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RECUPERATION OF CRITICAL METALS IN FLANDERS:
Scan of possible short term opportunities to increase recycling

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Executive summary

Proposal of short term opportunities

Underneath 12 opportunities are listed. They are derived from an extended literature review on possible next steps in collection, preprocessing and recycling of critical metals. There are many boundary conditions for the recycling of the here described opportunities, boundary conditions which to be further examined by discussion with experts and by further feasibility studies. The underneath short descriptions are only intended to trigger further discussion and to detect possible directions for even more resource efficient recycling.

O1a permanent magnets in a.o. hard disc drives, to recover Nd

Hard discs are easily detected. On average, the NdFeB magnet in Hard Disc Drives weighs 15g, of which 3,75 Nd. These magnets can be recovered as alloys to new magnets after hydrogen decrepitation (Hitachi's dismantling technology and the technology of the University of Birmingham with 95 % RE). Recycling is possible as well by hydrometallurgical methods (Ionic liquid methods, Selective leaching with 80-99 % RE for Nd), pyrometallurgical methods (Electroslag refining, Liquid metal extraction, Glass slag method, direct melting). The separation of magnet particles (minor components) from the component still is challenging. 88,5 % of Nd is applied in permanent magnets (all applications).

Other applications: (long term!): motors, actuators, microphones and speakers, Magnetic resonance imaging (MRI), frictionless bearings, magnetic refrigeration. Earphones might be an interesting niche waste stream (when disassembled).

Other elements: some of the permanent magnets also contain Dy and Pr, which are a critical elements as well.

O1b Hard disc drives, to recover Pt

A rather niche application of Pt is as part of the magnetic coating stack on hard discs in computers. Some 2% of the total Pt amount is used for this application, though it is interesting to further exploit the recovery of these layers because of the ease of detecting these components. The main challenge lays in the collection and separation of the components.

O2 Capacitors, to recover Ta

Although Ta is not considered anymore as a critical element, the amounts used and the ease to detect components with considerable Ta concentration (mainly capacitors) justifies a further evaluation of recycling specific Ta containing components. Capacitors mainly are present in portable electronics, automotive components (ABS, airbag, GPS…), medical appliances (hearing aids). The concentration and composition of an individual Ta capacitor can be found in the Full Material Declaration (FMD) sheet and varies between 24 and 42wt% with mixed concentrations of Ta and Ta_2O_5. Knowledge of the Ta content at board level for different applications is still lacking. Due to their characteristic colour and shape, they are relatively easy detectable at board level. Ta recycling is mainly an issue of physical identifications, up-concentration and logistics.

O3 Electronics for the recovery of Au and Ag

Although the recovery of Au and Ag out of electronics is well established and very efficient (due to the high economic value of the recovered, precious metals, metallurgical recycling efficiencies > 98% for Ag, Au are reached), there still is an efficiency gap in the collection of these materials. Relevant components are diodes, transistors, integrated circuits and semi-conductor memories, capacitors, resistors and electrical contacts, switches. It is found that only 12% of Ag and 26% of Au and Pd end-up in the appropriate Cu-waste-stream from which they can be extracted when mechanical shredding of waste material is performed. The amount of recovered Cu is 60% (average numbers for German ICT waste experiment). Selective disassembly of the PCB-parts is therefore recommended.

The main source of critical raw materials (CRM) can be found in the electronic components attached to the Printed Cricuit Board (PCB) and constituting the Printed Board Assembly (PBA). Noble finishes can be present at PCB level but most of the precious metals are coming from the component metallization layers and internal (Au) wire bonds. When further up-grading (in addition to the PCB separation) is still required, the highest Au containing components can be located in the advanced IC packages.

A special attention should be given to separate devices, such as USB sticks and memory cards. One FMD of memory chip shows 700ppm of Au at chip package level. Considering the ease of collection for separate devices, the potential for Au recovery is high, e.g. Au content in memory card (15mg) and Solid State Disk for USB stick (5mg). Further analysis of the composition and discussion on the delineation of WEEE is needed.

O4 Flat panel displays, to recover In

In is dominantly used (74% of the global usage) for the creation of Transparent Conductive Oxide (TCO) which is deposited on displays (TV, computer screens, tablets etc.). Although an absolute value of 0.05 to 5g per square m display is found, the concentration is very much diluted (far below 0.1wt%) due to the presence of the 'heavy' glass substrate. The complex construction of the display further complicates the disassembly process and potential up-grading. The ability to separate the different layers in flat panel displays is crucial. New technologies with leaching of In are more efficient, but still under development. It is recommended to first focus on the recovery of In during the manufacturing cycle (from process scrap and sputtering targets). One could also consider to separately collect the displays until recycling processing becomes available.

O5 LED screens, to recover In and Ga

First results show ranges from 30 to 170µg for In (this amount might even be an overestimation) and 30 to 530µg for Ga per individual LED die, but further research, including the disassembly and metallurgical processes, is needed. Although the amount of In and Ga in 1 LED is low, large assemblies of LEDs, such as LED screens or LED strings might be worth recycling separately.

Other applications: laser diodes to recover Ga.

O6 Computer and telecommunications products, to recover Be

Be is used as alloying element in CuBe alloys, in high performant connectors. The Be content in CuBe is as low as 2%, but the material could be recovered as alloy.

Other applications are as heat sink (BeO) in e.g. radio-frequency and radar equipment. BeO however is carcinogenic and should be removed anyway.

O7 Fibre optic systems and infrared optics, to recover Ge

Although Ge is highly dissipated in fibre optics, it is the main use of Ge, and due the scale in which optic fibres and other optics are introduced, recycling of post-consumer waste will be an issue in the future. Nowadays, recycling is mainly established for new scrap. The fibres and optics have a considerable life time, which makes that old scrap is not recycled yet, but shows a high potential for the future (Gus Gun, 2014)

Other applications: Ge devices are mainly expected for microelectromechanical systems (MEMS) applications where they can be used as capping substrates in bolometers which are used in movement sensors. Also for these devices, further research on the average critical material concentration is still required.

O8 Phosphors in (compact) fluorescent lamps, to recover Eu, Y, Tb

Phoshors constitute 3% of the weight of Compact Fluorescent Lamps (CFLs). They are easily detectable and removable, especially in larger CFLs, but suffer from the presence of mercury in the powder. Several separation technologies exist: Rhodia's process, OSRAM'S process with liquid-liquid extraction (RE>90 %), Flotation (RE>90 %) Direct re-use (low purity and RE). Note however that the economic value of the recuperated REE has dropped drastically last year (a.o. since the market for new CFL decreases because of the substitution with LEDs). The glass is not recycled yet because of contamination with Hg.

Other applications: flat-panel displays, liquid crystal displays

O9 Electronic control units and copper in motors, wiring, radiators, bearings in the automotive

For most End-of-Life Vehicles (ELV) components, end-processing is since long very well established, but dismantling of these components can yield higher efficiencies. The recovery of critical materials requires a dismantling step, prior to shredding. There is discussion going on whether such dismantling can be done in a cost-effective way, when aiming for enhanced material recovery. Quick wins should be sought in improving recycling systems and technologies that target a combination of materials that are present in those components that currently are being separated from the ELV, such as catalytic converters and batteries (O10a and b), or of which the removal may yield economic and environmental benefits in a foreseeable future, such as electronic control units (O4) and rare earth containing parts/alloys (braking systems contain e.g. up to 700g Nd).

O10a Li-ion batteries to recover a wide range of (cathode) constituents, and lead acid batteries for silver recovery

Processes are available (UMICORE) for refining pyrometallurgically obtained Co/Cu/Ni/Fe alloys for the recovery of cobalt as $LiCoO_2$ for Li-ion cathodes and of $Ni(OH)_2$. Bio-hydrometallurgical methods are currently under investigation. Several industries have developed (combinations of) mechanical and pyro and hydrometallurgical methods for recovery of $LiCoO_2$, $Li2CO_3$ or LiOH, Cu, Ni, Fe, Al, Co (e.g. RECUPYL, ACCUREC) that appear to achieve high functional recovery rates.

Recovery of silver from lead acid batteries can be achieved by pyrometallurgical methods, using the Parkes process with Mg addition, and by electrowinning.

O10b Nickel and cobalt rich batteries, to recover Li, Co, Ce, La and other REE

An electric vehicle contains on average 53 kg NiMH battery, which can easily be detected and removed. State-of-the-art industrial recycling of NiMH batteries is available, however, mainly Ni is functionally recovered from NiMH batteries and the REEs are lost in the smelter slags. Technological options are available to recover Ni, Co, Mn and REO (e.g. hydrometallurgical route from Zhang et al. (RE 97,8 %), Honda’s molten salt electrolysis, UMICORE/Rhodia’s Ultra High Temperature smelting and refining technologies). On the other hand, rare earths can also be recovered from NiMH slags enriched with RE-oxides. A wide range of other methods for the recovery of rare earths from NiMH is available, but their industrial applicability is still limited and subject to research. **Quick wins might be achieved from testing and/or upscaling of the most promising hydrometallurgical processes**.

The possibility exists of treating simultaneously several electrochemical systems of spent batteries using the same process, in order to overcome the high costs and difficulties of selective collection and sorting. The BATMIX process uses a single hydrometallurgical process of major battery systems (NiCd, NiMH and Li-ion) having Ni and Co as main metals.

Industrial capacity for pyrometallurgical based recovery of LiCoO2 from NiMH/Li-ion mixes, for secondary Li-ion cathodes, has been installed (UMICORE).

Remark:

Research results pinpoint that the highest material recovery not always results in the highest environmental benefits. However, at the moment, legislation does not distinguish between functional and non-functional recycling, and establishes weight based recycling targets, implicitly assuming that recycling rates are proportional with the environmental and economic benefits. In the case that increased recycling cannot be obtained without having a net negative impact on the sustainability of the recycling system, care must be taken to assure the accomplishing of the primary goal of waste management, minimizing the negative effects of the generation and management of waste on human health and the environment.

Contents

1. Introduction

This documents deals with the question whether yet unexploited opportunities for increasing the recycling rate of critical and value added elements could be increased in the near future by simple measures.

Simple measures could mean that a collection system is set up for specific products, or that a proper and simple pretreatment step is introduced to isolate components with a high concentration of a certain metal to be further recovered. We do not consider here improvements of the recycling technology itself, which also can increase the recycling rates of critical and value added materials, since it is out of the scope of the study. So, the possible “quick wins” should fit in existing extraction technologies, but means that collection or specific pretreatment is not existing, not sufficiently distinctive or not implemented. The needed technological development should be estimated as short term.

Finally, most elements discussed here are either used as an alloy or mixture with other elements, or as alloying element itself in e.g. steel, aluminium, or additive in plastics. The possibilities to recycle the alloy should also be considered and often results in a less energy-intensive recycling scheme, if a specific flow for the alloy can be organised and is economic feasible.

In a first chapter the viewpoint of the table of Mendeleev is taken. The elements considered critical or value added are discussed, their main applications listed as well as the share of the yearly production volume of an element going to these applications. This gives an general view on volumes and materials flows into specific applications.

The following chapters (3-5) start from the application side. Opportunities in specific waste streams of electrical equipment, batteries and vehicles respectively are discussed.

Chapter 2-5 are purely literature based. Chapter 6 summarizes the findings in 12 opportunities. These opportunities have been discussed with recycling experts and have been presented to a group of stakeholders. The comments of the experts and stakeholders are incorporated in the final text of the opportunities as presented in this report.

2. Use of critical and value added materials

2.1 Method

The table summarizing the use of elements in different applications (see excel file) is based on a vast amount of literature data. These data are not always consistent. It is very hard to compose a set of compatible and verified data. In the context of this assignment, we collected data starting from the CRM report 2014 of the EC (Commission, 2014b) and complemented it with data of other literature (e.g. Graedel et al., 2013; Chancerel et al., 2013; Buchert et al., 2012,...). The prices of the elements (better said: of a basic commercial alloy) are taken from the CES selector software, in August 2014. One has to bear in mind that the uncertainties are rather high for all these data, and that we did not spend effort nor would have the claim of being complete and compare all literature data in order to distill the "best" number. We do believe however that the quality of the data is high enough to allow for scanning possible unexploited opportunities for increasing the recycling rates of certain critical and valuable element.

Where possible, not only production amounts and typical applications of the elements are given, but also their presence in specific components, the content (mg per unit), the concentration (g/g component), and the physical potential (total weight of the element in a specific type of component).

Application areas of elements that are considered as not being a possible quick win opportunity, have got this label for different reasons: the recycling is already established (to a certain degree, in most cases efficiency can still be improved), not in the scope of the targeted applications, too difficult, ...

2.2 List of elements

The European Commission recently published an updated list of elements (Commission, 2014a) which are considered as being critical. The criticality is assigned to elements on basis of their economic importance for Europe, together with the risk of supply. This risk of supply is mainly depending on the political stability of the countries of origin. The list of critical elements now include: Antimony, Beryllium, Borates, Chromium, Cobalt, Coking coal, Fluorspar, Gallium, Germanium, Indium, Magnesite, Magnesium, Natural Graphite, Niobium, PGMs, Phosphate Rock, REEs (Heavy), REEs (Light), Silicon Metal, Tungsten. Because of lack of applications in the areas discussed in this report, coking coal, fluorspar, magnesite and phosphate rock are left out. On the other hand, some elements have been added in the discussion since they could represent an important economic value in recycling: gold, silver, tantalum (which was included in the previous list of critical elements of the EC, but dropped out of the updated list), tin, copper, zinc and molybdenum. In underneath list of elements, the current recycling and recycling opportunities as described by the report of the European Commission (Commission, 2014a) is summarized.

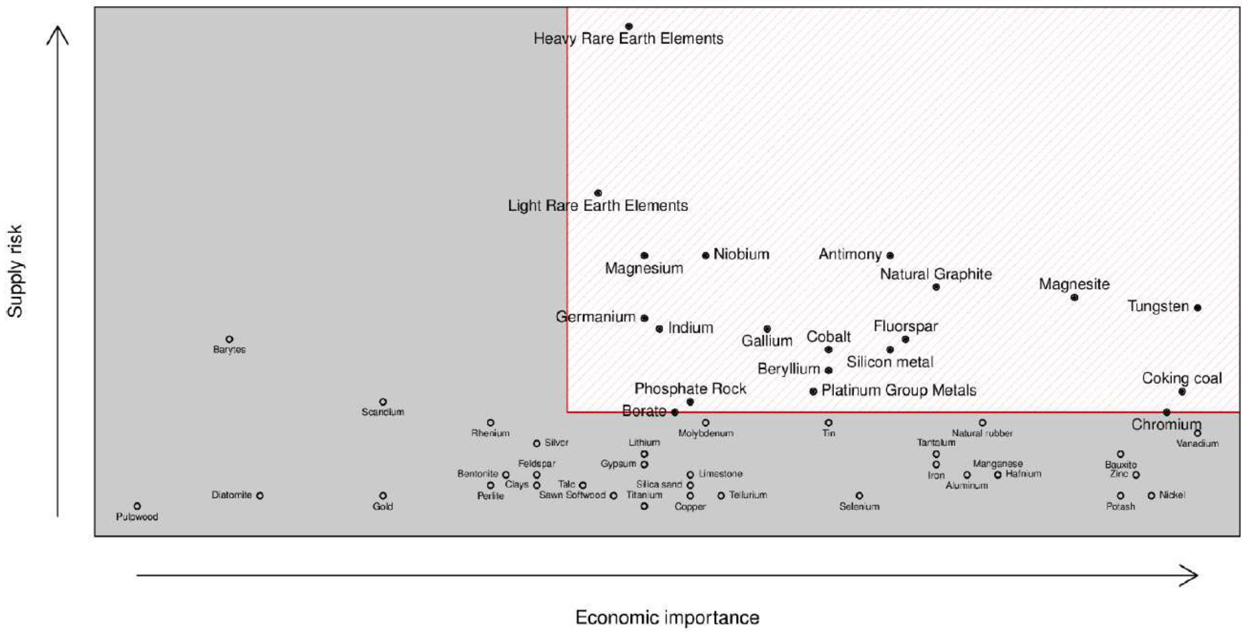

Figure 1: criticality of elements for Europe (Commission, 2014a)

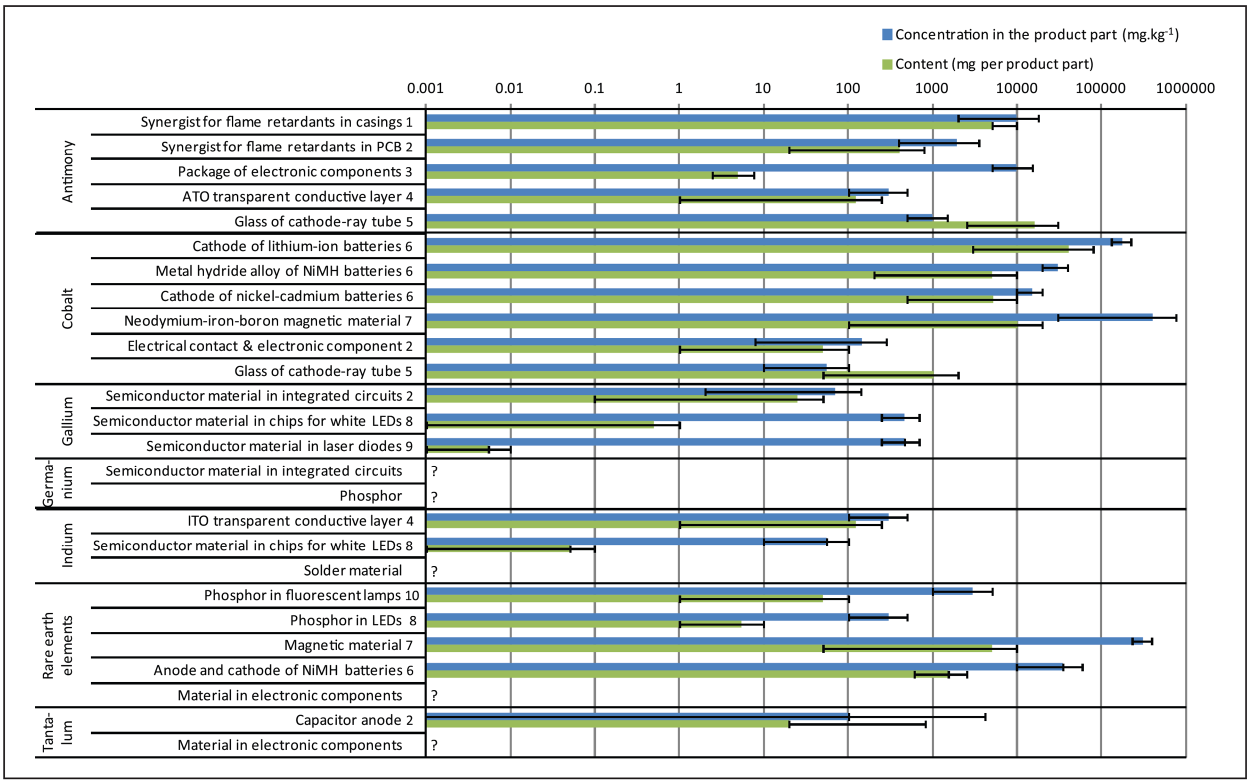

Figure 2: estimate of metal concentration and content for typical applications of some critical elements (Chancerel et al., 2013)

Critical elements

Antimony

Traditionally, Sb has been used in lead batteries. The recycling chain for these batteries is well established and the recycling is efficient. However, the use of this type of batteries is decreasing. Today, the major applications of Sb are as flame retardant in plastics, PCBs, and LCD screens (ATO layer). These are dissipative uses, and hard to recycle if not as secondary flame retardant plastic.

Beryllium

Beryllium recycling for end-of-life products is nearly nihil, while considerable amounts are recycled from new scrap. An opportunity could be in the recycling of Beryllium components (heat sinks e.g.) in computers, but has to be further studied. As to the Beryllium Science& technology Association (http://beryllium.eu/) recycling of Be out of computers would be interesting both from an economic as from an environmental point of view. Other applications of Be are quite scattered, making the opportunity for recycling at this moment rather small.

Chromium

Chromium is for 99% used as a alloying element in stainless steel, other steel grades and superalloys. It is therefore recommended to recycle e.g. stainless steel as alloy. Exact numbers of the recycling of stainless steel have not been found, but there is an established market for stainless steel scrap.

Cobalt

The recycling rate for cobalt is already high (estimated 68%). Cobalt is recycled for economic reasons (lower costs compared to cobalt extraction from ores) and for environmental reasons (to prevent damage caused by land filling of batteries). The only (short term) opportunity is to further increase the efficiency of collecting (and recycling) batteries.

Gallium

Recycling of new scrap of refined Ga for the semiconductor industry is established (capacity 198 tonnes/year), but there is no recycling of post-consumer scrap. Globally less than 1% end-of-life gallium is recycled (UNEP). In microelectronics, Ga is quite dispersed in the components and ends up in the slag when recovering other metals from the PCBs. For CIGS solar cells, there is a recycling of production waste (new scrap), but the amounts of postconsumer waste still are very low and it is not economically viable to set up a specific recycling scheme for Ga out of end-of-life solar cells at the very moment. Finally, there is a small potential for recycling Ga in the LEDs group of devices (Buchert, 2009), but a decent recycling system for LED seems not to be for the near future. A niche market could be the (infrared) laser diodes.

Germanium

Unlike industrial scrap, only very small amounts of germanium are recovered from post-consumer goods (less than 1% of end-of-life germanium is recycled according to UNEP). However, up to 80% of the Germanium containing optical fibres are reported to be recycled. It is to be further examined whether other Germanium containing infrared optics can be and are being recycled.

Indium

Only 1% of indium from end-of-use LCDs appears to be recovered. This is mainly due to the fact that only small concentrations are present in each device, thus a large number of screens would be required to make this economically viable. Several research projects are being undertaken in order to achieve indium recycling from LCDs.

Buchert estimates a mean value of 700 mg/m^2 In (present in the ITO layer) will be assumed for LCD displays as well as for plasma screens (Buchert et al., 2012), which equals 174 g/t of display waste. A specific niche are the low melting alloys, such as used in fuses.

Mg

Most magnesium is used as alloying element in Al alloys, which have to be recycled as alloy. There is room for improvement of recycling magnesium alloys used in automobile and mobile phones.

Natural Graphite

Although natural graphite is relatively abundant, it is catalogued as critical. Graphite is e.g. used in batteries, and is in the pyrometallurgical recycling of metals in batteries offered as reductant in the smelter. Recycling could be possible by using hydrometallurgical recycling routes for batteries.

Nb

Niobium is mainly used as alloying element in steels and superalloys. It is not recycled as such, but recycling of niobium-containing steel grades is recommended. Data on the absolute amount of niobium recycled are not available, but according to USGS it may be as much as 20% of apparent consumption

PGMs

Due to their high value, PGMs are well recycled, both in industrial and end user applications. The recycling of autocatalysts is well established, however the collection of autocatalysts (within Flanders, but especially in developing countries where used vehicles are exported to,) could be improved. The PGMs used as catalysts in industrial processes are recycled to a very high degree. A niche application of Pt and Ru is in hard disc drives, where the opportunity of improved recycling could be further studied.

Rare earth elements (RE)

End-of-life recycling rates of rare earth elements are very low. Opportunities to recycle rare earths are mainly in:

- The recycling of permanent magnets (Nd, Dy, Pr). They are used in electrical motors (e.g. in electrical vehicles; but also for driving automative windows in cars,...), in (off-shore) wind turbines where a minimum maintenance is required, and in hard disc drive heads.
- In the phosphors (Eu, Tb, La) of CFLs (compact fluorescent lamps). Some of the latter can be recuperated quite easiliy, but the Hg decontamination still has to be further developed.
- In NiMH batteris both NiMH batteries: from both portable electronics and hybrid/electric vehicles if they can be collected and identified.

Some rare earths are also used as alloying element in ceramics, where they are easily detected and could be recovered, but the cost of the extraction is currently too high compared with the RE market price.

Eu, Gd, Y are of importance in LED lights and therefore have a recycling potential for the future; this also applies to Y in flat screens (Buchert, 2009)

Silicon metal

Silicon used in Al is not recycled as such, but can be considered as recycled in the aluminium alloy. An opportunity might be in the recycling of Si in the solar cell and microelectronics industry. No further details about the recycling market and technologies have been documented yet.

Tungsten

Most tungsten is used in cemented carbides for cutting tools. The recycling of these cutting tools is well established. The concentration of tungsten in end-of-life products is many times higher than in ores, which makes recycling interesting.

Non-critical elements

Gold – Au

Because of its intrinsic value, gold has been recycled from nearly all applications. Although the metallurgical recovery of gold from electronic components is very efficient, the collection and pretreatment of gold-containing components still can be improved.

Silver - Ag

As for the end-of-life recycling rate (EOL-RR) for silver, this is greater than 50% worldwide. Jewellery, silverware and coins have very high recycling rates, typically greater than 90% due to the ease of collecting and recycling of these applications. Once these applications are excluded from the calculation; the end of life recycling rate for silver falls in the range 30%-50%.

However, the EOL-RR varies considerably by application:

- vehicles: 0%-5%
- electronics: 10%-15%
- industrial applications: 40%-60%
- others: 40%-60% (EC)

This means there is still room for (a lot of) improvement in recycling silver from electronics and vehicles.

Tantalum

The major application of Ta is in capacitors. However, capacitors are going together with the PCB to the smelter for the recovery of other metals, and Ta is not (yet) recovered. Ta capacitors contain 28 weight% Ta in post-consumer recycling, as determined by (Schöps 2011). The capacitors on all the PCBs in a notebook are estimated to have a total weight of 4.63 g, corresponding to a total quantity of Ta of around 1.7 g for a mean Ta content of approx. 36.7% (Buchert et al., 2012).

The second largest application area is the use of Ta as alloying elements in superalloys, for which it is recommended to recycle the alloy.

Tin

The infrastructure for reclaiming tin is well developed and recycling rates for the metal are high. Increase in recycling of solder alloys is possible.

Copper

Most copper is used in its metallic form for electrical wiring and tubes. The recycling is well established.

Zinc

Major amounts of Zn are used in galvanisation layers on steel. The scrap steel is recovered in a EAF, in which the Zn is emitted via the off-gases, and forms solid particles together with iron-oxides. Some of the Zn is recovered. Research is ongoing to improve the efficiency of the Zn recovery, however, this will only be implement on medium or long term. Other Zn alloys are well recycled.

Molybdenum

The main use of molybdenum is as alloying element in steel and stainless steel alloys, which should be recycled as alloy.

Lithium

Lithium is today mainly used in batteries and in ceramics and glass. Since 45% of batteries in portable electronics in the EU has to be recycled (by 2016), it could be expected that Li already is well recycled. However, in many cases the batteries are not recycled for the lithium content but for cobalt or ferromanganese, and the lithium is part of the slag e.g. used in road construction.

2.3 Interim conclusions

The data are listed in the accompanying excel sheet. An example of the application areas and found data is given in figure 3 for Sb.

The detected opportunities are listed in figure 4 and 5. They are ordered by the value of the total of material within the yearly production of the relevant application. Of course, this does not reflect the costs of the recycling, it just indicates what (financial) volume is concerned. A schematic overview of opportunities is given in figure 6.

Element	production (2010)	Application	Application details		% incorporated into application	Weight into application	prices	Economic value (Market price*weight)	Weight per component	Weight of the component	% weight within component	Ease of detecting the element and the component	Ease of liberating the material from the component
	tonnes					tonnes	Eur/kg *	MEUR	g	g			
Sb	150000	flame retardant	ATO (antimony trioxide) - incorparted mainly in plastics	plastic casings	43	64500	4,4	284	7	700	1		dissipative use mostly ends up in MSW
Sb				PCB					0,15	125	0,12		
Sb				LCD (ATO layer)					0,105	750	0,014		
Sb	150000	lead-acid batteries	mainly vehicle batteries		32	48000	4,4	211					established recycling
Sb	150000	plastics	catalysts		6	9000	4,4	40					dissipative use mostly ends up in MSW
Sb	150000	glass			<5		4,4		12	1091	1,1		
Sb	150000	microelectronics dopant			<5		4,4						
Sb	150000	alloys	lead alloys		5	7500	4,4	33					

Figure 3: Example of literature values for 1 element

Element	production (2010)	Application	Application details		% incorporated into application	Weight into application	prices	Economic value (Market price*weight)	Weight per component	Weight of the component	% weight within component
	tonnes					tonnes	Eur/kg*	MEUR	g	g	
RE - Nd	20000	Magnets	Used with praseodymium and other rare earth elements in high-intensity magnets	Computers	88,5	17640	138	2434	3,75 g	15 g of NdFeB magnet (on average) in HDDs	25 % in HDDs
Si	1860000	electronic and solar			8	148800	9,63	1433			
RE - Dy	850	Magnets	Used as a minor but important constituent of high-strength magnets	MRI	98,2	835	1197	999	39 kg	860 kg REPM	4,50%
RE - Pr	4950	Magnets	Used with neodymium and other rare earth elements in high-intensity magnets	Computers	72,8	3600	130	468	0,75 g	15 g REPM (on average) in HDDs	5 % in HDDs
Be	259	Computer and telecommunications products	Serves as both a structural support and heat sink in product applications such as computers, cellular phones, integrated circuits, and radars		50	129,5	861	111			
Ta	681	capacitors	portable electronics, automotive components (ABS, airbag, GPS…), medical appliances (hearing aids)…		40	272	388	106	0,15		
RE - Ce	45500	Batteries	Used in nickel-metal hydride batteries using nickel and mischmetal		2,8	1275	28	36	954 g	53 kg NiMH battery in an electric vehicle	1,8 % $
RE - Pr	4950	Magnets	Used with neodymium and other rare earth	MRI			130		43 kg	860 kg REPM	5%

			elements in high-intensity magnets					
RE - Pr	4950	Magnets	Used with neodymium and other rare earth elements in high-intensity magnets	Automobiles	130	75 g	1,5 kg of REPM/vehicle (in the electric motor)	5%
RE - Nd	20000	Magnets	Used with praseodymium and other rare earth elements in high-intensity magnets	MRI	138	198 kg	860 kg REPM	23%
RE - Nd	20000	Magnets	Used with praseodymium and other rare earth elements in high-intensity magnets	Automobiles	138	450 g	1,5 kg of REPM/vehicle (in the electric motor)	30%
RE - Tb	290	Magnets	Used as a minor but important constituent of high-strength magnets	Automobiles	2266	10,5 g	1,5 kg of REPM/vehicle (in the electric motor)	0,70%
RE - Dy	850	Magnets	Used as a minor but important constituent of high-strength magnets	Automobiles	1197	135 g	1,5 kg of REPM/vehicle (in the electric motor)	9%

Figure 4: list of most probable opportunities

Element	production (2010)	Application	Application details		% incorporated into application	Weight into application	prices	Economic value (Market price*weight)	Weight per component	Weight of the component	% weight within component
	tonnes					tonnes	Eur/kg*	MEUR	g	g	
Au	2635	electronics	diodes, transistors, integrated circuits and semi-conductor memories, capacitors and resistors		13	343	44100	15106			
Cu	15997172	automotive	motors, wiring, radiators, bearings…		10	1599717	7,37	11790			
Ag	23300	electronics	electrical contacts, switches and passive electronic components such as multi-layer ceramic capacitors		19	4427	805	3564			
Natural Graphite	1100000	batteries	Li-ion batteries		10	110000	11,1	1221			
RE - Eu	425	Phosphors	Used as a red phosphor in flat-panel displays, liquid crystal displays and fluorescent lamps	Compact fluorescent lamps	96,5	410	2840	1164		3 % of the weight of the lamp (for different lamp weights)	0,80%
Co	106000	batteries	recharcheable batteries	cathode of Li-ion batteries	30	31800	26,5	843	16	133	12
RE - Y	7650	Phosphors	Used in flat-panel displays, x-ray intensifying screens, and temperature sensors	Compact fluorescent lamps	78,7	6020	108	650	Not available	3 % of the weight of the lamp (for different lamp weights)	12,50%
RE - Tb	290	Phosphors	Used largely in compact fluorescent lights	Compact fluorescent lamps	70,7	205	2266	465		3 % of the weight of the lamp (for different lamp weights)	0,80%
In	662	flat panel displays	ITO	notebooks	56	371	668	248	0,039	250	0

RE - La	31500	Batteries	Used in nickel-metal hydride batteries using nickel and mischmetal		26	8185	29	237	2,65 kg	53 kg NiMH battery in an electric vehicle	5%
Pt	239	industrial - electrical	hard disk drives		2	4,7	41000	193			
RE - Y	7650	Ceramics	Y-stabilized zirconia (zirconium oxide) used in refractories and as jet turbine blade and nozzle coatings		20,9	1600	108	173	Not available	Not available	Not available
RE - Nd	20000	Ceramics	Used as a coloring agent		4,5	895	138	124	Not available	Not available	Not available
Ga	404	Optoelectronic devices	Includes laser diodes, light-emitting diodes, and solar cells	laser diodes	31	125	500	63	0,000008	0	0,017
RE - Sm	500	Magnets	Includes use in samarium-cobalt magnets		97	500	118	59	Not available	Not available	Not available
Be	259	Other	Includes appliances, automotive and medical applications, electronics, and industrial components		25	64,75	861	56			
RE - Gd	1020	Phosphors	Used as a green phosphor in flat-panel displays and in compact fluorescent lamps	Compact fluorescent lamps	22,6	230	239	55	Not available	$ 3 % of the weight of the lamp (for different lamp weights) $	0,30%
Ru	25	electrical	hard disk drives; resistive element in thick-film hybrid Ics		56	10,7	4600	49			
Ge	120	Fiber optic systems	Used in telecommunication infrastructure, cellular phones, and optical fibers		30	36	1340	48			
RE - Ce	45500	Phosphors	Fluorescent lamps(straight/curved), Compact fluorescent lamps (CFLs), LEDs, LCD backlights, Plasma screens	Compact fluorescent lamps	3,7	1690	28	47	Not available	3 % of the weight of the lamp (for different lamp weights) $	0,40%
Ge	120	Infrared optics	Used in lenses, windows, and		25	30	1340	40			

			infrared thermal imaging systems, mainly for military applications								
In	662	thermal interface mat	e.g. fuses		6	40	668	27			
Ge	120	Electronics and solar electric applications	Used in solar cells, automobile taillights, cameras, flashlights, cellular telephone display screens, televisions, and traffic signals		15	18	1340	24			
In	662	LEDs			3	20	668	13	0,000029	1	0
RE - La	31500	Phosphors	Fluorescent lamps (straight/curved), Compact fluorescent lamps (CFLs), LCD backlights, Plasma screens	Compact fluorescent lamps	1,4	455	29	13		3 % of the weight of the lamp (for different lamp weights) $	0,50%
RE - La	31500	Ceramics	Stabilizer in ceramics, ceramic capacitors, colourant		1,2	365	29	11	Not available	Not available	Not available
RE - Ce	45500	Ceramics	Stabilizer in ceramics, ceramic capacitors, colourant		0,8	365	28	10	Not available	Not available	Not available
Mg	755000	"	automobile				2,61				
Mg	755000	"	laptop/mobile phone				2,61				
RE - La	31500	Phosphors	Fluorescent lamps (straight/curved), Compact fluorescent lamps (CFLs), LCD backlights, Plasma screens	Flat panels			29		Not available	Not available	Not available
RE - La	31500	Phosphors	Fluorescent lamps (straight/curved), Compact fluorescent lamps (CFLs), LCD backlights, Plasma screens	LCDs			29		Not available	Not available	Not available
RE - Ce	45500	Phosphors	Fluorescent lamps(straight/curved), Compact fluorescent lamps (CFLs), LEDs, LCD backlights, Plasma screens	Flat panels			28		Not available	Not available	Not available
RE - Ce	45500	Phosphors	Fluorescent lamps(straight/curved),	LCDs			28		Not available	Not available	Not available

			Compact fluorescent lamps (CFLs), LEDs, LCD backlights, Plasma screens					
RE - Eu	425	Phosphors	Used as a red phosphor in flat-panel displays, liquid crystal displays and fluorescent lamps	Flat panel displays	2840	Not available	Not available	Not available
RE - Eu	425	Phosphors	Used as a red phosphor in flat-panel displays, liquid crystal displays and fluorescent lamps	LCDs	2840	Not available	Not available	Not available
RE - Gd	1020	Phosphors	Used as a green phosphor in flat-panel displays and in compact fluorescent lamps	Flat panel displays	239	Not available	Not available	Not available
RE - Tb	290	Phosphors	Used largely in compact fluorescent lights	Flat panel displays	2266	Not available	Not available	Not available
RE - Tb	290	Phosphors	Used largely in compact fluorescent lights	LCDs	2266	Not available	Not available	Not available

Figure 5: list of most additional opportunities

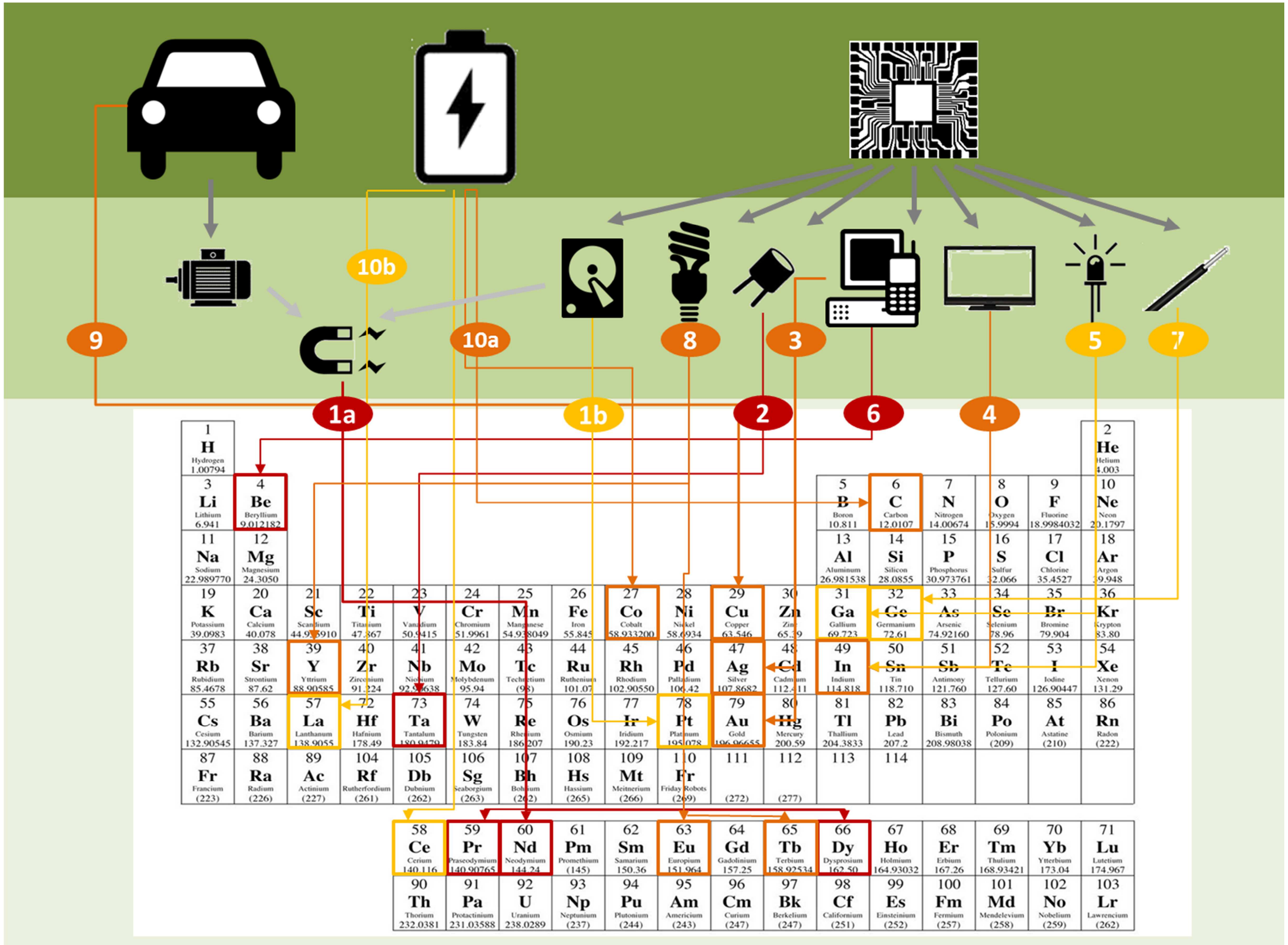

Figure 6: schematic overview of opportunities based on a scan of the main uses of the chemical elements

3. Weee

3.1 Introduction

3.1.1 Background

The **increased material complexity** and **continued miniaturization** for electronic components **lead to severe dilution** of many of the CRM elements in their global waste flow. Nevertheless, for some ‘high grade’ electronic categories, typical concentrations of precious metals (Au, Pd) are found to be higher in the Waste of Electrical and Electronic Equipment (WEEE) than in the presently mined, natural ores. Furthermore, the environmental impact of secondary recovery is much lower compared to the primary production. Both these conditions explain the large incentive for recycling. However, the heterogeneity of the waste flow makes recycling processes not straightforward. It is mentioned by Hagelüken (Hageluken et al., 2013) that *“**Recycling of consumer products and some industrial products is much more than metallurgy and requires a complete chain, starting with collection, sorting, and dismantling/ preprocessing to separate components containing valuable metals or to upgrade relevant fractions for subsequent metallurgical end-processing**”*.

UNEP has provided an overview study (UNEP Report, 2009) of the recycling performance for the different elements in which the **recycling rates** (end-of-life (EoL) functional recycling) (RR), **recycled content** (fraction of scrap metal in total metal input) (RC) and **old scrap ratio** (the fraction of post-consumer scrap in the recycling flow) are provided. Elements that have a poor recycling score on all of these performances are **Be**, **Ta**, Os, **Sb** and the rare earth elements (**REE**). Some elements have very low recycling rates (RR for EoL) but still have a reasonable amount of scrap metal into the final content used for (primary) metal production (RC). This holds for **In** and **Ge** and to a minor extent also for **Ga** which is an indication for recycling opportunities during the production chain (but not after ending up in the consumer product and waste). While the UNEP study focusses on the global element recyclability throughout all technology fields, following paragraph comments on the specific recycling opportunities and possibilities for WEEE as given by Hagelüken (Hageluken et al., 2013)

Recycling of WEEE has already been studied and is executed extensively. The different waste streams are currently optimized to recover mass-relevant materials like iron, aluminium, plastics and copper in which some of the trace elements can be lost (Chancerel et al., 2009) In total, it is stated that 17 metals are currently recycled. Cu can be recycled by pyro-metallurgical processes applied to PBA (Printed Board Assembly) WEEE and this recyclate contains high amounts of precious metals (**Ag**, **Au**, **Pt**, **Rh**, **Ru**, **Ir**). These can be subsequently refined by hydro-metallurgical processes. Side stream processes of slag and leaching residues further allow the recovery of some base metals (Pb, Sn, **Sb**, Bi) and specialty metals (**In**, Se, Te). The recovery efficiency of the precious metal purification processes are very high (above 90%, driven by the economic material value) but relatively low for **In** (10%) and **Sb** (47%) (Rotter et al., 2012). Further optimization of the latter processes or the extraction of other (not yet recovered elements like Ta, Be, REE, ...) lack a sufficient driver due to insufficient material recovery value. In order to stimulate and improve the recovery of more metals, a better knowledge of the usage and location of these elements is needed. This would allow a further up-grading of WEEE into separated fractions with a higher potential for recycling.

The purpose of this study is to search for as yet insufficiently exploited recycling opportunities in order to improve the recovery of some of the CRM elements that are present in WEEE by waste stream up-grading. The benefits of the increased recovery can be in terms of **economic**, **environmental** and/or **geo-strategic** gain that all contribute to the driving force or attractiveness for recycling of each of the different elements. It is not the aim of this search to prioritize in this matter nor to take into account technological difficulties and/or efficiencies of the recycling process. Whenever possible, comments, limitations and suggestions as found in literature about WEEE recycling are added but the main purpose of this investigation is **to locate the presence and form of the CRM elements in the WEEE**. This knowledge of the CRM presence is a prerequisite for being able to define recycling opportunities. However, in order to properly evaluate these opportunities, a combined study that focusses on market data, collection, separation and metallurgical recovery capabilities is still needed.

3.1.2 Waste stream categories and break-up test cases

A variety of EEE products exists and they are divided in several sub-categories as defined by the WEEE EU Directive (2002/96/EC). It is said that too many categories will hamper logistics, too little categories will result in a heterogeneous mixture of different 'grades' of waste with a higher risk for inefficient recovery. Separation of high-grade and low-grade electronics increases the effectiveness of the pre-processing operations as well as the subsequent recovery processes. The optimal conditions are a compromise between grade (quality) and recovery (quantity) (Chancerel et al., 2009).The Directive further specifies a certain weight fraction to be collected and treated for recycling. While this is a valuable approach to reduce the mass for landfill, the heaviest products not necessarily contain the most valuable elements. Several exercises have already taken place in which a breakdown study of different EEE is performed. The main focus of most of these studies was to retrieve the individual amounts of valuable precious metals present in the different products. The investigated types of products therefore mainly belong to the so-called 'high' grade categories.

In (Haig et al., 2012), a UK WRAP (*Waste Recovery Action Plan)* study, the **material composition for different product groups** is investigated. For each category, a list of several equipment pieces is specified and used for the analysis (done by FT-IR and XRF spectroscopy). A mass breakdown analysis shows that ferrous and plastic fractions account for the heaviest part for each of the products. These material fractions can be fed into existing/dedicated recycling streams but care must be taken not to lose other elements in the base metal fractions since they cannot be recovered from that. When looking at the portion of precious metals (**Ag**, **Au**, **PGM**) contained in the products, a large variation is found for the different categories explaining the 'high' and 'low' grade waste terms. The ***Au*** *content in waste coming from respectively IT and telecom (20ppm), consumer (15ppm), displays (12ppm), toys-leisure-sport (7ppm), small household equipment (1ppm) and finally electrical and electronic tools (0ppm) does not correlate to the individual product mass.* For the latter categories, a high mass count is expected and therefore scoring high in terms of potential mass-based recovery directives but not necessarily as critical metals source. The exercise shows that there is no correlation between mass and potential recovery of precious metals.

A summary of several elemental (**Ag**, **Au**, **Pd**, **Pt**) **breakdown analyses of PCB waste** from different products is given by (Chancerel et al., 2009) showing up to 1000 and 5000 ppm of **Ag** for personal computers (PCs) and mobile phones respectively. **Au** concentrations range from 80 to 600 ppm for

PCs investigated by different researchers over a period of more than one decade (1993 – 2007). The same work also reports on Substance Flow Analysis (SFA) investigations of the total valuable metal content (**Ag**, **Au**, **Pd**) in a representative mixture of waste of IT, telecommunications and consumer equipment (German group-3 WEEE category). Losses between the effective recovery and the predicted content are high: up to 35% of **Ag** is found in the ferrous outputs and 29% ends-up in the plastics recycling stream from which they cannot be recovered. **Only 12% of Ag and 26% of Au and Pd reach the appropriate (Cu) recycling stream**. To avoid this, unselective shredding should not be performed since severe shredding operations increase the risk for parts ending up in the wrong waste stream. It is stated that shredding should only be done when more knowledge is available about the location of the different elements, while for mobile phones it is found that a batch of untreated devices (no pre-processing steps) is most successful when recovering the precious metals.

In another research study (Rotter et al., 2012), the material flows in mobile phones for 9 trace elements are assessed and quantified. The investigated trace elements include **Ag**, **Au**, **Pd**, Ni, Bi, Sn, **Sb**, **In** and **Ta**. They are not all part of the CRM list and are probably chosen because of the presently existing recycling routes for most of these elements (Hageluken et al., 2013). Similar to what is found for the SFA for precious metals (Chancerel et al., 2009), significant recovery losses are found for **Sb** (<30% recovery), **In** (<10%) and **Ta** (0%). These losses are a combination of low recovery rates for the metallurgical end-processing (in contrast to values of above 90% for Au, Ag and Pd), losses during pre-processing (especially for mechanical dismantling) and most importantly because of high losses in the collection phase. Only 18% of the mobile phones are expected to end-up in the appropriate waste stream.

An overview of the different concentration levels found in so-called 'high-grade' waste and at the level of the PCB is given in table 1. More PCB-breakdown studies of other WEEE categories are given in (Huisman et al. ,2007).

Table 1: Overview of different precious metal concentration levels measured for waste and individual equipment.

	[**Error! Reference source not found.**] **IT waste UK** [ppm]	[**Error! Reference source not found.**] **Group3-waste Germany** [ppm]	[**Error! Reference source not found.**] **PC-PCB** [ppm]	[**Error! Reference source not found., Error! Reference source not found.**] **Mobile phone-PCB** [ppm]
Ag	60	70	600-1000	3600-5500
Au	20	10	80-600	370-980
PGM	10	4 (Pd only)	~100 (Pd only)	150-290
	Manual disassembly *(XRF, FT-IR)*	*Mechanical shredding* *(ICP-AES)*	*PCB = 13wt%*	*PCB = 22wt%*

Another representation of breakdown analyses is given by Johnson (Johnson et al., 2007) who uses Sherwood plots for specific equipment. In Sherwood plots, the dilution (1/concentration) is plotted against the metal price since a correlation is found between the dilution of ores used for refining and the final raw metal price. For the investigated PCB's, mobile phones and PC's, the measured precious metals (**Au**, **Ag**, **Pd**, **Pt**) dilution is much lower than for economically relevant dilutions of ores. The dilution of **Co**, **Mn**, **Cr** is found to be above or, for **Ga** and **Ge**, on the limit of economic relevance.

More recent work also focusses on the presence of other than the precious critical metals (Buchert et al., 2012). Breakdown analysis are shown for a variety of products (flat screens, notebooks and LED lighting). The elemental composition analysis is combined with a market analysis which allows the calculation of the expected total CRM consumption and ideal recovery potential. The predicted (mean) weight for **In** (used for the transparent conductive oxide ITO) ranges from 200 up to more than 2000 kg for LCD PC monitors and televisions respectively, as sold in Germany in 2010. These products are also sources of REE with **Y** being the most concentrated. This element is used as luminescent material and support matrix. A mass as high as 600 kg (for LCD televisions sold in Germany in 2010) can be found while for other REE only a few (tens of) kilograms are used (**Eu**, **La**, **Ce**, **Tb**, **Gd**). However, it is also mentioned that suitable separation and refining processes are currently missing for both **In** as well as the **REE** and for the time being, only storage can be recommended. It is furthermore mentioned that there is insufficient information available for the **Ta**, **In** and **Ga** content in mobile phones. More examples are discussed in the paragraph on specialty devices.

3.2 Build-up of EEE

As an example, a breakdown study of a notebook computer (Buchert et al., 2012) is shown in Figure 7. It contains up to 8 different parts that are relevant for recycling. All of the EEE products contain some structural parts, based on plastics and/or base metals (Al, Fe). The recycling routes for these materials are already well established, only caution must be taken not to lose any critical elements in these flows since they are inevitably lost. Furthermore, they contain cabling and electrical components like connectors, plugs, motors and transformers. These parts will be mainly composed of Cu alloys and some magnetic material in electric motors. And finally, they also contain one or more PBA's with specific components mounted on them. So roughly, EEE can be divided into structural, electrical and electronic parts. This report will focus on the electronic parts composed of PCB, electronic components and specific sub-devices (display, speakers, etc.). Their structure and composition depends on the target application and it is the purpose of this investigation to trace back specific components in which 'significant' amounts of CRM elements are used. By gathering information about the location, concentration and the composition of the CRM containing compound (in which pure versus doping concentrations are the two extreme cases) as well as information on the neighbouring compounds and the attachment procedures, potential recycling opportunities can be identified. The purpose is also to pinpoint the application where the components are preferably used.

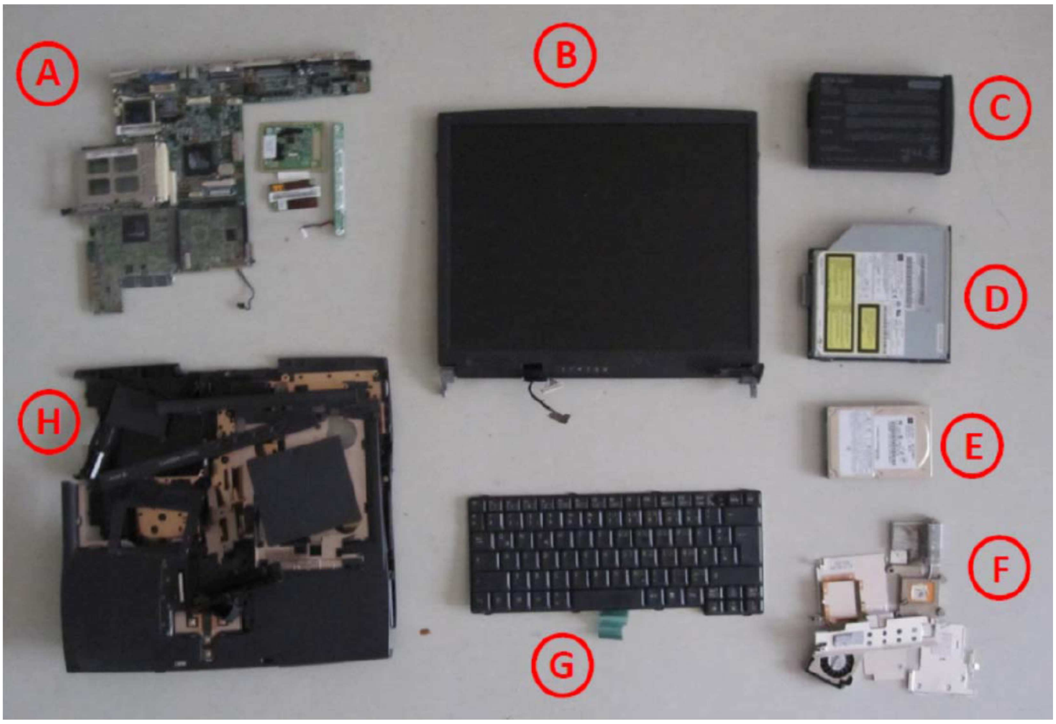

Figure 7: Notebook disassembly in 8 relevant sub-parts for recycling, taken from (Buchert et al., 2012) (photo Oeko-Institut). A. Motherboard and smaller PCB's, B. LCD screen, C. Battery pack, D. Optical drive, E. Hard disk, F. Steel elements (plates and cooling fans), G. Keyboard, H. Plastic components.

3.2.1 Printed Circuit Board

The PCB substrate is typically a polymer (epoxy) based laminate material with a large amount of Cu metallization providing the conductive routing layers for electrical signals. The following metal finish layers can be present on top of the Cu base metal to enhance the assembly performance (for instance for solderability) and durability (for instance corrosion resistance): Ni/**Au**, Ni/**Pd**/**Au**, solder or **Ag**. These finish layers are a source of precious metals, although their individual layer thicknesses (for **Ag**, **Au**, **Pd**) are usually low (between 0.05 and 0.5µm). For some applications, thicker (<2µm) , alloyed hard Au layers are used for electrical contacts such as edge connectors and key-pads. The solder finish thickness can be up to a few microns but contains little precious elements with an amount of Ag in Pb-free solders of only 3 to 5wt%. Overall, **large variations in metal content** can be found in PCBs used in different applications what is related to the PCB finish, electrical circuit density and size.

In most cases, the laminate itself is constituted of an epoxy based material with typically the Br-containing flame-retardant TBBP-A (FR4-PCB) and glass-based fibre and/or filler particles. It can further contain traces of Ba, Mg, (Al, Zn oxy-hydroxides) and **Sb**-trioxide as flame retardant additives (CRM Innonet). **Antimony** can be recovered from the Cu waste stream although the recycling efficiency is relatively low (47%, [**Error! Reference source not found.**,**Error! Reference source not found.**]). The mixed plastic fraction acts as an energy source for the pyro-metallurgical purifying processes.

3.2.2 Electronic components

According to the EU Innovation Network consortium (CRM Innonet) following critical materials are predominantly used for the fabrication of electronic components: **Ga** [70%], **Ru** [60%], **Ta** [50-60%], **Pd** and **Be** [20%]. The respective amounts being consumed by the electronics industry in relation to the global element usage is indicated in between brackets. Apart from **Pd**, the other elements are not extensively or not at all recycled and therefore particularly relevant to investigate the potential recycling opportunities. The constitution of these elements and their compounds define specific material properties (conductivity, thermal stability, etc.) that are needed to realize different functionalities of the electronic components. They will therefore end-up in specific components as will be investigated in the following paragraphs. The purpose is to also obtain more detailed information about the critical material location, concentration, compound formula and presence of other potential harmful elements that could counteract recycling possibilities.

All this information can be retrieved from FMD (Full Material Declaration) sheets when made available by the component suppliers. Sharing the material composition as such is not obliged and therefore, historically, little information is available. The producer's (not only for component suppliers but also for end-product manufacturers) obligation to provide information regarding the presence of hazardous substances (RoHS directive) and Substances of Very High Concern (SVHC) (Reach directive) in their products, strongly increases the availability of technical documentation in the supply chain which can be exploited to augment recycling.

3.2.2.1 Passive components

Table 2 shows the use of critical materials for passive components as defined in (CRM Innonet). Some other elements are added based on own research and internal database.

Table 2: Overview of expected critical metals for different electronic components.

	Innonet Report	This report Additional elements
capacitors	Ta, Pd, Nb	Nd, Sm-oxides, Mg, W
resistors	Ru, Ta	Ir, Rh, Cr, W
connectors	Ru, Be, Pd	Rh
inductors	Not specified	No CRM found
fuses	Not specified	No CRM found
transformers	Not specified	No CRM found

a) Capacitor

Following main categories of capacitor components exist: Ceramic, Film and Electrolytic capacitor (www.capacitorguide.com).

a. Ceramic capacitor

As suggested by its name, a ceramic material forms the dielectric part of the capacitor. The most often used capacitors are MLCC (Multi-Layer Ceramic Capacitors) which are built by a sandwich structure of a sintered granulate mixture of para-electric or ferro-electric materials and metallic electrode contact layers. The dielectric phase dominantly consists of one or a mixture of following compounds: Ti dioxide and/or Ba titanate. More complex stoichiometries with additions of Ca, Cu, Sr, **Co**, **Ta**, and **Mg** are possible as well. In order to increase the stability and dielectric performance of the capacitors, niobate's (**Nb**), tungstate's (**W**) and **Nd**, **Sm** and other **rare earth oxides** can be used.

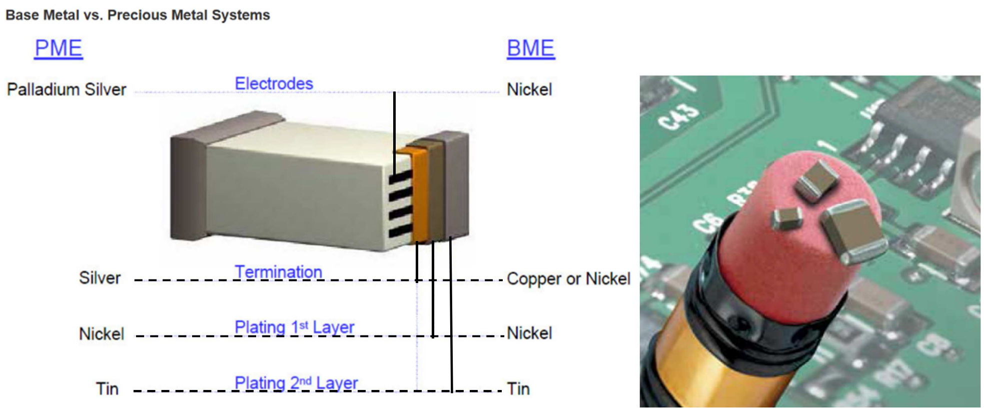

Figure 8: Schematic build-up of MLCC with different metal layers (left), Varying sizes of MLCC components (right). All images from supplier Johanson Dielectrics (www.JohansonDielectrics.com)

The electrode metal was historically made of **Ag** or **Pd**. This is still the case for applications in which high accuracy and stability is required (class I). For other applications, cheaper metals like Cu or Ni are nowadays used (class II). A schematic drawing is shown in Figure **12**, also indicating varying sizes for such components.

The terminals are typically created by subsequent layers of Ag, AgPd, Cu or Ni as contacting material to the electrodes, with Ni and Sn as solderable finish. Components with Ag, AgPd or even Au as finish layer exist as well and are typically used in combination with conductive adhesives.

The base area dimensions can vary between 0.34 x 0.15 mm^2 (smallest possible dimensions for component 01005) and several mm^2. For one specific dimension, different compositions are possible depending on the specific application requirements. Table 3 shows a comparison of two 0805 MLCC components from different categories.

Table 3: Comparison of different 0805 MLCC components with different dielectric compositions and metal contact choice, showing a large difference in CRM content.

0805A471JAT2A MLCC		
Material	Amount [mg]	[%]
Silver	**0.53**	**4.4**
Diboron trioxide	<0.01	0.0
Nickel	0.28	2.3
Tin	0.42	3.5
Palladium	**0.83**	**6.9**
(Ba,Ti) trioxide	2.20	18.3
(Bi,Ti) oxide	1.20	9.6
Nd oxide	**6.20**	**51.9**
Lead monoxide	0.36	3.0

0805ZD471KAT2A MLCC		
Material	Amount [mg]	[%]
Nickel	0.56	4.7
Copper	0.51	4.3
Diboron trioxide	0.01	0.1
Tin	0.35	2.9
(Ba,Ti) trioxide	9.22	76.8
Mn dioxide	1.35	11.3

Examples of applications in which the high quality, CRM containing MLCC's are found, are telecom, computer, automotive and non-consumer products.

b. Film capacitor

Film capacitors are made from thin plastic sheets. The use of critical materials is not suspected for this category.

c. Electrolytic capacitor

An electrolytic capacitor uses an electrolyte as dielectric through which the largest capacitance values can be achieved. The electrolyte can be a liquid but also a solid phase. The electrode material is commonly made of Al or Ta. While Al capacitors are used for many household applications, computers and power supplies, **Ta** capacitors are preferred when small sizes and higher stability and frequency response are required. They can be found in military and medical applications but also for commercial applications in laptops, cell phones and some audio amplifiers.

The Ta concentration in such capacitors can vary from 24 to 42% as reported in (Buchert et al., 2012). A schematic cross-section is shown in Figure 9. Pure Ta (wire) is used to make the anode contact, while Ta_2O_5 is used for the dielectric layer. Some suppliers do not distinguish both Ta-forms in their FMD material composition and only report the total content of Ta. For those that do indicate both Ta and Ta_2O_5 separately, varying composition ratios can be found as can be seen in Table 4.

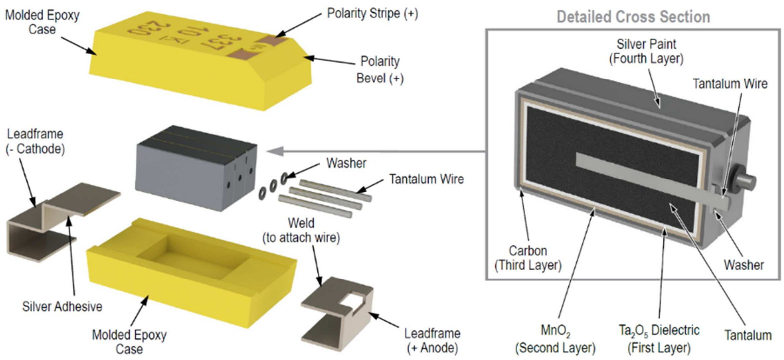

Figure 9: Schematic cross-section and build-up of Ta capacitor

Table 4: Comparison of different Ta capacitor components indicating different ratios of Ta and Ta_2O_5.

T495D106M035ZTE260		
Material	Amount [mg]	[%]
Nickel	12.60	2.8
Iron	18.84	4.2
Copper	0.45	0.1
Tin	1.59	0.4
Silver	8.58	1.9
Oxygen	84.56	18.9
Silicon	65.48	14.7
Carbon	43.06	9.6
Misc.	6.55	1.5
Tantalum	**145.27**	**32.5**
Ta_2O_5	**41.89**	**9.4**
Manganese dioxide	17.96	4.0
PTFE	0.02	0.0

TAJE476M035RNJV		
Material	Amount [mg]	[%]
Silver	7.31	1.4
CAS 68610-73-1	0.10	0.0
Tin	2.36	0.4
Nickel	0.93	0.2
CAS 25068-38-6	0.36	0.1
Copper	32.13	6.0
Iron	0.88	0.20
CAS 129915-35-1	55.94	10.5
Silica, vitreous	130.53	24.6
Ta_2O_5	**249.50**	**47.0**
Tantalum	**3.04**	**0.6**
Manganese dioxide	47.16	8.9
Graphite	1.10	0.2
PDMS	0.05	0.0
CAS 9002-84-0	0.02	0.0

Ta capacitors can be visually distinguished from other capacitors by their special appearance. They are often box-shaped compared to cylindrical for Al electrolytic capacitors. They have standardized dimensions which differ from ceramic capacitors, have L-bend shaped contactor pads and have different marker labels. An overview of various electrolytic capacitor types is given in Figure 10.

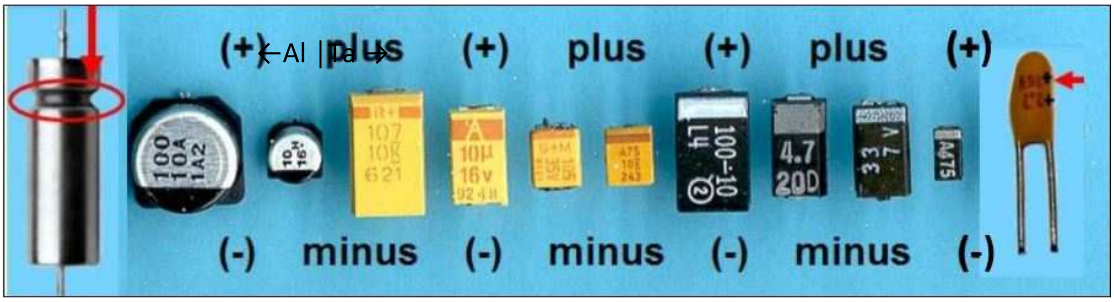

Figure 10: Images of various electrolytic capacitors (adapted from Wikipedia)

b) Resistor

Following main categories of resistor components exist: carbon composition resistor, wire-wound resistor and film resistor (www.resistorguide.com)

a. Carbon composition resistor

Carbon composition resistors were historically important but due to their low stability and accuracy they are – already since decades – mostly substituted by film resistors. Composition resistors are a mixture of C-containing (**graphite** or α-C) material, ceramic dust and a binder material (resin). They are still used today because of their low cost and due to their resistance to energy pulses.

b. Wire-wound resistor

This component consists of a resistive wire winded around an insulating ceramic or plastic core. The wire material is typically made from Cu or **Ag** alloys (including Ni, Sn or Mn). Alternatives are made from **Cr**-containing alloys (NiCr, NiCrFe, FeCrAl alloys) or pure **W** in the case of high temperature applications. These resistors are used for high precision and/or high power applications or for potentiometers. They can be used as circuit breaker, fuses or current/temperature sensors. Accurate potentiometers can be found in stereo devices, high precision resistors are used for measuring and calibration equipment.

c. Film resistor

For film resistors, a resistive layer is deposited on either a flat substrate (SMD chip-resistor) or on a cylindrical shape (axial resistor).The resistive material can be either carbon, metal or metal-oxide based. Metallic resistive layers may be composed of Ni-**Cr**, Sn-**Sb** and even **Au** and **Pt** alloys or **Ta**N. Metal oxide layers may consist of Sn-and **Sb**-oxide. The so-called thick and thin film resistor types are Surface Mount Devices. They not only differ in resistive layer thickness (<1um for thin films while >100um for thick films) but also in deposition method and in material composition. For thin film resistors, (reactive) sputtering or chemical vapour deposition is applied to deposit thin layers of Ni-**Cr** alloys**,** **Ta**N or different metal-oxides. Laser trimming or photo-lithographic processes are used for subsequent patterning. Considering the thickness dimensions and size, recovery of these thin film layers is negligible. Thick film resistors are formed by printing and firing of a paste material which is a mixture of a binder (glass frit), carrier (solvent) material and metal oxides. These metal oxides can be based on **Ir**, **Ru, Rh** or Re and may also include Pb, Bi, Ni. The presence of Pb in the glass or ceramic other than the dielectric ceramic for capacitors is excluded from RoHS by exemption 7c. The amount of **Ru**-oxide found in thick film resistors is only 1wt% and less with absolute values of less than tens of milligrams. The amount of resistors per board however can be high.

An overview of the schematic build-up of the different resistors is given in figure 11. These images give an indication of the possibility to visually distinguish such resistor components from other electrical components. While resistor chip packages have similar shapes and dimensions as ceramic capacitor chip packages, they can be separated from one another by their colour (black for resistors, brownish for capacitors) and their label markings.

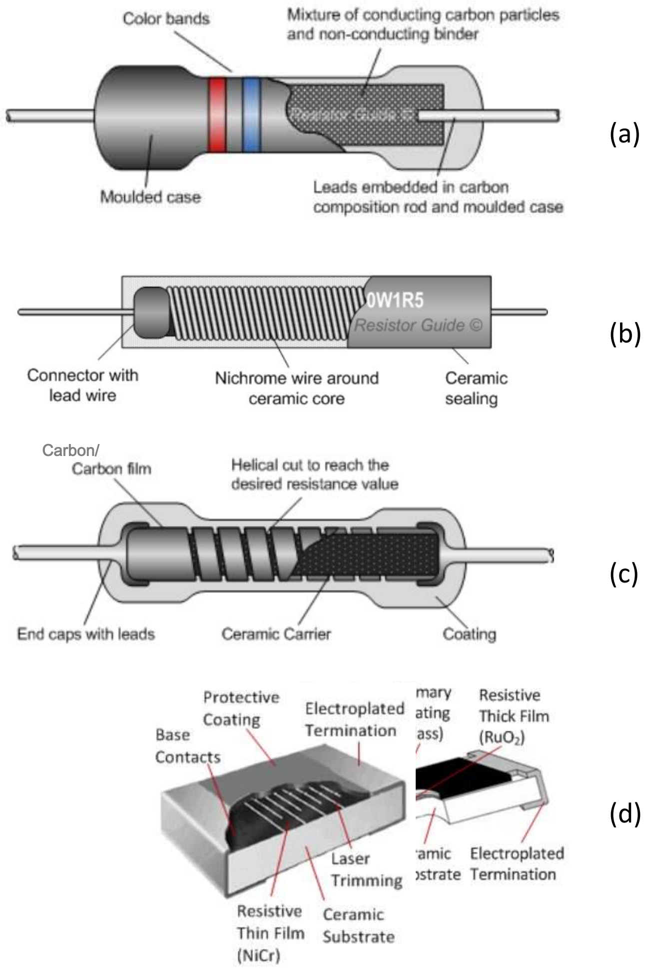

Figure 11: Overview of different resistor types with different material compositions and dimensions. (a) Carbon Composition Resistor, (b) Wire Wound Resistor and (c) Film resistor: carbon – metal – metal-oxide axial resistor (1) and thick (2) and thin (3) film chip resistor

c) Connectors (contacts and switches)

For most of the commodity products, terminals and connectors for electrical and electronic equipment are made out of brass or phosphor-bronze while for 'heavy duty' products **Be** alloyed Cu may be used. Large current electrical switches can also be made of **Cr** containing alloys. The **Be**-based alloys are also recommended for low current applications, for instance for low current battery or SIM card contacts in portable devices such as phones, laptops, camera's, ... and in general for all 'high performance' ICT and electronic applications. The amount of Be in Cu is ranging from very little up to 2wt%. This concentration will be often further diluted since other metallic parts contribute to the construction of a connector. Also, non-Cu parts like steel and Al can be part of a connector what can further complicate the recycling potential. As mentioned earlier, the extraction of **Be** out of the Cu fraction is currently not feasible and **Be** now ends-up in the slag of the Cu-recyclate (EPOW Report 2011). The possibility for the recovery of the Cu(Be) alloy as a whole needs further investigation regarding the recyclate thermodynamics.

Reed contacts are magnetically operating contacts and consist of **Ru** or **Rh**-coating layers on top of a ferro-magnetic core wire. These **PGM** elements are selected for their excellent material properties combining hardness, wear-resistance and electrical low-resistance performance. The use of Rh is mainly substituted by Ru because of its beneficial properties and excellent price. According to the commercial information of RRE (www.RRI.in, Reed Relays and Electronics India Limited), Reed switches and sensors are used in a variety of applications in electronics (switches and sensors in open door sensing devices (copiers, notebooks, ...), relays in fax-machines and modems, satellite dish position sensing devices and household appliances), as well as in other categories (automotive, marine, construction, ...). These reed devices should be easily detectable due to their glass encapsulation. The percentage of Ru or Rh obtained in such devices has not been found in literature. Investigations of layer thicknesses ranging from nm (sputtering) to 2μm (electroplating) layers have been reported (Shiskina et al., 2012). Regardless of the PGM concentration, these elements can be successfully and efficiently recovered in the Cu purification processes when the component remains attached to the PCB.

Similar to the Cu layers in PCB boards, a finish layer can be added to avoid degradation (oxidation, corrosion) of the connector core material. Finishes potentially include **Pd** due to its resistance to sparking, erosion and corrosion. Again, successful recycling is expected due to its chemical/physical connection to Cu.

d) Inductors

Inductors are metallic wire coil devices that may be wounded around a magnetic core material. Cu and **Ag** alloys are used for the metal coil and mainly Ni, Fe (Mo) magnetic materials are used. The presence of REE could not be confirmed in our database.

e) Fuses

No FMD datasheets found.

f) Transformers

From a material usage point of view, transformers are comparable to inductors being composed of (double) coils and potentially magnetic material. The presence of REE could not be confirmed in our database.

3.2.2.2 Active components

The **dominating semiconductor material is Si**. This material is recently added to the list of critical elements. Only a very small portion of purified Si is used for the electronics industry while most of it is used as alloying element for cast aluminium (Silicon Metal) Nevertheless, the Si material present in electronic (active) devices remains relatively pure: with very superficial alloying of doping elements to create p- or n-type FEOL (Front-End-of-Line)) semiconductor regions and with the addition of a BEOL (Back-End-of-Line) stack to create the FEOL interconnecting layers and additional (R,L,C)-functionalities, it only results in a few microns of thickness of 'contaminated' Si while the majority of the device is still constituted out of a bulky Si block of several hundreds of micrometres (Figure 11). Intentions or opportunities for recycling of Si out of electronic equipment have not been reported. Moreover, recycling routes starting from wafer production scrap or grinding dust from wafer thinning processes may be more beneficial and feasible. The original process wafer thickness of 700μm is often thinned down by mechanical/chemical grinding and polishing to below 400μm before fitting in a final device.

All **alternative semi-conductor compounds mostly consist of CRMs** and are usually compound formulations (except for **Ge**, the only other pure elemental semi-conductor, or SiGe) based on III-V elemental combinations such as **Ga**As, **In**P, or alloys thereof like **InGa**As,... but also ZnS, CdTe,... for II-VI compounds. These materials are being used for their superior performance for special and dedicated applications.

a) Si integrated circuits and packages

The **Si** chips need to be integrated into a 'package' in order to connect them to the operating board and allow (electrical) communication with other devices and the 'outside' world. A variety of package types exist and the choice for a specific package is depending on the functionality, die size, die density and operating conditions of the device. A direct attachment of the Si die onto the PCB (chip-on-board application) is usually not an option.

A package therefore usually consists of an intermediate or interposer board to bridge the gap between Si and PCB. The chip is mechanically connected to the interposer board either by gluing (by a so-called 'die-attach' material that is often containing a substantial amount of **Ag** particles to improve the thermal conductivity), or by flip-chip. In case of a flip-chip connection, both the mechanical and electrical connection is provided through this interconnection. The interconnect material for flip-chip is usually solder based (Sn or only seldom **In**-alloys) but can also be made of pure **Au** bumps. In case of a die-attach connection, wire-bonding is used to provide the electrical connection. The wire material can be Al or **Au** and recently also Cu wire bonding is considered as alternative due to lower resistance and lower cost. The interposer board material on which the Si IC (Integrated Circuit) is attached, can be either ceramic or organic. The ceramic material is usually a composite of alumina and silica but also compositions of **Be**O and **Mg**O are possible. The organic board material is similar to the epoxy-based composites as used for the PCB fabrication. The interconnections can be made by through-hole via's (vertical routing paths) or by a lead-frame material (peripheral 'pin' routing paths). The latter can also be used as interposer material for moulded plastic packages. The connection (combined mechanical and electrical) to the PCB is made by soldering (usually Sn-based alloys with a few wt% of Ag in the case of Pb-free solder). A solder connection can be made by solder balls, solder caps for connecting the leads or solder fillets to fix through-hole pin connections. Some cross-sectional examples of various IC packages are shown in Figure 12.

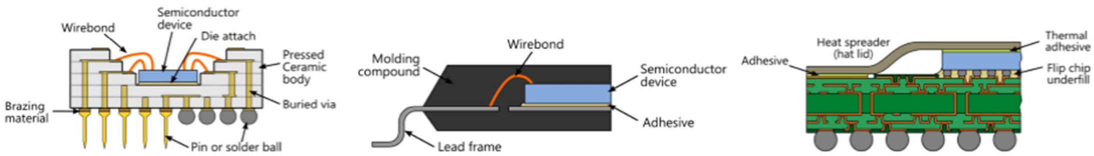

Figure 12: Schematic cross-section of various IC packages: (a) ceramic pin/ball grid array, (b) moulded plastic package, (c) flip-chip ball-grid-array (with heat sink)

A significant amount of metal can be present inside an IC package. Conductive routing layers are mainly composed of Cu or Cu-alloys and occasionally **W** or Mo for HTCC (high temperature co-fired ceramic) or **PGM** (Au, Au-Pt, Ag-Pd, Ag-Pt alloys) for LTCC (low temperature co-fired ceramic) packages. The lead frame material, heat sinks and pin connections can be made of Cu, Cu alloys, alloy 42 (42% Ni, Fe), Invar (36% Ni, Fe) or Kovar (54% Fe, 29% Ni, 17% **Co**) with possible noble finishes consisting of **Ag**, **Pd** or **Au**. The largest contribution to the Au fraction of a functional PBA (which is the board itself as well as the assembled components) is coming from advanced IC packages with a high count of Au wire bonds. These wire bonds have diameters of tens of microns and lengths up to several hundreds of microns and contribute in most applications more to the Au fraction than Au finishes which are usually only tens of nanometres in thickness.

The package further consist of organic composite materials used to encapsulate the package which may contain traces of $\mathbf{Sb}_2O_3$ flame retardant which are also found in PCB compositions.

The Si semiconductor chip itself is made of a bulky piece of pure Si with minimal amounts of other elements for doping, barrier layers, dielectrics, etc. Again, for these elements, recycling opportunities lie within the recovery of (metal) targets, process gasses and deposition scrap used and disposed during the production cycle. A cross-section of a Si flip-chip BGA package is shown in Figure 13, indicating size differences between on-chip layers and chip and package dimensions.

From the point of view of CRM recovery, packages are dominated by the precious metals. Large variations in **Au** content and concentrations can occur. This is clearly shown in table 5 that compares two FMD sheets for packaged chips: one of a commodity product frequently used with often multiple devices per board (clock oscillator die, offered at 1.63 €/die with a calculated Au content of 0.71 € based on a raw material cost of 31.5 €/g), containing high relative amounts of Au (13%) and an 'advanced' packaged imager chip, Al wire bonded, containing the double absolute Au value at the level of the ceramic substrate metallization but contributing to less than 1% of the package weight. As mentioned before, when remaining attached to the PCB, high recovery rates of the precious metals can be established.

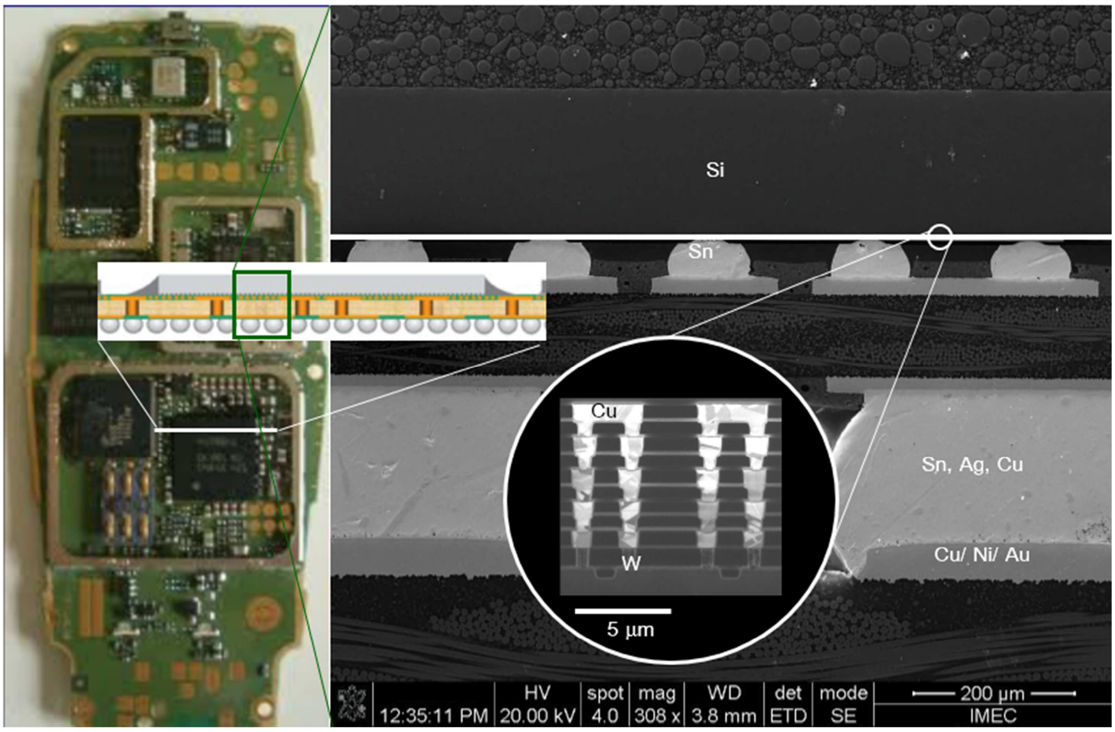

Figure 13: Cross-sectional SEM inspection of flip-chip BGA package showing dimensional differences between PCB, package and on-chip layers. Zoom-in of chip BEOL and FEOL layers is shown in circular insert.

Table 5: Comparison of different IC packages, showing high relative Au content for cheap commodity product (left) compared to advanced image sensor (right).

SM7745HEV25.0M		
Material	Amount [mg]	[%]
Nickel	13.30	7.9
Calcium oxide	0.50	0.3
Di-Cr trioxide	3.40	2.0
Magnesium oxide	0.50	0.3
Aluminium oxide	79.60	47.1
Titanium dioxide	0.90	0.5
Rubber, silicone	0.30	0.2
Quartz (SiO2)	1.30	0.8
Iron	23.30	13.8
Molybdenum	0.10	0.1
Silicon	0.10	0.1
Silver	**5.40**	**3.2**
Tungsten	4.70	2.8
Cobalt	**8.00**	**4.7**
Copper	0.20	0.1
Gold	**22.50**	**13.3**
Silicon dioxide	3.10	1.8
Silicone	1.80	1.1

NOIL1SC4000A-GDC		
Material	Amount [mg]	[%]
Ag	**6.40**	**0.04**
Epoxy	1.60	0.01
Bisphenol A, 25068-38-6	3.68	0.02
Filler - SiO2	0.32	0.00
Si	600	3.83
Al	7	0.04
Aluminum Oxide	11298	72.04
Silicon dioxide	1030	6.57
Magnesium Oxide	42.04	0.27
Titanium Oxide	1.35	0.01
Chromium Oxide	181	1.16
Tungsten	89.52	0.57
Molybdenum	4.06	0.03
Cu	13.56	0.09
Ni	373	2.38
Cobalt	**13.56**	**0.09**
Iron	472.02	3.01
Gold	**43.40**	**0.28**
SiO2	1100	7.02
Al2O2	19.65	0.13
B2O3	206	1.32
BaO	134	0.86
CaO	39.45	0.25

b) Transistors, diodes, ….

Some discrete active components can be used in a PCB design as well. Historically, **Ge** was used for the fabrication of transistors but this has been abandoned since the seventies due to the availability of cheaper purified Si. With minor exceptions for special audio-applications where Ge transistors are still preferred, these discrete components are nowadays Si-based devices.

c) Alternative semi-conductor materials

As mentioned earlier, alternative semiconductors are usually compound or alloy formulations based on **Ga**, **In** or **Ge**. These semiconductor materials are less attractive as substrate material for instance due to mechanical reasons (high brittleness) and are often processed by **additive technologies** on top of a 'parent' substrate (Si, SiC, quartz, ...) material. The CRM layer thicknesses are therefore usually small. On top of the limited material presence in such devices, it is mentioned by Hagelüken (Hageluken et al., 2013) that **In**, **Ge**, **Ga** (,Re, Mo) are refined as by-products from other ores (Zn, Al,...) and a source for recovery of these elements can be found by reprocessing of historical primary stocks with improved efficiency. Furthermore, similar to what is valid for Si-processing, recycling potential lies in the recovery during industrial processing (before EoL).

a. High power applications

Epitaxial grown **Ga**N, **In**Al**Ga**N, ... semiconductor layers can be used due to their superior performance to withstand high power conditions for the fabrication of power conversion devices for instance for solar applications, or other power supply devices. These layers are deposited on top of a Si substrate and contribute little to the total material mass.

b. High frequency applications

High frequency devices are used for satellite communication, mobile devices, radar and gps (positioning) systems. These high-end devices can make use of **SiGe** technology for better high frequency performance but these layers are similarly deposited by additive technology on top of a Si substrate, limiting the total amount of Ge in these devices.

c. Opto-electronic devices

Several semiconductor materials can be used for the fabrication of **image sensors**. These sensors convert the electro-magnetic (light) signal into an electrical signal. Depending on the wavelength spectrum of interest (Visible Spectrum for digital cameras versus Infra-Red (IR) detection for security or industry applications) different semiconductor materials are more suited as absorber material. The absorber material can be a thin layer of 'critical' semiconductor material which is deposited on a non-critical carrier substrate. The imager consumer market is dominated by Si CMOS and CCD (Charge Coupled Device) camera's. These are used for visible light and near IR applications (although for the latter window they suffer from a low detection limit and LED lights are needed to obtain sufficient (reflected) IR response). For more advanced IR-imaging, **In**P or **InGa**As substrates are needed in order to limit the crystal mismatch between the substrate and the absorber layer. However, after fabrication these substrates are thinned down before packaging. For high wavelength applications, bolometers (MEMS) are used. These can be found in most movement sensor applications. Although the sensor technology is based on Si and V-oxide, many devices are encapsulated with a **Ge** window cap (Hooylaerts, personal communication) which is transparent for the wavelength of interest.

Light Emitting Diodes (LED) are semiconductor devices in which the electrical current is converted into emitted light. This emission of photons occurs by recombination of electron-hole pairs at the p-n junction of an electroluminescent sensitive semiconductor. The colour (wavelength) of the emitted light is depending on the bandgap of the semiconductor material. While such devices were originally used for signalling or indicator lamps (for instance the red indicator lamps of digital clocks), the development of white light solutions has expanded its application range. They are nowadays also used for standard lighting applications as well as for integrated backlights of LCD screens. The semiconductors used for this purpose are the III-V semiconductors, mainly based on **Ga** combined with **In**, As, P, N. The solution to create white light is to either combine and mix different coloured LEDS or to use blue LEDS ((In)GaN) with a luminescent coating material to shift towards longer wavelengths. The stoichiometry of the semiconductor compound can change to create different bandgap materials and from that different wavelengths. The size of these chips is usually small, below $1mm^2$. The reported thicknesses of the dies vary strongly and range from 10 to 250μm according to Buchert (Buchert et al., 2012). In particular for In-alloyed LEDS, even these small thicknesses are questioned since In-based semiconductor layers are expected to be deposited by epitaxial growth (Balkenende, personal communication). This results in a material content of either 29 or 170μg of **In** and 33 or 530μg of **Ga** for a 2:3 In: Ga ratio of a single LED die. Furthermore, REE can be found in the luminescent material to convert the generated photon wavelength. The exact composition is proprietary information but it is mentioned by Buchert to contain **Y** (estimated 32μg/LED) or (**Gd** (15μg/LED), Y) Al garnet with **Ce** (2μg/LED) doping or traces of **Eu** (<1μg/LED) to change the spectral range.

Solar cells can be described as reverse LED's and generate electricity by absorption of light. Since solar cells are usually deployed in separate solar modules and less integrated in electrical/electronic devices, these devices are briefly discussed separately in paragraph 3.2.4.7.

d. MEMS applications

MEMS (Micro-Electro-Mechanical-System) devices can be used in different applications. Pressure sensors and accelerometers (for instance crash-detection in air bags) are most commonly used but it also includes RF switches, microphones, resonators, actuators, gyroscopes, optical mems, energy harvesters and micro-bolometers. These devices are usually built from Si**Ge** or Si.

e. Organic electronics

Not considered in this study

3.2.2.3 Mechanical accessories

The PBA can be furthermore equipped with specific structural devices that are needed to control the thermal, electrical and mechanical integrity of the products. With these devices are meant: heat sinks (thermally conductive plates, attached to heat generating devices), fans (for air circulation) and metal casings (for mechanical, magnetic and electrical protection). The metal parts may be composed of Al, Cu or Ni-Fe (Co) alloys, containing Be, Cr, Mg and possibly Nb alloying elements. Special care could be required in order to separate these parts from the PBA. Not only to reduce the risk for loosing valuable parts of the PBA into the base metal streams but also to minimize the amount of Al containing elements into the recommended Cu recyclate stream for PBA's which would hamper the recycling process (van Schaik et al., 2014).

3.2.3 Practical screening of electronic components

As part of the EU FP7 GreenElec project, a software tool is being developed at Imec in order to allow automatic reading and screening of product BOM files. Such a BOM (Bill of Materials) file consists of a list of all electronic components that the product contains, with their MPN (Manufacturing Part Number) code as unique identity code. For each of the components, the software searches the accompanying FMD (Full Material Declaration) sheet within the available database. One can than search for specific elements or compounds to check their presence in a product. The result of the screening is a list of component codes in which the compound of interest is found. For each of these components, a table with the material composition can be extracted when made available by the supplier. From this, the amount of a specific compound present on the full product board can be generated. If a design file is added to the BOM, one can also visualize the location of a specific compound. An example of such an analysis when searching for **Au** is shown in **Figure 14** what could be a guidance for selective disassembly.

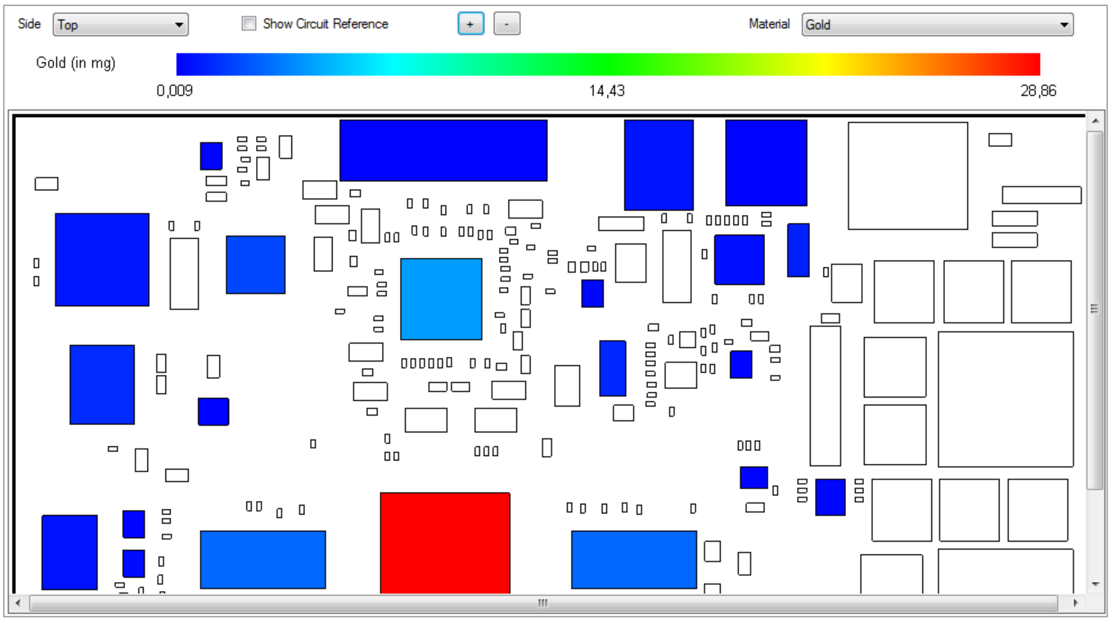

Figure 14: Au distribution for a given product board design. The lay-out is showing the location as well as the absolute amount of Au by means of the colored scale bar.

The usefulness of such a software tool is obviously depending on the available information. It starts with having the BOM of a specific product, for instance when offered for recycling. This is proprietary information and a close collaboration between OEMs and recyclers is therefore needed. Governmental regulations may be helpful to stimulate these interactions and information sharing. Furthermore it requires an extensive database in which the FMD sheets are available. So far, component manufacturers are not obliged to provide such a datasheet and even when available, the level of information accuracy is highly variable. Following the IPC 1752 standard(IPC 1752), the declaration can range from full material composition sharing (class D: Material Composition Declaration: homogeneous material level) to a basic classification specifying for instance 'EU RoHS' compliance or not (class A: Declaration Query/Reply).

A confirmation check (Table 6) of CRM presence is executed on our current available database with almost 2000 different components[1]. The software tool is used for screening the different CRM elements, apart from the precious metals. These metals have already high recycling rates at the PBA level and are not further investigated in this exercise. The reported values are only informative and do not claim to be valid for all (existing) components in that category. When the element is found in the database, the component with the highest amount of element mass is reported. The elements indicated in bold belong to the list of elements which are dominantly used by the electronics industry and do not have a current recycling route in place.

Table 6: Screening of FMD component database on CRM presence by the 'GreenElec' Recycling Calculator software tool.

Element	Compound formulation	Component	Amount [mg]	Amount [%]
Sb	Sb_2O_3	Connector (also heat shrink wire)	1800	< 20
Be	**Cu-Be alloy**	Connector		< 0.1%
Co		Clock oscillator		5.0
Ga	**GaP**	**LED**	**0.12**	**1.6**
Ge		Not FOUND		< 0.1%
In		Not FOUND		< 0.1%
Mg	Al-alloy	Heatsink	960	0.4
Nb	Oxide	MLCC Memory flash package	0.46 20	0.4 0.2
Ta	**Pure metal**	Ta electrolytic capacitor	**145**	**32**
	Oxide		**89**	**46**
W		RF module	12	7.6
Cr	Fe-alloy			<0.1%
REE_Yt	Oxide	MLCC	4.1	4.6
REE_Pr	Oxide	MLCC	0.82	16.3
REE_Nd	Oxide	MLCC	6.2	52.1
REE_Sm	Oxide	MLCC	0.9	12.2

[1] Some companies (for instance IHS or GreenSoft) offer a commercial component database with FMD datasheets. They do not necessarily contain a full material composition declaration at the homogeneous material level

3.2.4 Specific devices

In this paragraph, specific sub-devices that constitute a distinct functionality in many electronic equipment is discussed separately.

3.2.4.1 Hard disk

The core part of a hard disk drive (HDD) consists of the discs on which the actual data can be stored (the so called 'storage medium') and the recording head (both for reading and writing) mounted on a moveable arm. It furthermore requires a spindle to control the disc (or platter) rotation and an actuator to control the arm movement. The discs are built from Al or a glass/ ceramic composite material which require ultimate low surface roughness and thermal stability. On top of this carrier material, a magnetic layer is applied that allows the data storage. The data storage capacity has improved tremendously over the last decades. While the basic concept of the data storage has remained the same, improvements of materials and material deposition techniques have allowed for a data density increase of several orders of magnitude. The original spin-on Fe-oxide magnetic layers are replaced by sputtered coatings of (Co, Cr) or (Co, Pt, Cr, B) alloys. The magnetic material scaled down from several microns for the early used spin-on layers down to nanometer dimensions (<20 nm as reported in McFadyan et al., 2006). Since the beginning of the 21st century, layered hetero-structures are introduced to further improve the data storage which was facing its limits due to reached minimal grain sizes. In this concept, two ferromagnetic layers are separated by a thin Ru layer. Although the total layer thickness is small, one single disc area is relatively large with a common diameter of 3.74" (9.5cm) and one hard disk containing several discs. The precious metal content of Al and glass platters is investigated by Umicore and reported in (Buchert et al., 2012): significant amounts of Ag (850 mg/kg) are found in Al based platters while the largest amount of Pt (38 mg/kg) is found in glass-based discs. Both types contain about 7 mg/kg Ru. A potential drawback for the recovery of these layers can be the presence of the (Al, ceramic) carrier material. When hard disks are entered entirely into shredder systems prior to the metallurgical recycling, the small fraction of CRM may end-up in one of the base metal recyclate fractions and will most likely be lost.

Similar scaling as for the magnetic coating layers holds for the dimensions of the magnetic head for the writing and reading operations. While originally fabricated by manual mounting of inductive wiring around a magnetic core, the fabrication evolved to automated wafer-level processing ending-up in advanced multi-layer structures containing **Co**, **Cr**, **Ir**, **Ta**. For these layers, nanometer scale dimensions hold for both the thickness and the lateral dimensions what makes them unsuited for recycling.

Finally, the actuator that controls the movement of the arm is making use of an electromagnetic coil and permanent magnets. For decades, these magnets are **Nd**-based. Although the total magnet size per hard disk is relatively small, the amount of hard disks sold world-wide is several tens of millions a year (Constantinides). The amount and mass of magnets in notebooks is investigated by Buchert (Buchert et al., 2012). Up to 2000mg/notebook of **Nd**, 270 mg of **Pr** and 60 mg **Dy** is found which are distributed over the HDD and optical drive motor magnets and loudspeakers. Manual disassembly is recommended over shredding in order to recover the small amount of critical rare earth components. One has to take into account that recycling from these magnets may yield neodymium in its alloy-form as used for these applications and cannot be used for products that require the elemental form.

3.2.4.2 Storage devices

An alternative medium for data storage are devices known as SSD (Solid State Disc), memory cards or USB sticks. These devices contain a memory flash chip for storing digital information and a controller chip. They do not contain moveable parts as is the case for hard disks which makes them smaller and more resistant to mechanical shocks. They are therefore ideally suited for integration in smaller and portable devices (camera's, smartphones, ...) as well as for the fabrication of separate/isolated data storage devices (USB, memory card). The concept for data storage is based on a MOSFET device with an additional 'floating gate' (Solid Date Device). This floating gate is isolated by an oxide insulator what allows the storage of a certain charge of electrons. The presence or absence of this charge will define the 1 or 0 state of the digital data. The building of such devices is based on **Si**-CMOS (Complementary Metal Oxide Semiconductor) technology. Apart from precious metals used for packaging, little source of other CRM elements is expected inside the chip, as explained earlier. One memory and controller chip package example is found in our database and most relevant materials are shown in Table 7. Although relatively little Au is found in this particular device, especially for isolated memory cards and USB sticks which are not integrated inside a product, recycling could be relatively easy since disassembly is not needed.

Table 7: FMD of memory and controller chip (one example)

NOIL1SC4000A-GDC		
Material	Amount [mg]	[%]
Chromium	**600**	**7.36**
Copper	819.	10.05
Nickel	224	2.75
Manganese	41	0.50
Silicon	203	2.49
Aluminium	30	0.37
Iron	2881	35.33
Cobalt	**40**	**0.49**
Tungsten	**36**	**0.44**
Molybdenum	100	1.23
Niobium	**20**	**0.25**
Titanium	14	0.17
Silver	**6**	**0.07**
Tin	165	2.02
Gold	**5**	**0.07**
Magnesium	**0.03**	**0.00**
Palladium	**0.07**	**0.00**
Barium sulphate	24	0.30
Epoxy and acrylate Resin	30	0.36
Ruthenium oxide (RuO2)	**0.04**	**0.00**

3.2.4.3 Speaker / audio device

The most common type of loudspeakers are constructed in a similar way than the actuator of the hard disk, making use of an electromagnetic coil and permanent magnets in order to induce accurate movement of a foil to create sound waves. Also for the audio application market, **Nd**-based magnets can be used as alternative for the traditionally used ferromagnetic magnets for applications in which size and weight matters. Buchert et al. (2012) have measured the mass of permanent magnets to be 190mg for a mobile phone and 2.5g for a notebook. For the latter application, the composition of magnets has been analyzed and they contain 31% of REE with a **Nd**:**Pr** ratio of 5:1.

Apart from the known integrated loudspeaker devices, many portable devices are produced as well. They are either sold separately or can also be provided together with mobile devices. These products can range from high-quality earphones down to nearly disposable earbuds and could be easily separately collected.

3.2.4.4 Camera

The use of digital photography and video has increased significantly over the last few years, mainly due to the integration of such devices in smartphones and tablets. Furthermore, the continuous increase of pixel size and product performance has urged consumers to switch to newer versions and abandon the first generation devices. The dominant technology for these mainstream image sensor components is based on **Si**-technology. A study on the collection rate and recycling potential of small 'home' EEE appliances in Japan (Mishima et al., 2012) shows that next to mainly non-CRM elements, **Ta** and **Ag** in digital cameras have the recycling potential of a few tons. It is however not clearly mentioned whether this involves the yearly production, the expected disposal rate or any other product volume reference. Further research on actual material content is recommended.

3.2.4.5 Displays and screens

Nowadays, flat screens are integrated in many different devices. The largest screens can be found in TV appliances and monitors for computers. Buchert (Buchert et al., 2012) has analyzed such screens on their potential as source for CRM in detail. Three parts are extracted due to their relevance for CRM recovery: the display itself, the background lights and the assembled PCB. The latter part will no longer be discussed in this section since it is already extensively discussed in previous paragraphs. There are three different display technologies currently in use: LCD (Liquid Crystal Display), PDP (Plasma Display Panel) and OLED (Organic LED). For the fabrication of LCD screens, significant amounts of In are used: 74% of primary **In** is used for the fabrication of flat panel displays in the form of ITO (Indium Tin Oxide) (Götze et al., 2012). ITO has superior electrical and optical properties compared to other transparent conductive oxides. It can be easily patterned by etching and is shown to be stable in different environments what makes it the preferred option for high-resolution displays. ITO layers are applied on both sides of the liquid crystal matrix and are sandwiched between two glass plates. The reported ITO layer thicknesses and mass content per display varies significantly (Buchert et al., 2012; Götze et al. 2012) and is expected to be supplier dependent. Ranges from 5000 down to 50mg/m^2 are reported. The dominating mass fraction of the display is glass, secondly the plastics and liquid crystal material and finally the In content which is far below 0.1wt%. Apart from the low concentration, also the complicated sandwich structure hampers recycling. It is recommended to separately collect the LCD screens in order to avoid further dilution. Hagelüken (Hageluken et al. , 2013) mentions that recycling becomes more and more complicated throughout the whole production chain of displays, starting from the recycling of targets, the deposition scrapings from deposition tool chambers, broken or obsolete parts and finally full monitor screens. It is recommended to optimize recycling processes starting at the beginning of the production process.

For the background lighting of LCD displays, two different technologies are possible: either CCFL (Cold Cathode Fluorescent Lamps) or LEDs. The former technology is mainly used for older devices and televisions. The market share of LED background illumination in Germany (2010) is 30% for televisions and 90% for notebooks (Buchert et al., 2012). The LED technology is separately discussed before; the CCFL technology also contains various amounts of REE for the luminescent substances and support matrix. These CCFL tubes are smaller and less in amount for notebooks (1g) than for televisions (60g) with an estimated 2.1wt% of luminescent material. This material is mainly composed of **Y** but also traces of **Eu**, **La**, **Ce**, **Tb**, **Gd** can be found.

3.2.4.6 Lighting

LED's are previously described in section c (opto-electronic devices) in the paragraph on alternative semiconductor materials.

3.2.4.7 Solar cell

The use of photovoltaic energy for electricity generation has boomed over the last decade. With an expected module lifetime of 20 to 25 years, a similar exponential increase will be observed for the supply of obsolete PV modules, starting roughly 10 years from now. Different technologies are being developed and produced that make use of the photovoltaic principle to generate electricity from light. The dominant technology is based on bulk mono or multi-crystalline **Si** with roughly 80% of the market (Figure 15 - PV Technology Platform 2011). For this standard c-Si, the dominantly used CRM is **Ag**. With historic production processes, around 0.3 g/cell of Ag was consumed. Due to the high Ag prices and sustainability issues, strong efforts have been made to reduce this Ag consumption with present values of 0.14 g/cell and further reductions down to 0.04g/cell are predicted around 2020 (ITRPV Technology Roadmap (2014)). However, these newer modules with reduced amounts of Ag will only reach their EoL in roughly two decades from now. Considering 60 cells/module and an average module power of 200 – 250 Wp (for the dominant technology based on p-type mc-Si with 0.3g/cell), between 70 and 90 ton of Ag is present per GW power.

The second largest technology is based on thin film Si (TF-Si) requiring CTO (Conductive Transparent Oxide) as front contact layer what is usually **In** based (ITO). Similar to the display market, different company-depending stoichiometries and layer thicknesses are expected. The TF-Si market is recently caught-up by CdTe semiconductor technologies. Although little market share is currently based on CIGS (Cu **In Ga** Se) thin film modules or multi-junction concentrator cells (which are built by a stack of different semiconductor compounds based on **In**, **Ga** III-V compounds and **Ge**), due to the large global installed PV power of above 100GW, even 1% counts for a large amount of material consumption.Current recycling processes of PV-modules are focusing on the recovery of the frontsheet glass and the metal frames and cables.

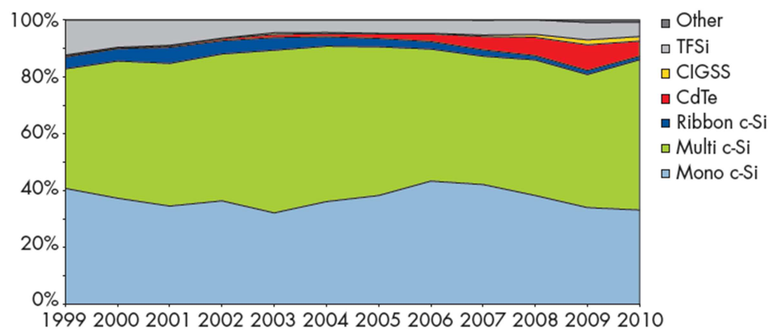

Figure 15: Market shares for different PV-technologies (from (PV Technology Platform (2011)))

3.3 Interim Conclusions WEEE

- Many of the CRM elements are found in (W)EEE. The complex build-up and small dimensions lead to diluted concentrations of these elements. However, due to the large sales count and often limited lifetime of these products, a large amount of waste is generated in which the total amount of CRM can be substantial. The purpose of this study is **to locate the presence and form of CRM elements in WEEE** in order **to support 'up-grading' activities** and **facilitate future recycling processes**.
- Extensive **recycling activities of WEEE are already taking place with major focus on the recovery of commodity elements** because of the weight-based recycling legislation and **precious metals**. Due to the high economic value of the recovered, precious metals, high metallurgical recycling efficiencies (> 98% for Ag, Au and Pd) are already established. These values **can only be achieved when appropriate pre-processing of waste is performed**.
- High losses are found when comparing the effective metal concentration in WEEE and the final recovered metal. Mainly due to inappropriate (automated) shredding operations, **most of the precious metals are lost in waste streams** (base metal or plastic fractions) from which they can no longer be recovered. An LCA-study of shredded ICT-waste shows that only **12% of Ag** and **26% of Au** and **Pd** end-up in the appropriate Cu-waste-stream from which they can be extracted. The amount of recovered Cu is 60%. **Selective disassembly of the PCB-parts is therefore recommended**.
- For small EEE like a mobile phone or a camera it is found that best recovery efficiencies can be obtained on untreated devices, without pre-processing. The ratio of precious materials to the total material content at which the optimal metallurgical recovery can be achieved is not clear. In other words, the level of required up-grading is not yet specified.
- The main source of CRM can be found in the electronic components attached to the PCB and constituting the PBA (Printed Board Assembly). Noble finishes can be present at PCB level but most of the precious metals are coming from the component metallization layers and internal (Au) wire bonds. When further up-grading (in addition to the PCB separation) is still required, the highest Au containing components can be located in the advanced IC packages.
- Of all elements, **Be**, **Sb**, **Ta** and the **REE**'s score low on all recycling indicators (recycling rate, recycled content and scrap ratio). To a lesser extent this also holds for **In**, **Ge** and **Ga** although these elements do have some recycling opportunities during the manufacturing cycle. Knowing that **Ga**, **Ru**, **Ta**, **Pd** and **Be** are dominantly used for the fabrication of electronic components and **In** is mainly used for the fabrication of displays, finding recycling opportunities for **Be**, **Ta**, **In** and **Ga** is most relevant.
- **In** is dominantly used (74% of the global usage) for the creation of Transparent Conductive Oxide (TCO) which is deposited on displays (TV, computer screens, tablets etc.). Although an absolute value of 0.05 to 5g per square cm display is found, the concentration is very much diluted (far below 0.1wt%) due to the presence of the 'heavy' glass substrate. The complex construction of the display further complicates the disassembly process and potential up-grading. It is recommended to first focus on the recovery of In during the manufacturing cycle (from process scrap and sputtering targets). One could also consider to separately collect the displays until recycling processing becomes available.
- **In** is further used for the fabrication of alternative semi-conductor materials, as is the case for **Ga** and **Ge** as well. While for most applications, these layers are deposited by additive technologies and actual thicknesses are small, some LED applications are expected to contain thicker In, Ga-based substrates. LED's are found in lighting applications, backlights for

displays and in some older equipment with the typical 'red' indicator lamps (for instance in alarm clocks). First results show μg ranges for In and Ga **per individual LED die**, but further research, including the disassembly and metallurgical processes, is needed. **Ge** devices are mainly expected for MEMS applications where they can be used as capping substrates in bolometers which are used in movement sensors. Also for these devices, further research on the average critical material concentration is still required.

- **WEEE REE** recycling options are currently non-existing and temporary storage is recommended until recycling processes are (commercially) available. REE are used as luminescent material in LED applications and as permanent magnet in components for hard disks and loud speakers (actuators). First material composition studies are executed to derive the respective content in notebooks. One particular test case could be to define the material composition in earplugs which is an easily collectable, mass (disposable) product. REE's are furthermore found in dielectric capacitor devices and some indicative material compositions are found in our FMD (Full Material Declaration) database. The amount of REO reaches up to 50wt%. Disassembly and identification procedures for such capacitors need further exploration.
- **Ta** is used for the fabrication of electrolytic capacitors. They provide the best ratio of capacitance value to component size and are used when small size, high stability and good frequency response are needed. The concentration and composition of an individual Ta capacitor can be found in the FMD (Full Material Declaration) sheet and varies between 24 and 42wt% with mixed concentrations of Ta and Ta_2O_5. Knowledge of the Ta content at board level for different applications is still lacking. Due to their characteristic colour and shape, they are relatively easy detectable at board level.
- **Be** is added in small quantities (less than 2 wt%) to alloy Cu in order to increase the electrical conductivity and improve the mechanical properties. The alloy can be used for the fabrication of connectors and heat sinks where it can be further diluted since other (non-Cu metals) may be used simultaneously. It is said to be used for the low current contacts for batteries and SIM cards. Be is furthermore used in BeO-compound substrates for power (high temperature) generating applications.
- Apart from the precious metals, little information is yet available at product level or waste category level for the other CRM categories. In this work, the presence of CRM in electronic components and specific sub-parts is screened. At the level of **individual components**, information on the concentration and composition can be found in FMD sheets (when available). The feasibility for component identification at board level is indicated. Following table highlights the CRM elements found in the different categories.

Component	CRM
Passives	
Capacitors	**MLCC** Ta, Co, Mg, Nb, W alloy additions to Ti dioxide and/or Ba titanate REE oxides (Nd, Pr, Sm) Pd, Ag **Ta capacitor** Ta (Ta_2O_5)
Resistors	**Thin film** (negligible content) *Ta*(N) **Thick film** Ru, Ir, Rh (oxides) (<1wt%) **Wire Wound** Cr, W
Connectors	Ru, Rh, Pd, Be
Actives	
IC packages	Mainly Au, some Cr
Alternative Si	Ge for MEMS, (movement) sensors and opto-electronic devices Ga,In for LEDs
Specific devices	
HDD	Ag, Pt, Ru (Co, Cr) in platters REE (Nd, Pr, Dy) in magnets
Speaker/audio device	REE (Nd, Pr)
Storage device	One FMD of memory chip shows 700ppm of Au at chip package level. Considering the ease of collection for separate devices (USB sticks, memory cards), the potential for Au recovery is high.
Camera	Ta, Ag
Displays	In in ITO REE for luminescent material
LED	REE for luminescent material In, Ga substrates

4. Batteries

4.1 Collection and recycling targets and rates

Collection targets for waste portable batteries and accumulators are contained in Directive 2006/66/EC, known as the ELV Directive. Article 10, paragraphs 1 and 2, of the Directive states that:

1. Member States shall calculate the collection rate for the first time in respect of the fifth full calendar year following the entry into force of this Directive.

Without prejudice to Directive 2002/96/EC, annual collection and sales figures shall include batteries and accumulators incorporated into appliances.

2. Member States shall achieve the following minimum collection rates:

(a) 25 % by 26 September 2012;

(b) 45 % by 26 September 2016.

Annex III of the Directive establishes minimum efficiencies of recycling processes:

Recycling processes shall achieve the following minimum recycling efficiencies:

(a) recycling of 65 % by average weight of lead-acid batteries and accumulators, including recycling of the lead content to the highest degree that is technically feasible while avoiding excessive costs;

(b) recycling of 75 % by average weight of nickel-cadmium batteries and accumulators, including recycling of the cadmium content to the highest degree that is technically feasible while avoiding excessive costs; and

(c) recycling of 50 % by average weight of other waste batteries and accumulators.

Article 12 (3) states that '*Where batteries or accumulators are collected together with waste electrical and electronic equipment on the basis of Directive 2002/96/EC, batteries or accumulators shall be removed from the collected waste electrical and electronic equipment*'.

4.2 Battery types and contents

Table 8 gives an overview of the different types of batteries put on the Belgian market in 2011, excluding car batteries. Approximately 53% of the portable batteries put on the market is separately collected by Bebat[2]. The total weight of the batteries that are separately collected by Bebat has been fairly constant since 2003. However, it is observed that the share of separately collected waste batteries with a positive recycling value is declining in comparison with their market share, while the share of non-rechargeable, primary batteries is still increasing (Bebat 2013).

Table 8: Batteries put on market in Belgium in 2011 (OVAM 2012)

Put on market 2011	Portable (in kg)	Industrial (in kg)
Zinc carbon	455.146	-
Alkaline	2.254.404	233
Silver oxide	5.056	3
Zinc air	5.125	118.171
Lithium	83.419	934
TOTAL primary	2.803.150	119.341
Nickel cadmium	401.219	26.548
Nickel hydride	295.880	17.451
Lithium rechargeable	803.592	77.588
Lead	97.588	10.998.277
Total rechargeable	1.598.279	11.119.864
Total	4.401.429	11.239.205

35% of the portable batteries are sold within an appliance. For the increasing amount of portable rechargeable batteries, this percentage is 68%. These integrated batteries will be collected as part of the WEEE, with an unknown share ending up in WEEE treatment processes.

4.2.1 Lead acid batteries (PbA)

Waste lead acid batteries have a positive economic value, and are heavily recycled, even allowing for close loop recycling. A typical new PbA battery contains between 60% and 80% recycled lead and plastic (Battery Council International, 2010). Plastic casings may contain antimony as a trioxide for flame-retardants. Lead acid batteries also contain **antimony** (or calcium) alloyed with the lead to suppress electrolysis of water during recharging. An industrial PbA battery contains 0 to 4% of antimony by weight, with an average of 1% (www.dekabatteries.com/assets/base/a.pdf) . Antimony will be present as an impurity in scrap lead to be processed for recycling. After reduction in a pyrometallurgical process (Farooq et al., 2012) , antimony ends up in a lead-antimony slag. The dual vessel BRM process uses the ISASMELT™ technology, where the lead-antimony slag is fed into a rotary furnace in order to produce a lead/antimony alloy plus a final low lead slag (www.isasmelt.com). The recycling of lead acid batteries is the main source of secondary antimony. In 2011 lead acid batteries constituted 25,9% of the global consumption of antimony by end-use.(Gunn, 2014)

4.2.2 Nickel cadmium batteries (NiCd)

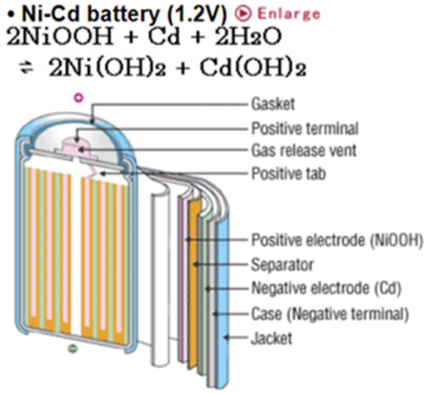

Figure 16: NiCd battery structure and reaction formula

The components of the battery are a cathode comprised of nickel hydroxy-oxide (Ni-OOH) on a nickel foam, graphite or iron substrate, an anode made of metallic cadmium pressed onto a nickel wire mesh, and potassium hydroxide (KOH) electrolyte (Sullivan et al, 2012). Graphite is an essential material in different battery types, as a chemically inert and highly oxidation-stable conductivity additive. 'In alkaline batteries graphite is used as a conductive additive in the cathode, together with electrolytic manganese dioxide (EMD). In lithium-ion rechargeable batteries, graphite is used as active material in the negative electrode of lithium and as a conductive additive in the positive electrode (http://criticalrawmaterials.org/critical-raw-materials/natural-graphite/).

'*Most of the graphite is synthetic and natural flake, mined, graphite accounts for only 5% of global demand for batteries. […] Synthetic graphite is very expensive to produce, deriving from petroleum coke and costing up to 10 times as much as the best natural graphite. But the game could turn in the next few years in favor of natural graphite because battery manufacturers are interested in increasing the proportion of natural graphite used in batteries to lower their production costs*'.[3] The application of graphite in batteries constitutes approximately 10% of the global use of graphite (natural and synthetic) (Northern Graphite Corporation and Mackie Research Capital, 2011). Although the recycling processes of graphite containing batteries yield a metal oxide containing graphite powder, the final destination of this graphite is not entirely clear. Possible applications include the use as a reductans in cobalt pigment production and in steelmaking. This occurs e.g. in some Li-ion battery recycling systems (see 2.2.7).

'*NiCd batteries are treated usually in a separate process as a function of two important reasons: the presence of cadmium that promotes some difficulties in the recovering of mercury and zinc by distillation, and the metallurgical difficulties associated with the separation of nickel and iron.*' (Bernardes et al, 2004)

4.2.3 Nickel-metal hydride batteries (NiMH)

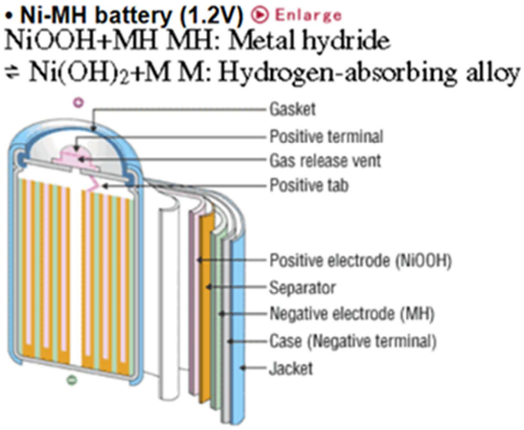

Figure 17: NiMH battery structure and reaction formula

The components of the batteries are: a cathode comprised of nickel hydroxyl oxide on a nickel foam substrate, an anode of mischmetal (Me) hydrides on a nickel or a nickel plated steel mesh, KOH electrolyte, and a separator of a porous polypropylene membrane. Mischmetals are metals from the lanthanide series, or **rare earths**, including metals from lanthanum (atomic number = 57) to luterium (71), which in the context of batteries are referred to the AB5 type. Even though it is not a lanthanide, **ytterium** (39) is also included in this group. Another group of metals used for NiMH anodes is the AB2 type, which includes **titanium** (Ti), **zirconium** (Zr), Ni, and **vanadium** (V). Spent NiMH batteries contain 36–42% nickel, 3–4% **cobalt** and 8–10% mischmetal consisting of **lanthanum**, **cerium**, **praseodymium** and **neodymium**. (OVAM 2012)

Today the discarded batteries are used in the steel industry as a cheap nickel-source (Bebat Jaarverslag 2013). **Cobalt** is not paid for and **rare earths (RE)** are slagged and lost for reuse. Technical recycling options are available, in which the dismantled and processed NiMH are melted in a DC electric arc furnace producing a nickel–cobalt alloy and a slag phase highly enriched with RE-oxides. A slag system with CaO–CaF2 showed a good melting behavior ensuring the best separation of NiCo alloy from the rare earth oxides. The slag consisted of 50–60 wt.% RE (Müller et al., 2006)

4.2.4 Zinc carbon and alkaline batteries

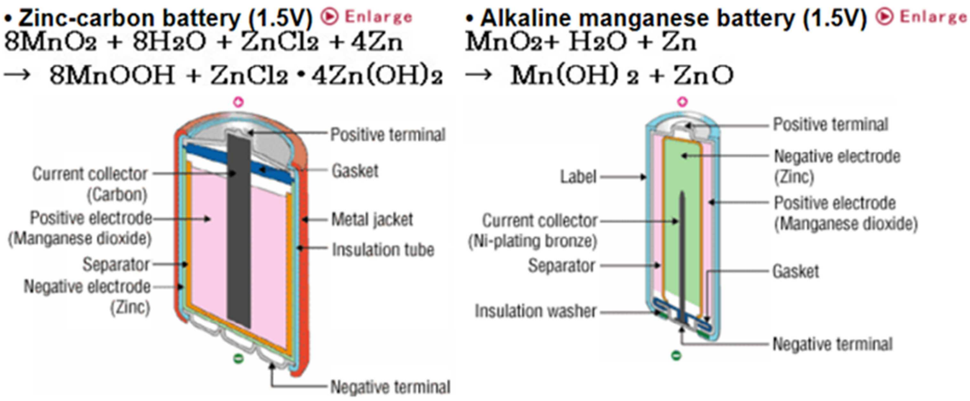

Figure 18: Zinc carbon and alkaline battery structure and reaction formula

*'Zinc carbon and alkaline waste batteries contain considerable amounts of **zinc**, **manganese** and **iron**. Metal recycling is the main objective of the available treatment options. Recycling is either done by hydrometallurgical processes or by pyrometallurgical processes. When applying a hydrometallurgical treatment scenario, the focus lies on zinc and iron recycling. When allowing manganese recycling, the energy demand of the hydrometallurgical process increases considerably. Both pyrometallurgical options recycle zinc, iron and manganese.' (*Briffaerts et al., 2009) The components of a mixed batch of alkaline (85%) and zinc carbon (15%) batteries are given in Table 9. This mix roughly corresponds to the relation between both battery types in the Belgian market mix.

Iron is recycled as ferromanganese in pyrometallurgical processes, or as iron scrap in a mechanical treatment. Zinc is recycled as metallic zinc, zinc sulphate, non-ferrous scrap or Waelz oxide. Manganese is recycled as ferromanganese in the pyrometallurgical scenarios, or as manganese dioxide. Part of the carbon content is used in the ferromanganese, or as fuel or reducing agent. Slags are often used as a construction material on landfills. The plastic fraction is valorised as a refuse derived fuel in cement kilns. (Briffaerts et al., 2009)

Table 9: Materials in a batch of zinc carbon (15%) and alkaline (85%) waste batteries (2006)

Comp.	Kg/ton	Comp.	Kg/ton
Zn	197	C	52
Mn	229	KOH	43
Fe	187	NH_4	3
Hg	0,13	Cl	5
Pb	1,9	H_2O	90
Cu	6,2	O_2	130
Cd	0,4	Paper	27
Ni	3,3	Plastic	25
		Total	**1000**

The recovery rates of different materials contained in non-rechargeable zinc carbon and alkaline batteries for different processing scenarios are given in Figure 19.

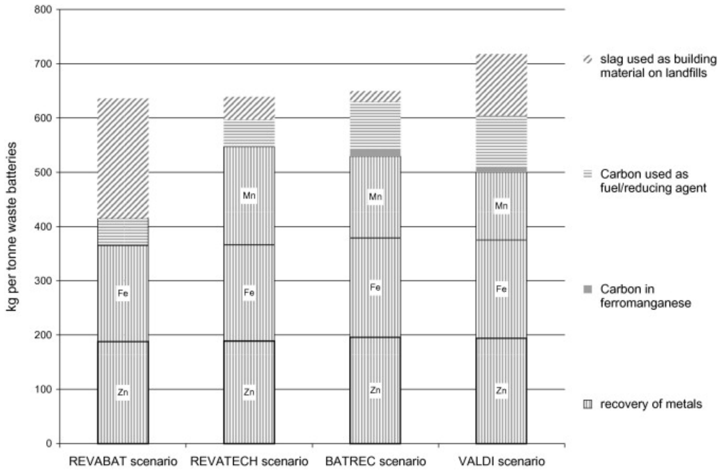

Figure 19: Recovery rates of materials zinc carbon and alkaline batteries for different processing scenarios (2006)

4.2.5 Silver oxide batteries

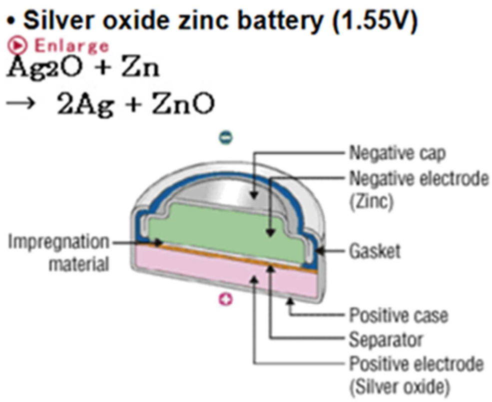

Figure 20: Silver oxide battery structure and reaction formula

Silver oxide batteries are also known as button cells. Button cells are used in watches, toys, calculators, hearing aids, digital thermometers, insulin pumps, portable medical monitors, etcetera. This size is of cells is approximately 35% **silver** by weight (https://www.silverinstitute.org/site-in-industry/batteries/). The complete material content is reflected in Table 10. In these batteries electrodes are separated by a semipermeable ion exchange membrane. The negative plate (cathode) is made of sintered fine silver oxide (Ag2O) powder, while the positive plate (anode) is composed of activated zinc.

Table 10: Composition of waste silver oxide button cell

(Sathaiyan N., Nandakumar V., Ramachandran P., 2006)

Components	Weight (%)
Zinc	10.4
Silver	30.3
Steel case	42.4
Mercury	0.8
NaOH	7.1
Paper/plastic	6.0
Water	2.6
Remainder	0.4

The silver can be recovered by various pyro and hydrometallurgical techniques (Aktas, 2010), and recently also a bio-hydrometallurgical method for silver extraction was proposed. (Umesh et al., 2013) A hydrometallurgical process to recover mercury from spent silver oxide button cells, apart from zinc oxide and silver, is available since some time (Aktas et al., 2011).

Table 11: Content of cell powder obtained from crushing, drying, grinding, sieving and homogenizing spent batteries (Aktas et al., 2011)

Elements	Ag	Zn	Hg	C	S	Fe	Pb	Cd	Ni
%	62.09	13.55	0.54	2.48	0.0088	0.0040	<0.0100	N/A*	N/A*

4.2.6 Zinc air batteries

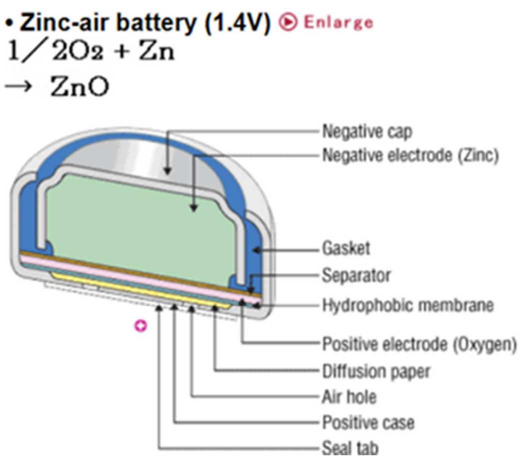

Figure 21: Zinc air battery structure and reaction formula

'Primary Zn–air batteries are well known for use in hearing aid devices (button-type cells), as hinted at in the introduction. Nevertheless, large primary Zn–air batteries have been also used to provide low rate and long-life power for applications such as seismic telemetry, railroad signaling and

navigational buoys as well as remote communications.' (Caramia et al., 2014) Research on electrically rechargeable zinc air batteries is ongoing, and the potential use e.g. for smart grid energy storage and in electric vehicles batteries are investigated. Zinc air batteries do not contain critical materials. **Zinc** as a metal is safer than lithium and can be fully recycled.

2.2.7 Lithium batteries

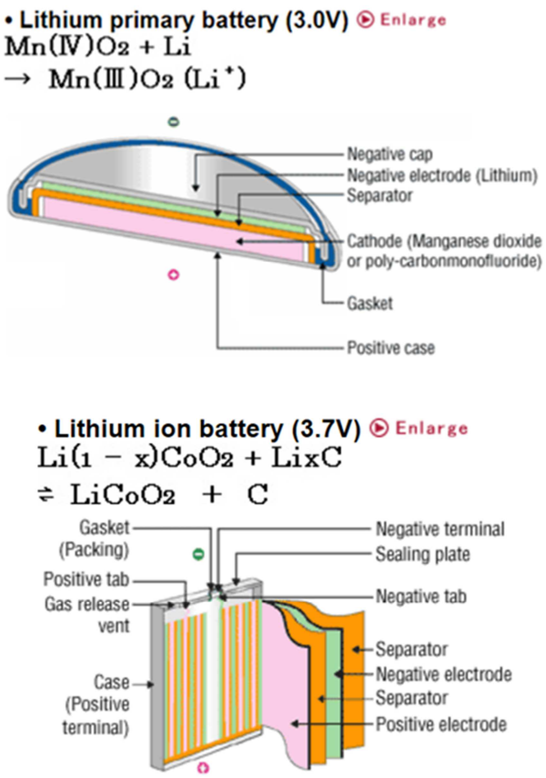

Figure 22: Lithium battery structure and reaction formula

In general, primary batteries are used in applications such as wristwatches, remote controls, electric keys and children's toys. Other applications of primary batteries are tire pressure gauges in cars and trucks, transmitters for bird tracking, pacemakers for heart patients, intelligent drill bits for mining, as well as light beacons and remote repeater stations. From the lithium batteries put on the Belgian market in 2011, almost 10% corresponds to primary lithium batteries.
The composition of Li-ion batteries is difficult to assess since many different types of Li-ion batteries have been put on the market (see Table 13 Gaines et al., 2010), and new types are continuously development and put on market. Overall, however, Li-Ion batteries include relatively large amounts of metals, contained in both casings, electrodes and electronic components. Typically at least one third of the production cost of a battery resides in materials (Georgi-Maschlera et al., 2012). Japan is currently the largest producer of Li-ion batteries and battery components. (www.mitsubishicorp.com/jp/en/mclibrary/business/vol1/page2.html)

Table 12: Average material content of portable Li-ion batteries

(Georgi-Maschlera et al., 2012).

Average material content of portable Li-ion batteries.

Battery component	Product data sheets in mass-%	Self-determined
Casing	~20–25	~25
Cathode material ($LiCoO_2$)	~25–30	~25
Anode material (graphite)	~14–19	~17
Electrolyte	~10–15	~10
Copper electrode foil	~5–9	~8
Aluminium electrode foil	~5–7	~5
Separator	–	~4
Others	Balance	Balance

Table 13: Different types of lithium ion batteries and their performance (Daimler analysis, 2010)

Name	LCO	LNO	NCA	NMC	LMO	LFP	LTO
Full name	Lithium Cobalt Oxide	Lithium Nickel Oxide	Lithium Nickel Cobalt Aluminium Oxide	Lihium Nickel, Manganese Cobalt Oxide	Lithium Manganes e Spinel	Lithium Iron Phosphat e	Lithium Titanate
Cathode	LiCoO2	LiNiO2	Li(Ni0,85Co0,1 Al0,05)O2	Li(Ni0,33Mn0,33Co0,33)O2	LiMn2O4	LiFePO4	e.g.: LMO, NCA, …
Anode	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Li4Ti5O12
Cell voltage	3,7 - 3,9V	3,6V	3,65V	3,8 - 4,0V	4,0V	3,3V	2,3 – 2,5V
Energy density	150Wh/kg	150Wh/kg	130Wh/kg	170Wh/kg	120Wh/kg	130Wh/kg	85Wh/kg
Power	+	o	+	o	+	+	++
Safety	-	o	o	o	+	++	++
Lifetime	-	o	+	o	o	+	+++
Cost	--	+	o	o	+	+	o

Li-ion batteries are mostly recycled in dedicated processes, but batteries can also be added into large-scale metallurgical processes (e.g. extractive cobalt or nickel metallurgy). Dedicated recycling processes consist of combinations of mechanical, pyrometallurgical and hydrometallurgical process steps. (Georgi-Maschlera et al., 2012) Overall recycling process requirements and the type of materials that are recovered in the useful output fraction will strongly differ between different process types. The main differences are summarized in Figure 23.

	Pyrometallurgical	Hydrometallurgical	Physical
Temperature	High	Low	Low
Materials recovered	Co, Ni ,Cu in alloy	Metal salts, Li_2CO_3 or LiOH	Cathode, anode, electrolyte, metals
Feed requirements	None	Separation desirable	Single chemistry required
Comments	New chemistries yield reduced product value	New chemistries yield reduced product value	Recovers potentially high-value materials; Could implement on home scrap

Figure 23: Main differences between different types of recycling processes[4]

It has been reported that in 2008 technologies of bio-hydrometallurgical processes (bio-leaching) had not gotten mature in their applications for recycling Li-ion batteries (Jinqiu et al., 2008).

Current recycling processes generate revenues principally from cobalt recovery. As Co use declines, other and more incentives will be required to make the business of recycling Li-ion batteries profitable. (Gaines et al., 2010) In the case of large (automotive) li-ion batteries, high-value cathode material could be recovered from clean (or in the future even mixed) Li-ion cathode streams. Indeed, the value of constituents is low for LMO and LFP cathodes, but the cathode itself has a high value (see Figure 24). (Gaines et al., 2013)

Cathode	Price of Constituents ($/lb)	Price of Cathode ($/lb)
$LiCoO_2$	8.30	12–16
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	4.90	10–13
$LiMnO_2$	1.70	4.50
$LiFePO_4$	0.70	9

Figure 24: Cathode constituents versus cathode values for automotive Li-ion batteries

In pyrometallurgical processes, lithium, aluminium, manganese and titanium end up in the slag. Hydrometallurgical processes that allow for the recovery of metals (Lupi et al., 2007), or of both metals and lithium (Li et al., 2013) have been proposed and tested. Also a so-called intermediate physical recycling process was developed to recover lithium carbonate and all metals (Gaines et al, 2013)

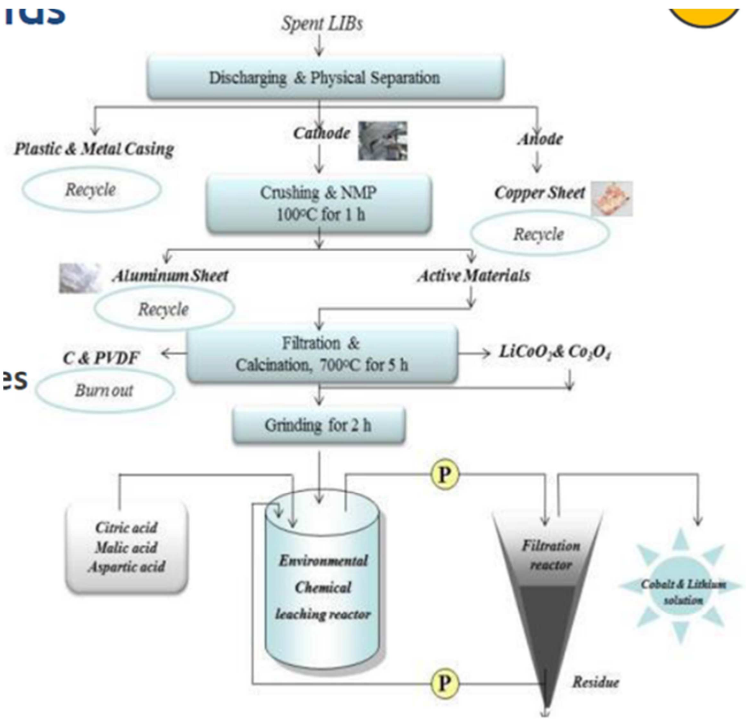

Figure 25: A hydrometallurgical process for metals and lithium from automotive Li-ion batteries Error! Bookmark not defined.

The recycling rates for the many metals that are used in Li-ion batteries will thus depend both on the ever changing battery composition and on the specific combination of recycling process steps.

Some of the currently industrially applied recycling processes of portable secondary Li-ion batteries yield complex alloys of different metals, of which the further processing efficiencies end-uses are difficult to assess. From a recent study (VITO, 2014), minimum and maximum functional recycling rates of existing recycling systems of portable Li-ion batteries were derived for **iron**, **copper**, **cobalt**, **aluminium** and **nickel** (see Table 14). Not functionally recycled metals usually end up in slags, some of which can be applied as building products.

Table 14: Minimum and maximum functional recycling rates of metals from dedicated Li-ion recycling systems

Metal	min.*	max.*
Cu	90%	100%
Ni	0%	100%
Fe	60%	80%
Co	90%	100%
Al	0%	60%

* rounded to one significant digit for confidentiality reasons

‘Lithium-polymer batteries can be dated back to the 1970’s. Their first design included a dry solid polymer electrolyte that resembled a plastic film. Therefore, this type of battery can result in credit card thin designs while still holding relatively good battery life. In addition, lithium-polymer batteries are very lightweight and have improved safety. However, these batteries will cost more to manufacture and have a worse energy density than lithium-ion

batteries.'(http://www.androidauthority.com/lithium-ion-vs-lithium-polymer-whats-the-difference-27608/) '*The lithium-polymer electrochemistry currently covers a wide range of active materials such as LiCoO2, LiNiO2, and its Co doped derivatives. Rather than the traditional metal can used by other small rechargeable cells, Lithium Polymer Batteries employ a thin (110 µm), polymer-based packaging material to contain the electrochemical materials. This allows the system to have a flat thin (2 to 5 mm) form factor*.(http://hardingenergy.com/wp-content/uploads/2012/06/6-Lithium-Polymer.pdf)

Recupyl has a patented process for the recycling of Lithium batteries which includes the evolution of the Lithium battery technology, including Lithium Polymer batteries.(http://www.recupyl.com/121-20-31-lithium-polymer-battery.html)

5. ELV

5.1 Recycling targets and rates

Recycling targets for ELV vehicles are contained in Directive 2000/53/EC, known as the ELV Directive. Article 7, paragraph 2, of the Directive states that:

2. Member States shall take the necessary measures to ensure that the following targets are attained by economic operators:

(a) no later than 1 January 2006, for all end-of life vehicles, the reuse and recovery shall be increased to a minimum of 85 % by an average weight per vehicle and year. Within the same time limit the reuse and recycling shall be increased to a minimum of 80 % by an average weight per vehicle and year;

for vehicles produced before 1 January 1980, Member States may lay down lower targets, but not lower than 75 % for reuse and recovery and not lower than 70 % for reuse and recycling. Member States making use of this subparagraph shall inform the Commission and the other Member States of the reasons therefor;

(b) no later than 1 January 2015, for all end-of life vehicles, the reuse and recovery shall be increased to a minimum of 95 % by an average weight per vehicle and year. Within the same time limit, the re-use and recycling shall be increased to a minimum of 85 % by an average weight per vehicle and year.

However, as stated in the report Metal Recycling – Opportunities, Limits, Infrastructure (UNEP, 2013), '*recycling rates as currently defined in EU waste legislation, such as the ELV and WEEE directives, do not refer to the actual recycling of individual metals in the recycling chain. Current system boundaries are the output of pre-processing steps and their resulting fractions, which again are a mix of different substances. The final smelting and refining step is not considered in the recycling rates. […] If smelting and refining are included, real recycling rates will be much lower, especially for precious and special metals*'.

5.2 Electro-mobility

Most predictions on the growth of the share of electric (EV) and hybrid electric cars (HEV) have been proven far too optimistic in most countries. In Belgium, 99,6% of the vehicles registered in 2013 had conventional combustion engines (ICE). The Netherlands, where a wider range of policy measures is in place, ambitions a EV/HEV share far below 5% for 2020 (http://www.rvo.nl/onderwerpen/duurzaam-ondernemen/energie-en-milieu-innovaties/elektrisch-rijden/stand-van-zaken/cijfers). Even in the case that a 5% share of EV and HEV vehicles were obtained in 2020, the number of EV and HEV would only start to be significant from 2025 or so, while at the same time over 95% of the ELV still would be equipped with a combustion engine. It will thus take at least another 10 years before a major offer of EV ELVs will have a noticeable impact on the material composition of the total ELV supply.

Furthermore, it is far from sure whether (H)EV ELV or parts with valuable or critical material content would become available on the currently existing recycling markets. Yet, leasing has proven to be an appealing formula to tackle the relatively high cost of electric car ownership (http://www.which.co.uk/cars/choosing-a-car/buying-a-car/buying-vs-leasing/leasing-a-battery-for-an-electric-car/), and offers producers both an opportunity and a responsibility to implement resource efficient logistics and innovation for upgrading, remanufacturing and recycling the cars and/or the batteries. In such context, EV production and recycling might develop as a single integrated business, in which advantages of scale lead to geographically centralized and resource efficient plants both for production and end-of-life processing. (http://www.luxresearchinc.com/news-and-events/press-releases/read/tesla-motors%E2%80%99-gigafactory-will-see-more-50-overcapacity-its-li)

Considering the above, we don't think that EV and HEV recycling offers opportunities for realizing quick wins (before 2025), and therefore we will consider trends regarding to ICE ELVs only. The OPTUM project investigated the potential of electromobility in terms of social acceptance and ecological contribution, by making an analysis of the resource aspects of the electro-mobility system, excluding batteries, taking account of recycling options and outlook; by identifying important new technological developments that impact on resource requirements, and; by making an early identification of possible bottlenecks or critical points in terms of resource policy, and development of corresponding strategies. (http://www.oeko.de/oekodoc/1354/2011-457-en.pdf)

5.3 State-of-the-art ICE ELV recycling

Galloo reported having treated in 2012 48.725 ELVs, on a total supply of 160.615 Belgian ELVs (30 %). The average ELV has a weight of 950 kg, consisting of 70 % steel, 5 % non-ferro metals and 25 % non-metals (polymers, glass, rubber and textiles).

(http://www.kenniscentrumvlaamsesteden.be/overhetkenniscentrum/Nieuwsbrief/Documents/2013/Urban%20Mining/MobieleMetalen%20-%20Rik%20De%20Baere%20-%20Galloo.pdf)

The Galloo ELV recycling process considers some dismantling of parts for reuse, after depollution. Nevertheless, most of the depolluted ELVs are fed into the shredder (see process in Figure 26).

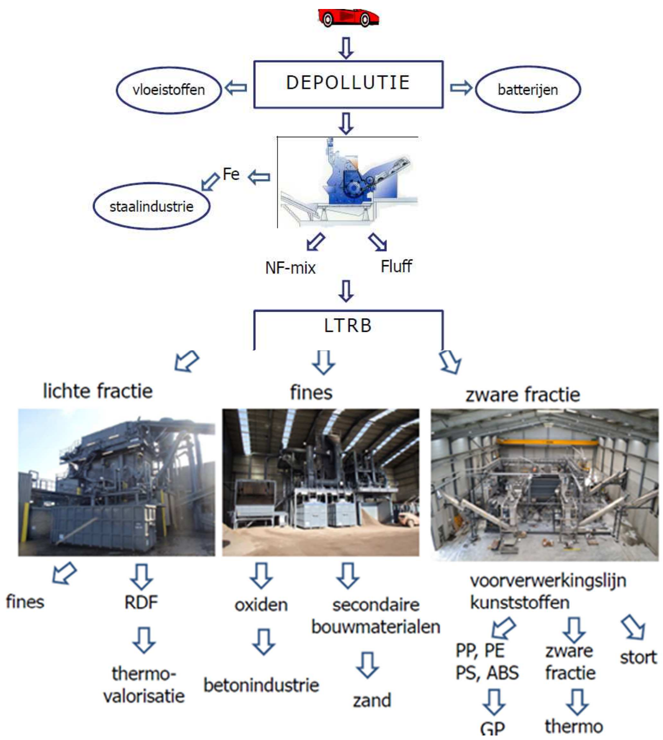

Figure 26: ELV treatment at Galloo Error! Bookmark not defined.

A recent study on collection targets and valorisation of Flemish large domestic appliances (excluding cooling appliances) (Nelen et al., 2014), of which the treatment process partially overlaps with that of ELVs, reveals the recycling efficiencies presented in Figure 27. The efficiencies for a material present in the recycling input are determined as the fraction of that material that is recovered in a useful output fraction in which the functionality of the material is conserved. The efficiencies are based on yield and purity estimates from mechanical treatment, with shredding, and also take into account secondary refining efficiencies where possible.

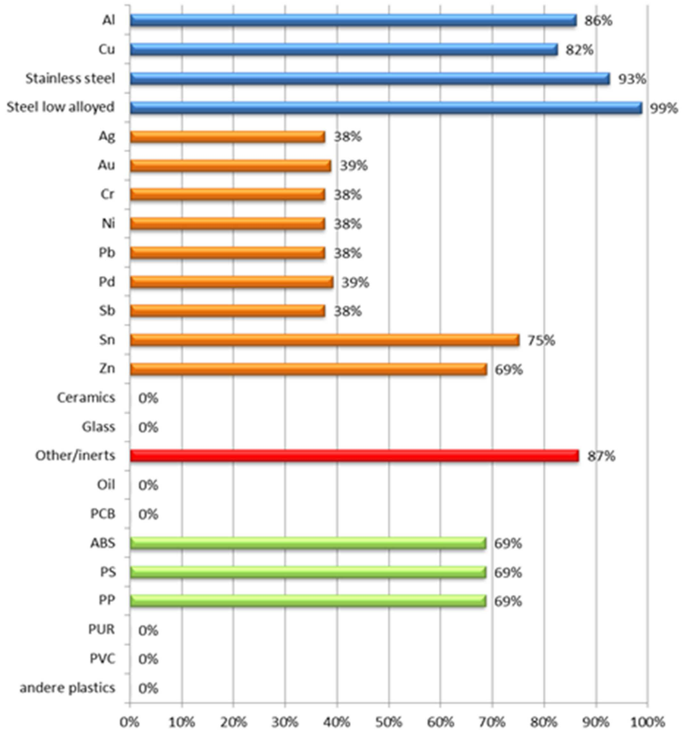

Figure 27: Recycling efficiencies of large household appliances

However, in a Product-Centric approach, in which recycling targets specific components of a product and their complexity at its End of Life (EoL), the recycling results for ELVs will differ substantially from those of white goods, also when they are fed into the same process, and even if their elemental material composition would be similar. For example, for white goods it is possible to achieve high recycling efficiencies for stainless steel, as this steel is mainly applied in the large washing machine drums that are easy to separate from the overall feed.

Ignatenko et al., 2008 developed a detailed flow sheet of an ELV processing optimisation model based on current and future future European Union car recycling scenarios.

Scenario	Al	Mg	Cu	Steel	Zn
1	0.78	0.89	0.78	0.97	0.82
2	0.78	0.89	0.78	0.97	0.82
3	0.72	0.84	0.74	0.95	0.81
4	0.55	0.58	0.67	0.84	0.73
5	0.74	0.82	0.77	0.93	0.76

Metal recovery for the defined scenarios after secondary metallurgy plants

- Scenario 1: Optimisation of ELV processing flow sheet without limitation of the thermal treatment stream;
- Scenario 2: Optimisation of ELV processing flow sheet with limitation of the thermal treatment stream restricted to 10% of the input (as required in the EU ELV Directive);
- Scenario 3: Maximum material and metal recovery scenarios with limitation of the thermal treatment stream restricted to 10% of the input (as required in the EU ELV Directive);
- Scenario 4: Minimum waste scenario without limitations for thermal treatment;
- Scenario 5: Maximum Al recovery scenario with limitation of 10% of the input to thermal treatment.

Figure 28: Metal recovery from ELV (From: Ignatenko et al., 2008)

- It can be observed in

Figure 28 that for all the studied scenarios, optimized recovery rates determined by rigorous thermodynamic modeling are still up to 10% lower than the recycling efficiencies calculated for large domestic appliances in Flanders (Figure 27). This reveals the presence of a significant ‘optimism bias’ in the yield and purity estimates from waste processors, that must be taken in account when predicting recycling potentials.

5.4 Material composition of ICE ELV and trends

In Belgium, the number of registered cars still increases. The total number of cars in 2013 was 5.392.908, representing an ‘urban’ stock of materials of an almost identical figure in tons. At the same time, in the last few years, a decrease in the number of ELVs can be observed in Figure 29. Both trend jointly result in an increase of the number of cars on the road. Over a longer period (2006-2012), the slope of the registered car curve is steeper than the slope of the ELV curve, indicating car life time extension. Effectively, between 1993 and 2013, the average age of Belgian cars went up from 6 years, 4 months, to 8 years, 1 month. (http://www.febiac.be/public/statistics.aspx?FID=23&lang=NL)

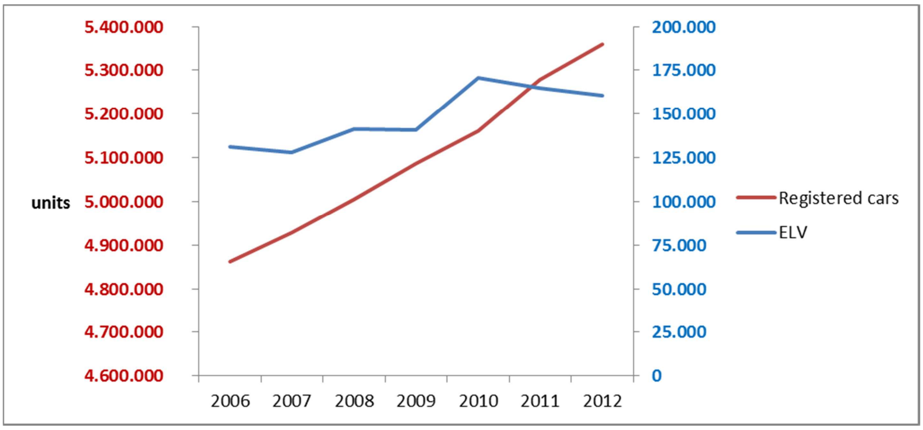

Figure 29: Number of ELV and registered cars in Belgium (2006-2012)

At European level assumed ELV 2015 composition is presented in Figure 30.

Material/Component	2003 ELV (% by weight)	2015 ELV (% by weight)
Ferrous Metal	68%	66%
Non Ferrous Metal	8%	9%
Plastics and Process Polymers	10%	12%
Tyres	3%	3%
Glass	3%	2%
Batteries	1%	1%
Fluids	2%	2%
Textiles	1%	1%
Rubber	2%	2%
Other	2%	2%
Total	100%	100%

Figure 30: composition of an 2015 ELV (right column), based on the composition of a 2003 new vehicle.

Plastics and nonferrous metals seem to increasingly replace steel and glass. The shift is clearly to more critical and strategic metals. (Pehlken, 2013). Cars have become heavier over the last decades, with an increasing value of the materials contained in electronic controls (see Figure 31).

Fahrzeug	Baujahr	Fahrzeug-gewicht	potenzielle Anzahl Steuergeräte	brutto Demontagezeit	potenzieller ET-Wert	potenzieller Neuwert
Golf 1	1974 - 1983	750 kg	1 Stck.	10 min.	130 €	514 €
Golf 2	1983 – 1992	845 kg	5 Stck.	80 min.	240 €	1.750 €
Golf 3	1991 - 1998	960 kg	9 Stck.	170 min.	487 €	2.379 €
Golf 4	1997 - 2003	1050 kg	16 Stck.	240 min.	1.530 €	3.798 €
Golf 5	2003 - 2008	1155 kg	28 Stck.	360 min.	2.744 €	6.268 €

Figure 31: Evolution of car weight and value of materials contained in electronic controls

(http://www.reecar.org/servlet/is/951/06-Knode-emontage.pdf?command=downloadContent&filename=06-Knode-Demontage.pdf)

'There is a trend in the automotive industry towards eliminating mechanical and hydraulic control systems and replacing them with electronic controls. Many traditional mechanical components can be

*eliminated such as shafts, pumps, hoses, fluids, coolers, cylinders, etc., which reduces the weight of the vehicle and improves efficiency. Electronic controls can also improve safety by facilitating more automated control functions like stability control. They also enhance the flexibility of automotive systems, making it easier to modify or upgrade vehicles. Electronic controls improve handling, enable better fuel efficiency and exhibit shorter response times in emergency situations' (*http://www.cvel.clemson.edu/auto/AuE835_Projects_2009/pillai_project.html) Electronic control units (ECU) usually consist of a printed circuit board inside an aluminum, steel or plastic frame. An example of the composition of printed circuit board from ECU is given in Figure 32. Control modules also contain multilayer ceramic chip capacitors, containing zirconate calcium, barium titanate or other mineral substances, and are connected with a wide variety of sensors.

Material	Resin board	Cu	Solder	Fe	Ni	Ag	Au	Pd	Bi, Sb, Ta	Others
Ratio (%)	70	16	4	3	2	0.05	0.03	0.01	0.02	4.91

Figure 32: Material composition (%) of PCBs in ELV ECU

'*As automobiles get more and more electronic, the number of ECU (Electronic Control Unit) devices in a single car can be between 10 and 100, resulting in a large number of wire harnesses criss-crossing the vehicle. Because the weight of these harnesses can reach several dozen kilograms, there is a tendency to position the ECUs in the engine room, thereby reducing the length of the harnesses and the related weight'.(* http://product.tdk.com/en/techjournal/archives/vol06_mlcc/contents03.html)

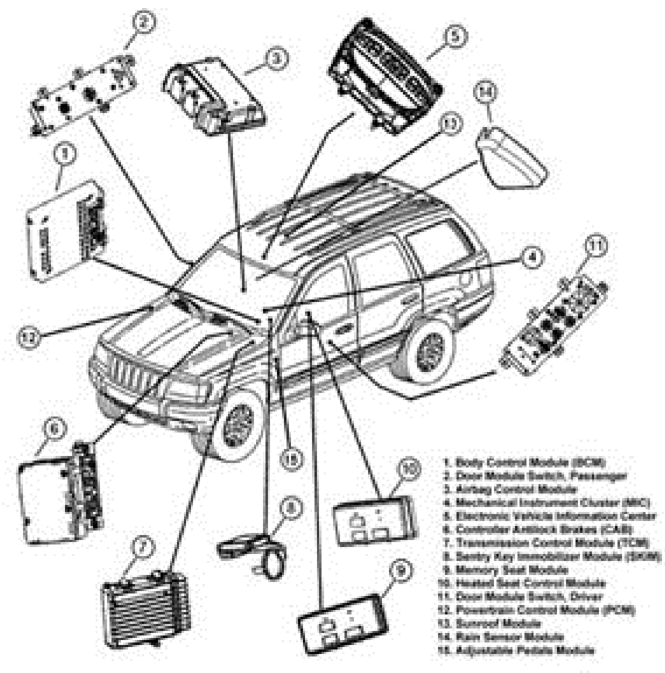

Figure 33: Electronic control modules in a Jeep Grand Cherokee (http://www.wjjeeps.com/ecm_02s.jpg)

The following list contains some of the electronic controls that currently can be found in ICE cars: **(http://www.reecar.org/servlet/is/951/06-Knode-emontage.pdf?command=downloadContent&filename=06-Knode-Demontage.pdf)**

- ECM
- Control unit for vehicle electrical system
- Telematics control unit
- Control unit for trailer towing
- Control unit for towing protection
- Phone and Blootooth controller
- Controller Gateway
- NOX sensor with control unit for exhaust gas control
- Controller Haldex clutch
- GRA-controller
- Control unit coming home
- Controller power stage
- Control unit for heater (receiver module)
- Control unit for multi-function steering wheel
- Controller for memory seat adjustment
- Navigation control unit
- Parking aid control unit
- Immobilizer control unit
- Telematics control unit
- Controller seat heating
- Transmission Control Module
- Climatronic control unit
- Airbag control unit
- ZV controller
- Controller seat heating
- lambda probe
- ABS control unit

When dismantled, the ECUs can be dealt with in the existing WEEE recycling systems that treat printed wiring boards (PWB). It is further believed that ELV ECU quality and reliability is superior compared to household appliance components. The harsh environment in cars and high requirements for quality of all automotive electronic components lead to many automotive-specific solutions for semiconductors, their packaging, and the process technologies used to manufacture them. (Wang et al., 2011) This make ELV ECU also an interesting component for reuse and remanufacturing purposes, of which the economic and environmental benefits largely outperform those of material recovery.

A hypothetical North American conventional mid-size sedan would contain 0,45kg of rare earths, distributed as showed in Figure 34. This rare earth content is concentrated in only 10 to 12 parts (see Figure 35).

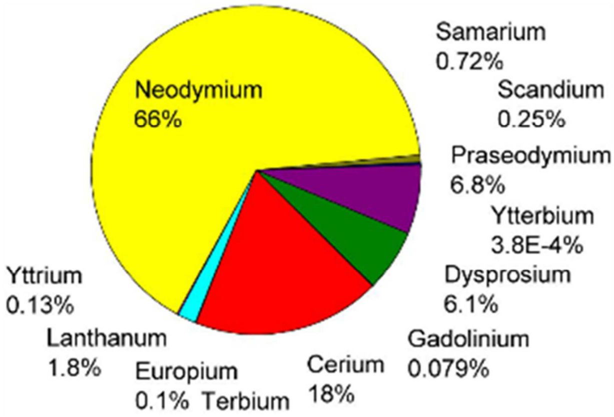

Figure 34: Rare earth distribution in a hypothetical North American conventional mid-size sedan [5]

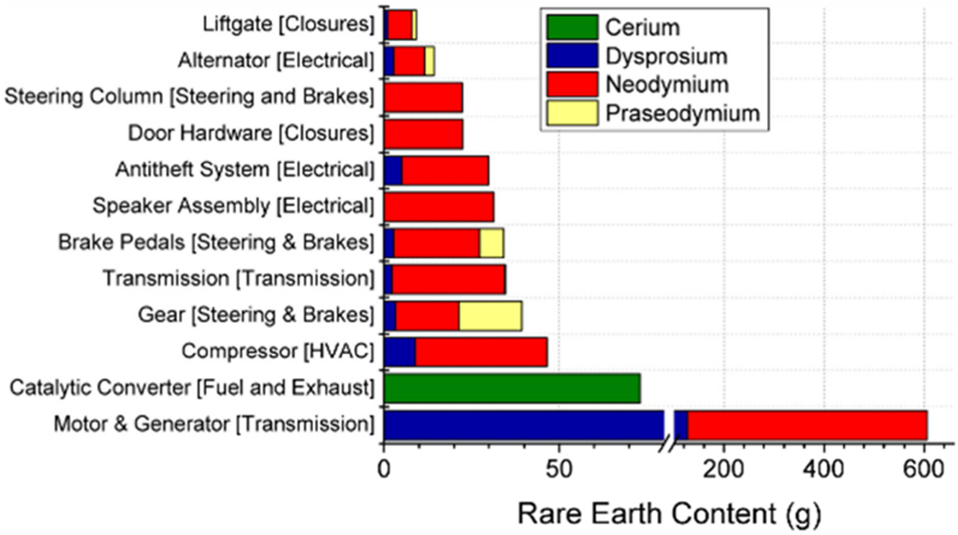

Figure 35: Vehicle parts and their rare earth content[5]

It is estimated that the automotive industry consumes approximately 16 to 25% of the global rare earth supply, excluding the rare earths consumed in the manufacturing process itself. (Alonso et al., 2012)

Other critical metals and minerals are contained in a high number of different auto parts (see Figure 36), often in alloys that aim for high strength and heat resistance, but also in particulate filters.

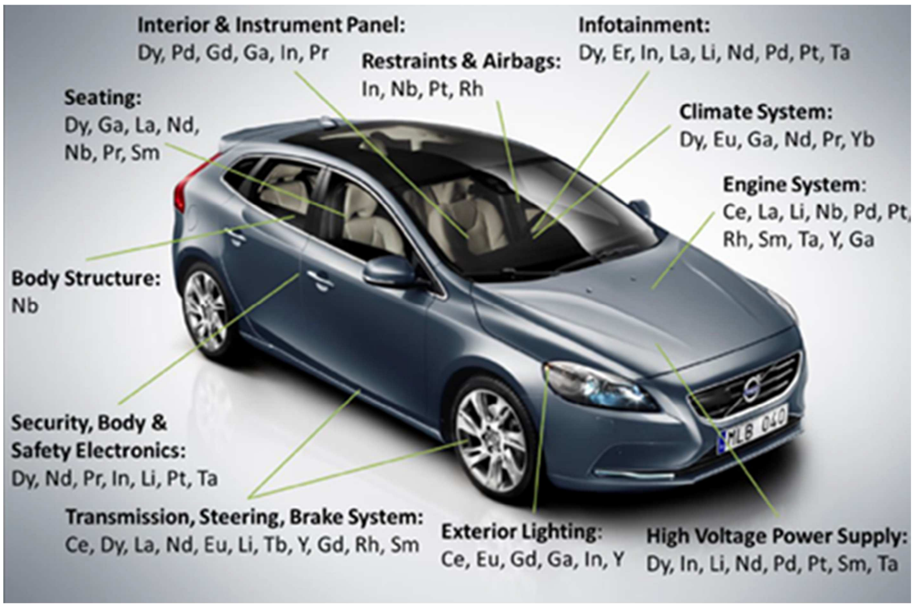

Figure 36: Rare earths and critical metals in auto parts Error! Bookmark not defined.

5.5 Optimization of ICE ELV recovery

The recovery of critical metals from ICE ELV requires the dismantling of car parts prior to shredding, since the functionality of most critical metals cannot or poorly be recovered after shredding (Figure 37 and Figure 38).

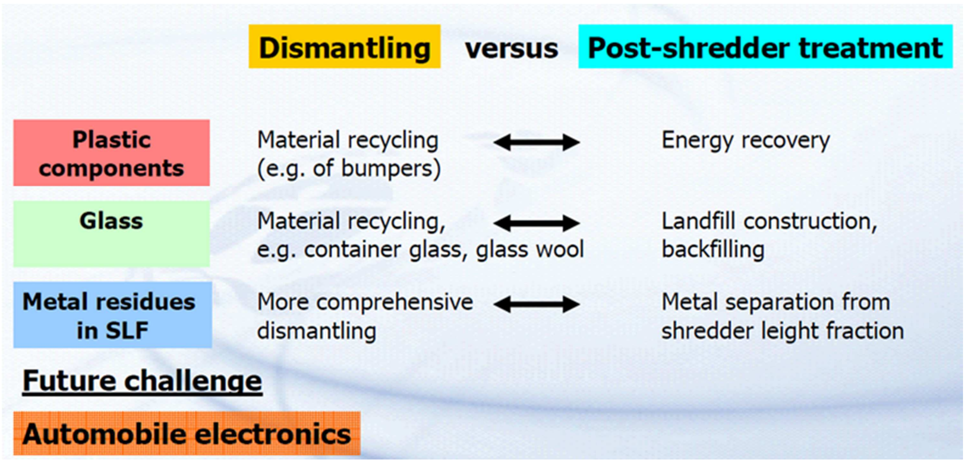

Figure 37: Comparison of applications dismantling and post shredder treatment output fractions (Kohlmeyer, 2012)

Component type	Metal	Re-use	Component recycling	Metals	Fines	SLF
Magnets	Nd, Dy			NFR	NFR	No R
Electronics	Au, Pt, Pd, Ta, Ga			FR (Au, Pt, Pd) NFR (Au, Ta, Ga, Pt, Pd)	NFR	No R
HSS and HT alloys	Nb	Re-use		FR NFR	NFR	No R
Catalytic converters and particulate filters	Pt, Pd Nd, Dy		FR (Pt, Pd) NFR (Nd, Dy)			

Figure 38: Current functional (FR) and non functional (NFR) recycling of scarce metals in ELV components (Söderman, 2013)

Dismantling enables the re-use or remanufacturing of components as well as the recycling of components in dedicated recycling systems, e.g. for recovery of precious metals together with PWB from WEEE (see Figure 39). This is particularly relevant for the increasing amount of ECUs.

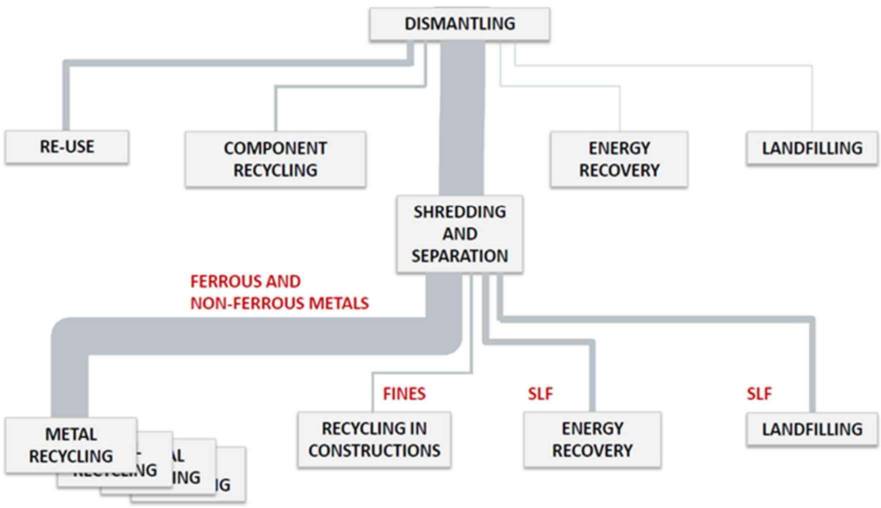

Figure 39: Swedish vehicle recycling 2010 Error! Bookmark not defined.

European waste management policies, in line with the waste hierarchy, tend to prioritize material recovery over energy recovery. At the same time, collection and recycling targets are measured at the entrance gate of the waste processors' facilities, and on a mass base. However, in a product centric approach environmental as well as economic benefits should be assessed by considering the overall outcome at the output side of the end-of-life management system applied to a particular product or product category. From the results for the different scenarios analyzed by Ignatenko et al. (2008), presented in

Figure 28, the authors conclude that '*Flexibility of the ELV recovery and processing system permits achieving high material and energy recovery quotas (rates) (over 95%) with the use of feedstock* *recycling and energy recovery for organic containing fractions if they cannot be suitably physically separated. The imposed legislative restriction on the amount of material that can be directed to thermal processing for energy recovery forces the system to include additional post-shredder treatment, with the result that material and energy recovery quotas are significantly lower at 88-91%, hence creating complex waste fractions.' (Ignatenko O, van Schaik, A, Reuter MA 2008)* The same approach should be followed to assess the benefits of recycling systems that allow for the reuse and remanufacturing of components.

A recent publication of the Scottish Government (Scottish Government, 2013) discusses strategies to face higher ELV recycling targets, citing a study from Coates et al. (2007): '*The study found that if ELV operators were to meet the 2015 recycling target by increased manual dismantling alone (i.e. assuming no improvements in post shredder technology - from the time of this 2006 study) then this would be done mainly by the removal of plastic and rubber components totalling 5%+ of the ELV weight. The study found that this would cost the ATF 12 Euro per ELV (taking into account the price received for the recovered material less labour and transport costs). Considering dismantling of only those components where it was economically feasible to remove, this would result in 0.75% of the ELV weight being extracted, with the target components being large, heavy sub-components (such as bumpers and internal trim). Obviously this is sensitive to labour costs and the market price for recovered material.*' The publication also indicates that '*this research is supported by other evidence (*Commission staff working document 2007) *on the manual removal of plastic parts from ELV. It suggested that the first 70kg "can be removed relatively cost-effectively.....with a steep increase in costs for removal of larger quantities of smaller parts"*'.

5.6 Challenges and preliminary conclusions

Research performed by the Chalmers University of Technology and the Swedish Environmental Research Institute (Södermann, 2013)**Error! Bookmark not defined.** concludes there is little incentive for scarce metal recycling, in policy as well as in practices, while information, practices and technology on the recycling of automotive electronics are still insufficient. The following organisational and institutional barriers to efficient vehicle recycling were identified:

- Little support from current policy: ELV-directive with total mass recovery target
- Low priority for policymakers: Supervision and compliance; Interpretation of concepts
- Low priority for automakers: "Material value should pay for recycling"
- Long, diverse and competitive actor chain: Payment models and investment risks; SMEs vs large companies

Research from Oldenburg University (Pehlken, 2013)**Error! Bookmark not defined.** suggests the need for:

- Proper sorting of car parts for metal concentrating
- More information on products composition
- Identification, dismantling and collecting of resource rich components
- New recycling technologies
- Environmental efficient product design with proper access to secondary resources

Hence, the following can be concluded from the literature review:

- The complete dominance of ELVs with an internal combustion engine (ICE) will last until beyond 2025. Quick wins are thus expected from optimization of ICE ELV.
- The Belgian supply of ICE ELVs is increasing at a rate below that of registered cars, as the average life time of cars is still rising.
- Determination of environmental and economic benefits of ELV treatment have to be approached from a product centric perspective.
- Critical materials are to be found mainly in electronic control units, catalytic converters, particulate filters, HSS and HT alloys and magnets.
- Current recycling targets and recycling systems focus on weight based material and energy recovery.
- The recovery of critical materials requires a dismantling step, prior to shredding. There is discussion going on whether such dismantling can be done in a cost-effective way, when aiming for enhanced material recovery.
- For dismantling of components to be environmentally and cost effective, reuse, remanufacturing and closed loop recycling must be considered, in that order of priority.

6. Opportunities

Underneath 12 opportunities are listed. They are derived from an extended literature review on possible next steps in collection, preprocessing and recycling of critical metals. There are many boundary conditions for the recycling of the here described opportunities, boundary conditions which to be further examined by discussion with experts and by further feasibility studies. The underneath short descriptions are only intended to trigger further discussion and to detect possible directions for even more resource efficient recycling.

O1a permanent magnets in a.o. hard disc drives, to recover Nd

Hard discs are easily detected. On average, the NdFeB magnet in HDDs weighs 15g, of which 3,75 Nd. These magnets can be recovered as alloys to new magnets after hydrogen decrepitation (Hitachi's dismantling technology and the technology of the University of Birmingham with 95 % RE). Recycling is possible as well by hydrometallurgical methods (Ionic liquid methods, Selective leaching with 80-99 % RE for Nd), pyrometallurgical methods (Electroslag refining, Liquid metal extraction, Glass slag method, direct melting). The separation of magnet particles (minor components) from the component still is challenging. 88,5 % of Nd is applied in permanent magnets (all applications).

Other applications: (long term!): motors, actuators, microphones and speakers, MRI, frictionless bearings, magnetic refrigeration. Earphones might be an interesting niche waste stream (when disassembled).

Other elements: some of the permanent magnets also contain Dy and Pr, which are a critical elements as well.

O1b Hard disc drives, to recover Pt

A rather niche application of Pt is as part of the magnetic coating stack on hard discs in computers. Some 2% of the total Pt amount is used for this application, though it is interesting to further exploit the recovery of these layers because of the ease of detecting these components. The main challenge lays in the collection and separation of the components.

O2 Capacitors, to recover Ta

Although Ta is not considered anymore as a critical element, the amounts used and the ease to detect components with considerable Ta concentration (mainly capacitors) justifies a further evaluation of recycling specific Ta containing components. Capacitors mainly are present in portable electronics, automotive components (ABS, airbag, GPS…), medical appliances (hearing aids). The concentration and composition of an individual Ta capacitor can be found in the FMD (Full Material Declaration) sheet and varies between 24 and 42wt% with mixed concentrations of Ta and Ta_2O_5. Knowledge of the Ta content at board level for different applications is still lacking. Due to their characteristic colour and shape, they are relatively easy detectable at board level. Ta recycling is mainly an issue of physical identifications, up-concentration and logistics.

O3 Electronics for the recovery of Au and Ag

Although the recovery of Au and Ag out of electronics is well established and very efficient (due to the high economic value of the recovered, precious metals, metallurgical recycling efficiencies > 98% for Ag, Au are reached), there still is an efficiency gap in the collection of these materials. Relevant components are diodes, transistors, integrated circuits and semi-conductor memories, capacitors,

resistors and electrical contacts, switches. It is found that only 12% of Ag and 26% of Au and Pd end-up in the appropriate Cu-waste-stream from which they can be extracted when mechanical shredding of waste material is performed. The amount of recovered Cu is 60% (average numbers for German ICT waste experiment). Selective disassembly of the PCB-parts is therefore recommended.
The main source of CRM can be found in the electronic components attached to the PCB and constituting the PBA (Printed Board Assembly). Noble finishes can be present at PCB level but most of the precious metals are coming from the component metallization layers and internal (Au) wire bonds. When further up-grading (in addition to the PCB separation) is still required, the highest Au containing components can be located in the advanced IC packages.
A special attention should be given to separate devices, such as USB sticks and memory cards. One FMD of memory chip shows 700ppm of Au at chip package level. Considering the ease of collection for separate devices, the potential for Au recovery is high, e.g. Au content in memory card (15mg) and Solid State Disk for USB stick (5mg). Further analysis of the composition and discussion on the delineation of WEEE is needed.

O4 Flat panel displays, to recover In

In is dominantly used (74% of the global usage) for the creation of Transparent Conductive Oxide (TCO) which is deposited on displays (TV, computer screens, tablets etc.). Although an absolute value of 0.05 to 5g per square m display is found, the concentration is very much diluted (far below 0.1wt%) due to the presence of the 'heavy' glass substrate. The complex construction of the display further complicates the disassembly process and potential up-grading. The ability to separate the different layers in flat panel displays is crucial. New technologies with leaching of In are more efficient, but still under development. It is recommended to first focus on the recovery of In during the manufacturing cycle (from process scrap and sputtering targets). One could also consider to separately collect the displays until recycling processing becomes available.

O5 LED screens, to recover In and Ga

First results show ranges from 30 to 170µg for In (this amount might even be an overestimation) and 30 to 530µg for Ga per individual LED die, but further research, including the disassembly and metallurgical processes, is needed. Although the amount of In and Ga in 1 LED is low, large assemblies of LEDs, such as LED screens or LED strings might be worth recycling separately.
Other applications: laser diodes to recover Ga.

O6: Computer and telecommunications products, to recover Be

Be is used as alloying element in CuBe alloys, in high performant connectors. The Be content in CuBe is as low as 2%, but the material could be recovered as alloy.
Other applications are as heat sink (BeO) in e.g. radio-frequency and radar equipment. BeO however is carcinogenic and should be removed anyway.

O7 Fibre optic systems and infrared optics, to recover Ge

Although Ge is highly dissipated in fibre optics, it is the main use of Ge, and due the scale in which optic fibres and other optics are introduced, recycling of post-consumer waste will be an issue in the future. Nowadays, recycling is mainly established for new scrap. The fibres and optics have a considerable life time, which makes that old scrap is not recycled yet, but shows a high potential for the future (Gus Gun, 2014)

Other applications: Ge devices are mainly expected for MEMS applications where they can be used as capping substrates in bolometers which are used in movement sensors. Also for these devices, further research on the average critical material concentration is still required.

O8 Phosphors in (compact) fluorescent lamps, to recover Eu, Y, Tb

Phoshors constitute 3% of the weight of CFLs. They are easily detectable and removable, especially in larger CFLs, but suffer from the presence of mercury in the powder. Several separation technologies exist: Rhodia's process, OSRAM'S process with liquid-liquid extraction (RE>90 %), Flotation (RE>90 %) Direct re-use (low purity and RE). Note however that the economic value of the recuperated REE has dropped drastically last year (a.o. since the market for new CFL decreases because of the substitution with LEDs). The glass is not recycled yet because of contamination with Hg.

Other applications: flat-panel displays, liquid crystal displays

O9 Electronic control units and copper in motors, wiring, radiators, bearings in the automotive

For most ELV components, end-processing is since long very well established, but dismantling of these components can yield higher efficiencies. The recovery of critical materials requires a dismantling step, prior to shredding. There is discussion going on whether such dismantling can be done in a cost-effective way, when aiming for enhanced material recovery. Quick wins should be sought in improving recycling systems and technologies that target a combination of materials that are present in those components that currently are being separated from the ELV, such as catalytic converters and batteries (O10a and b), or of which the removal may yield economic and environmental benefits in a foreseeable future, such as electronic control units (O4) and rare earth containing parts/alloys (braking systems contain e.g. up to 700g Nd).

O10a Li-ion batteries to recover a wide range of (cathode) constituents, and lead acid batteries for silver recovery

Processes are available (UMICORE) for refining pyrometallurgically obtained Co/Cu/Ni/Fe alloys for the recovery of cobalt as $LiCoO_2$ for Li-ion cathodes and of $Ni(OH)_2$. Bio-hydrometallurgical methods are currently under investigation. Several industries have developed (combinations of) mechanical and pyro and hydrometallurgical methods for recovery of $LiCoO_2$, $Li2CO_3$ or LiOH, Cu, Ni, Fe, Al, Co (e.g. RECUPYL, ACCUREC) that appear to achieve high functional recovery rates.

Recovery of silver from lead acid batteries can be achieved by pyrometallurgical methods, using the Parkes process with Mg addition, and by electrowinning.

O10b Nickel and cobalt rich batteries, to recover Li, Co, Ce, La and other REE

An electric vehicle contains on average 53 kg NiMH battery, which can easily be detected and removed. State-of-the-art industrial recycling of NiMH batteries is available, however, mainly Ni is functionally recovered from NiMH batteries and the REEs are lost in the smelter slags. Technological options are available to recover Ni, Co, Mn and REO (e.g. hydrometallurgical route from Zhang et al. (RE 97,8 %), Honda's molten salt electrolysis, UMICORE/Rhodia's Ultra High Temperature smelting and refining technologies). On the other hand, rare earths can also be recovered from NiMH slags enriched with RE-oxides. A wide range of other methods for the recovery of rare earths from NiMH is available, but their industrial applicability is still limited and subject to research. **Quick wins might be achieved from testing and/or upscaling of the most promising hydrometallurgical processes**.

The possibility exists of treating simultaneously several electrochemical systems of spent batteries using the same process, in order to overcome the high costs and difficulties of selective collection and sorting. The BATMIX process uses a single hydrometallurgical process of major battery systems (NiCd, NiMH and Li-ion) having Ni and Co as main metals.
Industrial capacity for pyrometallurgical based recovery of $LiCoO_2$ from NiMH/Li-ion mixes, for secondary Li-ion cathodes, has been installed (UMICORE).

Remark:
Research results pinpoint that the highest material recovery not always results in the highest environmental benefits. However, at the moment, legislation does not distinguish between functional and non-functional recycling, and establishes weight based recycling targets, implicitly assuming that recycling rates are proportional with the environmental and economic benefits. In the case that increased recycling cannot be obtained without having a net negative impact on the sustainability of the recycling system, care must be taken to assure the accomplishing of the primary goal of waste management, minimizing the negative effects of the generation and management of waste on human health and the environment.

7. List of interviewed experts

Name (company)	**Expertise**
Ruud Balkenende (Philips)	LED lighting
Marc Heyns (Imec)	Electronic wafer level processing and applications
Jan Huisman (TUDelft)	Materials recycling and sustainability
Jef Poortmans (Imec)	Photo-voltaics
Antoinette van Schaik (Maras)	Materials Recycling and Sustainability
Yongxian Yang (TUDelft)	Process fundamentals of metals extraction and refining
Bart Blanpain (KU Leuven)	Pyrometallurgy for metals recycling
Koen Binnemans (KU Leuven)	Ionometallurgy for recyling, Rare earth recycling
Tom Jones (KU Leuven)	Industrial Ecology
Tom Van Gerven (KU Leuven)	Sustainable inorganic materials management
Kim Eunyoung (VITO)	Hydrometallurgical processes, polymeric binders, lithium manganese oxide cathodes for lithium ion batteries
Catherine Lenaerts (Febelauto)	Collection, treatment and recycling of ELV in Belgium
David Wijmans (Campine)	Conversion of spent lead acid batteries and other lead-containing residues into raw materials that meet the quality requirements of the main lead user sectors

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