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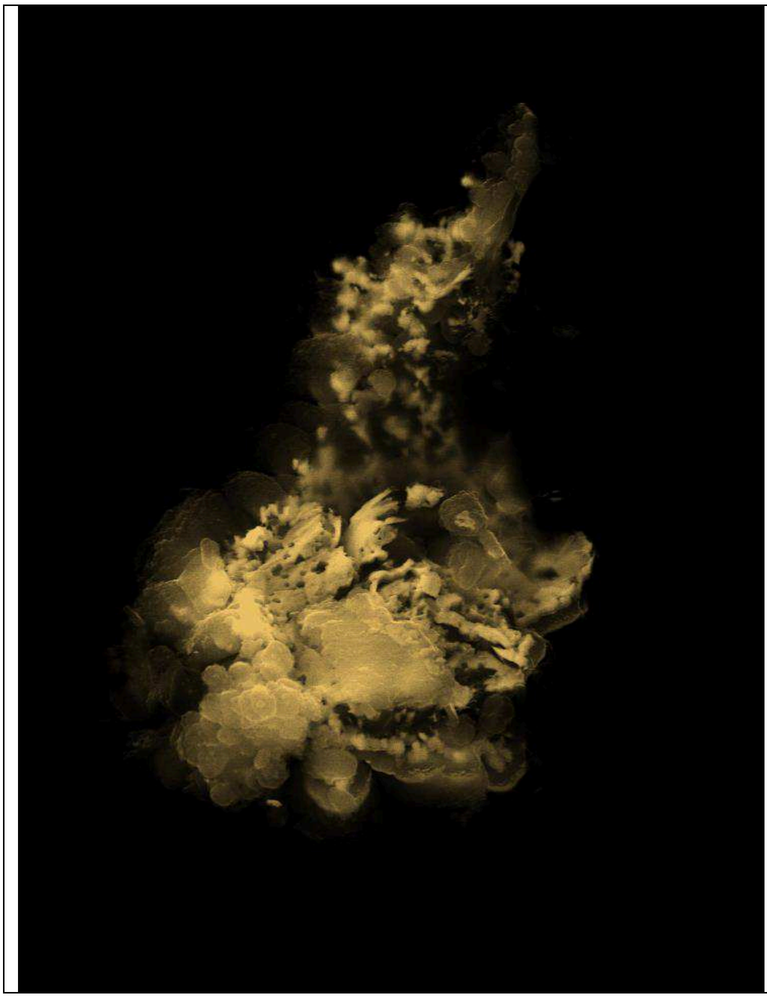
| Energimyndighetens titel på projektet – engelska<br>Precious Metals in Waste Material | |
| Universitet/högskola/företag<br>RISE | Avdelning/institution<br>Energi och cirkulär ekonomi |
| Adress<br>Box 857, 50115 Borås | |
| Namn på projektledare<br>Bo von Bahr | |
| Namn på ev övriga projektdeltagare<br>Henrik Jilvero, Sverker Sjölin, Glenn Bark | |
| Nyckelord: 5-7 st<br>WEEE, recycling, precious metals, gold, silver, rare earth elements, REE, SEM-analysis, characterization, fines | |



False-color image in secondary electron mode (© Glenn Bark) from scanning electron microscopy of a gold particle in WEEE.

The particle is 6 µm wide.



Box 310 • 631 04 Eskilstuna • Besöksadress Kungsgatan 43
Telefon 016-544 20 00 • Telefax 016-544 20 99
registrator@energimyndigheten.se
www.energimyndigheten.se
Org.nr 202100-5000

## Preface

This is the report from a Re:Source pre-project. The nature of the project is exploratory, and deals with the occurrence and behavior of precious metals (gold, silver and rare earth elements) in the fine fractions from electronic scrap recycling. So far, the recycling of WEEE (Waste Electrical and Electronical Equipment) has, in Europe, focused on quantity rather than quality, and it is also a well-known fact that significant amounts of gold and rare earth elements are lost in today's recycling processes.

The project has been carried through by three parts, Stena Technoworld, which is a major player in electronics recycling in Europe, Luleå University of Technology who contributed with analyzes and expert knowledge in the field, and finally RISE, Research Institute of Sweden (named SP Technical Research Institute when the project started) has taken part as a project manager.

The project group consisted of:

| | |
|---|---|
| Henrik Jilvero | Stena Recycling International AB |
| Sverker Sjölin | Stena Technoworld AB |
| Glenn Bark | LTU, Luleå University of Technology |
| Bo von Bahr | RISE, Research Institute of Sweden |

The project would like to thank Re:Source for funding that enabled the implementation of the project.

## Förord

Denna rapport utgör redovisningen av ett Re:Source förprojekt. Projektet är av undersökande karaktär och handlar om att lära sig mer om guld och sällsynta jordartsmetallers beteende och förekomst i fin-material från återvinning av elektroniksskrot. Hittills har återvinningen av elektronik varit fokuserad på kvantitet snarare än kvalitet, och man vet också att betydande mängder av guld och sällsynta jordartsmetaller går förlorade i dagens återvinningsprocesser. Problemägare är Stena Technoworld, som är en stor aktör på elektronikåtervinning i Sverige. Forskningsinstitutet RISE, Research Institute of Sweden (som hette SP, Sveriges Tekniska Forskningsinstitut då projektet startade) har fungerat som projektledare. Den tredje och sista parten i projektet har varit Luleå tekniska universitet som bidragit med analyser och expertkunskap på området.

Projektgruppen bestod av:

| | |
|---|---|
| Henrik Jilvero | Stena Recycling International AB |
| Sverker Sjölin | Stena Technoworld AB |
| Glenn Bark | LTU, Luleå University of Technology |
| Bo von Bahr | RISE, Research Institute of Sweden |

Projektet vill rikta ett tack till det strategiska innovationsprogrammet Re:Source, för medel som möjliggjort projektets genomförande.

# Innehållsförteckning

## Sammanfattning

Projektets syfte är att bättre förstå hur sällsynta metaller (guld, silver och REE, sällsynta jordartsmetaller) kan återvinnas från WEEE material. Idag går stora mängder av dessa metaller förlorade i återvinningsprocessen, dels för att de politiska målen för återvinning är kvantitativa snarare än kvalitativa, dels på grund av de nuvarande låga prisnivåerna för dessa material inte är en drivkraft för öka återvinningen av dessa material. Dock kan dessa två förutsättningar ändras förhållandevis snabbt i framtiden, och det är viktigt att generellt öka återvinningensnivåerna av dessa material för att röra sig mot en hållbar utveckling och att vara mindre beroende av import från Kina.

Den huvudsakliga verksamheten i projektet var att ta prover från WEEE, göra provpreparering, analysera proverna med olika metoder och slutligen dra slutsatser från detta. Ett viktigt faktum är att farligt avfall avlägsnades från WEEE-avfallet i ett första steg (enligt lagstiftningen) som följdes av bortplockning av lätt identifierade och värdefulla delar, t.ex. kablar, laptopskärmar och PCB (tryckta kretskort).

Det återstående WEEE-avfallet gick vidare i återvinningsprocessen. Från denna process faller det ut många olika fraktioner, och projektet har riktat in sig på de finkorniga fraktionerna från processen. Projektet har också samlat in kunskap via litteratursökning, och från andra industrisektorer, samt gjort en beskrivning av den nuvarande marknadssituationen för återvinning av sällsynta metaller.

Prover togs från Stenas återvinningsanläggning i Halmstad. De finkorniga utflödena var i fokus, eftersom ädelmetaller tenderar att hamna i dessa kategorier, enligt tidigare erhållen kunskap. Tre olika typer av finfraktioner togs det ut prover på; NF-finfraktion (icke järnhaltiga), Fe-finfraktion (järnhaltiga) och slam. Dessa tre typer av finfraktioner faller ut i olika skeden av återvinningsprocessen. En efterföljande siktningsprocess resulterade i tre sorteringar, vilket totalt gav nio olika prover. Detta provmaterial blandades med epoxy och gjöts till låga cylindrar, vilka bearbetades ytterligare för att vara lämpliga för undersökning med ett svepelektronmikroskop (SEM).

Proven undersöktes i SEM-mikroskop genom att manuellt avsöka varje provs horisontella yta. Totalt, undersöktes 2821 partiklar manuellt och i 82 av dessa hittades intressanta metaller; guld (16), silver (24) eller REE (42). Antalet prover och partiklar var emellertid för lågt för att kunna dra fasta slutsatser om den vanligt förekommande formen, partikelstorleken eller förmodade ursprunget av partiklarna. För att få statistiskt säkra slutsatser måste betydligt fler prover analyseras.

En analys av totalhalt gjordes också som ett komplement till mikroskopanalysen. Många ädelmetaller kunde detekteras, och den högsta totala halten av guld hittades i NF-fraktionen.

Energimyndigheten

Från de partiklar av guld som hittades, kan man konstatera att de alla har udda former, inte de tunna filmer (plätering o dyl) man kan förvänta sig då guldet från användning i elektronik. Detta tyder på att fragmentering och andra processteg har frigjort metallerna på ett ganska brutalt sätt.

Som förväntat så återfanns alltså guld och andra ädla metaller i de finkorniga fraktionerna. Dock är det ekonomiska incitamentet för att återvinna dessa specifikt, fortfarande mycket lågt. Om inte priserna ändras på dessa metaller, eller möjligtvis en förändring av lagstiftning sker med definierade återvinningsmål – så förväntas att status quo kommer att råda framöver.

## Summary

The project aim is to better understand how precious metals (gold, silver and REE, rare earth elements) can be recycled from WEEE material. Today, considerable amounts of these metals are lost in the recycling process, partly due to that the political recycling goals are quantitative rather than qualitative, partly due to the fact that the present low price levels for these materials are not a driver to increase the recycling rates. However, these two stipulations can change rather quickly in the future, and it is important to increase the recycling levels of these materials due to sustainability, and a less dependence on import from China.

The main activity in the project was to take samples from WEEE, make sample preparations, analyze the samples with different methods and finally draw conclusions from these activities. An important fact is that the hazard waste was removed from the WEEE stream as a first step, required by law. High value products were also removed from the WEEE-stream early in the recycling chain, such as laptop screens, cables and especially PCB (Printed Circuit Boards), and they are omitted in this work.

The rest continues to the recycling process, and the outputs consist of several materials in different particle sizes. There are some outputs consisting of fine materials, and these are in focus in this project, since some of the precious metals tend to end up in these categories. The project has also gathered know-how in the literature and from other industrial sectors, as well as a description of the present market situation for recycling of precious metals and REE.

Samples were taken from Stena Technoworld´s site in Halmstad. Three different types of fines were sampled; NF-fines (non-ferrous), Fe-fines (ferrous) and sludge. These three types of material drop out at different stages of the recycling process. A sieving process resulted in three sortings, ending up with nine different samples. These samples were casted to epoxy mounts, and further processed to be suitable for examination with a SEM (Scanning Electron Microscope) microscope.

The samples were examined in the SEM microscope by manually scanning the surface of the mounts. In total, the 2821 particles that were studied in detail, 82 of them included; Gold (16), Silver (24) or REE (42). However, the number of

particles was too low to make any solid conclusions on commonly occurring shape, particle size or presumed origin of the particles. For that many more samples have to be analyzed.
An analysis of the total content of precious metals was also done as a complement to the SEM-analysis. A lot of precious metals were detected and the highest total content of gold was found in the NF-fraction.

From the few particles of gold that were found, it is clear that they all have odd shapes, not the thin films you would expect coming from use in electronic equipment. This suggests that shredders and other process equipment have liberated the material in a rough manor.

As might be expected a lot of REE containing particles was also found in the fines fractions. However, the economic incentive for REEs' recovery is still very low. Unless there are regulatory or price changes, status quo is expected.

# Introduction and Background

## Problem description

As the products are becoming more complex, with higher demands and shorter life, the waste is becoming more complex, as well. Recycling industry is constantly adapting to treating new types of waste. Traditionally, recycling industry was focused on recovering key industrial metals, such as iron, copper and aluminum, from used cars and mixed metal waste. Recovery of precious metals (gold, silver, platinum and palladium) is common from waste streams included in producer responsibility acts, such as WEEE.

Today's products are usually more electrified, to expand their features while plastic is taking place of metals as construction materials. This is very evident in car industry. It is therefore needed to re-evaluate classification of waste and aims of recycling. It is likely that precious metals, platinum metals (rhodium, iridium and osmium), and rare earths (neodymium, dysprosium and europium) will be found in waste streams where they were not found before. Even though recovery of precious metals from WEEE is nothing new, studies show that large amounts of these metals are lost. Traditional recycling methods are designed for the large volumes of industrial metals that are easy to detect and quantify, not for metals of low quantities and physical characteristics of precious metals.

Gold is used in thin plating of conductive contact surfaces in electronics, because of its low conductivity and surface resistance. Standard recovery methods include various combinations of crushing, separation by density and magnetic separation. In these processes gold can easily be lost, because of its relatively high density (19.3 kg/dm$^3$) comparing to other materials (iron 7.8, copper 8.9, aluminum 2.7 and plastics 1-1.4) making gold fall on a bottom of a heap or in the non-reachable parts of the equipment.

Gold is difficult to characterize in heterogeneous waste streams, which contributes to loss of gold. Amount of analytical sample for chemical analyses are often about 5 grams. These few grams should represent a several kilograms of sample, which in its turn should represent several tons of the sampled material (Ore/WEEE). This puts large demand on sampling and subsampling procedures. Characterization of gold in ore normally includes several tens of thousands of chemical analyzes. Taking into account that chemical analyses are often performed by external accredited labs, the time aspect cannot be neglected.

Sampling of large amounts of material aiming at assessing metals in low concentrations, are questions that the mining industry has been grappling for a longer time than waste industry. This study is aiming at adopting proven methods for characterization of precious metals used in mining industry, and using them for characterization of WEEE in terms of gold. More knowledge on precious metals and their behavior during sampling and analyses, can potentially reduce losses of these valuable material and change the way of treating waste.

### Goal

This project aimed at developing methods for characterization and chemical analyses suitable for assessing precious metals in heterogeneous waste and recycled materials. Expected effects are improved collection, pretreatment and recovery of precious metals, leading to closed loop for these metals and avoiding their loss from the society.
Goals were as follows:

1. Mapping precious metals in WEEE (waste electric electronic equipment), including their amounts and chemical occurrence,

2. To compile relevant experiences from other industrial branches,

3. To test possibilities to implement characterization methods currently used in mining sector on the material of comparable content of precious metals,

4. Create conditions for the future innovation project; including mapping and analysis of the stakeholder needs, an actor constellation dedicated to the next stage of development, as well as a description of other relevant conditions

### Scope

The project is limited to precious metals with relatively high economic value and wide use in electronics, such as gold, silver and rare earth elements. The project concentrates on WEEE material only, and in specific the fine fractions resulting from the recycling activities from the WEEE-material. High value products which have been removed from the WEEE-stream early in the recycling chain, such as laptop screens, cables and especially PCB (Printed Circuit Boards), is omitted in this work. The remainder is a very inhomogeneous flow which is treated by a set of consecutive recycling processes. The fines from this treatment are investigated in this project.

### Technical-, policy- and market related conditions for recycling of precious metals.

Almost all domestic electronic and electric equipment (EEE) are in Sweden subjected to producer-responsibility system. Some specialized and non-household commercial EEE can be exempt from the producer-responsibility system. Stena Technoworld is the company responsible for WEEE recycling within the Stena Metall. The waste is collected from larger organizations and institutions (business-to-business) and through a producer-responsibility organizations (Elkretsen or EÅS) which collect waste from at municipal collection sites and shops.

#### *Stena Technoworld's recycling process*

The WEEE is transported to a first treatment facility where hazardous components (e.g. Ni-Cd batteries) and highly valuable components or products are separated (e.g. printed circuit boards, cellphones). The precious metal content of this

fraction is sufficient to treat separately. Other streams are transported to the processing facility, combining milling, sieving and magnetic and density separation.
Figure 1 present a very simplified schematic of streams produced during the valorization of the WEEE. The most difficult fractions to find any material or energy recovery for in all types of recycling are the fines fractions (here set to < 3mm). These fractions are characterized by a high mineral content (stones, glass, soil and concrete), low organic content and some residual metals. For these reasons, these fractions are in many cases landfilled. However, it is known that during milling of WEEE material, some of the precious metals are liberated as fine particles which eventually will end up in the fine fractions. The present project will mainly focus on these three WEEE fines' fractions:

- Fe-fines (Fe = ferrous)
- NF-fines (NF = non ferrous)
- sludge

The difference between the Fe-fines and the NF-fines is that the Fe-fines are magnetic, containing more ferrous material. The sludge is a waste fraction from the sink-and-float (density separation) process. Hence, the sludge will mostly consist of density regulating media, in this case being calcium carbonate.

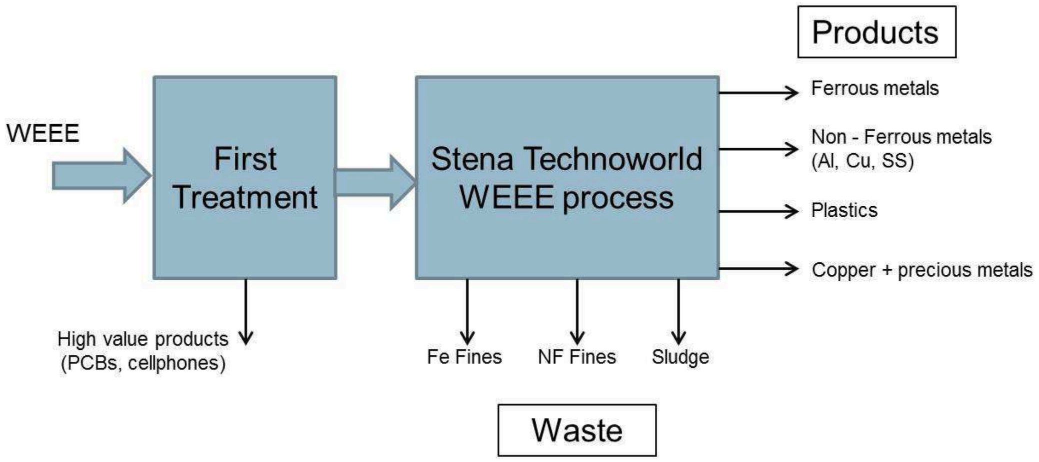
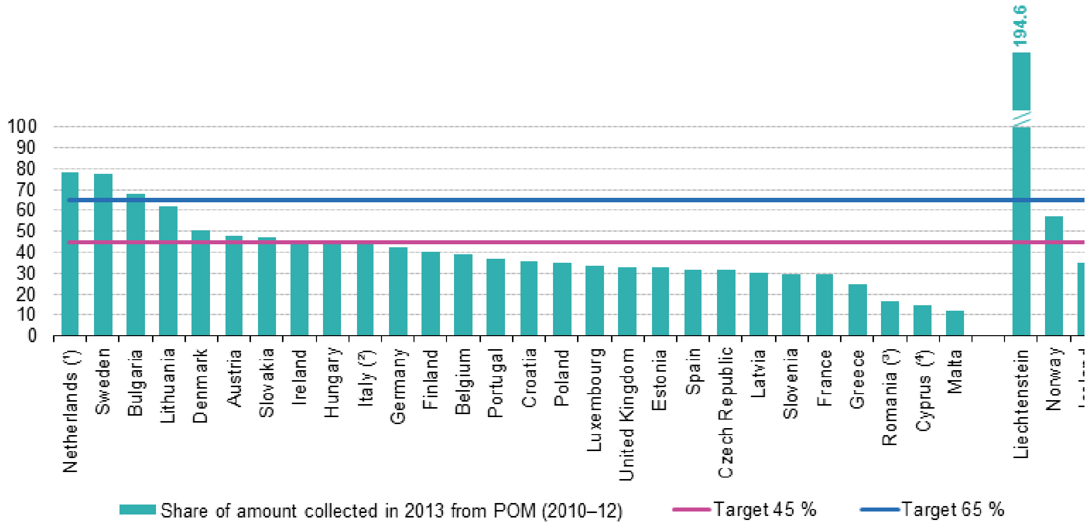



**Figure 1. A simplified schematic description of the Stena Technoworld valorization process for WEEE.**

### *Current policy on regulatory levels*

The policies governing the treatment of WEEE are in the EU covered by the current WEEE-directive "Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE)". The directive states that the minimum collection rate of the producer responsibility WEEE is 45% of what is put on market and it will increase to 65% by 2019.

Figure 2 show the collection rate of WEEE in the EU28+3. It shows that Sweden and the Netherlands approach an 80% collection rate.




(1) Products put on the market in 2010 and 2011: definition differs, see metadata.
(2) Waste collection: definition differs, see metadata.
(3) 2012 data.
(4) 2013: estimate.

**Figure 2. Collection rate of WEEE in EU28 member states plus additional countries [1].**

The recycling rates for different categories (Table 1) of WEEE are given in Table 2. The difference between the recovered and recycled rates are amounts allowed for energy recovery, while the residual fraction is allocated to landfills. The percentages stated in Table 2 are defined by weight, meaning that only the base materials of WEEE (plastics and major metals) are affected in the reality. As the precious and rare earth elements (REEs) are present in such a low weights, there is in reality no policy encouraging higher recycling. A recovery rate based on specific element, such in the battery directive, could potentially alter the ambitions in precious and REEs' recovery.

**Table 1. Categories of EEE according to the EU WEEE directive and Swedish directive** *"Förordningen* (2014:1075) om producentansvar för *elutrustning"*. **The categories are valid until August 14th 2018, after which new categories and more stringent rates are imposed.**

| Category nr | Description |
|---|---|
| 1 | Large household appliances |
| 2 | Small household appliances |
| 3 | IT and telecommunications equipment |
| 4 | Consumer equipment and photovoltaic panels |
| 5 | Lighting equipment |
| 6 | Electrical and electronic tools (except of large-scale stationary industrial tools) |
| 7 | Toys, leisure and sports equipment |
| 8 | Medical devices (with the exception of all implanted and infected products) |
| 9 | Monitoring and control instruments |
| 10 | Automatic dispensers |

**Table 2. Recovery and Recycling rates according to the WEEE directive. For description of the categories, refer to Table 1.**

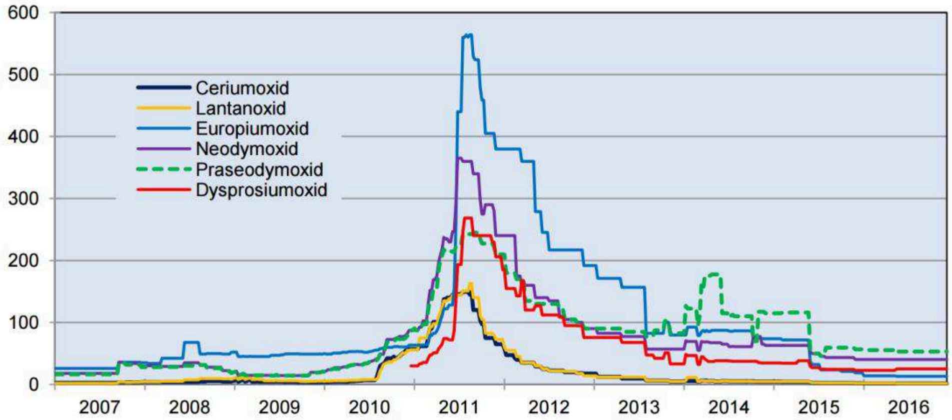
| | 15 August 2015 – 14 August 2018 | |
|---|---|---|
| **Category** | **Recovered (%)** | **Recycled (%)** |
| 1 and 10 | 85 | 80 |
| 3 and 4 | 80 | 75 |
| 2, 5, 6, 7, 8 and 9 | 75 | 55 |

Some of the larger actors in the region of precious metal recovery from WEEE are Boliden, Umicore and Aurubis. At Boliden´s Rönnskär facility a Kaldo oven is used to smelt copper along with the precious metals. The precious metals that are recovered at the Rönnskör Facility are gold and silver and they also produce a palladium/platina concentrate, which can be upgraded. The Umicore facility in Hoboken recovers 17 metals from their precious metals recycling process (Au, Ag, Pt, Pd, Rh, Ru, Ir, Cu, Pb, Ni, Sn, Bi, Se, Te, Sb, As, In). Aurubis is also a copper smelter company who additionally produce gold and silver.

The recovery of precious metals is today solely motivated by monetary means. As the material exchange prices constantly fluctuates so will the recycling methods. Figure 3 show historical data of the commodity prices of gold (a) silver (b) and REEs (c) [2]. Today the recovery of precious metals from WEEE is solely driven by market forces, thus there are no policy driven requirements to recover precious metals of REEs from WEEE. A higher material price will motivate a higher degree of disassembly in the first treatment. All commodities experienced a peak price during 2011-2012 and have since then progressive declined. This is especially true for REE which has declined significantly since this period. The reason for the large fluctuations in the REEs price is due to past alterations in China´s export quotas. At current prices the incentive to recover any REEs from WEEE is low. It is only in very specific applications where high concentrations and volumes of REEs are easily accessible, where recovery of REEs is motivated. One such example is the large neodymium magnets which can be salvaged from decommissioned wind mills.


a)


b)




c)

**Figure 3. Historical commodity prices of gold (a) and silver (b) given in USD/tr oz and REEs (c) given in USD/kg, Europiumoxide and Dysprosiumoxide in USD/hg.**

One of the future challenges with precious metals in WEEE is that the concentrations of precious metals might decrease. This is due to that the conductivity enhancing coatings of precious metals in electronic equipment is progressively getting thinner. Even though the total amount of precious metals used in WEEE is expected to increase the concentrations are expected to decrease, which consequently will make smelters more reluctant to pay for certain WEEE fractions.

REEs are primarily produced in China (Figure 4). Of the 124 000 tons of REEs produced world-wide in 2015, nearly 85% were produced in China. The consumption of REE-oxides in China is expected to increase from 98 000 tons in 2015 to 149 000 tons in 2020 [3].

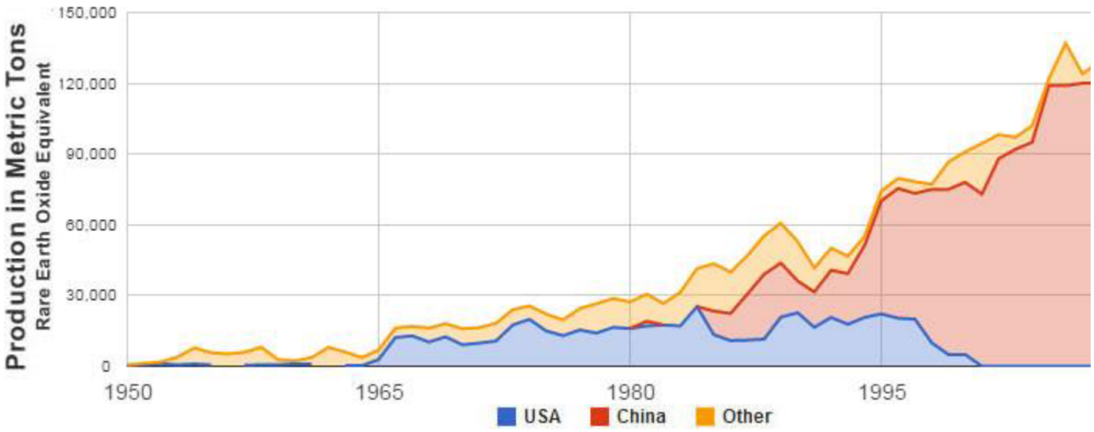



**Figure 4. The global production of REE [3].**

## Characterization of trace element ores (typically gold) in the mining industry

The mining industry has been doing different types of characterization for many decades. All sorts of metallic ores (e.g. Fe, Cu-Pb-Zn, Au) are subject to detailed characterization, to improve the understanding of the geological and structural settings of the ore, and thereby the recovery of the metals extracted. With a high degree of characterization, using state-of-the-art analytical equipment, it is possible to tune the mineral extraction processes so that larger revenue is accomplished.

Since detailed information on the occurrence of gold in the ore directly affects the metal recovery different types of analysis are used. The ore body is diamond drilled in a grid pattern, and samples (drill cores) are extracted from the ore, Figure 5. These drill cores constitute excellent material for subsampling, for use in various types of microanalytical techniques.

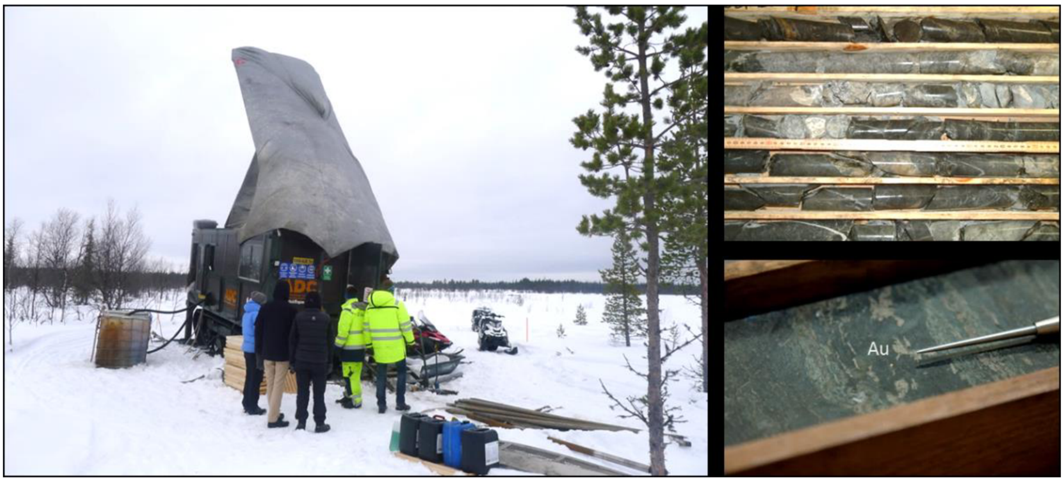



**Figure 5. Mineral exploration drilling in northern Sweden. This type of drilling generates rock drill core (upper right picture) that can be subsampled and further investigated in great detail. Lower right picture displays a minute gold grain in a drill core.**

### *Characterization of the drill cores*

All drill cores are manually logged and minerals of interest are noted. Since gold is a trace element and commonly has a grain size of <50 µm it is difficult to target when drilling the bedrock. However, when the gold ore was formed many million years ago the surrounding bedrock was affected, forming so called alteration minerals (for instance pyrite and arsenopyrite) that are related to the gold and that differs from the original background bedrock in that area, Figure 6. So, to target gold, the alteration minerals constitute a larger volume of bedrock and are therefore easier to target.

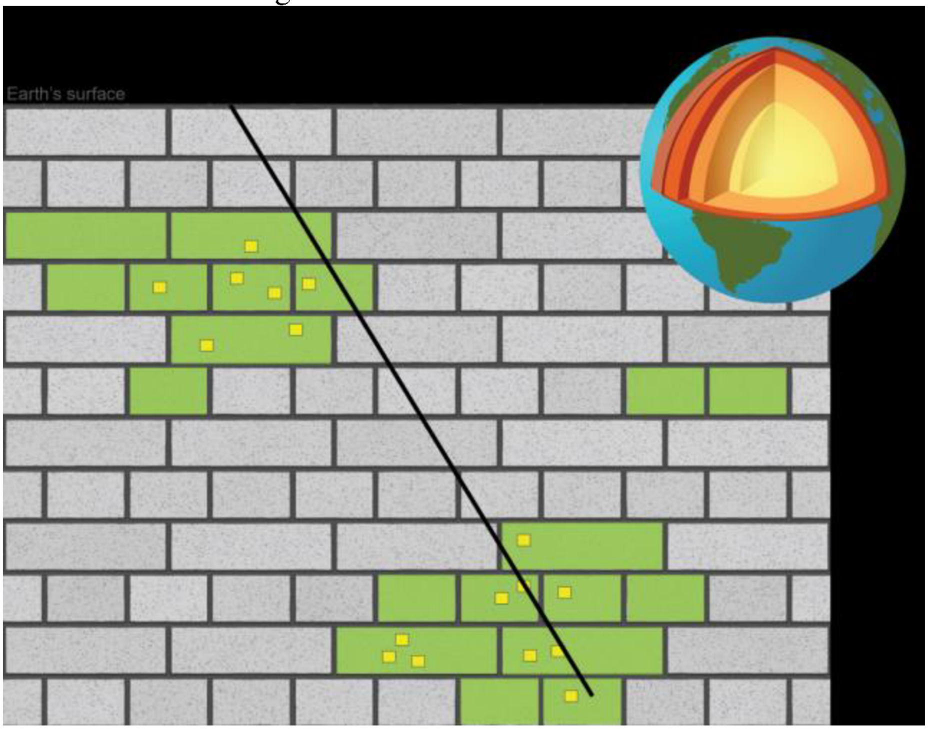



**Figure 6. Schematic view of a piece of the Earth's crust. The yellow specks represent gold and the green bricks indicator minerals that are commonly spatially associated with gold ore, alteration minerals. The grey bricks represent the huge amounts of common background minerals**

### *The occurrence of gold*

Once an ore body is discovered in the bedrock, through geological mapping and/or geochemical and geophysical measurements as well as boulder tracing (for gold), it is crucial to investigate how for instance the gold occurs in the bedrock. In process mineralogy, the two main types of gold ore are free milling gold and refractory gold.

Free milling gold means that the gold is fairly easy to extract, as it occurs in such a way that blasting and crushing/milling together with flotation is enough to reach a good recovery of gold (which for gold-only deposits is >90 %).

However, in many ore deposits fine-grained gold occurs to some degree locked inside sulphide minerals such as pyrite and arsenopyrite. One example is the Kittilä gold deposit in northern Finland where about 75 % of the gold is locked in arsenopyrite. Then an extra process step of cyanide leaching in closed tanks is used. There the sulphide minerals are dissolved in cyanide and the gold is liberated and possible to recover. Should the mining company be unaware of the locked gold, the gold would together with the sulphide minerals be deposited as waste and thereby lost.

An ore body is characterized in several different ways, with different intentions. Methods such as x-ray fluorescence (XRF) and hyperspectral imaging of the drill cores are used to define the alteration minerals (together with manual identification of minerals), which provides input to further exploration in the deposit area. This is also a way to delineate where the gold-related altered rocks are in the deposit area.

In this report, we will focus on the characterization methods used to improve the mineral process and metal recovery, since the approach and also the methods are directly applicable to the metal recycling industry.

*Mineral Liberation Analysis*

**Mineral Liberation Analyzer (MLA) and QEMSCAN**

To investigate how the gold (or other trace elements of interest) occurs in the ore (or WEEE), subsamples of the ore are used to perform a so called gold search. This is done in an MLA (Mineral Liberation Analyzer), or QEMSCAN (Quantitative Evaluation of Minerals by SCANning electron microscopy) that operates similar to MLA and provides the same output data (basically the same technique, but different manufacturers).

An MLA is essentially a computer-controlled SEM, coupled with multiple EDS detectors and software that scans the sample (for instance epoxy mounts, that were used in this study), recognizes particles and different phases within the particles and analyzes them all automatically according to the user-specified parameters. Currently its primary use is in the mineral processing industry, but it can be an extremely powerful tool for any investigations that could benefit from rapid data acquisition and compositional or mineralogical quantification of small inorganic particles such as any rock or mineral fragments, metals, ceramics, ashes or slags. MLA and QEMSCAN have been developed for the mining industry to solve some very specific problems or collect and quantify automatically scientifically valuable data which would be extremely tedious to collect manually.

*Using the instruments*

There are several different measurement modes available to solve different types of problems. One routine measurement mode used for crushed/powdered samples sets up the SEM so that all the interesting particles in the sample are recognized, measured and analyzed. This recognition is based on particles (usually minerals, for the mining industry) having a higher SEM image grey-scale value than the epoxy mount, which is set as background. If gold is searched for in the sample, then all particles with a higher grey-scale value than for instance 200 will be analyzed (the grey-scale goes from 0 to 255, where high values are seen as white particles in the SEM images). Particles with lower grey-scale values will be ignored in the analysis. The density of the particles, essentially their element composition, results in different shades of grey due to elastic scattering of primary electrons from the beam interacting with the sample. The instrument moves the sample automatically and collects data from all particles of interest in the sample (e.g. particle size, form, element association, degree of locking, chemical composition from EDS analysis). All EDS spectra are compared to a spectrum library and assigned a mineral name. The analytical parameters used are determined by the operator and there is always a compromise as to what sort of magnification to use, how long to collect each EDS spectra, what resolution to use for imaging etc.

*Collection of data*

All these parameters have an impact on the time the measurement runs and subsequently the cost. Analysis is often done as over-night automated runs, as it typically takes 3-4 hours for one sample if gold particles larger than 1−2 µm are to be detected and analyzed. The end result is a comprehensive statistical characterization of the sample, with typically data from more than 15 000 particles in each sample, given that there actually are >15 000 particles of interest in the sample. This is unlikely for a gold search, where the amount of gold particles per sample typically is anything from zero to a few hundred grains. Thus, to get acceptable statistics on the occurrence of gold in the deposit, many samples are required. For a gold ore deposit, commonly several hundred samples are used in the MLA characterization. MLA provides massive amounts of liberation data for the desired mineral phases, data that later guide the mineral process to improved metal recovery. Data over so called deleterious minerals in the ore is commonly also collected, as those minerals will negatively affect the mineral processing, resulting in loss of gold.

*Complementary characterization of the gold particles*

**Electron probe microanalyzer (EPMA)**

After the samples have been characterized with the MLA, typically the detected gold grains are analyzed in an electron probe microanalyzer (EPMA) that essentially is an SEM fitted with multiple WDS detectors (wavelength-dispersive spectrometry). In the EPMA, detailed compositional data from each gold grain can be generated. It is important to know the proportions of Au-Ag-Hg in the grains, as both Ag and Hg commonly occurs together with the Au in ore deposits. The proportions, mostly whether the particles are Ag-rich/poor, can affect the mineral processing negatively. Gold particles are notoriously difficult to analyze with the EPMA, as they are commonly very fine-grained and displays uneven surfaces. The unevenness is due to the polishing of the samples, to be able to use them properly in the SEM/EPMA. Gold is very soft and the polishing leaves groves and pits in the gold particles. These very small topographical features of the sample surface may seem insignificant, but is actually a major obstacle for the EPMA analysis as the topography will result in poor analyses and large portions of the data set may be rendered useless.

The EPMA is in addition to the spot analysis of particles of interest excellent for generating maps of the element distribution in the particles, Figure 7. For the mineral processing of the ore it is important to understand if the element of interest (e.g. gold locked in arsenopyrite) is evenly distributed in the host mineral or if it is concentrated in the core or rim of the host mineral. Should the Au be concentrated in the rims of the arsenopyrite, less time for cyanide leaching is required. Having this information lets the process mineralogist decide on a shorter leaching cycle, compared to if the gold was concentrated in the core of the host mineral, and thus reduces the cost for processing the ore.

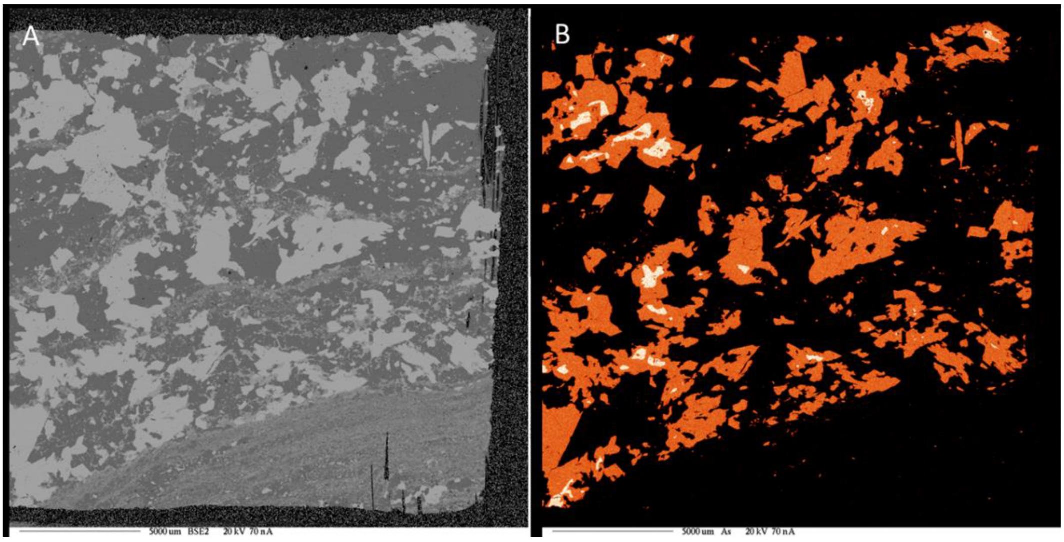



**Figure 7. Element mapping of a gold ore sample, using the electron probe microanalyzer (EPMA). A) Backscattered electron SEM-image of the sample, showing areas of different density in the sample. The intensity in the greyscale corresponds to differences in atomic number contrast in the sample. B) Same area as in A, but shown as an element map. Here, the area has been scanned with the electron beam and the EDS-detector shows the intensity of arsenic in the sample. The arsenic grains constitute the mineral arsenopyrite, which commonly is associated with gold in metallic ores.**

### Laser Ablation Inductively Coupled Plasma Mass Spectrometry, LA ICP MS

Another technique that is increasingly gaining interest from the mining industry (traditionally, it has been more common within academic research) is laser ablation inductively coupled plasma mass spectrometry (LA ICP MS), which is a powerful analytical technique that enables highly sensitive elemental and isotopic analysis to be performed directly on solid samples. In this instrument, a laser beam is focused on the sample surface to generate an aerosol of fine sample particles (laser ablation). The ablated particles are then transported through a plasma torch where the particles are digested and ionized (excited). The excited ions are subsequently introduced to a mass spectrometer, where element quantification takes place.

The LA ICP MS technique is in the front line of extreme element quantification of solid samples. It has been developed within academic environments for decades, and the instrument is similar to an EPMA, but generates far better element detection levels. Analysis down to the ppb level (parts per billion) is possible in spot analysis, compared to the EPMA that has a detection limit of ca. 100 ppm (parts per million). Laser ablation ICP MS is a destructive method since the laser digs micron-size craters in the sample, compared to the EPMA that can analyze the same spot over and over again. The spatial resolution is better in the EPMA, which typically works with a spot size of 1−5 µm. LA ICP MS commonly requires a laser spot size of a few tens of micrometers to get a good signal to noise ratio, in spot analysis mode. It is also capable of generating element maps of the sample and in those maps elements that cannot be detected in the EPMA are picked up and displayed nicely, Figure 8.

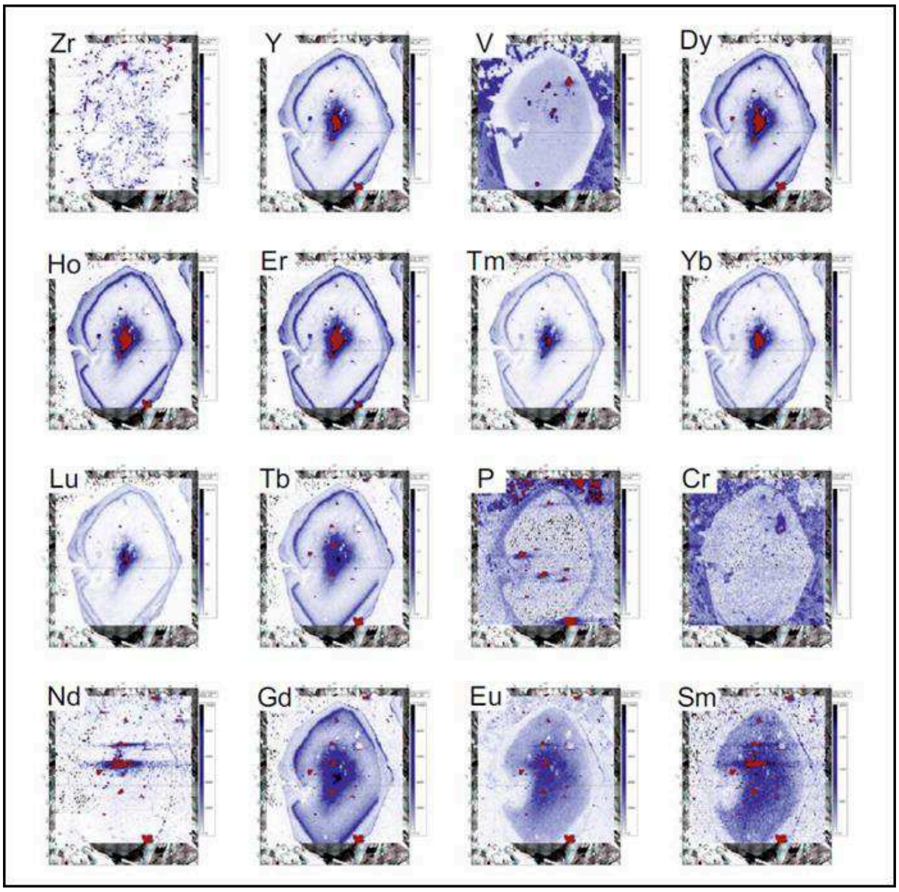



**Figure 8. Element maps of a garnet that shows distinct zoned distribution of trace elements. Data from a LA ICP MS mapping session, Luleå University of Technology.**

### Literature Review, methodology

The aim of the literature search was to scan the field and search relevant scientific publications regarding sampling and analysis of this type of material, i.e. inhomogeneous materials with a small content of precious or scarce metals. The scientific databases used in the project are listed in Table 3, together with a short description of the characteristics of the database, and relevant key words used. The key words listed in the table were used in different combinations.

**Table 3. Databases used in the literature search**

| Database | Description | Keywords used in several different combinations |
|---|---|---|
| Science Direct | Scientific database, which covers 3 800 journals and 35 000 book titles, published by Elsevier. All information in this database is also covered by Scopus, below, which means that this database has been used indirectly. It is mentioned here only because it is well-known. | precious metals<br>gold<br>sampling method<br>sampling strategy,<br>characterization<br>WEEE<br>Recycling<br>Waste<br>quantitative analysis |
| Scopus | The largest abstract and citation database of peer-reviewed literature: scientific journals, books and conference proceedings | |
| Google Scholar | A search engine which selects publications in the internet, classified as scientific literature. Updated very often. | |

### Literature review, findings

The literature search was done according to the description in previous section. A general observation is that there are a large number of articles about recycling of WEEE in literature, but only a small fraction of them includes precious metals. Many of the articles focus on treatment of PCB (Printed Circuit Boards) and not as much at handling the less valuable fractions from WEEE.

The number of articles and reports estimating the potential of recycling of precious metals from WEEE was surprisingly high. Methods for estimating this potential were different and in many cases the potential was assessed to be large, but with a rather high uncertainty. A common method used, was to multiply the assessed concentration in a fraction (e.g. laptops) with the amount of the fraction in a certain region, e.g. Europe. The general conclusion is that the potential for further material recovery is high, but not fully used, probably due to:

- low degree of collection in some countries or regions
- regulations focusing on quantity (of base metals) instead of quality (such as precious metals)

- difficulties to extract the precious metals due to that they are stuck to other materials
- not profitable to extract, at present price levels for virgin materials
- precious metals tend to accumulate in the finer fractions

Gold has a special status among the precious metals, both because it is a well-known precious metal and it has a lot of applications in the electronic industry. The articles found regarding precious metals tend to handle gold first and mention the other in more general terms. The reason for this is probably that gold has by far the highest economic value, which is corroborated by data from a new report from the Nordic Council of Ministers [4], (Figure 9). The value for gold in the figure is as high as 15.4 billions SEK, corresponding to about 44 tons of gold assuming price of 350 SEK/g gold. As a reference, the annual amount of gold produced at Boliden is about 15 tons. From an economic point of view it is motivated to focus on the recycling of gold, silver, palladium and cobalt, since these 4 corresponds to a 99.6 % of the economic value in WEEE.

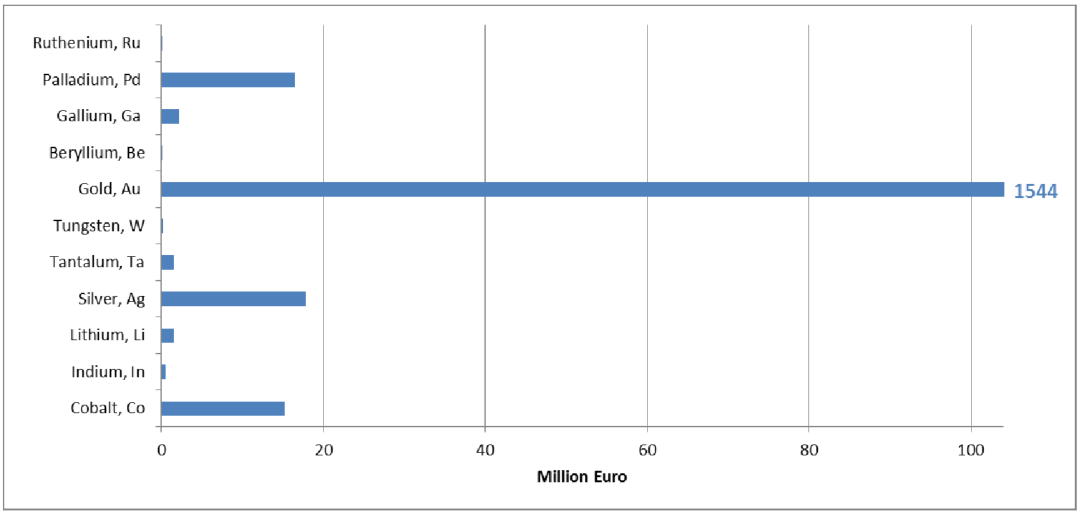



**Figure 9. The potential economic value of the critical metals present in the generated Nordic WEEE for 2015, dominated by gold [4].**

Another important reason to recycle gold and other precious metals is that the environmental impact from virgin production is very high compared to other metals. Especially regarding gold and the platina group metals. The climate impacts from production of these are between 10 – 100 times higher per kg than other precious metals. As things stand in the present study, gold represents over 97 % of the potential environmental savings from WEEE recycling – and gold, silver and palladium combined constitute over 99% of the potential savings [4].

Only a few references have been found that describes something similar to what has been done in this project. An article by Sun [5] describes the use of SEM-analysis in a similar way as in this project, but he studied the morphology and composition, not precious metals.

Other studies focus on the degree of liberation of all kind of particles, i.e. how "clean" the particles are [6][7]. Their finding is that the degree of liberation is quite high, but the liberated particles are often alloys, which requires further processing in the recycling chain to extract the pure metals.

Regarding geographical aspects, a lot of the research is and has been done in Asia, with a focus in China. China is the world leading producer of precious metals and they also handle a lot of WEEE.

Some conclusions from the literature search are:

- There are plenty of articles about WEEE, only a few focus on precious metals
- Articles regarding precious metals tend to focus on the potential of recovery of precious metals
- The recycling of PCB is very well investigated
- Recovering gold can be motivated both from an economic and environmental point of view
- There are only a few articles that deal with the question of how the precious metals occur in the waste.

The articles that were interesting have been compiled in Appendix B.

## Implementation of the project (genomförande)

This chapter provides an overall view of methodology used in this project which include a literature review, sampling process of the material (WEEE fines) and finally the (SEM-EDS) sample analysis. Figure 10 show a schematic view of the methodology that is used in the project. The literature review serves to assess each individual step in the methodology by evaluating previous work. The results from literature review also suggest appropriate sampling methods for more accurate on-line measurements of precious metals in WEEE fractions. The technical part of the project basically revolves around the analysis of 3 different fines fractions from the existing WEEE recycling process at Stena Technoworld. These fractions are, Fe-fines, NF-fines and sludge. The origin of these fractions is explained in 0. These fractions were sieved into three different size-fractions (>2mm, 0.5-2mm, <0.5mm). Thus, 9 different samples were analyzed in total. An elemental analysis of all the 9 samples was made to ensure the existence of precious metals and rare-earth metals, but is not a part of the official report.

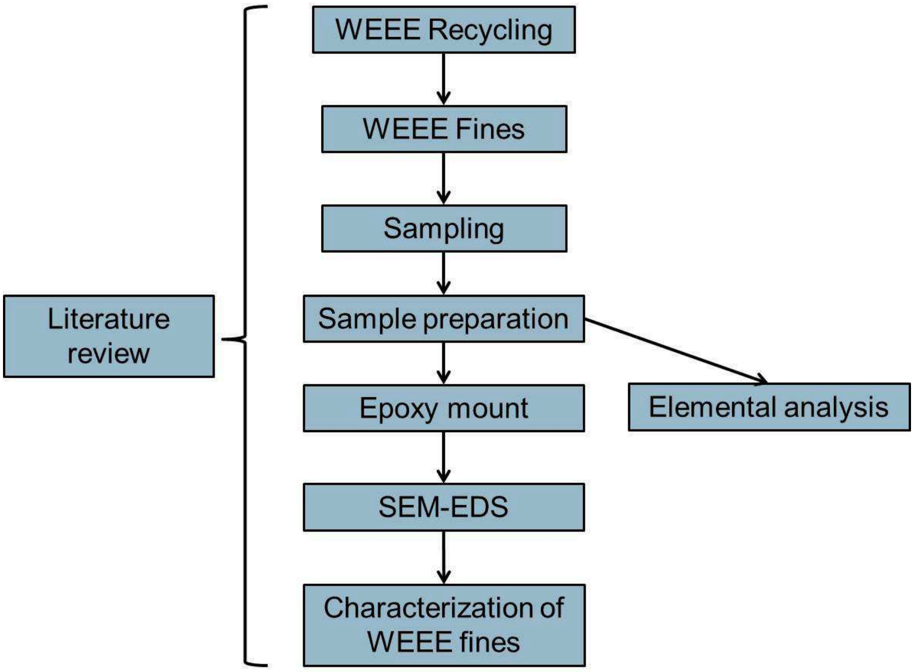



**Figure 10. An overview of the methodology and the scope of the project.**

### Sampling and sample preparation in Halmstad

The sampling was done according to established methods and standards in the waste sector. In Figure 11 below is a schematic description of the process to reach a final sample, appropriate for SEM analysis. The sampling procedure was different in the first step between fines and sludge, but similar in the consecutive steps. Three different materials (fractions) were sampled, and sieved in three different size-fractions (Figure 12), resulting in 9 individual samples.

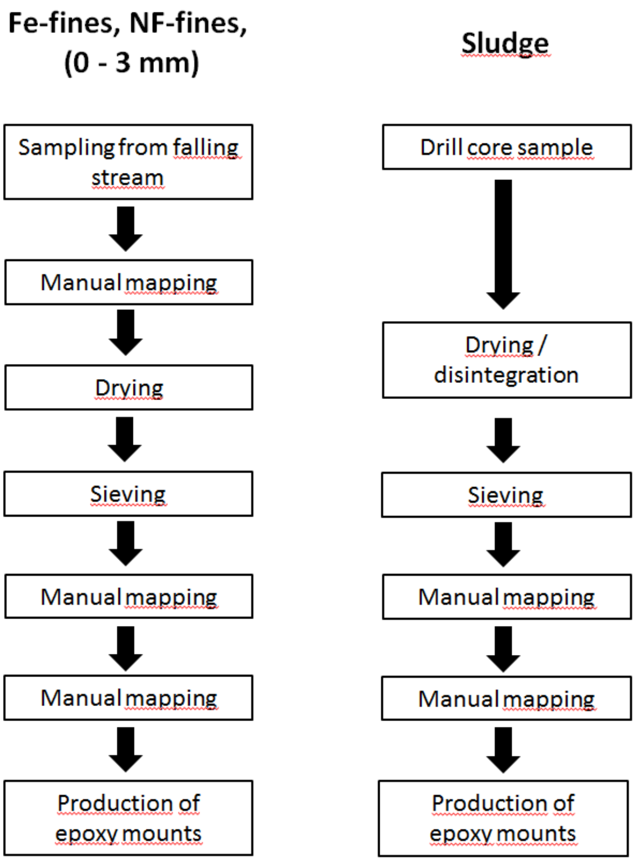



**Figure 11. Sampling process of fines and sludge. "Disintegration" of sludge in one of the boxes means a careful manual separation of parts that had been stuck together.**


**Figure 12. The sieving equipment. The sieving time differed from fraction to fraction and was stopped after visual inspection not after certain time span.**

*Sampling of fines*

The samples were taken from a falling waste stream during one day at approximately one hour intervals between sampling. About 2 kg of sample was collected at each occasion, resulting in about 20 kg of sample for each fraction. The samples of were collected in plastic boxes (Figure 13). Detailed tables of the sampling can be found in Appendix A.

**Figure 13. Collection of samples in plastic boxes. Approximately 20 kg of sample in each box.**

Dry content was determined by drying at 105°C for 8h and was 95% för Fe-fines and 86% for NF-fines.

**Figure 14. Appearance of the samples after drying but before sieving. Fe-Fines (left) and NF-fines (right).**

The subsequent step was to sieve the fractions into three particle size intervals, >2 mm, 0.5 – 2 mm, < 0.5 mm. After sieving, the last mapping was done. The outcome from this step was used to produce the epoxy mounts that were analyzed.

**Figure 15. The final samples of NF-fines fraction used to produce the epoxy mounts. Left: > 2 mm, center: 0.5 – 2 mm, right: < 0.5 mm.**

### *Sampling of sludge*

For sampling of sludge a steel pipe was used to take the sample from the pile of fines, a method which can be compared with taking a sample by using a drill (producing a drill core), which is the common method for mineral exploration. Figure 16 below shows the cylinder formed samples just taken out from the pipe. In Appendix A, a more detailed schedule of the sampling is described. All sludge was dried during 24h and a part of that time in 105°C. After the drying and before sieving, a mortar was used for further separation of the material. This was followed by sieving and the same consecutive steps described for the material in section 0.

**Figure 16. Samples of sludge, taken with a pipe.**

**Figure 17. Sludge after drying.**

### Sample preparation and analysis

Nine WEEE samples collected at Stena Technoworld in Halmstad were reduced through conventional sample splitting at LTU, into two subsamples from each sample. The subsample volume was approximately 10 $cm^3$, (Figure 18A). The subsamples were then  shipped to a sample preparation laboratory (Petrolab Ltd) in England, and to ALS Scandinavia for elemental analysis. The remainder of the samples were archived at LTU.

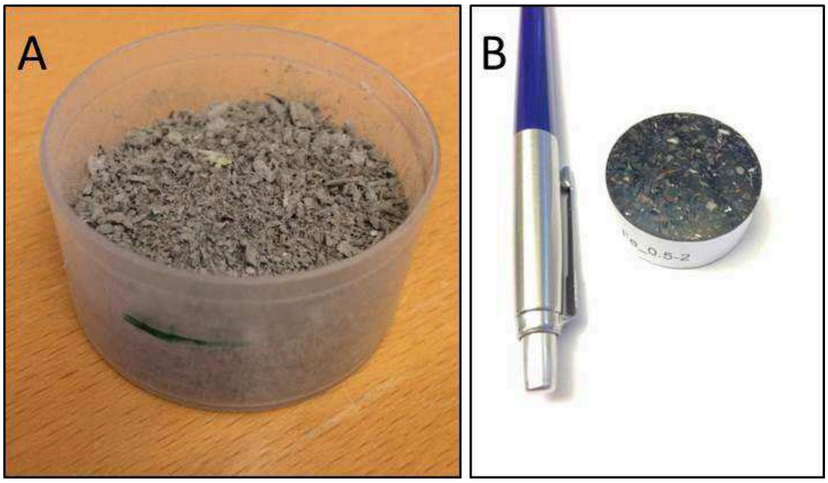



**Figure 18. WEEE sample. A) Sample volume required for one sample. The plastic cup measures 35 mm in diameter with a height of 20 mm. B) Polished epoxy sample (30 mm in diameter), prepared for SEM analysis.**

An English laboratory (Petrolab Lt), which specializes in technical support services to the mining, minerals processing and materials industries worldwide, prepared the samples into 30 mm circular polished epoxy mounts (Figure 18 B). This is a sample type suitable for analysis with SEM.

The individual granular samples, together with a graphite powder, were poured into epoxy glue and thoroughly mixed together (Figure 19). The graphite powder was introduced into the sample to prevent settling of heavier particles during hardening of the epoxy. The rounded graphite granules (powder) act as a physical barrier for the particles in the WEEE samples, and thus prevents the heavier particles to settle to the bottom of the mount  (which would render them impossible to analyze by SEM). When the samples had hardened, they were cut in half (using a machine saw) and the flat surfaces of the becoming samples were polished in an automated polishing machine until the surfaces reached an acceptable planeness and roughness which is crucial to SEM analysis (Fig B).

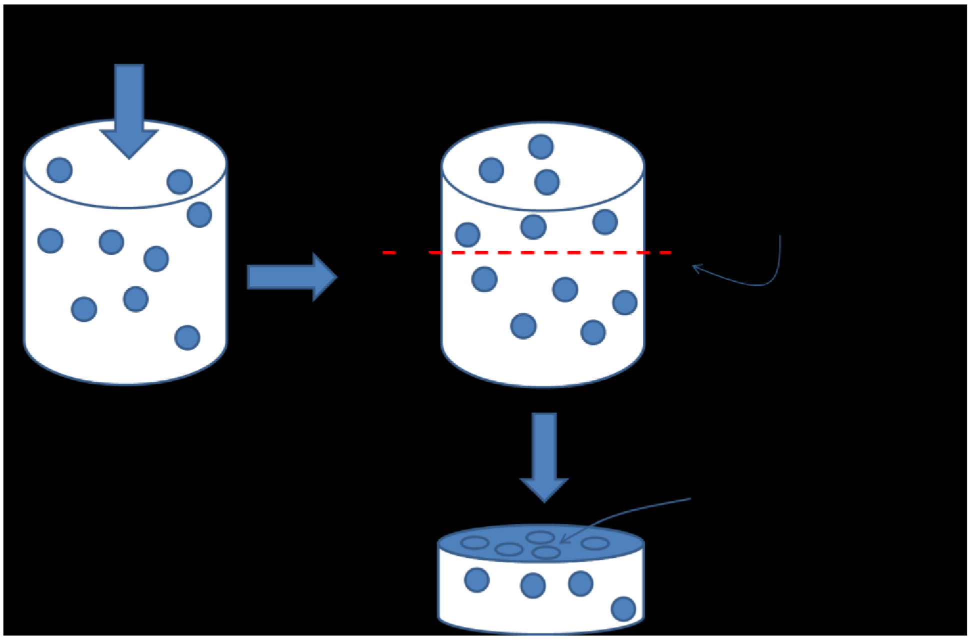


**Figure 19. Sample preparation of granular WEEE samples for analysis with a scanning electron microscope.**

As a final stage of sample preparation, the samples were given a thin coating (a few tens of nanometers) of carbon on the sample surfaces. This was done in a carbon coater (Figure 20), at LTU, where carbon was evaporated onto the samples. Thermal evaporation of carbon is widely used as sample preparation for SEM.

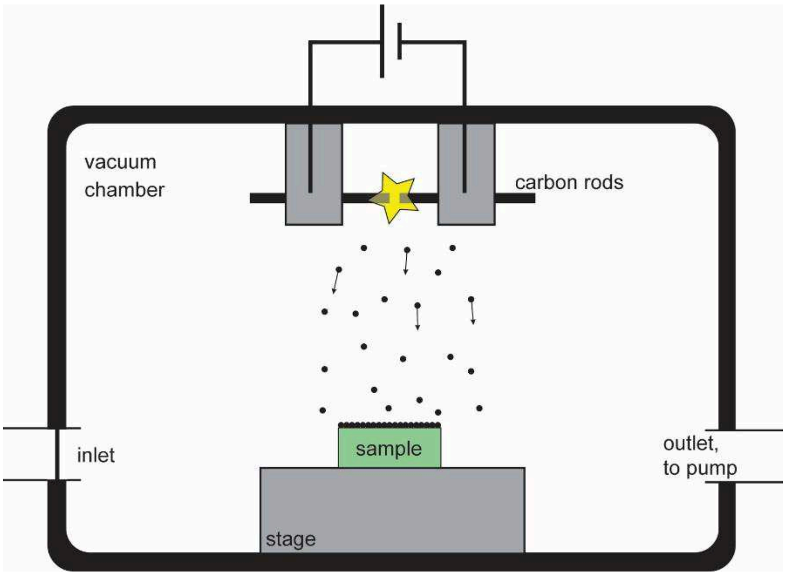



**Figure 20. A carbon source (carbon rods) is mounted in a vacuum system between two high-current electrical terminals. When the carbon source is heated to its evaporation temperature, a fine stream of carbon particles are deposited onto the samples that are positioned below the carbon source.**

Carbon coating is needed for samples that are non-conductive, as electrons from the electron beam in the SEM will otherwise not be able to escape from the point of analysis (electron beam spot), generating image and analytical artifacts called charging effects. The fine carbon layer is transparent to the electron beam of the SEM, thus enabling improved imaging, chemical analysis and removal of excessive electrons at the sample surface.

After the coating procedure, the nine samples were cleaned with alcohol and plasma cleaning, removing any residues from the sample preparation and un-gloved handling of the samples.  After this, the samples were ready for analysis with SEM.

### Microanalytical characterization techniques

At Luleå University of Technology (LTU), an array of different microanalytical labs is available for characterization of solid samples. The laboratory for scanning electron microscopy (SEM-EDS), used in this study, is part of a chain of analytical techniques that commonly are used in the characterization of metallic ores. Apart from an energy-dispersive spectrometer (EDS), the SEM is also fitted with a wavelength-dispersive spectrometer (WDS). This gives the SEM almost the same analytical capacity as the electron probe microanalyzer (EPMA), even though analysis is slower than a traditional EPMA which has 4 or 5 WDS detectors that operates simultaneously. In addition to the analytical SEM-EDS/WDS, there is another SEM lab that is dedicated for extreme imaging (image resolution is ca. 0.5 nm). In the near future LTU will also establish a QEMSCAN lab (Quantitative Evaluation of Minerals by SCANning electron microscopy) for automated mineralogical characterization, capable of a high sample through-put.

At LTU there is also a new lab for laser ablation inductively coupled plasma mass spectrometry (LA ICP MS). This lab focuses on analysis (spot/mapping) of low concentration trace elements in sulphide minerals. The focus area of the LTU lab is unique in Sweden, as other LA ICP MS labs tend to avoid sulphide analysis due to the analytical difficulties it can render. LTU has since long an excellent relationship with University of Tasmania (CODES), that is world-leading in sulphide analysis, and the senior LA ICP MS technician at LTU is a former CODES employee. LTU also has laboratories for x-ray diffraction (XRD), x-ray tomography, Raman etc., readily available for LTU researchers, where particle-related research and analysis can be performed.

**Basic principles of scanning electron microscopy (SEM)**
In scanning electron microscopy (SEM), a focused electron beam is used to generate a variety of signals from the interaction between the electron beam and the sample, under vacuum conditions (Figure 21). The different signals provide information on surface morphology, chemical composition, crystalline structure and orientation of materials making up the sample. The electron beam is scanned over a selected area (commonly micrometer to millimeter size) and data are collected from the surface of the sample, and a two-dimensional image is generated that displays spatial variations in these properties.

Two types of images are generated, one which uses the secondary electrons (SE) that are generated from the surface of the sample when the primary beam is focused on the selected area. The other type is so called backscattered electron images, which use electrons that are generated from inside the sample, at depths down to a couple of micrometers, when the primary beam interacts with the sample. SEM is considered a non-destructive surface technique even though some signals are generated from the sub-surface. The magnification of samples is typically in the range 100 – 50 000x, with an image resolution of approximately 1 nanometer.

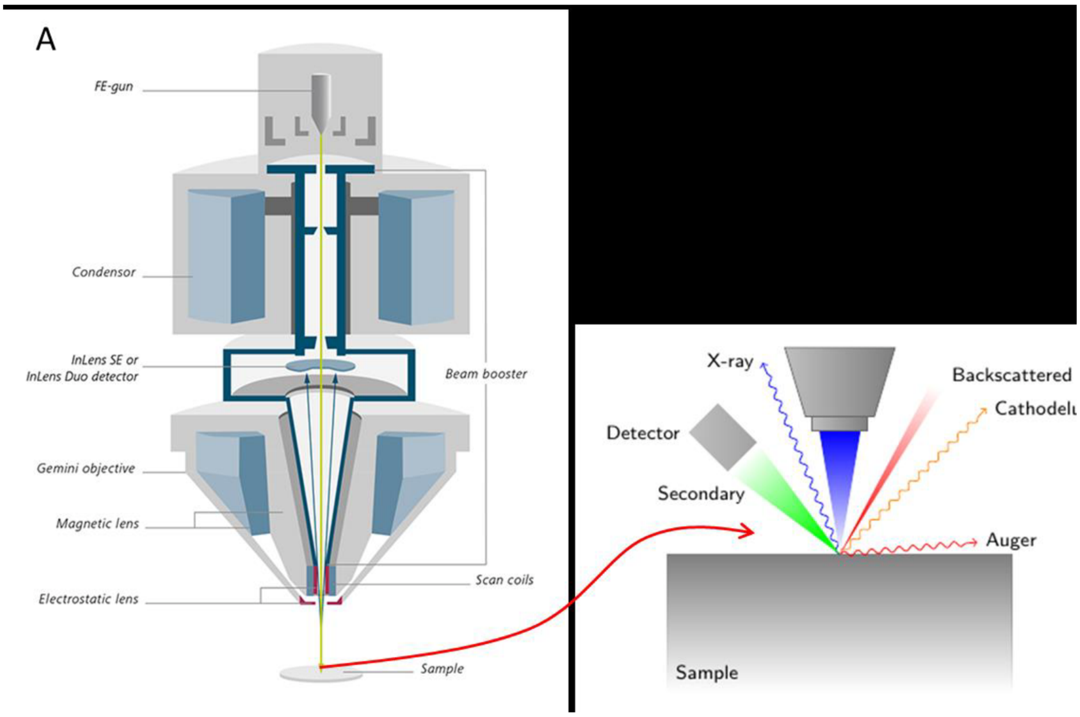



**Figure 21. SEM schematics. A) Basic principle of an SEM, showing the electron beam being focused through an array of different condensers and lenses before reaching the sample at the bottom. B) Signals generated in an SEM, from the interaction of a primary electron beam (in blue) and the sample. The signals used in this study were the x-rays and the secondary/backscattered electrons. Image courtesies of zeiss.com and texample.net.**

Besides generating extreme magnification/resolution images, the SEM can also generate chemical data when fitted with an energy-dispersive spectrometer (EDS) and/or a wavelength-dispersive spectrometer (WDS). In this study an EDS detector was used to generate chemical data from the samples. These spectrometers record the different energies and wavelengths of the x-rays that are generated from the electron-sample interaction and provide data on the elemental composition and distribution in the sample surface. Characteristic x-rays are produced for each element in the sample that is "excited" by the primary electron beam.

The SEM technique stems from the 1930´s and is a mature technique which is particularly suitable for a wide range of applications in the earth sciences, materials science, machine element, chemical technology, metallurgy, food science, biology, waste technology etc. Thus, SEM is ideal for analysis of very fine-grained gold particles in electronic waste.

### Analytical process

Nine WEEE samples were analyzed in a high-resolution Zeiss Merlin Scanning Electron Microscope, fitted with a large-area EDS-detector, at LTU, Sweden (Figure 22). The software Aztec 3.1, from Oxford Instruments Nanotechnology Tools Ltd, was used for the data acquisition and post-processing. Every sample was analyzed in the same way, and the rest of this section is a description of the analytical protocol that was used for all nine samples.

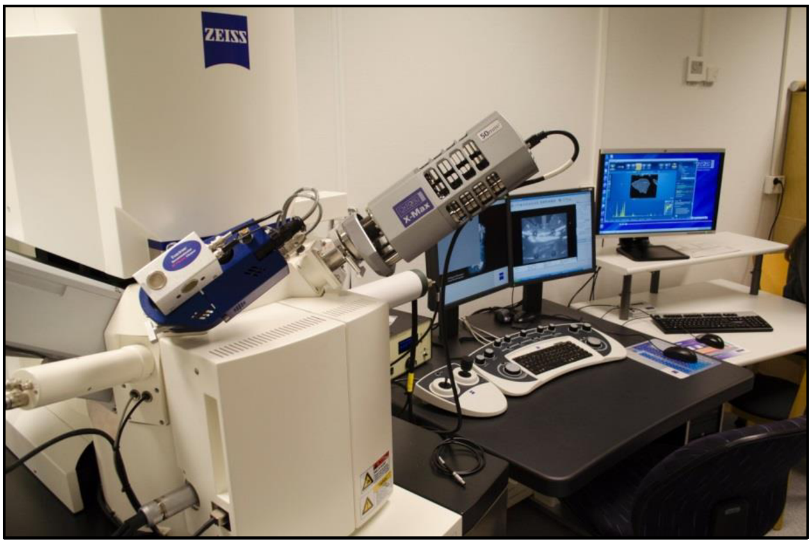



**Figure 22.** **Laboratory for scanning electron microscopy (SEM) at LTU.**

After the sample was introduced into the high-vacuum sample chamber, the analytical beam parameters were set to 20 kV accelerating voltage with a 1 nA beam current. Under these conditions, the electron beam was focused using the signal from the secondary electrons and image contrast (greyscale) was set so that heavier particles (likely gold particles) were emphasized.

Then the sample was manually investigated in a grid-like pattern, covering the whole sample surface area. Heavy particles are very bright (white) on the screen and all white particles were analyzed by increasing the magnification to have a first ocular inspection and then by focusing the electron beam on that particular particle and do a qualitative element analysis (point analysis) with the EDS detector to determine the main composition of the particle of interest. Gold-bearing particles would then show Au in the EDS spectra (Figure 23).

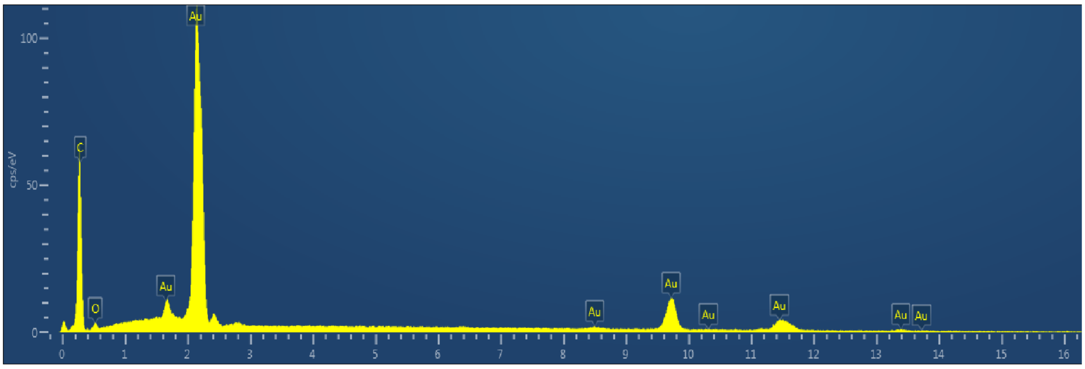



**Figure 23. Energy-dispersive spectra of gold-bearing particle. The carbon peak represents the carbon coating of the sample.**

When detecting a particle of interest (Au, Ag and REE-bearing particles) the particle, together with the immediate surroundings of the particle in the sample, was set up for element mapping. During the mapping the electron beam is continuously scanned over the particle area and all elements that the EDS detector can detect were mapped. This was done to investigate which elements for instance Au was associated with in the particle. Element detection limits for the EDS are approximately 0.1 wt%.

After the element analysis of the particle of interest, secondary electron images were made of the particle. When using the secondary electron signal it was possible to emphasize the 3D-features (surface topography) in the particle. From these images the particle size was estimated.

# Results

### Aspects on sampling at Stena Technoworld

The challenge for Stena Technoworld is to find a sampling method for gold and precious materials that is reliable and affordable. The gold is present in the material but the spread is large and the particles are very small, sometimes fixed to other metals as well. A more common sampling situation is when the material is well known and the concentration is higher. One example of this is for LKAB that produce iron pellets from iron ore. The average concentration of iron oxide is about 60 % in the ore. The challenge here is not to find what you are looking for, it is instead to take a large sample and be able to handle it. LKAB have invested a lot in machinery for correct splitting of the samples, and the following analyzes.

To estimate the random error in the sampling, the recommendation is to follow the methodology in NTR 604-report "Uncertainty from sampling" [8], in which the recommendation is to decide the measurement uncertainty by using double samples. This is a method to decide the final measurement uncertainty, by estimating the uncertainty in the sampling and analysis respectively. The report NTR 604 is an extract of and based upon the principles, methods and text of the international Eurachem Guide Estimation of measurement uncertainty arising from sampling [8].
Unfortunately the materials in this project have other characteristics than iron ore, and resemble more like a "hot-spot"-situation, as described in the previous section, i.e. the gold particles are very small and also very scattered in the material. To resolve this situation, it is possible to follow one of these alternatives:

- Take a big sample, or
- Use screening technology

The first method is used by the mining industry, e.g Boliden handle the sampling as described below for every batch of WEEE that comes to them.

- The batch consists for example of about 500 tons
- A sample is taken from the batch by taking out a number of subsamples in a falling stream, to obtain an aggregate sample (sample A) of about 400 kg.
- The A-sample crushed and then splitted down to a B-sample of 50 kg.
- The B sample is homogenized in a melting step, to get a "melt-stone" which is considered to be fully homogenized

**Pros:** Good representativeness between the test results and batch.

**Cons:** Expensive and cumbersome, requires a lot of equipment, including a furnace, requiring third-party control since Stena Technoworld has no testing equipment in the form of melting furnaces, etc.

The other alternative is to use some kind of screening test, i.e. take a large number of samples and do quick repeated tests on these, e.g. with XRF. If the sample material is comprehensive it is possible to apply the methodology with double samples according to Nordtest, which was mentioned earlier. Stena has used XRF to some extent for screening tests but the methodology can probably be developed.

### Technical analysis

From the analytical protocol described above, a number of interesting particles were detected, imaged and analyzed, Table 4. From manually analyzing 2821 particles that appeared interesting from image contrast conditions (basically appearing white on the screen), 82 particles contained Au, Ag or REEs (ca. 2.9 % of the total analyzed particle population).

**Table 4. Number of particles of interest in the three sample types that were analyzed (NF-fines, Fe-fines and sludge). Each sample type was sub-sampled in three different size fractions (from sieving).**

| Sample name | Sieve fraction >2 mm | Sieve fraction 0.5-2 mm | Sieve fraction <0.5 mm |
|---|---|---|---|
| **NF-fines** | | | |
| Au | | | 1 |
| Ag | | 1 | 4 |
| REE | 2 | | 5 |
| **Fe-fines** | | | |
| Au | 12 | | |
| Ag | | 3 | 5 |
| REE | 5 | 3 | 12 |
| **Sludge** | | | |
| Au | | 3 | |
| Ag | 2 | 1 | 8 |
| REE | 1 | 3 | 11 |

#### *Gold-bearing particles*

All analyzed sample types, and sieve fractions, contain gold-bearing particles. The gold-bearing particles range in size from 5 to 25 µm, with a mean size of 13.6 µm (Figure 24). In the sludge 0.5-2 sample two larger particles (25 µm) were detected. If these are excluded the mean particle size of the total gold particle population ends up at 12.2 µm.

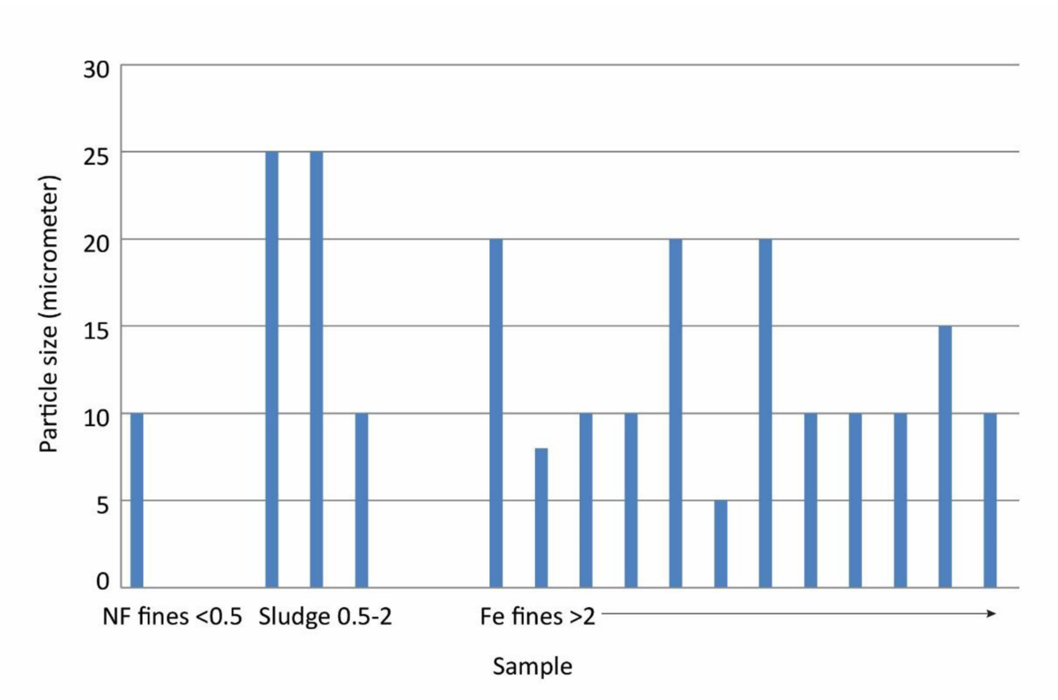



**Figure 24. Particle size distribution for the gold-bearing particles. The sample with the better statistics, Fe >2, shows a mean particle size of 12.6 µm.**

Energy-dispersive spectrometry reveals that the gold particles mainly are of two different compositions. Gold either occurs as essentially pure gold or associated with Al (Figure 25 - Figure 27). The gold particles have three different textures, one that looks rather eroded (Figure 25A), one with a knobbly texture (Figure 25B) and one that appears more solid (Figure 26). All three types show an association between gold and aluminum, and 10 out of 16 gold particles show gold as the only detectable element in the SEM-EDS analysis (Figure 27).

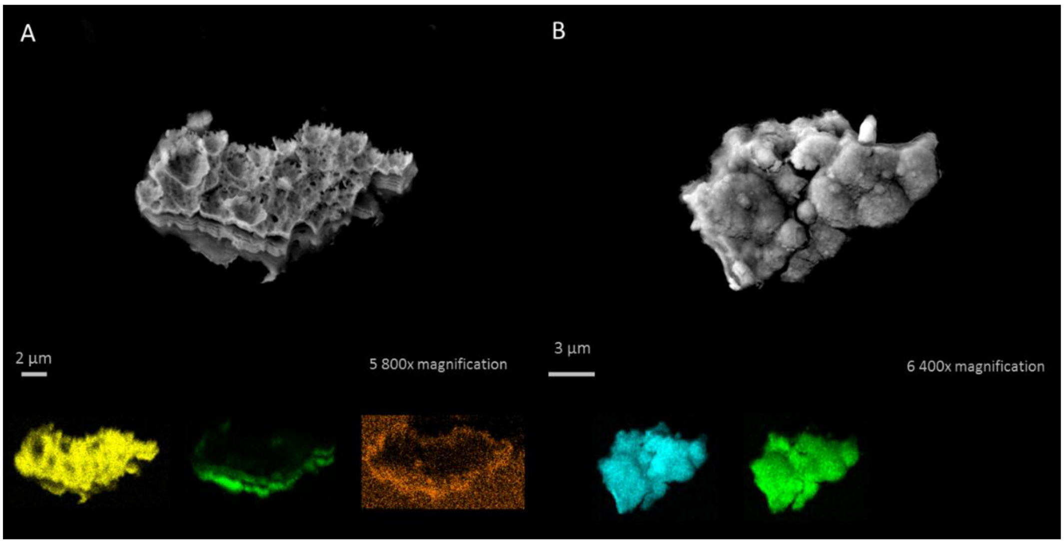



**Figure 25. SEM images, and energy-dispersive spectrometric maps (in color) of gold particles in the sample Fe>2. A) Gold particle with a rather eroded appearance. Aluminum (and oxygen) is enriched at the bottom of the particle. B) Knobbly gold particle that also shows Al intensity.**

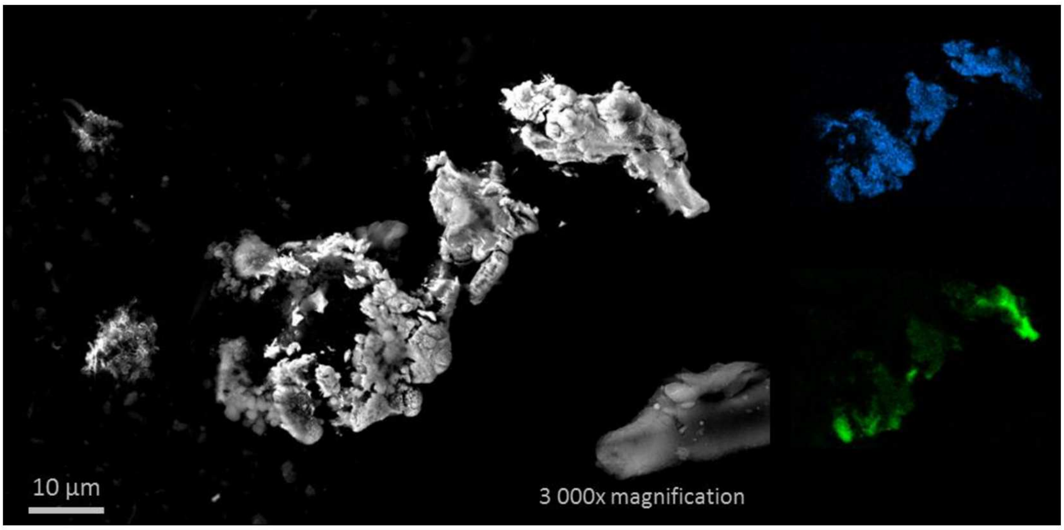



**Figure 26. Scanning electron microscope image of the more solid particle texture. Also here is gold associated with aluminum.**

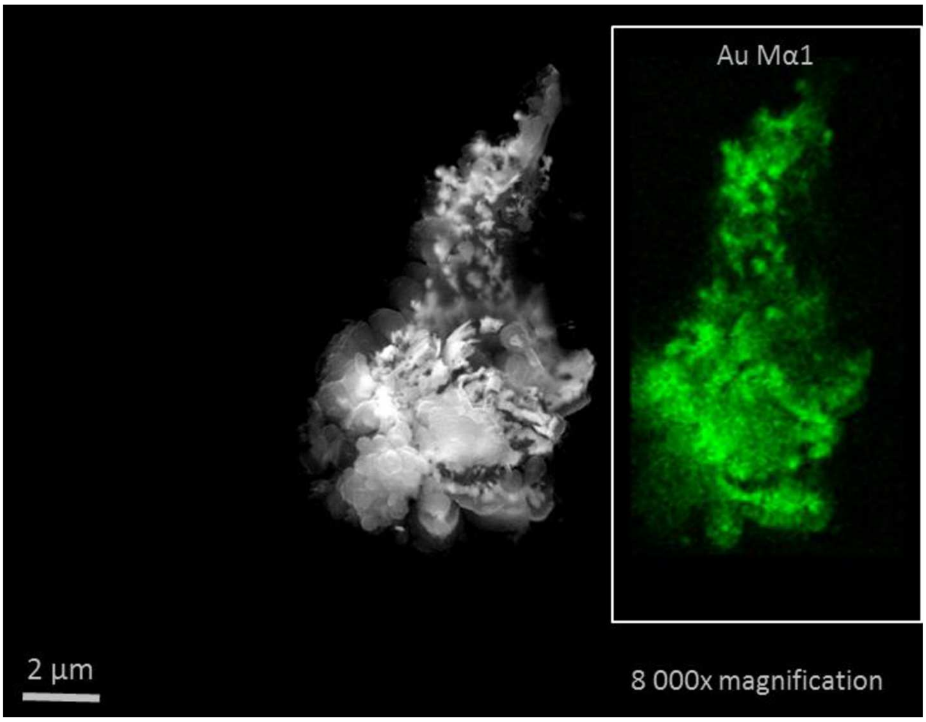



**Figure 27. Scanning electron microscope image of a knobbly particle of gold. No other elements were detected in the EDS analysis.**

*Silver-bearing particles*

All analyzed sample types, and sieve fractions (except the samples Fe>2 and NF>2), contain silver-bearing particles in various amounts (Figure 28). The majority of particles were detected in the sludge samples, where eleven Ag-particles were found, compared to 5 and 8 in the two other sample types. The silver-bearing particles range in size from 3 to 1000 µm, with a mean size of 31,9 µm (if excluding the 1000 µm outlier-particle).

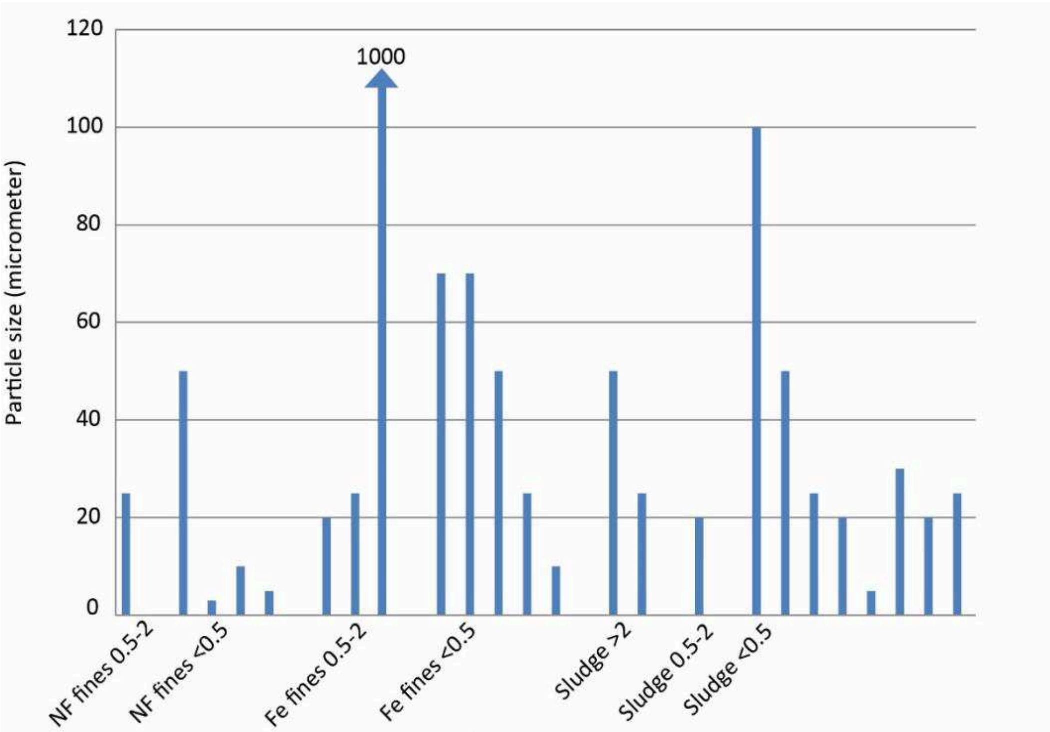



**Figure 28. Particle size distribution for the silver-bearing particles. In samples Fe >2 and NF>2, Ag particles were not detected so those samples are excluded from the plot.**

From the EDS analysis (energy-dispersive spectrometry) it is evident that Ag has mainly three different element associations: Ag-S, Ag-halogens and pure Ag. In the particles that show Ag together with S, the Ag appears to be secondary, forming overgrowths of the primary particle (Figure 29 - Figure 31). Where Ag are associated with the halogen group (Br, Cl, I) the particles appear more solid, and Ag is likely attached to some substrate (Figure 30 and Figure 31). In Figure 31A the substrate seems to be made of silicon. The samples also show particles that are essentially Ag-only particles, with various traces of ± Cu, Zn, Nb, Fe, Ca, Mg, Ti, Bi and Ta (Figure 32).

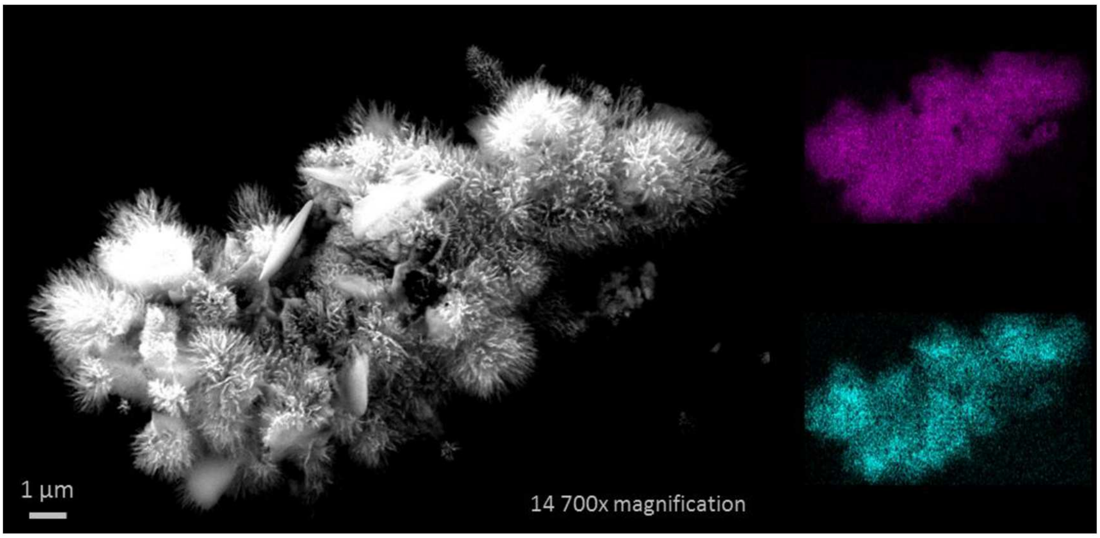



**Figure 29. Scanning electron microscope image, and energy-dispersive spectrometric maps (in color) of a silver particle (secondary overgrowth?)**

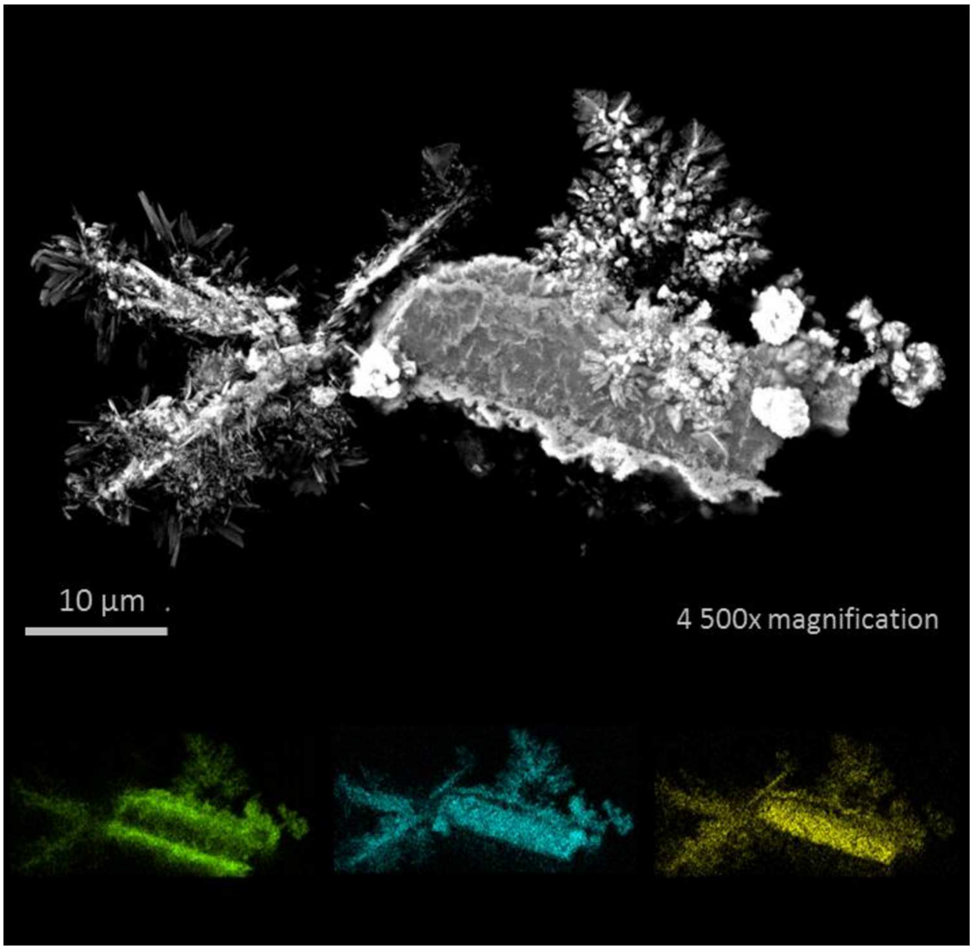



**Figure 30. Scanning electron microscope image, and energy-dispersive spectrometric maps, showing the association between Ag and S (plus in this particle Cu).**

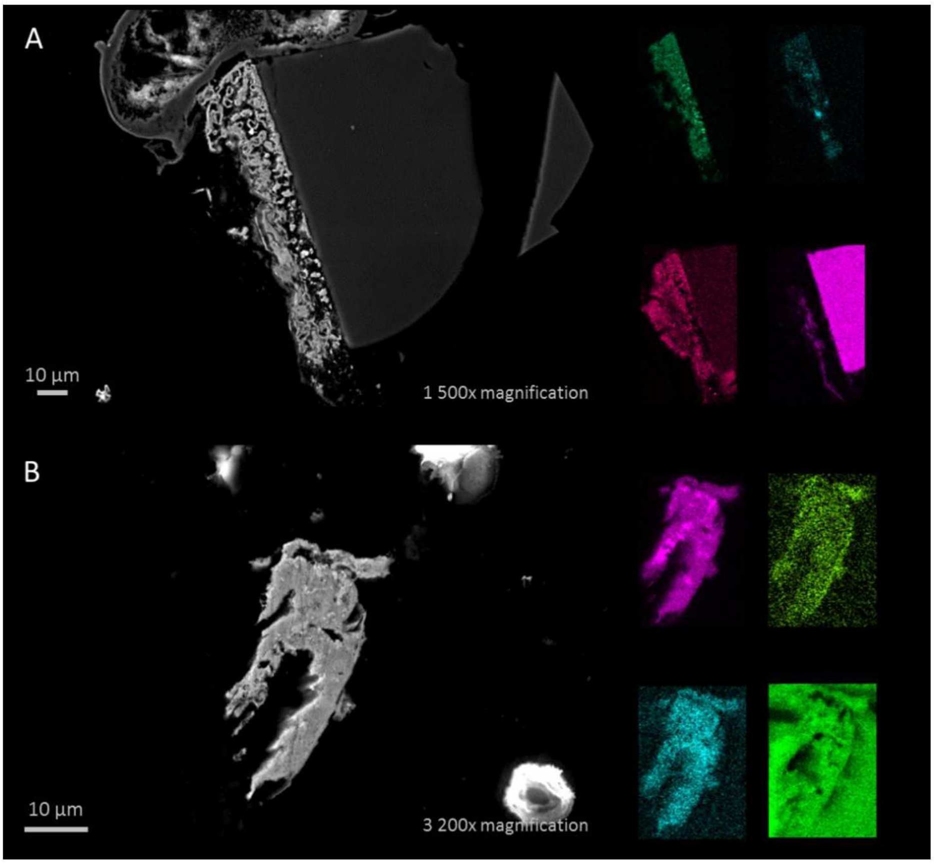



**Figure 31. Scanning electron microscope images, and EDS maps, showing Ag together with the halogens (Br, Cl and I). A) Ag particle, where Ag appears to be attached to a Si substrate. B) Ag together with Cl and I, with Br more dispersed over the analyzed area.**

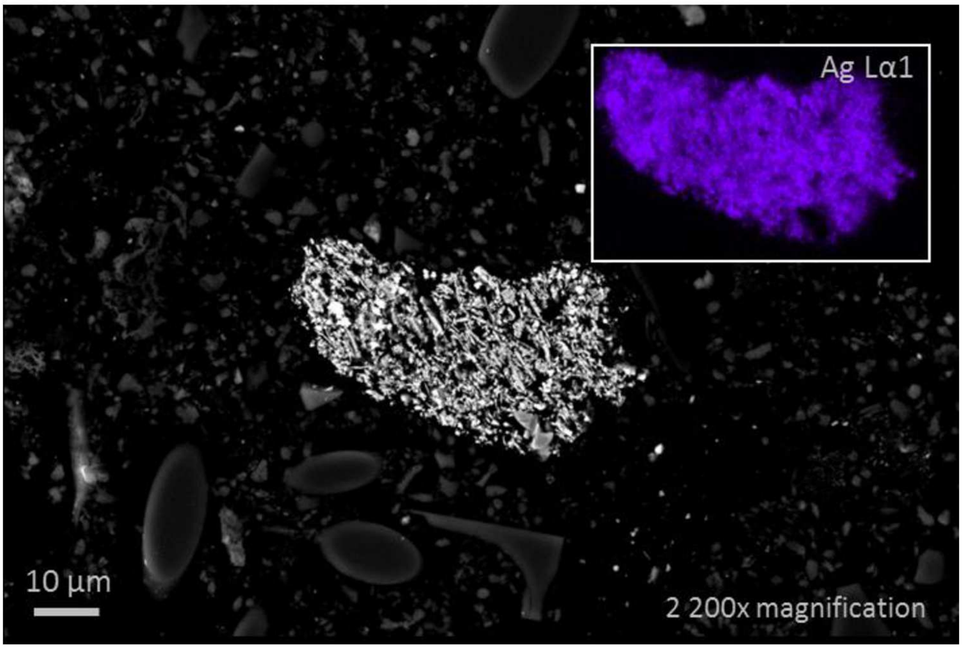



**Figure 32. Scanning electron microscope image, with an EDS map as inset, showing a cluster of very fine-grained Ag particles.**

*Rare Earth Element-bearing particles*

All analyzed sample types, and sieve fractions (except the sample NF 0.5-2), contain REE-bearing particles in various amounts (Figure 33). The majority of particles (n=21) were found in the Fe and sludge samples, where 19 and 15 particles were detected respectively (out of a total of 40 REE particles). The REE-bearing particles range in size from 3 to 100 µm, with a mean size of 16.7 µm for the NF samples, 34.5 µm for the Fe samples and 24.7 µm for the sludge samples.

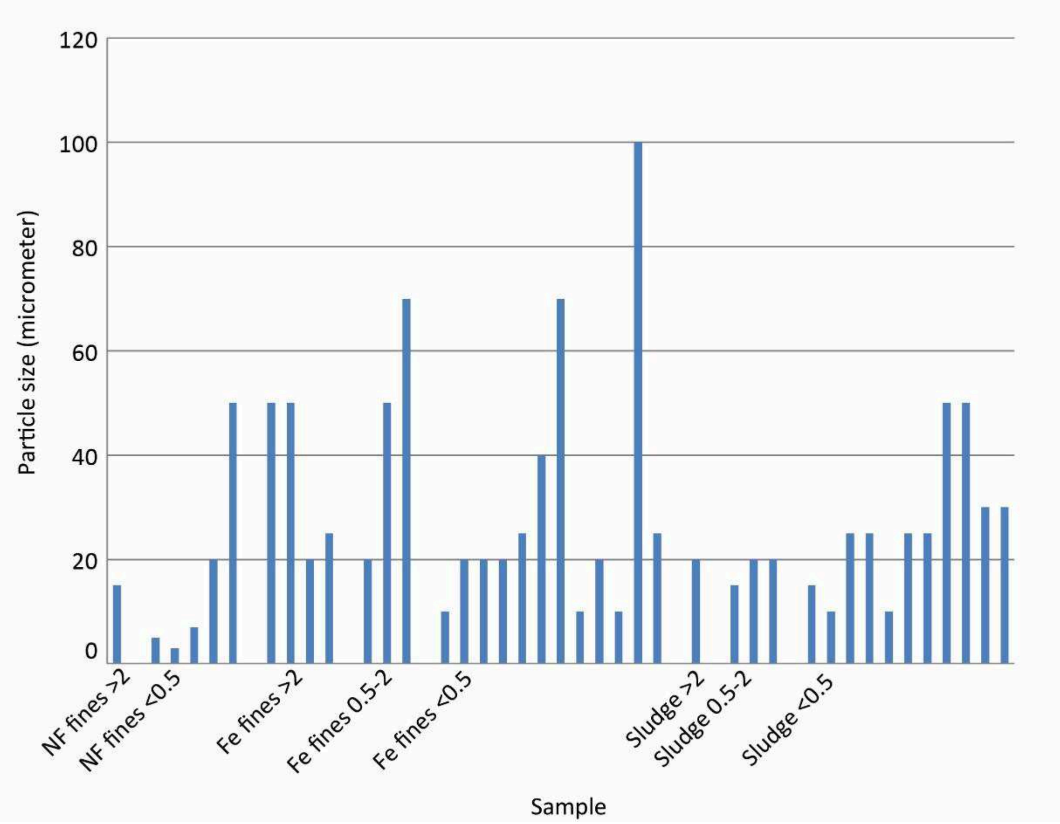



**Figure 33. Particle size distribution for the REE-bearing particles. Thirty-four out of 40 particles were detected in the Fe and sludge samples.**

Analysis by SEM-EDS reveals that REE particles (essentially La, Ce and Nd) occur in all sample types. The composition of the REE particles is dominated (21 of 40) by a Ni-La-Ce-Co compound, with various amounts of Si, Mn and Fe (Figure 34). The second most common (n=5) composition is Ce-Si-La-Al-P-Nd-Fe (Figure 35). The rest of the particles are made up of various combinations of the elements Nd, Fe, Pr, Pb, Zn and P. All REE particles that were detected appear rather solid in texture (granular).

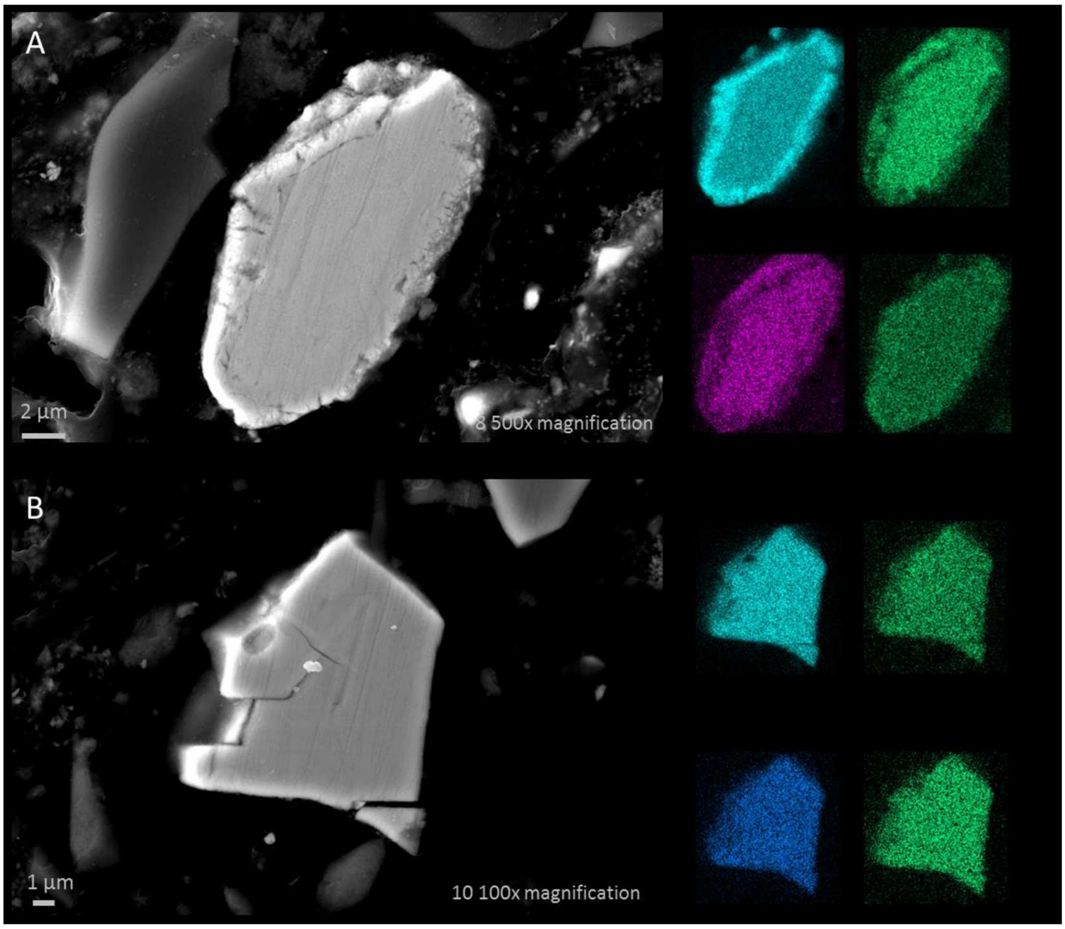



**Figure 34. Scanning electron microscope images, and EDS maps, showing granular REE particles of the element association Ni-La-Ce-Co. A) Zonation of the particle is evident, where a higher concentration of Ni is seen in the rim of the particle. B) More homogeneous particle, where an imaginary zonation is seen on the left-hand side of the particle. This is most likely due to topographical effects in the particle, resulting in lower element intensities in those areas.**

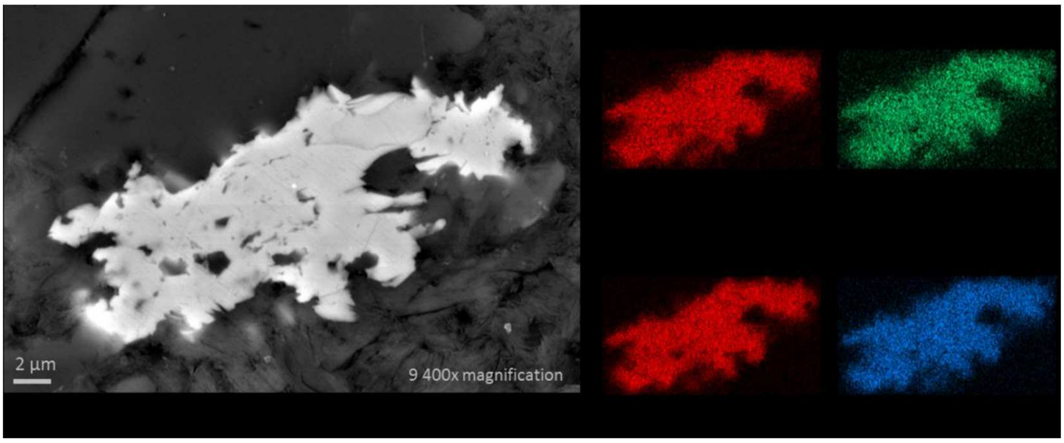



**Figure 35. Scanning electron microscope image, with associated EDS maps (in color) showing the intensities of Ce, La, P and Nd.**

## Conclusions

In this work three different waste fractions (WEEE fines) from an existing WEEE recycling process is collected and analyzed with respect to precious metals and rare-earth elements. It is known from previous studies that a lot of material value is lost to these fractions. By employing state-of-the-art analytical equipment which today is used in the mining industry it is possible to characterize the lost precious metal particles with respect to size, shape and adjacent elements or matrix. The aim of the project evaluate if, by analyzing the precious metals particles based on the aforementioned parameters, there might be ways to recover the lost material or alter the process to avoid them reaching the fines fraction.

The methodology is based a literature review of previous work, sampling of the material and SEM-EDS analysis of the samples. Three different WEEE fines fractions where collected (Fe-fines 0-3mm, NF-fines 0-3mm and sludge). Each of the three fractions was in turn sieved into three different size-fractions, >2 mm, 0.5 – 2 mm, < 0.5 mm, making a total of 9 samples.

As mentioned in the discussion, the major conclusion from this work is that the methodology employed by the mining industry for characterization of precious metal ores, work for waste fractions as well. Of the 2821 particles that were studied in detail, 82 of them included Gold (16), Silver (24) or REE (42). However, the number of particles was too low to make any solid conclusions on commonly occurring shape, particle size or presumed origin of the particles. For that many more samples have to be analyzed.

From the few particle of gold that was found it is clear that they all have odd shapes, not the thin films you would expect coming from use in electronic equipment. This suggests that shredders and other process equipment have liberated the material in a rough manor.

As might be expected a lot of REE containing particles was also found in the fines fractions. However, the economic incentive for REEs' recovery is still very low. Unless there are regulatory or price changes, status quo is expected.

## Discussion

The aim of the project was to detect and characterize the precious and rare-earth elements that are lost in the fines from WEEE recycling. In the attempt to accomplish this, methodologies and experience from the precious metals mining industry where employed. From both an environmental and economic point of view, gold is the most interesting element to focus on and depending on how it occurs in the waste fines it might be possible to recover more gold from the recycling process and thereby increase revenue.

However, to introduce additional process steps to increase gold recovery, the characterization would need to provide robust statistics on the gold occurrence in the fines. In this reconnaissance study, nine samples were taken from the fines to try to detect gold in the fines and to characterize the particles detected. From elemental analysis (not presented in the report) it is shown that the NF-fines contain more gold than the other sample types. However, in the particle characterization part of this study it is evident that gold particles occur in all sample types (Table 4). Through utilizing well-established analytical techniques such as scanning electron microscopy and energy-dispersive spectrometry, which are common methods in the mining industry, 16 gold particles were characterized in the samples. In addition to these results, 24 silver particles and 42 REE particles were analyzed. Apart from the Au, the REEs are of particular interest since they belong to the CRM group (https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_sv), as classified by the European Union.

Scanning electron microscopy stems from the 1930s and is a mature technique when it comes to characterization of solid conductive and non-conductive samples in a variety of technical branches. It has been used before in characterization of recycled WEEE [6][7], but not focused on the characterization of gold in WEEE. In this project we have proven that the employed methodology can be very well suited not only for natural ores with precious metals, but also waste fractions of WEEE. The only hindrance for further conclusions is that the amount of precious metal particles are too few. The total number of gold particles found where 16, which it not enough for any statistically reliable conclusions. With poor statistics it is not really possible to trace the origin of the particles found, but based on the material composition it is possible to speculate.

**Gold:** The gold found where typically misshaped particles of only gold (10 of 16), which is most likely gold plating from electronics which have been deformed in the mill. In four out of 16 particles, gold is attached to aluminum (Figure 25 - Figure 26). The aluminum is probably a ceramic alumina ($Al_2O_3$) substrate that is used for conductive films in electronics.

**Silver:** The silver-sulphur combination seen in Figure 30 is most likely not the original product, rather a product from a reaction, judging the look of the particle. It is probably the same reaction as silverware get over time. The silver reacts with sulphur forming ($Ag_2S$) a blackish discoloring to the silver. The use of silver-halogen particles are still unknown.

**REEs:** The combination of Ni-La-Ce-Co are well known from utilization as cathode material in batteries and combinations of Nd-Pr are found in strong permanent magnets which now is common in many types of electronics.

To gain a better understanding of how Au, Ag and REE occur in the WEEE fines, improved statistics are necessary. In the gold mining industry, these types of statistics are generated from the use of two SEM-based techniques; MLA (Mineral Liberation Analyzer) and QEMSCAN (Quantitative Evaluation of Minerals by SCANning electron microscopy). The two techniques are rather similar in the approach to characterize a material, both are computer-controlled SEM, coupled with multiple EDS detectors and software that scans the sample, recognizes particles and different phases within the particles and analyzes them automatically, according to the user-specified parameters. Presently, it is heavily used in the mineral processing industry, but it can be a very powerful tool for any investigation that could benefit from swift data acquisition on particle composition, form and association, such as fines from WEEE. MLA and QEMSCAN were developed for the mining industry, to deal with specific problems or collect and quantify automatically scientifically valuable data that would be very tedious to collect manually. Both techniques generate large amounts of data, and are dependent on having particle databases setup, to compositionally recognize the detected particles and to properly classify and group them. Larger mining companies have their own MLA labs, enabling a more accurate mineral database since the input data comes from the companies own mine/mines, which thus improves the results from the MLA analysis.
With improved statistics, the costs of setting up additional process steps to recover more of the gold (and Ag, REE) in the WEEE process can be addressed. The gold particles analyzed in this study could possibly be recovered using additional gravimetric techniques.
Since we have investigated material where circuit boards already have been removed we can look at improved mechanical separations steps as well as evaluate leaching on fines. The most preferred process for minimal losses, manual dismantling, is already implemented so future development needs to focus on complementary processes. And evaluating improvements in the recycling process, having the results in this project in mind, sampling and analysis are crucial.

## Suggestions for future work

There are a number of different options for future work. For a statistically more accurate results more samples should be analyzed. Considering the results from this work a sample volume of about 100 samples should suffice for more statistically more accurate results. These samples should be analyzed in a MLA or QEMSCAN, to gain the best possible statistics of the particles of interest in the fines.

The literature review also proved that there is a lack in work done on on-line sampling methods for WEEE materials. The ones that exist are very costly and its details are proprietary knowledge.

Other material that could be of interest with this kind of methodology is to analyze the fines material of bottom ash from municipal solid waste incinerators. Studies have shown that this fraction will include precious metals which today also is allocated to landfills.

## Publication list

Not relevant for this project

## Reference list

[1] Eurostat, Waste statistics - electrical and electronic equipment, November 2016, http://ec.europa.eu/eurostat/statistics-explained/index

[2] Nyheter från SGU, Metallpriser i december 2016, https://www.sgu.se/om-sgu/nyheter/2017/januari/metallprisernas-utveckling-under-2016/

[3] http://geology.com/articles/rare-earth-elements/

[4] Bakas, Herczeg, Vea, Fråne (IVL), Youhanan, Baxter, 2016, "Critical metals in discarded electronics", a report from the Nordic Council of Ministers to study this strategical question.

[5] Sun, Z.H.I. et al, 2015, Characterisation of metals in the electronic waste of complex mixtures of end-of-life ICT products for development of cleaner recovery technology

[6] Ogunniyi, M. K. G, Vermaak, and D. R. Groot, Chemical composition and liberation characterization of printed circuit board comminution fines for beneficiation investigations. Waste Management, 2009. 29(7): p. 2140-2146

[7] Guo, C. et al., Liberation characteristic and physical separation of printed circuit board (PCB). Waste Management, 2011. 31(9–10): p. 2161-2166

[8] NTR 604, Uncertainty from sampling - a nordtest handbook for sampling. Based upon the euroachem international guide "Estimation of measurement uncertainty arising from sampling", Christian Grøn, Jette Bjerre Hansen, Bertil Magnusson, Astrid Nordbotten, Mikael Krysell, Kirsten Jebjerg Andersen, Ulla Lund, ISSN 0283-7234, Nordic Innovation Centre 2007

[9] M H Ramsey and S L R Ellison eds. Eurachem/EUROLAB/CITAC/ Nordtest/AMC Guide: Measurement Uncertainty arising from sampling: a guide to methods and approaches Eurachem (2007). ISBN 978 0 948926 26 6. Available from the Eurachem secretariat

# Appendix A

More detailed description of the sampling is described in 0. The fractions FE and NF were taken in a falling stream with 1 hours interval. The sludge was sampled 9 times with approximately 1 hour between the samples.

**Table 5. Sampling of fine fractions**

| Time | Falling sample (g) | Falling sample (g) |
|---|---|---|
| | Fe | NF |
| 06:00 | 1564 | 2484 |
| 07:00 | 1572 | 2354 |
| 08:00 | 1460 | 2488 |
| 09:00 | 1548 | 1934 |
| 10:00 | 1426 | 2388 |
| 11:00 | 1544 | 2018 |
| 12:00 | 1658 | 2196 |
| 13:00 | 1344 | 2214 |
| 14:00 | 1312 | 2198 |
| **Sum** | **13428** | **20274** |

**Table 6. Sampling of sludge**

| Time | Sampling with pipe (g) |
|---|---|
| 06:15 | 330 |
| 07:05 | 174 |
| 08:00 | 178 |
| 09:00 | 528 |
| 10:00 | 304 |
| 11:00 | 262 |
| 12:00 | 352 |
| 13:00 | 248 |
| 14:00 | 290 |
| **Sum** | **2666** |

The following articles and reports were found in the literature search. Only a few of them are very relevant for this project and they are mentioned in section 0.

# Appendix B

The following articles and reports were found in the literature search.

**Table 7. The most relevant articles for recycling of precious metals.**

| Source | Description |
| --- | --- |
| Bakas et al. 2012 | **Present and potential future recycling of critical metals in WEEE**<br>The report analyses the potential of precious materials in the WEEE fraction. There is a review of pre-processing techniques for WEEE and corresponding estimated losses of precious metals (section 5.3). Their recommendation to increase the yield of gold and precious materials is to use "multi-level deep manual dismantling" as far as possible.<br><br>Some of the conclusions relevant to this project:<br>• Great losses due to mechanical treatment<br>• The recycling rate in the pre-processing is rather high (90-95%) for some metals (Ag, Co, Te, Au, Pd, Ru) but 0 % others (W, Ta, Ga, Ge)<br>• There are thermodynamic limitations if the precious metals are connected to other materials.<br><br>Copenhagen Research Institute, November 2014, www.cri.dk<br>Christian Fischer (project manager), CRI, Adrian Harding, Environment Agency, England & Wales, Sabine Haselsteiner, CRI et al. |
| Dominy, S.C., Minnitt, R.C.A, 2011 | **Design of Grade Control Sampling Programs for Underground Gold Mines**<br>The article describes how to design a sample program in the mining industry to achieve as much gold as possible.<br><br>Eight International Mining Geology Conference / Queenstown, New Zealand, 22-24 August, 2011 |
| Guo Chao, Wang Hui, Liang Wei, Fu Jiangang, Yi Xin, 2011 | **Liberation characteristic and physical separation of printed circuit board (PCB)**<br>The article describes shredding and treatment of PCB and assess the faith of the metals in the different fractions. The article is very relevant for this project, but focuses solely on copper.<br><br>Waste Management 31 (2011) 2161–2166 |
| Mulenshi, J.M., 2015, LTU | **Processing of residues from recycling of waste electrical and electronic equipment (WEEE)**<br>A report from Luleå Technical University about sieving of |

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| | fine materials and what types of metals that this fraction contains. Gasification is described followed by extraction of metals from the ash.<br><br>Senior Design Project in mineral Processing and Metallurgy, M7005K and P7007K,Luleå Technical University, 2015 |
| Ogunniyi, I.O., Vermaak, M. K., Groot, D.R.,2009 | **Chemical composition and liberation characterization of printed circuit board comminution fines for beneficiation investigations**<br>The article is about the content of metals in fines from PCB.<br><br>Waste Management, 2009. 29(7): p. 2140-2146 |
| Palmieri, R., Bonifazi, G., Serranti, S., 2009 | **Recycling-oriented characterization of plastic frames and printed circuit boards from mobile phones by electronic and chemical imaging**<br>The article describes research regarding characterization of metals with established and also innovative techniques, as hyperspectral imaging in short wave infrared field. Some of the pictures describe how gold and other precious materials are situated in the material.<br><br>Waste Management 29 (2009) 2140–2146 |
| Sun, Z.,I., Xiao, Y., Sietsma, J., Agterhuis, H., Visser, G., Yang, Y., 2015 | **Characterisation of metals in the electronic waste of complex mixtures of end-of-life ICT products for development of cleaner recovery technology**<br>The article describes shredding and sieving of ICT-materials and investigates the faith of metals regarding in which fractions tend to occur. Some of the conclusions are that ICT is a very complex material. Most of the metals, except copper is in the form of alloys or trapped in other materials.<br><br>Waste Management 35 (2015) 227–235 |
| Sun, Z., Xiao, Y., Agterhuis, H., Sietsma, J., Yang, Y., 2016 | **Recycling of metals from urban mines, a strategic evaluation**<br>An evaluation of two index regarding recycling of metals from urban waste. A resource index and a technology index. The discussion about “fines” is relevant for our project.<br><br>Journal of Cleaner Production 112 (2016) 2977e2987 |
| Sun, Z., Xiao, Y., Sietsma, J., Agterhuis, H., | **A Cleaner Process for Selective Recovery of Valuable Metals from Electronic Waste of Complex Mixtures of End-of-Life Electronic Products**<br>The article is about gold and other precious metals, how it |

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| Yang, Y.,<br>2015 | situated in the waste and how it can be dissolved in a leaching process.<br><br>Environ. Sci. Technol. 2015, 49, 7981−7988 |
| Upgrade 2012-2015,<br>Chancerel, P.,<br>Rotter, V.S. | **UPgrade - Closing Material Loops in the Extended Value Chain**, - Project for the improved valorization and integrated recovery of trace metals in Waste Electronic and Electric Equipment<br>A very interesting project between 2012-2015 ”Project for the improved valorization and integrated recovery of trace metals in Waste Electronic and Electric Equipment. Some of the conclusions:<br>• A high metal potential of minor metals do not imply a technical and economical feasible recycling<br>• The actual knowledge base for WEEE does not comply with the information demand from the recycling industry.<br>• Recydling of precious metals from WEEE if only possible if materials can be liberated and concentrated in a “recovery compatible composition”.<br><br>http://www.upgrade.tu-berlin.de/eng_index.html |
| Bakas, I.,<br>Herczeg, M.,<br>Eldbjørg, B.V.,<br>Fråne, A.,<br>Youhanan, L.,<br>Baxter, J.,<br>2016 | **Critical metals in discarded electronics**<br>The report was written due to an interest from the Nordic Council of Ministers to study this strategical question. Experts in the Nordic countries has written the report, among them IVL.<br>The content of the report is that estimations are made both regarding the amount of WEEE in the Nordic countries in different categories, and the concentration in each category, resulting in a total estimation of the potential for recycling of precious metals. Other estimations are done regarding the environmental and economical issues, and it is stated that it is worth to recycle from both these aspects, especially for Au.<br><br>ISBN 978-92-893-4569-9 (PRINT)<br>ISBN 978-92-893-4570-5 (PDF)<br>ISBN 978-92-893-4571-2 (EPUB)<br>http://dx.doi.org/10.6027/TN2016-526<br>TemaNord 2016:526, ISSN 0908-6692<br>© Nordic Council of Ministers 2016 |
| Bizzo, W.A.,<br>Figueiredo, R.A.,<br>de Andrade, V.F., | **Characterization of Printed Circuit Boards for Metal and Energy Recovery after Milling and Mechanical Separation**<br>The article characterizes PCB regarding content and have some rather common conclusions in the area:<br>The precious metals content has fallen recent years, and that |

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| 2014 | the metal content is larger in the fine fractions<br><br>Materials 2014, 7, 4555-4566; doi:10.3390/ma7064555, ISSN 1996-1944, www.mdpi.com/journal/materials |
| Chancerel, P., Marwede, M., Rotter, V.S., Ueberschaar, M., TU Berlin, 2014 (?) | **Design challenges for recycling of critical metals**<br>A study regarding which types of metals that are present in different types of electronics.<br><br>*Supplementary material for the paper "Design for recycling* of critical materials embedded in electronics products – *technology and policy recommendations"* |
| Chancerel, P., Rotter, S., 2009 | **Recycling-oriented characterization of small waste electrical and electronic equipment**<br>An article that describes the presence of metals in WEEE.<br><br>Waste Management, Volume 29, Issue 8, August 2009, Pages 2336-2352 |
| Chancerel, P., Meskers, C.E.M., Hagelüken, C., Rotter, V.S., 2009 | **Assessment of Precious Metal Flows During reprocessing of Waste Electrical and Electronic Equipment**<br>An extensive research article focusing on whether or not substance flow analysis (SFA) is a relevant method to assess losses of critical metals. The conclusion is that SFA is a good method for the purpose. The flows are illustrated with Sankey diagrams. A statement on page 802 is interestin; "However, it is most likely that shredding indeed has a negative impact on the precious metal recovery".<br><br>Journal of Industrial Ecology, Volume 13, Number 5<br>DOI: 10.1111/j.1530-9290.2009.00171.x |
| Cucchiella F., D'Adamo, I., Koh, S.C.L., Rosa, P., 2015 | **Recycling of WEEEs: An economic assessment of present and future e-waste streams**<br>The article estimates amounts of a large number of materials in 14 different types of WEEE-streams, and make an economic assessment of the value of these materials. Gold dominates and represents about 50 % of the revenues in a scenario where a couple of precious metals are recycled.<br><br>Renewable and Sustainable Energy Reviews, 51, (2015) 263–272 |
| Duygan, M., Meylan, G., 2015 | **Strategic management of WEEE in Switzerland – combining material flow analysis with structural analysis**<br>The study assess the recycling sector for laptops and cell |

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| | phones in Switzerland during 2011 and states that the recycling methods are governed by cost of labour, metals and energy.<br><br>Resources, Conservation and Recycling 103 (2015) 98–109 |
| Jirang, C.,<br>Lifeng, Z.,<br>2008 | **Metallurgical recovery of metals from electronic waste: A review**<br>The article is a review of pyro metallurgical processes and bio metallurgical processes to extract gold.<br><br>Journal of Hazardous Materials 158 (2008) 228–256 |
| Oguchi, M.,<br>Murakami, S.,<br>Sakanakura, H.,<br>Kida, A.,<br>Kameya, T.,<br>2011 | **A preliminary categorization of end-of-life electrical and electronic equipment as secondary metal resources**<br>The article discusses the content of metals in some categories of WEEE.<br><br>Waste Management 31 (2011) 2150–2160 |
| Lu, Y.,<br>Xu, Z.,<br>2016 | **Precious metals recovery from waste printed circuit boards: A review for current status and perspective**<br>A very recent review article of present methods for precious metals recovery and suggestions for improvements. It is relevant both regarding the pre-processeing and the recovery stage. It is included in this survey due to the fact that it is recently published and that it gives a good overview of the area.<br><br>Resources, Conservation and Recycling 113 (2016) 28–39 |