CHALMERS
UNIVERSITY OF TECHNOLOGY

Enhanced Soil Washing

A Study on Treatment of Copper Polluted Soil and Bark

Master's Thesis in the Master's Programme Infrastructure and Environmental Engineering

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Cover:
Investigated site at Långö in Köpmannebro.

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ABSTRACT

According to a survey performed by the county administration boards in Sweden, there are over 80 000 sites where the levels of contamination vastly exceeds its surroundings. Many of these pollutants are the remains from former industrial operations, such as chemical industry, tree impregnation, mining and dry cleaning. When it comes to metal contamination, excavation followed by landfilling is the most commonly used treatment method. However, as a consequence of stricter EU legislations along with the fact that many of the landfills of today are beginning to reach their maximum capacity, the need for new remediation methods is substantial.

In this study, a lab scale evaluation was made on the effectiveness of enhanced soil washing on soil and incinerated bark from a site at Långö outside Köpmannebro. The material at this site was heavily polluted by copper, which is the substance of interest in this study. The report focuses on the leaching capabilities in large samples compared to previous research conducted at Chalmers University of Technology. In the leaching experiments, the leaching agent consisted of an acidic process water, a waste product from the flue gas cleaning after waste incineration. After the initial experiments a precipitation test was conducted on the leachate in order to evaluate the possibilities to extract the copper from the solution.

The leaching experiments showed a large variation in the success of copper removal from the solid material. In the soil samples 71-74 percent was successfully removed, while the ash leaching had a removal rate of 9-50 percent. An attempt to reach a higher removal rate on the ash was made, using a mix of process water and 3M HCl, which then successfully removed 87 percent initial copper. This gives a strong indication of the impact that pH has on the copper removal rate, which is why further investigations regarding optimal pH for this method is needed.

A precipitation of copper was attempted in leachate. The attempt was more successful in the ash leachates, with ~99.9 percent effectiveness, while the soil leachates precipitated between 68-81 percent of the containing copper.

Key words: Contaminated soil, Soil washing, enhanced soil washing, acidic leaching, copper, mercury, precipitation

Förstärkt Jordtvätt
En Utredning av Behandling av Kopparförorenad Jord och Bark

Examensarbete inom masterprogrammet Infrastructure and Environmental Engineering

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SAMMANFATTNING

Enligt en undersökning utförd av länsstyrelserna i Sverige finns det över 80 000 platser där föroreningsnivåerna kraftigt överstiger dess omgivningar. Många av dessa föroreningar är resterna från tidigare industriverksamhet, i huvudsak från den kemiska industrin, träd impregneringsindustrin, gruvindustrin och kemtvättsverksamheter. När det gäller metallföroreningar är urschaktning och deponi den vanligaste behandlingsmetoden. Men som en följd av skärpt EU-lagstiftning tillsammans med det faktum att många av dagens deponier börjar nå sin maximala kapacitet, är behovet av nya saneringsmetoder stort.

I denna studie har en laboratorieutvärdering av effektiviteten för en jordtvättsmetod utförts på jord och förbränd bark som hämtats från Långö utanför Köpmannebro. Materialet på denna plats var kraftigt förorenat av koppar, som är metallen i fokus i denna studie. Rapporten syftar till att undersöka urlakningens effektivitet i större prover jämfört med tidigare forskning som bedrivits vid Chalmers Tekniska Högskola. I urlakningsexperiment har ett surt processvatten från rökgasrening efter förbränning av avfall, använts som lakmedium. Efter de initiala experimenten utfördes fällningsförsök på lakvattnet för att utvärdera möjligheterna att utvinna koppar från lösningen.

Lakningsförsöken visade en stor variation i framgång för avlägsnande av koppar från det fasta materialet. I jordprover har 71-74 procent av kopparn avskilts, medan ask-urlakningen avlägsnade 9-50 procent av totalmängden koppar i materialet. Ett försök att nå en högre urlakningsgrad på askan gjordes med hjälp av en blandning av processvatten och 3M HCl. Med hjälp av denna metod lyckades 87 procent av det initiala kopparinehållet avlägsnas. Detta gav en tydlig indikation på hur pH inverkar på urlakningsprocessen, vilket tyder på att mer undersökningar gällande vilket pH som är effektivast för denna metod behövs.

Fällningsförsöket var mer framgångsrik för askans lakvatten, med ~99,9 procent av all koppar utfälld, än för jordens lakvatten som fällde ut mellan 68-81 procent av det totala kopparinnehållet.

Nyckelord: Förorenad mark, jordtvätt, förstärkt jordtvätt, sur lakning, koppar, kvicksilver, fällning

Contents

Preface

This study regarding enhanced soil washing of soil and ash has been conducted at Chalmers University of Technology during spring semester 2015. We would like to extend our deepest gratitude to our supervisor Karin Karlfeldt Fedje for her incredible support and guidance during the course of this project. We would also like to express a warm thankfulness to Mona Pålsson for her company, moral support and continuous assistance in the lab. Without their help, writing this report would never have been possible.

We would also like to thank Jesper Knutsson for assistance with ICP-MS analysis and preparation, Ann-Margret Strömvall for guidance and support and Britt-Marie Wilén for assistance with dissolving of solid samples.

Notations

BV/h – bed volumes per hour
Enhanced soil washing – a variation to soil washing where adjustments of liquid medium, leaching time or number of sequential leaching steps can be made, to allow less soluble metal pollutants to be removed from the material
Ion-exchange resin – a material which can adsorb ions in exchange for other ions
KM/MKM – criteria with guideline values for sensitive and less sensitive land use
L/S ratio – the relationship between liquid and solid material
Leachate – the liquid medium after a leaching experiment
Leaching agent – the liquid medium used in a soil washing process
Leaching time – the time a material is exposed to mechanical mixing with a leaching agent.
Lewatit® TP 214 – the ion-exchange resin used in this study for removal of mercury
Process water – the liquid rest product from flue gas cleaning after waste incineration, used in this report as leaching agent
Soil washing – a remediation technology which uses liquids, often water together with some sort of mechanical process to scrub soils
A3 – Ash sample with L/S 3 used in the batch leaching experiment
A3w – washing water from sample A3
A5 – Ash sample with L/S 5 used in the batch leaching experiment
A5w – washing water from sample A5
A7 – Ash sample with L/S 7 used in the batch leaching experiment
A7w – washing water from sample A7
A5a – Ash sample with L/S 5 (leached with addition of 3M HCl) used in the batch leaching experiment
S3 – Soil sample with L/S 3 used in the batch leaching experiment
S3w – washing water from sample S3
S5 – Soil sample with L/S 5 used in the batch leaching experiment
S5w – washing water from sample S5
S7 – Soil sample with L/S 7 used in the batch leaching experiment
S7w – washing water from sample S7
Report 1 – Report previously conducted at Chalmers (Eriksson & Johansson, 2013)
Report 2 – Report previously conducted at Chalmers (Khmilkovska, 2014)
Kemakta – Report previously conducted by Kemakta Konsult AB (Kemakta Konsult AB, 2012)

1 Introduction

The report is divided into two blocks; initially the studied area is presented together with a review of the current legislation in the field of soil remediation and landfilling in Sweden. Further, a literature study is presented, containing facts and information relevant for the experimental procedures in block two. The second block presents the practical laboratory work, followed by results and conclusions.

1.1 Aim and objectives

The aim of this project is to investigate a method for leaching copper from contaminated soil and bark. The report will focus on assessing the effectiveness of the method for large samples, removal of mercury from the leaching agent and characterising the extracted metal product to evaluate its quality and recycling potential.

More specifically the objectives of the report are to:

- Attempt to remove mercury, present in the leaching agent, using an ion-exchange resin.
- Remove copper from soil and ash samples by leaching with an acidic process water.
- Evaluate if the effectiveness of the leaching experiment using larger samples then in previous studies at Chalmers University of Technology.
- Extract copper from the leachate by precipitation with sodium hydroxide (NaOH)
- Briefly investigate the access to acidic process waters in Sweden and the industrial interest for the copper product, regarding purity and quantity.
- Give recommendations for further research.

1.2 Limitations

All sample material in the report will be gathered from a site in Långö outside Köpmannebro. The leaching experiments will be performed with an acidic process water from the flue gas cleaning at Renovas municipal waste incineration plant.

1.3 Research questions

- How effective is the leaching experiment in larger samples compared to the previous studies?
- Can the mercury be successfully removed from the acidic process water?
- Is it possible to precipitate copper out of the leachate and is the purity of the copper sufficient for recycling?
- Can the solid remains be deposited at a landfill with regards to the Swedish landfill legislation?

2 Background

According to a survey performed by the county administration boards in Sweden, there are over 80 000 sites where the levels of contamination vastly exceeds its surroundings (Nordin, 2013). Many of these are the remains from former industrial operations, such as the chemical industry, tree impregnation, mining and dry cleaning.

When it comes to metal contamination, excavation followed by landfilling is the most commonly used treatment method. Landfilling of contaminated material in Sweden 2008 amounted to 377 000 tons out of which a large portion originated from contaminated soil (Karlfeldt Fedje, et al., 2014). Sweden had at that time 157 landfills open, out of which 28 were open for contaminated waste (SEPA, 2014a). Today landfills throughout the country are beginning to reach their maximum capacity, while it is more difficult to get permission to open new ones. This is a consequence of the EU directive for landfilling came around in 2009. Since then, many of the landfills have been closed and more are closing each year as a result of the stricter legislations concerning landfilling of toxic material. Because of this, new methods for remediation are needed in order to meet the demands for the future.

Even if the primary goal with soil remediation is to reduce the environmental hazards, reports indicate that out of a socioeconomic point of view, it might be of interest to extract the metals and at the same time reduce the spread from the landfilling area (SGU, 2014a). During 2013, 46 sites contaminated with various substances were remediated with governmental funding (SEPA, 2014b). This is the highest number yet and an increase of more than 50 percent from the previous year. In addition, over 530 sites were treated by private actors under the same year. Since the 1980’s, over 2300 sites among risk class 1 or 2 have been treated out of which 373 objects falls under risk class 1 (Nordin, 2013).

2.1 Studied site

The site investigated in this report is located on the small peninsula of Långö, south of Köpmannebro which is presented in Figure 2.1. Up until the late 1920’s, the site was used by Televerket (formerly known as Kungliga Telegrafstyrelsen), housing an industry for impregnation of telephone poles (Kemakta Konsult AB, 2012). Logs were shipped by boat to Långö, where they were impregnated according to the Boucherie method. The Boucherie method involves injecting copper sulphate through the root-end of a tree, into the sap stream, until the liquid started dripping from the branches and the top of the log. Since copper sulphate is a fungicide, highly toxic to microorganisms, a saturated pole was considered to be completely impregnated. When the process was completed after 5-15 days, the twigs and bark were removed from the log and left at site. The bark then contained high concentrations of copper, which has leached into the soil over time, and is the main source of the contamination. It has been estimated that 30 tonnes of copper is present in the area, valued to approximately 1.5 million SEK.

Due to the limited decomposition of bark, there is a complete absence of vegetation in the contaminated area, which can be seen in Figure 2.2. To the south, the site neighbours 5 private properties, while it is bordering to Dalsjön in the western and northern parts (Kemakta Konsult AB, 2012). To the east, there is a sharp line where the contaminated area turns into to vegetated woodland.

Figure 2.1. Location of the investigated site, Långö in Köpmannebro, (Google, 2015).

The investigated area covers around 20 000 m^3 and consists of clay, till, peat and large deposits of bark. The upper soil layers measure 50 to 17100 mg Cu/kg dry material while the deeper sediments measure slightly less, about 70 to 7400 mg Cu/kg dry material (Springfors, 2001). The thickness of the bark varies between 0.2 and 1.8 meters, and covers around 8000 m^2 of the total area (Kemakta Konsult AB, 2012). Thus, the contaminated bark volume have been approximated to 8000 m^3. In the bark there is a present copper concentration of 2900 to 37200 mg/kg dry material (Springfors, 2001).

The surface in the area is generally covered with bark with the exception of a few outcrops of rock. As can be seen in Figure 2.2, there is complete absence of plants or other types of vegetation in the area.

Figure 2.2: A part of the investigated area at Långö, Köpmannebro. The picture is taken in a northbound direction (Kemakta Konsult AB, 2012).

3 Literature review

This literature review includes information about existing techniques, as well as some of the latest findings, in the fields of metal recovery and treatment of contaminated soil. Current knowledge regarding the two metals, Cu and Hg, is also presented in the following chapter.

3.1 Contaminated sites

Contaminated sites are often associated with improper disposal or spillage of a substance, causing an excess amount of the material in an area. The contamination is of concern when it poses a threat to the land owner or user, the environment and/or the second hand users of the land (SEPA, u.d.). Depending on what type of substance that is causing the contamination and the conditions at the site; plants, wildlife and human health might be at risk of harm. It may also be of concern to the land owners due to financial and legal implications. Over time, leaching of contaminants may occur, causing the pollutants to enter bodies of water, such as streams and lakes. This can have a negative impact on the aquatic life and the water as a source for drinking.

3.2 Legislation

When dealing with contaminated material, there are several systems and guidelines that classifies the material, based on its content. These classifications can be used to determine the treatment priority for a contaminated site or how to dispose of the material.

3.2.1 MIFO classification method

The MIFO risk classification (Method for inventories of contaminated sites), according to which the contaminated sites have been divided, contains four different classes as presented in Table 3.1 (SEPA, 2003). In order to assess the risk class at any given site, four different issues are evaluated related to the overall risk:

- Hazard assessment
- Contamination level
- Potential for migration
- Sensitivity/protection value

Each of the four aspects contains one to four levels and ultimately all four aspects are weighed together in a final assessment to assign a specific site its corresponding classification.

Table 3.1. The different risk classes in the MIFO classification.

Classification	Description
Class 1:	Very high risk
Class 2:	High risk
Class 3:	Moderate risk
Class 4:	Low risk

So far, basically all governmental funding is provided for sites of risk class 1 and 2 (Nordin, 2013). Since the 1980’s, over 2300 sites among risk class 1 or 2 have been treated out of which 373 objects falls under risk class 1.

3.2.2 Limits for contaminated land

In addition to the classification method presented in MIFO, the Swedish EPA has developed a simplified model to produce limit values for contaminated land. These limit values are derived from calculations on typical conditions at contaminated sites in Sweden (SEPA, 2009).

The model has been produced for two different types of land use, sensitive land use (KM) and less sensitive land use (MKM). Limits for the KM- and MKM-criteria have been developed with four different objects in mind which are presented in Table 3.2.

Table 3.2. Parameters of interest for classification according to the KM-MKM criteria (SEPA, 2009).

Protected object	KM – Sensitive land use	MKM – Less sensitive land use
People present in the area	Full time stay	Part time stay
Soil conditions in the area	Protection of the soils ecological function	Limited protection of the soils ecological function
Groundwater	Protected within and adjacent the area	Protected 200 m downstream from the area
Surface water	Protection of surface water and water living organisms	Protection of surface water and water living organisms

The limits from the model presented in Table 3.3 states a level of contamination for which the risk of negative impact on humans and/or the environment is generally acceptable. It is important to point out that the limits produced for this model are to be used as a guide in risk assessment and are not legally binding.

Table 3.3. Limits in solid material according to the KM-MKM criteria (SEPA, 2009).

Substance	KM [mg/kg]	MKM [mg/kg]
Sb	12	30
As	10	25
Ba	200	300
Pb	50	400
Cd	0.5	15
Co	15	35
Cu	80	200
Cr	80	150
Hg	0.25	2.5
Mo	40	100
Ni	40	120
V	100	200
Zn	250	500

3.2.3 Landfilling legislation

In cases where the contaminants exceed the values for KM and MKM, landfilling may be considered

In 2004 a new regulation on material disposal by landfilling came out (SEPA, 2007). The main purpose was to reduce the negative impacts imposed by landfills on the environment with regard to surface water, groundwater, air as well as the greenhouse effect. This is why, contrary to KM and MKM, the landfilling classifications are describing concentrations in the leachate caused by precipitation.
In Sweden, each landfill needs to be categorised as one of three following classes:

- Landfill for inert waste
- Landfill for non-hazardous waste
- Landfill for hazardous waste

In order to assess according to which class a certain contaminated soil or other material should be disposed, shaking or percolation tests are to be performed and compared with the limits presented in Table 3.4 at a liquid to solid, L/S, ratio of 10 (SEPA, 2007).

Table 3.4. Limits for leachates evaluated with the SS-EN 12457-3 standard leaching test, developed as a tool for classification of waste material (SEPA, 2007).

Element	**Inert waste**	**Non-hazardous waste**	**Hazardous waste**
As	0.5	2	25
Ba	20	100	300
Cd	0.04	1	5
Cr	0.5	10	70
Cu	2	50	100
Hg	0.01	0.2	2
Mo	0.5	10	30
Ni	0.4	10	40
Pb	0.5	10	50
Sb	0.06	0.7	5
Se	0.1	0.5	7
Zn	4	50	200
Cl^-	800	15 000	25 000

3.3 Mercury

Mercury is an element that exists naturally in air, water and soil. It is most familiar in its pure form as a liquid metal, also referred to as quicksilver due to its volatility (Green Facts, 2015). However, it is more commonly found in inorganic mercury compounds, or mercury salts, in the shape of powder or crystals.

The largest sources of mercury emissions to the air caused by humans are coal-burning power plants and small scale gold mining (SEPA, 2014). Other sources of mercury contamination include burning of hazardous waste, chlorine production and improper treatment and disposal of products containing mercury. In the past it has been commonly used in products such as thermometers, batteries, light bulbs and cosmetics.

Mercury is a highly volatile metal, which is easily transported over great distances in the atmosphere (SEPA, 2014). Since mercury is not degradable, it assimilates in soil, water and living organisms. Once it has been deposited, micro-organisms can methylate inorganic mercury and form methylmercury, MeHg (Swedish Environmental Protection Agency, 2014). Methylmercury is accumulated in the aquatic food chain and consumption of seafood is the most common way of human exposure (US Environmental Protection Agency, 2014). High levels of mercury can cause damage to the nervous system and unborn babies, still developing their nervous system, are the most sensitive to exposure (Swedish National Food Agency, 2014). Research shows that children, whose mothers consumed larger quantities of methylmercury, suffer from slower growth and development than others.

3.4 Removal of heavy metals with ion exchange resin

As has been revealed in previous research conducted at Chalmers University of Technology, the concentration of Hg in the final residues has been sharply increased after the acidic leaching with the process water (Khmilkovska, 2014). Thus, this report will make an attempt to reduce the Hg concentration in the process water in order to obtain a final product of better quality.

Ion exchange methods can be used for the purpose of removing heavy metals from flue gas residuals. The ion exchange process is an interchange of ions between a solid (the ion exchange resin) and a liquid, as shown in Figure 3.1. In this report a *Lewatit® TP 214*, which has shown great selective for Hg(II) ions, was operated in order to remove mercury from the process water (Dąbrowski, et al., 2004). According to Andersson[1] at Lanxess, the resin has a high affinity towards Hg as well as noble metals, such as Au and Ag, and platinum metals, such as Rh and Pd. Heavy metals, such as Cu, Zn and Pb, might also bind to the resin. However, when a metal with higher affinity to the resin passes through, it will switch places with one of lower affinity. Thus, the resin will not be saturated prematurely from a solution containing too much Pb, but rather keep it until there are more Hg ions to exchange it for.

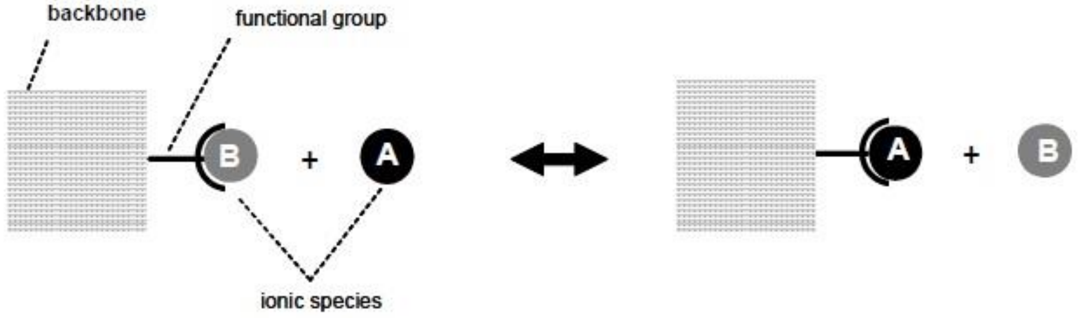

Figure 3.1: The ion exchange reaction is based on the interchange of ions between a solid (resin) and a liquid, without changing the structure of the solid (Neumann, u.d.).

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[1] Stefan Andersson Lanxess, e-mail conversation, 2015-03-25.

3.5 Copper

Copper is a metallic element mainly found in ores containing copper sulphide minerals. It has a high thermal and electrical conductivity, which makes it suitable for applications such as heat exchangers, heat sealing devices, wires and cables (European Copper Institute, u.d.). When copper is exposed to the atmosphere it is able to form stable compounds, in form of oxide layers and basic salts, which act as protection from corrosive attacks. The corrosion process is therefore relatively slow compared to most of the common metals. Because of these properties, copper is the third most consumed industrial metal, only beaten by iron and aluminium in terms of quantity (U.S. Geological Survey, 2015). The general access to copper is good, which can be explained by the fact that 40-80 percent of the used copper is recycled, accounting for about 9 percent of the total copper consumption in the United States and up to 50 percent of the annual copper consumption in Sweden (U.S. Geological Survey, 2014) (Swedish National Heritage Board, 2013).

The consumption of copper has increased significantly since 2004, mainly due to a rising demand in Brazil, China and India (Seth, 2012). The increased demand has also led to a doubling of the copper price, from about 2500 Euro/t in 2004 to about 5000 Euro/t in early 2015, see Figure 3.2. This is one of the reasons to evaluate the possibilities to use the method described in this report for extraction and recycling of the copper product.

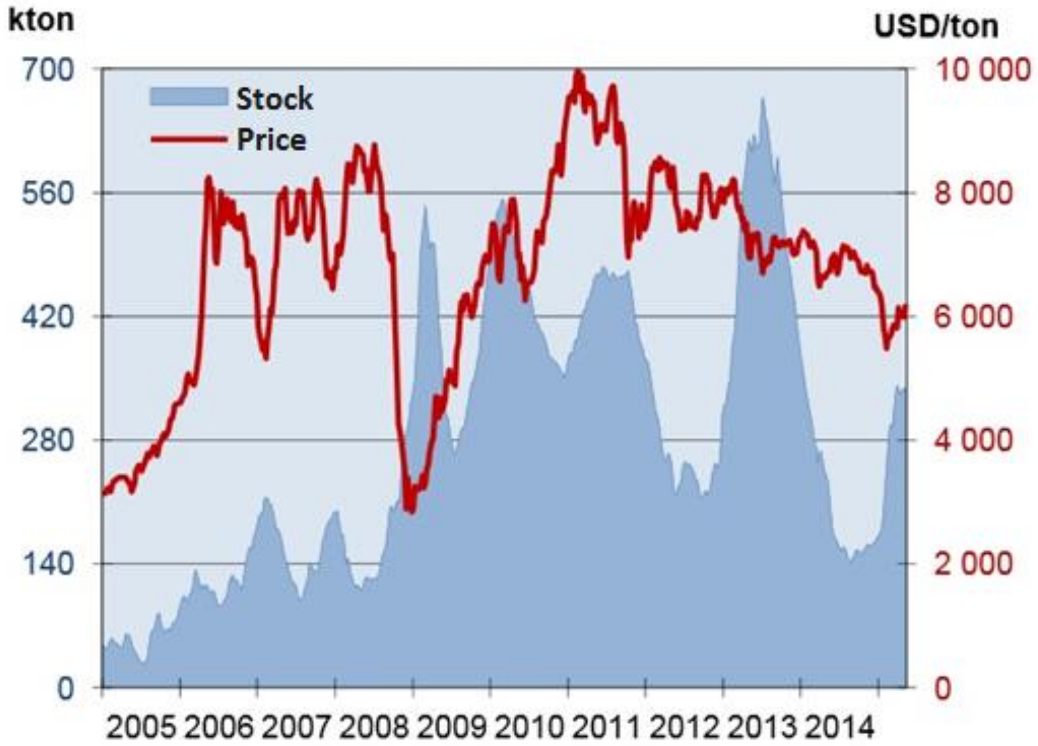

Figure 3.2: The price of copper over the past 10 years (SGU, 2015).

3.5.1 Copper contamination

Copper, in different forms, exists naturally in soil and is essential for the growth of plants (Schulte & Kelling, 1999). The concentration usually ranges from 2 ppm to 100 ppm, with an average of 30 ppm. However, excessive amounts of copper in the soil can be toxic and have negative effects on the environment. High levels will disrupt the nutrient cycle and prevent the mineralisation of important nutrients. Leachate entering nearby waters has also proven to be harmful to the aquatic life. However, depending on the chemical composition and the presence of water in the area, the solubility of copper can be low and will therefore not have a significant impact on the surroundings. This also means that if no treatment is applied to the area, these conditions will persist for a long time.

3.6 Incineration

According to current legislations, the polluted material at Köpmannebro cannot be deposited as waste at a landfill since it mainly consists of bark, which is an organic material (Kemakta Konsult AB, 2012). To take care of the masses, incineration of the bark has been considered as the main alternative. Incineration would also be advantageous if the material were to be treated through enhanced soil washing. Since bark is highly absorbent and the organic content can form strong chemical bonds to metals, incinerating the material would not only decrease the volume but also release more of the metals during a leaching process (Eriksson & Johansson, 2013).

3.7 Treatment methods

There are several existing solutions for treating contaminated soils, both in-situ and ex-situ. Some techniques are based on extracting the contaminants from the soil, while others focus on preservation in order to prevent the contaminants from leaching to a greater area.

There are also several ways and additions to the soil washing procedure. Depending on the conditions in the polluted material, different techniques can be applied to optimize the extraction of contaminants, while limiting the use of leaching agents.

3.7.1 Containment

One group of treatment procedures called containment methods include techniques such as caps, vertical- and horizontal barriers. These methods aim to restrict the water flow in to and out of the contaminated area (USEPA, 1997). Caps refer to covering the surface of a landfill or contaminated site, in order to minimize the infiltration of groundwater, improve the stability and aesthetics of the surface and to control the emissions of gases and odour. Vertical barriers are created by techniques such as grouting boreholes, filling trenches with slurry and forming sheet-pile walls around the contaminated area. The vertical barriers will restrict the movement of groundwater in the area, keeping the contaminants from leaching. Horizontal barriers are created to seal off the contaminated area from underneath without having to remove the contaminated material.

3.7.2 Solidification/Stabilisation Technologies

Solidification and stabilisation technologies refers to a group of techniques that involve mixing or injecting the polluted material with treatment agents (USEPA, 1997). These techniques can be used for several reasons, including:

- Solidifying a contaminated material that is in the form of a liquid or semi-liquid.
- Reducing the solubility of the contaminants in order to keep them restricted in the specific area.
- Reducing the permeability of the contaminated material in order to limit the contact with liquids.

Solidification/stabilisation is most commonly used by mixing the treatment agent to form a solid container around the waste particles, restricting their movement and contact with their surroundings.

3.7.3 Vitrification

By inserting electrodes into the ground of the contaminated site, an electric current can be passed between them in order to melt soil (CPEO, u.d.). The process starts at the ground surface and as the soil melts, the electrodes move deeper in to the ground. The organic material is pyrolised, while the metals melt and become a part of the vitreous mass. This process is called vitrification. When the current is turned off, the soil cools down and creates a solid block, much like the solidification technique, preventing the contaminants from leaching and keeping them within the contaminated area.

3.7.4 Phytostabilisation

Phytostabilisation refers to minimizing the mobility of metals in soil by using vegetation as a soil stabiliser (The University of Hawaii, u.d.). The plants can protect the contaminated area from erosion, caused by wind and rain, and reducing the solubility of the pollutant. The mobility is also restricted through adsorption, accumulation and precipitation within the root zone. Phytostabilisation is useful at large-scale areas having low contamination, where other remediation methods are not feasible due to extensive costs.

3.7.5 Phytoextraction

Phytoextraction, or phytoremediation, is a technique to restore contaminated areas by extracting the pollutants through plants (Lasat, 2002). The plants can accumulate high concentrations of inorganic material, especially metals, and thereby removing it from the soil. When the plants are fully grown and stocked with contaminants, they are harvested and disposed of according to what contaminants they have accumulated. The effectiveness of this method depends on several factors, for example, geographical location, extent of the contaminated area and type of plant, soil and contaminant. It is also limited to the area and depth of the plants root system.

3.7.6 Soil flushing

Soil flushing is similar to soil washing in terms of treating the soil by extracting the contaminants from the polluted material (Shammas, 2009). Soil flushing is however performed in-situ by injecting water, or a water based solution, in to the ground. Once it has passed through the contaminated zone, the water is collected at strategically placed wells and the contaminated elutriate is recovered by pumping the water back up to the surface again.

3.7.7 Soil washing

Soil washing is a treatment method commonly used in both Europe and the United States. The method can be divided into physical separation technologies and chemical extraction processes (Dermont, et al., 2008).

Physical separation

In some cases, the pollutants are concentrated to a certain fraction of the soil. When this is the case, the leaching procedure could be optimized by adding a physical pre-treatment, separating the particles through sieving, and treating the fractions based on their content. To achieve a more accurate separation than sieving, there are several methods commonly used to separate different sized particles.

One technique is hydrocyclones, which is a type of centrifuge that separates particles greater than 10–20 µm (Mulligan, et al., 2001). A fluidized bed uses floatation and settling to separate particles smaller than 50 µm. In the case of Köpmannebro, a previous report indicated that the concentration of copper was equally distributed over all tested fractions (Khmilkovska, 2014).

Gravity concentration is another method which involves separating particles based on their gravity (Sierra Fernández, 2013). The method utilizes the particles relative movement in a viscous fluid which commonly means water or air. To be able to use the method successfully, there is an absolute necessity to have a difference in density between the contaminated material and the material that is considered clean.

Magnetic separation is a method which takes advantage of the fact that measurements can be made to show how strong a correlation is between the magnetic properties of a soil and its pollutant contents (Sierra Fernández, 2013). This method utilizes this correlation to remove the pollutants from contaminated soil, where materials with a positive susceptibility are attracted by the magnetic field while those with a negative susceptibility are repelled.

Chemical extraction

This refers to technology which desorbs and makes metals present in the contaminated soil or other material soluble by using a chemical reagent (Sierra Fernández, 2013).

Conventional soil washing is a technology which uses liquids, often water together with some sort of mechanical process to scrub soils (USEPA, 1996). A simple explanation of the process could be to compare it with a conventional washing machine for laundry, where the soil is mixed with the scrubbing solution and placed in some sort of scrubbing unit before being agitated. The wash water is then drained out for the material, which can be done for instance with a centrifuge or similar device. The remaining soil is then washed with clean water in order to get the remaining contaminants out of the material.

Enhanced soil washing can be used to describe the soil washing technique where adjustments are made with regard to liquid medium, leaching time or number of sequential washing steps. For instance by addition of acid, the solubility of cation metals increase with the lowering in pH, while addition of a base agent works in an opposite manner (SGI, 2012). In previous studies, acidic process water from the wet flue gas cleaning at a waste incineration plant has shown great leaching capabilities for Cu, which is why enhanced soil washing is the technique chosen for the experiments in this report (Karlfeldt Fedje, et al., 2013).

3.8 Metal recovery

Recovery of metal from contaminated soils is today a field with very limited experience in Sweden. Experiments have been made on lead contaminations, where a combination of soil washing and on-site electrolysis, after which the metals have been processed (SGI, 2012).

One of the main challenges with recycling of metals in highly contaminated soils is that the metal contents are generally too low to be handled in a metallurgical process, and that the risk of contaminating the final product with other trace metals is high.

This chapter will go through some of the available techniques to extract metals from the leachate after the soil washing procedure.

3.8.1 Precipitation of metals

Heavy metals are common contaminants in industrial wastewaters (Armenante, 1997). Because of their toxicity, it is often beneficial with removal prior to discharge. One of the most common methods to remove heavy metals is by alkaline precipitation with hydroxides. The precipitation generally follows the reaction presented in Equation 1.

$$M^{+n} + nOH^{-} \leftrightarrow M(OH)_n \qquad \text{Equation 1}$$

Since many heavy metals are amphoteric, their solubility reaches a minimum at a specific pH. For Cu this specific pH level is 9, which is also the pH the report aims to reach during the precipitation experiment.

3.8.2 Electrolysis

One way to recover copper from a copper-containing solution is to use electrolysis. It is a common and often crucial step in the industrial production of large quantities of copper (Davenport, et al., 2002). The acidic solution dissolves the copper compounds leaving Cu^{2+} ions. An electric current is connected to an anode and a cathode to create a flow of electrons and a redox-reaction. The copper ions are reduced at the cathode by receiving electrons and thus forming Cu. This process requires a lot of energy and is therefore quite expensive.

3.8.3 BES

Copper has previously been successfully recovered from leachate using a Bioelectrochemical System (BES). The procedure is a type of electrolysis but instead of using an external power source the BES is used as a microbial fuel cell (Karlfeldt Fedje, et al., 2014). This process allows for spontaneous current flow where no additional electrical energy is needed. First a salt solution, containing copper, is acclimatised in the cathode compartment during a period of four weeks. When the acclimatisation is complete, the actual leachate from the soil/ash can be used in the copper-recovery process. In the study conducted by Karlfeldt Fedje, et al., (2014) on similar leachates that are used in the present study, it was shown that copper could be selectively extracted from the leachate with only minor contaminations from other metals.

3.9 ICP-MS Analysis

Inductively Coupled Plasma–Mass Spectrometry, or ICP-MS, is an instrument used to detect trace elements (PerkinElmer, Inc., 2011). In the ICP-M S, the analysed solution is turned into an aerosol, which is hit by argon plasma with a temperature of about 6000 °C. The aerosol is dried and its atoms are separated and charged by the removal of one electron. This process forms singly-charged ions, which are sent to the mass spectrometer. The mass spectrometer is a filtering device, scanning through the mass range and only letting particles of a certain mass-to-charge ratio pass by at a time. When the ions pass through the mass spectrometer they hit an electron multiplier, setting of an electric pulse. The software compares the pulses to a standard calibration curve and is thereby able to determine the concentration of each element.

The samples analysed in ICP-MS are usually divided into two categories: liquids and solids. Before analysing the contents, the samples need preparation in order for the results to be as accurate as possible (Chalmers University of Technology, u.d.). Common preparation for samples includes addition of internal standard, acidification, filtration and dilution. The solid samples are normally digested in a microwave, where the content of the sample is dissolved in a strong acid under high temperature.

4 Method

4.1 Sampling

In this study, samples from previous investigations will be combined with new samples, gathered from Långö outside Köpmannebro. Samples from previous investigations includes all soil samples and a minor amount of the total bark mass. The previously collected bark was taken at ÅF5, KEM1300 and KEM1 presented in Figure 4.1. The sampling took place at ÅF7 and KEM8 on FIGURE. The sampling was done at approximately 30 cm depth with stainless steel shovels. A large plastic sack was used to transport the material back to the lab, in which it was later stored for the duration of this project.

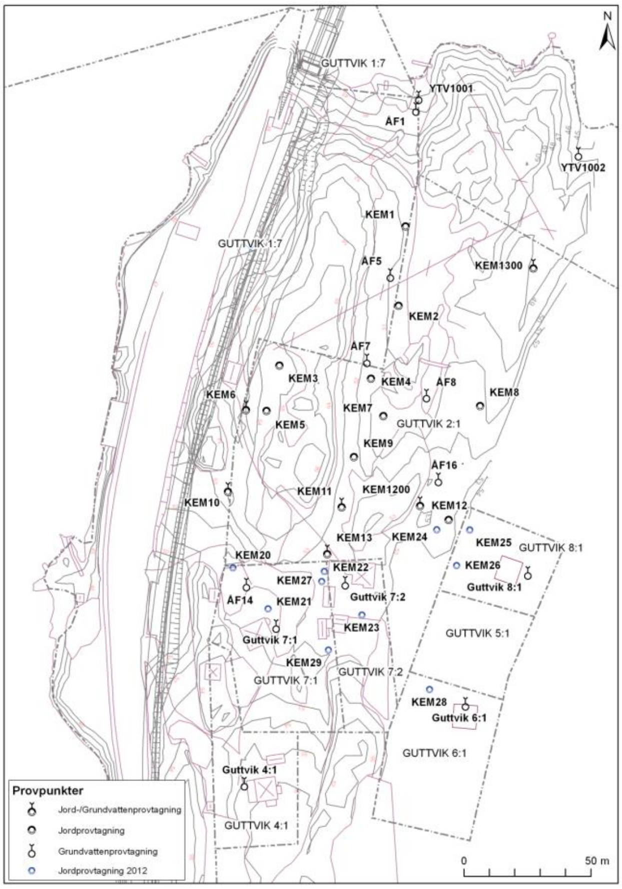

Figure 4.1. Sampling locations at Långö in Köpmannebro.

4.2 Experimental procedure

For the laboratory work to be as smooth as possible, it is important to plan ahead each step of the working process. For this reason, a flow chart, describing each step in the laboratory, was produced, see Figure 4.2.

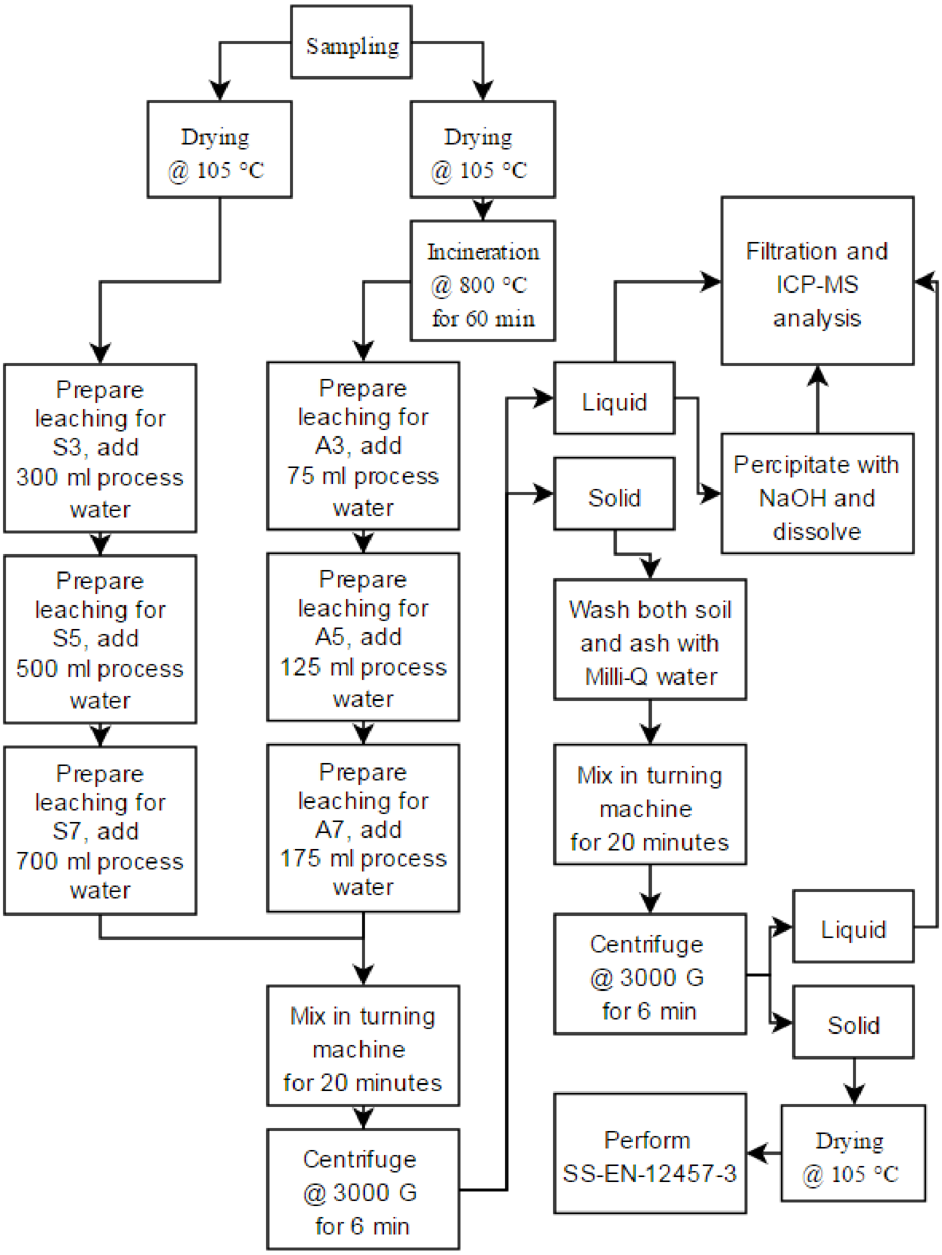

Figure 4.2. Descriptive flowchart of the experimental procedure.

4.3 Laboratory work

4.3.1 Sample preparation

Initially, the bark and the soil samples presented in Figure 4.3 a) and b), are weighed before they are separately put into the oven at 105 °C, to be dried for approximately 24 hours. The bark and soil samples, are then weighed again after being stored in a desiccator until they have reached constant weight. The bark sample is then incinerated at 800 °C for one hour and put in a desiccator for cooling, see Figure 4.3 c). The resulting ash is weighed in order to calculate the material loss from the incineration process. Figure 4.3 d) shows the soil after being mechanically ground by a mortar.

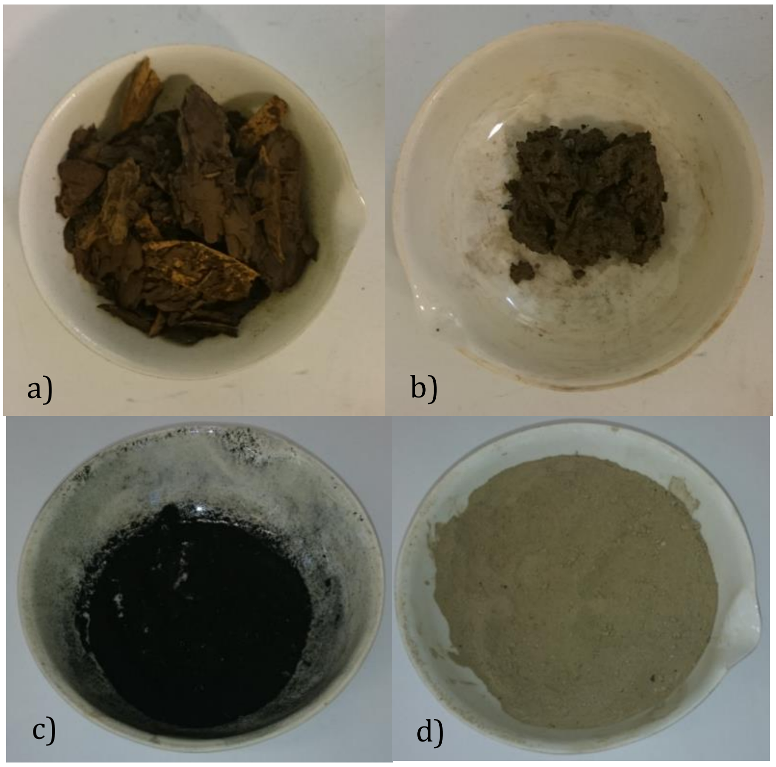

Figure 4.3. a) Bark before incineration, b) Soil before drying, c) Bark (ash) after incineration, d) Soil after drying and grinding.

4.3.2 Incineration

Two kinds of ovens were used in the incineration process of the bark. First it was dried along with the soil in a Thermo Scientific Heratherm oven for at least 24 hours, at 105°C. Once dry, it was transferred into a CSF 1200 carbolite furnace which is presented in Figure 4.4. In the initial trials the bark was put into the oven at 650°C, for 1 hour. Since the resulting incineration rate was not satisfying, the temperature settings of the oven were changed to 800°C. The dried bark was hereinafter transferred into the oven at room temperature, heating up along with the oven in a process that takes approximately 1.5 hours. When the temperature reached 800°C, a timer was set to 1 hour. When the time was up, the incinerated bark was brought out of the oven and kept in a desiccator to cool down, before it was finally grinded into a fine powder in order to enhance the upcoming leaching process. Due to the size of the oven and the ventilation capacity, an amount of approximately 50 grams of bark could be incinerated at a time.

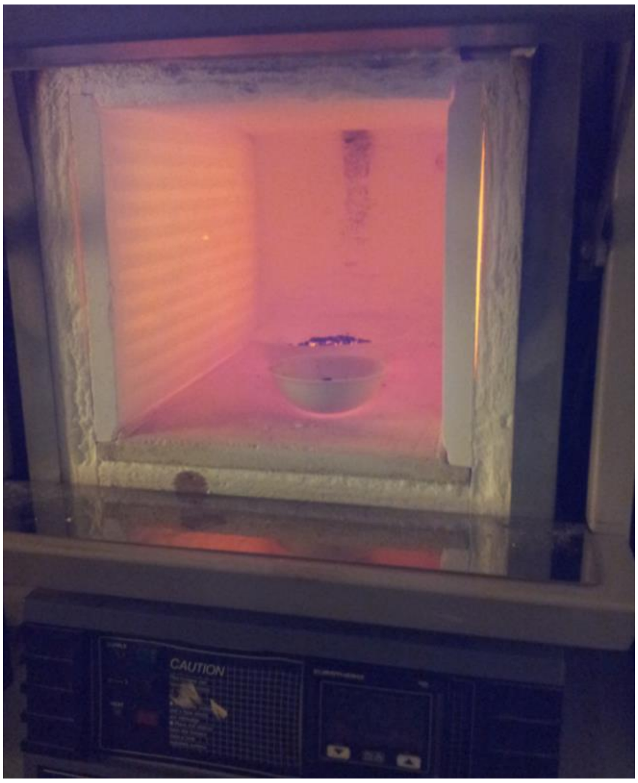

Figure 4.4. Bark incinerated in a CSF 1200 carbolite furnace heated to 800 °C.

4.3.3 Solid samples

In order to analyse the content of the solid samples, such as the original metal concentrations in the soil and ash, the samples need to be dissolved in a solution prior to the ICP-MS analysis.

From each solid sample, 0.25-0.5 grams of dried material was accurately weighed in and added to a PTFE test vessel, customised for the sample carousel in the microwave oven which are both displayed in Figure 4.5. To each vessel, 5 ml of Milli-Q water and an equal amount of nitric acid was added. The vessels were placed in protective sleeves, sealed with expanded plastic caps and heated in the microwave oven. After a cool-down process, the samples were weighed and transferred into 14 ml Falcon tubes. Any weight difference was compensated for by addition of a solution consisting of 1:1 Milli-Q water and nitric acid. The readily soluble elements are at this point considered to be dissolved in the solution and the sample can be analysed in the ICP-MS using a dilution rate of 1:100.

The ICP-MS analysis of the dissolved ash samples showed unreliable concentrations compared to what have been previously seen in Report 1. For this reason, a sample of the original ash was sent to an external laboratory for a second analysis. Results from the external analysis is presented in section 5.1.

Figure 4.5. a) Sample carousel used in the microwave oven. b) MARS5 Microwave oven.

4.3.4 Removal of Hg from the leaching agent

Previous studies have discovered that mercury, present in the leaching agent, has a tendency to adsorb to the solid material during leaching (Khmilkovska, 2014). The aim of the laboratory test is to investigate the effectiveness of the *Lewatit® TP 214* resin with regard to chemical and physical adsorption of mercury.

The ion-exchange unit was built by tightly packing glass wool in the bottom of a column, using it like a filtering device, to keep the resin from going through the column. A specified amount of *Lewatit® TP 214* was mixed with Milli-Q water and added on top of the wool as can be seen in Figure 4.6. The column was then rinsed with small amounts of process water, in order to prevent the water in the resin from diluting the final product. The rest of the column was filled with process water and the tap was opened slightly to allow the acid to slowly filter through the ion-exchange resin. A desired specific velocity for such a filtration test is in the range of 1 BV/h to 100 BV/h (Neumann, u.d.). Once the column started to run out of process water, it was immediately refilled or stopped, always keeping the resin surface from getting in contact with the air.

Figure 4.6. The Lewatit® TP 214 column set up for operation.

For the process water used as a leaching agent in this report, the column kept a constant flow with a specific velocity of about 3 BV/h. The effectiveness of this treatment method was evaluated by analysing the content of the solution in an ICP-MS. For future reference, a trial run with a specific velocity of 15 BV/h was also analysed in the ICP-MS.

4.3.5 First cycle

Prior to the main leaching test, a downscaled trial version was carried out in order to evaluate the leaching technique. In order to produce the leaching agent, Hg-treated process water was diluted 3:1 using Milli-Q water, according to a method tested in a previous report from Chalmers University of Technology (Khmilkovska, 2014). Diluting the process water allows for a more sustainable leaching process, since the volume of process water can be reduced.

5 g of dried soil was weighed into 9 different sample tubes, numbered 1 to 9. The samples were divided into groups of three where 15 ml, 25 ml and 35 ml of the leaching agent was added to each of the groups respectively, in order to study the influence of L/S. To create an optimum leaching procedure, the samples were mixed using a modified Edmund Bühler 7400 Tübingen SM25, shaking table (see Figure 2.2). The samples from each L/S-ratio, were shaken for 20, 30, and 40 minutes respectively, creating a matrix with unique combinations of L/S-ratios and leaching times. A summary of the experimental set-up is presented in Table 4.1.

Figure 4.7. Principle picture, showing the setup of the Edmund Bühler 7400 Tübingen SM25 shaking table.

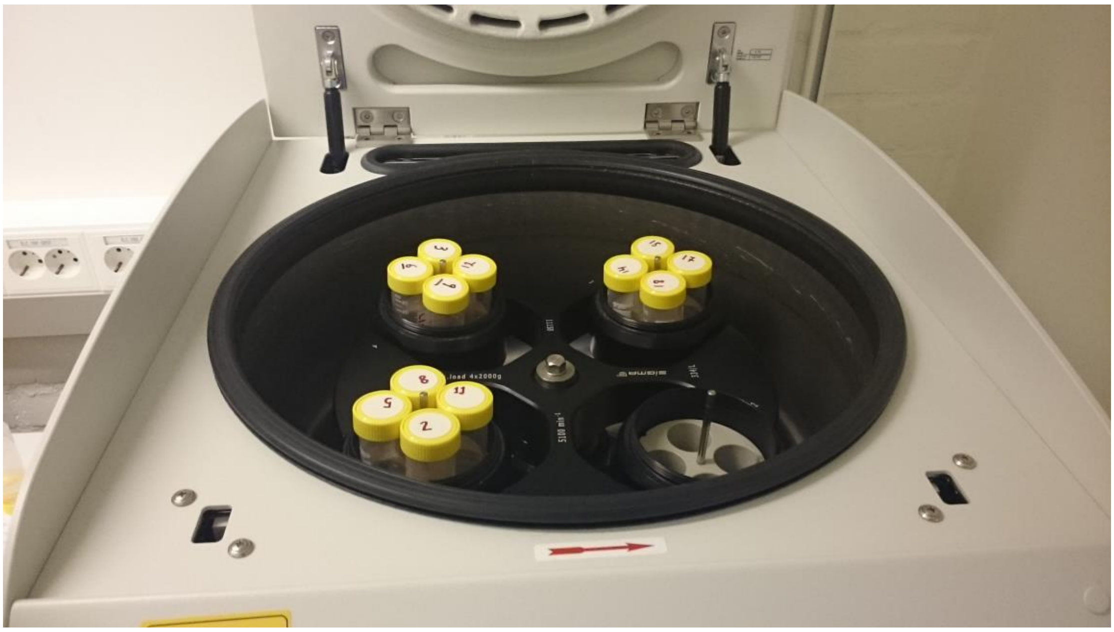

Figure 4.8. Samples prepared for separation in Sigma 4-16.

To separate the leachates from the soil, the sample tubes were put in a Sigma 4-16 centrifuge at 3000G for 15 min, see Figure 4.8.

Table 4.1. The experimental set-up for the first cycle, where the leaching time was optimised.

Sample nr	L/S ratio	Leaching agent (ml)	Leaching time (min)	Centrifuge (min)
2	3	15	20	15
3	3	15	30	15
4	3	15	40	15
5	5	25	20	15
6	5	25	30	15
7	5	25	40	15
8	7	35	20	15
9	7	35	30	15
10	7	35	40	15

From the separated samples, a micropipette was used to extract 5-10 ml of leachate out of each sample tube which was used to create new samples, solely containing leachate. Each new sample was diluted 1:100 with Milli-Q water and sent to ICP-MS analysis.

4.3.6 Batch leaching

For the batch leaching, 100 g samples of dried soil and 25 g samples of ash were measured into one-litre plastic storage bottles. To each sample, leaching agent was added to form L/S-ratios of 3, 5 and 7 respectively. From this point, the samples will be denoted as A7, A5 and A7 for ash and S7, S5 and S7 for soil. The bottles were placed in a Styrofoam box, using foam rubber to keep them in position. The box was fastened in a turning machine, borrowed from the geotechnical laboratory, which was used to mix the samples during the leaching process which is presented in Figure 4.9. Based on the small scale leaching of soil samples, it was concluded that an increased leaching time, from 20 to 30 or 40 minutes, had a negligible impact, see results in section 4.3.5. It was therefore decided to leach both the soil and the incinerated bark for 20 minutes respectively.

Figure 4.9. Leaching in progress using a turning machine borrowed from Chalmers geotechnical laboratory.

When the leaching process was finished, the samples were transferred into 500 ml pp-bottles, custom-made for the centrifuge. To separate the liquids from the solids, the samples were then centrifuged in a Sigma 4-16. In order to create a balance in the centrifuge, the samples were weighed in and symmetrically matched with blank samples. The centrifuge was set to 3000 G for 3+3 minutes to ensure that the solids were not too tightly packed in the bottom of the bottles.

From each separated sample, 10 ml of eluate was extracted, filtered and prepared for ICP-MS analysis. To cover the possibility that the filter would not completely withstand the acidic environment, another 10 ml of each sample was extracted and prepared for the same analysis, unfiltered.

In addition to the batch leaching, one more sample was leached with slightly different settings. In a similar fashion as the samples in the first cycle, a 1 g ash sample was leached using L/S 5 but with a modified leaching agent. Instead of diluting the process water with milli-Q, the leaching agent consisted of 4 parts process water and 1 part 3M HCl, in order to keep the alkaline ash from affecting the pH level.

4.3.7 Washing of soil residues

Following the batch leaching process, a washing step with the intention of further inducing a release of copper ions from the residue was performed. In an earlier study conducted at Chalmers University of Technology, the washing step was done by pipetting milli-Q water onto a bed of solid residues and letting it stand for two minutes to allow the water to soak into the material (Khmilkovska, 2014). The water was then sucked out of the residues with a vacuum filtration device as presented in Figure 4.10.

Figure 4.10. Principle set-up of the vacuum filtration device used in the project.

In this report, the washing was done in a similar manner but with some alteration. After the batch leaching was completed and the residues had been separated from the leachate, milli-Q water was added to the residues at an L/S ratio of 0.6. The samples added to 500 ml plastic PP-bottles and placed in a padded Styrofoam box. The box was put in a turning machine, acquired at Chalmers geotechnical lab, for 20 minutes to make sure that all material were in contact with the water. When the mixing was complete, the washing water was separated from the residues by means of vacuum filtration.

The washing water and the residues are then stored for further analysis.

4.3.8 Precipitation of Cu from leachates

The experiment was performed using a Heidolph MR Hei-Mix magnetic stirrer and NaOH pellets in order to obtain the required conditions for precipitation of the metal product. To begin with, a specific volume of leachate from three ash samples and three soil samples was measured in 14ml Falcon tubes and poured into a beaker, see Table 4.2. The beaker was put onto the magnetic stirrer followed by addition of NaOH pellets. The pellets were added carefully, while monitoring the pH with a Multiline WTW 350i pH-meter to be able to reach a pH level of 9, where copper ions are the least soluble (Palmer & Bénézeth, 2008). Small precipitants began to form between pH 4-5, increasing until only a turbid slurry was visible in the beaker. The experiment was cancelled at pH 9 and the slurry was allowed to settle for a few minutes. The precipitation was extracted from the solution, using a vacuum filtration device with a Munktell 1.6 µm, 47mm Ø filter. The filter containing the precipitants was removed and placed in aluminium foil bowls which was put in a Thermo scientific HERATherm oven at 105 °C for 24 hours. The samples were then weighed and put in desiccators for further analysis.

Table 4.2. The volumes of leachate added during the precipitation experiment along with start and end pH after addition of NaOH.

Sample ID	Volume [ml]	pH start	pH end
A3	15.5	4.1	9.9
A5	19.0	3.3	9.8
A7	15.5	3.2	9.1
S3	15.5	0.3	9.0
S5	20.0	0.4	9.0
S7	15.5	0.4	9.0

4.3.9 SS-EN 12457-3

To determine if the treated material could be disposed of as waste, it is characterised through a Swedish Standard Leaching Test SS-EN-12457-3. In the two step standard leaching test, a sample mass of 175 g is required. For practical reasons, this report used a downscaled version of the test with 4 g sample mass for each L/S ratio. Residues from A3-A7 and S3-S7 was weighed and put into six 50 ml PP-bottles. Milli-Q water was then added to the sample material at an L/S ratio of 2, before they were put in an Edmund Bühler 7400 Tübingen SM25, shaking table for 6 hours. After step one was completed, the samples were centrifuged for 6 min and filtered by vacuum filtration. For the next step, the same procedure was repeated with an L/S ratio of 8 and a shaking time of 18 hours.

This was done by leaching the dried samples with Milli-Q water in a two-step process. The samples were first leached for 6 hours ± 30 min, with an L/S-ratio of 2, and then for another 18 hours ± 30 min, using an L/S-ratio of 8. After each step, the samples were centrifuged and the eluate was filtered and then analysed using ICP-MS. By determining the concentrations in the eluates, the material can be classified as either inert, non-hazardous or hazardous waste and disposed of accordingly.

4.3.10 Chloride content

To assess the content of chloride in the solutions, a *Visocolor® ECO Test 5-18* was performed. In order to fit the range of the test, an interval from 1 to 60 mg/l, the samples were diluted to different degrees depending on their original chloride concentrations. From each diluted sample, 5 mL was added to the test tube, along with 10 drops of Cl-1, a solution provided by the test kit. The samples were mixed by shaking, before another 10 drops of Cl-2, a solution also provided by the test kit, was added. Depending on the concentrations of chloride, the colour of the samples shifted into different tones of orange. The chloride content could then be determined by comparing each sample to a reference sample on a colour scale, provided by the test kit.

4.3.11 ICP-MS Preparation

Initially an inventory of all samples was prepared and presented in APPENDIX I. When the samples were prepared for ICP-MS, high metal concentration made it necessary to dilute them with milli-Q water to avoid falling outside the machines detection range. For the ash samples, a dilution of 1/1000 was decided based on previous lab results, indicating a high concentration of metals in the leachate. This hypothesis was further strengthened by observing the blue colour of the samples which can be seen in Figure 5.1 section 5.5.

For the soil samples, a dilution of 1/100 was decided, since previous investigations has shown a lower concentration of metals in soil leachate compared to leachate from ash. The same dilution is used in all samples concerning the standard leaching test which also can be expected to have a lower metal content than the ash leachate.

The pH was measured to less than one in all leachates from the enhanced acidic leaching. However, in the samples from the standard leaching test, the pH was measured to approximately 5 in both the first and the second leaching step. To be able to obtain reasonable results from the ICP-MS, their pH needed to be lowered, which is why 100 µl nitric acid with a concentration of 65 percent was added to each sample.

Before the ICP-MS is run it is important to prepare standard solutions, with a known concentration of metals. The internal standard is added to compensate for deviations in the results caused by matrix effects, instrument drift and dilution errors (Chalmers University of Technology, u.d.). It consists of an element which would not exist naturally in the sample, often Indium or Rhodium. The standard solutions were prepared using acid-washed 50 ml volumetric flasks in order to get an accurate solution, which were then introduced into the ICP-MS instrument before the samples.

4.4 Voices from the industry

In order for the method to be feasible in a large scale operation, access to acidic process waters is necessary. Therefore, an attempt to assess the availability of acidic wastewaters was performed. The waste incineration- and paper industry was identified as possible sources for acidic wastewaters. The interview questions were:

1. Do you have access to acidic process waters similar to what have been used in this report?
2. What is the annual produced quantity of process water at your facility?

The selected companies for the evaluation and their answers are presented in APPENDIX II. During the investigation two of the seven companies stated that they have an acidic process water from the flue gas cleaning. The others either had a pH which was well above the requirements for a successful leaching process, or produced acidic process water at an insignificant level. Although it may seem like the access to acidic process waters is low, the enquiry suggests that there is a need for a more thorough investigation regarding the process water supply throughout the country. Worth to mention is that Vattenfall, which is one of the larger stakeholders in the enquiry, produces 15-20 times more flue gas condensate than Vetab for example, indicating that many of the smaller industries in the assessment is not of any significant importance to the overall result.

5 Results and discussion

5.1 Original contents in the soil and ash

In comparison to previous studies, the concentration of copper in the untreated ash of this study is significantly higher. The results are not directly comparable since different types of incineration has been applied to the bark. There does not seem to be a coherent factor of enrichment as the content of some of the analysed metals, such as Cu and Zn, are higher in this study compared to Report 1, while others, such as Pb and Cr, are lower. A problem that was noticed during the ICP-MS analysis of the dissolved samples, was that the copper content in the ash was significantly higher compared to the results from Report 1. For this reason, the sample was also sent for analysis in an external laboratory. The results from this analysis is denoted "External analysis" in Table 5.1, and are also accepted as the basis for comparison in the report. The deviation in the results measured in the report in comparison with Report 1 and the external analysis raises the question whether the method for dissolving solid material has been successful.

Table 5.1. Comparison of original content in ash to previous studies and external analysis.

Original content in Ash [mg/kg]			
	Measured values	Report 1[2]	External analysis[3]
Sb	11.2	-	-
As	0.5	11	-
Ba	840	930	970
Pb	168	360	-
Cd	<0.1	1.3	-
Co	0.0	7.5	-
Cu	214 000	130 000	161 000
Cr	5.0	50	-
Hg	0.03	<0.01	-
Mo	<0.1	2.4	-
Ni	25.3	26	-
V	12.1	38	21.9
Zn	440	260	-

Based on the results from the ICP-MS, the concentrations of several of the analysed elements had too low deviation from the concentrations of a milli-Q sample and were therefore regarded as being below the detection limit of the instrument. The concentration of copper in the soil is similar to the levels measured in previous studies, as shown in

Table 5.2. According to the study made by Kemakta, the soil is heterogeneous and the copper levels in ten analysed clay samples fluctuate between 33 mg/kg and 5400 mg/kg, with an average of 1252 mg/kg (Kemakta Konsult AB, 2012).

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[2] (Eriksson & Johansson, 2013)

[3] ALS Scandinavia

Table 5.2. Comparison of original content in soil to previous studies.

Original content in Soil [mg/kg]				
	Measured values	Report 1[4]	Kemakta[5]	Report 2[6]
Sb	<0.1	-	-	-
As	<0.1	0.59	0.7	0.4
Ba	<0.1	500	79.5	526
Pb	<0.1	7.9	11.1	8.2
Cd	<0.1	0.032	0.1	0
Co	<0.1	2.2	4.8	2.1
Cu	2202	1100	1252	2390
Cr	<0.1	42	8.6	25.7
Hg	<0.1	<0.04	0.2	<0.04
Mo	<0.1	0.29	-	-
Ni	<0.1	3.1	6.2	3.9
V	<0.1	44	19.8	46.1
Zn	19.4	14	26.1	13

5.2 Incineration

The incineration process proved to be more problematic than expected. Due to the heterogeneity of the samples, the resulting amount of ash from each incineration could differ between 2 to 14 percent of the original bark material. This had an obvious impact on the time plan for the experimental procedure, where it was hard to guarantee a specific time to reach the desired ash mass of 150 g divided in three batch leaching experiments. It became clear during the course of the report that the incineration was too time consuming for the length of this project, which is why the experiment had to be adjusted to use 75 g of ash, divided in three batch leaching samples, instead.

5.3 Removal of Hg from the leaching agent

The initial runs in the ion exchange resin with 3 BV/h obtained an almost total removal of Hg which is presented in *Table 5.3*. The concentration reached a satisfying reduction and falls well below the KM and MKM criteria for mercury. Even though the initial mercury concentration was below the criteria as well, it was considered necessary to reduce it to avoid accumulation in the solid material after leaching in higher L/S quotes. As previously mentioned in chapter 4.3.4, a trial run with 15 BV/h was also executed in order to evaluate if the process could become more effective. The results from the trial run are also presented in *Table 5.3* and show that the concentration of Hg is lower in the trial run by comparison. This raises the question if the removal of Hg should be optimised as well, with attempts to increase the number of BV/h even further.

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[4] (Eriksson & Johansson, 2013)

[5] (Kemakta Konsult AB, 2012)

[6] (Khmilkovska, 2014)

Table 5.3. Metal concentrations in process water before and after Ion-exchange.

	Hg-content [µg/l]	Removal rate [%]
Before Ion-exchange	86.4	-
After Ion-exchange 3 BV/h	5.9	93
After Ion-exchange 15 BV/h	2.4	97

5.4 First cycle

The first leaching cycle, performed only on soil samples, was done in order to evaluate the effect of different shaking times. In the results from this evaluation, presented in Table 5.4, it can be seen that the shaking time in samples of L/S 5 and 7 had little to no effect on the methods effectiveness with less than five percent fluctuation between each sample and the mean Cu-concentration for the corresponding L/S quote. In samples with L/S 3 large fluctuations can be observed. However, it does not appear to follow any specific pattern which is why these variations are disregarded in this report. It is hard to draw general conclusions based on such a limited sample supply, which is why it was decided to use a shaking time of 20 minutes to be as efficient as possible. In this study three shaking times were evaluated and since the effect is low according to Table 5.4, future research could attempt to reduce this parameter further.

Table 5.4: Copper concentrations in the leachate after the first cycle of the leaching experiment.

L/S [-]	Shaking time [min]	Cu-content [mg/l]	Mean Cu-content [mg/l]
3	20	527.0	546.9
3	30	460.2	
3	40	653.5	
5	20	392.1	405.0
5	30	415.2	
5	40	407.8	
7	20	268.3	273.3
7	30	282.2	
7	40	269.3	

As can be seen in *Table 5.5*, the highest copper content was achieved in the leachate with L/S 5 during the small scale test in the first leaching cycle.

Table 5.5: Copper concentrations in the leachate after the first cycle of the leaching experiment

Soil mass [g]	L/S [-]	Mean Cu-concentration [mg/l]	Cu-content in solid sample [mg/g]
5	3	546.9	1.6
5	5	405.0	2.1
5	7	273.3	1.9

5.5 Batch leaching

The pH of the leaching agent was initially below 0.1. During the leaching process the pH changed, especially after being in contact with the ash. As shown in Table 5.6, the soil only slightly affected the pH, while the ash is more alkaline and decreased the acidity of the leachate to levels around pH 3-4. Since results from previous studies have indicated that the leaching of copper can be highly effective in an acidic environment, the increased pH-levels could be considered as a factor that affects the results in this report. As seen in Table 5.6, a lower L/S-ratio in ash samples results in a higher pH because of the materials alkaline character.

Table 5.6. pH in the leachate.

	Soil			Ash		
Sample ID	S3	S5	S7	A3	A5	A7
pH	0.3	0.4	0.4	4.14	3.25	3.15

The samples obtained from the batch leaching experiment involved leachate and washing water from soil and ash which are presented in Figure 5.1.

Figure 5.1. a) Leachates from batch leaching, from the left sample 1-3; S3-S7. Sample 4-6; A3-A7 b) Washing water after batch leaching, from the left sample 1-3; S3w-S7w. Sample 4-6; A3w-A7w.

5.5.1 Soil

Regarding the original content in the soil, the concentration of copper is the only one which exceeds the guideline values for "sensitive land use", KM, presented in Table 5.7. However, the concentration of copper also exceeds the limiting values for "less sensitive land use", MKM, by far. The copper levels are not surprising, matching the results of previous studies quite well, as shown in Table 5.7 and Figure 5.2.

Table 5.7. Metal content in original soil sample, compared to remaining concentrations after leaching and washing. (As, Ba, Pb, Cd, Co, Cr, Hg, Mo, Ni, Sb and V were also analysed but were all below the detection limit).

mg/kg	Soil orig	S3 residues	S3w residues	S5 residues	S5w residues	S7 residues	S7w residues	KM	MKM
Cu	2200	700	650	700	600	700	550	80	200
Zn	19	17	16	17	17	17	17	250	500

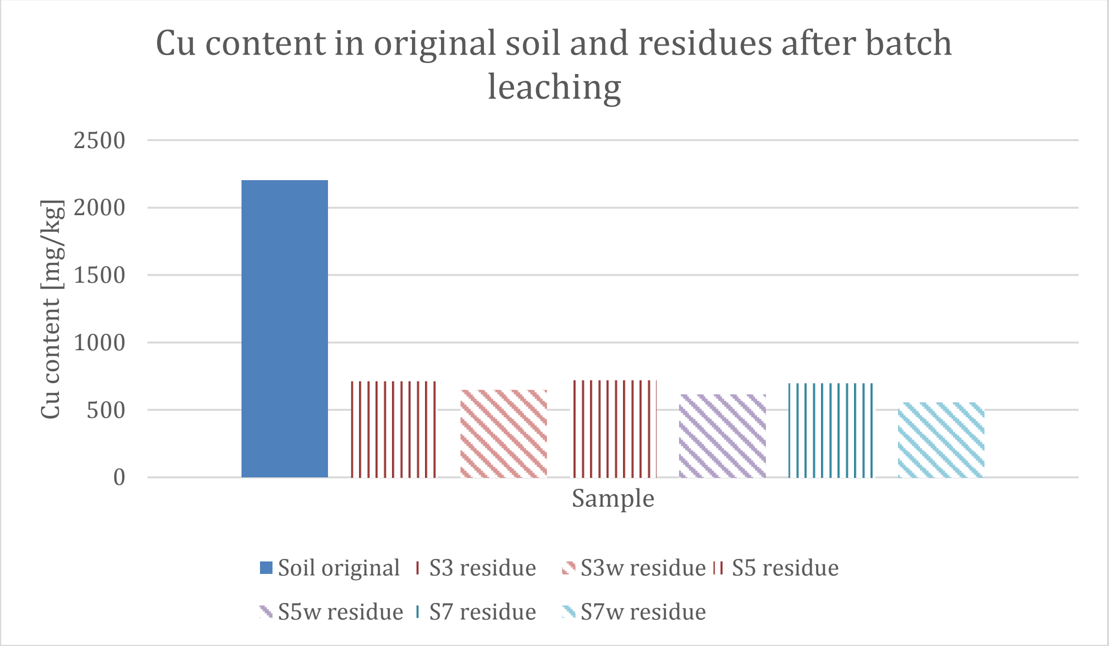

Figure 5.2. Cu content in residues after batch leaching of soil.

The results show that the batch leaching has mainly affected the copper in the soil, while Zn has been slightly reduced.

After the batch leaching, roughly one third of the original concentrations of copper remained in all three samples, S3-S7. A higher L/S does however seem to release slightly more copper from the soil, seeing that the copper removal rate after the following milli-Q wash was:

- 75 percent, after S7w
- 72 percent, after S5w
- 71 percent, after S3w

In order to reach the upper limit of MKM, at a concentration of 200 mg/kg, a removal rate of approximately 91 percent is required. Consequently, none of L/S-ratios in the batch leaching were effective enough to reach the guideline values for either KM or MKM.

5.5.2 Ash

Due to the incineration process, several of the metals have been enriched in the ash and Ba, Pb, Cd, Cu and Zn are all well above the limiting guideline values for KM, as presented in Table 5.8 and Figure 5.3.

Table 5.8. Metal content in original ash sample, compared to remaining concentrations after leaching and washing. (As, Cd, Co, Hg and Mo were also analysed but were all below the detection limit).

mg/kg	Ash orig	A3 residue	A3w residue	A5 residue	A5w residue	A7 residue	A7w residue	KM	MKM
Sb	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	12	30
Ba	972	972	972	972	972	972	972	200	300
Pb	168	168	168	168	168	168	168	50	400
Cu	161 000	149 600	145 500	125 700	110 900	99 000	82 300	80	200
Cr	33.8	33.8	33.8	33.8	33.8	33.8	33.8	80	150
Ni	13.3	13.3	13.3	13.3	13.3	13.3	13.3	40	120
V	21.9	21.9	21.9	21.9	21.9	21.9	21.9	100	200
Zn	441	397	372	383	359	371	352	250	500

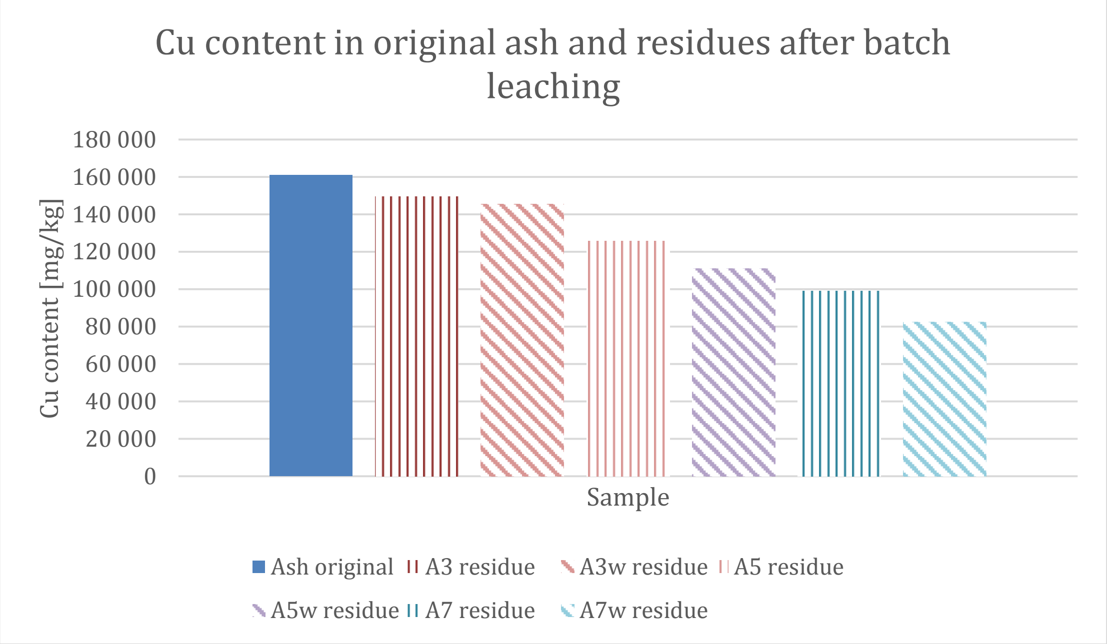

Figure 5.3. Cu content in residues after batch leaching of ash.

The L/S-ratio had a major impact on the leaching of copper from the ash. While none of the tested L/S-ratios were very successful in terms of leaching percentage, there was still a noticeable relative difference between them. It is also important to point out the pH is less affected by the alkaline ash in the samples with a higher L/S ratio, which is one of the reasons why these perform better in terms of leaching. The removal rates of copper for the tested L/S-ratios, including the appurtenant milli-Q wash, were as follows:

- 48.9 percent, after A7w
- 31.1 percent, after A5w
- 9.6 percent, after A3w

Based on the original concentrations in the ash, gained from the incineration applied in this report, a removal rate of 99.9 percent would be required to reach the upper limit of MKM.

Since the leachate was separated from the residues by centrifuge, there is reason to believe that there is still some leachate left in the material. Therefore L/S 0.6 in the washing step might not be sufficient to remove all metal pollutants still present in the material. Worth mentioning is also that another mechanical mixing has been used during both leaching and washing compared to previous studies.

Since the increased pH was a probable cause to the unsatisfying leaching rates, a new smaller trial leaching was conducted. In order to keep an acidic environment during the leaching process, the leaching agent was composed of 4 parts undiluted process water and 1 part 3M HCl. Since the experiment was conducted in the end of the study, with a purpose of evaluating the impact of pH, only one smaller sample of 1 g was tested with L/S 5 and with no appurtenant washing step.

The leachate stayed acidic during the leaching process, with pH<1. The concentration of copper in the leachate was 3.5 times higher than the concentration in the corresponding L/S 5, previously run in the batch leaching.. As can be seen in, the leaching has improved significantly and results in a removal rate of 78 percent without adding a washing step.

Table 5.9. Comparison of copper content remaining after each consecutive treatment step, between A5 and A5a.

[mg/kg]	Original	After Leaching	After washing
A5	161000	126 000	111 000
A5a	161000	35 000	-

5.6 Chloride content

In order to evaluate the accuracy of the test, a reference sample containing tap water was tested and compared to data gathered by *Kretslopp och vatten*, the local water administration in the city of Gothenburg. According to their report, the chloride concentration in tap water fluctuates between 7 and 15 mg/l (City of Gothenburg, 2015). These values correlate well with the values measured using the Visocolor® ECO Test 5-18, which showed a concentration of 7 to 12 mg/l, as presented in Table 5.10.

Table 5.10. Chloride content in samples, using a Visocolor® ECO Test 5-18

	Dilution ratio	Test result (mg/l)	[Cl] in eluate (g/l)	[Cl] in solid material (g/g)
Tap water (ref)	1:1	7-12	0.007-0.012	-
Process water	1:500	50	25	-
Precipitation S7	1:10	<1	<1	-
Precipitation A7	1:50	25	1.25	0.03
SS-EN Step 1 S7	1:100	12	1.2	-
SS-EN Step 1 A7	1:500	15	7.5	-
SS-EN Step 2 S7	1:50	2	0.1	-
SS-EN Step 2 A7	1:50	20	1	-

As shown in Table 5.10, the process water, which is highly acidic due to a high concentration of HCl, also shows a high content of chloride. The dissolved copper precipitates, from both the soil and the incinerated bark, were also tested, since chloride is unwanted in the final product. The copper precipitate from the ash leachate contained 0.03 g/g of solid precipitate, while the precipitate from the soil showed no traces of chloride according to this test.

5.7 SS-EN 12457-3 Leaching test

Since the results from the batch leaching test proved insufficient to match the criteria for KM and MKM a standard leaching test was performed. This is done to simulate how the contaminants in the material are transported with the rainfall runoff at a landfill. The two leachates were analysed with ICP-MS in order to evaluate the metal concentrations. To evaluate how well the samples comply with the landfill regulations, the two leaching steps are used calculate the release of metals at a cumulative L/S of 10.

The results from the calculations are presented for soil in Table 5.11 and for ash in Table 5.12.

Table 5.11 Quantity of constituent leached from the soil in leaching step one and the cumulative release from step one and two. (As, Ba, Pb, Cd, Co, Cr, Hg, Mo, Ni and Se were also analysed but were all below the detection limit).

soil	**Cumulative release in L/S 10**					
	S3	S5	S7	Inert waste	Non-hazardous waste	Hazardous waste
Cu	491	339	414	2	50	100
Sb	0.1	0.1	0.1	0.06	0.7	5
Zn	8.8	8.5	9.8	4	50	200
Cl^-	-	-	1900	800	15000	25000

The L/S quotes stated in Table 5.11 describes for which sample the results are valid. In the three rightmost columns the limits for different landfill classes are stated to compare with the results.

The evaluation shows that Cu exceeds the limits for hazardous waste while the remaining substances are placed in the category for Non-hazardous waste or below. In the case of copper this is not surprizing, keeping in mind that the amount of leached copper from the batch leaching experiment indicate that high levels of copper are still present in the soil material.

As earlier research has shown a lower leaching of Cu in the standard leaching test, placing the soil material below the criteria for non-hazardous waste, there are reasons to believe that the washing step has not worked sufficiently with the method described in this report (Khmilkovska, 2014).

In order to be able to deposit this material at a landfill, further treatment is needed. A recommendation based on earlier research at Chalmers, could be to introduce additional leaching steps (Eriksson & Johansson, 2013).

Table 5.12 Quantity of constituent leached from the ash in leaching step one and the cumulative release from step one and two. (As, Ba, Pb, Cd, Co, Cr, Hg, Mo, Ni and Se were also analysed but were all below the detection limit).

ash	**Cumulative release in L/S 10**					
	A3	A5	A7	Inert waste	Non-hazardous waste	Hazardous waste
Cu	2412	9974	5142	2	50	100
Sb	0.1	0.1	0.1	0.06	0.7	5
Zn	14.4	24.1	18.4	4	50	200
Cl^-	-	-	13400	800	15000	25000

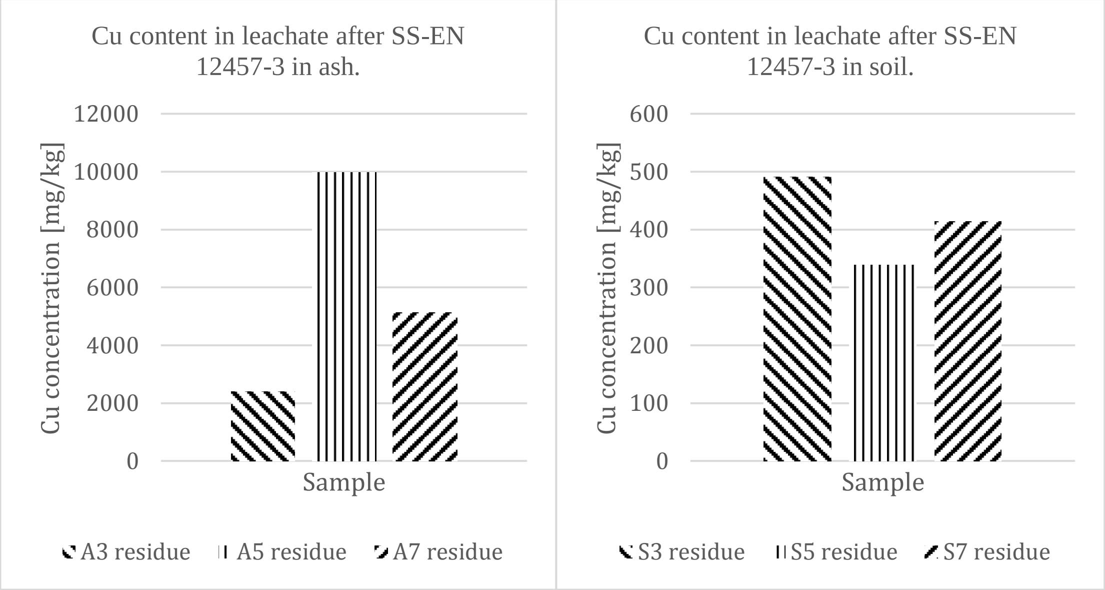

Figure 5.4 Concentrations of Cu in leachate after standard leaching test.

According to Table 5.12 the leachate from the ash was also above the limits for hazardous waste. The concentration of copper was also significantly higher in the ash leachate than in its soil counterpart, as can be seen in Figure 5.4. Since the batch leaching for the ash proved less effective than for the soil, a higher percentage of copper from the original ash is still present in the material after the first leaching. Adding the fact that the original concentration of copper was significantly higher in the ash than in the soil makes it reasonable to think that the concentration of copper in the standard leaching of the ash would be vastly greater than in the soil. Although, this is not further considered in this report.

To be able to deposit the material at a landfill the ash also need some kind of additional treatment. Again, a recommendation could be to increase the number of leaching steps. However, a problem that arouse in the method was that the pH-level in the batch leaching ranged from 3.1-4.2 in the ash leaching compared to the soil leaching which was performed at a pH around 0.4. Since the method is more effective in the lower range of pH, this is definitely something that can impair its performance. Because of this, the report conducted an additional test with pH with more satisfying results.

5.8 Precipitation

In order to separate the copper from the leachate, NaOH-pellets were added to increase the pH and create conditions where copper is the least soluble. Since the ash was more alkaline than the soil, the pH of the ash leachate was already at levels around 3-4, while the leachate from the soil was still highly acidic with a pH of 0.3-0.4, as presented in Table 5.6.

The leachate that was remaining after the precipitation of copper was completed, was analysed in order to determine the effectivity of the precipitation method. The original leachate from the ash contained significantly higher concentrations of copper than the leachate from the soil. However, as presented in Table 5.13, the precipitation method worked a lot better for the ash, resulting in an almost complete removal of copper. For the soil leachate, the effectivity of the method was not consistent and between 68 and 81 percent of the copper precipitated.

Table 5.13. Rate of precipitation for Cu, from soil and ash samples.

Sample ID		Cu in leachate after precipitation [mg/kg]	Original Cu in leachate [mg/kg]	Rate of precipitated Cu [%]
Ash	A3	2.6	3801	99.9
	A5	11.6	7057	99.8
	A7	4.5	8850	99.9
Soil	S3	94.2	498	81.1
	S5	66.6	297	77.6
	S7	67.9	216	68.5

The leachate from the ash contained higher concentrations of copper than the soil and consequently resulted in a larger amount of precipitate, as can be seen in Table 5.14. The precipitate from the ash leachate also contained a higher concentration of copper, 40 - 44 percent, in comparison to the precipitate from the soil, which consisted of a mere 11 - 14 percent of copper.

Table 5.14. Amount of precipitation and proportion of Cu in precipitate.

	Ash			Soil		
	A3	A5	A7	S3	S5	S7
Precipitate from leachate (g/l)	9.83	15.91	21.84	2.86	1.61	1.31
Cu content (%)	40	42	44	14	13	11

It is hard to point to one specific reason why the precipitation was less successful in the soil leachate. A possible scenario could be that the copper has stronger bonds to chemical complexes, such as humic acids, present in the soil (Hwang, et al., 2015). Another parameter that could affect the result is the temperature. When adding the NaOH-pellets, the soil leachates had an increase in pH from about 0.3 to 9, which consequently led to a higher increase in temperature in comparison to the ash leachates that started out at pH 3-4. Since the solubility of copper increases along with temperature, this might affect the precipitation (Etacude, 2008).

An indication of the copper content in the precipitate is the visual characteristics. The filtrated precipitate from the ash formed a turquoise solid with clear blue crystals, while the soil counterpart formed a similar but completely brown solid. After the precipitates were dried in an oven at 105 °C, the solid from the ash leachate was still somewhat intact, with fractures of higher intensity inversely proportionate to the mass of the solid. The precipitate from the soil had decreased significantly in mass while drying and, consisting only of 11-14 percent copper, it had no trace of blue in its colour. Further visual confirmations on the high copper content in the ash compared to the soil is the colour of the samples with dissolved precipitate, seen in Figure 5.5.

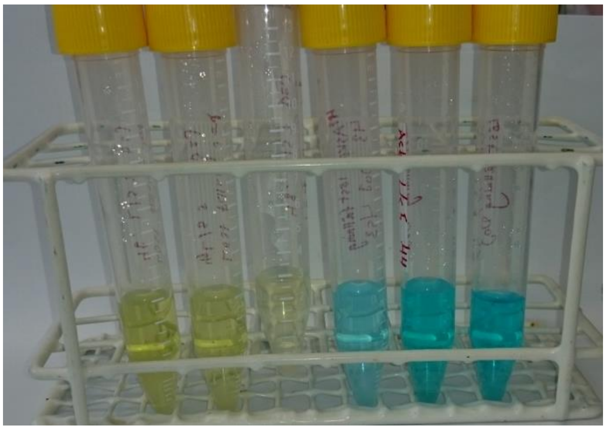

Figure 5.5. Precipitations dissolved in HNO$_3$. The three leftmost samples: soil L/S 3-7. The three rightmost samples: ash L/S 3-7.

6 Conclusion

The batch leaching experiments showed a large variation in the success of copper removal from the solid material. In the soil samples the 71-74 percent was successfully removed while the ash leaching had a removal rate of 9-50 percent. An attempt to reach a higher removal rate on the ash was made, using a mix of process water and 3M HCl, which then successfully removed 87 percent initial copper. This indicates that the leaching is more effective in pH below 1 than in pH 3-4.

Compared to previous studies, the leaching was less effective in this project. However, if this has to do with the sample size or the fact that the methods are somewhat different is not entirely certain.

After the SS-EN12457-3 standard leaching test, the results showed that the material could not be deposited at a landfill for hazardous waste. However, the only exceeding substance was copper with about four times the criteria for hazardous waste in the soil samples and 100 times the criteria for the ash worst ash sample. Since earlier studies has shown the importance of a washing step, these results indicate that a well implemented washing step after the batch leaching is needed.

A precipitation of copper was attempted in leachate. The attempt was more successful in the ash leachates, with ~99.9 percent effectiveness, while the soil leachates precipitated between 68-81 percent of the containing copper. Possible reasons for this are related to temperature and that the soil contains humic acids that may have strong bonds to Cu.

The acidic process water had an original Hg concentration of 86 µg/l. The removal rate after treatment with *Lewatit® TP 214* was in the range of 92 - 97 percent.

7 Further recommendations

As a recommendation for additional research in this field, this paper has discovered that there is a need to evaluate at which pH the leaching of ash is working optimally.

The experiments with ion-exchange resin has shown that the removal is working in an acceptable manner. However, the process could be optimized further to reduce the time consumption.

Finally, there is a need to evaluate the possibilities to recycle the metals. For this an assessment of the industrial demands for the metal product is needed as well as an analysis of its purity.

8 References

Armenante, M. P., 1997. *Precipitation of Heavy Metals from Wastewaters.* Newark: New Jersey Institute of Technology.

Chalmers University of Technology, n.d. *ICP sample preparation introduction,* Gothenburg: Chalmers.

City of Gothenburg, 2015. *Dricksvattnets kvalitet: Göteborgs stad.* [Online]
Available at: http://goteborg.se/wps/portal/invanare/bygga-o-bo/vatten-och-avlopp/dricksvatten
[Accessed 20 May 2015].

CPEO, n.d. *Vitrification: CPEO.org.* [Online]
Available at: http://www.cpeo.org/techtree/ttdescript/ssvit.htm
[Accessed 28 January 2015].

Dąbrowski, A., Hubicki, Z., Podkościelny, P. & Robens, E., 2004. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere,* 56(2), pp. 91-106.

Davenport, W. G., King, M., Schlesinger, M. & Biswas, A. K., 2002. Chapter 18 – Solvent Extraction Transfer of Cu from Leach Solution to Electrolyte. In: M. Davenport, ed. *Extractive Metallurgy of Copper.* s.l.:Elsevier B.V., pp. 307-325.

Dermont, G., Bergeron, M., Mercier, G. & Richer-Laflèche, M., 2008. Soil washing for metal removal: A review of physical/chemical technologies and field applications. *Journal of hazardous materials,* Issue 152, pp. 1-31.

Di Palma, L., Ferrantelli, P., Merli, C. & Biancifiori, F., 2003. Recovery of EDTA and metal precipitation from soil flushing solutions. *Journal of Hazardous Materials,* 103(1-2), pp. 153-168.

Eriksson, A. & Johansson, P., 2013. *Soil Washing: Optimization of Acid Leaching of Copper from Contaminated Soil,* Gothenburg: CHALMERS UNIVERSITY OF TECHNOLOGY.

Etacude, 2008. *Chemicals: Etacude.* [Online]
Available at: http://chemicals.etacude.com/c/more/cuso4.html

European Copper Institute, n.d. *About Copper: Properties.* [Online]
Available at: http://www.copperalliance.eu/about-copper/properties/chemical-properties
[Accessed 20 January 2015].

Google, 2015. *maps.google.se.* [Online]
Available at:
https://www.google.se/maps/dir/58.7681771,12.507367//@58.2708478,12.2436951,9z
[Accessed 24 06 2015].

Green Facts, 2015. *Mercury: GreenFacts.* [Online]
Available at: http://www.greenfacts.org/en/mercury/l-2/mercury-1.htm

Hwang, B., Kim, E., Yang, J. & Baek, K., 2015. Extractive and oxidative removal of copper bound to humic acid in soil. *Environmental Science and Pollution Research,* 22(8), pp. 6077-6085.

InfoMine, 2015. *Charts and Data: InfoMine.* [Online]
Available at:
http://www.infomine.com/ChartsAndData/ChartBuilder.aspx?z=f&gf=110563.USD.lb&dr=max&cd=1
[Accessed 20 January 2015].

Karlfeldt Fedje, K., Modin, O. & Strömvall, A.-M., 2014. *Copper recovery from polluted soils using acidic washing and bioelectrochemical systems,* Gothenburg: Chalmers University of Technology.

Karlfeldt Fedje, K., Yillin, L. & Strömvall, A.-M., 2013. Remediation of metal polluted hotspot areas through enhanced soil washing - Evaluation of leaching methods. *Journal of Environmental Management,* Issue 128, pp. 489-496.

Kemakta Konsult AB, 2012. *Kompletterande huvudstudie för förorenad mark vid f.d. stolpimpregnering på Långö, Köpmannebro, Mellerud kommun,* Stockholm: Kemakta Konsult AB.

Khmilkovska, N., 2014. *Soil Washing Optimisation and Assessment of the Residues with Focus on Copper: a Method to Treat Metal,* Gothenburg: Chalmers University of Technology.

Lasat, M. M., 2002. Phytoextraction of Toxic Metals: A Review of Biological Mechanisms. *Journal of Environmental Quality,* Volume 31, pp. 109-120.

Mulligan, C. N., Yong, R. N. & Gibbs, B. F., 2001. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology,* 60(1-4), pp. 193-207.

Neumann, D. S., n.d. *Working with Ion Exchangers - A Practical Guide -,* s.l.: Lewatit; LANXESS.

Nordin, A., 2013. *Lägesbeskrivning av arbetet med efterbehandling av förorenade områden,* Stockholm: SEPA.

Palmer, D. A. & Bénézeth, P., 2008. *Solubility of Copper Oxides in Water and Steam.* Oak Ridge, Oak Ridge National Laboratory.

PerkinElmer, Inc., 2011. *PerkinElmer: The 30-Minute Guide to ICP-MS.* [Online]
Available at:
http://www.perkinelmer.com/pdfs/downloads/tch_icpmsthirtyminuteguide.pdf
[Accessed 5 February 2015].

Schulte, E. E. & Kelling, K. A., 1999. *Understanding Plant Nutrients: Soil and Copper,* Wisconsin: University of Wisconsin-Extension.

SEPA, 2003. *Introduction to a method - For inventories and risk classification of contaminated sites,* Stockholm: SEPA.

SEPA, 2007. *Mottagningskriterier för avfall till deponi - Handbok 2007:1,* Stockholm: CM Digitaltryck AB.

SEPA, 2009. *Riktvärden för förorendad mark - Modellbeskrivning och vägledning - Rapport 5976,* Stockholm: CM Gruppen AB.

SEPA, 2014a. *Naturvårdsverket.* [Online]
Available at: http://www.naturvardsverket.se/Miljoarbete-i-samhallet/Miljoarbete-i-Sverige/Uppdelat-efter-omrade/Avfall/Om-deponering-

av-avfall/
[Accessed 20 01 2015].

SEPA, 2014b. *Naturvårdsverket - Större fokus på att åtgärda förorenade områden.* [Online]
Available at: http://www.naturvardsverket.se/Miljoarbete-i-samhallet/Miljoarbete-i-Sverige/Uppdelat-efter-omrade/Fororenade-omraden/Resultat-2013/
[Accessed 21 01 2014].

SEPA, 2014. *Naturvårdsverket: Miljöarbete i samhället.* [Online]
Available at: http://www.naturvardsverket.se/Miljoarbete-i-samhallet/EU-och-internationellt/Internationellt-miljoarbete/miljokonventioner/Kvicksilver/
[Accessed 19 January 2015].

SEPA, n.d. *Scottish Environment Protection Agency: Contaminated land.* [Online]
Available at: http://www.sepa.org.uk/land/contaminated_land.aspx
[Accessed 21 January 2015].

Seth, S., 2012. *Dramatic copper demand growth expected from China, India, Brazil.* [Online]
Available at: http://www.mineweb.com/archive/dramatic-copper-demand-growth-expected-from-china-india-brazil/
[Accessed 20 January 2015].

SGI, 2012. *Kunskapsläge och förutsättningar för återvinning av metallförorenade massor,* Linköping: SGI.

SGU, 2014a. *Uppdrag att utföra en kartläggning och analys av utvinnings- och återvinningspotential för svenska metall- och mineraltillgångar,* Uppsala: SGU.

SGU, 2015. *Utvecklingen av metallpriser i april: SGU.* [Online]
Available at: http://www.sgu.se/om-sgu/nyheter/2015/maj/utvecklingen-av-metallpriser-i-april/
[Accessed 26 May 2015].

Shammas, N. K., 2009. Removal of Heavy Metals from Soil. In: L. K. Wang, N. K. Shammas & Y. Hung, eds. *Waste treatment in the metal manufacturing, forming, coating, and finishing industries.* Boca Raton, Florida: Taylor & Francis Group, LLC, pp. 381-432.

Sierra Fernández, C., 2013. *Remediation of mining and metallurgy Brownfields by means of Physical Separation Procedures,* Oviedo: University of Oviedo.

Springfors, A., 2001. *Kartläggning av föroreningssituationen i mark, grundvatten och sediment, förenklad riskbedömning, översiktlig åtgärdsutredning samt riskbedömning för föreslagna eferbehandlingsåtgärder för Långön, Köpmannebro,* Stockholm: ÅF.

Swedish Environmental Protection Agency, 2014. *Mercury Management in Sweden,* Stockholm: SEPA.

Swedish National Food Agency, 2014. *Kvicksilver - fördjupning.* [Online]
Available at: http://www.slv.se/sv/grupp1/Risker-med-mat/Metaller/Kvicksilver/Kvicksilver---fordjupning/
[Accessed 19 January 2015].

Swedish National Heritage Board, 2013. *Materialguiden,* Visby: Swedish National Heritage Board.

The University of Hawaii, n.d. *Hawaii.edu: Technologies.* [Online]
Available at: http://www.hawaii.edu/abrp/Technologies/phystab.html
[Accessed 30 January 2015].

U.S. Geological Survey, 2014. *Annual Publications (2014): Copper,* s.l.: USGS.

U.S. Geological Survey, 2015. *Copper - Statistics and Information.* [Online]
Available at: http://minerals.usgs.gov/minerals/pubs/commodity/copper/

US Environmental Protection Agency, 2014. *About: Mercury.* [Online]
Available at: http://www.epa.gov/mercury/about.htm
[Accessed 19 January 2015].

USEPA, 1996. *A Citizen's Guide to Soil Washing,* Cincinnati: USEPA.

USEPA, 1997. *Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb,* Washington, DC: Engineering Bulletin.

APPENDIX I

Table 1: Description of samples analysed with ICP-MS

Sample ID	**Content**
0	Blank
1	L/S 3 soil unfiltered
2	L/S 7 soil unfilt.
3	L/S 3 soil filt.
4	L/S 7 soil filt.
5	L/S 3 soil washed in 0.6 milli-Q
6	L/S 7 soil washed in 0.6 milli-Q
7	L/S 7 ash filt.
8	L/S 7 ash filt.
9	L/S 3 ash filt.
10	L/S 3 ash filt.
10A	Blank
11	L/S 7 ash washed in 0.6 milli-Q
12	L/S 3 ash washed in 0.6 milli-Q
13	L/S 5 soil unfilt.
14	L/S 5 soil filt.
15	L/S 5 ash filt.
16	L/S 5 ash washed in 0.6 milli-Q
17	L/S 5 soil washed in 0.6 mQ
17A	Blank
18	SS-EN L/S 3 soil (step1 – L/S 2)
19	SS-EN L/S 5 soil (step1)
20	SS-EN L/S 7 soil (step1)
21	SS-EN L/S 3 ash (step1)
22	SS-EN L/S 5 ash (step1)
23	SS-EN L/S 7 ash (step1)
23A	Blank
24	SS-EN L/S 3 soil (step2 – L/S 8)
25	SS-EN L/S 5 soil (step2)
26	SS-EN L/S 7 soil (step2)
27	SS-EN L/S 3 ash (step2)
28	SS-EN L/S 5 ash (step2)
29	SS-EN L/S 7 ash (step2)
30	Process water
30A	Blank
31	L/S 5 Ash filt. fr precip
32	L/S 5 Ash filt. fr precip Washed MQ
33	L/S 5 Soil filt. fr precip
34	L/S 5 Soil filt. fr precip Washed Mq
35	L/S 7 Ash filt. fr precip
36	L/S 7 Ash filt. fr precip Washed MQ
37	L/S 3 Ash filt. fr precip
38	L/S 3 Ash filt. fr precip Washed MQ
39	L/S 3 Soil filt. fr precip
40	L/S 3 Soil filt. fr precip Washed MQ
41	L/S 7 Soil filt. fr precip
42	L/S 7 Soil filt. fr precip Washed MQ
43	L/S 3 Ash precip. Dissolved

44	L/S 3 Ash precip. Dissolved
45	L/S 5 Ash precip. Dissolved
46	L/S 5 Ash precip. Dissolved
47	L/S 7 Ash precip. Dissolved
48	L/S 7 Ash precip. Dissolved
49	L/S 3 Soil precip. Dissolved
50	L/S 3 Soil precip. Dissolved
51	L/S 5 Soil precip. Dissolved
52	L/S 5 Soil precip. Dissolved
53	L/S 7 Soil precip. Dissolved
54	L/S 7 Soil precip. Dissolved
55	Ash ref
56	Ash
57	Ash
58	Soil
59	Soil
60	Vällsjön
61	Vällsjön

Table 2: Raw data from ICP-MS analysis

	Sb	As	Ba	Pb	Cd	Co	Cu	Cr	Hg	Mo	Ni	V	Zn
S0	0.00	0.00	0.02	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	-0.01	0.00	0.00
S3	0.58	0.00	3.41	1.24	0.18	-0.32	524.07	-0.27	0.01	0.28	-0.77	0.25	0.96
S5	0.60	0.00	3.18	0.66	0.17	-0.34	219.04	-0.30	0.01	0.13	-0.65	0.05	0.44
S7	0.58	0.00	3.41	1.23	0.18	-0.32	497.66	-0.28	0.01	0.08	-0.73	0.25	0.92
S4	0.60	0.00	3.21	0.66	0.17	-0.33	215.57	-0.30	0.01	0.05	-0.67	0.06	0.43
S5	0.51	0.00	4.00	0.42	0.17	-0.32	108.12	-0.29	0.01	0.03	-0.62	0.07	0.95
S6	0.51	0.00	3.18	0.75	0.18	-0.32	236.56	-0.28	0.01	0.02	-0.68	0.22	0.66
S7	5.09	0.02	21.71	4.50	1.85	-3.39	8814.49	-3.22	0.06	0.09	-5.22	-1.33	9.78
S8	5.09	0.02	21.81	4.55	1.85	-3.39	8886.17	-3.21	0.05	0.09	-5.20	-1.39	10.11
S9	5.01	0.00	21.93	2.01	1.91	-3.27	3810.59	-3.43	0.04	0.09	-4.26	-1.68	14.65
S30	5.01	0.00	21.96	2.01	1.92	-3.27	3790.91	-3.43	0.04	0.12	-4.27	-1.67	14.40
S30A	0.00	0.00	0.02	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	-0.01	0.00	0.00
S31	5.02	0.00	22.20	2.10	1.80	-3.42	6980.91	-3.41	0.03	0.07	-5.32	-1.68	8.25
S32	4.99	0.00	21.21	1.69	1.82	-3.32	1707.56	-3.43	0.03	0.07	-4.70	-1.69	10.62
S33	0.62	0.00	3.34	0.84	0.17	-0.33	311.24	-0.29	0.00	0.01	-0.68	0.11	0.49
S34	0.62	0.00	3.35	0.84	0.17	-0.33	296.95	-0.29	0.00	0.01	-0.69	0.12	0.54
S35	5.06	0.01	21.48	3.05	1.87	-3.39	7056.66	-3.37	0.04	0.02	-5.07	-1.58	11.61
S36	5.01	0.00	21.03	1.99	1.82	-3.41	6182.94	-3.43	0.03	0.04	-5.16	-1.67	9.96
S37	0.52	0.00	3.59	0.66	0.19	-0.32	175.17	-0.29	0.00	0.00	-0.64	0.16	0.74
S37A	0.00	0.00	0.02	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	-0.01	0.00	0.00
S38	0.50	0.00	4.92	0.19	0.20	-0.06	312.73	-0.28	0.00	0.00	-0.35	-0.14	5.04
S39	0.50	0.00	5.77	0.18	0.18	-0.14	213.37	-0.30	0.00	0.00	-0.46	-0.14	4.55
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S50	0.51	0.00	6.02	0.18	0.18	-0.11	214.11	-0.29	0.00	0.01	-0.38	-0.12	4.48
S51	0.50	0.00	8.70	0.18	0.20	-0.32	481.78	-0.34	0.00	0.00	-0.44	-0.16	6.46
S52	0.51	0.00	7.26	0.22	0.19	-0.32	1612.44	-0.34	0.00	0.01	-0.31	-0.16	7.09
S53	0.51	0.00	5.68	0.20	0.21	-0.32	1461.73	-0.34	0.00	0.01	-0.46	-0.16	8.61
S53A	0.00	0.00	0.02	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	-0.01	0.00	0.00
S54	0.50	0.00	3.03	0.16	0.17	-0.33	21.48	-0.34	0.00	0.00	-0.59	-0.17	0.43
S55	0.50	0.00	3.09	0.16	0.17	-0.33	19.80	-0.34	0.00	0.00	-0.59	-0.17	0.55
S56	0.50	0.00	3.11	0.16	0.17	-0.33	24.70	-0.33	0.00	0.00	-0.58	-0.17	0.63
S57	0.50	0.00	2.22	0.16	0.18	-0.34	208.03	-0.34	0.00	0.00	-0.57	-0.17	1.09
S58	0.50	0.00	3.01	0.18	0.19	-0.34	890.36	-0.34	0.00	0.00	-0.52	-0.17	2.08
S59	0.50	0.00	2.48	0.16	0.19	-0.35	432.33	-0.34	0.00	0.00	-0.57	-0.17	1.42
S70	0.68	0.01	2.15	0.16	0.17	-0.35	-1.16	-0.31	0.00	0.01	-0.61	-0.05	0.29
S70A	0.00	0.00	0.02	0.00	0.00	0.00	-0.02	0.00	0.00	0.00	-0.01	0.00	0.00
S71	0.50	0.00	2.19	0.16	0.17	-0.35	11.57	-0.34	0.00	0.00	-0.61	-0.16	-0.01
S72	0.50	0.00	2.10	0.16	0.17	-0.35	-0.67	-0.34	0.00	0.00	-0.61	-0.16	-0.06
S73	0.53	0.00	3.66	0.16	0.17	-0.35	66.62	-0.34	0.00	0.04	-0.61	-0.11	0.40
S74	0.52	0.00	2.34	0.16	0.17	-0.35	5.94	-0.34	0.00	0.05	-0.61	-0.14	0.02
S75	0.50	0.00	2.19	0.16	0.17	-0.35	4.53	-0.34	0.00	0.01	-0.61	-0.16	-0.02
S76	0.50	0.00	2.10	0.16	0.17	-0.35	-1.68	-0.34	0.00	0.01	-0.61	-0.16	-0.05
S77	0.50	0.00	2.21	0.16	0.17	-0.35	2.61	-0.34	0.00	0.00	-0.58	-0.16	0.07
S78	0.50	0.00	2.12	0.16	0.17	-0.35	-0.36	-0.34	0.00	0.00	-0.61	-0.16	-0.05

	Sb	As	Ba	Pb	Cd	Co	Cu	Cr	Hg	Mo	Ni	V	Zn
S79	0.51	0.00	3.97	0.16	0.17	-0.35	94.15	-0.34	0.00	0.03	-0.61	-0.11	0.53
S40	0.50	0.00	2.26	0.16	0.17	-0.35	13.52	-0.34	0.00	0.04	-0.61	-0.15	-0.05
S41	0.53	0.00	4.05	0.16	0.17	-0.35	67.91	-0.34	0.00	0.07	-0.61	-0.12	0.54
S42	0.50	0.00	2.17	0.16	0.17	-0.35	1.29	-0.34	0.00	0.06	-0.61	-0.15	-0.07
S43	5.02	0.01	21.83	2.22	2.04	-3.14	6067.99	-3.40	0.01	0.05	-3.54	-1.68	23.29
S44	0.53	0.01	3.31	0.60	0.41	-0.10	4148.63	-0.33	0.00	0.00	1.13	-0.17	18.89
S45	5.22	0.03	22.64	5.63	2.11	-3.22	17567.07	-3.15	0.01	- 0.03	-3.42	-1.64	29.46
S46	0.74	0.02	3.97	4.75	0.56	-0.07	16919.31	-0.07	0.00	0.02	2.96	-0.09	34.01
S47	5.19	0.03	22.66	7.25	2.00	-3.28	18070.28	-2.96	0.01	- 0.05	-4.17	-1.14	20.74
S48	0.73	0.03	4.07	7.16	0.48	-0.11	18627.74	0.17	0.00	0.03	2.41	0.47	26.18
S49	5.19	0.01	24.05	4.92	1.71	-3.40	1249.06	-3.19	0.01	- 0.08	-6.38	-0.60	2.13
S50	0.70	0.01	5.19	3.87	0.19	-0.26	1170.10	-0.09	0.00	0.00	-0.95	0.88	2.66
S51	5.24	0.02	23.81	3.86	1.71	-3.44	727.48	-3.25	0.01	- 0.08	-6.26	-1.11	1.08
S52	0.76	0.01	4.92	2.34	0.18	-0.29	700.50	-0.15	0.00	0.00	-0.73	0.43	1.71
S53	5.05	0.01	21.80	2.25	1.70	-3.48	185.98	-3.37	0.01	- 0.09	-6.14	-1.54	0.10
S54	0.57	0.00	3.10	0.81	0.17	-0.33	191.90	-0.27	0.00	- 0.01	-0.67	0.01	0.51
S55	12.15	0.43	800.39	162.61	5.51	-3.79	196100.08	3.53	0.03	1.41	23.77	11.61	432.20
S56	11.05	0.45	825.92	165.87	5.67	-3.74	213860.80	2.84	0.03	1.37	26.98	11.66	433.27
S57	11.27	0.46	849.54	169.30	5.68	-3.64	214616.61	7.08	0.03	1.46	23.52	12.46	447.77
S58	10.42	0.06	71.27	11.04	3.58	-4.90	2048.52	-1.98	0.02	- 0.12	- 16.96	11.86	17.40
S59	10.31	0.08	79.79	12.77	3.56	-4.62	2356.41	-0.97	0.02	- 0.12	- 19.06	17.74	21.49
S60	10.58	0.64	306.13	54.13	5.57	11.37	37.00	57.13	0.02	1.16	81.22	96.87	915.89
S61	10.38	0.65	300.57	55.53	5.50	11.80	32.32	53.50	0.02	1.03	84.90	96.47	933.26

APPENDIX II

Carina Hall, Skövde Värmeverk	Skövde Värmeverk has a waste incineration facility where 60 000 tonnes waste are handled per year. Approximately half of it is household waste and the rest comes from different types of industries. In this process we have a flue gas treatment step where we produce an acidic process water. Approximately 13 000 m^3 condensed process water is produced annually.
Bengt Brunberg, Billerud korsnäs	After consulting two of our environmental engineers I have come to understand that our process water is well above your desired pH levels. The pH of our filtered process water is kept at 6.7 and does therefore not seem like a relevant trace for your research.
Bengt-Olof Andersson, Lidköpings Värmeverk	Regarding your questions on our process water, we have nothing with the low pH you desire. However, the condensed flue gas water we generate has an annual quantity of approximately 50 000 m^3.
Peter Nilsson, Vetab Vetlanda	Vetab has a flue gas treatment step but our rinsing circuit is maintained at pH 6.5. During 2014 we had an outtake of 9900 m^3 condensed process water.
Anna Karlsson, Vattenfall	We produce somewhere between 150 000 – 200 000 m^3 process water annually. I would like to point out that it can be complicated to extract the process water at such a low pH as is given in the report, normally the pH is increased to around 2, before being recirculated into the condensing process again. A part of the product is taken out at this point for cleaning. However, it is possible to rebuild the process in order to have an outtake at lower pH levels.
Annie Grann, Jönköping Energi	Yes we have water with low pH in the flue gas cleaning, which is called ”the acidic step”. This is not something that is treated for emission and is instead recirculated back into an earlier step in the cleaning process. For this reason, it is not something that we monitor the quantities of either. We don’t have any discharge of water from our flue gas cleaning facility, only from the condensation.
Björn Pettersson, Norrköping Värme	In Händelöverket we don’t have the flue gas cleaning that is most commonly used for waste incineration furnaces in Sweden, because the incineration process is working a bit differently than the typical application. We do however have a flue gas condenser connected to our bio-furnaces but the

	condensate circuit is pH adjusted to around 7 and is, after flocculation precipitation and ammonium separation, slightly higher.