqueous phase by 1 mol/L Cyanex 923. The starting materials for testing of this process were the leachates described in Table 8. The leaching removed 70~100% of the copper, 80% of the zinc and significant fractions of the aluminum, calcium, sodium, potassium, iron, cadmium, and lead from the ash. The removal of iron, cadmium, and lead is a problem due to co-extraction with zinc using Cyanex 923, as shown in the extraction experiments described in earlier sections. On the other hand, leaching of cadmium and lead from the ash matrix may present a way to remove these metals from the environment. Fe(III) can be separated from zinc and copper using TBP in chloride medium. However, this complicates the process by adding an additional extraction [112]. Alternatively the selective stripping or reductive cementation by addition of zinc metal powder to separate iron and other undesired elements from zinc that was investigated in this work can be used.

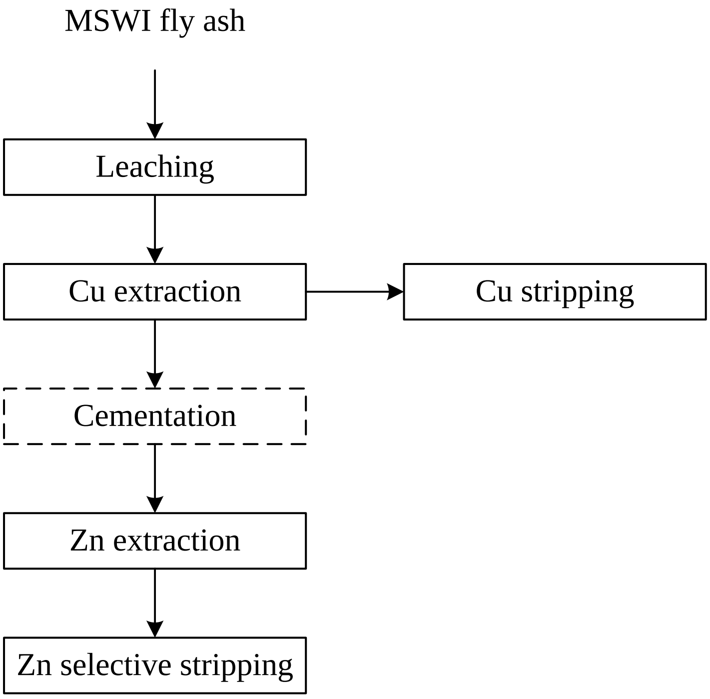

Fig. 32. Schematic of suggested flowchart based on the results

A summary of the overall results obtained in laboratory size experiments for the combined process for leaching and extraction of copper and zinc from MSWI fly ash is presented in Table 9. The copper and zinc recovery results refer to those obtained from leaching at pH 2 with hydrochloric acid, extraction of copper and zinc using 1 mol/L LIX 860N-I and 1 mol/L Cyanex 923, respectively, diluted in Solvent 70 and stripping copper and zinc from organic phases using 1.5 mol/L sulfuric acid and 1 mol/L nitric acid, respectively. All phase volume ratios used in the extractions and stripping were 1.

Table 9. Recovered amounts of Cu and Zn in the leaching-extraction procedure. All results are shown in % of the content in the original ash and in the flow going in to the respective process. Paper III [74].

	Ash A	Ash B
Cu yield in %		
Leaching	70.2 ± 2.2	100.0 ± 1.4
Extraction	100.0 ± 0.0	100.0 ± 0.0
Stripping	98.4 ± 0.1	87.3 ± 0.1
Total yield	69.1 ± 2.2	87.3 ± 1.9
Zn yield in %		
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
Total yield	75.2 ± 2.1	80.9 ± 0.7

The metal yields obtained from Ash A were quite reasonable, but were lower than those obtained from Ash B. Similar differences in copper recovery yields from grate-fired combustor fly ash and fluidized bed fly ash have been observed in earlier work and was indicated to depend on the copper speciation [41, 96]. Differences in fly ash composition at one combustion site will also occur, due to differences in composition of the input municipal waste. However, it is important to recognize that although the recovery yield of copper and zinc in the leachate will vary between different ashes, the extraction process is robust enough to be able to handle considerable variations in metal concentrations.

4.4.Laboratory pilot scale test

Based on the experimental experience obtained (Papers I, III, and IV) on MSWI fly ash leaching and solvent extraction separation and purification, one set of process steps was chosen for upscaling tests in mixer settlers. The upscaling work is described in Paper V.

Table 10 shows the chemical composition of fly ash A and the HCl based leachate from the pilot scale test. The leaching of copper and zinc were similar to what was measured earlier in Paper I and other laboratory experiments [41, 60, 91]. In the pilot scale experiments 58% of the copper and 80% of the zinc was leached out from the fly ash, respectively, whereas the earlier laboratory scale leaching released 69% copper and 79% zinc [91]. This difference in copper results may be due to the low content in the ash (840 mg/kg), since with a low total concentration small variations from the average concentration of copper within the ash sample taken for leaching leads to significantly different leaching results.

Table 10. Metal content in MSW fly ash A and leachates; nd=not detected (20 h leaching time, liquid to solid (v/w) = 20, pH = 2)

Element	Fly ash mg/kg dry ash	Leachate mg/L Pilot scale
Al	36,100	1,090±1.8
Ca	180,000	4,570±53.3
Cd	83	1.9±0.02
Cr	450	3.5±0.04
Cu	840	24.3±0.2
Fe	20,100	83.2±1.9
K	21,100	1,030±27.4
Mg	18,100	687±12.2
Mn	1,100	27.2±0.4
Na	26,100	1,290±26.3
Pb	3,000	45.2±1.8
Ti	14,100	nd
Zn	17,100	680±4.6

Experiments aimed at acquiring data for the construction of McCabe Thiele diagrams were performed to determine the number of the solvent extraction stages and stripping stages needed in the mixer-settler system to obtain purified individual copper and zinc solutions for further treatment. The reactions between extractants and the copper and zinc ions were described above in Eq. (11) and (2) [78, 113]. The chemistry involved in these reactions has been described.

$$Cu_{aq}^{2+} + 2RH_{org} \leftrightarrow R_2Cu_{org} + 2H_{aq}^{+} \quad \text{(Eq.11)}$$

$$ZnCl_{2aq} + 2TRPO_{org} \leftrightarrow ZnCl_2 \cdot 2TRPO_{org} \quad \text{(Eq.2)}$$

Two molecules of extractant are involved in the transfer of one metal ion for both copper and zinc. However, the zinc ions are extracted as chloride complexes, which could influence the zinc stripping. There is 0.0004 mol/L copper and 0.01 mol/L zinc in the pilot leachate (Table 11). According to Eq. 2 and 11, 0.001 mol/L LIX860N-I and 0.02 mol/L Cyanex 923 are needed to completely extract 0.0005 mol/L copper and 0.01 mol/L zinc from the leachate. Considering the fact that co-extraction of other metal ions might occur, 0.01 mol/L LIX860N-I and 0.1 mol/L Cyanex 923 in the organic phases were chosen for the experiments used to build the McCabe Thiele diagrams.

The kinetics of copper extraction and zinc extractions using a phase ratio of 1 are shown as the changes in the distribution ratios (D) in Fig. 33. The time required for extraction of copper or zinc to reach equilibrium is also less than 1 min here, as in other systems of different phase ratios. 1 min was therefore chosen for the bench scale extraction experiments to construct the McCabe Thiele diagrams. The pH adjustment was unnecessary for copper extraction due to the low concentration (less than 25 mg/L of copper in aqueous solution). The pH change influenced by the copper extraction cannot be detected by an electrode.

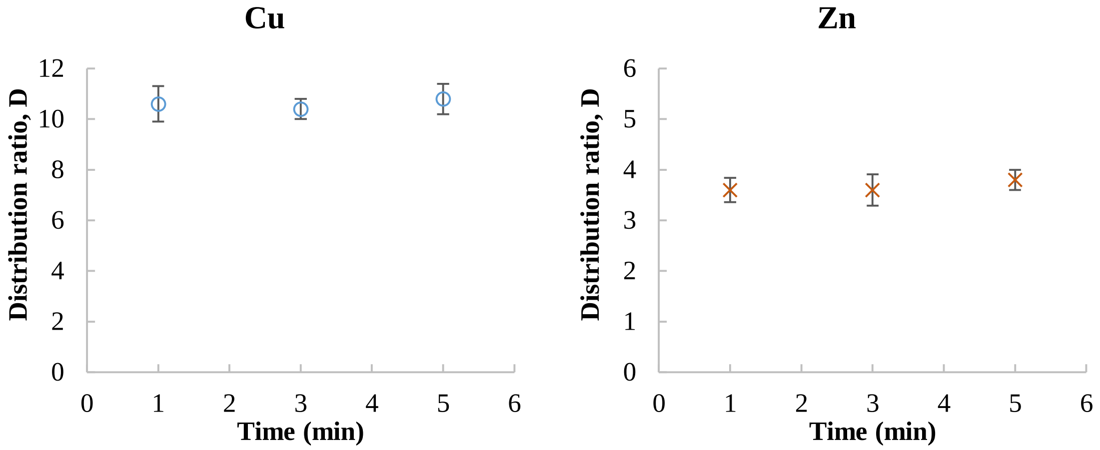

Fig.33. Kinetics of copper extraction using 0.01 mol/L LIX860N-I (left) and zinc extraction using 0.1 mol/L Cyanex 923 (right). The phase ratio O:A was 1.

The McCabe Thiele diagrams describing the extraction of copper and zinc from the ash leachate are shown in Fig.34. The vertical line shows the concentration of metal in the feed solution (24.3 mg/L for copper and 680 mg/L for zinc) at the intersection on the x-axis, and the dashed lines represent the theoretical stepwise evaluation of the number of extraction stages. A lower phase ratio (O:A) could yield more metal concentrated in the organic phase, but it would also result in the need for more operational stages. Therefore the phase ratios (O:A) 1:2 for copper and 1:1 for zinc were adopted as the respective operating ratios for the subsequent investigations using the mixer-settler system. The extraction stages for theoretical complete extraction of copper and zinc were found to be 2 and 3, respectively. The theoretical model predicts that roughly 60% of the copper can be extracted in the first stage and an additional 32% in the second stage (in total 92% of the copper), roughly 70% of the zinc can be extracted in the first stage and in total 93% of the zinc could be extracted in the first two stages.

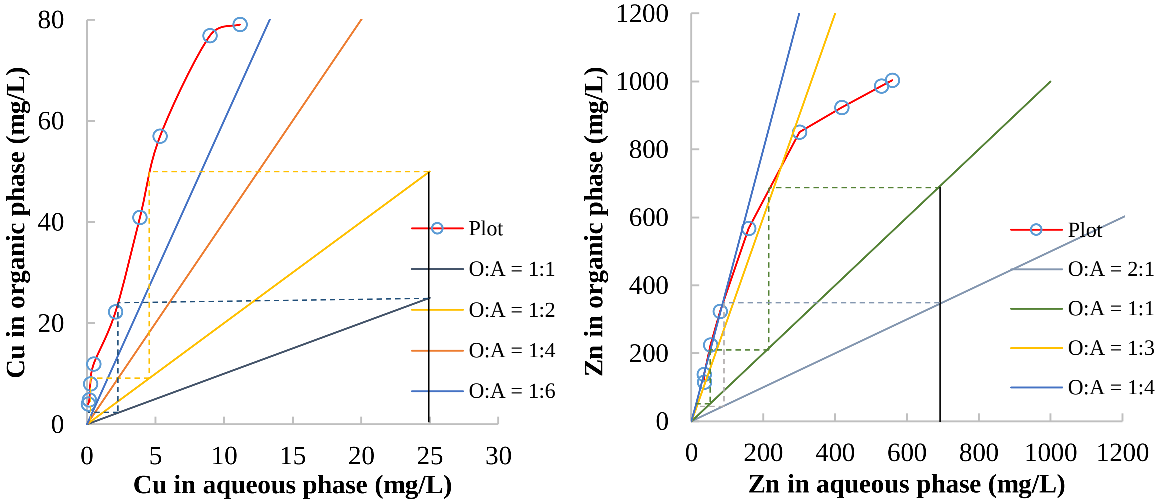

Fig. 34. McCabe Thiele diagram with theoretical operational steps for the extraction of Cu and Zn with 0.01 mol/L LIX860N-I and 0.1 mol/L Cyanex 923 in kerosene. The slopes of the operating lines for Cu extraction are O:A = 1:2 and for Zn extraction O:A = 1:1, respectively. The contact time was 1 min.

The aqueous feed from filtration was pumped into a set of two mixer settler units for copper extraction with a flow rate of 6 mL/min. The counter current flow rate of the organic phase using 0.01 mol/L LIX860N-I in kerosene was 3 mL/min. The volume of the mixer chamber is approximately 55 mL, thus the contact time is 6 min calculated from Eq. 10, which is enough to reach the equilibrium. This arrangement enabled a O:A ratio of 1:2 to be achieved. Aqueous samples were taken from each chamber every half hour and the metal concentration of those samples and in the aqueous feed, raffinate I, were measured.

Fig. 35a presents the copper extraction results. More than 90% of the copper was selectively extracted from the aqueous feed with no other co-extraction except less than 1% iron in two mixer settler stages. The separation factor of Cu/Fe is larger than 1000, indicating that it is feasible to separate those two elements in this system [69].

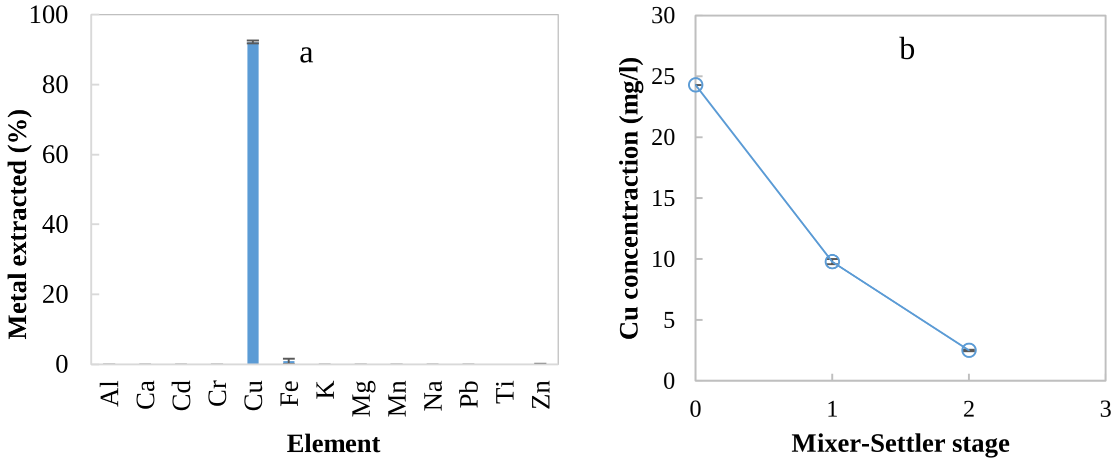

Fig. 35. Results of Cu extraction; a) percentage of copper extracted, b) Cu concentration in each chamber. The O:A ratio was 1:2.

The concentration of copper in the aqueous phase after each of the two mixer settler chambers used is shown in Fig. 35b. The copper concentration in the aqueous phase in the 1st and 2nd stages was 9.8 mg/L and 2.5 mg/L, respectively, which corresponds to approx. 61% and 90% copper extracted. These results correspond very well to the prediction results of the McCabe Thiele diagram (~60% and 92%). As the O:A ratio was 1:2 the copper was concentrated in the organic phase I.

Raffinate I (aqueous phase) collected from the copper extraction was used as the feed solution for the zinc extraction. The flow rate for both aqueous and organic phases in this process was 6 ml/min to obtain an O:A phase ratio of 1:1 and the contact time was more than 4 min. The mixer-settler system consisted of three stages and the aqueous phase in each chamber and the raffinate II were sampled. The total equilibrium extraction efficiencies of zinc and co-extracted metals using 0.1 mol/L Cyanex 923 are presented in Fig.36. Approximately 99% of the zinc was extracted and the co-extraction of cadmium, iron and lead was 26%, 90% and 57%, respectively.

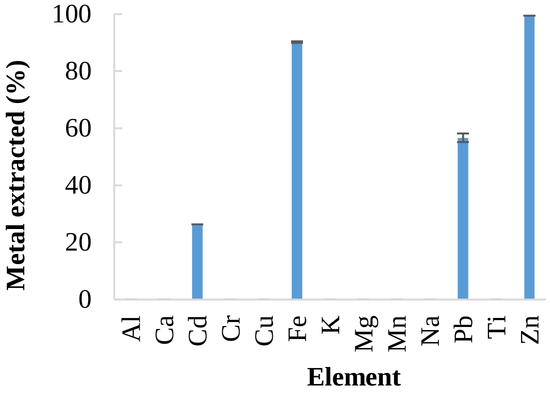

Fig. 36. Extraction results for Zn and co-extracted Cd, Fe and Pb in the mixer-settler system using an O:A ratio of 1:1 and 0.1 mol/L Cyanex 923 in 3 steps.

More detailed information about the results from each reaction chamber for zinc extraction is shown in Fig 37. The concentrations of zinc and iron decreased rapidly in the 1st stage, from 680 mg/L to 140 mg/L for zinc and from 82mg/L to 53mg/L for iron. There was no significant change in the lead concentration and the concentration of cadmium remained almost constant, 1.9 mg/L in the first stage, indicating that zinc and iron were favored to be extracted. The extraction priority of Cyanex 923 followed the order Zn, Fe>Pb>Cd under the experimental conditions used, which may be due to zinc and iron having higher equilibrium constants than that of lead and cadmium under these conditions. The reason may also be that zinc could form a complex with more lipophilic characteristics with Cyanex 923 than the other metal ions do [78], which would favor the extraction of Zn. The formation priority of metal-extractant complex can be adjusted by changing the extraction conditions, e.g. with different acids as stripping agent. [114].

Table 11: Concentration of metals at each stage: after leaching, in the raffinates after copper and zinc extraction, as well as in the stripping products. nd = not detected.

Element	Solution type and metal concentration (mg/L)				
	Leachate	Raffinate I (Cu extraction)	Stripping product I (Cu extraction)	Raffinate II (Zn extraction)	Stripping product II (Zn extraction)
Al	1,089.3	1,090 ± 12.9	nd	1,093 ± 4.2	nd
Ca	4,570	4,582 ± 23	nd	4,582 ± 14	nd
Cd	1.9	1.9 ± 0.0	nd	1.4 ± 0.0	nd
Cr	3.5	3.5 ± 0.0	nd	3.5 ± 0.0	nd
Cu	24.3	1.9 ± 0.1	43.6 ± 0.3	1.9 ± 0.0	nd
Fe	83.2	82.5 ± 1.0	nd	8.1 ± 0.2	0.1 ± 0.0
K	1,030	1,036.3 ± 16.0	nd	1,037.1 ± 5.7	nd
Mg	686.5	687.5 ± 9.2	nd	688.0 ± 6.4	nd
Mn	27.2	27.3 ± 0.9	nd	27.5 ± 0.1	nd
Na	1,290	1,300 ± 7.7	nd	1,300.2 ± 9.3	nd
Pb	45.2	45.2 ± 0.9	nd	19.6 ± 0.7	nd
Ti	nd	nd	nd	nd	nd
Zn	680.3	679 ± 8.1	nd	3.7 ± 0.1	613.9 ± 3.3

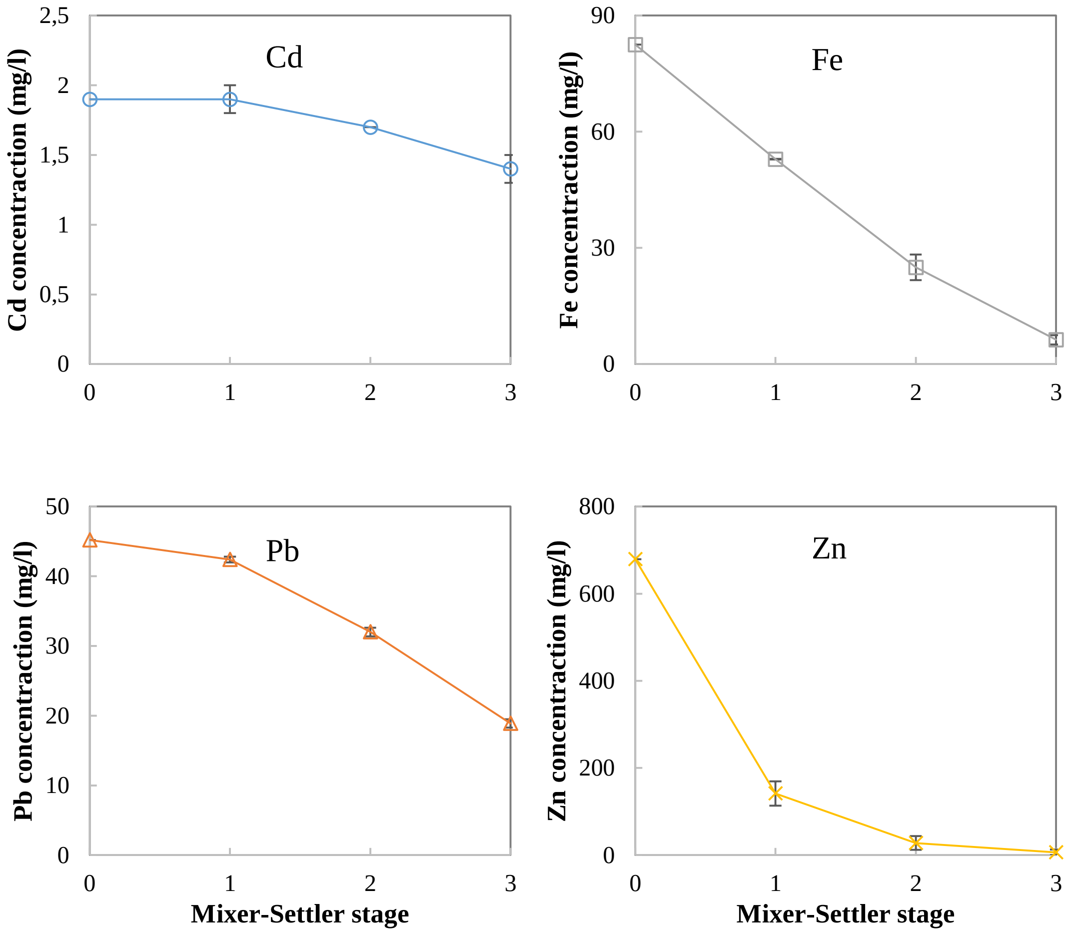

Fig. 37. Extraction behavior of zinc and co-extracted metals in a mixer settler system comprised of three stage. The extraction was carried out with 0.1 mol/L Cyanex 923 in kerosene. The O:A ratio was 1:1.

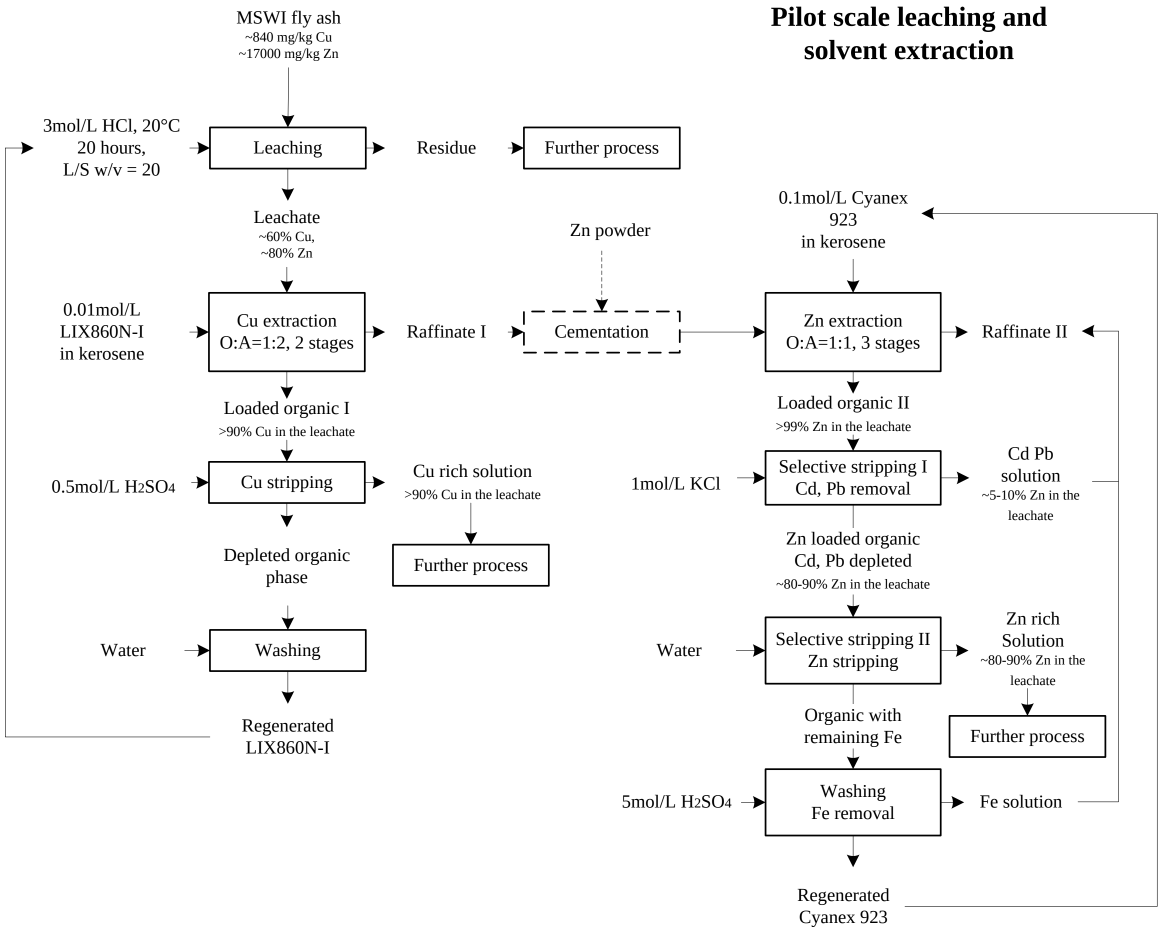

Fig. 38. Mass flowscheme of the leaching-extraction process in pilot scale using counter current mixer-settlers, presented in Paper V [109].

A mass flow overview of the pilot scale process results is presented in Table 11 and Fig.38. The feed material is dry MSWI fly ash. Leaching was done for 20 hours at pH 2 with a liquid to solid ratio (v/w) of 20 using 3mol/L HCl as the acidifying and leaching agent and more than 50% of copper, 80% of zinc and other metals in the ash were leached out. This ash has a rather low copper concentration and low leachability of the copper, but other fly ashes have been shown to give much higher copper yields in similar leaching (see for example fly ash B in Table 8). Copper was separated first from other constituents via solvent extraction with LIX860N-I in kerosene. A 0.01 mol/L solution extracted more than 90% of the copper in two stages from aqueous feeds containing roughly 25 mg/L Cu with an O:A ratio of 1:2. The extraction is highly selective, so the amount of co-extracted impurities is negligible. A reductive cementation by zinc powder addition is suggested before the zinc extraction to remove the impurities that can be co-extracted, i.e. cadmium, iron and lead. Zinc extraction in the aqueous feeds is achieved using Cyanex 923. A concentration of 0.1 mol/L Cyanex 923 in kerosene can completely extract the zinc in three stages at an O:A ratio of 1:1. If the cementation step is not used, the co-extracted impurities can be removed by selective stripping with minor loss of zinc using a chloride solution, as described above.

5. Conclusions

This thesis reports the development of a new potential hydrometallurgical process based on combining leaching and sequential solvent extraction to recover copper and zinc from MSWI fly ash. The investigations were carried out at bench scale and laboratory pilot scale.

The grate-fired combustor bottom ash, which is rich in glassy slag and metal pieces, was very difficult to leach due to its glassy matrix. The bottom ash released a large amount of iron to the leachate and the leachate gave a gel-like precipitate in a short time, making itunsuitable 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.

Fly ash from MSWI facilities was used for the study 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 found that hydrochloric acid is relatively efficient, dat solubilizing copper (68.2 ± 6.3%) and 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, which can make the ash residue less environmentally problematic. However, investigation of the toxicity of the residue is needed to verify this.

The commercial extractant LIX860N-I (an aldoxime) worked well for the Cu extraction. No third phase formations or phase separation problems were observed and the Cu extraction gave a good extraction yield with high selectivity. Only a very small amount of Fe was co-extracted from one of the ash leachates. The extracted copper in organic phase was stripped, with good results, in a one stage process using selected sulfuric acidic solution (1.5 M).

For the zinc extraction three commercial extractants, Cyanex 272, Cyanex 572 (both acidic extractants) and Cyanex 923 (a solvating extractant) were used. Under the experimental conditions used Cyanex 272 has a lower extraction efficiency for zinc than Cyanex 572 and co-extracts more of the undesired, dissolved iron. In addition, it is more difficult to take iron out from the organic phase during stripping when using Cyanex 272 than when using Cyanex 572. Cyanex 923, on the other hand, is more effective and no pH adjustment of the aqueous phase is needed since it is a solvating extractant, but it co-extracts cadmium and lead besides iron. Therefore, the stripping process to obtain a high purity of zinc product solution gets more complicated with this extractant than when using Cyanex 572. Extraction was favored when the extractant was dissolved in aliphatic diluents rather than aromatic diluents and long chain alcohols. An increased temperature, in the range of 20 to 60 °C, has only a slight influence on the zinc extraction but gives a significant increase in iron co-extraction, which led to a significant decrease in the separation factor between zinc and iron.

The zinc that had been extracted by Cyanex 572 can be separated from iron in a stripping step using 1 M nitric acid, followed by the removal of iron from the organic phase with 3 M hydrochloric acid. The regenerated organic can be reused. For the extraction using Cyanex 923 it was shown that cadmium and lead could be stripped from the organic phase using a chloride-containing agent with a loss of zinc in the range of 5~10%. Zinc could then be stripped out by water and the remaining iron by sulfuric acid. With this treatment the organic phase can be recirculated in the process. It was also shown that reductive cementation by the addition of zinc powder is a feasible alternative method for removing contaminating metal ions from the aqueous phase prior to zinc extraction.

McCabe Thiele diagrams modelling the sub-processes with respect to the number of stages needed in mixer-settler systems showed that only a few mixer settler stages will be needed for each sub-process. The total solvent extraction process was then demonstrated in pilot scale mixer settler equipment consisting of two stages for copper extraction and three stages for zinc extraction. This gave a recovery of 90% of the copper and ~100% of the zinc in the leachate.

The overall results indicate that the recovery of copper and zinc from MSWI fly ash using leaching and extraction is feasible up to pilot scale. Since mixer settlers show a near linear scale-up behavior these results are promising for further scale-up to industrial scale.

6. Future work

The following aspects of the process are required to improve the yield of metals:

1. Further optimization of the leaching process to reduce the volume of secondary waste.

2. Further optimization of solvent extraction with regard to the organic to aqueous ratio, in order to minimize the secondary waste.

3. The stripping process can also be further optimized.

4. Further optimization of the cementation process to simplify the recovery of zinc.

5. Further treatment of the waste stream and residue generated during the process.

6. Investigation of the leaching mechanism of other elements, e.g. lead and cadmium, by investigating the speciation using XAS.

7. Process assessment for the fly ash recycling operated by mixer-settler system.

8. Investigation of the possibility to design a process for the utilization of the bottom ash.

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Abbreviations and terms

°C	Degree Celsius
θ	Phase volume ratio
>	More than
<	Less than
%E	Extraction percentage
wt.%	Percentage weight total
Approx.	Approximately
Aq.	Aqueous
Cyanex 272	Bis(2,4,4-trimethylpentyl) phosphinic acid
Cyanex 572	Mixture of phosphinic and phosphonic acids
Cyanex 923	Mixture of four slightly different tri-alkyl-phosphine oxides
D	Distribution ratio
Diluent	A liquid phase (organic in this thesis) that dissolves extractant
EXAFS	Extended X-ray Absorption Fine Structure
Extractant	A compound (in this thesis an organic compound) that transfers solute from a liquid phase to another in solvent extraction
Feed	The liquid phase that contains solutes to be extracted along with impurities for the solvent extraction process
g	Gram
h	hour
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
kg	kilogram
L	Liter
Leachate	An aqueous solution that contains materials released from a solid after contact
LIX860N-I	5-nonylsalicylaldoxime
L/S	Liquid to solid ratio (volume mL to weight g)
M	Molar concentration (mol/L)
min	Minute
mL	Millilitre
MSWI	Municipal solid waste incineration
O:A	Organic to solid volume ratio
Org.	Organic
pH_{eq}	Equilibrium pH
pH_{in}	Initial pH
pH_{pzc}	pH where the number of positively and negatively charged surface groups of the mineral are the same
ppm	Part per million
Raffinate	A liquid phase from which materials have been extracted by an immiscible liquid phase
rpm	Rounds Per Minute
$SF_{A/B}$	Separation factor
TOPO	trioctylphosphine oxide
TRPO	tri-alkyl-phosphine oxides, Cyanex 923
v/w	Volume/weight
XANES	X-ray Absorption Near-Edge Structure
XAS	X-ray Absorption Spectrometry
XRD	X-ray powder Diffraction

Appendix

Appendix A: Analytical Techniques

ICP-OES

Inductively Coupled Plasma – Optical Emission Spectroscopy is an analytical measurement technique for the metal concentration in aqueous solution or gas sample. The instrument used here is a Thermo Fisher iCAP 6500 ICP-OES. As reported by the manufacturer, the detection limits in the range of 1-50 µg/L (ppb), the sample was introduced into the instrument with a carrier gas (argon) as aerosol, then is atomized by heating with argon plasma to a high temperature (6000 – 7000 K). The type of elements in the sample is identified by the difference of particular photon wavelength, and the intensity of the emitted photons is proportional to the amount of element presented in the sample, which is used to quantify the element concentration by external calibration.

IC

Ion Chromatography is used to separate analytes based on their respective charges with ion exchange mechanism. Ion exchange chromatography uses a charged stationary phase to separate charged compounds including anions, cations, amino acids, peptides, and proteins, the instrument used in this experiment is Thermo Scientific Dionex, DX-100 IC, which is used to determine the anions concentration in liquid sample by external calibration.

XAS

X-ray Absorption Spectroscopy is a widely used technique for determining the local geometric and/or electronic structure of matter.The X-ray absorption spectroscopy measurements were carried out at the beam line I811 in the Maxlab Swedish national synchrotron facility at Lund University that was operable until recently. The beam line was situated on the 700MeW ring MaxIII [89]. Zn K-edge and Cu-K-edge spectrum data were collected using a Si(111) double crystal monochromator. All Zn spectra were calibrated by assigning the first inflection point of the Zn metal K-edge to 9.959 keV. The Cu spectra were calibrated by assigning the first inflection point of the Cu metal K-edge to 8979keV.

The sample spectra were collected in fluorescence mode by a Lytle detector. Zinc or copper foil data for energy calibration were simultaneously collected in transmission mode by ionisation chambers filled with Ar. The intensity of the primary beam, I_0, was measured using ion chambers filled with N_2 to 1.1 bar. The intensity of the beam after passing the sample (I_1) and after passing the metal foil (I_2) were measured using ion chambers filled with Ar to 0.1 bar and 2 bar, respectively.

Appendix B: Mixer-Settler system

Mixer-settler units consist of a mixing chamber and a part where the aqueous and organic phases can separate due to the density difference. Combinations of mixer settlers are used for small-scale continuous tests of solvent extraction processes, as well as in large scale industrial applications. The mixer-settlers can be arranged in many different flow schemes, such as counter-current, which gives a good phase contact. Mixer-settlers are easy to manage and they can handle quite a wide range of flow ratios. The process efficiency can be improved by adding more extraction stages at a low cost. In addition, the results based on small scale mixer-settlers can be linearly scaled up from small scale to full industrial scale [69]. A sample of mixer-settler system setup used in section 4.4 is shown in Fig. 39.

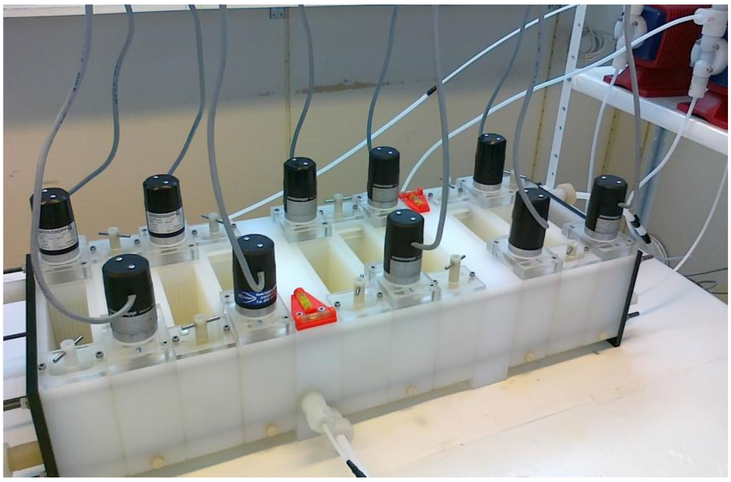

Fig. 39. A sample of mixer-settler system for copper and zinc extraction from MSWI fly ash leachate.