Study of the sequential extraction of Copper and Zinc from MSWI filter fly ash.

Master of Science Thesis in Chemical Engineering

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I ABSTRACT

In every country each year a large amount of municipal solid waste is produced and different strategies are used to mitigate the environmental impact that the handling of this waste may have.

The strategy known as *"Waste to Energy"* is an efficient way to reduce the solid waste volume while allowing energy recovery from the waste. However, the municipal solid waste (MSW) fly ash produced is a hazardous residue that is rich in heavy metals.

Copper and zinc are often present in the filter fly ash and to clarify their speciation a sequential extraction scheme based on previous works was used in this work with the aim to determine how these metals are sequestered in the fly ash.

The purpose of this study was to analyze the effects of the different variables involved in the sequential extraction scheme in order to have a better understanding of how the conditions applied influence the speciation of metals obtained. The Plackett-Burman experimental design and the Lenth´s approach for a deeper data analysis were used.

The results showed that the presence of alkaline compounds and fine particulate carbon in the ashes affect the metal speciation results obtained. It is suggested that the pH in the extraction liquid is controlled in each step and that the possible re-adsorption of metal ions to carbon is taken into account when evaluating sequential extraction results. Probably, an optimization of the method has to be done for each ash sample type.

II DEFINITIONS AND ABREVIATIONS

- **[NTA],** concentration of nitrilotriacetic acid.
- **[HH],** concentration of hydroxilamine hydrochloride.
- **L/S 1,** liquid to solid ratio of the water extraction.
- **L/S 2,** liquid to solid ratio of the exchangeable fraction.
- **L/S 3,** liquid to solid ratio of the carbonates bound fraction.
- **L/S 4,** liquid to solid ratio of the reducible fraction.
- **L/S 5,** liquid to solid ratio of the organic bound fraction.
- **t1,** time of extraction of the water extraction.
- **t2,** time of extraction of the exchangeable fraction.
- **t3,** time of extraction of the carbonates bound fraction.
- **t4,** time of extraction of of the reducible fraction.
- **t5,** time of extraction of the organic bound fraction.
- **AmAc**, dilution percentage of the ammonium acetate solution.
- **Carbon added,** carbon active added on the sample in g.
  m, independent effects.
- **τ^2,** variance.
- **PSE,** pseudo standard error quantity called.
- **DOE++,** name of the software used to perform the analysis.
- **Y,** response.
- **A0,** intercept.
- **An,** coefficient of the nth factor.
- **n,** number of levels.
- **k**, maximum number of variables.
- **N,** an integer multiple of 4.
- **SES**, Sequential extraction scheme.
- **FM**, fractionating methods.
- **MSWI,** Municipal solid waste incineration.

III OBJECTIVES

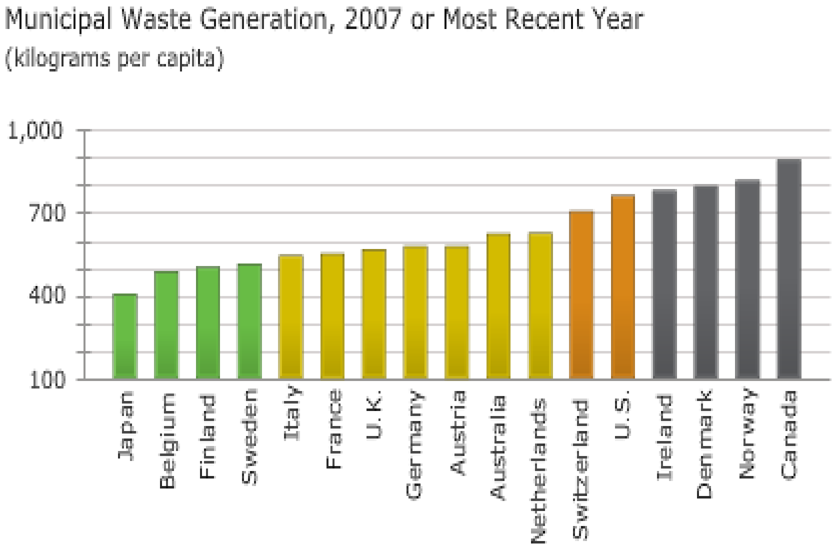
- Compare different SES through a reproducible analysis model.
- Find a method to improve the SES.
- Understand the effects of the variables for each target sample.
- Acquire knowledge about the Copper and Zinc distribution and speciation in specific samples.

1.INTRODUCTION

The handling of municipal solid waste (MSW) is a problem to solve in each society in the world. The major concern is to reduce the environmental impact caused by waste management [48].

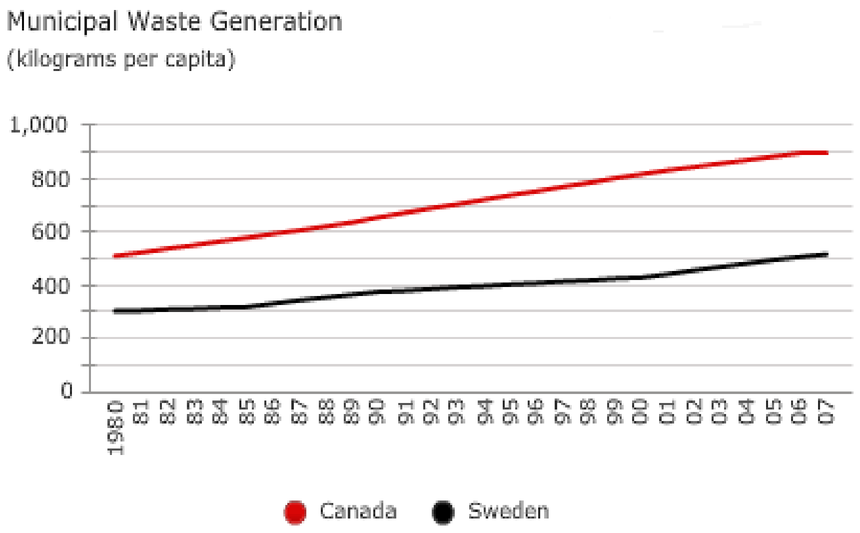
A socio-economic study made by Institute university of Natural Resources and Applied Life Sciences Vienna for the main European cities, shows a distribution of the waste production against a variable called prosperity level which includes different socio-economic factors. The point of view taken in this work can have important applications for recycling and to generate new and more efficient strategies for the solid waste usage, since relevant information as the distribution of materials among the wastes is needed for that purpose [WR13].

It is evident that the volume of waste is mainly dependent on the resources of a society, its culture related to waste topics, as well as the strategy of wasted management used. Graphic 1 shows the differences of Kilograms per capita per country. The countries have different waste management strategies, culture and resources which lead to large differences in amounts of waste produced[WR14].



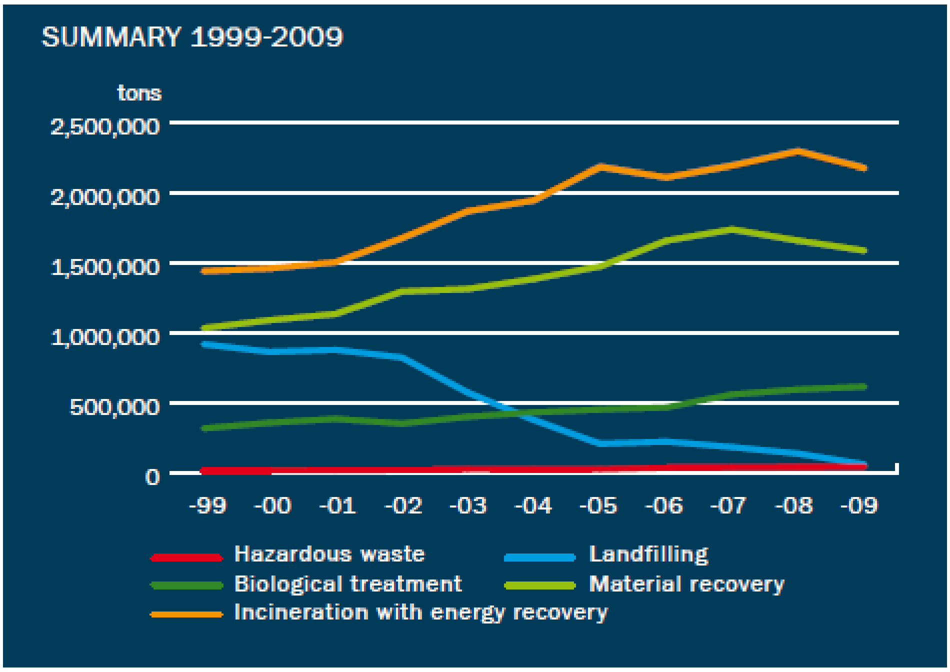
Graphic 1. Municipal waste generation per country, 2007. Source: Industry Survey: Business and Government Sectors 2008 (Ottawa: Statistics Canada, 2010).

An interesting comparison was made between the amounts of waste produced in Sweden and Canada during the period 1980 to 2007 (graphic 2)[WR14].



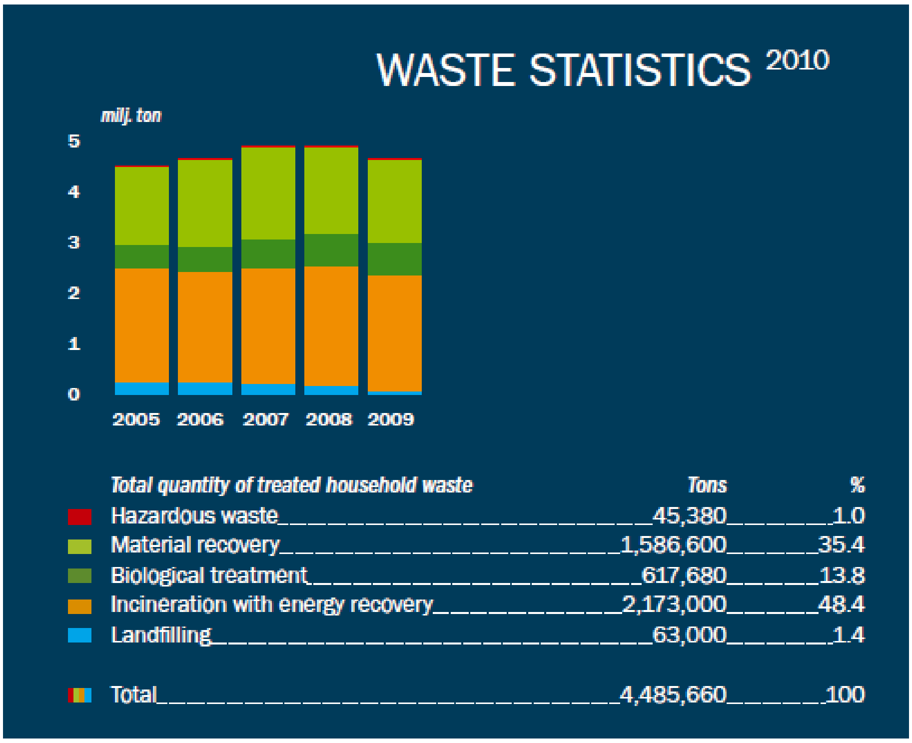
Graphic 2. Municipal waste generation, major producer (Canada) and Sweden. Source: Industry Survey: Business and Government Sectors 2008 (Ottawa: Statistics Canada, 2010).

In Sweden, significant efforts have been put into developing environmental policies and waste management techniques. As shown in graphic 3, the amount of municipal solid waste going to landfill has decreased in recent years and more is going to biological treatment, material recycling and incineration. However, since the amount of waste produced is still rising, the efforts are now directed towards waste prevention and increased recycling.



Graphic 3. Treatments of the waste and volume in tons, source: Avfall Sverige.

The process of waste incineration has become popular. It is an effective method to treat solid waste, as it reduces mass and volume in very high percentages, up to 70%. It also has a very important advantage which is the production of energy by using different methods of incineration, the most common processes being mass burn combustors and fluidized bed combustors [48]. Waste to energy strategy is a growing alternative, in Sweden 48% of the MSW was used for this management strategy in 2010.



	Total quantity of treated household waste	Tons	%
🟥	Hazardous waste	45,380	1.0
🟩	Material recovery	1,586,600	35.4
🟩	Biological treatment	617,680	13.8
🟧	Incineration with energy recovery	2,173,000	48.4
🟦	Landfilling	63,000	1.4
	Total	4,485,660	100

Graphic 4. Treatments of the waste and volume in millions of tons and percentages, source: Avfall Sverige.

Under normal conditions municipal solid waste incineration (MSWI) produces two types of ash: bottom ashes (BA) and fly ashes (FA) [48]. The main problem with the ashes is that they contain components that are toxic and may leach into the environment, and therefore most ashes are considered to be hazardous waste [48].

The definition of hazardous waste is mainly related to the leaching properties of the toxic components in the waste, such as dioxins and heavy metals that get attached to the matrix of the ashes during the combustion process [38].

2. INDUSTRIAL COMBUSTION [1]

The energy recovery from waste makes use of existing technologies. The main technologies used are:

- Fixed-bed combustion.
- Fluidized bed combustion.
- Powder combustion.
- Grate furnace fired boiler

Below there is a short resume of the main characteristics of these technologies. It is shown how the fuel and the air supplies are employed in each system, as well as the technical differences that create different environments of combustion.

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[1] *(Fragments extracted from Sjaak van loo and Japp Koppejan, combustion and co-Firing [39])*

Fixed bed combustor systems have underfeed stoker furnaces. The main flow of air passes through the so called fixed bed, in which the processes of drying, gasification, and combustion take place. The gases are burned once the secondary addition of air occurs, this happens in a combustion zone that is separated from the fuel bed [39].

Fluidized bed combustor technology has been used since 1960 for the purpose of treating solid waste. Some different types of combustor designs exist with differences in the velocity of the fluidization, i.e. Bubbling Fluidized Bed (BFB) and Circulating Fluidized Bed [39].

Bubbling Fluidized Bed combustor is an interesting technology for a nominal boiler capacity over 20 MWth. In this case a bed material is used and disposed in the bottom of the furnace. The primary air is supplied over a nozzle distributor plate that fluidizes the bed with a low fluidizing velocity. The bed material is usually silica sand and dolomite when sulphur binding is needed. The secondary air comes in through the several inlets arranged in the upper part of the furnace [39].

A great advantage of the BFB furnaces is their flexibility concerning particle size and moisture content of the biomass fuels [39].

The sample denominated in this work as ash 1 comes from a BFB system.

Circulating fluidized bed combustor When the fluidizing velocity is increased to 5 to 10 m/s and using smaller bed material particle sizes (0,2 to 0,4 mm in diameter) a CFB is achieved. The bed material and the fuel particles are carried with the flue gas, separated in a hot cyclone or a U-beam separator and fed back to the combustion chamber. The temperature conditions are controlled by external heat exchangers cooling the recycled sand. The high turbulence results in an improved heat transfer as well as more homogeneous conditions in the combustion chamber [39].

Powder combustion Systems for combustion of powdered fuel have pneumatical fuel injection into the furnace, the start up is done by an auxiliary burner, when the system comes to a certain temperature the start up system is shut down and the fuel feeder starts. In these systems the fuel quality has to be constant, the fuel particle size needs to be keep between 10 and 20 mm, and the moisture content can not exceed 20 wt%. Due to the explosions-like gasification of the small particles the fuel has to be highly controlled. Is notable that fuel gasification and charcoal combustion take place at the same time because of the small particle size of the fuel, therefore quick load changes and an efficient load control can be achieved [39].

Grate fired boiler The moving grate is commonly used at capacities **larger than 1-2 MW**, but even in the lower capacity region, there are many boilers with moving grates. Since the fuel bed is mixed mechanically, moving grates are more fuel flexible than fixed grates. For fuels with high contents of ash, like straw and residues from arable land, a moving sloping grate should be used. Otherwise, there is a risk for sintering of the ash; fuels with varying particle sizes also require a moving grate.

The most common fuel type used in grate boilers is wood chips, but also mixtures of wood chips/peat, wood chips/shavings from saw-mills, briquettes and residues from arable land and waste are frequently used. This is also a suitable combustion technique for MSW since the moving grate can deal with large variability in fuel particle size.

The sample denominated in this work as ash 2 comes from a GFB system.

2.1 INDUSTRIAL AIR EMISSIONS AND DEVICES OF CONTROL

The main gaseous products of MSW combustion are steam, carbon dioxide, HCl (g), NOx. In addition, the flue gas contains some particulate matter. The organic chlorine contained in the solid municipal waste is in high proportion converted into HCl (g) and Cl_2 and in a minor quantity to polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The chlorinated organic compounds are normally adsorbed on the surfaces of fly ash. In some cases process of adsorption using activated carbon are set up to enhance retaining of organic pollutants [56].

2.2 AIR POLLUTION CONTROL SYSTEMS

Settling Chambers The first collector of the entire system is often a chamber that removes the biggest particles that may clog the filters or produce fouling. Cyclones are normally used as a device for particulate matter removal; their cost efficiency is very high. Its working methodology is very simple, as the flue gases move in a circular path the biggest particulate matter hits the wall and then is collected in a hopper after passing through a conical section [56].

In electrostatic precipitators the flue gases pass through an array of wires and plates where particle surfaces are charged., The wires are kept at a large positive or negative electrical voltage with respect to the plates and this difference of voltage produces a charge on the surface of the ash particles. The particles are then attracted to the plates and wires to be collected. Particles size of 0,1 to 50 µm are effectively removed by this system[56].

Fabric filters. In this system the flue gases are directed through fabric filter bags. These filters are effective at the removal of particles larger than 5 µm. It can be adjusted to remove smaller diameter size particles but the resistance of the air to pass through the filter increases. Before the contact with the filter, the flue gases must be cooled to avoid fire risk[39][56].

3. PROCESS AND MECHANISM OF ASH FORMATION [2]

The main constituents of ashes are present as salts in the biomass; some of them are bound to the carbon structure. the so called inherent ash. They can be also present as mineral particles from dirt and clay added during the transportation, handling and disposal of the burning material, this is known as entrained ash [39].

The compounds in inherent ashes are homogeneously dispersed in the fuel and their mobility is higher than the entrained ash[39], in the process of combustion, a fraction of the ash forming compounds in the fuel is volatized and released to the gas phase, the amount of the volatile ash components depends on the characteristics of the fuel, the gas atmosphere and the combustion technology that is being used; High temperatures and a reducing atmosphere enhance the volatilization of heavy metals [39].

When these fractions are released from the combustion material as vapours, they can form primary particles in the boundary layer of the combustion particles; this is caused by the re-oxidation and nucleation of matter [39]. Highly volatile elements like Cd, Zn and Pb, will pass through the boundary layer and move to the furnace environment in their gaseous state, probably reacting with S, Cl, and K [39].

Primary particles that are formed during the vaporization are very small with a size of about 5 to 10 nm. During the transport in the flue gas they grow by coagulation, agglomeration and condensation and form the basis of the fine ash fly ash [39]. The non-volatile ash compounds remaining in the char may melt and coalesce inside and on the surface of the char, depending on the temperature and chemical composition of the particles. This results in residual ash particles with a wide range of compositions shapes and sizes related to the characteristics of the parent mineral particles [39].

Depending on the temperature of combustion, combustion technology, density and size of residual ash particles a fraction of this as h flow will be entrained with the flue gases and will form the coarse fraction of the fly ash, while the remaining large particles will stay on the grate to form the bottom ash [39].

Upon the process of cooling the flue gases in the convective heat exchanger section, vapourous compounds condense or react on the surface of pre-existing fly ash particles in the flue gas. Due to the large surface of the

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[2] *(Fragments extracted from Sjaak van loo and Japp Koppejan, combustion and co-Firing [39])*

fine fly ash compared to the coarse fly ash an enrichment of heavy metal in the fine fly ash is a common phenomenon [39].

If the concentration of inorganic vapours in the flue gas and the cooling rate in the heat exchanger are both high, super saturation,i.e. the formation of new particles can occur by the process of nucleation [39].

When biomass is burned the main volatile element is the K that comes from the inherent ash part. The entrained ash minerals are much more stable than the inherent ash is, as it consists of very stable mineral silicate compounds that are not going to be vaporized [39].

According to chemical equilibrium calculations vaporized K is mainly present as KCl or KOH at high temperatures. As the temperature decreases the chloride and hydroxide are converted to sulphate by homogenous gas phase reactions. Gaseous K_2SO_4 has a very low vapor pressure and becomes highly saturated as soon as it is formed. This is a primary step to form new primary particles by homogeneous nucleation. However, not all of it will react so the remaining potassium will nucleate as KCl or K_2CO_3 or condensate in similar forms on pre existing particles at significant low temperatures. Furthermore, solid KCl and K_2CO_3 in the ash particles may undergo heterogeneous reactions with SO_2 (g) and form solid K_2SO_4.

Bottom ash: The ash fraction produced on the grate and in the primary combustion chamber, often mixed with mineral impurities contained in the fuel like sand, stones and earth or with bed material in fluidized bed combustion plants, can cause slag formation, due to a lowering of the melting point, and sintered ash particles in the bottom ash.

The Cyclone fly ash: Fine, mainly inorganic, ash particles carried with the flue gas and precipitated in the secondary combustion zone, in the boiler and especially in multicyclones placed behind the combustion unit. This ash fraction mainly consists of coarse fly-ash particles.

The filter fly ash: Second and finer fly-ash fraction precipitated in electrostatic filters, fibrous filters or as a condensation sludge in flue gas condensation units (normally placed behind the multicyclone). In small scale biomass combustion plants without efficient dust precipitation technology, this ash fraction is emitted with the flue gas. A small part of the filter fly-ash remains in the flue gas anyway and causes dust emissions. This ash fraction also contains some aerosol size particles (submicron ash particles).

4. ASH CHARACTERIZATION

The main properties of ashes are [48]:

Physical properties

- Particle size distribution.
- Moisture content.
- Bulk density.
- Compressive strength.
- Permeability.
- Porosity.

Chemical properties

- Chemical composition.
- Loss on ignition.
- Heavy metals and leachability.
- Organic constituents.
- Chloride content.

4.1 CHARACTERIZATION OF INCINERATION ASHES

The composition of municipal solid waste depends on the lifestyle and waste recycling processes of a region or country, which means that after the process of incineration the ashes may vary in composition as well.

Under normal conditions in an incinerator the final properties of the ashes will mostly depend on:

- Raw municipal sewage waste.
- Incinerator technology used.
- Operational conditions.
- Environmental controls (seen as processes of decontamination).

4.2 CHEMICAL COMPOSITION

The chemical composition shows that the major elements are Si, Al, Fe, Mg, Ca, K, Na and Cl, further, SiO_2, CaO, Fe_2O_3, MgO and TiO_2, are the common oxides present in ash. CaO is the most abundant compound that exists in MSWI fly ash, which constitutes up to 46%, but SiO_2 is the most abundant compound that exists in MSWI bottom ash, containing up to 49% [48]

In the work by Camerani with fly ash of a bubbling fluidized bed it is shown that the most abundant constituents are Ca, Al, K and Si, and in MSW filter ashes are mostly chlorides, hydroxides, sulphates of alkaline earth metals, this characteristic speciation has been reported by many authors [37].

When speciation is carried out for biomass ashes abundant forms of easily soluble compounds of Ca, Na and K, such as CaO, $Ca(OH)_2$, NaCl, KCl, $CaCO_3$, $CaSO_4$and CaClOH are found, Aluminosilicates are scarce unless the ash contains some sand.

5. COPPER AND ZINC

5.1 COPPER

Copper is a reddish metal with a face-centered cubic crystalline structure. It reflects red and orange light and absorbs other frequencies in the visible spectrum, due to its band structure, so it has a nice reddish color. It is malleable, ductile, and an extremely good conductor of both heat and electricity [WR7].

The cupric ion, Cu^{2+}, and hydroxide complexes, $Cu\,OH^+$ and $Cu(OH)_2$, are present in natural water. Copper forms strong solution complexes with humic acids. The affinity of Cu for humates increases as pH increases and ionic strength decreases [WR7]. Because copper is released both naturally and through human activity it is very widespread in the environment, copper is often found near mines, industrial settings, landfills and waste disposals [WR7]. Most copper compounds will settle and be bound to either water sediment or soil particles. When copper ends up in soil it strongly attaches to organic matter and minerals. As a result it is not transported very far after release and it hardly ever enters groundwater. In surface water copper can be transported great distances, either suspended on sludge particles or as free ions [WR7].

Soluble copper compounds form the most important threat to human health among the different copper compounds [WR7]. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's disease; it is characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea [WR7]. The cupric ion (Cu^{2+}) is the most toxic species of copper, but cooper toxicity has also been demonstrated for $Cu(OH)^+$ and $Cu_2(OH)_2{}^{2+}$ [WR7].

5.2 ZINC

Zinc [WR6] is a lustrous bluish-white metal. It is found in group IIb of periodic table. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen.

Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids, Zn may precipitate as $Zn(OH)_2$ (s), $ZnCO_3$(s), ZnS(s), or $Zn(CN)_2$ (s).

Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may coprecipitate with hydrous oxides of iron or manganese (Smith et al., 1995). Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increases as pH increases and salinity decreases.

Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters. Large quantities of zinc can be found in soils. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater.

6. SEQUENCIAL EXTRACTION SCHEMES (SES)

The quantification and characterization process of different species of an element present in a sample is denominated “Speciation”. Speciation is often done using a leaching process, normally divided in different steps, and these steps are related to a designated fraction. These procedures are widely known as sequential extraction schemes (SES), but they are also known as fractionation methods (FM). A large number of investigations published by researchers include single extractions and different steps extractions that vary from 3 to 8 stages. The most used fractions have denominations such as “exchangeable”, “metal soluble in water under acidic conditions”, “ reducible associated to Fe-Mn oxides” , “oxidizible” or bound to organic matter and sulfur and “residuals or associated with silicates”.

Nevertheless the use of the following fractions seems to be a common agreement.

1. Exchangeable.
2. Bound to carbonates.
3. Bound to Fe-Mn oxides
4. Bound to organic matter.
5. Residual.

Fraction 1.

The exchangeable fraction is susceptible to :

1. Ionic composition.
2. PH variability.

Fraction 2.

The trace elements can be associated to carbonates, often as mixed carbonates, such as $(Ca, Cd)CO_3$, where Ca is exchanged for Cd in some places in the crystal structure.

Fraction 3.

Bound iron and manganese oxides existing as nodules, concretion, and cement between particles, are excellent scavengers for heavy metals.

Fraction 4.

The metals can be bound to organic matter. Complexation and peptization are well known processes that involves metals, as well as the process of bioaccumulation and their mechanisms are important ways to sequester metals.

Fraction 5.

Primary and secondary minerals including trace metals. This fraction consists of silicates, aluminates and other sparingly soluble oxides. The trace metals bound in this fraction can only be released by dissolution in HF using high temperature.

Many authors have designed different methods to do this sort of extractions. The procedures normally used have focused their main parameters on selectivity, leaching efficiency and avoiding problems with carry over of metals from one step to another.

Major factors in the schemes:

- Chemical properties of the reagents.
- Selectivity and efficiency of extraction.
- Experimental conditions.
- Order of the steps in the scheme.
- Cross-contamination.
- PH buffering
- Re-adsorption.
- Physical associations of the solid fractions.
- Ecology.

The commonly used order of reagents is:

1. Unbuffered salts.
2. Weak acids.
3. Reducing agents.
4. Oxidizing agents.
5. Strong acids.

Examples of extraction agents:

- ***Exchangeable:*** $CaCl_2$, $MgCl_2$, NH_4OAc, $BaCl_2$.
- ***Acid soluble***: HAc/NaAc.
- ***Easily reducible:*** $NH_2OH.HCl$.
- ***Easily oxidisable:*** $K_4P_2O_7$, NaOCl.
- ***Moderately reducible:*** NH_4Ox/HOx, $NH_2OH.HCl/HAc$
- ***Oxidisable (oxides and sulphites):*** H_2O_2, H_2O_2/NH_4Oac
- ***Poorly –reducible Oxides:*** DCB, NH_4Ox/AA.
- ***Residual***: H,HF+HNO_3

When it comes to uniformity of the schemes there have not been general agreements in the researcher community. However, similar designs are found in many of the SES especially in the first steps, i.e. the exchangeable fraction and in the carbonate associated fraction. There is more disagreement on the work conditions and reagents used to extract the least mobile metal fractions, especially the fraction of metals associated to organic matter, which is the most problematic.

7. COMPARISON AMONG DIFFERENT SES

7.1 REAGENTS AND METHODS USED IN OTHER STUDIES

Below some of the schemes used by the researchers to analyze samples are presented, many of which were mentioned in the comparisons among schemes.

1. **Tessier sequential extraction Procedure.**

Table 1. Tessier sequential extraction procedure.

FRACTION	OPERATIONAL DEFINITION	CHEMICAL REAGENTS AND CONDITIONS
1	Exchangeable	1 g is extracted at room temp. For 1 h with 8 ml of 1 M $MgCl_2$ (pH 7) with continuous agitation.
2	Carbonate	To the step 1 residue add 8 ml of 1 M NaAc adjusted to pH 5 with HAc shake for 5 h at room temperature.
3	Reductible	To the residue of step 2 add 20 ml 0,04 M $NH_2OH.HCl$ in 25% HAc at 96 °C for 6 h.
4	Oxidizible	To the residue of step 3 add 3 ml of 0,02 M HNO_3 and 5 ml of 30% H_2O_2 (pH 2) and heat to 85 °C for 2 h; add 3 ml of acidified H_2O_2, heat to 85°C for 3 h; finish with 5ml of 3.2 M NH_4Ac in 20 % HNO_3 and agitate for 0,5 h.
5	Residual	To the residue of step 4 add 3 Ml of Concentrated $HClO_4$ and 10 ml of HF, heat to dryness add 1 ml of $HClO_4$ and 10 ml of HF, heat near to dryness, finish with 1 ml of $HClO_4$, with the residue dissolved in 12 M HCl.

2. **BCR sequential extraction procedure.**

Table 2. BCR sequential extraction procedure.

FRACTION	OPERATIONAL DEFINITION	CHEMICAL REAGENTS AND CONDITIONS
1	Acid-extractable	1 g aliquot, 40ml of 0,11 M HAc, shake for 16 h at ambient temperature, separate extract from solid residue by centrifugation at 1500X g for 20 min
2	Reductible	To the residue of step 1 add 40 ml 0,1 M $NH_2OH.HCl$ (Acidify to pH 2 with HNO_3), shake for 16 h at ambient temperature, separate extract from solid residue by centrifugation at 1500X g for 20 min.
3	Oxidizible	To the residue of step 2 add 10 ml H_2O_2 (pH 2) for 1 h at room temperature; heat to 85°C for 1 h, add a further 10 ml of H_2O_2, finish with 50 ml of 1 M NH_4Ac (pH 2), shake for 16 h at ambient temperature, , separate extract from solid residue by centrifugation at 1500X g for 20 min.
4	Residual	Digest Step 3 residue on a hot plate using $HF/HNO_3/HClO_4$ in Teflon dish

3. **BCR optimized**

Table 3. BCR Optimized sequential extraction procedure.

FRACTION	OPERATIONAL DEFINITION	CHEMICAL REAGENTS AND CONDITIONS
1	Acid-extractable	1 g aliquot, 40ml of 0,11 M HAc, shake for 16 h at 22 ± 2 °C, separate extract from solid residue by centrifugation at 3000X g for 20 min.
2	Reductible	To the residue of step 1 add 40 ml 0,5 M $NH_2OH.HCl$ (Acidify to pH 2 with HNO_3), shake for 16 h at 22 ± 2 °C separate extract from solid residue by centrifugation at 3000X g for 20 min.
3	Oxidizible	To the residue of step 2 add 10 ml H_2O_2 (pH 2) for 1 h at room temperature; heat to 85 °C for 1 h, add a further 10 ml of H_2O_2, finish with 50 ml of 1 M NH_4Ac (pH 2), shake for 16 h at ambient temperature, separate extract from solid residue by centrifugation at 3000X g for 20 min.
4	Residual	To step 3 residue add 3ml of distilled H_2O, 7,5 ml of 6 M HCL and 2,5 ml of 14 M HNO_3, leave overnight at 20 , boil under reflux for 2 h cool and filter.

4. **GSC Geological Survey of Canada sequential extraction procedure.**

Table 4. GSC sequential extraction procedure.

FRACTION	OPERATIONAL DEFINITION	CHEMICAL REAGENTS AND CONDITIONS
1	Exchangeable, adsorbed and carbonate.	1 g Aliquot, 20 ml of 1 M NaAc adjusted to Ph 5 , shake for 6 h at room temperature, centrifuge 10 min at 2800 rev /min, and conduct a second leach with 1M NaAc.
2	Amorphous Fe / Mn oxyhydroxide	To the step 1 residue ad 20 ml of 0,25 M of $NH_2OH.HCl$ in 0,05 M HCl heat in water bath (60 °C) for 2 h, centrifuge for 10 min, repeat leach and heat for 0,5 h.
3	Crystalline Fe / Mn Oxide	To the residue of step 2 add 30 ml 1 M $NH_2OH.HCl$ in 25% HAc at 90 °C for 3 h, centrifuge for 10 min and repeat 1 M $NH_2OH.HCl$ leach and heat for 1,5 h.
4	Oxidizible	To the residue of step 3 add 0,75 g of $KClO_3$ and add 5 ml of 12 M HCl and 15 ml of H_2O, centrifuge for 10 min, add 10 ml of 4 M HNO_3, heat in water bath at 90 °C for 20 min, centrifugate for 10min , rinse the residue with 5 ml of H_2O.
5	Residual	To the residue of step 4 add 2 ml of 16 M of HNO_3, heat on a hot plate at 200 °C, add 2 ml of 12 M HCl, heat for 20 min at 90 °C in a water bath, and add 5 ml of concentrate HF, 3 ml of concentrated. $HClO_4$ and 2 ml of concentrated HNO_3, heat for 1 h at 90 C in a water bath; evaporate at approx. 70 °C overnight, add 1 ml of 12 M HCl and 3 ml of 16M HNO_3.

5. **Kersten and Förstner sequential extraction**

Table 5. Kersten and Förstner sequential extraction procedure.

FRACTION	OPERATIONAL DEFINITION	CHEMICAL REAGENTS AND CONDITIONS
1	Exchangeable	1 M NH_4Ac, pH 7, 2 h
2	Carbonate	1 M NaAc, pH 5 (HAc), 5 h
3	Easily reducible	0,1 M $NH_2OH.HCl$ in 0,01 HNO_3 12 h
4	Moderately reducible	0,1 M Oxalate buffer pH 3, 24 hide in the dark.
5	Sulphidic/Organic	30% H_2O_2,pH 2 (HNO_3), 2 h at 85 °C, extracted with 1 M NH_4Ac in 6% HNO_3, 12 h.
6	Residual	Hot HNO_3, concentrated.

6. **Camerani's sequential extraction scheme.**

Table 6. Camerani's sequential extraction procedure.

FRACTION	OPERATIONAL DEFINITION	CHEMICAL REAGENTS AND CONDITIONS
1	Water soluble	Samples of 0,1 g, 2 ml Deionized water for 10 mins. Centrifugated at 13000 rpm (20000g) for 30 min.
2	Ion exchangeable	The sample is extracted at room temp. For 1 h with 2 ml of 1 M $MgCl_2$ (pH 7) with continuous agitation. Centrifugated at 13000 rpm (20000g) for 30 min.
3	Surface oxide and carbonate bound metal ions	To the step 2 residue add 2 ml of 1 M NaAc adjusted to Ph 5 with HAc shake for 5 h at room temperature. Centrifugated at 13000 rpm (20000g) for 30 min.
4	Reductible	To the residue of step 3 add 5 ml 0,04 M $NH_2OH.HCl$ in 25% HAc at 90 °C for 6 h. Centrifugated at 13000 rpm (20000g) for 30 min. Centrifugated at 13000 rpm (20000g) for 30 min.
5	Oxidizible	To the residue of step 4 add 0,5ml of 0,002 M nitric acid and 2,5 ml of 30% hydrogen peroxide solution pH 2, the mixture was slowly heated in a water bath at 90±3 °C as before, After 3 h, 1,5 ml of 1.2 M ammonium acetate in 10% (v/V) nitric acid was added, samples were diluted to 8 ml and agitated for 30 mins. Centrifugated at 13000 rpm (20000g) for 30 min.
6	Residual	To the residue of step 5 add 2,5 ml of "aqua regia" and 0,5 ml of 30% hydrogen peroxide and stored overnight. Then, 1,5 ml of concentrated hydrochloric acid and 2,5 ml of ultra pure water added and the solution was heated for 30 min. The extract was made up to 25 ml and stored in a Teflon bottle. Centrifugated at 13000 rpm (20000g) for 30 min.

After the comparison, there are some positive factors of each of them as well as negative factors for the purpose of having the best performance at the SES. The following table summarizes the pros and cons of the reference scheme used in this study.

The main issues are linked to the focuses that the scientist in the moment of the analysis did, the target sample, the selectivity of the reagents, time of extraction and the diversity of methods involved in having a right approach to a better speciation sequence. There was included in the next table all the critics and evidence collected from other scientists concerning to the different factors involved in the SES.

Nonetheless more studies related to MSWI fly ash are need to be done to understand how each variable affects the final recovery of metals, because the different problems have been not properly focused.

Table 7. Pros and cons of different SES.

SCHEME	PROS	CONS
TESSIER	Good selectivity of reagents. Good total recovery of metals, complete dissolution Higher recovery yield for Zn when this method is compared to other sequential extraction, such as Kersten or B.C.R [34]. Less time consuming than the other schemes. Pretty good reproducibility. Main reference.	The dissolution of carbonates might not be complete. A higher recovery yield of the reducible fraction can be reached by increasing the concentration of Hydroxilamine hydrochloride. Dissolution of organic matter might not be complete. Do not use pure water as a leaching agent. Susceptible to resorption process.
BCR	Includes the use of centrifuge to minimize resorption. As it is an evolved scheme from Salomons and Förstner, some conditions increase the selectivity and the accuracy of the method, such as times, temperatures, and concentrations [34].	There is a lot of information useful for environmental analysis by including the acid soluble fraction as whole block. The SES is susceptible to readsorption and resorption.
BCR MODIFIED	It minimizes the resorption and distribution problem compared to the original BCR. Higher amount of metals are extracted in the reducible fraction, $HONH_2 \cdot HCl$	A still susceptible to some resorption process, but it is less exposed to it. Selectivity of reagents has to be studied.

	concentration is higher. • The residual treatment is more specified. • Good reproducibility	
GSC	• High amounts of Cu are recovered.	• Low comparability to other schemes.
KERSTEN AND FÖRSTEN	• High levels of metals in the acid soluble fraction. (NH_4Ac). • Good reproducibility, its results are very similar to the BCR.	• Possible attack of other targets. • High probability of attack on carbonates.
CAMERANI	• Includes a pure water extraction, important to see potential harm to the environment. • Some measures had been improved to prevent resorption such as centrifugation.	• Higher potential of the reductible fraction can be reached. • Probably includes some problems of performance of Tessier's scheme.

7.2 MENTION OF RELEVANT COMPARISONS

Concerning to the comparison among different schemes an additional problem can appear when the physical conditions of the experiment change, for instance a small change in pH, temperature, contact time, solid to liquid ratio, particle size, or moisture change can lead to a considerable change of the distribution of the fractions.

These methods (SES) have been mostly applied to soil analysis, sediments, clays, sewage sludge and, quite recently, ashes. Numerous varieties of SES have been described in literature; Kersten and Förstner have reported more than 25 different sequential extraction schemes [31]. Nowadays there are two methods that are most known, the method proposed by *Tessier et al* and the method proposed by the community bureau of reference (BCR)[1][7]). The results obtained in a study analyzing these two main methods showed that the best reproducibility was related to the Tessier´s acid soluble, reducible and residual fractions. It was not very successful for the steps for exchangeable and oxidisable fractions [1].

The lack of selectivity for the oxidizible fraction was related to the complexation of metal ions to organic matter or to an incomplete dissolution of sulfides in this fraction, for the second problematic phase (the exchangeable fraction) incomplete dissolution could be one reason. Another explanation suggested was the low accuracy obtained in atomic absorption spectrometry when measuring samples containing a high concentration of $MgCl_2$, which causes an important matrix synergy [1], however a problem like matrix synergy can be solved by analyzing the leached samples with the ICP-MS or ICP-OES techniques.

Improvements and more experiments are needed, to develop more reliable metal speciation by sequential extraction. Based on results and discussions published in literature, it is probable that specialized schemes for each sample type has to be developed. [31].

Efforts to harmonize the SESs have been done, for example the BCR improved method attempts to reduce the impact of the problem of the readsorption and the solid to liquid ratio[1], the BCR method has been proposed to unify the extraction techniques of Cu, Cd, Cr, Pb, Ni and Zn in sediments, soils, sewage sludge and industrially contaminated grounds. The result of a test of robustness led to an improvement of this process in the second step by using hydroxylamine hydrochloride and a 3000 g centrifugation speed, called BCR optimized method [50].

There is also a divergences between the BCR and the optimized BCR in fractions such as the reducible species. The optimized approach removes more Cu, Zn, and Pb than the standard BCR, due to the higher concentration of the hydroxylamine hydrochloride used. These sorts of differences have had repercussion in other experiments that had modified this parameter and the result became an increased concentration of the hydroxylamine hydrochloride in the scheme by Tessier [31].

In the same study of R.A.Sutherland, it is said that in one of the most widely used methods, the Tessier´s one, the acid-soluble species extraction does not dissolved all the carbonates. Hall et al. (1996a) found that the second application of NaAc leach solution dissolved about the equivalent of 35-40% of the Cu, Fe and Zn extracted in the first application, this performing problem is also mentioned by Tack and Verloo (1996), their estimation was that a 10-25% of the metals extracted of a calcareous sediment in the reducible fraction was related to the dissolution of carbonates non dissolved previously. There was also reported that metal-specific differences exist in the Tessier´s procedure [31].

In other study with fly ashes sample was concluded that development of the BCR procedure with water extraction as the first step is recommended because the extraction of water soluble species yields very important information necessary to evaluate the risk of environmental pollution[37][38].

As it is generally seen there is a lot of profitable knowledge available in the studies, but when comparing a pair or more methods important differences can be found. Such problems are present if for instance a comparison between Tessier and BCR (Optimized or not) is done, because the acid soluble fraction in the BCR may correspond to the sum of the exchangeable and acid soluble fractions in the Tessier´s method [34]. To try to do a comparison study a lumping of very probable equivalent fractions was done to make a better reading of data but it obviously had an adverse effect on the precision of the comparability [31].

An important comparison among Tessier´s method, BCR and Meguellati schemes applied to sediments showed that the first scheme was the most effective and precise for evaluation of metal mobility in iron oxide sediments. The difference lays in the concentration of hydroxylamine hydrochloride, 0,04 M vs. 0,1 M. The latter studies showed that comparing BCR and Kersten and Förstner 5 stage scheme, no significant differences were observed for Zn and Cd [51].

A comparison among the modified Tessier´s method, Stover´s method and the BCR made in the Department of Environmental Technology at the Wageningen University suggest that the reproducibility and repeatability of the Tessier´s and BCR extraction schemes were good for application in fractionating methods, but the one of Stover was not very efficient at the extraction of sulphur from the sulphide fraction and its reproducibility was significantly lower than the others [1].

A study made with marine sediments compared the BCR, Kersten and Tessier methods, and the results of BCR and Kersten were found to be similar. It was also shown that the residual fraction in the Tessier´s method is higher, the researchers attribute that to the use of hydrofluoric acid because at high temperatures it dissolves the silicates [34], In the same study the results for the acid soluble fraction the Kersten and BCR method are higher than those obtained in the Tessier method, even when the results for the first two were similar for Cu and Pb, being the Kersten method the one that had higher levels of concentration. The study attributes the differences to the liquid to solid ratio which is lower in the Tessier´s method [34]; Thus, the release of these metals would be determined by solubility, i.e. the equilibrium concentrations would have been reached.

For the reducible fraction, the results are dependent on the metal, the Kersten´s method gives the highest levels of concentration for Cu, Cr and Fe, the Tessier ´ s method shows the highest levels of Zn and Pb, this sort of selective results may be influenced by the selectivity of the previous steps, because if carbonates were not well dissolved the result can be higher or vice versa if a part the iron and manganese oxides were previously extracted [34]. Concerning to the oxidizible fraction the results were very similar for the three methods, however the Tessier's method shows the lowest concentration and this is probably due to extraction time which is shorter in Tessier method than in the other methods.

The suggestion of a high dependence of the pH conditions of the leachate as the main factor for the mobility in heavy metals was made by a study with MSWI [7], who stated that a lower ph than the neutral would release higher amounts of metals. This conclusion may be relevant in order to be aware of the potential of pollution of the ashes in the environment [37] as well as for the general understanding of the extraction sequences. At this point it is convenient also to be also aware of the effect of water leaching because even if it is not in an acidic range it can harm the environment, some researchers have include a water leaching step in the sequential extraction scheme to study this process[38] [37].

The possible re-adsorption or re-precipitation during the extraction sequence is a difficulty that every study has to face. In fact probably most of the differences among SES can be directly affected by this process, so studying and solving this problem can probably lead us toward a reliable harmonization process, some studies have shown that the use of some reagents can slow down this process or partially block it. For instance in a study made by the Department of Geology of Wayne state University applied to sediments it was found that the use of nitrilotriacetic acid (NTA) was very effective to counteract resorption[18]. Their results suggest that the use of 400 mg/l or more of NTA in each step of the extraction scheme can substantially help to hinder the resorption without causing significant dissolution of non targeted fractions; some other agents like EDTA can attack carbonates lowering the selectivity and accuracy of the study [19].

The use of NTA can preferably be applied when high levels of contamination are expected in the sample which is the main condition to have serious problems of resorption [18]; the use of other chelating agents that can act to prevent resorption can also be contemplated to further studies, such as the DTPA (Pentetic acid). DTPA has been widely used to measure the bioavailability of metals in soils, and it is a good option to study the prevention of resorption and re distribution of metals in a sequential extraction scheme by this chemical.

A common conclusion suggested by many researchers is that the main variations in extraction results were caused by the origin of the waste more than by the total content in the ashes matrix. This is an important issue because if some day an industrial process is developed to extract heavy metals a daily routine of analysis might be required in order to know the quantity of reagents that should be used to carry out the extraction. Then a fast and reliable process must be found.

Summarizing this section of comparisons, there have been several achievements at the understanding of the methods of extraction but there is a huge need in improving them, the next topics are the most relevant points to develop in future investigations:

- Harmonized sampling techniques.
- Harmonized sequential extractions schemes, and increased comparability among them.
- Optimization of the conditions of selectivity for the reagents.
- Resorption and redistribution problem during the procedure removed.
- Alternative and focused Schemes that can be used for a target sample, for instance two conditions could be important for this objective: the type of sample and the metals studied.
- Lack of studies with solid waste incineration residues, such as ashes, fly ash and airborne dust, more research studies must be done.
- Characterization of pollution sources.

A general suggestion to deal with the main problems such as the comparability, harmonized sequential extraction schemes, resorption and redistribution problem and alternative SES addressed to target samples can probably be the use of more robust statistical analysis, covering wider ranges of the main factors as well as the interaction of variables involved [35][36].

8. Speciation of copper and zinc in the literature

In most extractions sequences reported in literature the Cu major percentage has been extracted in the oxidizable fraction, whereas Zn has been mostly removed under acidic conditions, as well as in the exchangeable fraction. In a study of MSWI-BA, the copper was in a major part extracted under oxidizing conditions (40-79%), indicating that copper can be bound to organic ligands by complexation when incomplete combustion of the waste happens, the same study showed that over 40 % of the Zinc is likely to be released under soft acid conditions and between 25 to 35 % under strongly acid conditions. This emphasizes the idea of the strong dependence of the pH for the Zinc leaching. For the reducible and oxidizing conditions smaller amounts of Zn were found, reductible fraction (6-14%) and oxidizing conditions (7-18%) [3].

In a similar study for MSWI ashes, it was shown that when the pH of the extractant fall below neutral range, the extracted amounts of heavy metals rise substantially due to the released metals bound to the carbonate fraction [4] [3], this study also mention that the conditions of precombustion, combustion and the composition of the waste are strong conditions for the ash speciation. It was referred that under reducing conditions in the combustor some metals are released in the gas phase and later absorbed onto the fly ash. This is a very likely process for the Zinc.

There is an interesting study that concerns to the speciation evolution of heavy metals during a sewage sludge incineration process. The authors conclude that the acid soluble fraction in the raw sludge for Cu and Zn has a great tendency to volatilize during incineration. It was also seen that the volatilization is likely to happen by two ways, inner transition control and volatilization control, in the case of copper in a sample with no moisture content, the inner speciation transformation occurred [49].

A remarkable point was that there is a considerable impact of moisture content for Cu, Zn, Pb and Cr speciation in the ash. It was also found that the residual fractions of Zn, Pb and Cr came from hydrolysis processes. The mechanism probably is related to the conversion of Zn and Pb chlorides under moderated moisture presence to hydroxides forms and then when they are dewatered to oxides which are much less volatile forms [49].

In a characterization of industrial waste incineration fly ash using, water, HNO3 and aqua regia, the released amount of heavy metals as Cu and Zn was significant, moreover it was found that some particles with hollow structures contained various kinds of elements such as Cr, Fe Zn and Ti. In this case of study the metals of group 12 like Zn were leached in more than 60% and 80%, with HNO3 and aqua regia, the results indicated that Zn were mostly in the acid soluble form, they suggest that those forms could be chlorides. If they had used a water leaching step, the presence of chlorides would have been possible to verify. For metals of the group 11, leachabilities were very different from one element to other, Cu (group 11) the leachability was pretty high (90%), but for Fe it was as low as 5%, which indicates that more stable forms are present (oxides)[7].

9. MAIN IDEAS APPLIED TO THIS STUDY

Based on the review of the investigations published in recent years the following plan was made for this investigation:

- An optimization technique is going to be applied, as it is the best way to study a group of factors that affect the results of the experiment.
- An appropriate experimental design has to be used to do a good reliable management of the information.
- A modified Tessier Scheme can be taken as a base procedure, being aware of the limitations mentioned by many authors.
- The use of water as a leaching extractant should be included in the SES as the variations showed by Zareen Abbas [56] and Camerani [37] are very important for the environmental repercussion.
- The use of a centrifuge in each fractionating step will prevent resorption and it is a better option than filtration.
- The use of **NTA** could be used to prevent resorption and redistribution and rising the level of precision (The comparison among other chelating agents and the selection procedure of NTA is included in the annexes).
- Different ratios of L/S in the extraction steps can be used to study this procedure variable, which could be useful for further optimization studies.
- In the carbonate bound fraction extraction it could be useful to lower the pH and if possible try to evaluate the effect of applying this change in other fractions as well.
- Leaching times can be analyzed and optimized.
- Measure the C content in the ash samples, as it is linked to adsorption of Cu.
- A standard method of drying the sample should be used.

10. PROPOSED ANALYSIS

First of all a characterization of the different variables was made, followed by a selection of the ones susceptible to be modified and controlled during the experiment, once that number of the controllable variables was defined, the search for a method of statistical analysis started.

As this is a screening study, the method of Plackett-Burman experimental design was selected due to their main characteristics that allow saving time of experimental work and collect the maximum information with an optimized number of experiments; the reliability of the method will be discussed in the experimental design chapter.

The variables of the study are listed below:

10.1 Controllable variables

- **NTA** concentration (not applied to the water extraction and the exchangeable fraction).
- pH adjustment in fraction 3, (bound to carbonates).
- Hydroxylamine hydrochloride concentration.
- Liquid to solid ratio in extraction 1, 2, 3, 4, 5.
- Extraction time in 1, 2, 3, 4, 5.
- Concentration of Ammonium Acetate in the reducible fraction.
- Temperature at extraction 4 is set to 90 ± 3 °C.
- Temperature at extraction 5 is set to 90 ± 3 °C.

10.2 Non-controllable variable

- Amount of Carbon in the sample (linked to the Fe content).

As the amount of carbon is a characteristic of the ash in itself, hence it is not a parameter that can be modified, but by adding known amounts of Carbon a study of the effect of the presence of it can be done.

The option of adding Carbon to the sample of analysis is the only way to create a different level of carbon in the sample so this non controllable variable is turned into a semi-controllable one. The added carbon most probably does not have the same characteristics as the carbon of the ash matrix.

11. EXPERIMENTAL DESIGN

11.1 Factorial design.

An important tool of the experimental design which has been used by chemists is the factorial design, the most common are two level factorial designs, these sorts of designs are mainly used for screening, that is to determine the influence of factors on a response, and which are important. When it comes to a large number of factors involved in a study, an important limitation related to the number of experiments can come out; because the number of experiments must be equal to a power of two, this makes this experimental configuration inefficient for a screening study [41].

As an example, for a 10 factors design experiments at two levels 1024 experiments are required, in this study 15 factors will be studied, that is equivalent to 32,768 experiments. For a screening study this is not useful at all, fortunately there are ways to reduce this number of experiments.

11.2 Fractional factorial designs

If an experimental design is condensed there are a number of important features to take in account [41]:

- Each column of a factor must be different.
- In each column of a factor there must be equal number of levels, in this case (-1) and (+1).
- For each experiment at a level of (+1) there are an equal number of experiments.
- For each experiment at level (+1) there are an equal number of experiments for the rest of the factors that are at levels (+1) and (-1), and so on for every combination.

The last property is called *orthogonality,* it means that each factor is independent of each other. If this is not well established, it will not be easy to distinguish the effect of two factors varying separately [41].

However after the reduction the interaction between factors is said to be confounded in a certain degree, for all that not all these effects are likely to be significant, and the purpose of a screening study is to determine which effects factors should be studied in detail later.

In a complex and reduced experiment it is then understandable than some information among the different interactions is reduced, nevertheless this methods will enable the possibility of selecting significant variables that are of interest [41].

The known restrictions of the two levels fractional design are [41]:

- There are no quadratic terms, as the experiments are performed in just two levels.
- There are no replicates.
- The design only provides an approximation within the experimental region.
- The number of experiments must be a power of two, for instance a matrix may not have 5, 6, 9 or 11 runs of experiments, the number has to be 4, 8, 12, 16 and so on.

11.1 PLACKETT-BURMAN

The Placket-Burman approach propose a number of two levels factorial designs, whose number of experiments is a multiple of and whose number of factors is one less than the number of experiments, reducing the number of experiments required [41], an important assumption of the method is that the variables are independent, hence the interactions of the factors are also taken as negligible, this means that the confounding effect is minimum.

It is important to notice that when interactions between factors are not negligible, they are confounded in Plackett–Burman designs with the main effects, this means it is hard to distinguish between certain main effects and certain interactions, this is commonly known as confounding, nevertheless for this study the assumptions taken avoid this sort of effects.

The most important properties that this design keeps its orthogonality, that is needed to make consistent the independence state of the variables for a 15 factors matrix. This can be understood by examining its main properties.

- There are 8 instances in which factor 1 is at a high level, and 8 at the lower.
- For each of the 8 instances at which factor 1 is at a high level, in 4 cases the rest of the variables will be at a high level and in other 4 cases the rest of the variables will be at a lower level.
- Any combination of factor is related in the same way.

This design has some restrictions such as [41]:

- The number of experiments must be a multiple of 4.
- There are only certain and specific arrangements that have these properties.

In order to determine the significance of the variables the statistical analysis method was made according to the Lenth´s method. This is an analysis included in the software used (DOE++).

11.2 THE METHOD OF LENTHS

The Lenth´s analysis is an objective method for deciding which effects are active in the analysis of unreplicated experiments, when the model is saturated (This study works with a saturated model) and hence there are no degrees of freedom for estimating the error variance [57]. Lenth´s method assumes that there are *m* independent effects and they have all the same variance, τ^2 , in an orthogonal two-level experiment on N observations [57], the last enunciate shows a disadvantage of the method, when the contrast of variables is done with the assumption that all the variables have the same variance τ^2 [57].

In an orthogonal two-level experiment on N observations, where (+) denotes the high level and (-) the low level.

Each contrast has the form :

$$C = \bar{y}_{(+)} - \bar{y}_{(-)}$$

Equation 1. Contrast form.

Where $\bar{y}$ (+) is the average of the N/2 observations at the “high” level of a factor and $\bar{y}$ (−) is the average of the N/2 observations at the “low” level [57].

Each such contrast has variance:

$$\tau^2 = (4\ \sigma^2 / N)$$

Equation 2. Variance equation.

Where σ^2 is the error variance.

Let c1, c2, cm denote the m contrast estimates.

As usually the model is saturated, we have m = N −1. The calculation has two steps.

First, let

$$s_0 = 1.5 \cdot \text{median } \{|c\ j|\}$$

Equation 3. First stage of the pseudo standard error.

Then, let

$$\text{PSE} = 1.5 \cdot \text{median } \{|c\ j| : |c\ j|\ \_\ 2.5\ s_0\}$$

Equation 4. Pseudo standard error.

The second step exclude the effects that exceed 2,5 $s_{0.}$ PSE is termed the pseudo standard error, and it is an estimate of τ.

Lenth proposed a method for the estimation of a pseudo standard error quantity called PSE, where the effects are judged to its relation to the PSE, and then it is decided if the effects are significant or not [57].

Hence in this study the Lenth' s method is an appropriate approach for a screening study, since the Plackett-Burman method does not include replicates.

A saturated Plackett–Burman factorial design is used in this study to correlate dependent and independent variables with the purpose of estimate the importance and the effect of each variable in the final total extraction of an element, in this case Cu or Zn [41].

The polynomial disposition of the method enables the use of different variables related to a final effect.

$$Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + - - - + A_nX_n$$

Equation 5. Polynomial disposition of the variables.

Where Y is the response, A0 (intercept), and A1 to An are the coefficients of the response values [41].

The approach to understand the coefficients is explained below.

The coefficients determined the effect of the variable related, for instance if the coefficient A1, has the value of 10, it means that the effect of the variable X1, increases the response in a 10% when the level is raised from (-1) to (+1) [41].

It is important to note that A0, is the intercept, and the coefficients have this point as a reference. This point must be very close to a state where all the factors at the level (-). Hence a very negative or positive effect can have higher values than 100, and it has to be interpreted from a physical point of view to understand it clearly [41].

11.2 VARIABLES SET UP

Total controllable variables for a statistic analysis in a complete experiment: 15

For each variable the value will have two levels, an inferior and a superior, the assignment will be +1 or -1 to determine which is the state of each variable.

For instance in the use of NTA the options will be 0 assigned to the low level (-) and 200 mg/ l assigned to the high level (+) in the matrix of the experimental design, or L/S ratio which could be 20 for the low level (-) and (40) for the high level (+).

Note: As the samples are going to be of 0,1 g, the liquid to solid ratio will be expressed in reference to the first sample weight, and will be written in the next table as a ratio and the milliliter used to reach that ratio.

Table 8. Different variables and set up levels.

Number of variable	FACTOR	LOW LEVEL (-)	HIGH LEVEL (+)
1	NTA concentration	0	200 mg/L
2	pH adjustment in fraction 3	pH 4,5	pH 5
3	Hydroxilamine hydrochloride concentration	0,04 mol/l	0,5 mol/L
4	Liquid to solid ratio fraction 1, expressed as ml used.	30 (3ml)	60(6ml)
5	Liquid to solid ratio fraction 2 expressed as ml used	30 (3ml)	60(6ml)
6	Liquid to solid ratio fraction 3 expressed as ml used	30(3ml)	60(6ml)
7	Liquid to solid ratio fraction 4 expressed as ml used	50 (5 ml)	100 (10 ml)
8	Liquid to solid ratio fraction 5	3,5 ml per aliquot 0,5 ml of inhibitor of resorption. (Ammonium acetate in nitric acid)	7ml per aliquot 1 ml of inhibitor of resorption. (Ammonium acetate in nitric acid)
9	Extraction time 1	10 minutes	20 minutes
10	Extraction time 2	10 minutes	20 minutes
11	Extraction time 3	5 hours	6 hours
12	Extraction time 4	6 hours	7 hours
13	Extraction time 5	5 hours	6 hours
14	Concentration of inhibitor step 5	Ammonium acetate at 10% (v/v) nitric.	Ammonium acetate at 20 % (v/v) nitric acid.
15	Carbon added	0g	0,01g

11.3 MATRIX USED IN THE STUDY

The Plackett-Burman matrix was extracted from Optimizing Engineers Design figures (j. Krottmaier), once the data is fulfilled, the software (DOE++ from reliasoft) is used for further analysis.

For this case of study the experimental design has the following characteristics:

- Orthogonal matrix, because n = 2, which corresponds to the number of levels.
- The number of the experiment must be a multiple number of 4 as the theory of optimization suggest.
- The maximum number of variable is subjected to the formula:

$$K= (N-1)/(n-1)$$

Equation 6. Maximum number of variables in the experiment.

Where k, number of variable, N a multiple of 4, and n the number of levels.

So for this case the size of the matrix is 16, which means that the maximum number of effects studied is 15, in a 2 level experiments.

With the factor from 1 to 15 assigned in order to the table showed before, a run is equivalent to an experiment.

There will be two responses, total Zn concentration and Cu total concentration at the extraction per each run.

Table 9. Matrix that shows the values configuration of each SES.

FACTOR	**1 [NTA]**	**2 pH**	**3 [HH]**	**4 L/S 1**	**5 L/S 2**	**6 L/S 3**	**7 L/S 4**	**8 L/S 5**	**9 Ext time 1**	**10 Ext time 2**	**11 Ext time 3**	**12 Ext time 4**	**13 Ext time 5**	**14** AmAc **Step 5**	**15 Carbon added.**	**Total Zn and Cu recovered**
1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
2	-	-	-	-	-	-	-	+	+	+	+	+	+	+	+	
3	-	-	-	+	+	+	+	-	-	-	-	+	+	+	+	
4	-	-	-	+	+	+	+	+	+	+	+	-	-	-	-	
5	-	+	+	-	-	+	+	-	-	+	+	-	-	+	+	
6	-	+	+	-	-	+	+	+	+	-	-	+	+	-	-	
7	-	+	+	+	+	-	-	-	-	+	+	+	+	-	-	
8	-	+	+	+	+	-	-	+	+	-	-	-	-	+	+	
9	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	
10	+	-	+	-	+	-	+	+	-	+	-	+	-	+	-	
11	+	-	+	+	-	+	-	-	+	-	+	+	-	+	-	
12	+	-	+	+	-	+	-	+	-	+	-	-	+	-	+	
13	+	+	-	-	+	+	-	-	+	+	-	-	+	+	-	
14	+	+	-	-	+	+	-	+	-	-	+	+	-	-	+	
15	+	+	-	+	-	-	+	-	+	+	-	+	-	-	+	
16	+	+	-	+	-	-	+	+	-	-	+	-	+	+	-	

12. SEQUENTIAL EXTRACTIONS INVOLVED IN THE STUDY

The steps used in the sequential extraction schemes are: Dry the samples at 105 °C and then take 0,1 g sub-samples.

Extraction 1.

Water soluble fraction

Variables:

- **4 Liquid to solid ratio 30 or 60 related to 0,1 sub-samples.**
- **9 Time of leaching, 10 mins or 20 mins.**
- **15 Amount of carbon added to the starting sample, 0 or 0,01g.**

Extraction made with continuous agitation; 3ml or 6 ml of deionized water are used for this purpose during 10 or 20 minutes in presence of 0,01 of carbon added or in absence of it.

Extraction 2

Exchangeable fraction

Variables:

- **5 liquid to solid ratio, 30 or 60.**
- **10 time of leaching, 10 mins or 20 mins.**
- **15 Amount of carbon added to the starting sample, 0 or 0,01g.**

This extraction is made using 3 ml or 6 ml of a 1 M $MgCl_2$ solution at pH 7 with continuous agitation during 10 or 20 minutes.
In presence or absence of 0,01 of carbon added of it in the first extraction of the procedure.

Extraction 3

Bound to surface oxides and carbonates.

Variables

- **1 use of NTA, concentration 0 or 200mg/l.**
- **2 pH at 4,5 or 5.**
- **6 Solid to liquid ratio 30 or 60.**
- **11 time of leaching 5 or 6 hours.**
- **15 Amount of carbon added to the starting sample, 0 or 0,01g.**

This extraction is carried out with 3 ml or 6 ml of a solution of sodium acetate and acetic acid adjusted to pH 4,5 or pH 5 during 5 or 6 hours time, continuous agitation.
In presence or absence of NTA at 200mg/l.
Presence or absence of 0,01g of carbon added of it in the first extraction.

Extraction 4

Metal ions bound to Fe and Mn oxides.

Variable

- **1 use of NTA, concentration 0 or 200 mg/l.**
- **3 Concentration of hydroxylamine hydrochloride 0,04 or 0,5.**
- **7 solid to liquid ratio 50 or 100.**
- **12 Time of leaching 6 or 7 hours.**
- **15 Amount of carbon added to the starting sample, 0 or 0,01g.**

Extraction with occasional agitation, with 10 ml 0,04 or 0,5 M of hydroxylamine hydrochloride in 25 % (v/v) acetic acid, during 6 or 7 hours, at 90 ± 3 °C.
In absence or presence of NTA at 200mg/l.
In absence or presence of 0,01g of carbon added of it in the first extraction.

Extraction 5

Metallic ions bound to organic matter and sulphides.

Variables

- **1 use of NTA, concentration 0 or 200 mg/l.**
- **8 solid to liquid ratio, expressed in 3 or 6ml per aliquot added.**
- **13 time of extraction 5 h or 6 h.**
- **14 concentration of the inhibitor, 10% or 20 % in volume.**
- **15 Amount of carbon added to the starting sample, 0 or 0,01g.**

The residue of extraction 4 is extracted with 1 ml or 0,5 ml of 0,02 M nitric acid and 2,5 (if 0,5 of nitric acid is added) or 5 ml (if 1 ml of nitric acid is added) of 30% hydrogen peroxide solution (adjusted to pH 2). The mixture is slowly heated in a water bath to 90 ± 3 °C, after 2 hours a second aliquot (0,5 ml for the first case or 1 ml in the second one) of 30% hydrogen peroxide was added and the mixture heated to 90 ± 3 °C as before. After 3 hours, 3 ml of 1.2 ammonium acetate in 10 or 20 % (v/v) nitric acid are added, and samples are diluted to 10 ml (if the aliquot is 3ml) or 20 ml (if the aliquot is 6ml) and agitated for 30 min.

After each extraction, the liquid phase is centrifugated in tubes of 50 ml at 15 000 rpm (22 614 g) for 30 min. In a JA-17 Beckman Coulter, serial No0 07E 451. The supernatants were decanted and stored in Teflon bottles.

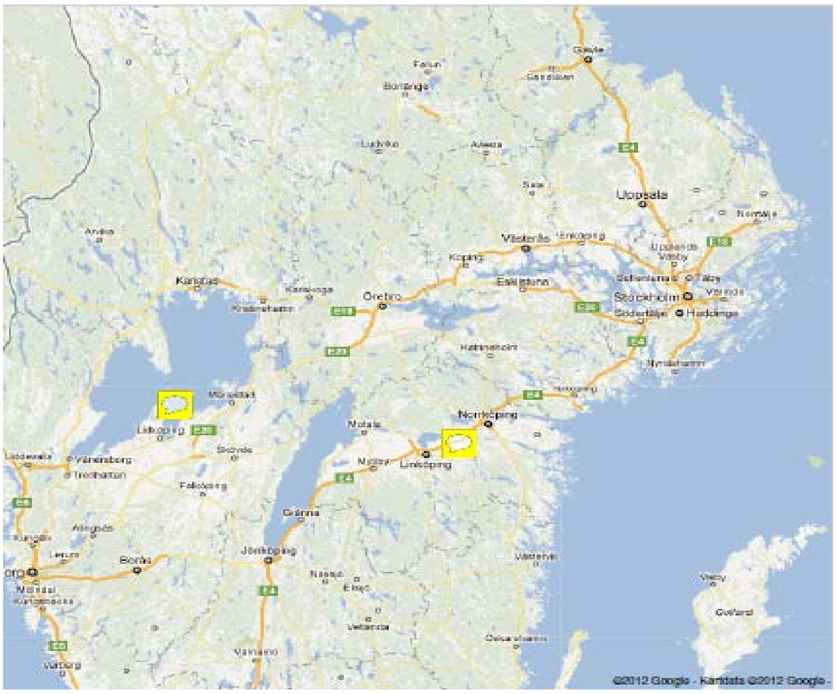
Each sample was keep at 4 °C until they were analyzed.

13. SAMPLES

Fly-ashes used in this work were taken from two different places, Lidköping [WR-17] and Linköping [WR-16]. In both cities the waste is burned to generate heat, which is used afterwards for district heating. This process is commonly known as waste to energy. The combustion unit in Lidköping is a bubbling fluidized bed boiler and that in Linköping is a grate fired boiler.

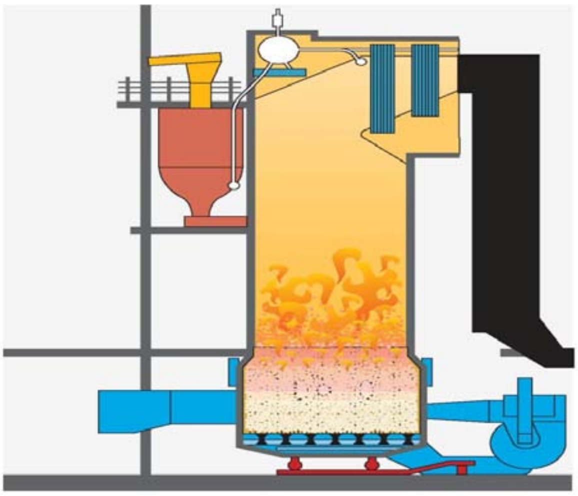
The fly ash from Lidköping is richer in Ca and Cu than the fly ash from Linköping., The Lidköping ash also has a lower concentration of unburned matter than that of the Linköping ash (Table 10).

It is important to point out that the ash from Linköping, has 5 times less Cu content than the one of Lidköping, and 3 times more Zn, also a higher content of unburned matter is present. This differences are due to the raw material used as waste and the technology of incineration.



Graphic 5. Location of the places were the samples were taken from, Lidköping left and Linköping right.

- Ash 1 comes from a fluidized bed boiler in Lidköping; the combustion system is showed in the next graphic.



Graphic 6. Bubbling fluidized bed system Fly-ash1.

- Ash 2 is a Fly-ash from a grate fired boiler firing waste in Linköping represented in the graphic below.

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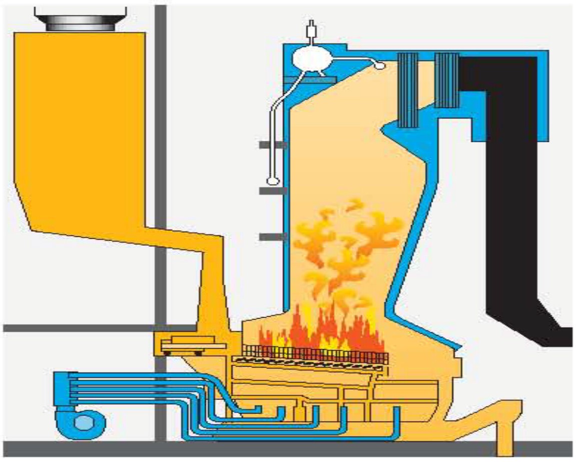


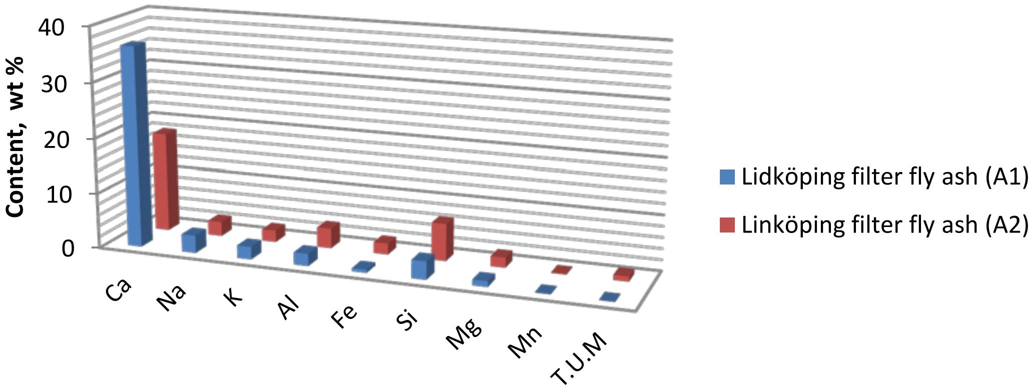
Graphic 7. Grate fired boiler system Fly-ash2.

The total analysis for both samples is presented in Table 10. Note that the concentrations of some elements have significant differences between the samples.

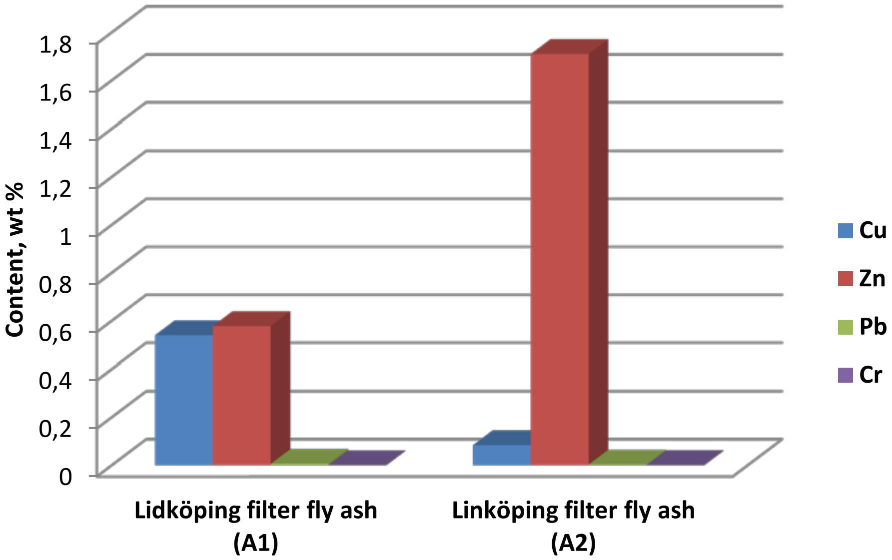
Table 10. Total analysis of samples 1 and 2.

	LIDKOPING	**LINKÖPING**
ELEMENTS	**(mg/Kg of filter fly ash)**	**(mg/Kg of filter fly ash)**
Ca	363000	180700
Na	31800	26100
K	22800	21100
Al	22200	36100
Fe	5600	20100
Si	32700	67300
Mg	10100	18100
Mn	574	1100
P	4000	5000
As	82,8	240
Ba	766	140
Be	1,17	< 2,5
Cd	88,6	83
Co	18,8	34
Cr	194	450
Cu	5400	840
Hg	2,81	<0,045
Mo	13	22
Ni	31,9	220
Pb	5730	3000
Sn	23,8	380
Ti	1860	14100
V	14	70
Zn	5780	17100
Cl$^-$	157000	31000
S (%by weight)	0,69	8,15
Total unburned matter (% by weight)	0,02	0,9

A diagram with the composition of fly ash samples of this work showed below, these values are subjected to variations depending on the sampling technique.



Graphic 8. Major elements in the samples analyzed in this work.



Graphic 9. Main trace elements in the samples analyzed in this work.

14. RESULTS AND DISCUSSION

Immediately after performing the 16 sequential extraction schemes on 2 different ashes, the different fractions were analyzed for Cu, Zn, using the ICP-MS and ICP-OES techniques. Subsequently the recovery was calculated, as well as, the metal recovery yields for each SES involved in the study.

14.1 METAL RECOVERY YIELDS

The metal recovery yields for the Lidköping sample were high (around an 80%) for the Cu and medium-high for the Zn (60%). Most of the values were below 100% due to the lack of a stage of total dissolution. The fraction left can be associated to silicates and other stable forms such as coated species which are very hard to leach. Similar yields are frequent in other similar studies [23] [37] [39].

For the sample of Linköping, the Zn yields were around the expected values (60%), but the Cu recovery yields were extremely high. This behavior suggests that there is an important error related to the measurement of the total Cu in the sample or to the measurement of the samples obtained. This variation can be attributed to the inhomogeneous characteristics of the fly-ash as well as the low content of Cu in the sample.

Table 11. Metal recovery yields in percentage.

METAL RECOVERY YIELDS (%)				
PLACE	**LIDKÖPING**	**LIDKÖPING**	**LINKÖPING**	**LINKÖPING**
ELEMENT	Cu	Zn	Cu	Zn
SES1	85	64	>100	54
SES2	87	68	>100	50
SES3	94	74	>100	73
SES4	70	54	>100	23
SES5	76	60	>100	49
SES6	87	64	52	39
SES7	97	64	88	61
SES8	128	94	97	46
SES9	92	67	>100	85
SES10	85	61	66	60
SES11	80	65	78	60
SES12	89	71	>100	62
SES13	86	68	>100	45
SES14	82	65	>100	53
SES15	96	69	>100	50
SES16	95	62	>100	40

14.2 METAL RECOVERY

Moreover the amounts of ash recovered were used to do the yield calculations are shown in the next table, these values are used as the final response for the Plackett-Burman experimental design.

Table 12. Metal recovery per SES, expressed in mg/Kg of filter fly ash.

METAL RECOVERY (mg/Kg of ash)				
PLACE	**LIDKÖPING**	**LIDKÖPING**	**LINKÖPING**	**LINKÖPING**
ELEMENT	**Cu**	**Zn**	**Cu**	**Zn**
SES1	2023	1639	5038	9282
SES2	1651	1378	1998	8470
SES3	1016	860	5347	12560
SES4	1130	936	886	3970
SES5	736	620	1336	8400
SES6	1128	893	436	6620
SES7	2092	1476	737	10400
SES8	1999	1568	815	7830
SES9	2180	1707	2470	14566
SES10	2156	1653	558	10209
SES11	1211	1046	659	10310
SES12	1152	984	1092	10650
SES13	1118	944	4337	7730
SES14	1109	936	3764	9022
SES15	1496	1162	3253	8530
SES16	2056	1441	1905	6839

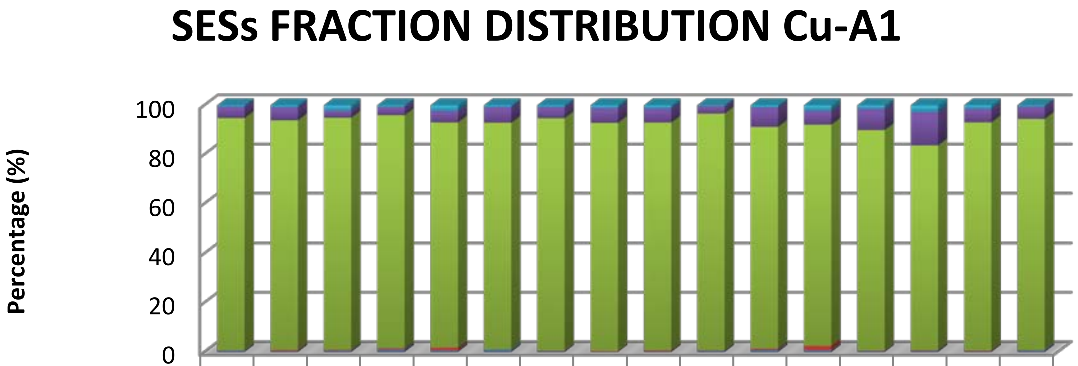
14.3 FRACTIONS DISTRIBUTIONS

The distribution of the leached fractions is shown in the following graphics to give an overview of the results. However, major conclusions cannot be made from these graphics since multiple variables are involved in each step.

14.3.1 COPPER from Lidköping fly ash.

The predominant fraction in this case was the carbonates and oxides surface bound copper, followed by the Fe-Mn oxides bound fraction. The third fraction was the organic bound fraction followed by the exchangeable fraction, and the least important fraction is the water soluble. However, regardless of the low contribution of water soluble Cu, the concentration in the leachate is still close to the legal limits of copper in drinking water (*the world health organization has established this limit value in 2 mg of Cu/L*)[WR-21]. This fact shows the hazardous potential of this sample [WR-7].

Linking this distribution to an analysis performed on this sample with the X-ray absorption spectroscopy (XAS) technique (Lassesson and Steenari), the species $CuSO_4.5H_2O$ (solubility in water, 2033 g/L (100 °C)) and CuOHCl (ionic character) were found, it is possible to suggest that these species are leached in the main fraction (Carbonates bound fraction) due to their solubilities [WR-19] [58].



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
🟦 Organic	0,5	0,8	2,2	0,7	2,4	0,8	0,7	1,2	1,3	0,3	0,9	2,3	1,5	2,8	1,5	0,5
🟪 Fe-Mn	5	5	3	3	5	6	5	6	6	3	8	6	9	14	5	5
🟩 Carbonatic	94	93	94	95	91	92	94	93	92	96	90	90	89	83	93	94
🟥 Exchangeable	0,1	0,6	0,4	0,5	1,1	0,1	0,2	0,3	0,5	0,2	0,5	1,7	0,2	0,4	0,3	0,1
🟦 Water	0,5	0,2	0,5	0,9	0,6	0,9	0,3	0,0	0,2	0,4	0,8	0,7	0,3	0,4	0,2	0,6

Graphic 10. SES Fraction distribution Fly-ash1 (Lidköping).

14.3.2 ZINC, FLY ASH FROM LIDKÖPING.

Concerning Zn, similar distributions were seen as for Cu (Lidköping). However, significant differences were observed for the carbonates bound fraction which was lower for Zn than for Cu and the fraction bound to Fe-Mn oxides that was higher.

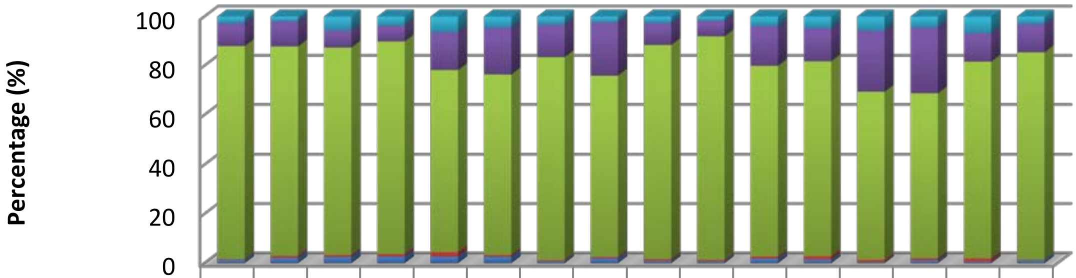
A higher hazardous potential was also observed for this sample compared to the second sample which its characteristics are going to be discussed later on this report[WR-6] ,for this purpose is important to point out that the world health organization stated a legal limit of 5 mg Zn^{2+}/L in drinking water[WR-7].

As this method is a sequential extraction procedure the deviation in the accuracy is accumulative, when the step of the extraction of the metals bound to carbonates is reached, the reagents agresivity increases. At this point the accuracy of the method is more susceptible to be affected, hence it is very important to have a good experimental practice and assure the experimental conditions. Once this fact is understood it is possible to observe that there is a relation between the selectivity and accuracy of the carbonates and the reducible fraction. Usually if the selectivity is high for the carbonates it is usually high for the reducible fraction. This phenomena occurs when there is no attack of unintented targets by the reagents involved in the extraction step of metals bound to carbonates.

When a lower attack of the carbonates fraction occurs a left fraction of the carbonates bound metal ion is very likely to be released in the reducible fraction, hence the accuracy of the extractions drops, a similar case occurs when the reducible fractions is attacked when the target is the carbonates bound fraction, the accuracy of both extractions drops. As the selectivities of these fractions are strongly linked, these two steps still a weak point in the sequential extraction design, a new method to evaluate and improve the accuracy related to this steps have to be developed, in this case the a parallel study made with the XAS technique gives out some ideas to have a reliable approach.

It was found with the XAS technique that the compound $ZnFe_2O_4$ is present in a level close to 30% of the total content of Zn in the Lidköping fly ash (Lassesson & Steenari, 2012)[58], this data is relevant, because it can be an important clue to increase the reliability of the measure of the selectivity for the fractions mentioned, when a comparison of that concentration is done with each SES, the closer value of concentration for the target specie ($ZnFe_2O_4$) is found in the SES 14 with a 27% of $ZnFe_2O_4$ in the total content extracted, It is interesting to point out the configuration of the pH (Main driving force in this extraction) for that singular SES in the carbonates bound extraction step, its value is (pH=5).

SESs FRACTION DISTRIBUTION Zn-A1

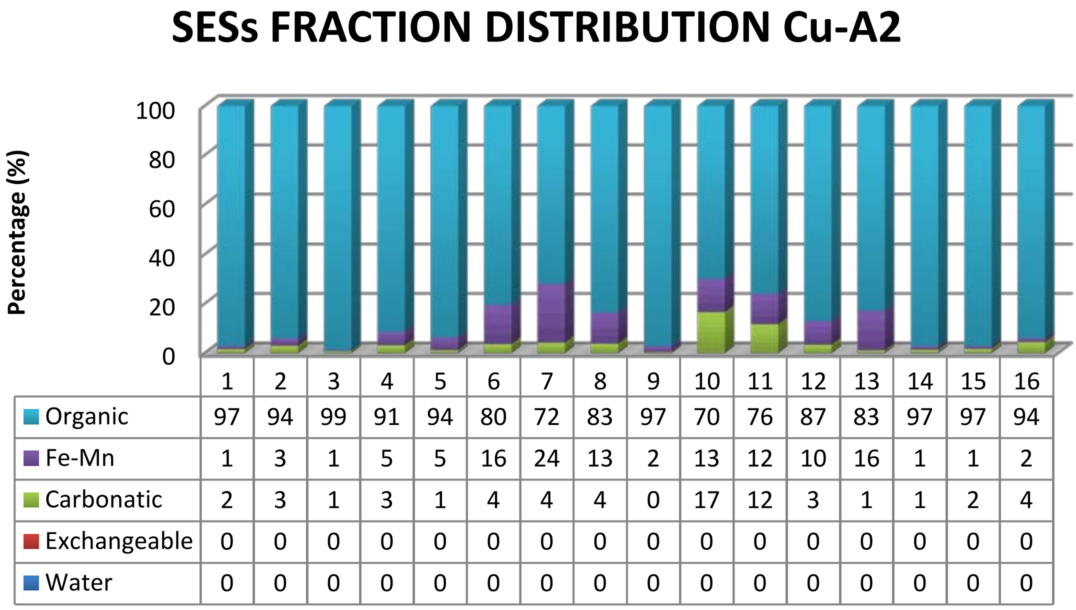


	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
🟦 Organic	2,8	2,0	5,6	3,8	6,4	4,6	3,4	2,4	2,7	1,7	3,9	4,8	5,8	4,5	6,8	3,2
🟪 Fe-Mn	9	10	7	6	15	19	13	22	9	6	16	13	25	27	12	11
🟩 Carbonatic	86	85	84	86	74	73	82	73	87	91	77	79	68	67	80	84
🟥 Exchangeable	0,4	0,8	0,8	1,0	1,8	0,8	0,5	0,5	0,7	0,6	0,9	1,4	0,9	0,9	1,3	0,3
🟦 Water	1,2	2,1	2,4	2,6	2,6	2,5	0,7	1,9	0,9	0,7	1,8	1,4	0,4	1,1	0,6	1,1

Graphic 11. SESs fraction distribution Zn Fly-ash 1 (Lidköping).

14.3.3 COPPER, FLY ASH FROM LINKÖPING

In contrast to the ash of Lidkoping, for the Cu distribution in the sample from Linköping was observed a predominant organic matter bound fraction. The influence of the water extraction and the exchangeable fraction for Cu in the general distribution was null. This characteristics can be explained because this ash contains activated carbon used for mercury adsorption in the flue gas channel.



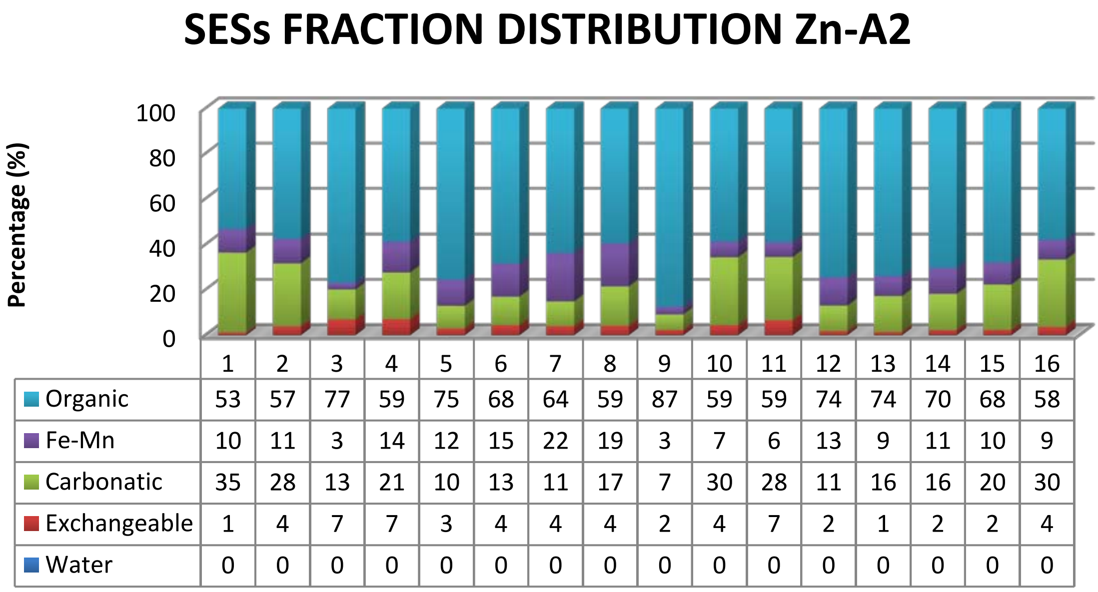
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
🟦 Organic	97	94	99	91	94	80	72	83	97	70	76	87	83	97	97	94
🟪 Fe-Mn	1	3	1	5	5	16	24	13	2	13	12	10	16	1	1	2
🟩 Carbonatic	2	3	1	3	1	4	4	4	0	17	12	3	1	1	2	4
🟥 Exchangeable	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
🟦 Water	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Graphic 12. SES fraction distribution Cu-ash 2 (Linköping).

14.3.4 ZINC, FLY ASH FROM LINKÖPING

The general distribution of fractions is slightly different for Zn comparing it to the Cu distribution of the Linköping sample since Zn was found to be present in each fraction except for the water extraction step.

The general leaching behavior for Zn in this sample shows a predominant organic fraction, followed by the carbonates fraction, in a third rank there is the Fe-Mn oxides fraction and in the last place is the exchangeable fraction. The water extraction values were statistically null.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
🟦 Organic	53	57	77	59	75	68	64	59	87	59	59	74	74	70	68	58
🟪 Fe-Mn	10	11	3	14	12	15	22	19	3	7	6	13	9	11	10	9
🟩 Carbonatic	35	28	13	21	10	13	11	17	7	30	28	11	16	16	20	30
🟥 Exchangeable	1	4	7	7	3	4	4	4	2	4	7	2	1	2	2	4
🟦 Water	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Graphic 13. SESs fraction distribution Zn Fly-ash 2.

14.4 DATA ANALYSIS AND TEST OF SIGNIFICANCE

With the Plackett –Burman experiment we can determine the direction and magnitude of an effect, some of them are positive or negative. The coefficient indicates how each variable affect the final response in percentage. These coefficients can be arranged in an equation to determine the optimum state for the best performance of each extraction related to each target.

The analysis of significance is determined with the Lenth´s method mentioned in the experimental design chapter.

NOTE: This chapter was condensed due to the **several coincidences in the effects of the variables for metals in the same sample, for this reason the following description of the Cu variables effect in both ashes allows this study to observe the main effects and their trends per sample,** regardless this shortening, relevant information and comparison of the effects with Zn is shown, (for further interest the Zn data is included in the annexes).

14.4.1 COEFFICIENT ANALYSIS

Once that the coefficients are obtained and knowing their main significance (variability in percentage of the metal recovery) it is important to recall a previous note for a proper read of the data: *It is important to note that A0, is the intercept, and the coefficients have this point as a reference, this point must be very close to a state where all the factors at the level (-). Hence a very negative or positive effect can have higher values than 100, and it has to be interpreted from a physical point of view to understand it clearly [41].*

Furthermore the method analyzes the effects of the variation of the factor levels, obtained through a mathematical treatment, not the factor in itself.

Table 13. Plackett-Burman coefficients for fly-ashes from Lidköping and Linköping.

TARGET	Cu LIDKÖPING	Cu LINKÖPING	Zn LIDKÖPING	Zn LINKÖPING
TERM	COEFFICIENT	COEFFICIENT	COEFFICIENT	COEFFICIENT
[NTA]	0,3	-6	0,2	-9
pH	-32	257	-37	88
[HH]	1,4	-17	0,8	78
LS1	0,4	-15	0,1	-22
LS2	0,9	-11	0,6	-18
LS3	-3,3	13	-2,2	18
LS4	0,4	-14	0,1	-22
LS5	-2,0	60	-1,3	98
t1	-4,7	113	-2,7	183
t2	-0,9	-22	-0,8	-34
t3	7,3	-236	2,2	-245
t4	17,5	-682	10	-1001
t5	30,8	-643	17	-958
AmAc	-2,9	66	-1,9	108
Carbon added	-821	-30600	-280	-44900

The different signs of the coefficients suggest that several variables have different effect for different target samples. To understand why these specific characteristics occur it is necessary to discuss the different effects more in detail.

The most relevant effect is that produced by the carbon added. The effect of carbon addition is negative in both cases; however in the Lidköping sample the effect value is less intense than for the Linköping sample. As was previously mentioned the Linköping filter fly ash was treated with active carbon.

The high adsorption potential of the active carbon is widely known, it has a large available surface of adsorption, frequently higher than 500 (m^2/g) [WR-19]. This increases substantially the available sites for adsorption. The presence of activated seems to enhance the process of resorption in both samples. The effect of carbon present has a significant bias because the exact amount of carbon added in the final treatment of the ash that comes from Linköping is not known.

Once the carbon effect was understood is easier to understand the behavior of the rest of the other effects; the Lidköping ash was free of a carbon treatment and the effects are coincident with the expected values.

For instance in the Lidköping sample a higher pH resulted in a lower release of Cu (as well as of Zn), higher concentrations of the reagents and times of extraction result in higher release of metals except for the ammonium acetate concentration which showed an opposite effect probably due to a major effect of the nitric acid in which it was diluted.

Note: For the Lidköping fly ash the pH concentration linked to the nitric acid present was more important than the ammonium acetate effect, in the lower level the proportion of nitric acid was the 90% in volume compared to an 80% in volume of the ammonium acetate solution in the higher level.

The variations in liquid to solid ratios were observed to give a low magnitude in the coefficients which means that these ratios are not very significant but still susceptible to be optimized, the trend that orientates the right direction for the optimization was detected.

Analyzing the Linköping sample, the higher magnitude effects were the same as for the Lidköping fly ash sample, but their sign was opposite, this may be linked to the carbon effect. Since the presence of carbon surface sites is so large it probably hides the effects of variations in other parameters.

This data suggest that probably higher values of metals release were reached in the sample from Linköping at the highest factors configuration (pH, concentration and times of extraction) but the availability of the centers of adsorption was abundant, hence the speed of the resorption process was higher than the leaching in the different steps of the SES, resulting in lower values for some of the high levels used in some factors.

14.4.2 OPTIMIZATION OF THE FACTORS

The optimum combination of variables was determined by optimization of the equation (1). Nonetheless is important to mention that the mathematical optimization value of the pH was 4.5, but due to the paired observation with the XAS technique of the compound $ZnFe_2O_4$ in a level close to 30% of the total content of Zn in the Lidköping fly ash (Lassesson & Steenari, 2012)[58], was possible to determined that the pH 5 was more convenient to reach a higher selectivity and efficiency of the method in the carbonates bound and iron and manganese fractions (Highlighted in the table 14).

In the table below the optimization of the different targets is shown. The setup of Lidköping is more reliable than the Linköping due to the observed effect of the carbon present in the resorption process. Hence the improvement of the SES is reliable and valid for the Lidköping filter fly ash sample but it is not for the Linköping filter fly ash sample.

Table 14. Optimized set up for Cu and Zn from Lidköping and Linköping

PLACE	Cu LIDKÖPING	Cu LINKÖPING	Zn LIDKÖPING	Zn LINKÖPING
[NTA]	200 mg/L	0 M	200 mg/L	0 M
pH	5	5	5	5
[HH]	0,5 M	0,04 M	0,5 M	5 M
LS1	20	N/A	20	N/A
LS2	20	N/A	20	30
LS3	60	60	60	60
LS4	100	50	100	50
LS5	90	90	90	90
t1	10 min	N/A	10 min	N/A
t2	10 min	N/A	10 min	10 min
t3	7 h	5 h	7 h	5 h
t4	7 h	6h	7 h	6 h
t5	7 1/2 h	7 1/2 h	7 1/2 h	5 ½
AmAc	10%	20%	10%	20%
Carbon added	0	0	0	0

14.4.3 TARGET EFFECT OF THE VARIABLES.

In Table 15 the ratios (CZn/CCu) and (CCu/CZn) show how each factor contribute to the final response comparing the two metals studied.

For the most relevant sample (Lidköping) due to the higher reliability of the results for that sample, the factors have more impact on Cu than on Zn, with the exception of the pH, which is more relevant for Zn. This indicates a higher mobility of the Zn species than for the Cu species present in this ash.

Another effect is the contribution of the carbon showing that Cu has a higher affinity to carbon than Zn does.

In the second sample a significant part of the Cu available is probably already attached to the activated carbon added in the flue gas treatment, hence the effect of the variables on the leaching behaviour of the Cu is lower for this ash than for the Lidköping sample.

Table 15. Effect of the SESs on each metal Fly-ash1 and Fly ash 2.

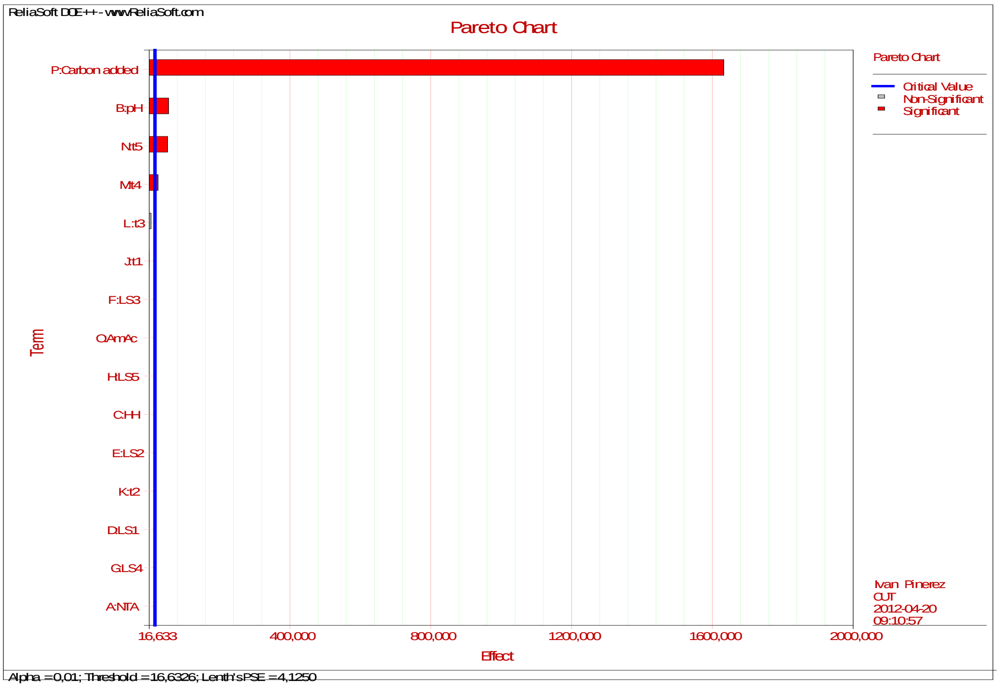
PLACE	**LIDKÖPING**	**LINKÖPING**
TERM	**(CZn/Ccu)*100**	**(Ccu/CZn)*100**
[NTA]	56	65
pH	117	291
[HH]	56	22
LS1	31	66
LS2	70	62
LS3	68	71
LS4	35	63
LS5	66	61
t1	58	62
t2	83	67
t3	30	96
t4	59	68
t5	56	67
AmAc	64	61
Carbon added	34	68

14.4.4 TEST OF SIGNIFICANCE

In the Pareto chart, the variables are organized in decreasing order of effect. There is also included a study of the level of significance of the variables with a 99,9% of confidence accoding to the Lenth´s method, the hierarchy order is shown in the graphic.

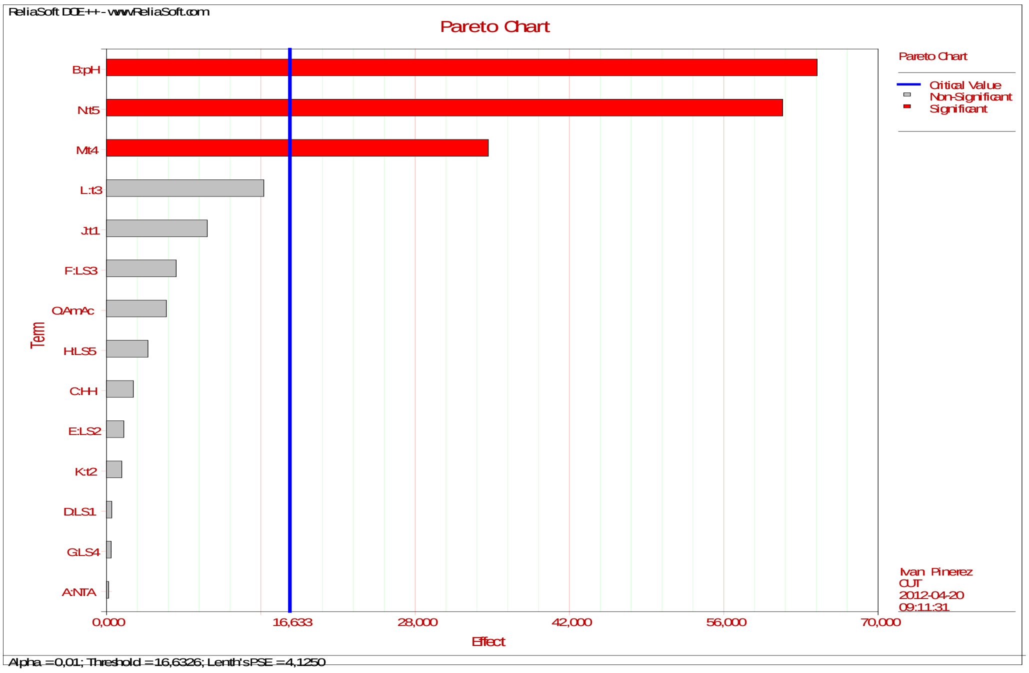
The hierarchy of the effects caused on each factor is in decreasing order for Cu (Lidköping) as follows, Carbon added, pH, t5, t4, t3, t1, L/S 3, [NH4Ac], L/S 5, [HH] , L/S 2, t2, L/S 1,L/S 4 and [NTA] . The threshold of a risk level of 0,01 indicates the division between the significant and non-significant variables, **being the significant ones the Carbon added, pH, t5 and t4**, the significant variables were coincident in the hierarchy of importance with the Zn results.

There were differences in the order for the non-significant variables, but this is meaningless according to the test of significance.

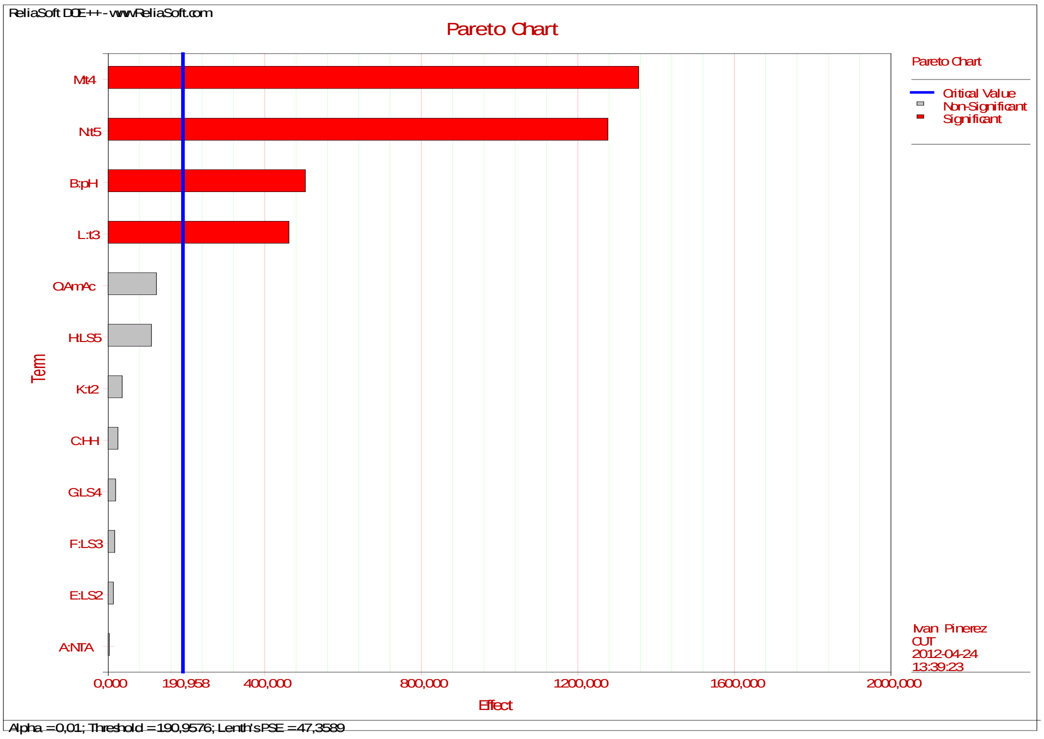


Graphic 14. Variables pareto chart Cu Fly-ash1.

As the effect of the presence of carbon is very strong a second chart where the effects of other variables are magnified is presented below.



Graphic 15. Variables in the pareto chart without the Carbon effect, Cu Fly-ash2.

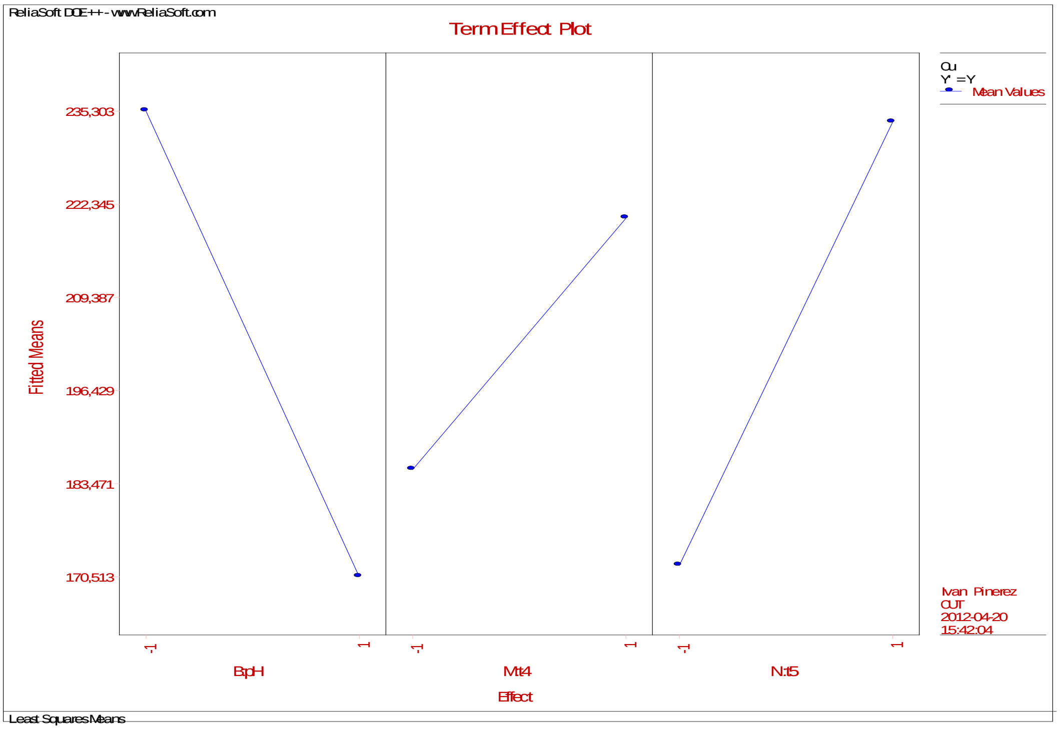


Graphic 16. Variables in the pareto chart without the Carbon effect, Cu Fly-ash2.

14.4.5 TERM EFFECT

In the following chart the term effect for the significant variable for the Cu (Lidköping) is presented, considering the two states for each variable. As the presence Carbon effect is strongly negative and does not allow a good visualization, it was eliminated from the graphic.

Here it is possible to see the negative effect of rising the pH level, as well as the positive effect of increasing the time of extraction of the Fe-Mn oxides bound fraction and the Organic matter bound fraction. Similar trends were observed for the Zn (Lidköping).



Graphic 17. Term effect of significant variables without the Carbon effect Cu Fly-ash1.

For the significant values in Cu (Linköping) was found that:

- The effect of the Carbon presence was strongly negative.
- The effect of increasing t4 was negative.
- The effect of increasing t5 was negative.
- Theeffect of increasing the pH to 5 was positive.
- The effect of increasing t3 was negative.

The general meaning of this results were discussed previously.

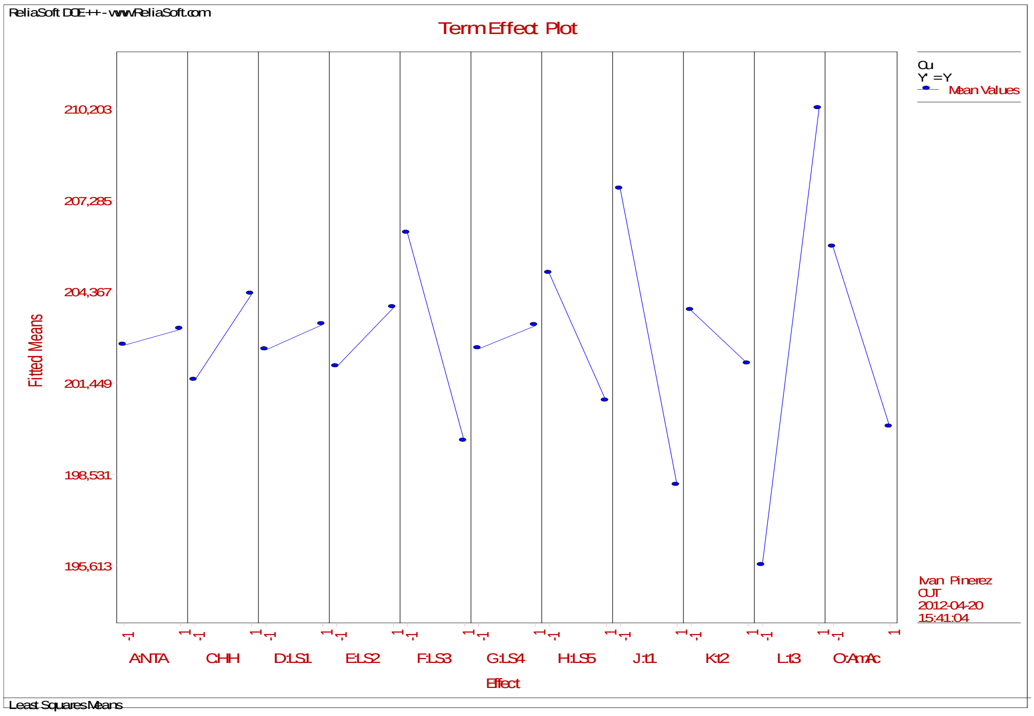
14.4.6 NON-SIGNIFICANT VARIABLES

According to the theory, the presence of non-significant variables is not very relevant at the time of state a clear hierarchy of the main effects in order to realize the final optimization, nevertheless their effect can be physically interpreted with the term effect chart.

The statistical effect of the non-significant variables for the Cu (Lidköping) are shown in the next figure. The graphic shows the effect of increasing each variable set up level from (-1) to (1). The trends were the same for the Zn in the same sample.

The general trends are resume like this for non-significant variables:

- NTA has a positive effect when it is used.
- An increased concentration of Hydroxilamine Hydrochloride enhances the extraction in the reducible fraction.
- Increasing L/S 1 has a positive effect.
- Increasing L/S 2 has a positive effect.
- Increasing L/S 3 has a negative effect.
- Increasing L/S 4 has a positive effect.
- Increasing L/S 5 has a negative effect.
- Increasing t1 has a negative effect..
- Increasing t2 has a negative effect.
- Increasing t3 has a positive effect.
- An increase in ammonium acetate concentration has a negative effect.



Graphic 18. Term effect of non significant variables Cu Fly-ash1.

In the case of the Linköping samples the effects of other variables was unclear due to the presence of carbon as it was previously discussed, anyway the trends are presented below.

- NTA has a negative effect when present.
- Hydroxilamine Hydrochloride enhanced the extraction in the reducible fraction by having a lower concentration.
- Increasing L/S 2 has a negative effect.
- Increaing L/S 3 has a positive effect.
- Increasing L/S 4 has a negative effect.
- Increasing L/S 5 has a positive effect.
- Ammonium acetate concentration has a positive effect when it is increased.

14.4.7 RESUME OF EFFECTS

- The effect of the presence of carbon was very large, giving a low leachability of both Cu and Zn. This effect is probably related to the available surface for adsorption on the carbon. It is very likely that it has enhanced the resorption of metal ions.

- The presence of NTA was positive but not significant, probably due to the strong effect of the Carbon which was its antagonist driving force. However, these results showed that the NTA was not an aggressive chelating agent.

- The increased concentration of Hydroxilamine hydrochloride resulted in a higher release of reducible metal species, as well as a higher liquid to solid ratio and time of extraction, reinforcing the idea of an incomplete extraction in other SES such as the Tessier one.

- The increased concentration of the inhibitor of resorption Ammonium Acetate was negative which was not expected. Since it was diluted in Nitric acid it can be suggested that the volume of nitric acid used in the dilution its more important than the Ammonium Acetate present is.

- Concerning to the liquid to solid ratios, they were positive in L/S 1(Water), L/S 2(Exchangeable) and L/S 4(Reducible), using lower ratios could cause saturation of ion metals in the extraction liquid for the fraction 1, 2 and 4.

- The behaviour of the L/S 3(Carbonates) and L/S 5 (Organic) was unexpected and negative, for some unknown reasons by increasing the liquid to solid ratios disminishes the leaching yields. This effect should be further investigated.

- In relation with the data refered to time extractions set up, the time in extraction steps 1(Water extraction) and 2 (Exchangeable) show that these two extraction steps are susceptible to resorption.

- On the other hand increasing the t3(Carbonates), t4(Reducible), and t5(Organic) was positive for the metal extraction yield. In these three fractions chemical reactions occur that would need time to react properly with the susbtrate, and if this time is not optimized the selectivity of the extraction may be low.

- A drop in the accuracy of the analysis of the fly ash from Linköping is due to the high potential of resorption present in the filter fly ash (Active Carbon treatment).

Comment: in the anexes are included several squares diagrams were all the interactions per fraction can be seen. They were used to confirm the optimization values and the effect interaction of the parameters per fraction, its effect is resumed in the optimizated set up of variables per each metal in each ash sample.

15. CONCLUSIONS

15.1 SAMPLES

- The final treatments made on the ashes have a huge effect on the metals distribution, Lime added (Lidköping), activated Carbon added (Linköping).
- Higher recovery yields for Copper than for Zinc in both samples were observed.
- For the carbonates bound fraction, Zinc is more susceptible to be leached under acidic conditions in a filter fly ash that has not been treated with active carbon. For a filter ash that includes activated carbon a lower pH in the leaching of carbonate bound Cu leads to a higher release.
- Lidköping filter fly ash contains more of water soluble Cu and Zn compared to the Linköping fly ash.
- For a determined ash and using the ratios made from the Plackett-Burman coefficients, it was observed that the effects of the different factors had different repercussions for each metal.

15.2 VARIABLES

- Times of extraction t4 and t5 should be optimized in first place when a SES is improved.
- The pH set up is a critical factor that could increase the accuracy of the method.
- Liquid to solid ratio and concentrations were not significant variables but their trends towards to the optmization were detected.
- NTA Effect was probably masked by the presence and huge effect of Carbon, but its non-significance characteristic is a positive result related to the low agressivity of the chelating agent, hence its selectivity can be very appropiated to lower the resorption problem.
- In the fractions were NTA was not used, the resorption process was more evident, being the time of contact the main variable.

15.3 SEQUENTIAL EXTRACTION SCHEMES.

- A comparability through a multivariable analysis of different SES was succesfully applied to different SES.
- The significant variables and non significant variable in order of importance were detected for each metal using different configurations of the SESs.
- Each variable effect involved in the study effect was observed on a determined ash and metal.
- A Semi-optimum SES has been proposed for each target.
- Accuracy can be improved by linking other techniques (total analysis and XAS).
- Clear differences and different distribution of species were seen and explained for the ashes analyzed with these schemes, so they probably are a good approach to understand the metal speciation, but their accuracy must be increased.

- Positive suggestions of previous studies were included (water extraction, NTA, new concentrations).
- Ideas of previous studies were analyzed and more valuable data has been acquired.

16. SUGGESTION FOR FURTHER STUDIES

- Perform a similar analysis on an artificial ash substrate to measure the accuracy of an optimized SES.
- Study the pH and the leaching behaviour within the context of the SESs.
- Evaluate the effect of the variables without the presence of carbon.
- Increase the levels of study to reach the real optimum for each sample.
- Perform replicates of the experiment to reduce the variability of results in order to perform more reliable contrast tests.
- Perform more studies in different ashes.
- Link the SES to the speciation with synchrotron based X-RAY absorption spectroscopy metal speciation results.

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AGRADECIMIENTOS

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