Recovery of Zinc from Municipal Solid Waste Fly Ash

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II

Preface

This masters project was carried out at the Chemistry Department at the University of Oslo, from August 2016 to May 2018, under supervision by Professor Grethe Wibetoe and Dag Eriksen.

I would like to thank my supervisors for giving me an interesting topic, and for providing guidance and feedback. I also want to thank Anne-Marie Skramstad for teaching me the instrumentation.

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Abstract

The availability of many elements is decreasing due to extended use. One possible solution to this problem is the recovery of metals from waste. Fly ash from municipal solid waste (MSW) incineration contains many metals and can therefore be considered a resource. This project focuses on the recovery of zinc from MSW fly ash.

A total analysis of the fly ash was performed using ICP-OES after decomposing the sample in a microwave oven. MSW fly ash contains silicates, and the content of the zinc trapped in the silicates was measured. An insignificant amount of the zinc was trapped in the silicates, making it unnecessary to dissolve the silicates for a good yield.

Leaching is a common way of dissolving metals from fly ash. In this project, leaching experiments were performed in a process reactor, and the eluate was analyzed with ICP-OES and IC. The fly ash was first pre-leached with water to remove water-soluble salts. Sulfuric acid and ammonia solution were studied as possible leachates for zinc recovery. Using sulfuric acid resulted in immediate formation of gypsum, making this leachate problematic. The leaching experiments with ammonia showed good results, making ammonia solution a possible leachate for recovery of zinc from fly ash.

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APC	Air pollution cleaning
CRM	Certified reference material
EDTA	Ethylenediaminetetraacetic acid
IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectrometry
L/S ratio	Liquid-solid ratio
LOD	Limit of detection
LOQ	Limit of quantification
min	Minute
MSW	Municipal solid waste
NOAH	Norsk Avfallshåndtering
PP	Polypropen
ppb	Parts per billion
ppm	Parts per million
rpm	Rounds per minute
S/S	Solidification/stabilization
XRF	X-Ray fluorescence

1 Introduction

1.1 Background

1.1.1 Scarce metals

The world is facing a major problem; the availability of many elements is decreasing. An analysis in 2011 was performed by the Chemistry Innovation Knowledge Transfer Network, UK, to get an overview of the situation. After the analysis, 44 elements were labeled "endangered elements" [1]. The phrase "endangered element" refers to an element that soon will be in limited supply. The 44 elements were divided into three groups: (1) will be at a serious threat within 100 years, (2) rising threat from increased use, and (3) limited availability, future risk of supply. Zinc, Zn, was placed in the first group, along with He, Ga, Ge, As, Ag, In, Te and Hf.

The same prediction has been done by other studies [2, 3]. For instance, in 2012, the scarcity of the elements was calculated using the extraction rate from natural resources, with an estimated yearly increase of 3%, compared to the available amount of Zn in the earth's crust. It has been assumed that if nothing is done, virgin Zn will be gone by 2097 [3]. Recovery of Zn was not taken into account in this analysis.

Since there is no established method for deciding the scarcity of an element, variations in the lists and research done were expected [4]. For instance, Zn is not on the List of Critical Raw Materials published in 2017 by the European Commission [5]. This list is made by comparing economic importance and supply risk of the elements. When calculating supply risk, governance and trade risks are considered.

The increasing loss of elements is mostly due to increase in population, and the use of new technology [6]. Fortunately, there might be ways to solve this problem: replacing the scarce elements with polymers, optimizing the use of the elements so smaller quantities are needed, and recycling and recovery.

In the search for new resources, the expression urban mining was introduced. The definition of urban mining is "the process of reclaiming raw materials from spent products, buildings and waste" [7]. The use of waste as a resource for metals could help solve the problem with

the "endangered" elements. Parts of the metal recovery industry already uses both industrial and municipal waste. Ash from municipal solid waste has recently gained recognition as a resource.

1.1.2 Incineration as waste treatment

Mass burn incineration is the most common type of thermal treatment for municipal waste. The combustion is done at a temperature between 850 - 1450 °C, depending on the treatment plant [8]. The high temperature of the incineration process decompose organic and bioactive materials in the waste [9], removing most of the hazardous components. The high temperature produced by the combustion is used to generate steam, which is then used as district heating or for production of electricity. Pollution is removed from the gasses formed by the decomposition of the waste before it is released into the environment. Incineration fly ash is carried with the flue gas and is collected in cleaning filters.

The incineration produces gases that needs to be cleaned before being released. This step is called air pollution cleaning (APC) and has seen much development over the last decades. A common type of APC is scrubbing. Scrubbing uses alkaline sorbents, typically $CaCO_3$, to remove acidic gases, such as HCl, HF and SO_2 [8]. Another type of APC is addition of active carbon to the flue gas. The main purpose of the active carbon is to remove Hg.

Incineration reduces the mass and volume of the MSW remarkably. The volume can be reduced by up to 90% and the mass by 75% [9]. It has been estimated that the worldwide generation of MSW has increased with 90% from 2002 to 2012 [8]. Attention to environmental effects, has made the deposit fee higher, so it is no longer appealing to deposit as landfill [10].

A disadvantage with incineration is the production of solid residue; bottom ash and fly ash. Incineration of 1 metric ton municipal solid waste (MSW) generates 15-40 kg hazardous waste [10]. The bottom ash is a mixture of sludge, glass and other unburned materials, and contains mostly silicates, oxides and carbonates [8]. In many countries, the bottom ash is used as raw materials for construction materials like cement. During the last couple of decades, much research has been done on pre-treatment of the bottom ash to prevent leaching of heavy metals into the environment [11]. This ash is also used for recovery of metals, mostly iron and aluminum scraps.

1.1.3 Municipal solid waste incineration fly ash

Fly ash is a fine, grey powder with particle size ranging from µm to mm. Figure 1 shows a typical MSW fly ash. Its color ranges from dark to light grey, depending on its contents.

Figure 1 MSW incineration fly ash (Photo: J. Kessel)

The three ash samples, used in this project, contain carbon particles after APC with activated carbon. The carbon particles vary in size. Figure 2 is a picture of fly ash with 10x magnification, taken with an Olympus BH2 microscope. The carbon particles can be seen as black spots.
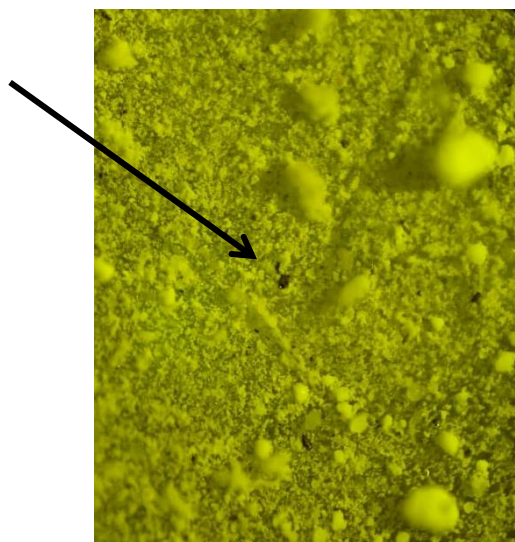
Figure 2 MSW fly ash with 10x magnification showing the particles of active carbon. (Photo: J. Kessel)

The contents in fly ash depend on both the solid waste that was incinerated, and the method used as APC. The dominant elements are Na, K, Ca, Al, Si, Cl and O, and they are present mostly as oxides [12]. It is believed that the fly ash is formed by condensation of volatile compounds, like lead and cadmium chloride, on particles of metal oxides [13]. The usage of new technology, which takes advantage of new materials, makes the municipal waste more complex both in structure and content.

Characterization of the fly ash has been tried many times, but due to a great number of different compounds at low concentrations, it is not an easy task and the results varies. Table 1 lists the most common crystalline compounds in MSW fly ash found by various studies. Some research has shown that the composition of main compounds depends on the particle size [14].

Table 1 Main crystalline compounds in MSW fly ash determined with XRD

	Lima, Ottosen et al. (2008) [15]	*Zhang, Su et al. (2014) [16]*	*Li, Xiang et al. (2004) [17]*	*Fermo, Cariati et al. (1999) [18]*
Al_2O_3	X			X
$CaSO_4$	X	X	X	X
CaO				X
$CaCO_3$	X	X	X	X
Fe_2O_3	X	X		X
KCl	X		X	X
$NaCl$	X		X	X
SiO_2	X	X	X	X

The ash also contains some organic matter and heavy metals. The organic compounds include polycyclic aromatic hydrocarbons (PAH), chlorobenzenes (CB) and furans (PCDF), which are all toxic. The heavy metals present in the fly ash varies, with lead and zinc commonly with the highest concentration [10]. The zinc concentration is usually in the range of 0.5-5% [12].

Due to the high concentration of heavy metals, chloride and toxic organic material, MSW fly ash is labeled hazardous [19]. Thus, proper treatment is vital before deposition.

1.2 Use of fly ash today

Today, most of the fly ash is deposited as landfill. To avoid heavy metals leaching into the environment, the fly ash is treated before deposition. There are three main types of treatment: separation, thermal treatment and solidification/stabilization (S/S) [10].

Pre-leaching with water is the most common type of separation treatment. Water dissolves the water-soluble salts, like NaCl and KCl, and makes the ash more stable for later use. Research has been done on recovery of salts from eluate after leaching with water [20] Separation is typically combined with S/S treatment.

Thermal treatment is further incineration of the fly ash. The temperature depends on the thermal method used, but is usually between 1000-1500°C [10]. At these high temperatures, the elements rearrange and make up other compounds. Furthermore, CaO goes from soluble to insoluble, which reduces the pH significantly. Since the solubility of the heavy metals depends on the pH, the drop in pH makes them more soluble.

Thermal methods reduce the volume and creates more bottom ash that could be used for instance as building materials. However, it is expensive since the process uses large amounts of energy.

Like MSW incineration, thermal treatment of fly ash produces more fly ash, called secondary fly ash. Due to volume reduction, this ash has a high concentration of heavy metals, for instance Zn. Studies has shown promising results for recovery of Zn and Pb [21].

Solidification/stabilization (S/S) uses additives and binders to immobilize the contaminants. The goal is to make the contaminants into less soluble or less toxic compounds. This is a beneficial method as the fly ash is made useful, e.g. stabilization in cement or other building materials. A study from 1994 showed that immobilization of most of the contaminants, except the chlorides, is possible [22]. Then again, the solidification is not effective for soluble salts, and the ash therefore needs pre-treatment like separation.

The most promising S/S-treatment is addition ofphosphoric acid [19]; the idea is that the heavy metals will be entrapped in a matrix of phosphate minerals and will therefore not leach out to the surroundings.

In Norway, MSW fly ash is transported to NOAH (Norsk Avfallshåndtering) at Langøya, Holmestrand. NOAH is a Norwegian waste management company that specializes in hazardous waste. They handle from both consumers and industry. At Langøya they use S/S treatment: the fly ash is combined with sulfuric acid to make gypsum. The gypsum is then used to fill up old limestone mines. Figure 3 shows Langøya from above. The green "lake" is the acid pool where the sulfuric acid is stored. The red "lake" is one of the mines filled with gypsum. The colors of the lakes are due to high concentrations of iron. The acid contains Fe^{2+} which is green. When the acid reacts with the fly ash, the iron ions is oxidized to Fe^{3+} which is red.
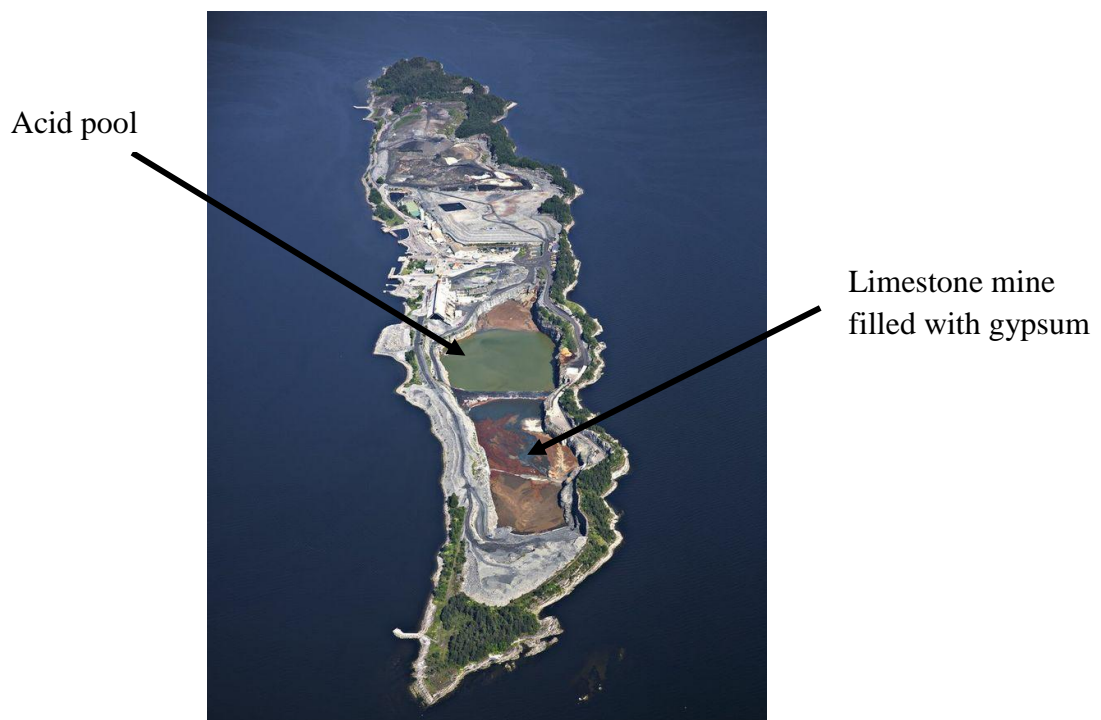
Figure 3 Langøya from above [23] (Used with kind permission from NOAH)

Examples of established methods of recovering valuable compounds from MSW fly ash are HALOSEP and FLUREC. HALOSEP uses scrubber water to neutralize the fly ash and recover chloride in the form of NaCl and KCl [24]. The acidic scrubber water will also dissolve a lot of the metals, and the eluate can therefore be used to recover for instance Zn. FLUREC combines acid washing and leaching with NaOH to produce Zn with purity >99.9% [25]. This process is used in large scale in Switzerland.

In 2012, 26% of the world's zinc supply was produced by recycling [2]. Many of the recovery methods are expensive, thus making them unattractive [26]. In 2015, a study concluded that,

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with the current market price for zinc and the currently established methods, recovery of zinc from fly ash is not economically viable [25].

The overall goal is to find efficient and low-cost methods for recovery of Zn from MSW fly ash. The method must also be robust enough to withstand the large variation in the contents of MSW fly ash.

1.3 Objectives

Municipal solid waste fly ash has been considered as a resource for a few decades, and much research has been done on recovery of salts and metals from the ash. The aim of this project is to study ammonia solution, sulfuric acid and water as leachates for effective leaching of Zn from MSW fly ash. The eluate will be analyzed with ICP-OES, using methods that need to be optimized for each leachate.

To calculate the yield after leaching, the total concentration of metals of interest needs to be determined. Before analysis, the sample needs to be totally decomposed. This is done in a microwave oven with an established method for decomposition of fly ash. The method did not work, hence a need subobjective was to optimize the method for decomposition of MSW fly ash.

MSW fly ash does contain some silicates which complicates both the leaching and the decomposition. A decomposition of the sample without dissolving the silicates was performed to measure the amount of Zn trapped in the silicates.

ICP-OES is used for analysis of the decomposed sample, and the method used needs to be optimized considering the choice of wavelengths and sample preparation.

2   Theory and methods

2.1 Decomposition

Total analysis of fly ash is often performed with X-ray instruments [14, 21, 27-29], but analysis with ICP-OES after decomposition is also widely used [14, 29, 30]. Using ICP-OES requires more pre-treatment, and only metals can be measured. However, a large advantage is that it gives accurate and precise results.

The samples are decomposed in closed vessels in a microwave oven. This is an efficient way of decomposition due to the high temperature and pressure. Also, the closed vessel minimizes contamination and the loss of sample.

For this decomposition, a combination of HNO_3, HCl and HF is used. HNO_3 dissolves metals by forming nitrates and oxidize organic matter. HCl dissolves many metals by forming complexes. A 3:1 (molar) combination of HNO_3 and HCl is called aqua regia. In some studies, the fly ash is decomposed using only aqua regia as the solvent [21].

Despite this, the content of silicates in the fly ash demands the use of HF for decomposition. Due to possible hazards using HF, the amount should be as small as possible. The amount of HF needed to completely decompose fly ash is debated [31], but methods using this acid have been widely used [14, 30]. The HF reacts with silicates as shown in equation 1

$$SiO_2 + 6HF \leftrightarrow H_2SiF_6 + 2H_2O \qquad\qquad \text{Eq. 1}$$

Because of the dissolution of silicates, it is important to use equipment made of organic polymer, e.g. polypropen (PP), when using HF, unless the fluoride is neutralized. Boric acid is often used to neutralize HF, making fluoroboric acid, HBF_4, as shown in equation 2 and 3.

$$H_3BO_3 + 3HF \leftrightarrow HBF_3(OH) + 2H_2O \qquad\qquad \text{Eq. 2}$$

$$HBF_3(OH) + HF \leftrightarrow HBF_4 + H_2O \qquad\qquad \text{Eq. 3}$$

Like HF, fluoroboric acid is classified as acute toxic, but it does not react with silicate, making it possible to use glassware [32-34].

HF has a strong reactive nature. Since the ash contains a great amount of Ca, it is reasonable to assume that it will be formed CaF_2, which is an insoluble salt.

For the sample to be analyzed with the ICP-OES, the sample must be fully decomposed. One option for dissolving fluoride salts is to add boric acid. When calculating the amount of boric acid needed, it is estimated that all the precipitate is CaF_2. See Appendix 2 for calculation of the needed boric acid.

Boric acid dissolves CaF_2 by the following reaction

$$CaF_2 + H_3BO_3 \leftrightarrow BF_4^- + 2Ca^{2+} + 3OH^- \qquad\qquad \text{Eq. 4}$$
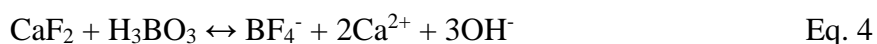
The manufacturer of the microwave oven used, Milestone, has provided a method for decomposing fly ash. The method used is based on the method from Milestone, but with some alterations to the amount of acids.

2.2 Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES is a quantitative technique used for multi-element analysis. This instrument can measure metals at low concentrations, with typical detection limits of $10 - 0.01$ ppb [35].

An important part when developing a method for ICP-OES is to choose the most suitable wavelengths. When selecting wavelengths, it is important to think about interfering lines from other elements. If the line selected is close to a line from an element with a high concentration, the peak from the selected line will not be distinguishable from the high intensity peak. For elements present at high concentrations, wavelengths with high intensity should be avoided to ensure that the concentration is within the limits of the line [36].This mostly concerns Ca, K and Na. For elements present at low concentrations, it is usually wise to use the line with highest sensitivity to avoid interferences. Also, both atomic and ionic lines should be selected for each element. A great difference in atomic and ionic lines is often caused by matrix interferences.

Poly boost is needed to measure wavelengths below 190nm [36]. Poly boost purges the chamber with argon gas to get rid of O_2. Oxygen gas absorbs the low wavelengths before they reach the detector and must therefore be removed.

Minimum two or three wavelengths are chosen for each element during method development. One of the wavelengths was chosen for each element and was for calculations. The other

wavelengths were used to monitor spectral interferences. Optimal wavelengths are given in table 16 in Appendix 4.

2.2.1 Limit of detection and limit of quantification

Limit of detection (LOD) is the smallest concentration that can be distinguished from the blank with a selected confidence level [37]. LOD is given in concentration units and is calculated by the formula

$$C_{LOD} = 3x\ S_{Blank} \qquad\qquad \text{Eq. 5}$$

For determination of LOD six different blanks, as described in subchapter 3.2.3, were used. The concentrations in the blanks were measured between the standards and the samples.

LOD for all optimal wavelengths used is given in table 16 in Appendix 4.

2.3 Leaching

The most promising leaching methods so far uses acidic and alkaline leachates. Research on recovery of metals using bio-leaching, i.e. leaching with bacteria or fungus, has given promising results [38, 39]. Leaching assisted by radiation, for instance microwave acid extraction [28], is also an option.

Leaching is often followed by solvent extraction and electrowinning to recover the desired metal(s).

2.3.1 Pre-leaching with water

The fly ash was pre-leached with water to dissolve as much water-soluble salts (Na, K, Cl etc.) as possible. Alkaline metals and alkaline earth metals are present in the ash as basic salts and will react with the acid in the leaching process. Therefore, if they are not removed, more acid is needed to dissolve the metals of interest, making the process more expensive. Also, the separation of Zn from the eluate will be more complex if the salts are not removed [21].

Most of the research done on pre-leaching of fly ash use high liquid-solid (L/S) ratios, usually 30:1 – 40:1. [21, 27, 38]. The use of large amounts of water is not favorable in an industrial

setting considering post-treatment and handling of the water. Thus, in this project, the pre-leaching experiments will be performed with a lower L/S ratio, 5:1.

Often, the pre-leaching with water is performed with up to 30 hours leaching time, but it has been determined that the optimal leaching time for dissolving K, Ca and Na is one hour [27].

Research shows that Zn is present in the fly ash as amphoteric compounds [21], mainly as hydroxides and chlorides [40]. Hence, the Zn should be extractable in both acidic and basic solutions. In this project the leachates used is sulfuric acid and ammonia.

2.3.2 Sulfuric acid

Studies on leaching MSW fly ash with sulfuric acid has shown that it is possible to dissolve a high amount of Zn. It has been shown that the reaction is not very temperature dependent and can thus be done at room temperature, saving much energy [21, 41].

Nagib and Inoue (2000) found that 5 minutes was sufficient time for acidic leaching of fly ash, with 20% acid concentration and a L/S ratio of 7:1 [21]. Having a longer leaching time will have minimal effect on the quantity of zinc dissolved, but will increase the amount of other metal ions dissolved, such as Al, Mg and Fe, and is therefore not favorable.

Another study, performed by Fedje et al. (2010) used an acid concentration of 1.5M and a L/S ratio of 10:1, and obtained a yield of 100% for Zn [27]. A study by Tang et al. (2015) leached with a L/S ratio of 20:1 and a constant pH = 2, and dissolved 80% of the chloride [41].

Even though using sulfuric acid has many advantages, it also has some disadvantages. Both Pb and Hg forms insoluble salts with sulfate and will thus precipitate. To be able to dispose of the ash as non-hazardous waste, the concentration of the heavy metals needs to be below the limits given by the state. Therefore, leaving the lead in the ash may lead to the need for more treatment of the ash before disposal.

Another problem with using sulfuric acid is the possible formation of gypsum. Gypsum might entrap desired metals, and will also make the filtration difficult. However, if the pre-leaching of the ash removes most of the Ca, this will not be a problem.

2.3.3 Ammonia

Concentrated ammonia solution (14.8M) has a pH > 12.5, and since ZnO is soluble in pH greater than 12.5, the ammonia will dissolve some of the Zn. A mentioned, the most common form of Zn in the ash is as $Zn(OH)_2$ and $ZnCl_2$ (with hydrates). Zinc chloride is soluble in water, hence zinc hydroxide is the presumed form of Zn. Equation 6 and 7 shows the reaction of ammonia with water and the reaction of zinc hydroxide in basic solution.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \hspace{3cm} \text{Eq. 6}$$

$$Zn(OH)_2 + 2OH^- \leftrightarrow [Zn(OH)_4]^{2-} \hspace{3cm} \text{Eq. 7}$$
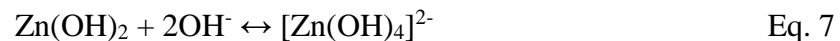
A basic leachate will only dissolve amphoteric compounds, and therefore only Zn, Pb and Cd compounds will dissolve. This makes the separation process after leaching easier

Ammonia makes complexes with many metal ions especially with Cu, but also with Zn as shown in equation 8.

$$[Zn(OH)_4]^{2-} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+} + 4OH^- \hspace{2cm} \text{Eq. 8}$$
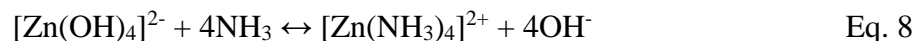
A literature study showed no previous research with recovery of Zn with leaching with ammonia solution. However, some research has been done on leaching with ammonium solution. Fedje et al. (2010) tried leaching MSW fly ash with 3M ammonia nitrate, NH_4NO_3, for 24 hours with a L/S ratio of 5:1. The yield was 29% for Zn, and 16% when the ash sample was pre-leached with water. Hopefully, the higher pH in the ammonia solution will result in a higher yield.

2.3.4 Other leachates

Sodium hydroxide - NaOH

NaOH is a strong alkaline leachate, giving the advantage of only dissolving amphoteric compounds. However, research has found that alkaline leaching is not as efficient as many acidic leachates. Gong and Kirk (1994) found that NaOH dissolves about half of the Zn dissolved when using HCl as leachate [13].

A study performed by Nagib and Inoue (2000) found that the amount of Zn dissolved is very dependent of the NaOH concentration [21]. The amount of Zn dissolved increase with the

concentration of NaOH. However, at higher concentrations they encountered problems with formation of $Zn(OH)_2$, making the filtration step difficult. The maximum amount of dissolved Zn with just NaOH was found to be 28%.

Hydrochloric acid - HCl

HCl is one of the most promising leachates for recovery of Zn from MSW fly ash. Studies have shown that it is possible to dissolve close to 100% of the Zn at 20°C with acid concentration > 1M of HCl [13, 42]. Both temperature and L/S ratio has minimal effect on the dissolution of Zn [21, 41], making the use of HCl easy and low-cost. The leaching is very pH dependent, thus a good pH control is important. Tang and Steenari, 2016, showed that at pH = 2, the yield of Zn was about 75%, and at pH = 4, the yield was about 55% [41].

As stated earlier, HCl is removed in the air pollution cleaning step after the incineration by scrubbing. A large advantage of using HCl is therefore the possibility of using the scrubber solution, making this a cheap leachate.

Another advantage of using HCl as the leachate is that it dissolves a lot of the heavy metals due to the strong acidic nature, and the complexation of chloride with many metals. Hence, the ash residue after leaching will have low concentrations of heavy metals and can be used as e.g. raw material for cement or deposited without further treatment. On the other hand, dissolving other metals will make the eluate more complex and might make it difficult to separate Zn from the solution. Also, due to low stability of silica in water, high concentration of HCl may lead to formation of silica gel. Silica gel will make the solution almost impossible to filtrate, making treatment of the solution difficult [13].

Nitric acid - HNO_3

Nitric acid is a strong acid and has many of the same advantages as HCl. However, nitrate is rarely used as ligands and will therefore not make complexes like the chloride in HCl.

Tang and Steenari (2016) found that the amount of Zn dissolved depends greatly on pH [41]. When pH was increased from 2 to 4, the yield of Zn decreased by 13%. The maximum amount of Zn was obtained at pH 2, with a L/S ratio of 20:1, giving a yield of 65%.

Another study, performed by Gong and Kirk (1994) dissolved 4-5 mg/g Zn with 2M nitric acid and a L/S ratio of 20:1 [13]. They found that the amount of Zn dissolved increase with increasing leaching time.

Organic acids

Organic acids have also been tried as leachates. In addition to lowering the pH, some organic acids make complexes with some metals. Research has shown that the amount of Zn leached with acetic acid depends greatly on the concentration of the acid. The Zn yield was highest at 3.4M (20%) acid concentration, with 62% of the Zn leached from the ash [21]. A different project reports leaching with formic, acetic and lactic acids and all three leachates gave a yield $< 1\%$ Zn and they concluded that organic acids are not suitable leachates [27]. The low yield is most likely due to the low acid concentrations, 0.1M. Of the organic acids, citric acid is the most promising, dissolving about 80% of the Zn with a concentration of 0.5M and a L/S ratio of 100:1 [39]. Despite the high yield, this method has a high L/S, making it less favorable.

Ethylenediaminetetraacetic acid - EDTA

EDTA is a strong complexing agent. The reactivity of EDTA depends strongly on pH, thus pH control is important when using this leachate. Research conducted by Fedje et al. in 2009 [27] showed that 40% of Zn dissolved in EDTA with pH adjustment (initial pH =0, end pH = 8.8), and only 1% without pH adjustment. Another project, performed by Hong et al. in 2000 [43], showed that it is possible to get a yield of 80-100% with pH adjustment, but that the yield depends widely on the fly ash sample.

Combinations

Combinations of leachates has proven successful for dissolving Zn. It is usually a combination of acidic and alkaline leachates, i.e. the fly ash is first leached with an acid and then with an alkaline leachate, or vice-a-versa. Leaching with NaOH and then washing the residue with HCl, gave good results with 98% Pb and 68.8% Zn and no significant amount of other metals [21]. Another study showed that leaching with NaOH followed by H_2SO_4 dissolved over 90% Zn [42].

2.4 Ion chromatography

Ion chromatography is an easy way to determine anions, with a limit of detection suitable for this application. The method used for the IC in this project is based on an established method [44].

The instrument setup has no suppressor to reduce the eluent conductivity. Hence, to lower the background signal, a mobile phase with low conductivity is needed. The mobile phase used is based on a phthalate buffer, giving a limit of detection of < 1ppm [45].
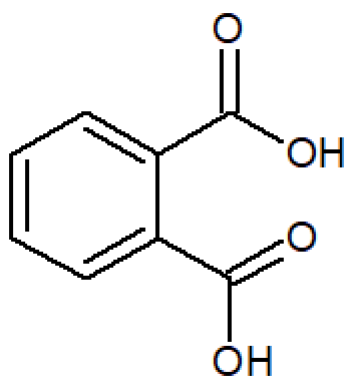
Figure 4 Ortho-phthalic acid

The stationary phase used is a strong anion exchanger with trimethyl ammonium groups as the functional group.

The chloride content in the eluate is measured after pre-leaching with water, with the second sampling method. The concentration of sulfate is not crucial in this context and was therefore only measured after pre-leaching with the first sampling method.

The solutions after leaching with concentrated ammonia solution have a high pH and is thus not suited for this method.

3 Experimental

3.1 Chemicals and samples

3.1.1 Chemicals and labware

The reagents used, with concentration and purity grade, are listed in table 2.

Table 2 Details about the reagents used.

Reagent	Concentration (%)	Density (kg/L)	Purity grade	Producer
HNO_3	65	1.39	EMSURE® ISO	Merck (Damstadt, Germany)
HCl	35	1.19	EMSURE® ISO	Merck (Damstadt, Germany)
HF	40	1.13	Suprapur®	Merck (Damstadt, Germany)
H_3BO_3 (s)	99.99	-	Suprapur®	Merck (Damstadt, Germany)
H_2SO_4	95-97	1.84	EMSURE® ISO	Merck (Damstadt, Germany)
NH_3	28	0.90	Normapur®	VWR (Radnor, US)

Unless stated otherwise, the water used were type II water (15.0 MΩcm) purified with a Milli-Q® Integral Water Purification System from Merck Millipore, Damstadt, Germany.

All standards were made using stock solutions from Teknolab AS, Ski, Norway. Due to large difference in concentrations, all stock solutions were single element. See table 3 for concentrations.

Table 3 Concentration of analyte in stock solutions used for preparation of calibration standards

Stock solution concentration (µg/mL)	Elements
1000	Ag, Al, As, Ba, Cd, Ce, Co, Cr, Cu, Hg, Fe, La, Mn, Ni, P, Pb, Sb, Si, Sn, Tl, U, V, Y, Zn
10 000	Ca, K, Mg, Na

Volumetric flasks (100 ± 0.2mL) made of PP were used when the solution contained HF. Volumetric equipment of glass (100 ± 0.1mL, 250 ± 0.1mL) were used for the remaining solutions.

Before use, all labware, unless stated otherwise, was washed with 6.5% HNO_3 for minimum 4 hours, usually 24 hours, and then rinsed with water.

3.1.2 Samples

Three different ash samples were used, labeled (by NOAH) G-04207, G-04500 and G-08980. Hereafter, the three samples are termed ash 1, ash 2 and ash 3 respectively. The samples were provided by NOAH, Langøya.

Results from routine analysis at NOAH were provided and listed in Appendix 1. The total contents of the samples were determined by analysis with X-ray fluorescence (XRF), with an internal method. The samples were leached in water and the eluate were then analyzed with ICP-OES with standard method NS-EN 12457-2 "Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)". The concentration of CaO and CO_3^{2-}, and total solid residue were also measured, with, respectively, an internal standard, ISO 10694 "Soil quality — Determination of organic and total carbon after dry combustion (elementary analysis)" and internal method. The results are given in Appendix 1.

3.2 Quality measures

3.2.1 Certified reference material

A certified reference material (CRM) is a material where the amount of some, or all, of the present elements has been certified by a valid procedure, often done in more than one laboratory. The material of the CRM is ideally the same material as the sample. The use of a CRM gives an idea about the accuracy of the method. The accuracy may vary from element to element.

When doing the total analysis, a CRM was used through the whole procedure. The CRM was BCR 176R: Fly ash (trace metals). The concentrations of the CRM are listed in table 4.

Table 4 Certified concentration of metals in CRM

Element	Certified value (mg/kg)	Uncertainty (mg/kg)
As	54	5
Cd	226	19
Co	26.7	1.6
Cr	810	70
Cu	1050	70
Fe	13100	500
Ni	117	6
Pb	5000	500
Sb	850	50
Se	18.3	1.9
Tl	1.32	0.21
Zn	16800	400

3.2.2 Analysis of residue after leaching

After leaching with water, the solid residue, after filtration and drying, was decomposed and analyzed. This was done as a quality control of the method. The amount of analyte in the eluate and in the solid residue should add up to the total amount in the ash before leaching. The method used for measuring total content in the residue is the same method used for measuring total content in the sample.

3.2.3 Use of blanks

Blanks were done for all experiments. The blanks were treated like samples and followed the whole experimental procedure.

Two blanks were used for each decomposition. The dedicated vessels were added the same combination of acids as the other vessels. For leaching experiments, one blank was used for each leachate/temperature. The preparation of the blanks was done as described for the leaching experiment, with the same volume of leachate and the same conditions. For the blank to be representative, the blank leaching was done between the other leaching tests.

All blanks were analyzed with ICP-OES, after the standards and before the samples. Blanks with significant concentration of metals of interest are taken into account when calculating the sample concentration.

3.3 Decomposition in microwave oven

The water content of the ash was determined using a gravimetric method [46]. All three ash samples were found to contain approx. 1% water, hence the results were not corrected according to dry mass.

The microwave oven used were an ETHOS PLUS from Milestone with a HPR-1000/10S high pressure rotor and Teflon vessels.

Before each run, the vessels were washed using the same procedure as for the decomposition.

For each run, five replicates, two blanks and one CRM were analyzed. The vessels were added 0.25g sample, followed by addition of HNO_3, HCl and HF. The amount of acid added is shown in table 5.

Table 5 The amount of acid used for decomposition of MSW fly ash

Run	HNO3 (mL)	HCl (mL)	HF (mL)	Comment
1	8	1	0	Result used for determination of content in silicates.
2	7	1	1	Trial
3	7	1	1.5	Trial
4+	5	2	2.5	Results used for total analysis

Temperature and time of the decomposition program are shown in table 6. Figure 24 and 25 in Appendix 3 show the power and pressure of a typical decomposition.

Table 6 Decomposing program for MSW fly ash in microwave oven

Temperature (℃)	Time (min)	
140	3.5	Slope
200	3.5	Slope
240	4	Slope
240	30	Plateau

After the decomposition program, the vessels were left for cooling in the microwave oven until they reached about 70℃. They were then moved to an ice bath for approximately 30min.

Before addition of the decomposed sample, each volumetric flask were added 0.95g boric acid.

The decomposition was done one time with glass flasks, and the rest of the time with plastic flasks. Only the results when using plastic flasks were used for measurement of metals in the sample.

3.4 Leaching

All leaching experiments were done with ash 1 as the sample.

3.4.1 Instrumentation

An automated process reactor was used for the leaching experiments. See figure 5 for instrumental setup.
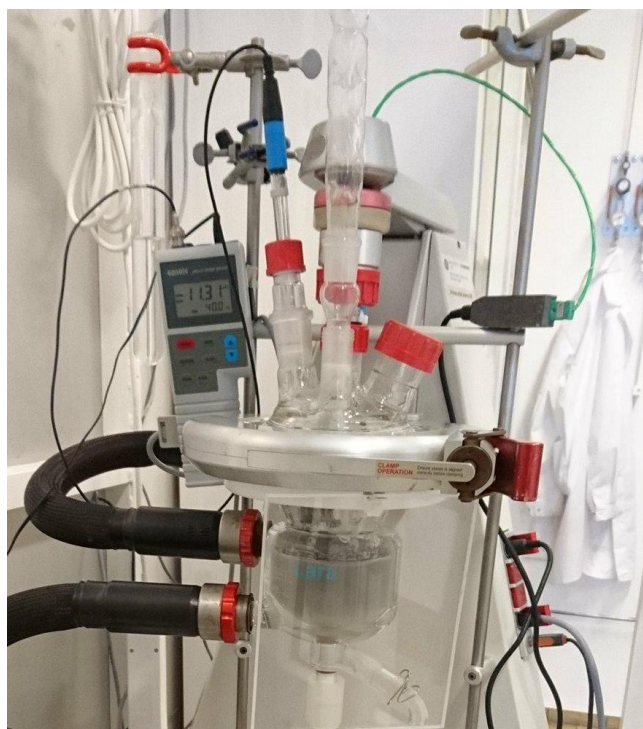
Figure 5 LARA reactor with filtration system used for the leaching experiments.

The reactor was a 250 ml jacketed glass batch process reactor. An 80mm top mounted agitator was used. Four baffles, with width 10mm, were inserted from the top and leveled approximately 10 mm above the agitator. The baffles create turbulence in the liquid, increasing homogeneity.

The temperature was controlled using a Haake F3 Cooler/heater circulator. The temperature was measured using a PTFE coated K type thermocouple. pH measurements were done using a Jenco 6230N pH meter. When not in use, the pH meter was placed in a storage solution.

LabView was used to control stirring and temperature, and continuously measure pH, mV signal, temperature and time. Figure 26 and 27 shows the measured pH and temperature over time for two leaching tests.

The setup of the LARA reactor was done by Svein Ræstad for his master thesis [47].

For filtration of the sample after leaching, a Buchner funnel and a suction flask were used. The filter paper used was grade 1 with diameter 7.0 cm from Whatman, Maidstone, UK. For suction when filtrating, the suction flask was connected to a vacuum pump.

Before each run, the reactor was rinsed with 10 % HNO_3 at 40°C for 30min, and then washed with water.

3.4.2 Pre-leaching with water

First, 200mL water was transferred to the reactor. After the water reached the specified temperature, an 40g ± 0.5g sample was added, and the stirring was initiated. The conditions for the leaching experiment are shown in table 7.

Table 7 Conditions used for pre-leaching of fly ash with water

L/S-ratio (V/w)	5:1
Stirring	600 rpm
Temperature	25 °C and 40 °C
Time	15, 30, 60, 90 and 120min

The sampling was done two ways. First, samples were taken out at 15, 30, 60 and 90 min. The stirring was turned off and the solids settled before 5mL of the eluate was transferred to a 100mL volumetric flask. This was done at both 25 and 40 °C. This sampling method did not suffice and the results were discarded.

The rest of the leaching tests with water were performed for 15, 30, 60 and 120min, without any sampling during the leaching time. Four replicates were done for each leaching time.

The eluate was then filtrated from the ash residue using the filtration setup described in subchapter 3.4.1. After filtration, the eluate was transferred to a 250mL volumetric flask.

The reactor was then washed with 200mL water. The washing water was allowed to run through the ash in the Buchner funnel and was collected in a filtration flask. It was then transferred to a 250mL volumetric flask.

The samples taken out during the run, the eluate and the washing water was analyzed with ICP-OES and IC.

3.4.3 Leaching with sulfuric acid

The sample used in this experiment was first washed with water at 25°C and dried. The washing was done as described in subchapter 3.4.2. This leaching experiment was performed to observe if gypsum is formed, hence the process reactor was not used for this experiment.

A beaker was added 4g sample, followed by addition of water and the sulfuric acid needed to gain the specified concentration and a L/S ratio of 5:1. The beaker was left with magnetic stirring for 30min in room temperature.

This was done with acid concentration of 1.88M (10%), 2.81M (15%), 3.75M (20%) and 4.69M (25%).

3.4.4 Leaching with ammonia solution

The leaching experiments with ammonia solution were done using the same procedure and setup as pre-leaching with water. The samples used were not pre-leached prior to leaching with ammonia. The conditions used is shown in table 8.

Table 8 Conditions used for leaching with ammonia

Ammonia concentration	14.8M (28%)
Temperature	25°C
Time	30, 60 and 120 min
L/S-ratio (V/w)	5:1
Stirring	600 rpm

One experiment was conducted where the ash was leached with ammonia two times. The leaching followed the same procedure and conditions as described above. The solid residue was washed, but not dried between leaching.

The eluate and washing water was then analyzed with ICP-OES.

Analysis of precipitate

A beaker with about 25mL eluate (after leaching 60min) was left without cover for two days. The solution was then separated from the precipitate. The precipitate was dissolved in 25mL 2.8M nitric acid and analyzed with ICP-OES.

3.5 ICP-OES

3.5.1 Instrumentation and conditions

The instrument used is a Varian Vista AX CCD simultaneous ICP-OES with a Sturman-Masters nebulizer and V groove spray chamber. This ICP-OES uses an axial torch. The parameters used are shown in table 9.

Table 9 Instrumental conditions on ICP-OES

RF power (kW)	1
Plasma Ar flow (L/min)	15
Auxiliary Ar flow (L/min)	1.5
Nebulizer Ar flow (L/min)	0.75
Sample flow rate (mL/min)	1.0*
Reading time (s)	1
Reading per replicate	3

* The flow rate was determined using a measuring cylinder and a timer

A fitted gaussian background correction with two points per peak was used.

Two to four wavelengths were chosen for each element. Wavelengths that did not give sufficient peaks were removed.

Between the analysis of the standards and the samples, the instrument was flushed with 5% nitric acid to minimize memory effect. A blank test was done after the flushing, and the

samples were not analyzed until the blank test showed insignificant concentrations of the measured metals.

3.5.2 Calibration standards

The same elements were added to the standards used for total analysis and for analysis of eluate after leaching. Since many different elements were to be analyzed, they were divided into two groups, labeled STA and STB. For analysis of eluate after leaching with ammonia, many of the elements were not present, and it was just made one type of standard, labeled STN.

After analysis, the standards were adjusted to more appropriate concentrations. The elements that could not be measured, due to low concentrations, were removed from the standards.

The concentrations in the calibration standards are based on the total content determined by NOAH given in table 11 in Appendix 1. Concentrations and preparation of the calibration standards are given in Appendix 2.

3.6 Ion Chromatography

3.6.1 Instrumentation, parameters and procedure

The ion chromatograph used were Metrohm 690 Ion Chromatograph with constant volume piston pump. The column used was an anion exchanger, type PRP-X100, 125 x 4.0 mm. The system was connected to a computer with Chromeleon 7 software by Thermo Scientific. The pH-meter used was an Orion 420A+ from Thermo Scientific.

The eluent conduct (range) and the full scale (sensitivity) were set to 500 µS/cm and 50 µS/cm respectively, giving a real full scale at 10 µS/cm. The eluate conduct obtained was in the range of 230 – 240 µS/cm. The flow rate was 1.0 mL/min.

When injecting the sample, the injection loop (50 µL) was flushed two times. This was to make sure that the volume injected was the same every run.

A solution with known concentration of chloride and sulfate was measured two times.

3.6.2 Samples, standards and mobile phase

The sample used is the eluate from the leaching of the ash with water. The samples were diluted 1000 times for measurement of chloride, and 100 times for measurement of sulfate.

Three standards were used. For the concentrations of the standards, se table 10.

Table 10 Concentrations of standards used for measuring chloride and sulfate with IC

	Concentration of Cl^- (mg/L)	Concentration of SO_4^{2-} (mg/L)
Standard 1	30	10
Standard 2	50	15
Standard 3	70	25

Preparation of the mobile phase is described in Appendix 2.

4 Results and discussion

4.1 Decomposition

The first decomposition was done using only HCl and HNO₃ to measure the concentration of metals that are not trapped inside the silicates. As can be seen in figure 6, the sample did not get totally dissolved. The white particles observed in the flask are silicate, which needs HF to be dissolved.

Figure 6 The ash sample after decomposition with HCl and HNO₃ (without HF) (Photo: J. Kessel)

The other decompositions were done with HF, HCl and HNO₃, as described in table 5. When using HF, one would like to use as little of the acid as possible due to hazards, thus increasing amounts were added to find the minimal amount needed to dissolve all the silicates. The decompositions with HF clearly showed precipitate. The precipitate looked more like a slurry than the particles as seen before. Since the ash has a high concentration of Ca, the precipitate is most likely fluoride salts, particularly CaF_2.

To remove the precipitate, boric acid was added to the decomposed sample as described in chapter 3.3.

After decomposition, the carbon particles mention in1.1.3 were still present. This was expected as acids will not alter the carbon structure itself [48], but will dissolve minerals absorbed by the carbon.

The use of 5mL HNO_3, 2mL HCl and 2.5mL HF including the addition of 0.95g H_3BO_3 completely dissolved all three ash samples, i.e. gave clear solutions without any visible particles. This mixture of acids was therefore determined to be suitable for decomposition of MSW fly ash.

Analysis of the samples in glass volumetric flasks gave very high blank values for some metals, some over 100% more than expected value in sample. The metals with the highest blank values were Al, K, Na and Si, indicating a reaction with the glass equipment. This means that the boric acid does not neutralize the HF fast enough to use glass equipment as describes in the literature. However, adding the boric acid to the vessel instead of the volumetric flask, neutralizing the HF before coming in contact with the glass, might have worked. The results from the experiments with glass flasks were rejected, and all later decompositions were done using plastic flasks.

4.2 Total contents

The concentrations (± one standard deviation) of the most abundant metals in the three fly ash samples are shown in figure 7. For the experiment, 13 replicates were analyzed for ash 1 and 10 replicates for ash 2 and 3. The measured amount of the metal was compared to the total mass of the sample, to obtain the mass fraction. The concentrations of all measured metals are listed in table 16 in Appendix 4.
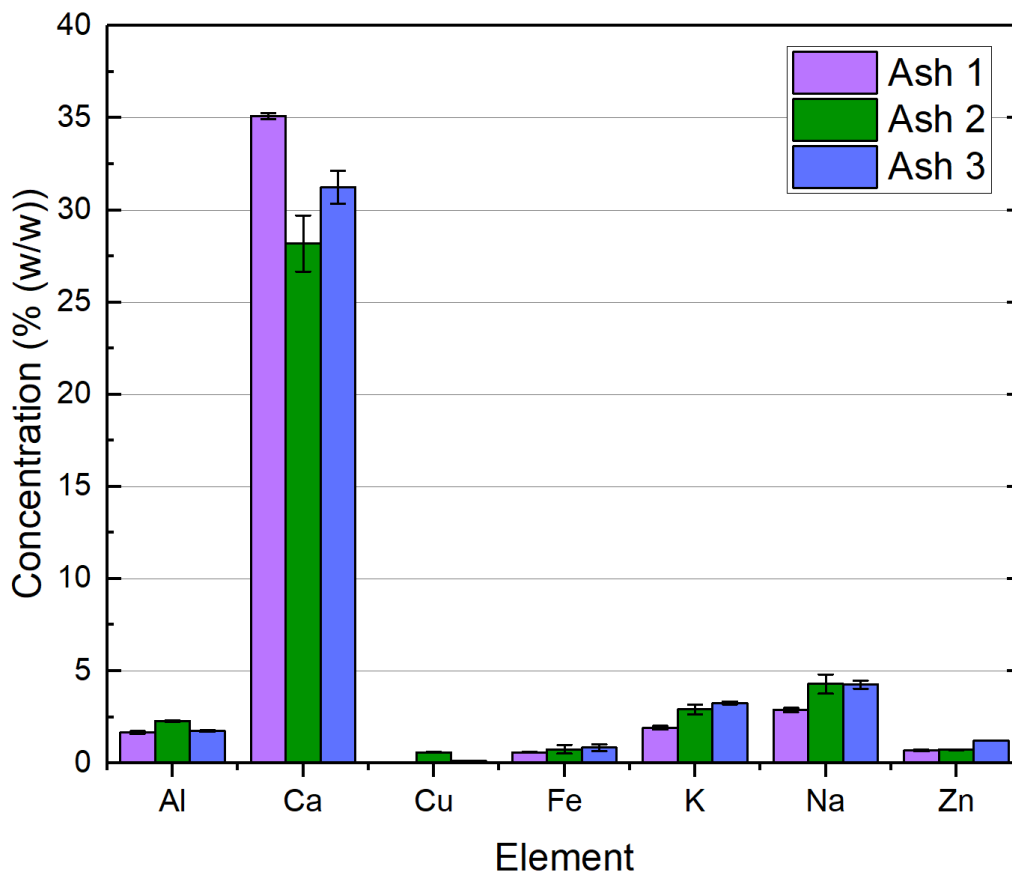
Figure 7 Total contents of the main metals in the three ash samples

As expected, the three samples show some difference in concentration, but the main metals were the same in all samples. The results were in the same concentration range as found in the literature for other MSW fly ash samples [e.g.18, 29, 41, 42]. The large concentration of Ca in all samples are due to the addition of $CaCO_3$ to the flue gas in the air pollution control step during incineration.

The measured amount of metals makes up about 45% for the total mass of the fly ash. The last 55% may be mainly oxygen, chloride and sulfur, which cannot be measured with ICP-OES. The total analysis from NOAH, shown in table 11, showed that 1-3% of the ash is Si.

Si could not be measured due to problems with contamination, i.e. a calibration curve could not be drawn due to large errors between data points. As discussed in 4.1, the HF was not completely neutralized and the remaining HF might have reacted with the inner quartz tube in the plasma torch and dissolved Si. For future experiments, a more suitable torch should be used, for instance one made of aluminum oxide.

A CRM was decomposed and analyzed with every total analysis, i.e. six replicates were measured. A standard procedure for comparison of measured and certified results was used as described in the CRM report [49]. The results were also compared by calculating relative error which is shown in table 11.

Table 11 Relative error of measured concentration in CRM compared to certified values.

Element	Certified concentration (mg/kg)	Error (%)
Cd	226 ± 19	-13.6
Co	26.7 ± 1.6	31.7
Cr	810 ± 70	-18.7
Cu	1050 ± 70	-6.0
Fe	13100 ± 500	-1.9
Pb	5000 ± 500	-8.0
Sb	580 ± 50	33.7
Zn	16800 ± 400	-8.86

All results agreed with the certified concentration according to the standard procedure, except for Zn and Sb.

Comparing the measured concentrations with the results found by XRF by NOAH showed big differences, and no apparent pattern between the ash samples. However, the concentrations found by NOAH were calculated from only one replicate, giving a big uncertainty. This, combined large uncertainties for the method, up to 30% for some metals, makes the concentrations questionable.

MSW incineration fly ash contains, as mentioned, some silicates. In most cases, HF is needed to dissolve the silicates. The use of HF makes the process expensive and demands extra precautions. A comparison of the ash decomposed with and without HF reveals the amount of Zn trapped in the silicates. If a great amount of the Zn is trapped, dissolving silicates might be the only solution.

Figure 8 shows the concentration (± one standard deviation) of several metals in ash 1 after decomposition without HF compared to the total concentration of the metals. For analysis of sample decomposed without HF, 5 replicates were used. Exact values are listed in table 17 in Appendix 4.
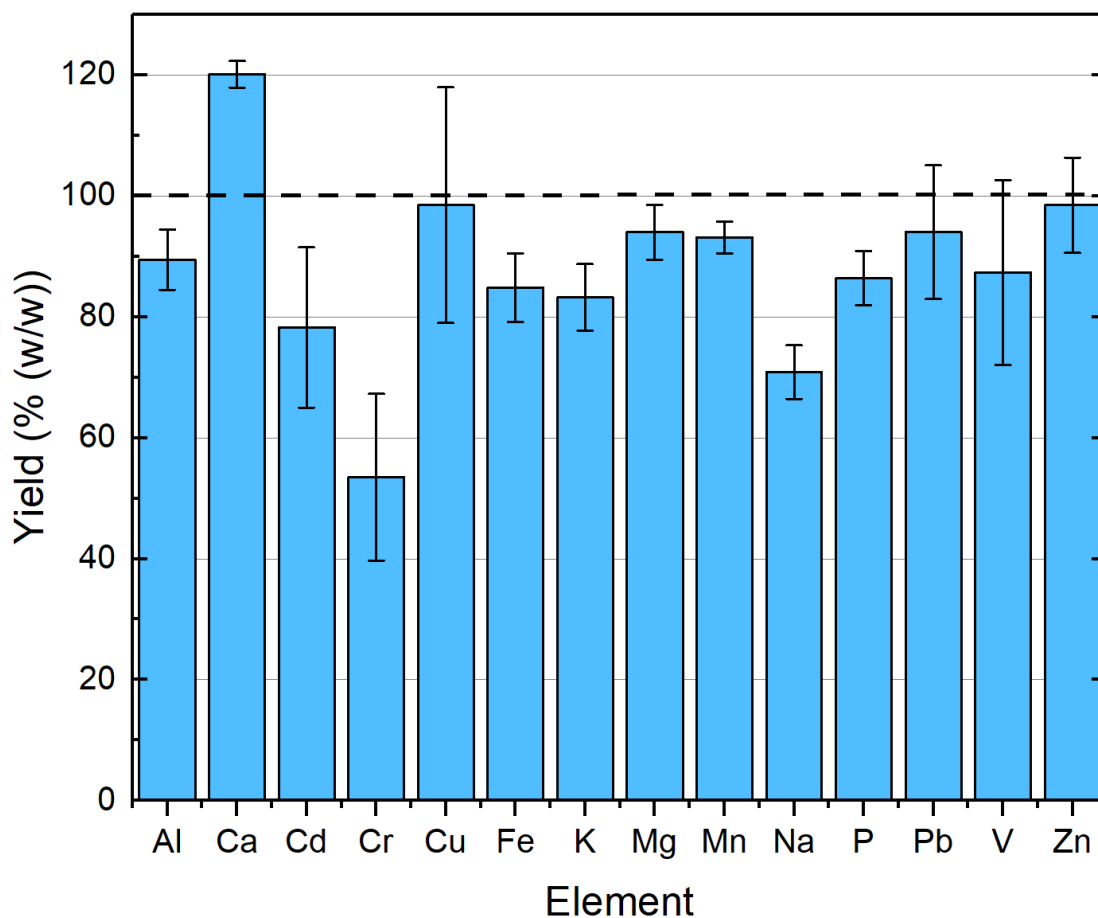
Figure 8 Yield of several metals after decomposition with HCl and HNO₃ (without HF)

The standard deviation, which can be seen as vertical black lines on top of each bar in figure 8, is alarmingly high for some metals, especially Cd, Cr and Cu. These are metals with low total concentration in the ash and are closer to LOD, giving the results a high uncertainty. Besides, the number of replicates used for determination of metals not trapped in the silicates were low.

As seen in figure 8, Ca has a yield of 120%. As discussed earlier, when decomposing the ash, Ca precipitates before being dissolved with boric acid. If some of the calcium salts were not dissolved before analysis of the sample, the total concentration of Ca would be too low, i.e. the measured amount of Ca outside the silicates could be higher than the determined total amount of Ca. Still, an excess amount of boric acid was used, hence the amount of Ca that did not dissolve should not be significantly large.

The high yield of Ca might be a result of contamination caused by for instance poorly cleaning of equipment or contamination of reagents. However, this is not a likely cause since

all equipment is thoroughly washed before use. Also, the same equipment, with the same washing method, and the same regents are used for all other experiments and should therefore have given high Ca values in all results. The high yield may also be a coincidence.

All the measured elements, except Cr and Na, gave a yield > 80% when decomposed with only HCl and HNO_3. Since $98 \pm 8\%$ of the Zn is dissolved without HF, the silicates in the fly ash might not need to be considered when recovering Zn. The expenses and possible hazards of using HF to dissolve the silicates are greater than being able to recover all the Zn.

4.3 Leaching

4.3.1 Water

Results from pre-leaching with water where sampling was done during the leaching are shown in Appendix 5. For most elements measured, the yield was about 0% and then increased significantly at 120min. This is likely due to the samples taken out at during the leaching not being representative for the whole solution. Since the solution settled before the samples were taken out, much of the dissolved elements might have been absorbed by the ash and was thus not collected when the sample was taken. The sampling procedure is not optimal, and these results was only used for method development.

Comparing the results at 120min, there is only a small difference between the two tested temperatures making the increase at 40°C insignificant. Therefore, following experiments were done at 25°C. Heating of water requires much energy, therefore, at a bigger scale, high temperatures should be avoided to make the cost small.

All later experiments were done with specified times, i.e. one experiment for 15min, one for 30min and so on. The results are presented as concentration in eluate in figure 9 and 10. Figure 11 shows the yield of Ca, Na, Pb and Sn. See table 19 and 20 in Appendix 5 for raw data. All results are given with ± one standard deviation. The yield (% (w/w)) is calculated by comparing the amount in the eluate with the total amount previesly measured.
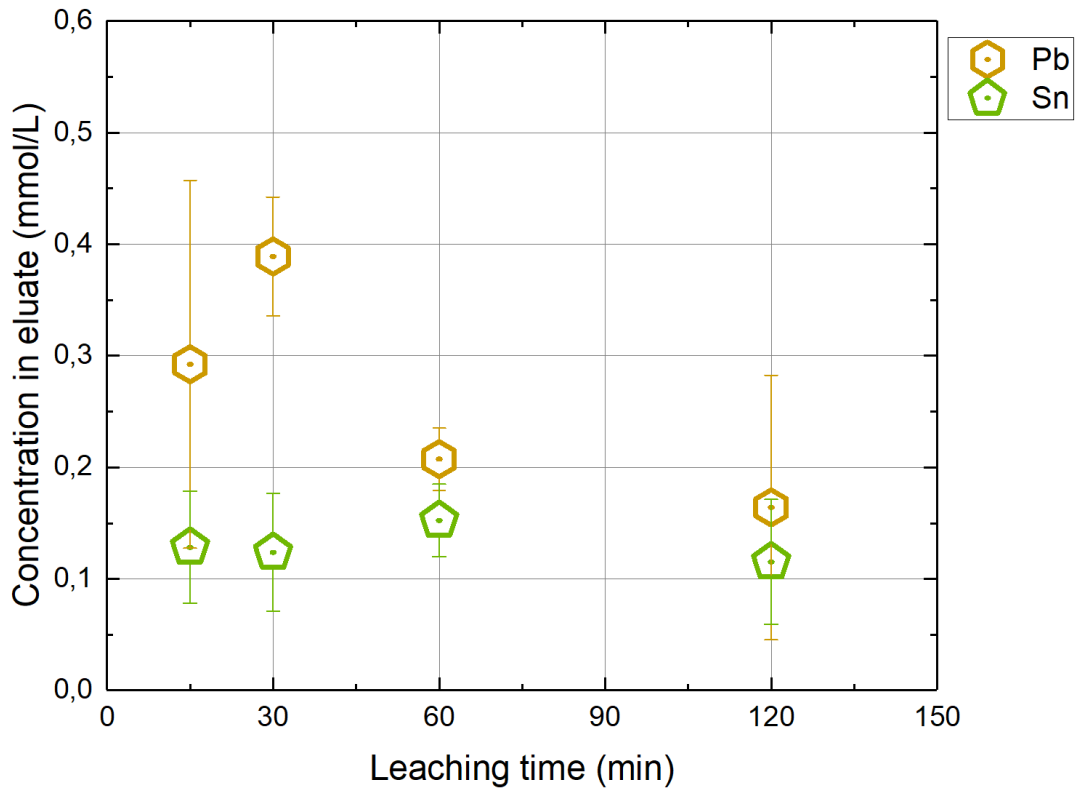
Figure 9 Concentration of Pb and Sn in eluate after leaching MSW fly ash with water.
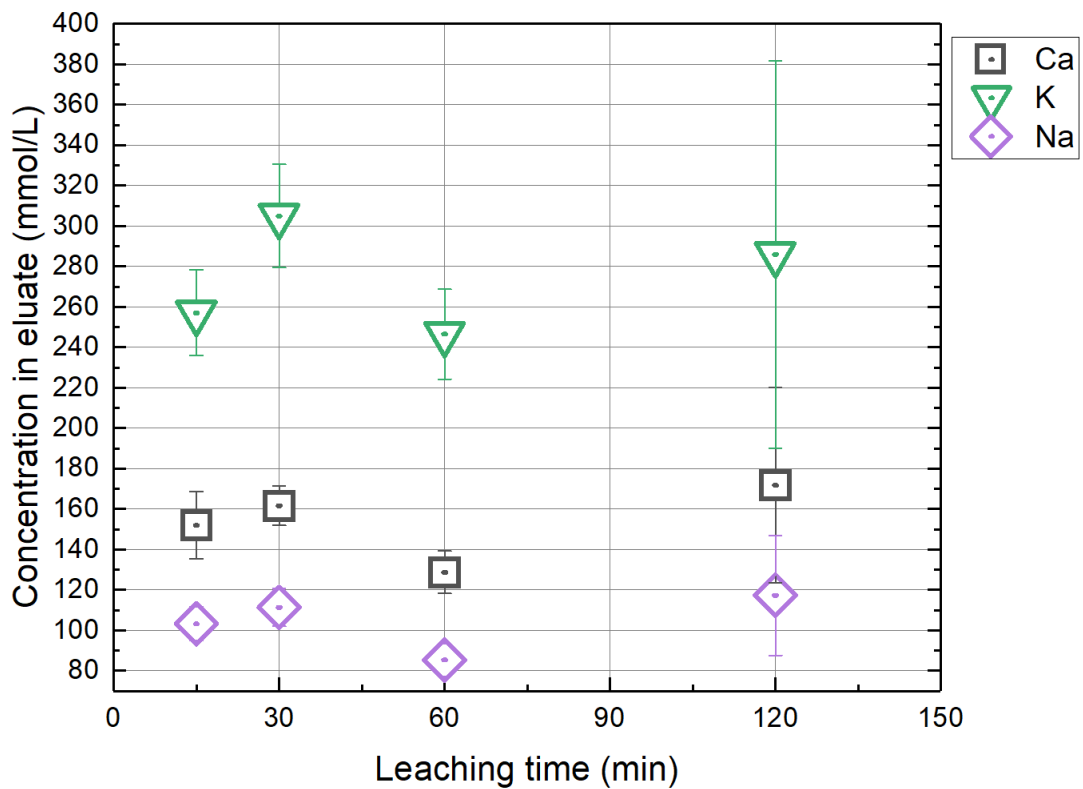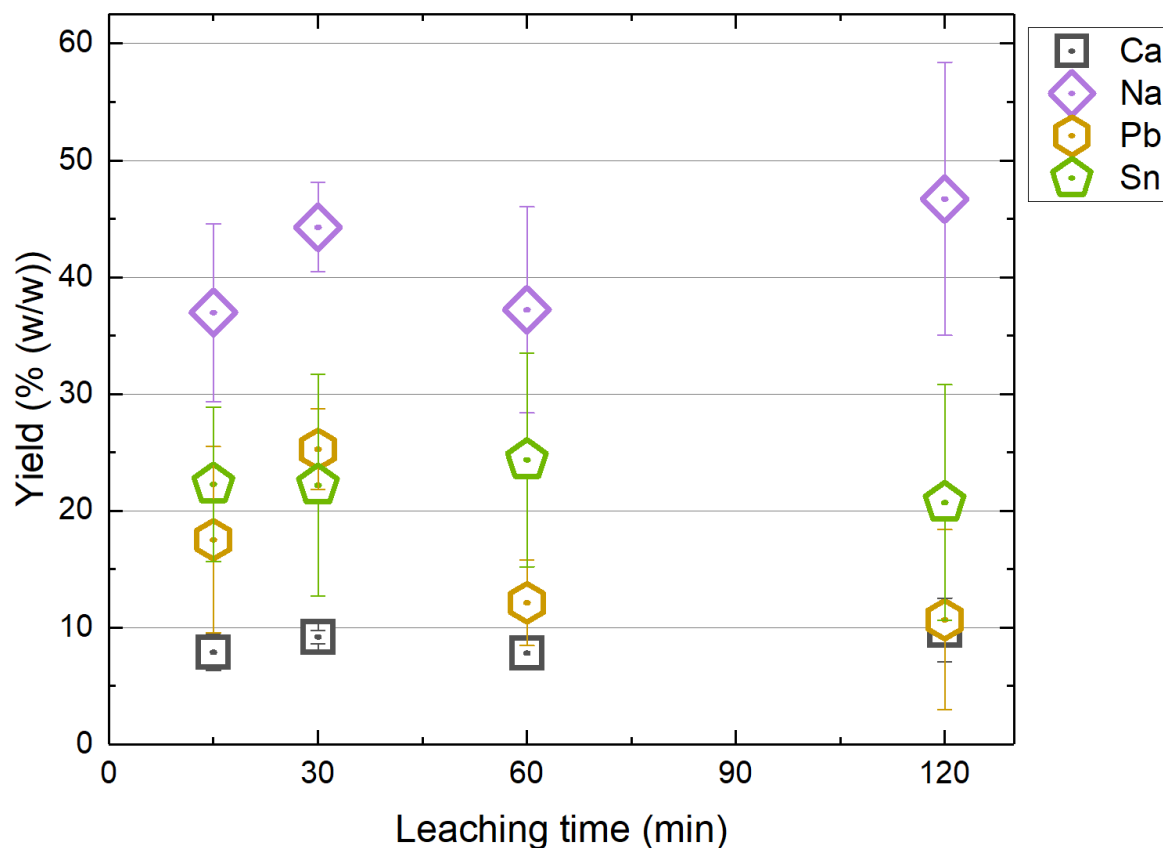

Figure 10 Concentration of Ca, K and Na in eluate after leaching MSW fly ash in water.

Figure 11 Yield of Ca, Na, Pb and Sn after pre-leaching with water

The metals shown in the figures above, in addition to K, were the only metals with measured concentration > LOD (given in table 15). As expected, much of Ca, Na and K dissolved since they are mostly present as soluble salts. Results for K are shown in table 19 and 20.

With a yield of over 200% for K, there were obviously some contamination or interferences. The blank sample showed significant values of K, which was removed from the measured concentration. High blank values usually mean large uncertainty, making the measured concentration unreliable. Even after removal of concentration from blank value, the yield is over 200%. All equipment, with the same washing method, are used for all other experiments, which makes it an unlikely contamination source. The same goes for interferences, as the same ICP-OES method were used for all experiments, but none of them showed high K values. This issue was not investigated further due to time limitations.

The yield achieved for Na and Ca is lower than the yield found in many studies using a higher L/S ratio. For example, Fedje et al. dissolved 71% Na and 31% Ca with a L/S ratio of 50:1

and a leaching time of 24 hours [27]. The difference might be caused by longer leaching time, higher L/S ratio or a combination of the two.

Due to the alkaline compounds in the sample, the leaching solution obtained an end pH of 11-12.

Figure 9 shows that about 0.2-0.4 mmol/L Pb was dissolved when leaching the ash with water. This corresponds with the leaching experiments performed by NOAH, where about 0.3 mmol/L was dissolved, and with the research done by Fedje et al. (2010) [27]. The majority of Pb in MSW fly ash is present as $PbSO_4$ [14], which is slightly soluble in basic solutions [50]. In alkaline solutions, $PbSO_4$ will dissolve to form hydroxide complexes, as shown in equation 9 below.

$$PbSO_4 + 4OH^- \rightarrow [Pb(OH)_4]^{2-} + SO_4^{2-} \qquad \text{Eq. 9}$$

This corresponds to the fact that some sulfate also dissolves when leaching the ash with water.

No characterization of Sn in MSW fly ash were found during the literature study for this thesis. Tin obtains the oxidation stage +2 or +4 [51]. Stannous oxide, SnO, is somewhat soluble in basic solutions which could be an explanation for the dissolved Sn. The reaction of SnO with hydroxide is shown in equation 10.

$$SnO + OH^- + H_2O \rightarrow [Sn(OH)_3]^- \qquad \text{Eq. 10}$$
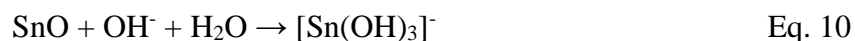
Both Pb and Sn were measured at low concentrations, resulting in in uncertain value. For this reason, the high yield of both the metals might be a coincidence or the result of contamination. Especially the dissolved Sn raises suspicion as it has not been mentioned in other studies with leaching of MSW fly ash in water.

Figure 11 shows a decrease in concentration for all metals, except Sn, at 60 min. The pre-leaching test done at 60 min were done in-between the other pre-leaching tests, and with the same method and equipment as the other tests. For these reasons, the decrease in concentration at 60min should not be caused by contamination as this would have shown in all samples. Because of high uncertainties, the decrease is most likely a coincidence.

The metals with concentration measured lower than LOD did not significantly dissolve in water.

Figure 12 shows the yield of Ca, Na, Pb and Sn when the concentration from the washing water was added.
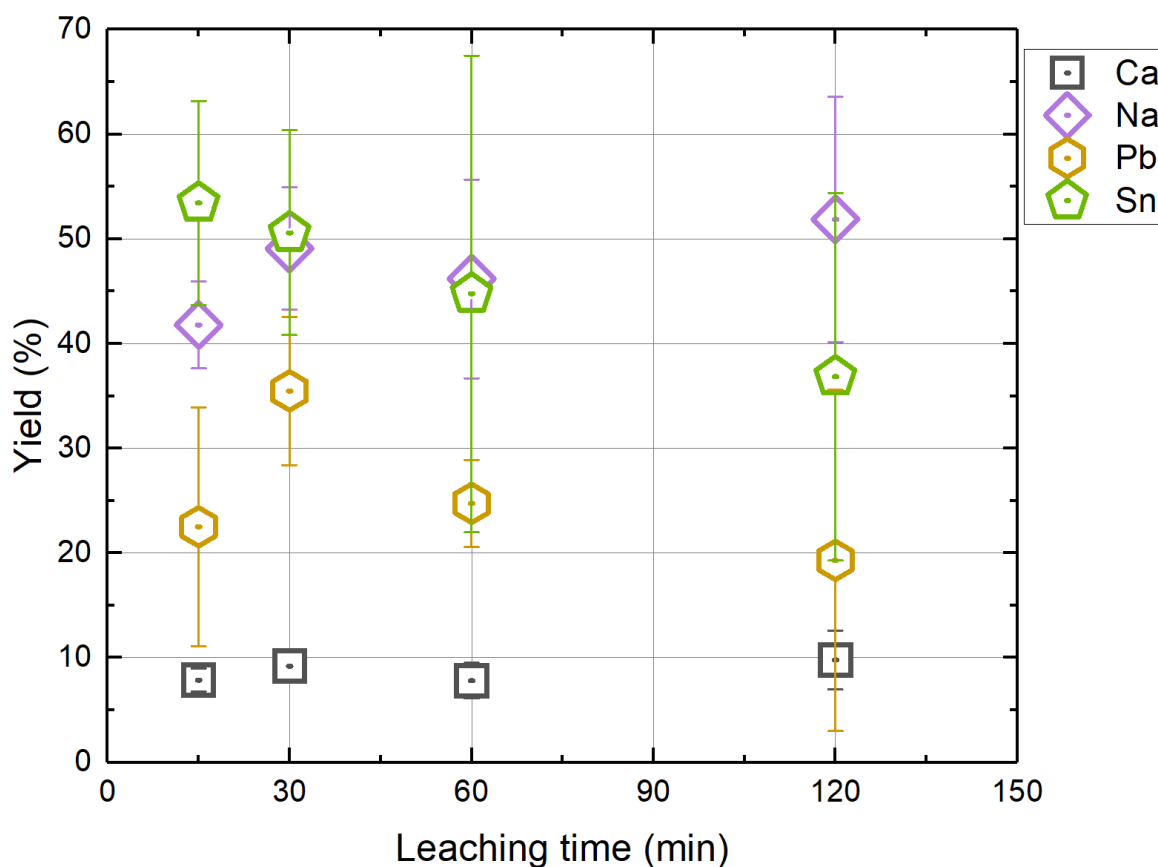
Figure 12 Yield of Ca, Na, Pb and Sn after pre-leaching with water and washing

Comparing figure 11 and 12 reveals that the concentration of Na, Pb and Sn increases when the residue is washed with water after leaching. This increase in concentration shows the importance of washing the solid residue. Some of the eluate might not be separated from the ash during filtration. When washed, the water will release the trapped eluate from the solid residue.

The concentration of both Sn and Pb decreased with increasing leaching time. This may be due to formation of insoluble salts. In the presence of chloride, Pb will form lead(II) chloride, $PbCl_2$, as in equation 11.

$$Pb^{2+} + 2Cl^- \leftrightarrow PbCl_2 \qquad\qquad \text{Eq. 11}$$

However, if the concentration of chloride is high, the lead will form complexes with the chloride, making it re-dissolve.

The decrease of Sn might be caused by formation of tin(II) hydroxide, $Sn(OH)_2$ which is an insoluble salt.

$$[Sn(OH)_3]^- \leftrightarrow Sn(OH)_2 + OH^- \qquad\qquad \text{Eq. 12}$$
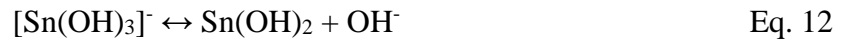
For equation 12 to shift to the formation for $Sn(OH)_2$, OH^- needs to be removed from the solution. Other studies has shown decrease in dissolved heavy metals with increase of leaching time due to precipitation of hydroxides [40]. As mentioned, the tin may also be present as Sn^{4+}, which will form tin(IV)hydroxide, $Sn(OH)_4$.

The eluate after pre-leaching with water was also analyzed for chloride with IC. The results are shown in figure 13 and 14. When calculating the yield of Cl^-, the measured total amount of chloride by NOAH was used.
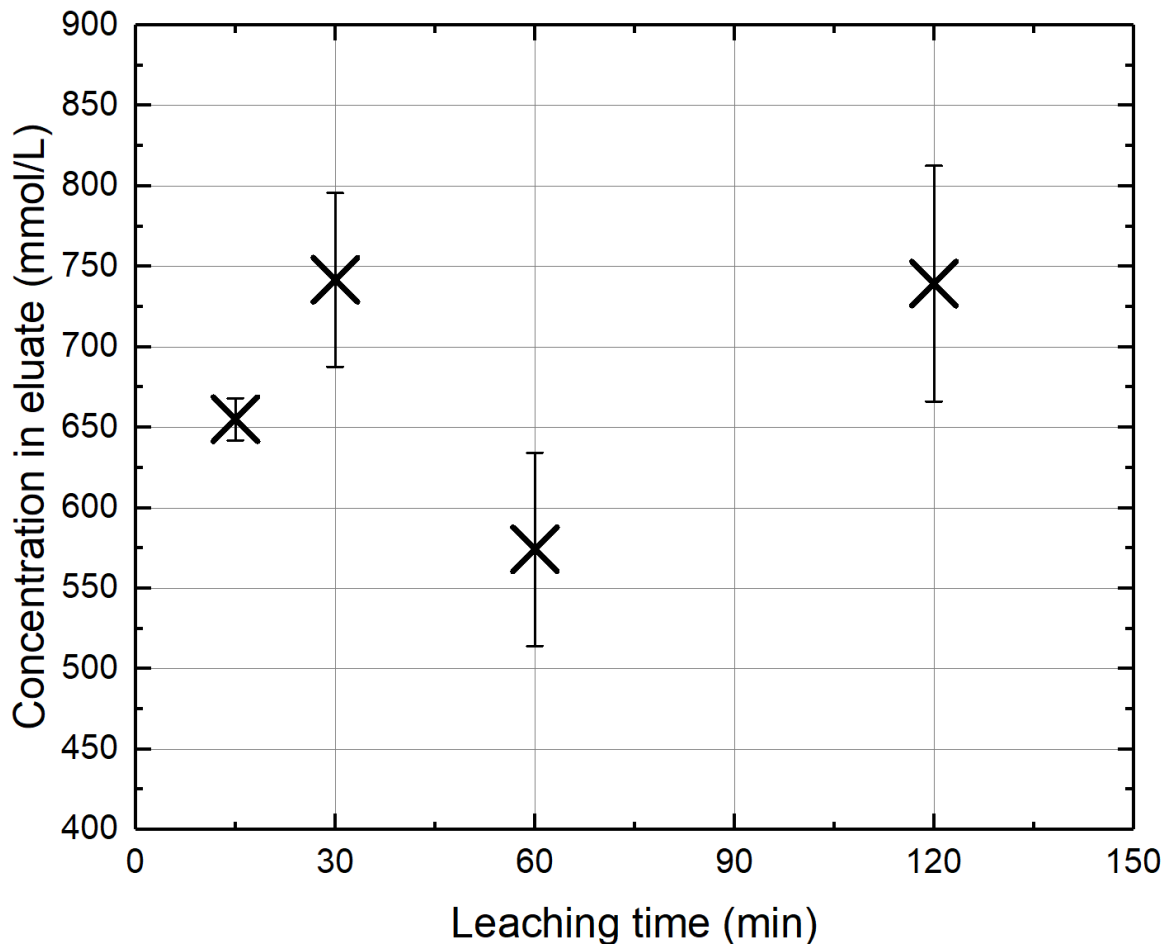
Figure 13 Concentration of chloride in eluate after pre-leaching MSW fly ash with water
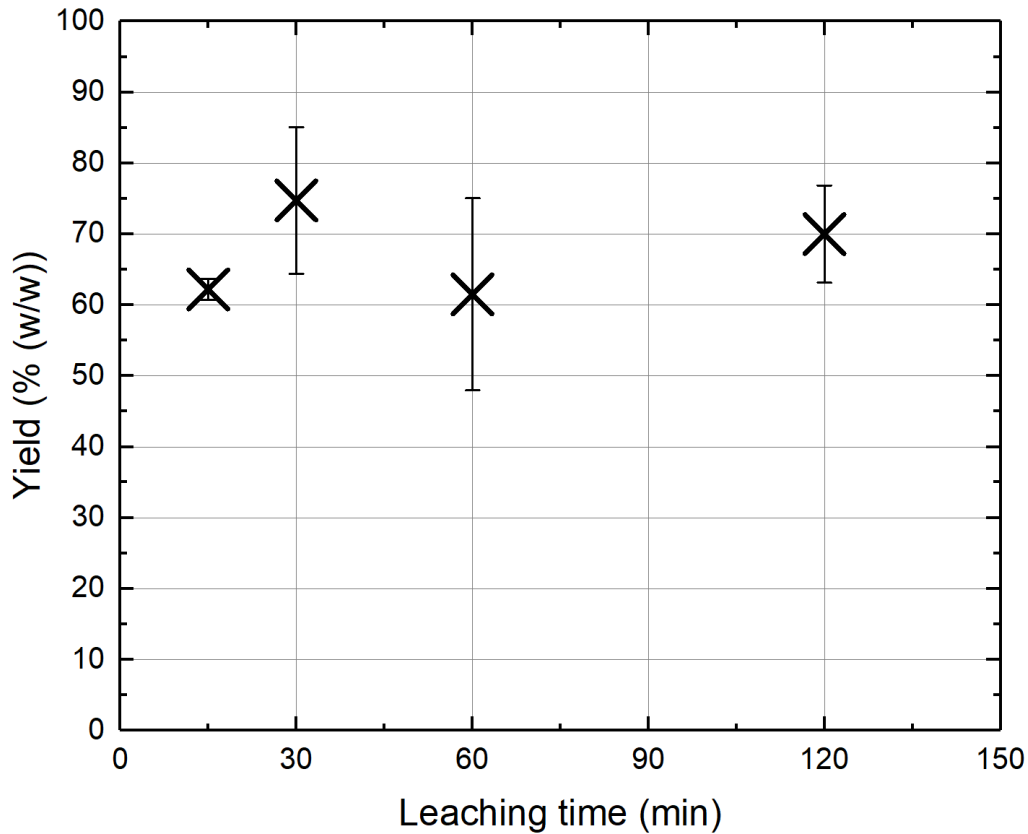
Figure 14 Yield of chloride in eluate after pre-leaching with water

None of the washing solutions contained chloride. The relative error found by comparing the measured concentration of the known sample with the actual concentration was 7.9%.

As with the cations, the chloride concentration decreases at 60min, probably caused by the same reasons: precipitation and/or coincidence. The concentration of the anions is a bit higher than of the cations, but they are in the same range.

As mentioned, one of the routine analysis done at NOAH is leaching the ash in water using NS-EN 12457-2. This method uses a L/S ratio of 10:1 and a leaching time of 24 hours, and the achieved yield was 100%. This yield is higher than obtained in this project and might be due to higher L/S and the long leaching time.

Doing the leaching in steps might dissolve more chloride Funari et al. in 2016 pre-leached the ash in three steps with a L/S ratio of 10:1 dissolving over 80% of the chloride [38]. Performing the pre-leaching in steps gives a good yield without having to use large quantities of water.

The eluate contained 10.4-12.5 mmol/L sulfate. Yield could not be calculated because the total concentration of sulfate is not known. The concentration of sulfate in the eluate corresponds with the dissolved Ca and Pb as discussed above.

As seen, the eluate contains mostly Na, K, Ca and Cl and might be suitable for recovery of salts. Research on use of salts recovered from MSW fly ash as road salts has shown promising results [20]. In Scandinavia, the amount of road salts used each year is high, and this might be a motivation for more research on this possibility.

4.3.2 Sulfuric acid

When sulfuric acid was added to the beakers with the sample, the solution thickened immediately. This is due to the formation of gypsum, $CaSO_4 \cdot 2H_2O$. Figure 15 shows the beakers after the leaching process described in subchapter 3.4.3.

Figure 15 Ash samples after addition of sulfuric acid

In the literature, use of sulfuric acid as leachate has given sporadic results, but overall the leachate shows promising results, up to 100% yield of Zn [21, 27, 38]. Neither of the studies express problems with formation of gypsum. This might be because of higher L/S ratios than 5:1 which was used in this experiment, but this is not likely since the difference in L/S ratio is not that large. Using a high L/S ratio will prevent the formation of gypsum, but it will decrease the amount of Zn leached [52, 53]. Due to the change in contents of MSW fly ash, the increased L/S ratio must be able to withstand great varieties in Ca concentration in the ash.

As mentioned, one of the purposes of pre-leaching the fly ash with water before leaching with sulfuric acid, is to dissolve as much Ca as possible to prevent the formation of gypsum. This

leaching experiment revealed that pre-leaching might not dissolve enough of the Ca for the ash to be leachable with sulfuric acid.

Both possibilities, higher L/S and better pre-leaching, requires large quantities of reagents, especially water, which need to be handled after use. Both the increase of reagents and need for post-treatments will increase the cost of the method.

4.3.3 Ammonia solution

When adding ammonia to the ash, the solution turned blue almost imidiatly. Figure 16 shows the leaching solution before initiating stirring. The strong blue color is caused by copper complexes.
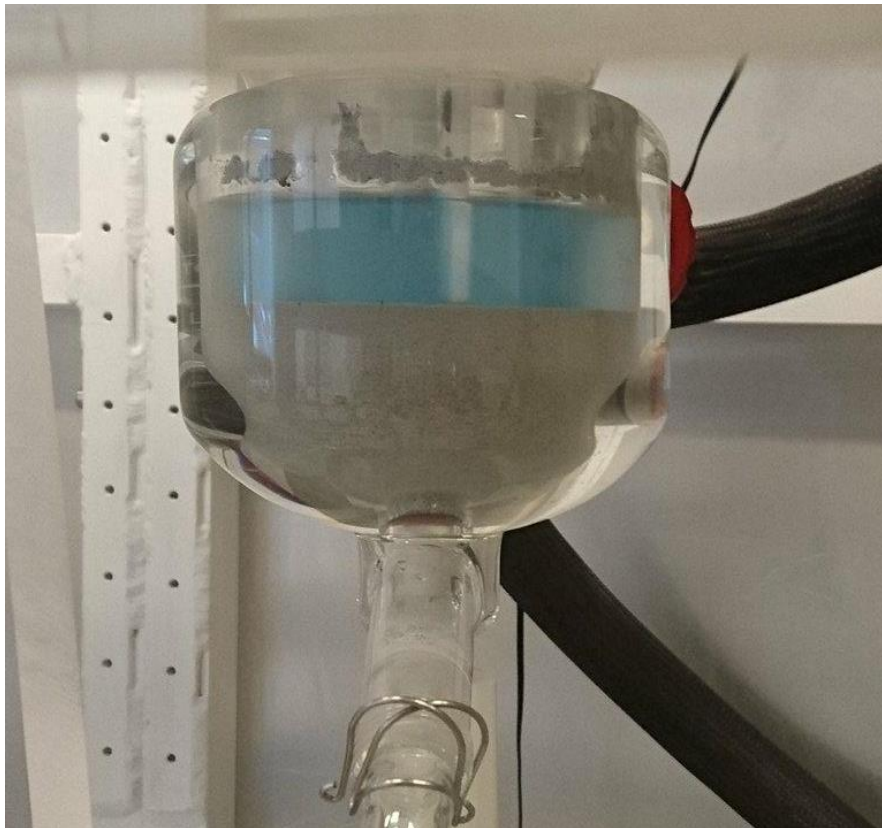
Figure 16 Reactor with MSW fly ash and ammonia solution before initiation of stirring

The results from leaching the fly ash with ammonia are shown in figure 17, 18 and 19 as concentration in the eluate and yield. The yield is calculated by comparing the amount in the eluate with the previusly measured total amount. Other metals measured had a concentration lower than LOD or 1%.
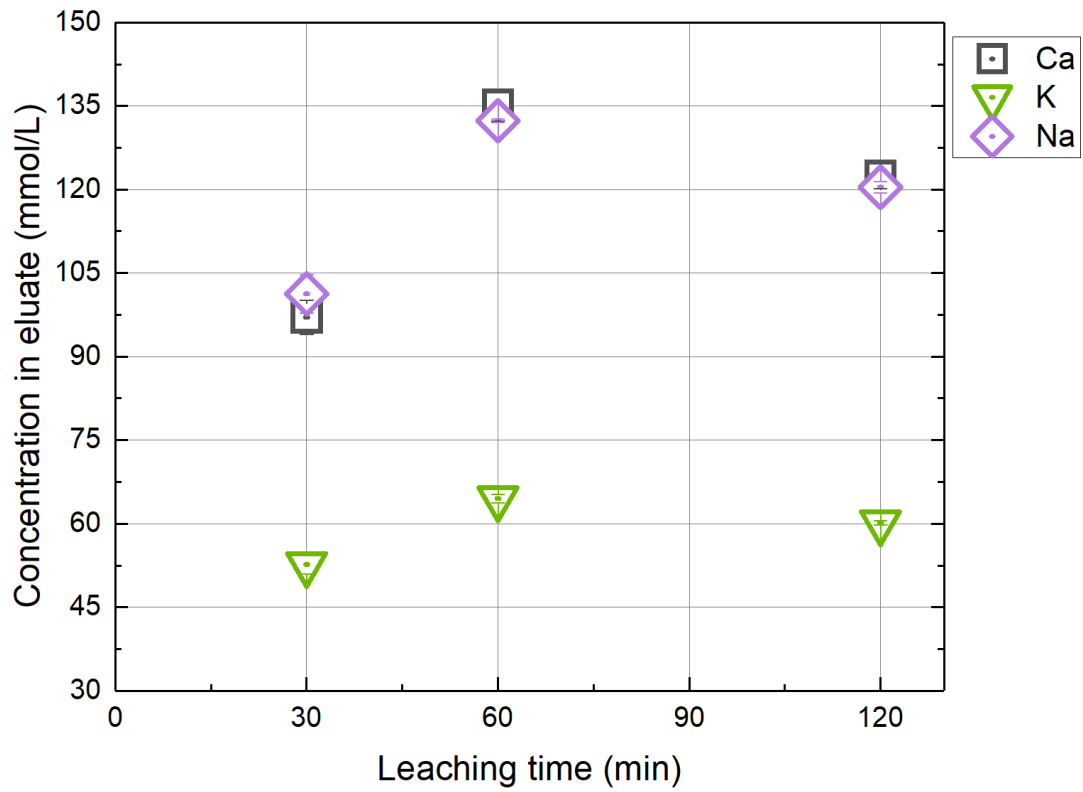
Figure 17 Concentration of Ca, K and Na in eluate after leaching MSW fly ash with ammonia solution
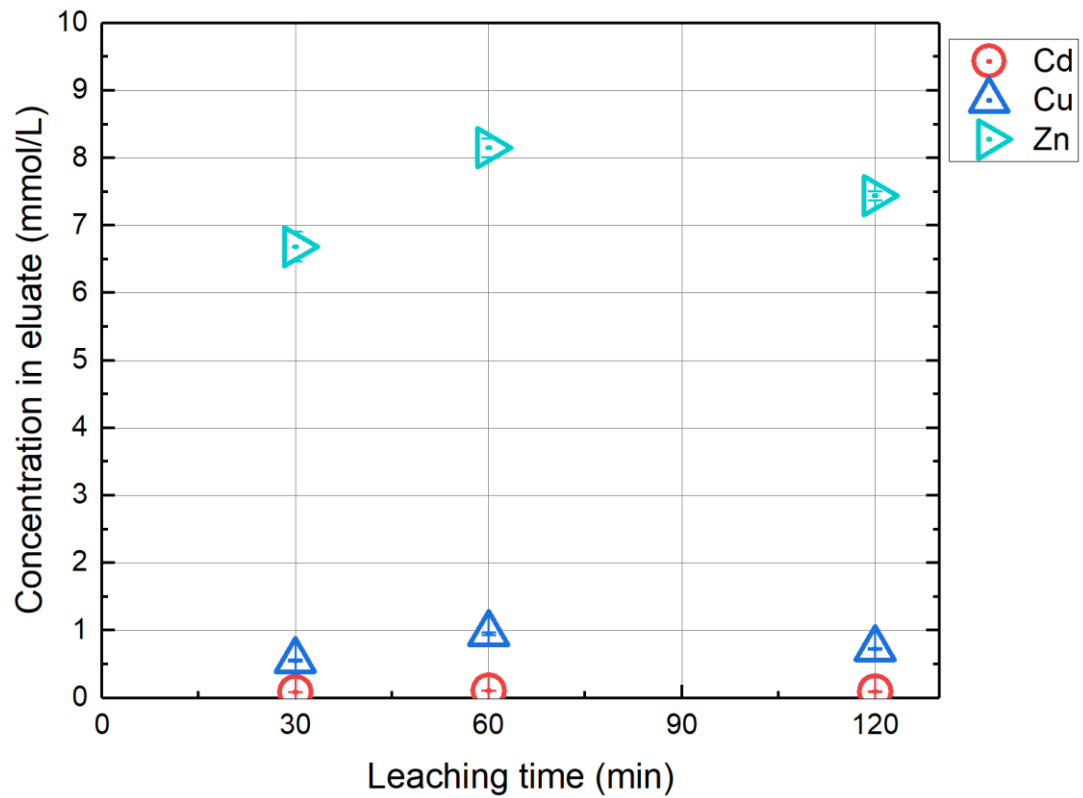
Figure 18 Concentration of Cd, Cu and Zn in eluate after leaching MSW fly ash with ammonia solution
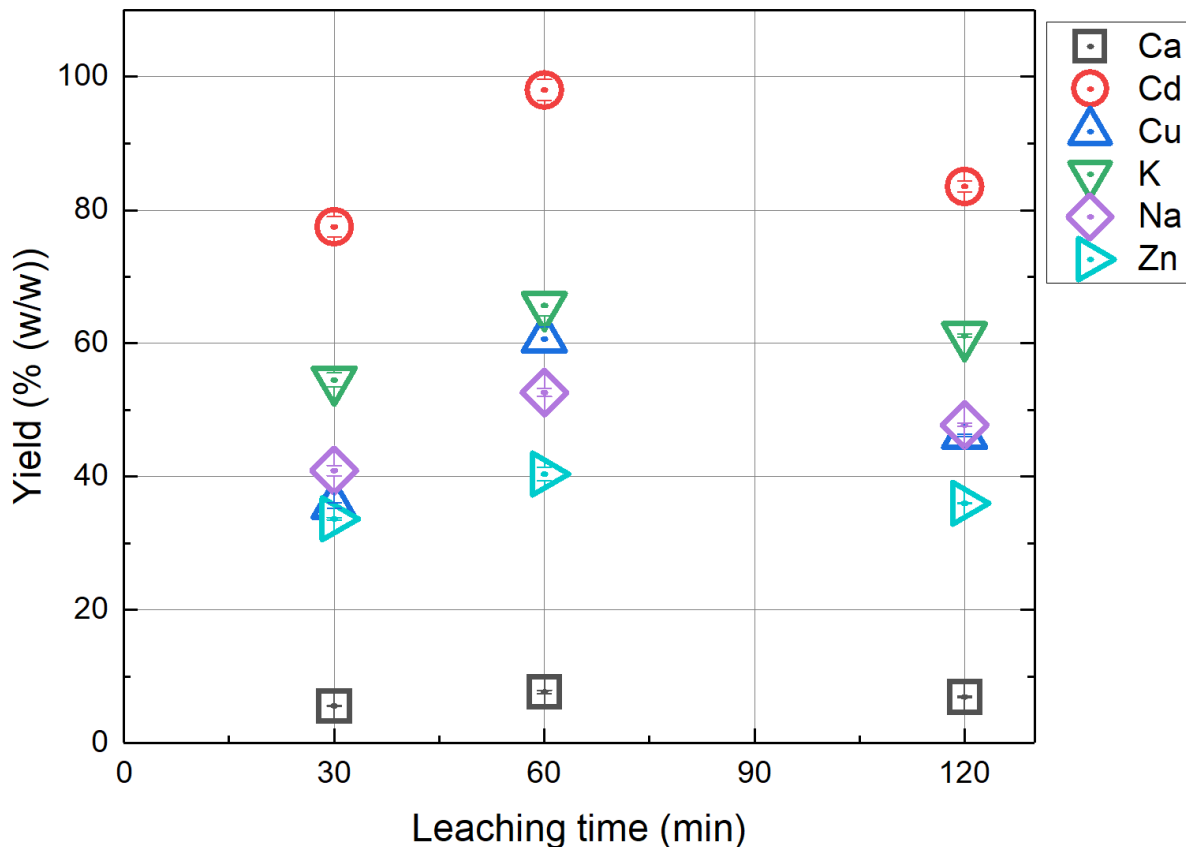
Figure 19 Yield of several metals after leaching with ammonia

Na and K dissolved because of the water in the ammonia solution. Since much of the Na and K is present in the ash as chloride salts, the eluate will probably contain some chloride. The eluate was not analyzed with IC due to high pH.

The initial pH was about 13, and the end pH was approx. 12.5. Cu, Cd and Zn is amphoteric and will therefore dissolve in basic solutions. Cu forms strong complexes with ammonia, hence a high yield was expected for Cu. Cd and Zn do form ammonia complexes as well, but none as strong as Cu. The high yield of Cd might be partly because of low concentration of Cd in the fly ash.

Compared to the results from leaching with 3M ammonium nitrate, NH_3NO_3, found by Fedje et al. (2010) [27], the results was about the same for Na and K. The amount of Ca and Cu dissolved was higher in ammonium nitrate, possibly because of the difference in pH. The pH difference might also be the reason for the difference in dissolved Zn. With ammonium nitrate, 29% Zn dissolved, but with ammonia solution about 40% dissolved. Difference in leaching time might also be a reason for the different yields; the leaching done with ammonia

nitrate had a leaching time of 24 hours and the leaching with ammonia solution was performed at 2 hours.

Comparison of the two leachates reveals that ammonium nitrate may be a good leachate for recovery of Cu, but ammonia solution might be a good option for recovery of Zn.

Figure 20 shows the yield of Ca, Cd, Cu, K, Na and Zn when the concentration from the washing solution is taken into consideration.
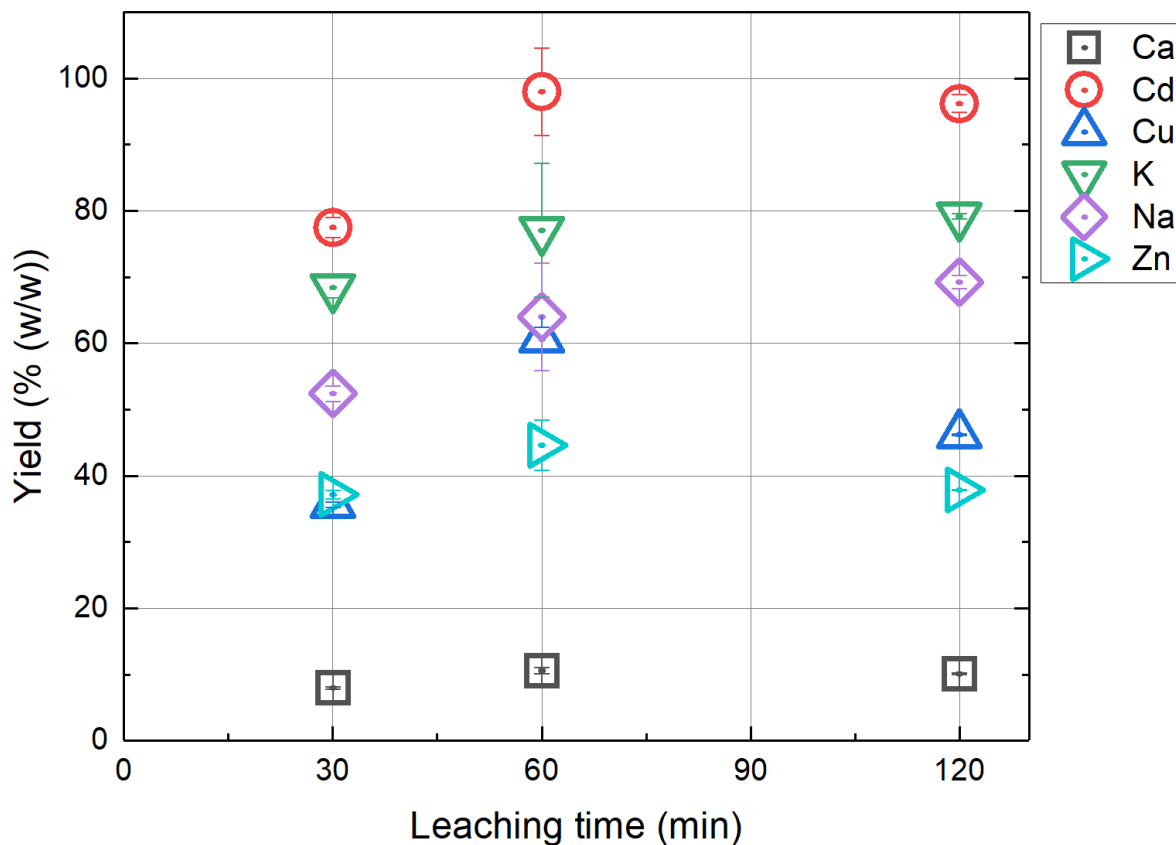
Figure 20 Yield after leaching with ammonia and after washing

When the amount from the washing solution was added, the concentrations increased. The concentration of all the measured elements show a decrease at 120min leaching time, except for Na and K. The decrease might be caused by slow precipitation of hydroxides. Cd, Cu and Zn all form insoluble salts with hydroxide, and there might be a competition between the reaction with ammonia and the hydroxide.

The formation of hydroxides could be used as an advantage, to separate Zn from the eluate. If the ammonia is evaporated from the elute, the equilibrium for Cu complexation shown in equation 13 will shift to the formation of a hydroxide complex.

$$[Cu(NH_3)_4(H_2O)n]^{2+} + (4\text{-}n)H_2O + 2OH^- \leftrightarrow [Cu(H_2O)_4(OH)_2] + 4NH_3 \qquad \text{Eq. 13}$$
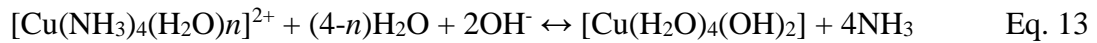
When equation 13 shifts to the right, OH^- will be removed from the solution. The decrease in the concentration of hydroxide will result in precipitation of zinc hydroxide as in equation 14.

$$[Zn(OH)_4]^{2-} \leftrightarrow Zn(OH)_2 \text{ (s)} + OH^- \qquad \text{Eq. 14}$$

The removal of OH^- from the solution corresponds to the decrease in pH with increasing leaching time as seen in figure 27 in Appendix 3.

The precipitation can then be filtrated from the solution. If the concentration of other metals than Zn is low in the filtride, it can hopefully be used as raw material for zinc production. The filtrate might be used for recovery of Cu and/or salts, mainly NaCl and KCl. The evaporated ammonia can be dissolved in water and be reused as leachate.

A beaker with eluate after leaching MSW fly ash with ammonia was left without cover for two days. After one day, the solution clearly showed precipitate and the blue color had faded. Figure 21 shows the solution after one day compared to the eluate.
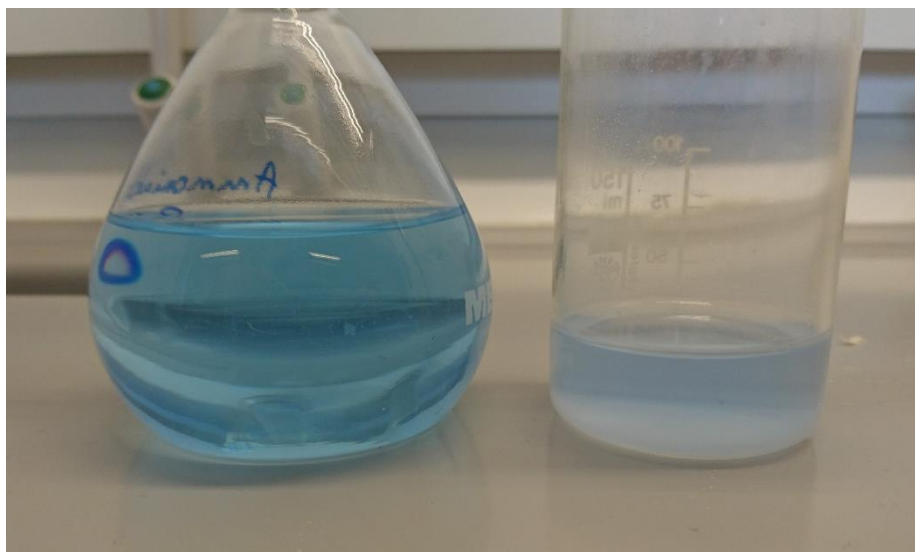
Figure 21 Color of solution after one day without cover compared to the eluate

After two days, the solution was all white and more precipitate had formed. All the visible precipitate was sticking to the beaker. Figure 22 shows the precipitate after the removal of the solution.
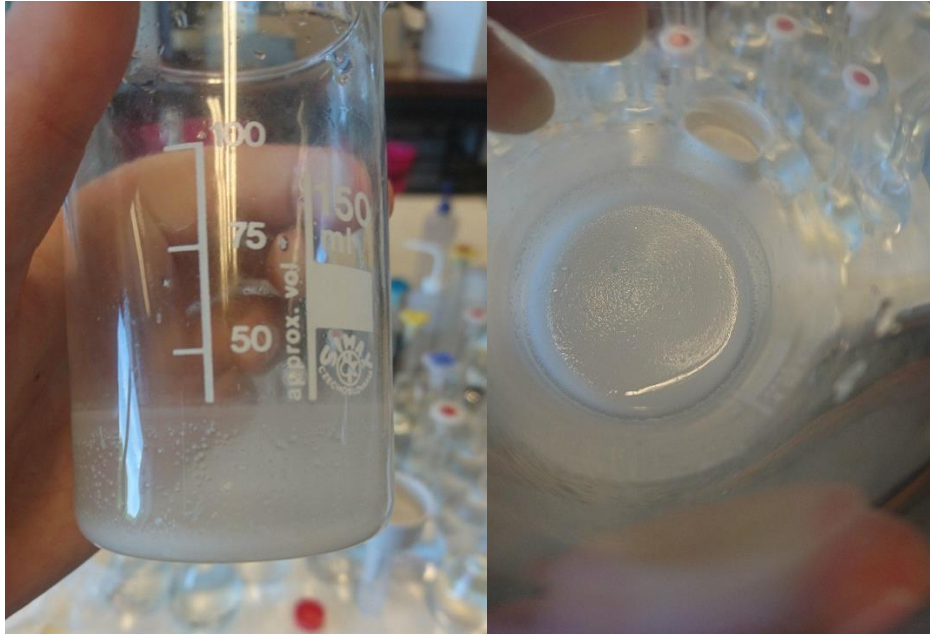
Figure 22 Precipitate after evaporation of ammonia from eluate after leaching MSW fly ash with ammonia solution

Qualitative analysis of the precipitation showed significant amounts of Ca, Cd, K, Na and Zn. The solution was probably left for too long, allowing other compounds to precipitate. If the residue was separated from the solution earlier, it might be purer $Zn(OH)_2$. In an industrial setting, heat would probably be used for fast evaporation.

For the recovery of Zn from MSW fly ash after leaching with ammonia solution to be possible, the chloride concentration must be minimized. If the chloride is not precipitated with $Zn(OH)_2$, further separation is not needed. However, if this is not the case, the chloride needs to be removed from solution by other means. An option may be to pre-leach the fly ash with water to dissolve the water-soluble chloride salts, before leaching with ammonia.

One experiment was performed where the sample was leached with ammonia two times, as described in 3.4.4. The total yield after being leached two times was not higher than when the ash was leached one time.

Possible flowsheet for leaching of Zn with ammonia solution

Figure 23 shows a possible flowsheet for leaching of Zn from MSW fly ash using ammonia solution as leachate, based on results discussed above.
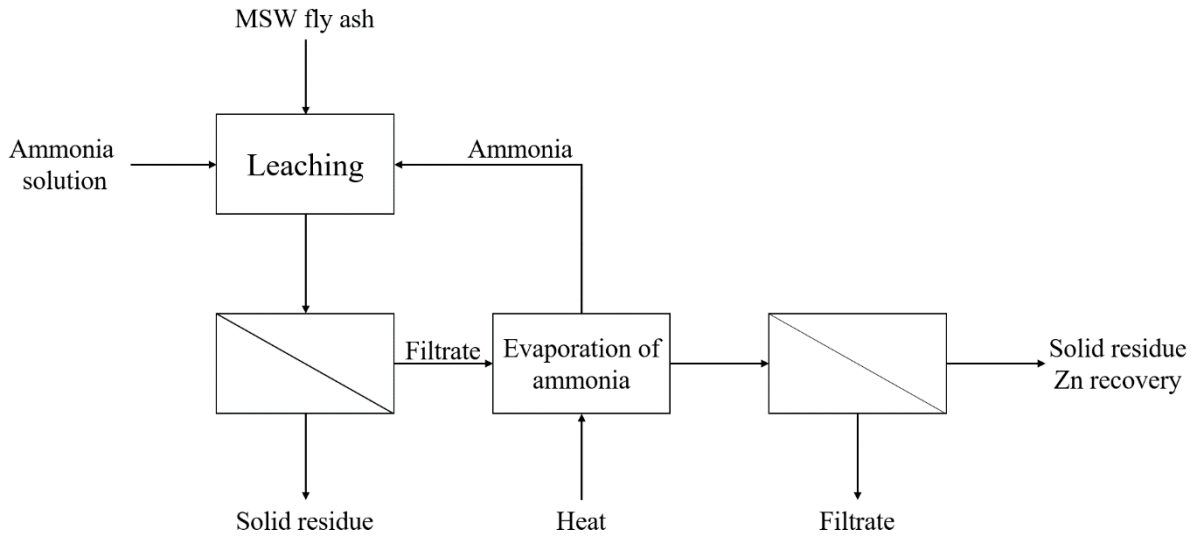
Figure 23 Possible flowsheet for leaching of Zn from MSW fly ash with ammonia solution

The solid residue after the first filtration could be deposited. Since only Zn, Cu and Cd are the only heavy metals that dissolved, the residue is still hazardous, but the volume and mass is reduced. This residue could also be leached with an acidic leachate, releasing the heavy metals for further metal recovery.

The filtrate after the second filtration could be used for salt recovery. This filtrate will hopefully contain mostly K, Na, Ca and Cl, making it ideal for salt recovery.

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5 Conclusion

Municipal solid waste fly ash has been considered as a resource for a few decades, and much research has been done to recover salts and metals from the ash. In this study, the behavior of water, sulfuric acid and ammonia solution were studied. The eluate was measured with ICP-OES and IC.

Pre-leaching with water dissolved K, Na, Ca, Pb, Sn, Cl$^-$ and SO$_4^{2-}$ at significant values. The conditions used for pre-leaching were not optimal for dissolving Na, K, Ca and Cl$^-$ compared to results from other studies. A higher L/S ratio and/or a longer leaching time will dissolve more of the water-soluble salts.

According to literature, leaching with sulfuric acid can yield up to 100% Zn at various conditions. However, gypsum formed immediately after addition of sulfuric acid, making the process difficult. Other acidic leachates had been proven to give equal or better results without similar problems, and are thus probably better choices for leaching of MSW fly ash.

Ammonia solution dissolved about 40% Zn, along with K, Na, Ca, Cd and Cu. After removal of ammonia from the eluate, Zn(OH)$_2$ precipitated. A possible process was found for recovery of zinc from MSW fly ash using ammonia as leachate.

A decomposition of the fly ash was done without dissolving the silicates. It was found that < 10% of the Zn is trapped in silicates, making dissolution of silicates unnecessary for obtaining a good yield.

Addition of boric acid after microwave decomposition with HCl, HNO$_3$ and HF proved to be a suitable method for total decomposition of MSW fly ash. The decomposed fly ash was analyzed with ICP-OES to measure the total concentration of some metals. By analysis of a CRM, the method gives results with reasonable accuracy and good precision, and is considered suitable for this purpose.

5.1 Future work

A lot of research has already been done on leaching of MSW fly ash with water. However, more attention should be given to leaching in steps for the possibility of obtaining high yields without using high L/S ratios.

More research needs to be done on recovery of Zn using ammonia solution for the proposed process to be profitable. The leaching step needs optimization in terms of L/S ratio, leaching time and concentration. Leachability of the solid residue after leaching with ammonia should be studied to determine if recovery of more Zn or other desired metals is possible. If further metal recovery is not beneficial, the residue should be analyzed to determine if more treatment is needed before deposition.

Only a superficial, qualitative analysis was done of the $Zn(OH)_2$ precipitate after removal of ammonia. Therefore, the contents of the precipitate should be further analyzed. The evaporation of ammonia should also be optimized to get the precipitate as pure as possible. Conditions to be studied are mainly temperature and time.

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Appendix 1: Analysis provided by NOAH

The results from routine analysis at NOAH, as described in chapter 3.1.2, are shown in table 12 – 14.

Table 12 Concentration in the three fly ash samples measured with an internal method.

	Concentration (mg/kg dry ash)		
	Ash 1 G-04207	Ash 2 G-04500	Ash 3 G-08980
Ag	24.1	37.7	16.5
Al	9010	20600	7780
As	143	21.8	23.6
Ba	676	1350	701
Ca	295000	287000	366000
Cd	151	97.3	74.6
Ce	7.2	< 8.10	9.2
Cl	187000	163000	109000
Co	36.9	35.5	28.3
Cr	320	320	170
Cs	< 4.00	11.5	< 3.90
Cu	1200	5830	458
Fe	7120	9520	4680
Hg	8.5	29	8.7
K	31000	27700	20000
La	< 5.80	7.4	< 5.80
Mg	6310	8800	5170
Mn	461	725	406
Mo	19.9	22	15.7
Na	69200	63300	46600
Ni	51.1	19	28.7
P	1680	4960	1910
Pb	2800	2680	1560
S	26300	22300	24600
Sb	954	309	597
Se	6.9	3.8	4.3
Si	18600	28700	15800
Sn	586	368	428
Ti	4340	18300	4830
Tl	9.6	< 5.00	6.6
U	32.3	31.9	33.2
V	< 84	< 120	< 78
Y	5.9	5.5	6.9
Zn	11800	7590	6640

Table 13 Concentration in eluate after leaching fly ash with water with an internal method.

	Concentration in eluate ($\mu g/L$)		
	Ash 1 G-04207	Ash 2 G-04500	Ash 3 G-08980
As	< 40	< 40	< 40
Ba	1000	178	2480
Cd	< 2	5	< 2
Co	< 10	< 10	< 10
Cr	19	495	43
Cu	2010	6220	64
Mo	155	214	116
Ni	< 20	< 20	< 20
Pb	55800	42300	18100
Sb	< 40	< 40	< 40
Se	< 30	< 30	< 30
Sn	< 10	< 10	< 10
Tl	< 30	< 30	< 30
V	< 10	< 10	< 10
Zn	4090	10400	4230

Table 14 Concentration of CaO and CO_3^{2-} measured with an internal method and ISO 10694, respectively.

	Concentration (% (w/w dry ash))		
	Ash 1 G-04207	Ash 2 G-04500	Ash 3 G-08980
CaO	22.5	26.6	34.5
CO_3^{2-}	1.92	4.88	4.46

Appendix 2: Preparation of solutions

<u>Calculation of needed amount of boric acid</u>

Calculation of the amount of boric acid needed to neutralize the HF used for decomposition of the fly ash sample, as described in 2.1.

C(HF added) = 0.023 mol/mL

V(HF added) = 2.5mL

n(F$^-$ before decomposition) = <u>0.056 mol</u>

From equation 2 and 3, the boric acid reacts with fluoride in the ratio of 1:4.

n(H$_3$BO$_3$) = 0.056 mol / 4 = <u>0.014 mol</u>

m(H$_3$BO$_3$) = 0.014 mol x Mm(H$_3$BO$_3$) = <u>0.873g</u>

To ensure an excess boric acid, 0.95g was used.

<u>Mobile phase (IC)</u>

1. 700mL type II water and 200mL 20 mmol/L phthalic acid are transferred to a 500mL beaker.

2. Using a pH meter and magnetic stirring, the pH is adjusted to between 4.1-4.5 with 10% (w/v) NaOH.

3. Then, 100mL acetone is added to the beaker.

4. The solution is then transferred to a plastic container and degassed for 10 min with helium.

Calibration standards

Concentration of metals in the calibration standards used for analysis with ICP-OES.

Table 15 Concentration of metals in calibration standards

	Element	Concentration (mg/L)				
		Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
STA	Al	10	20	30	40	50
	Ca	400	600	800	1000	1200
	Co*	0.04	0.06	0.08	0.1	0.12
	Cr	0.2	0.6	1.2	1.8	2.5
	Cu	0.5	5	10	15	20
	Fe	10	15	25	30	40
	K	100	150	200	250	300
	Mg	5	10	15	20	25
	Mn	0.5	1	1.5	2	2.5
	P	2.5	5	7.5	10	12.5
	Sn	0.5	1	1.5	2	2.5
STB	Ag*	0.02	0.05	0.08	0.1	0.15
	Ba	1	2	4	8	12
	Cd	0.2	0.4	0.6	0.8	1
	Ce*	0.005	0.01	0.02	0.03	0.04
	La*	0.005	0.01	0.02	0.04	0.08
	Na	100	200	300	400	500
	Pb	2.5	5	7.5	10	15
	Sb	0.5	1	2	3	4
	Si	0.5	1	2	3	4
	V*	0.05	0.1	0.2	0.3	0.4
	Y*	0.002	0.005	0.01	0.015	0.02
	Zn	10	20	30	40	50

* The stock solution was diluted to 10 mg/L before use in the calibration standard.

For analysis of decomposed sample, the calibration standards were added HNO_3, HCl, HF and H_3BO_3 to matrix match the decomposed samples. The stock solutions contain some HNO_3 which was considered when adding HNO_3.

For analysis of eluate after leaching with ammonia solution, the calibration standards were added ammonia solution to obtain the same concentration as in the samples.

Appendix 3: Instrumental output

Figure 24 and 25 shows the temperature program used for decomposition with power and pressure respectively.
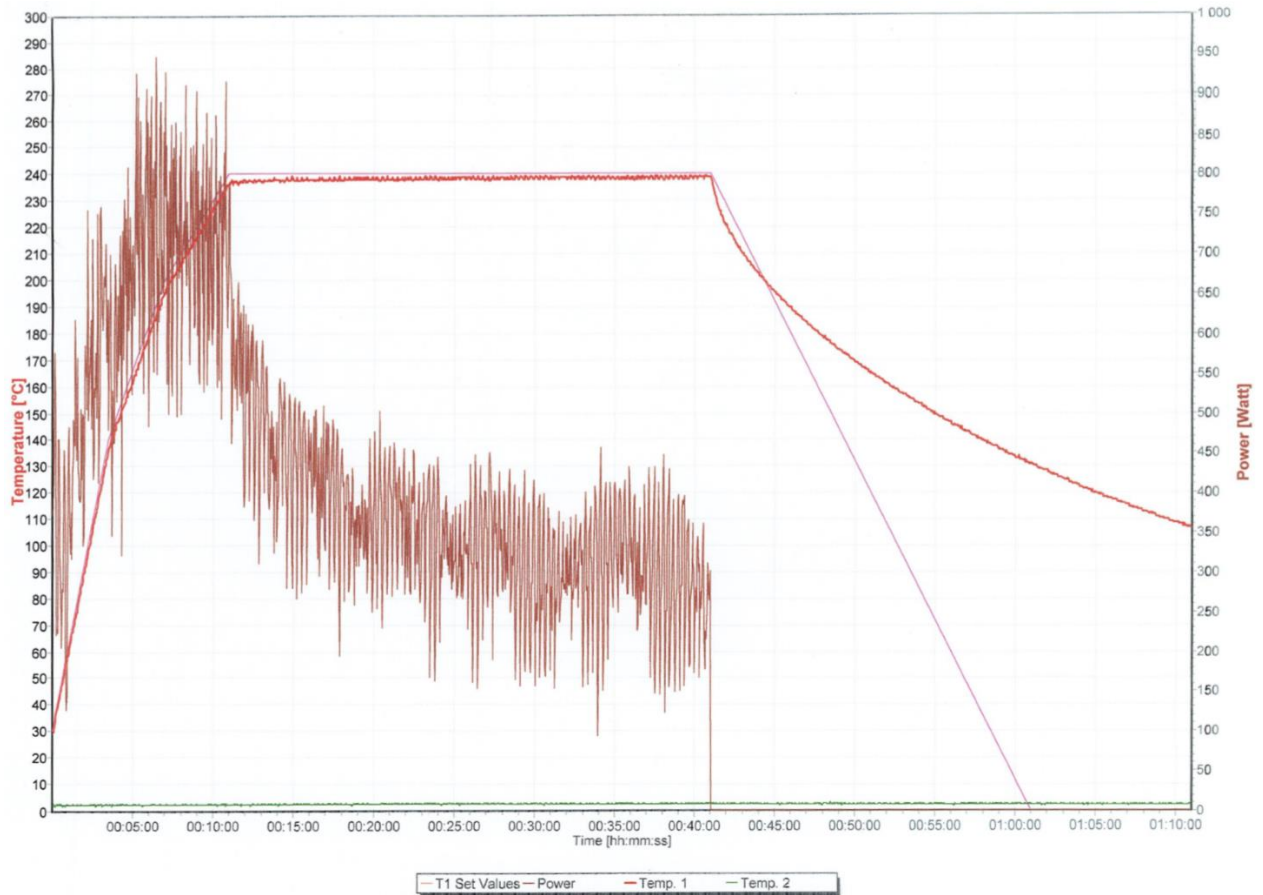
Figure 24 Temperature program and power when decomposing MSW fly ash with HCl, HNO$_3$ and HF
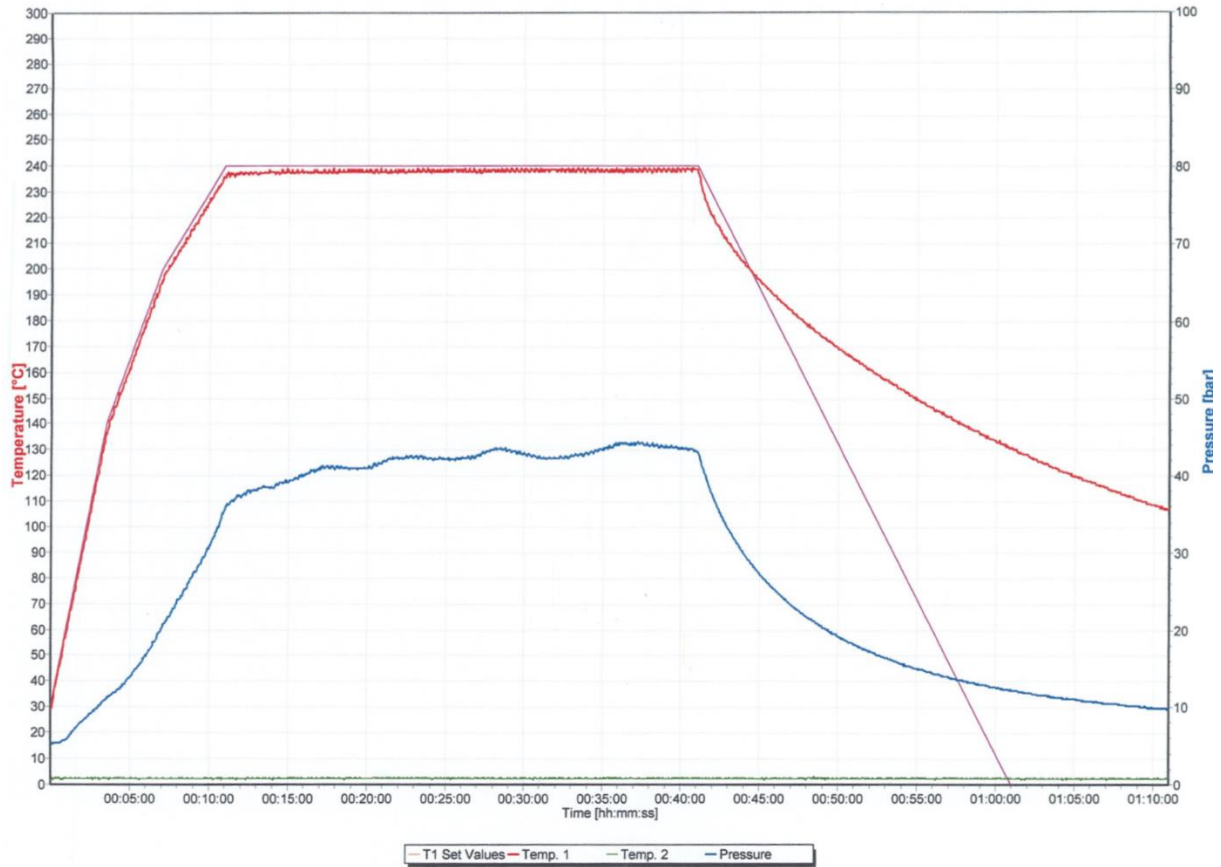
Figure 25 Temperature program and typical pressure when decomposing MSW fly ash with HCl, HNO₃ and HF

Figure 26 shows pH and temperature as a function of leaching time for pre-leaching with water. pH generally varied from 11-13, so this leaching test was in the higher pH range. The sudden increase in pH and decrease in temperature at the beginning are caused by addition of fly ash to the reactor.
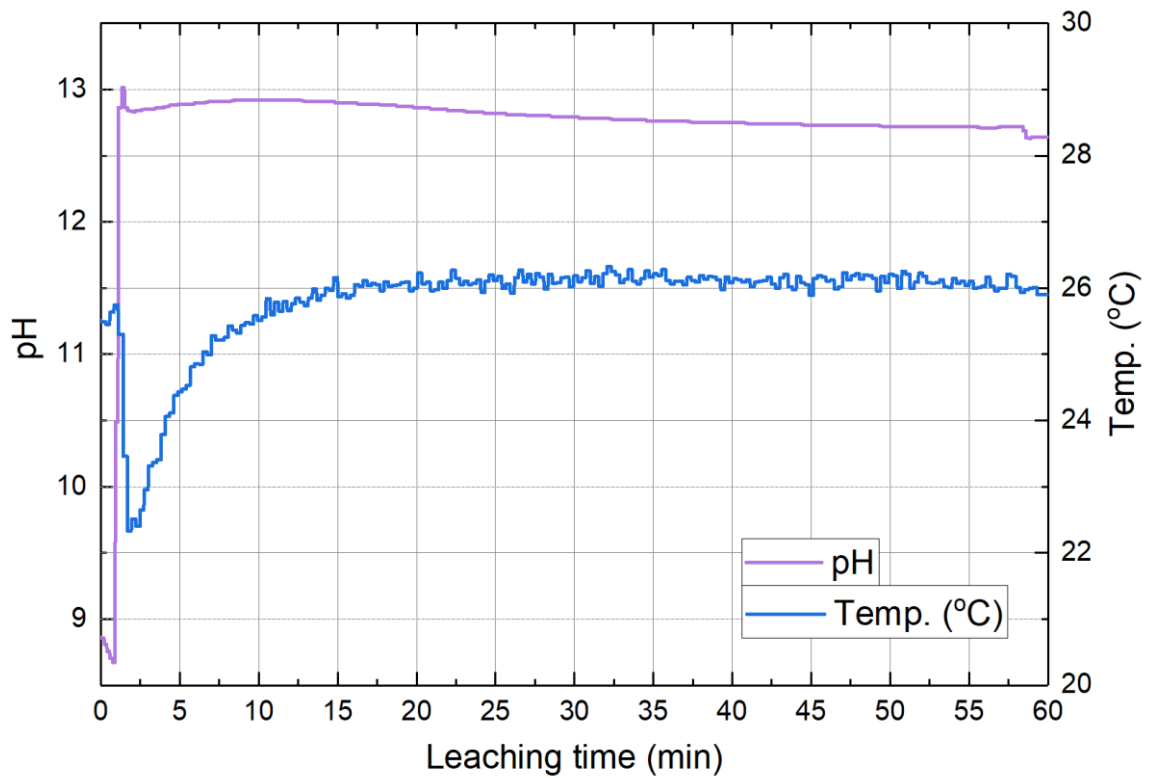
Figure 26 measured pH and temperature during pre-leaching of MSW fly ash with water

Figure 27 shows pH and temperature as a function of leaching time for leaching with ammonia solution. The decrease in pH and increase in temperature at the beginning are caused by addition of the ammonia solution.
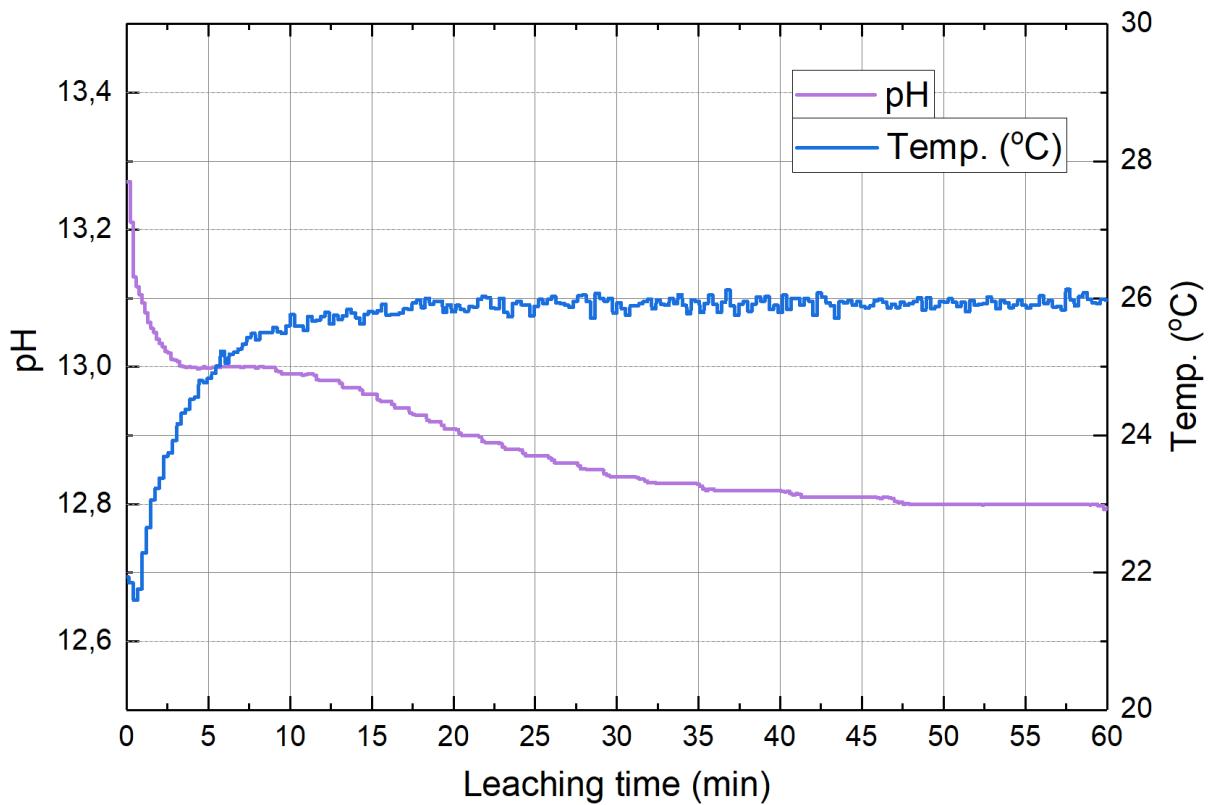
Figure 27 measured pH and temperature during leaching of MSW fly ash with ammonia solution

Figure 28 shows an example of a peak at wavelength 334.502 used to calculate the concentration of Zn.
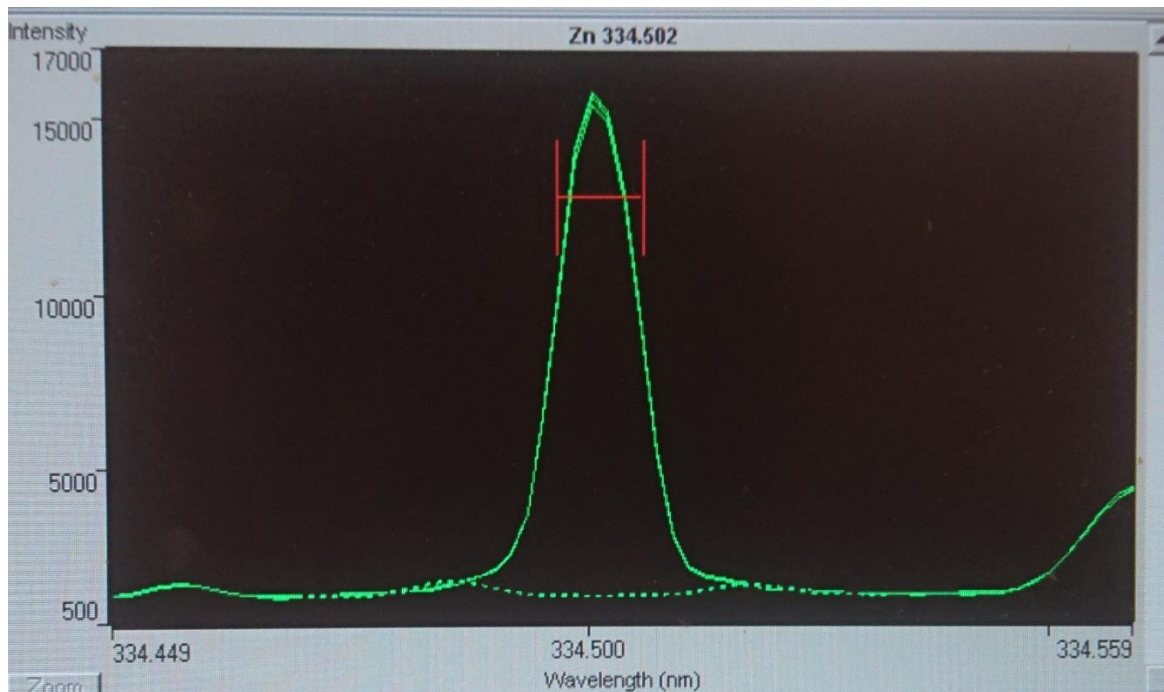
Figure 28 An example of a peak for Zn obtained with ICP-OES

Figure 29 shows an example of a calibration curve for Zn used for calculating concentration of Zn in eluate after leaching with ammonia solution. This calibration curve has a $r^2 = 0.999$
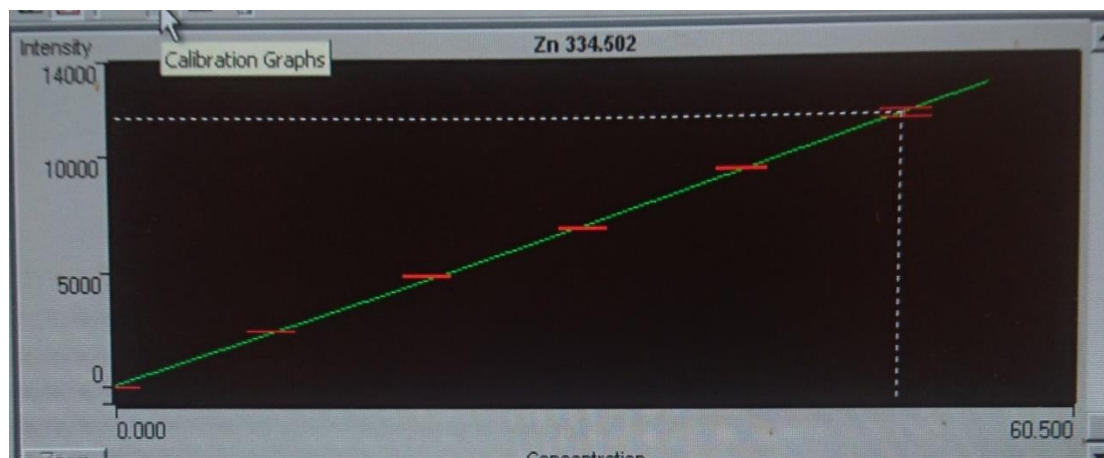
Figure 29 An example of a calibration curve used for measurement of Zn

Figure 30 shows an example of a chromatogram measured with IC. The retention time of the anions follow the order $Cl^- < NO_3^- < SO_4^{2-}$.

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mV*min	mV	%	%	n.a.
1		2,443	98,525	572,862	63,70	82,07	n.a.
2		3,524	6,256	27,548	4,04	3,95	n.a.
3		8,412	49,888	97,571	32,25	13,98	n.a.
Total:			154,668	697,980	100,00	100,00	
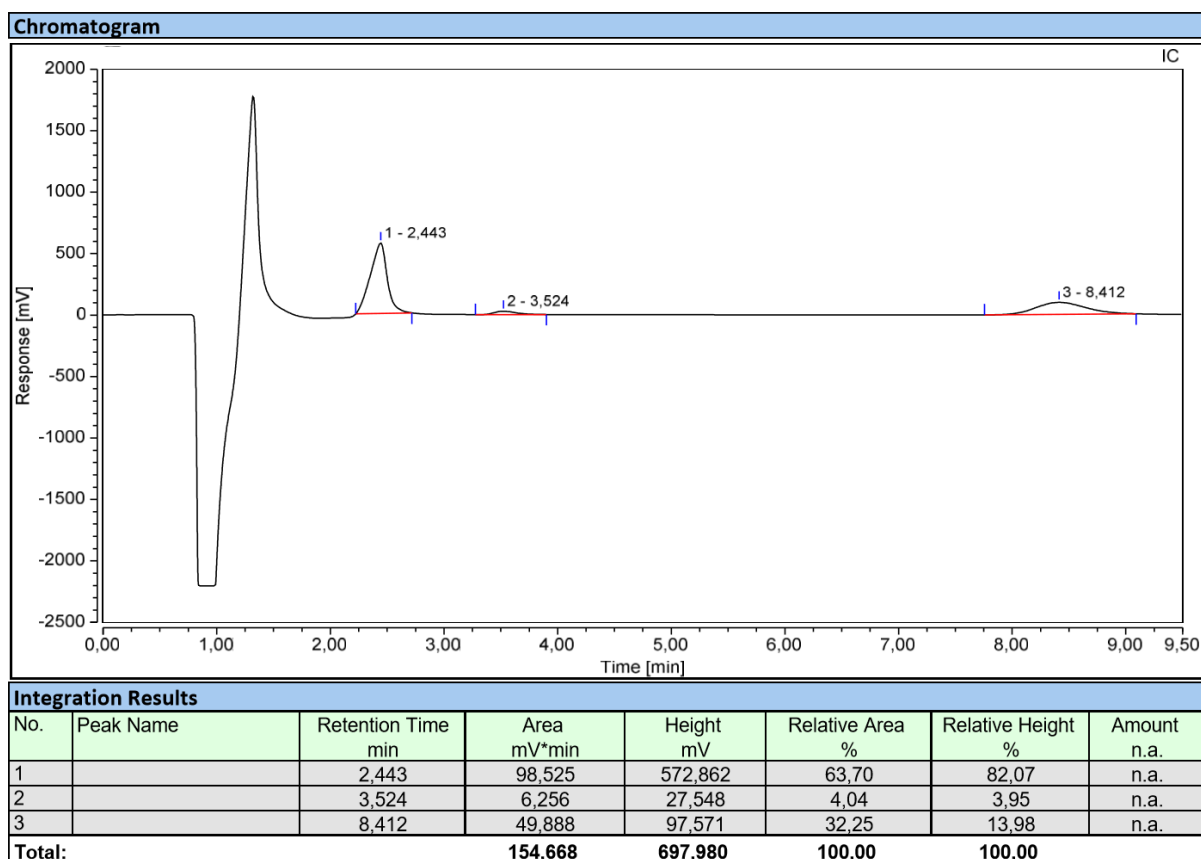
Figure 30 A typical chromatogram of eluate after leaching MSW fly ash in water, showing the peaks for chloride, nitrate and sulfate.

Figure 31 shows a calibration curve used for calculating the concentration of chloride in eluate after pre-leaching with water.

60
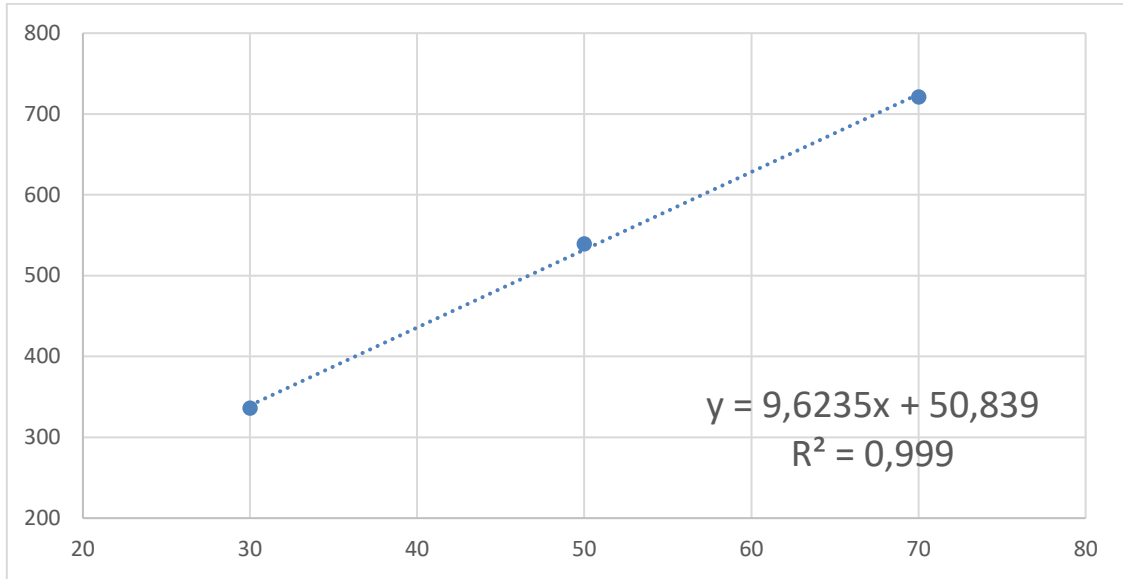
Figure 31 A calibration curve used for calculating concentration of chloride in eluate after pre-leaching with water

Appendix 4: Results from total analysis

Table 16 shows the optimal wavelengths used for analysis of decomposed sample and eluate after leaching, with LOD calculated as described in 2.2.1.

Table 16 Optimal wavelengths with measured LOD

Element: wavelength	LOD (mg/L)	Element: wavelength	LOD (mg/L)
Ag: 328.068	0.004	Al: 396.152	0.4
Ba: 455.403	0.1	Ca: 210.324	25
Cd: 214.439	0.01	Co: 230.786	0.04
Cr: 267.716	0.04	Cu: 327.395	0.2
Fe: 238.204	0.3	K: 766.491	2
La: 379.477	0.003	Mg: 280.270	0.1
Mn: 257.610	0.03	Na: 588.995	12
P: 213.618	0.2	Pb: 283.305	0.3
Sn: 283.998	0.1	V: 311.837	0.009
Y: 371.029	0.0005	Zn: 334,502	0.6

The determination of the LOD was done one time and is thus only meant as an indication.

All results from analysis of total contents in the three fly ash samples are shown table 17.

Table 17. The measured concentration of metals in the three fly ash samples

Element	Wavelength	Contents (%) Ash 1	Contents (%) Ash 2	Contents (%) Ash 3
Ag	328.068	0.001 ± 0.001	0.0035 ± 0.0005	0.0014 ± 0.0001
Al	396.152	1.67 ± 0.08	2.27 ± 0.04	1.74 ± 0.05
Ba	455.403	0.0756 ± 0.003	0.143	0.0791 ± 0.0001
Ca	210.324	35.1 ± 0.2	28 ± 2	31 ± 1
Cd	214.439	0.006 ± 0.001	0.0079 ± 0.0002	0.0140 ± 0.0001
Co	230.786	< 0.04	< 0.04	0.0017
Cr	267.716	0.0210 ± 0.0002	0.037 ± 0.003	0.029 ± 0.004
Cu	327.395	0.05 ± 0.01	0.59 ± 0.03	0.1262 ± 0.0003
Fe	238.204	0.58 ± 0.03	0.7 ± 0.2	0.8 ± 0.2
K	766.491	1.9 ± 0.1	2.9 ± 0.3	3.2 ± 0.1
La	379.477	< 0.003	< 0.003	< 0.003
Mg	280.27	0.809	< 0.1	1.0146
Mn	257.61	0.043	0.0647	0.05
Na	588.995	2.9 ± 0.1	4.3 ± 0.5	4.3 ± 0.2
P	213.618	0.31 ± 0.01	0.538	0.294
Pb	283.305	0.16 ± 0.02	0.27 ± 0.01	0.294 ± 0.002
Sb	206.834	0.062	< 0.05	< 0.05
Sn	283.998	0.033	0.0402	0.0845
V	311.837	0.0017 ± 0.0002	0.00179	0.00243 ± 0.00004
Y	371.029	0.00061	0.00055	0.000682
Zn	206.2	0.68 ± 0.05	0.73 ± 0.02	1.2

Comparison of the total amount and the amount of metals dissolved without decomposition of silicates is shown in table 18.

Table 18 The amount of metals decomposed with HCl and HNO₃ compared to the total amount

Element	Total concentration (g/kg)	Decomposed without HF (g/kg)	Decomposed without HF (%)	Relative STD (%)
Ag	0.011	0.0031	28	72
Al	16.7	14.9	89	5
Ca	351	421	120	2
Cd	0.062	0.049	78	13
Cr	0.210	0.11	53	14
Cu	0.50	0.49	98	19
Fe	5.9	5.0	84	6
K	19	15.9	83	6
Mg	8.1	7.6	93	5
Mn	0.43	0.40	93	3
Na	28	20.4	70	4
P	3.1	2.65	86	5
Pb	1.6	1.49	94	11
V	0.017	0.015	87	15
Y	0.006	0.006	90	36
Zn	6.8	6.7	98	8

Appendix 5: Results from leaching

The results for Ca and Na from experiment 1 when pre-leaching in water are shown in figure 32 and 33 respectively. All other elements measured gave the same pattern. These results were rejected as discussed in 4.3.1.
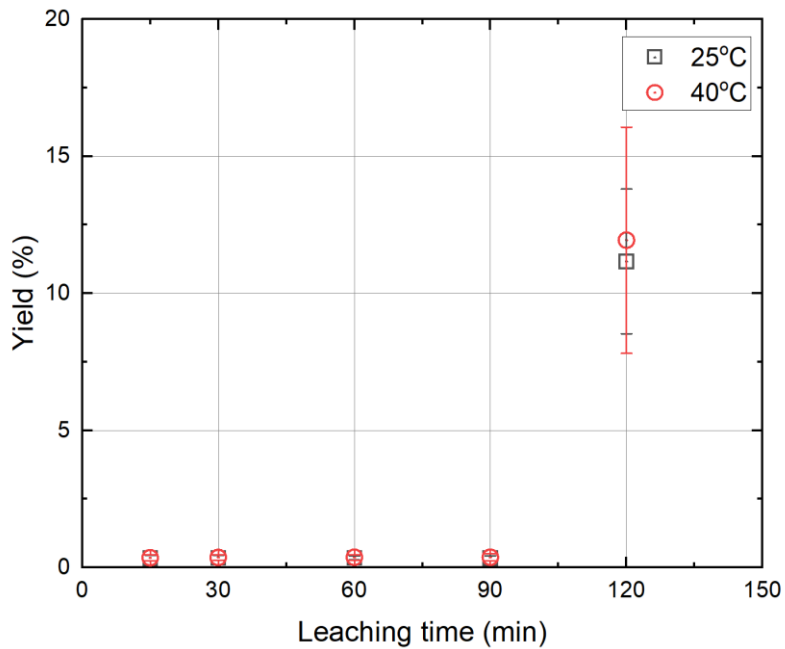

Figure 32. Yield of Ca after pre-leaching with water, using the first sampling method.
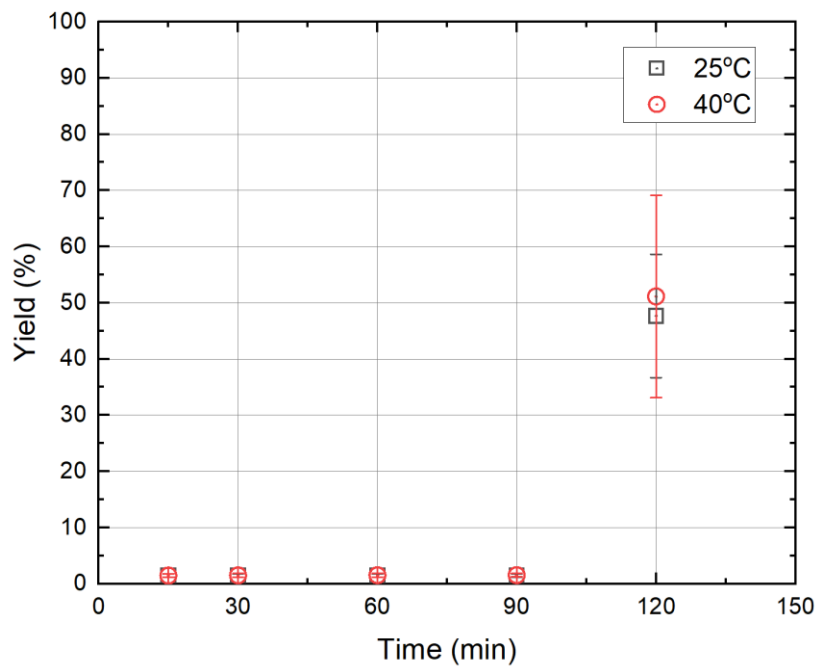

Figure 33 Yield of Na after pre-leaching with water, using the first sampling method.

Results from pre-leaching with water, as shown in figure 9, 10 and 11 are listed in table 19 and 20 as molarity and yield respectively.

Table 19 Concentration of Ca, K, Na, Pb and Sn in eluate after pre-leaching with water.

Time	Concentration (mmol/L)				
	Ca	K	Na	Pb	Sn
15	152 ± 17	257 ± 21	103 ± 8	0.3 ± 0.2	0.13 ± 0.05
30	162 ± 10	305 ± 26	111 ± 9	0.39 ± 0.05	0.12 ± 0.05
60	129 ± 11	247 ± 22	85 ± 8	0.21 ± 0.03	0.15 ± 0.03
120	172 ± 48	286 ± 96	117 ± 30	0.2 ± 0.1	0.12 ± 0.06

Table 20 Yield of Ca, K, Na, Pb and Sn from pre-leaching with water.

Time	Yield (%)				
	Ca	K	Na	Pb	Sn
15	8 ± 2	220 ± 47	37 ± 8	18 ± 8	22 ± 7
30	9.2 ± 0.6	294 ± 26	44 ± 4	25 ± 3	22 ± 9
60	8 ± 1	258 ± 61	37 ± 9	12 ± 4	24 ± 1
120	10 ± 3	194 ± 158	47 ± 12	11 ± 8	21 ± 10

Results from leaching with 28% ammonia solution, as shown in figure 17, 18 and 19 are given in table 21 and 22 as concentration and yield.

Table 21 Concentrations in eluate after leaching with ammonia

Time	Concentration (mmol/L)					
	Ca	Cd	Cu	K	Na	Zn
30	97 ± 3	0.085 ± 0.003	0.55 ± 0.01	53 ± 2	101 ± 3	6.7 ± 0.2
60	135 ± 3	0.109 ± 0.002	0.95 ± 0.02	64 ± 1	132 ± 0.3	8.2 ± 0.1
120	123 ± 2	0.093 ± 0.002	0.73 ± 0.01	60.2 ± 0.4	120 ± 1	7.44 ± 0.07

Table 22 Yield of Ca, Cd, Cu, K, Na and Zn after pre-leaching with water

Time	Yield (%)					
	Ca	Cd	Cu	K	Na	Zn
30	5.60 ± 0.03	77 ± 2	35.7 ± 0.4	55 ± 1	41 ± 1	37.2 ± 0.6
60	7.5 ± 0.3	94 ± 7	57 ± 7	65 ± 2	52 ± 2	43 ± 4
120	7.0 ± 0.2	84 ± 1	46.2 ± 0.1	61.1 ± 0.2	47.8 ± 0.3	37.9 ± 0.1