Leaching and recovery of metals from municipal sold waste incineration ashes.

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Abstract

As the demand to obtain a more sustainable and green society researchers and engineers has been pushed beyond their limits to find new solutions to match their demands. As various types of ashes are collected from different incineration techniques, these ashes need to be managed before it is to late. These ashes, fly ash, bottom ash and boiler ash, contain high concentrations of toxic metals compounds that are very hazardous from an environmental point of view and from a health perceptive. The toxic containment in these ashes has to be taken care rapidly for several reasons. Scientists has conclude that in the near future their will be a lack of metals that is one reason why these ashes should be taken care of so the contained metals could be recovered from these ashes. This can be done through chemical leaching; researchers have determined that leaching of ashes should be carried out in acid solutions. It has been shown that metals leach most efficient at lower pH value but for some metals the release rate of metals are still as efficient at higher pH value. In this thesis project, two different ashes at different particle fractions has been leached with hydrochloric acid and the metal content was determined with ICP-MS at an external lab by analyzing the various leachate mixtures. The obtained results in this experiment showed that Zinc had the highest percentage of leaching from the various ashes that was examined.

Keywords: MSWI, ashes, fly ash, incineration, pH.

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1. Introduction

The European Union sets the framework for regulation of waste management for the countries across Europe and on these parameters the Swedish parliament decides how to manage the waste and the whole management system should be designed. The strive for a more sustainable and green society has guided Sweden towards an environmental waste management. Due to all regulation that the Swedish government has set, all waste in the country has to be handled and managed in the most optimum environmental way as possible. To achieve these goals everyone (municipalities, producers, households, companies, organizations and citizens) has to participate and play their part in order to maintain sustainable society [2].

Municipalities have the responsibility for collection of household waste and that the waste is transported to a treatment facility for recycling. This doesn't only apply for household but even for restaurants, shops, offices etc. The waste must be disposed of in an environmentally sound manner. Manufactures shall ensure that appropriate collection schemes and treatment methods. They also have obligation to inform about sorting and collection. The aim of the producer is that the products that are manufactured consumes the least possible amount of natural resources, they should be easy to recycle and do not contain hazardous substances[2][5].

During 2013 in Sweden, the treated household waste amounted to 4,447,880 tons. Researchers have come to found out that every Swede generate 461.2 kg of household waste in 2013 compared to 460.3 kg per person during 2012. Apart from energy recovery, which decreased during 2013, table1 show how the different waste management tools increased during 2013 from 2012. While figure 1 shows the development for various techniques since 1975 to 2013.

Technique	Increase (ton)	+/- %	Kg/person
Material recycling	1467200	+3,2	152,1
Biological recycling	711450	+5,7	73,8
Energy recovery	2235930	-1,5	231,8
Landfilling	33300	+2,1	3,5

Table 1. Data shown how various techniques increased/decreased from 2012 to 2013 in Sweden.

Waste incineration is a well-used management tool for municipal solid waste, MSW. The composition of MSW varies from region to region, depends on consumer behavior and changes on a daily basis [7]. In Sweden it usually gives rise to about 200 000 tones of fly ash [2]. Due to potential toxic metal compounds and soluble chlorides, the fly ash is often classified as a hazardous material and has to be landfilled even tough landfilling is not the most sustainable treatment process for MSW incineration (MSWI). That is the reason why incineration is increasing both in Sweden and in other countries across Europe [2]. Due to the toxic compounds in fly ash, production of ashes must be handled in ways that ensure that there are no negative effects on the environment or human health [4]. Ash it self is not a consistent substance but more like a combination of various different metals, materials and minerals and other chemical compounds. These compounds contain metal compounds such as, metal chlorides or oxides. Therefore a huge range of scientists and researchers around the world set their time to research about this complicated complex and how to extract those containing minerals and metals in the most efficient and environmentally sensitive manner.

Previously, the main focus of MSWI research was mainly on how to obtain prevention of leaching of metals and chloride and the spread of these hazardous chemicals. During early 2000s the fly ash was typically disposed in the landfills for hazardous waste [9][17].

However, a major issue with MSWI fly is that it contains leachable heavy metals. With the strive for a more sustainable and greener society, companies and organizations are trying to find out various solutions techniques to solve the problem, metals recovery. A possible solution to this problem is, leaching. Some of these metals can be seen in the list below [6].

- Copper, Cu.
- Lead, Pb.
- Zinc, Zn.

Calculation has shown that the net worth of Zn in Swedish MSWI fly ash is approximately 7 million Euros per year [3][1]. The corresponding value for EU is about 60 million Euros per year. For Vanadium, a very rare soft metal element, the net value in Sweden for this metal is approximately 3 millions/ year with a prize of 280 Euro/kg. However, as the metals in fly ash aren’t present in metal pieces it’s not possible to directly recover them using physical methods hence chemical leaching is needed [1].

2. Aim

The main aim of this thesis work is to leach two different ashes, A and B These ashes are sieved into different particle fractions. . It is also know ashes contain a high content of various metal and the main objective of this project is to study the leaching process of these various metals from ash A respective ash B.

3. Theory

3.1 Waste Incineration

In recent years, due to new regulation the waste management in Sweden has gone through a lot of changes. The growth of waste incineration has played a big part of this development. Almost 50% of the MSW is today being energy recovered while less then 5% is being landfilled [9].

According to the report of RVF (Avfall blir värme och el 2005,02) waste incineration has increased with 50% since 1985 with an average increase of 100 000 tons per year.

Today there are two dominant techniques regarding waste incineration, mass burn- and fluidized bed technology.

Each year, Swedish waste incinerators cause about 200 00 tons of fly ash and 700 000 tons of bottom ash. To name one of very many applications for bottom ash is the application of construction material at waste deposits. For fly ash application area is much more complex due to all toxic chemicals.

The amount of each ash residue that is produced at waster incinerator may vary on several factors, waste composition, air pollution control system or incinerator technology. Table 2 shows a general calculation of the amount different ash residues produced per ton of waste incinerated. Fly ash normally contributes to a small quantity of the total volume of residue from a waste incineration facility; the amount of fly ash is approximately from 5 to 20 %of the total ash.

Type of residue	Typical amount produced, kg/ton of feed waste
Bottom ash	250-420
Boiler ash	2-12
Econmizer ash	Small
Fly ash	10-30

Table 2. Typical amounts constructed, kg/ton of waste feed

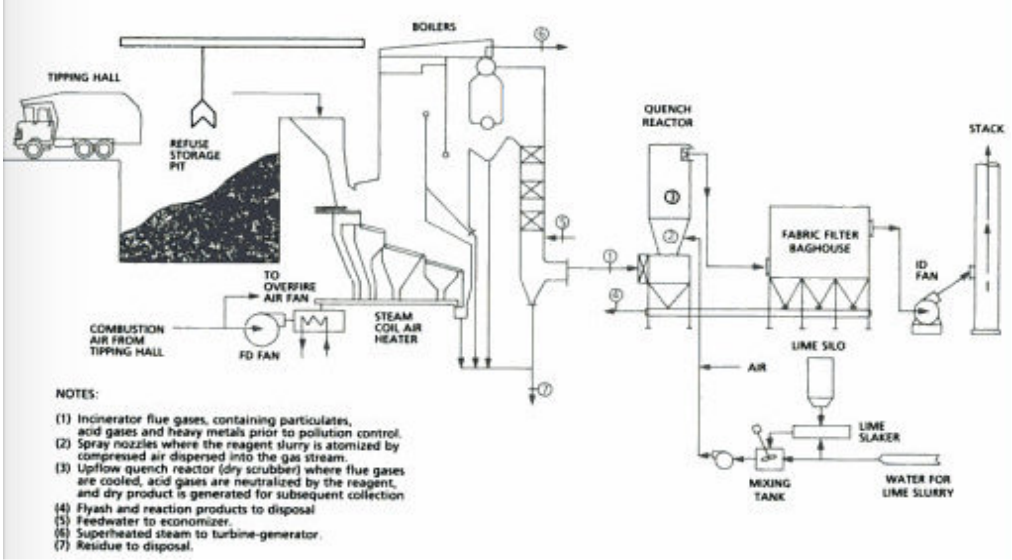
3.1.2 Mass burn-combustor

In this technique, the combustion of waste is done with grate, made of rods. The rust is variable and the rod motion moves the waste gradually forward into a fireplace, while it's distributed and mixed for combustion to be as complete as possible [11].

At lately, usage of water-cooled roaster rods has increased rapidly, since the waste fuels has obtained a more increased heating value, as a result of quantity of industrial waste has increased [9].

The combustion takes place at temperatures between 850 and 1100 ° C. Investigations has shown, in order to burn one ton of waste as efficiently as possible 4000-5000m^3 air is needed to be consumed. To maintain an efficient combustion as possible the air is added in different zones [10].

The gases from the combustion of the fuel in the furnace rise at while the incineration in the combustion boiler chamber continues. While these hot gases rise up, a portion of heat from these gases are transferred to the water that circulates in tubes built in the boiler walls. The flue gases are still at a high temperature, between 200 and 600°C when leaving the boiler. A schematic scheme of this method can be seen in figure2 [10][11] .



NOTES:

(1) Incinerator flue gases, containing particulates, acid gases and heavy metals prior to pollution control.
(2) Spray nozzles where the reagent slurry is atomized by compressed air dispersed into the gas stream.
(3) Upflow quench reactor (dry scrubber) where flue gases are cooled, acid gases are neutralized by the reagent, and dry product is generated for subsequent collection
(4) Flyash and reaction products to disposal
(5) Feedwater to economizer.
(6) Superheated steam to turbine-generator.
(7) Residue to disposal.

Figure 1. Schematic scheme of a mass burning facility

3.1.3 Fluidized bed

Waste incineration in fluidized beds, FB, is carried in a sand bed. By blowing combustion air through the bedplate it will occur as a liquid.

The temperature of the fluidized combustion is generally around 850- 900°C. The formation of nitrogen oxides (NO_X) is minimized since the oxidation process of nitrogen in the air is supplied for increased combustion. A plant with fluidized beds requires a finer and more homogeneous fuel, which puts a great demand on the pretreatment of the incoming waste. The fluidized bed combustion technique requires a size reduction and pre- sorting of waste [3]. The extraction process for energy recovery in a FB-pan is similar roast technique [10] [11].

The characteristic of fluidized beds is that, this method has a good and efficient combustion from an environmental perspective. This method also places high demands on the waste that enters the process, that it is dispersed and pre-treated. This means that pretreatment of the incoming MSW is being handled properly, which in turn means that, as much as possible metal is removed from the MSW and that material is crushed so that it has a size of 10x 10cm. [13]

When the waste is incinerated the temperature in the system should be above 1000°C. The incinerations ovens should hold a Reynolds number greater then 50 000. At the end of this process the fuel gas is cooled down from 450 °C to 250°C. To prevent the emission of dioxins and other hazardous compounds bag filtration are used. Figure 2 below illustrates a schematic of a fluidized bed combustor.

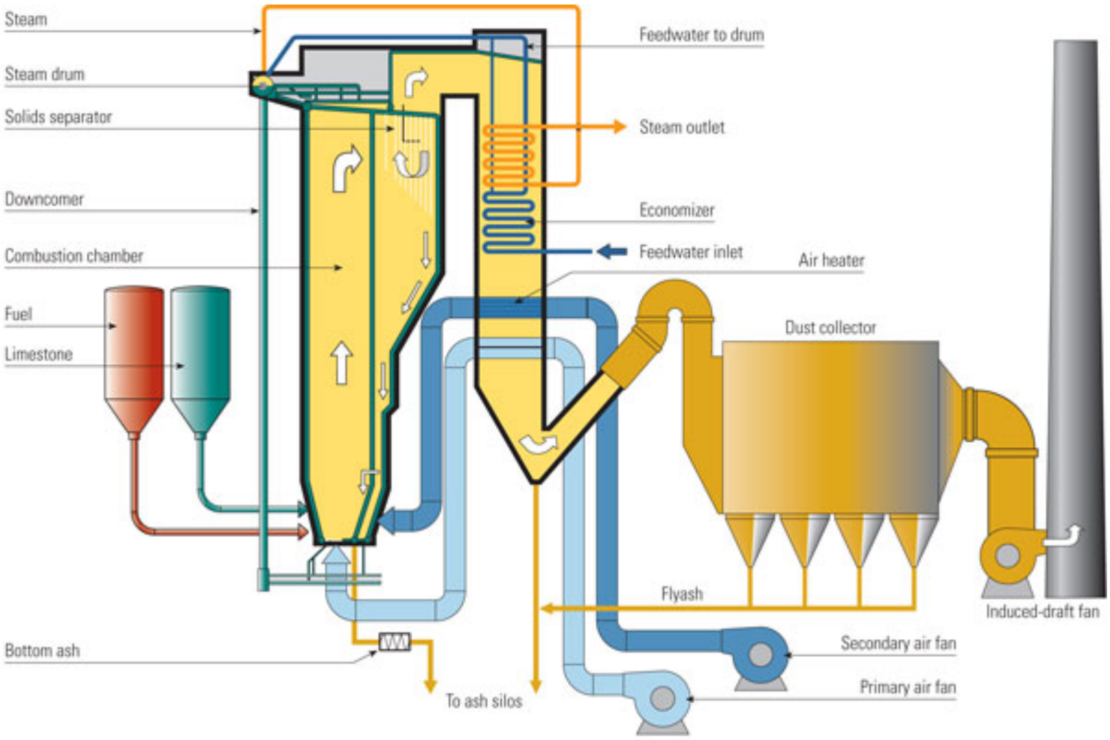


Figure 2. Schematic scheme of a fluidized bed combustor.

3.2 Fly Ash

In this report the main focus will be on Fly ash. Fly ash is the smallest ash particles generated during incineration. Fly ash is residue in any combustions process from any incineration facility; whether it is municipal solid waste that being incinerated or anything else. From a general point of view, one can say, that the chemical and physical properties of fly ash can depend on a variety of factors, such as, air pollution control system design or what type of incineration method is applied etc.

However, the metals get vaporized while they are incinerated and also that they get absorbed at the surface causes the high content of heavy metals in fly ash.

According to a study made of Charles H. and his colleagues, they found out that eight elements differed from all other elements in their chemical compositions in fly ash, Si, Al, Fe, Mg, Ca, Na, K and Cl. CaO was the richest compound in the fly ash, 46% [12]. Due to the high containment of heavy metals, the risk for, damage the environment and effect mankind in a negative terms, is quite high if they don't get managed in the right way.

In general, laboratory-leaching tests are made for measuring different properties of the material that is being analyzed. For example some of these parameters could be, solubility, release rate or availability. Table 2 shows a more brief description of these parameters. [14]

Property	Definition	Characteristic	Unit
Availability	A specific amount of any species that may leach under specific time period.	High L/S, small particle sizes of material to be tested, contact time which allows the resolution to be achieved.	Mass leached/mass of initial material (e.g. mg Pb/kg ash)
Solubility	Concentration of elements in solution.	Low L/S, contact time which allows equilibrium between the solid and liquid phase.	rate per mass or surface area basis (e.g., mg released/sq material/day)
Release rate	Is used to estimate "discharge" for specific element from a material.	_____	_____

Table 3. Description of different properties of the material thats being analyzed through the laboratory leaching test.

3.3 Leaching of metals from ash

A definition of leaching could be defined as, any suspension of a soluble "body" from a solid phase into a solvent. The cause of chemical reactions that takes place in the waste particles is why leaching occurs and the mass transport processes from the fluid moving through the solid particles.

However, the amount of the metals release from municipal waste can be expressed as a function of the availability for leaching which in turn represents the amount of the total content of various compounds in the waste matrix itself. When a fluid or particle diffuse though a waste matrix, the portion of metals that is released can be determined by the solubility restrictions, thus this process can be referred as a *solubility controlled leaching* process. In other circumstances of very soluble mineral phases, leaching could be defined as *availability controlled leaching.*

Scientist and engineers has put a lot of time for developing new strategies in order to obtain a reduction rate of releasing metal compounds from deposited ash. Tough this can be done by removing metals from the ash. A review of thermal treatment processes for MSWI ash reviled that, metals present in a reduced environment had an increased in the release rate compared to metals present in a oxidizing environment. [3] Due to the high energy consumption in thermal treatment this process may be very expensive. [25] A way to stabilize ashes and make it more "solider" is to mix it with cement and water, which results in agglomeration of the material. By making ashes more stabilized it has shown a decrease in leaching of metals and sulphates [3][1][4].

Leaching is a very common wet treatment for releasing metals from ashes. Metals forming soluble compounds such as NaCl or KCl gets released more or less independently of pH in the solution while many the solubility of other metal compounds is very depended by the pH.[14] For example, cadmium solubility, increases greatly with lower pH values, when the pH > 8 and the is applied for Lead when the pH is less than 6 and when the pH is greater than 10. The reason for why Lead can easily release metals at pH greater then 10 and pH lower then 6, because many metals has the ability to form soluble cations in environments with low pH values and likewise can form hydroxides at higher pH solution. [3][14]

Nevertheless, even tough it seems that the pH is the most dominant factor for the releasing of metals from ashes it not the only factor. Another strong factor that influence the release rate is, the size of particle it self, the mineralogy of the ash, the chemical speciation of the metals, the redox potential in the mixture, the ability of building ligands in the leaching liquid and the liquid-solid ratio, $\frac{L}{s}$. [1][4]

The amount of leachate that interacts with a known amount of waste is usually referred as *liquid-solid ratios*. The liquid solid ratio influences the release rate (concentration) of metals. The $\frac{L}{S}$ ratio is a result of climatic circumstances and the features of the waste material. The solubility regulated leaching processes that was mentioned above is characterized by the $\frac{L}{S}$ which is almost linear depended by the increased amount released of metals. [1][14]

Complex formation increases the leached amount while mineralogical changes in the ash matrix, such as carbonation, as well as red-ox reactions, can lead to both increased and decreased leaching. By using various types of leaching agents, is another way to obtain a greater leaching so metals get released from the ashes. The most common leaching method is; *the acidic leaching.* Many metal compounds have greater solubility at lower pH solutions. Figure 4 below shows how the total amount leached is depended by the and how the factors mentioned earlier effects the leaching. [1][3][4][14]

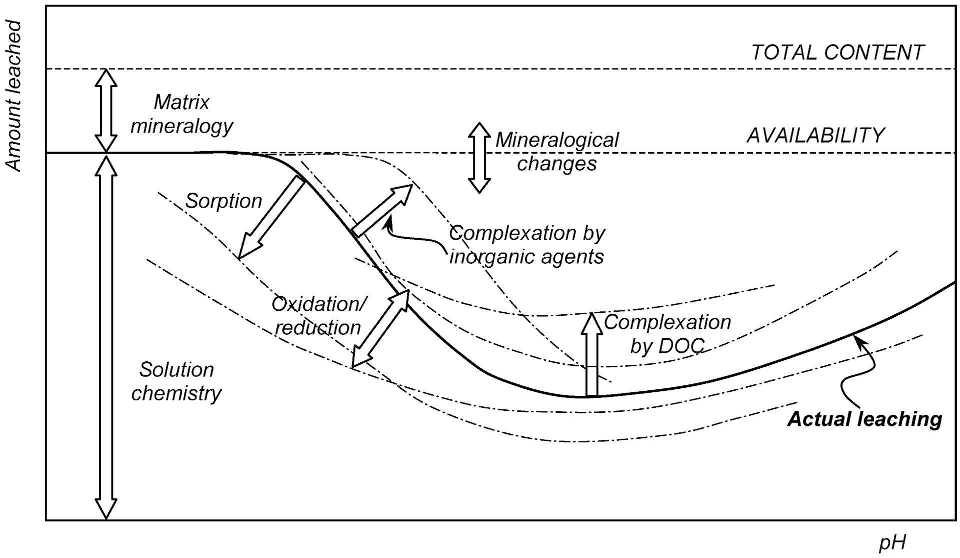


Figure 3. Influence of different processes on the metals solubility as a function of pH. Based on [14]

3.4 Recovery methods

As mentioned earlier, heavy metals can cause a lot of damage on mankind. Serious health effects such as, reduced growth and development, cancer, organ damage, nervous system damage and even in some extreme fall cause death, can be consequent if human life gets exposed to these kinds of chemicals [20]. To prevent mankind from getting exposed from these kinds of chemicals, engineers are constantly developing new technologies for the metal recovery from municipal waste.

When the metals are finally leached out from the ash they are present in ionic form in the leachant. To obtain a valuable worth of these metals, the ions need to be recovered with recovery methods, which depends on various factors [20][21].

3.4.1. Chemical precipitation

This technique has long been one of the primary methods for the treatment of metals in industrial waste. This process involves the conversion of soluble metals to insoluble salts that will precipitate. By using filtration the precipitate can be removed from the treated water. [20]

3.4.2. Flotation

Flotation is more rapid and appropriate than filtration or centrifugation, and it is suitable for operation at sampling spots[22]. There is mainly three types of flotations process. This method is strongly depended by the formation of precipitate and the removal by attachment to air bubbles. Due to the metal concentration, the precipitation may proceed through metal hydroxide formation or as a salt with a specific anion.

3.4.3. Adsorption

Adsorption is mass transfer process where the material are transferred from a liquid phase to surface of a solid phase. The metals that are present in ionic form are adsorbed into a material or surface. This process offers a high quality on the effluent, flexibility both in design and operation as well as it now well recognized as an effective and low cost method for heavy metal wastewater treatment [21][22][30].

3.4.4. Ion exchange

Ion exchange is another popular method for the removal of metals from industrial waste. Depending on its surrounding material the ion exchanger is capable of exchanging cations or anions. A disadvantage of this method is the matrix get easily fouled by organics and another solid in the waste water and that's why this method is not the most accurate at handling solution that is concentrated with metals. That it can't handle concentrated metal solution because the matrix other wise this method has a high removal efficiency and high treatment capacity. [21][24]

3.4.5. Membrane filtration

Even though the mechanism is the same this method divided into four sub categories, microfiltration, ultrafiltration, nanofiltration and reverses osmosis. For each of these techniques, the main driven force can either be pressure, concentration, vacuum or an electric field. The solids in the liquid are removed by setting a barrier that prevent the solids to diffuse to the "other side". Figure 5 shows an illustration of membrane filtration. [22]

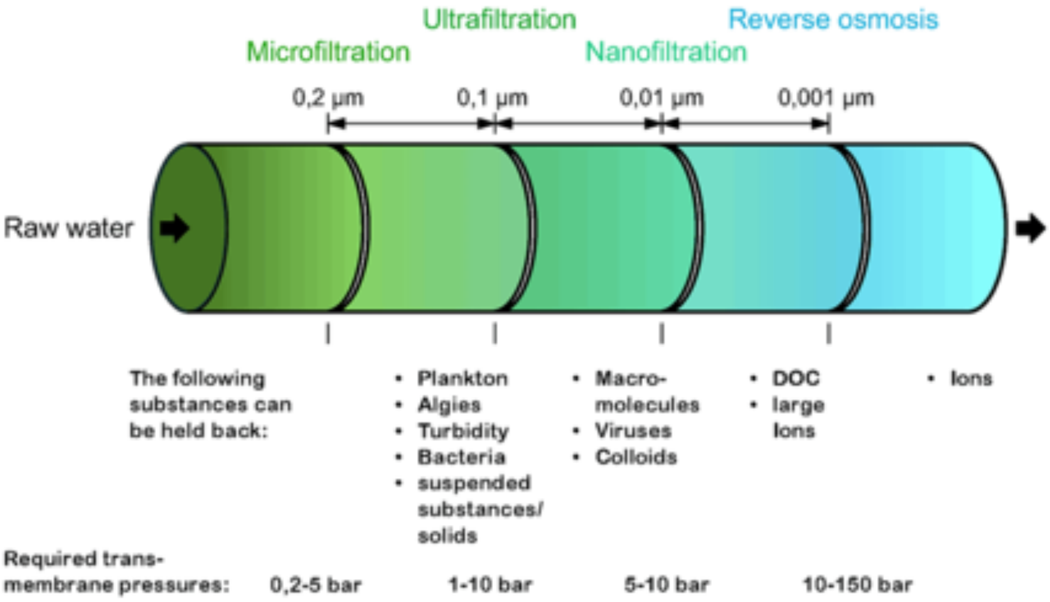


Figure 5. An illustration of membrane filtration.

In this thesis work, the analysis of metals concentrations from the leachate Inductively coupled mass spectrometry; ICP-MS will be used as an analytical method that will further be explained in details in section 4.4.

4. Experimental

4.1 Description of ashes

Two MSWI ashes have been selected for investigation in this experiment, ash A and ash B. Where the latter one is an ash collected from a fluidized-bed with lime additives. Ash A is from collected from a mass combustor with the help of an electric filter. No additives were added in this ash. See table 4 for an easy overview of the ashes.

Ash	Technique	Additives
Ash A	Mass- combustor	None.
Ash B	Fluidized-bed	Lime.

Table 4 An overview of investigated ashes.

4.2 Particle fractions

Ash A and ash B were both divided into different particle fraction by sieving. Particle size of each ash can been seen below in table 5.

Size (µm)				
Ash A	36	64	150	300
Ash B	Botten	36	63	-

Table 45 Particle size distribution for respective ash.

Figure 6 shows the different ash particles size for ash A that was used in the experiment. Figure 7 shows the three sizes that was used for ash B.

Figure 6. Particle fractions 36, 63, 150 and 300 µm for ash A.

Figure 7. Particle fractions "botten", 36, 63 µm for ash B.

Figure 9 below shows the percentage of each particle fraction for ash A and B.

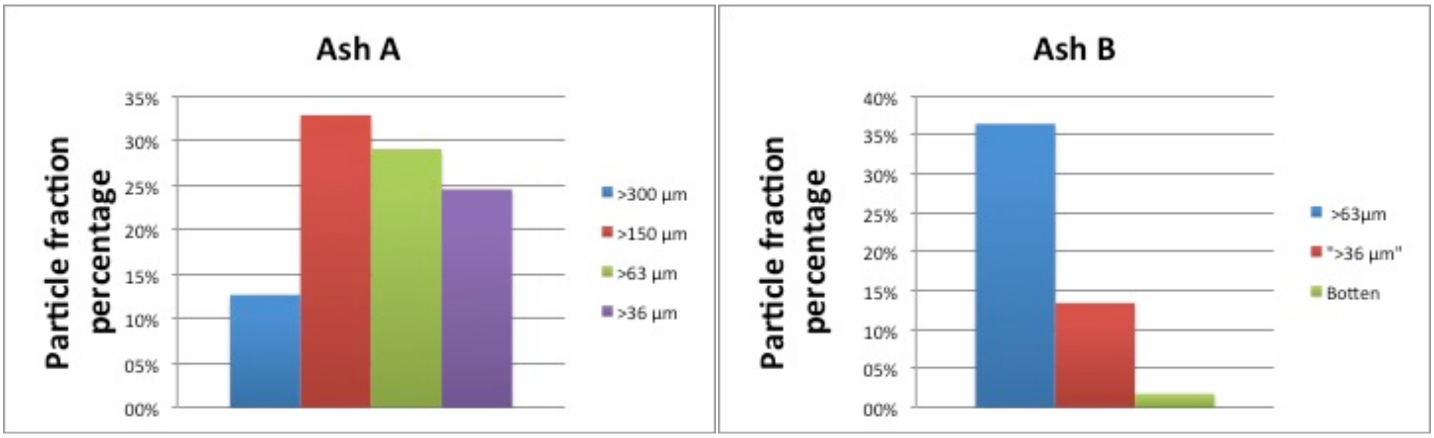


Figure 8. An illustration of each particle fraction in percentage for respective ash.

Worth mentioning is that, due the shortage of some particles (ash B) at the different particle fraction same sizes couldn't be applied.

4.3 Experimental procedure

3 grams of specific ash particle fraction is weighed and dissolved into vials with a solution of 9 ml 1 molar hydrochloric acid, HCL, $\frac{L}{S} = 3$. Thereafter, the solutions are placed on a shake table for 20 minutes so the mixtures could be stirred and dissolve properly. After this the mixtures is put in a fume cupboard for five minutes so that the leaching process can be started. In order to obtain an ash residue and leachate water the samples are centrifuged at 3000 G for three minutes.

Figure 10 shows the four samples after the first centrifugation. The liquid phase (leachate water) of each sample is transferred to new vials and to be further analyzed with ICP-MS. 1.8 ml milli-Q was poured down in the vials contained the solid phase (ash residue), $\frac{L}{S} = 0.6$. The main purpose with washing the ash residue with milli Q water is because so the ash residue gets "clean" from various solutes that may be left from the first step.

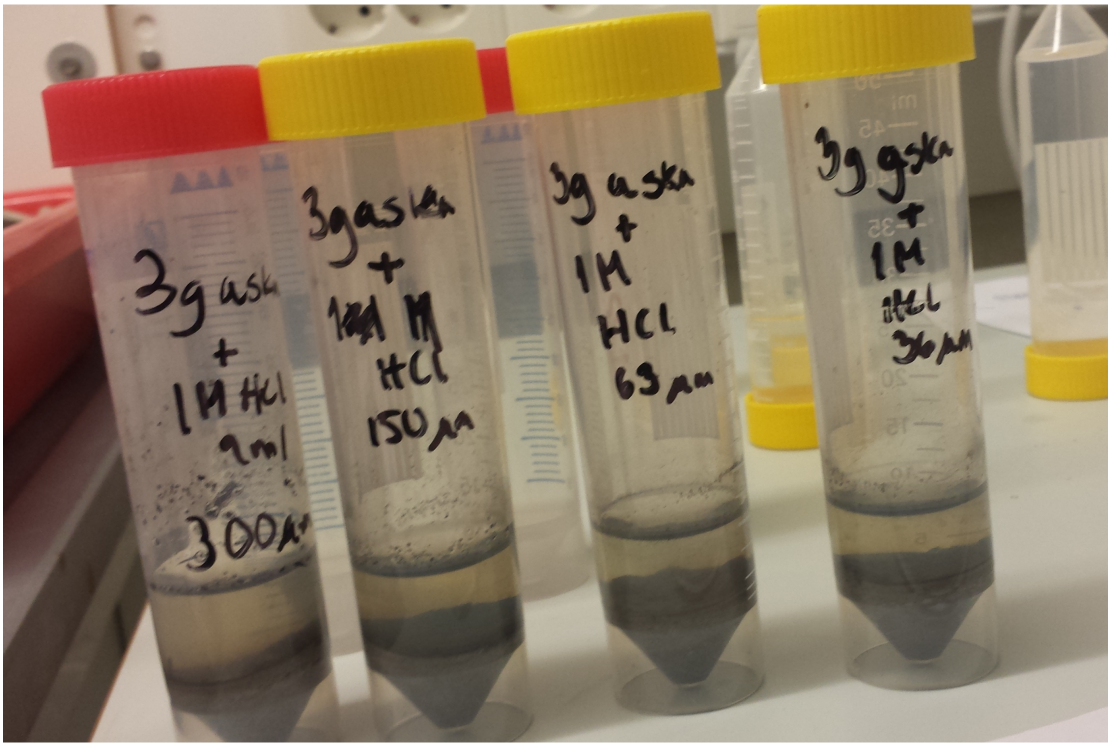


Figure 10. Illustration of different particle fractions of ash A mixtures after the first centrifugation.

Again the samples is placed on a shake table for 20 minutes to get a mixture between the ash and the Milli-Q water, then the samples where placed a in a fume cupboard where they are leached for five minutes. After the leaching the mixtures are centrifuged. Like mentioned above, the leachate water is transferred to new vials. To dry the ash residues (solid phase) these vials was placed in an oven at 105 ° C.

The leachate was later filtered by suction so it could be totally separated from the sludge and the residues. Figure 11 show the leachate for the different ashes at various particle fractions.

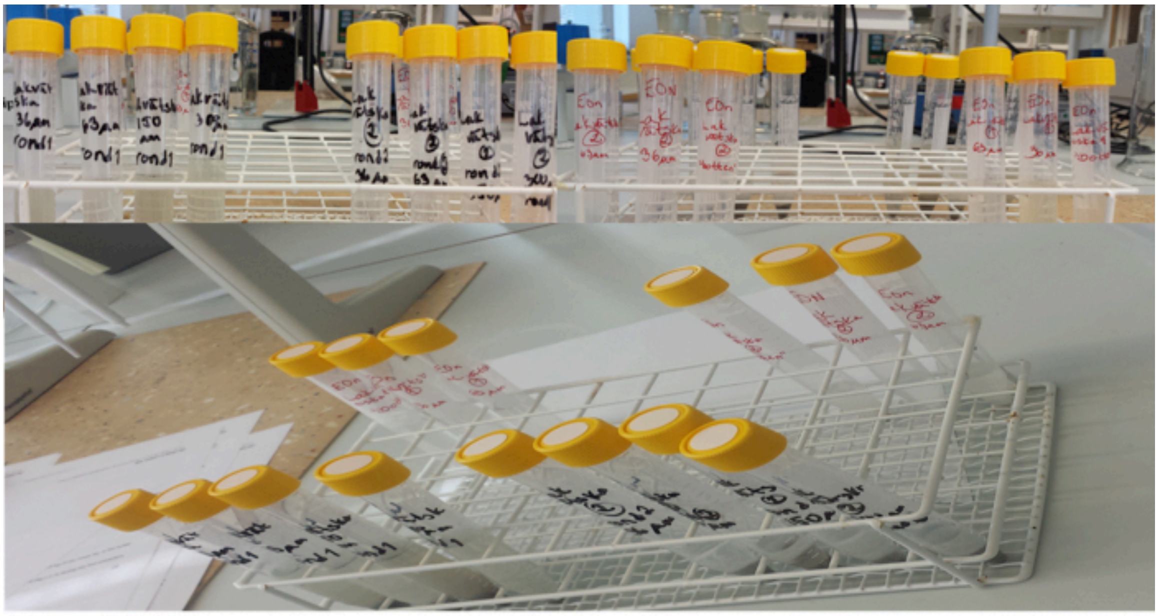
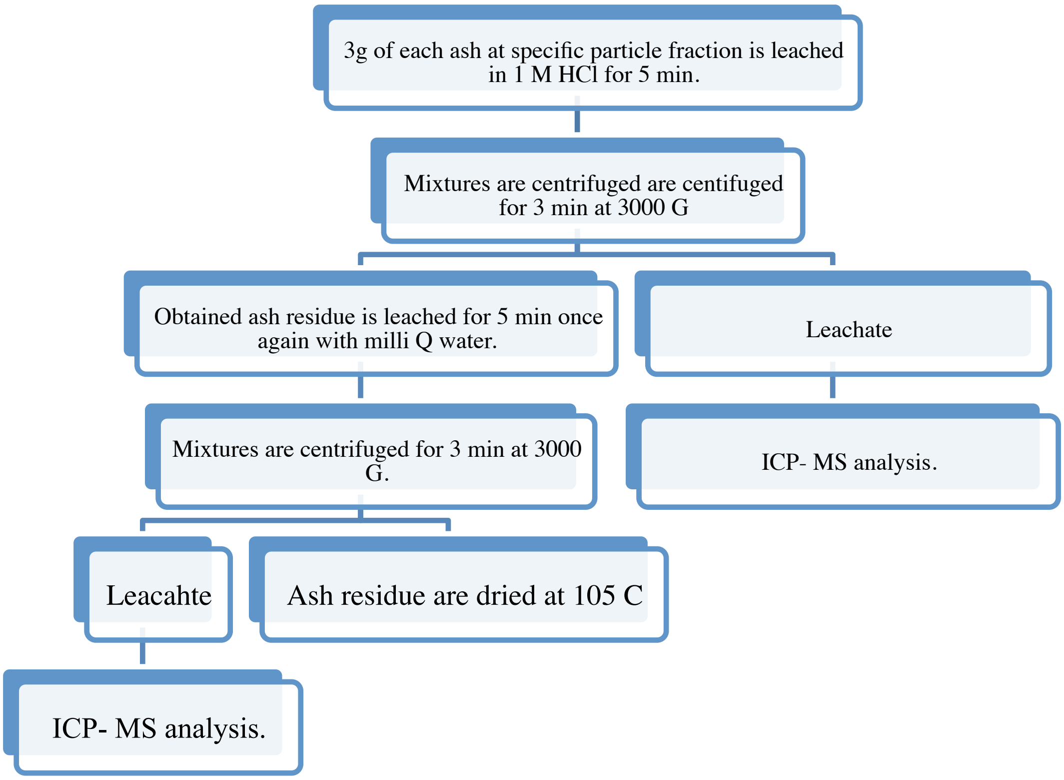


Figure 11. Leachate for ash A and B for various particle fractions.

Figure 12 shows a shemactic flow scheme of the lab process



4.4 Analytical method- ICP-MS

After the filtration and the drying process all samples were further analyzed at an external lab with *Inductively coupled plasma mass spectrometry, ICP-MS.* Figure 12 shows the instrumental setup for ICP- MS.

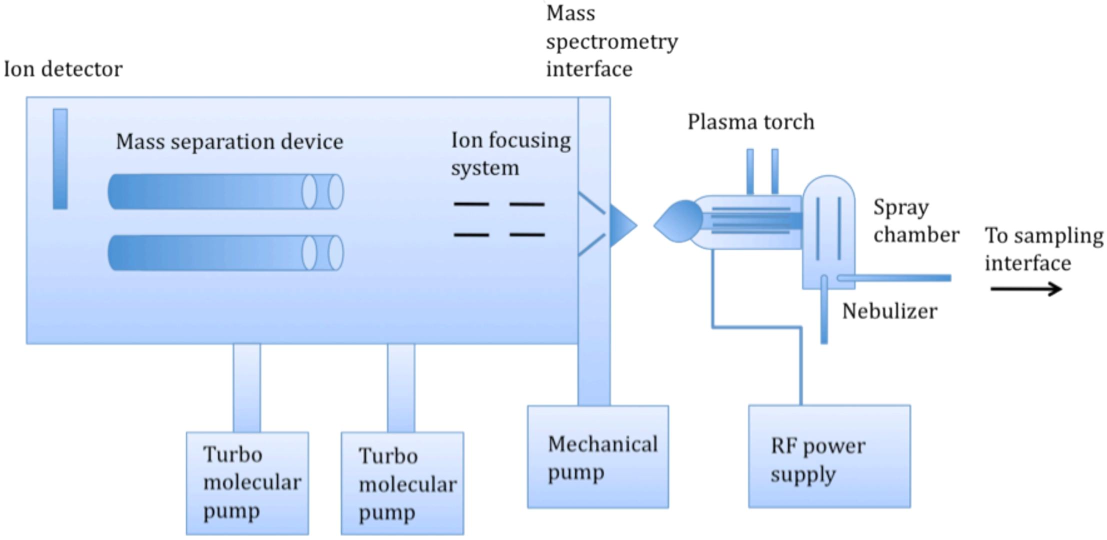


Figure 12. Basic instrumental setup for ICP-MS. Adapted from R. Thomas, Practical Guide to ICP-MS: A Tutorial for Beginners, CRC Press, Boca Raton, 2nd edn. (2008).

ICP- MS is a worldwide technique and is unquestionably the fastest growing technique for tracing various elements.[27] This technique was commercially introduced in the early 1980’s.[26] ICP-MS allow the detection of most elements in the periodic table. Figure 13 shows elements that can be detected with this technique.

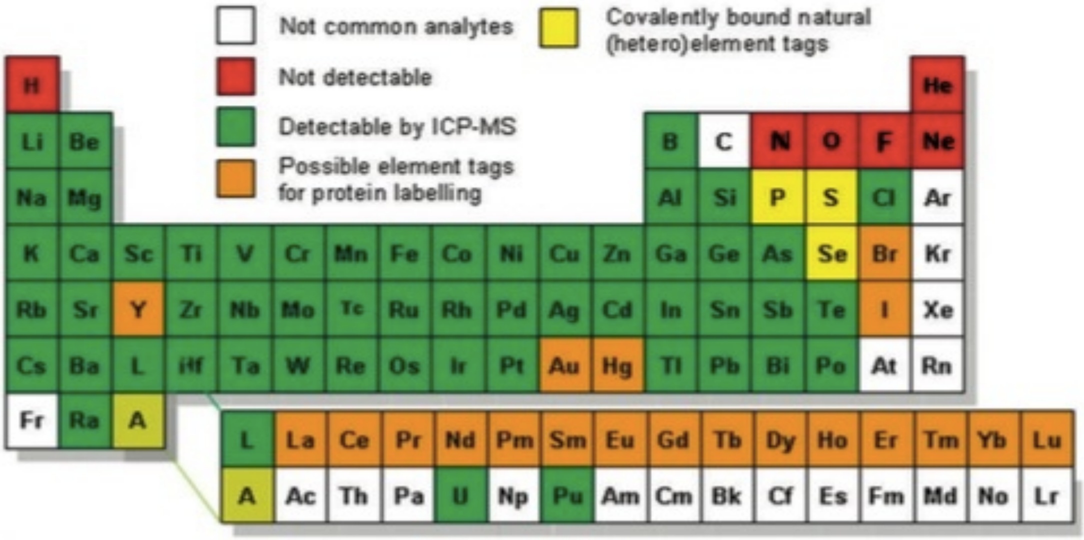


Figure 13. Elements that is detectable with ICP- MS.

Because of the high temperature, approximately 7000K, that occurs within the plasma ICP- MS suitable for liquid samples, such as leachate. ICP- MS gives a number of advantages such as,

- Multi element analysis
- Quantification to metals
- High sensitivity
- Detection limits
- The ability to get isotopic information
- Handling of complex matrices
- Determination of isotope ratio information
- Speed of detection/analysis. [18][27][26]

When the samples are introduced in the ICP-MS system the atoms of each element are ionized with the help of a nebulizer or using a laser to directly convert the samples into ions. To enter the mass spectrometer theses samples are carried out in argon gas. Once the ions reach the mass spectrometer they are separated by using the *quadruople mass separator*[18]. Figure 14 illustrates this separation technique.

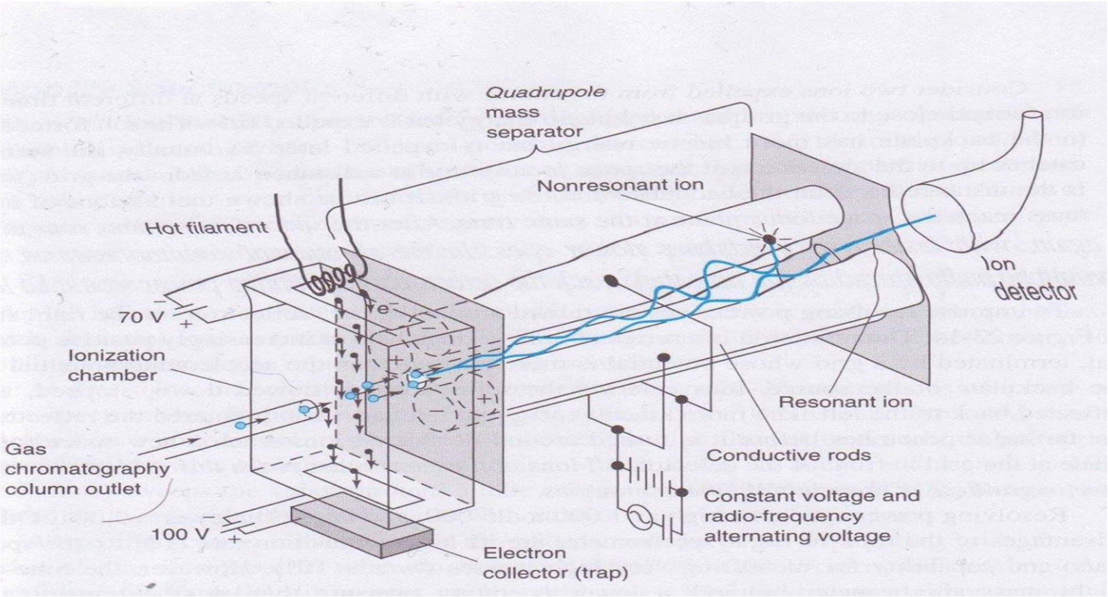


Figure 14. Illustration of the quadurople mass separator.

The quadurople mass separator is mainly build up by four different rods to which are applied both a constant voltage and a radiofrequency voltage. Since this specific voltage that is applied to the rods only a few ions with the most accurate $\frac{mass}{charge}$ ratio manage to travel through the ion chamber to the analyzer. Other ions collide with the rods and are lost before they reach the detector.

4.5 pH measure

The pH values were measured with for each leachate for particle fraction 63µm using a WTW pH-electrode SenTix 41-3 with a Muliti 35i.

5. Results

5.1 Total content of Cu, Pb and Zn in ash A and B at various particle fraction.

The main focus in this results section will be on Copper, Lead and Zinc because of the fact that both ash A and ash B had the most highest content of these three metals element which is presented in table 6 below.

	Solvent	*Cu, $_{initial,}$(mg/kg)*	*Pb, $_{initial}$(mg/kg)*	*Zn, $_{initial}$ (mg/kg)*
Ash A 36µm	Acid	**2600**	**4150**	**36400**
Ash A 36µm	Water	**2600**	**4150**	**36400**
Ash A 63µm	Acid	**2050**	**3200**	**26700**
Ash A 63µm	Water	**2050**	**3200**	**26700**
Ash A 150µm	Acid	**2500**	**4970**	**38100**
Ash A 150µm	Water	**2500**	**4970**	**38100**
Ash A 300 µm	Acid	**2570**	**5130**	**37800**
Ash A 2 300µm	Water	**2570**	**5130**	**37800**
Ash B < 36	Acid	**6280**	**3470**	**10700**
Ash B < 36	Water	**6280**	**3470**	**10700**

Ash B 36µm	Acid	**5320**	**2830**	**9050**
Ash B 36µm	Water	**5320**	**2030**	**9050**
Ash B 63µm	Acid	**4160**	**1910**	**32400**
Ash B 63µm	Water	**4160**	**1910**	**32400**

Table 6. Illustration of the total containment of Cu, Pb and Zn in the ashes.

5.2 Release of metals

Further below in this section, three tables will be presented, one for each metal element. In these tables there are two interesting parameters; $C_{released}$ and *% total release*. Where the latter one is a measure of how much of each element leached of the ash matrix at specific particle fraction, which is expressed in percentage. The first parameter, $C_{released}$, is how much metals are released from the ashes, expressed in mg/kg. These three tables will be filled with data so to clarify these table, three graphs will also be presented for each element for the illustration of total release expressed in percentage of each metal at various particle fraction.

5.2.1 Leaching of Copper

Sample	***Solvent***	***$C_{released}$ (mg/kg)***	***% Released***	***% Total release***
Ash A Leachate 1 36µm	Acid	**693**	27	**28**
Ash A Leachate 2 36µm	Water	**289**	1	
Ash A Leachate 1 63µm	Acid	**325**	16	**16**
Ash A Leachate 2 63µm	Water	**9**	0	
Ash A Leachate 1 150µm	Acid	**537**	21	**22**
Ash A Leachate 2 150µm	Water	**5**	0	
Ash A Leachate 1 300µm	Acid	**609**	24	**25**
Ash A Leachate 2 300µm	Water	**13**	1	
Ash B Leachate 1 < 36	Acid	**11**	0	**0,2**
Ash B Leachate 2 < 36	Water	**1**	0	
Ash B Leachate 1 36µm	Acid	**2**	0	**0,0**
Ash B Leachate 2 36µm	Water	**0**	0	
Ash B Leachate 1 63µm	Acid	**11**	0	**0,3**
Ash B Leachate 2 63µm)	Water	**2**	0	

Table 7. Amount of Copper leached from the ash A and B.

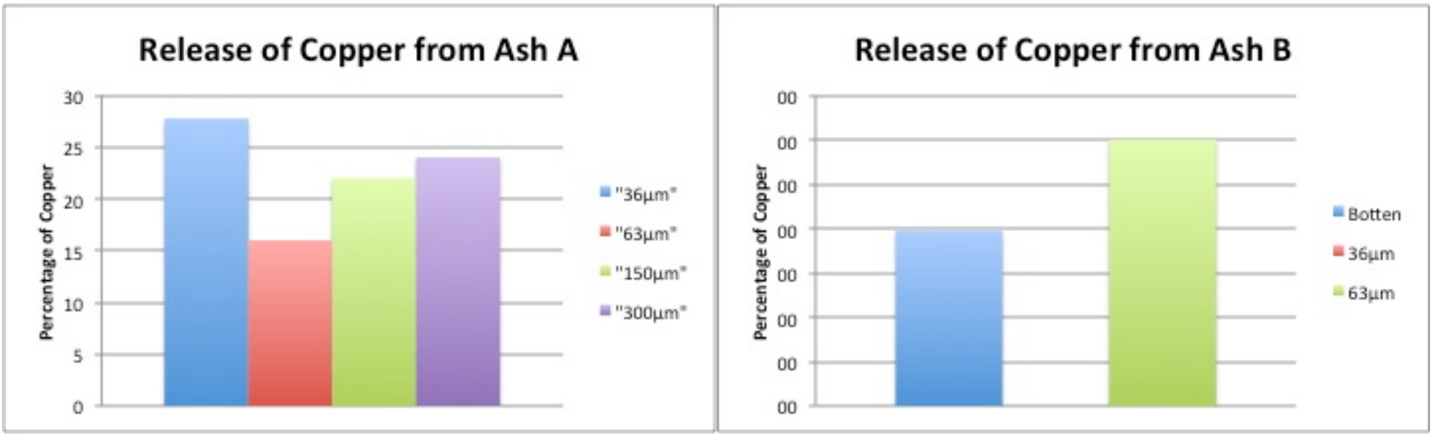


Figure 15. Two plots showing the percentage of the Copper release at each particle fraction for both ashes.

5.2.2 Leaching of lead

Sample	***Solvent***	***$C_{released}$ (mg/kg)***	***% Released***	***% Total release***
Ash A Leachate 1 36μm	Acid	**1377**	33,18	**35**
Ash A Leachate 2 36μm	Water	**77**	1,87	
Ash A Leachate 1 63μm	Acid	**723**	22,59	**30**
Ash A Leachate 2 63μm	Water	**234**	7,33	
Ash A Leachate 1 150μm	Acid	**1470**	29,58	**30,**
Ash A Leachate 2 150μm	Water	**22**	0,45	
Ash A Leachate 1 300μm	Acid	**1608**	31,35	**31**
Ash A Leachate 2 300μm	Water	**27**	0,53	
Ash B Leachate 1 < 36	Acid	**23**	0,65	**1**
Ash B Leachate 2 < 36	Water	**0,9**	0,03	
Ash B Leachate 1 36μm	Acid	**1**	0,04	**< 1**
Ash B Leachate 2 36μm	Water	**0**	0,00	
Ash B Leachate 1 63μm	Acid	**38**	1,96	**1,98**
Ash B Leachate 2 63μm	Water	**0**	0,02	

Table 8. Amount of Lead leached from ash A and B.

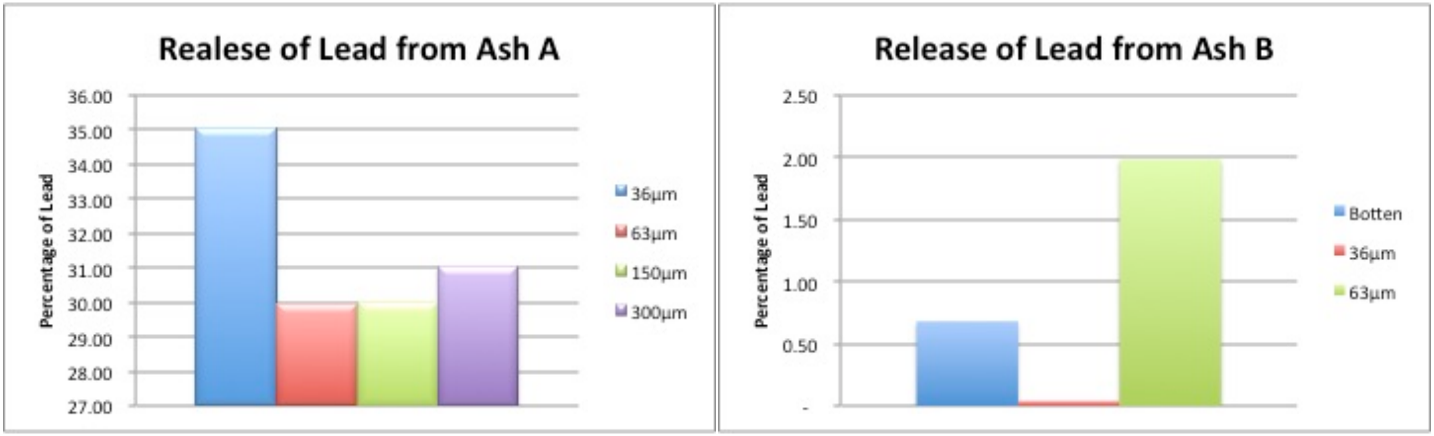


Figure 16. Two plots showing the percentage of the Copper release at each particle fraction for both ashes.

5.2.3 Leaching of Zinc

Sample	*Solvent*	*C $_{released}$ (mg/kg)*	*% Released*	*% Total release*
Ash A Leachate 1 36µm	Acid	**16710**	45,91	**51,51**
Ash A Leachate 2 36µm	Water	**2040**	5,60	
Ash A Leachate 1 63µm	Acid	**10170**	38,09	**42,18**
Ash A Leachate 2 63µm	Water	**1092**	4,09	
Ash A Leachate 1 150µm	Acid	**16650**	43,70	**47,20**
Ash A Leachate 2 150µm	Water	**1332**	3,50	
Ash A Leachate 1 300µm	Acid	**16470**	43,70	**47,32**
Ash A Leachate 2 300µm	Water	**1416**	3,75	
Ash B Leachate 1 < 36 µm Ash B Leachate 2 < 36 µm	Acid Water	**104,1** **571,2**	0,97 5,34	**6,31**
Ash B Leachate 1 36µm	Acid	**118,2**	1,31	**3,29**
Ash B Leachate 2 36µm	Water	**179,4**	1,98	
Ash B Leachate 1 63µm	Acid	**209,4**	0,65	**5,04**
Ash B Leachate 2 63µm	Water	**1422**	4,39	

Table 9. Amount of Zinc leached from ash A and B.

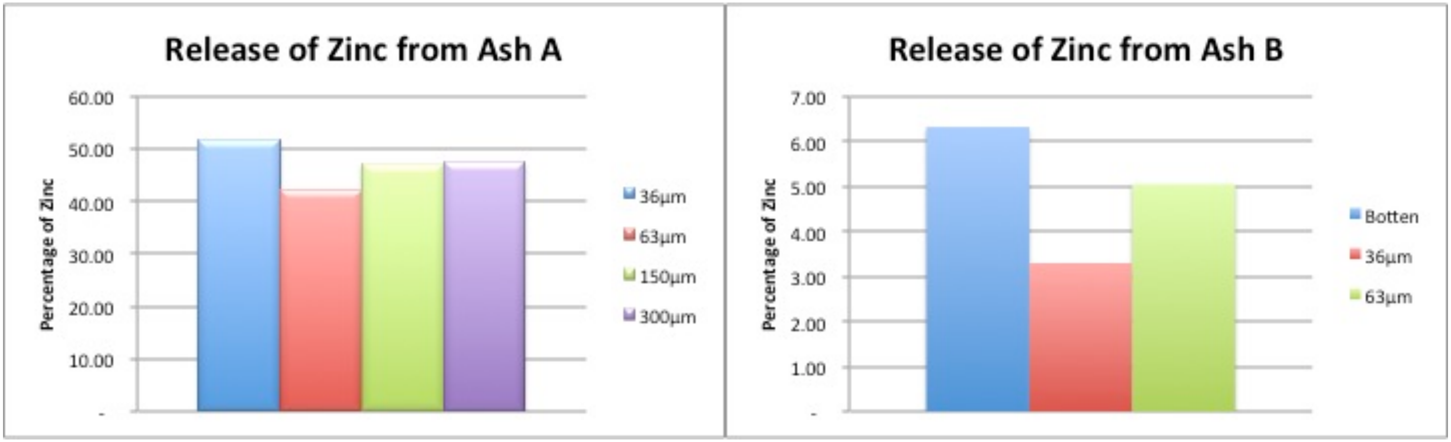


Figure 17. Two plots showing the percentage of the Lead release at each particle fraction for both ashes.

5.4 pH Value

The pH value for all leachates for both ashes at particle fraction 63µm was measured by using a pH meter. Table 10 below shows the obtained pH values for each leachate.

Ash Sample	Particle Fraction	pH Value
Ash A leachate 1	63µm	1,97
Ash A leachate 2	63µm	4,20
Ash B leachate 1	63µm	3,05
Ash B leachate 2	63µm	4,85

Table 10. pH value of each leachate for particle fraction 63µm for both ash.

6. Discussion

As expected, the results from the tables and figures shown in 5.3 that the leaching percentage of the various is much greater in the smallest fraction for all metals. The metals concentration increased while the particle size decreased. This is mainly because of that smaller particles contain more metals then bigger particles [4][12]. The results were similar for respective ashes for each element. The highest release percentage was obtained from Zinc at total release percentage at 51,5 which can be seen in table 10 in 5.2.3. The Zinc will react with the HCl according to the reaction1 below.

$$Zn + 2HCl \longrightarrow H_2 + ZnCl_2 \qquad (1)$$

Reaction 1 is an example of a redox reaction. The Zinc will further reacts with the hydrochloric acid it will lose an electron while the hydrogen will be reduced by gaining the electron to form a neutral molecule, H_2. The second highest release percentage can be seen in table 9 in 5.2.2 which was obtained for Lead at 35,0 %. Like wise reaction 1, Lead will also react with the hydrochloric acid as it results in hydrogen gas in the mixture and a chloride compound as in reaction 2.

$$Pb + 2HCl \longrightarrow H_2 + PbCl_2 \qquad (2)$$

The results also indicate that there is a huge difference between ash A and ash B. From all three tables in section 5.2 one can clearly see that the total amount release of each element in ash B is much lesser comparably with ash A. This can be because of the fact that ashes are collected from different treatment processes, fluidized bed and mass burn combustor. Ash B is much more “compact” (see figure 7 in 4.2) then ash A that can also be an explanation that it more difficult to recover metals from ash B. That it may demand more energy to leach out various metals from the ash matrix. Another way to leach out a higher rate of metals from ash B could also be to lower the pH value, as the leaching is strongly depended by the pH value. Several researchers, such as Karlfeldt and co workers, have declared that, at lower pH value the release rate of leaching metals is increased. However, this may not totally true because of the fact that some metals, e.g., Pb and Zn, also increase their leaching ability at higher pH values (>9). From the tables obtained in section 5.2 it’s quite clear that Zinc is the element with the highest percentage that leached out of the ashes. But what has to be mentioned is that even though Zinc was the element with highest release percentage one still has to consider the initial amount of Zinc in the ash, 36400 mg/kg (table 6) for the particle fraction 36µm. But in this scenario, the Zinc for 36µm also had the most initial mass rate that also can be the reason why it leached out as much as it did. But just because of the fact that Zinc had the highest intial amount, it doesn’t always has to the element with the highest content that leaches out the most. For example let say that what if we had 3 Copper particles in a specific fraction, and 2 of them leached out from the ash matrix, then automatically that will result in 63% leached out, which in this example is very unessential. The result also confirmed that theory about that there are higher amount of metals in smaller particle fractions is true for ash A, while this theory may differ a bit for ash B. The highest release percentage for ash B was found for Zinc (36µm) with an initial amount of 10700 mg/kg (table 6) and 104,1 mg/kg (table 9) leached out. But for Copper and Lead the highest percentage was leached out for particle fraction 63µm. For lead it was 1,98% and for Copper 0,3%.

Like mentioned previously, the theory about finding higher amount of metals in smaller particle fraction differed a bit for ash B. For Copper the smallest particle fraction released 0,2 % and for Lead it was 0,68%. For Lead this theory only differed with 1.3 %(=1,98-0,68) and for Copper 0,1%(=0,3-0,2). But what also need to be mentioned, even though the highest leaching percentage for Copper was at particle fraction 63µm compared to < 36µm the initial amount of Copper was higher for the smaller fraction with, 6280 mg/kg while the initial amount for 63µm was at 4160 mg/kg and the same was for Lead. The highest leaching percentage was obtained for particle fraction 63µm for Lead and the second highest leaching percentage was for particle fraction < 36 µm and it differed with 1,3 %. The initial amount of Lead for < 36 µm was only 3470 and it leached out 22,7 resulting that only 0,68% leached out for this particle fraction.

However, the leaching percentage and the recovery of each element seems quite low even for Zinc (51,51%). To optimize and to further obtain a higher release percentage of these metal elements, this process can be further be optimized by using a lower pH value, other values on L/S or maybe even use a longer time for the leaching process.

Another part that could also influence of leaching of metals is the L/S ratio, which can be confirmed by table 7,8 and 9. The leachate 2 of both ashes obtained very low concentration values for various metals and this is can vary on the low L/S ratio (=0,6) that was used in these mixtures compared to the L/S ratio (=3) used in the leachate 1.

The fact that Copper may has the highest reduction potential value at 0,34 while Lead has -0,13 and Zinc -0,76 may also be an explanation that Copper had the lowest concentration among the metals.

The results from 5.4 showed that leachate 2 for Ash B had the highest pH value at 4,85 (table 10) while the leachate 1 for ash A had the lowest. This may be because of leachate 2 for ash B only consist the ash residue and the milli-Q water, that was added to the mixture for removal of various solutes on the ash matrix and that it had a much smaller L/S ratio then leachate 1 for ash A. The leachate 1 for ash A contained hydrochloride acid and the ash matrix with various metals that reacted with the acid forming metals in ionic which in turn may influence the pH value.

What also need to be mentioned is that there is studies that has revealed that in the near future there will be lack of metals. So by using these kind of techniques for the recovery of metals is necessary

The idea of sieving ashes in various particle fraction is a unique way to leach out metals because of the fact that if sieving is not applied it may be harder to get out a greater amount of metals. In this experiment one can see that the incineration technique for these ashes also plays a huge role as the leaching ability for ash B differs quite much from ash A. An explanation to this could also be that in ash B lime is added as a additive that may inhibit the metals to leach from the ash matrix.

7. Conclusions

- The highest concentration of the metals was Zinc.
- The results confirmed that, low pH value influences the release rate of metals.
- The results conclude also that lower particulate levels contain more metals
- The results show, that the leaching ability can vary widely due what incineration technique has been applied.

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