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**GREEN RECYCLING OF EEE:
SPECIAL AND PRECIOUS METAL RECOVERY FROM EEE**

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Abstract

Electronic and Electric Equipment contains a range of components made of a wide variation of metals, plastics and other substances. Up to 60 elements can be found in complex electronic equipment: base metals, precious metals and special metals in circuit boards and batteries. Because of its amount WEEE represents a considerable metal resource with a higher special and precious metal content than found in ores. The Umicore integrated smelter and refinery recovers and supplies back to the market 17 different metals from EEE. Pre-treated materials enter state of the art, material and energy efficient metallurgical processes for environmentally sound recovery of metals and treatment of off gasses and hazardous substances. The organics in the feed function as reducing agent and alternative energy source during smelting for precious metal recovery. Lithium-ion batteries are treated using a dedicated process. As a result the environmental footprint of metals produced from EEE is much smaller than primary production.

Introduction

Electronic and electric equipment (EEE) contains a wide range of components made of metals, plastics and other substances. Some of these are valuable (precious and base metals), some are hazardous (halogens, Hg, Cd) and some are both (e.g. Pb) [1]. A mobile phone can contain over 40 elements (figure 1) including base metals (Cu, Sn), special metals (Co, In, Sb), and precious metals (e.g. Ag, Au, Pd). Metals represent on average 23% of the weight of a phone, the majority of this is Cu as precious metals are present in low concentrations. Furthermore, the Lithium battery contains several grams of Co [2]. At first sight this appears to be very little, but taking into account the global sales of phones this leads to a significant metal demand in total (table 1).

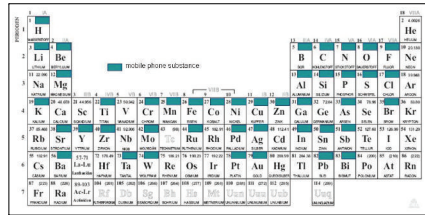


Figure 1: The elements present in a mobile phone.

The combined metal demand for mobile phones and personal computers only add up to about 3% of the world mine supply of Au and Ag, to 13% of Pd and to 20% of Co. For In and Ru this is much more. Almost 80% of the world's demand of In is used for LCD panels and over 80% of Ru is used for hard disks. Taking into account the highly dynamic growth rates, it becomes clear that EEE are a major driver for the demand (and prices!) of several metals [3]. The large amount of EEE in use also represents an enormous metal resource that could come available for recycling when the devices have reached their End-of-Life. Excellent recovery of valuable metals from WEEE contributes to the future metal supply for manufacturing EEE, to the efficient use of resources and to a sustainable life cycle for EEE.

The recycling of WEEE is mandatory in Europe (directive 2002/96/EC), but its weight-based recycling targets do not provide a direct incentive for the recovery of the special and precious metals. Precious metals are recovered for their economic value as they often account for the biggest share of the intrinsic scrap value. In a mobile phone they account with less than 0.5% of the weight for over 80% of the value. Copper represents 5-15 % of the value with 10-20% of the weight. Iron, aluminium and plastics, which dominate the weight, have only small

value contributions. Recycling of less valuable elements such as Pb, Sn, In, Ru from EEE is only economically feasible because valuable elements such as Au, Pd, Ag and Cu are present [4]. Most of the precious and special metals are contained in the printed circuit boards (PCB) present in PCs, mobile phones etc. where they are mixed with or connected to other metals in contacts, connectors, solders; connected to ceramics in capacitors, ICs and connected to resins in the layers of the circuit boards [1]. These complex combinations of metals and materials in WEEE require appropriate pretreatment and metal recovery processes that can deal with this mixture of metals and recover them with high efficiency.

Table 1: Average metal content per piece and total metal demand based on global sales in 2007 for mobile phones (1200 million) and PC & laptops (255 million).

	Mobile phone		PC & laptop	
	per piece (mg)	total (t)	per piece (mg)	total (t)
Ag	250	300	1000	255
Au	24	29	220	56
Pd	9	11	80	20
Cu	9 000	11 000	500 000	128 000
Co*	3 800	4 500	65 000	6 500**

* assuming all batteries are Li-ion. ** from 100 million laptops.

Recycling Chain for EEE

The efficiency of the entire recycling chain (collection, sorting & pretreatment, metal recovery) depends on the efficiency of each step. Collection of the discarded EEE is of crucial importance as this determines the amount of material that is actually available for recovery. Many collection programs are in place but their efficiency varies from place to place and also depends on the device, as small devices such as mobile phone are not so easily collected. About 3% of the people bring the phone to a collection point for recycling or reuse. About half of the phones are 'hibernating' at consumers and the rest is given away or sold for reuse [5].

After sorting the equipment enters a pre-treatment step to separate the materials in different streams from which the valuable metals can be recovered efficiently. Furthermore hazardous components such as batteries and capacitors have to be removed prior to further (mechanical) pre-treatment. During mechanical pre-treatment considerable losses of precious and special metals in PCB occur [1, 6]. One of the causes is unintended co-separation of the minor metals with a major metal due to incomplete liberation of the complex materials. Another cause is the losses of precious metals, particularly Pd, in dust

and fine particles due to shredding of the ceramic components on the PCBs circuit boards. Manual removal of the circuit boards from telecommunication and IT equipment prior to shredding will prevent these losses, and the complex combination of metals in PCBs can be treated very efficiently using metallurgical processes [1]. The pre-treatment process yields among others precious and special metal containing fractions that are suitable for treatment in an integrated smelter-refinery and batteries suitable for metal recovery. Extensive pre-treatment of EEE is not always necessary, small electronic devices such as mobile phones, MP3 players etc. can after removal of the battery also be treated directly.

Recovery of Metals from EEE Materials

Umicore Precious Metals Refining operates an integrated smelter and refinery in Belgium, which recovers and supplies back to the market 17 metals (Au, Ag, Pd, Pt, Rh, Ir, Ru, Cu, Pb, Ni, Sn, Bi, In, Se, Te, Sb, As) from complex precious metals bearing materials such as EEE materials, automotive and petrochemical catalysts and industrial wastes as well as from by-products out of the non-ferrous industries. In total over 200 different types of raw materials, about 350 000 t, are processed each year in a highly flexible flow sheet (figure 2) optimized for the treatment of a wide range of materials. The plant is one of the world's largest precious metal recycling facilities with a yearly capacity of 50 t Platinum Group Metals (PGMs), equal to about 7% of the world mine production, of 100 t Au and of 2400 t Ag.

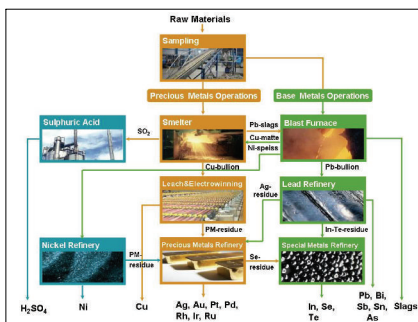


Figure 2: Flowsheet of the integrated smelter-refinery.



Figure 3: Examples of EEE feed materials: PCB and IC.

Feed Materials

The EEE materials treated are specifically the fractions that contain precious metals (figure 3):

- Printed circuit boards: production scrap or from EoL products such as IT, telecommunication, audio and TV equipment as well as unpopulated boards with precious metals.
- Components: multi-layered ceramic capacitors (MLCC), integrated circuits (IC), contacts etc.
- The fractions with a high PCB-content or other fractions with precious metals from shredding and sorting operations i.e. metallic granules, mixed plastic fractions with residual metals and (precious) metal-containing dusts.
- Overstock or obsolete material of small EEE devices after removal of the battery.

EEE materials are further categorised based on their gold content in very low grade (< 50 ppm), low grade (50-100 ppm), medium grade (100-200 ppm), high grade (200-400 ppm) and very high grade (> 400 ppm) material. To illustrate the difference between the devices the average precious metal concentration in PCBs of different electronic devices is given in table 2. The difference can easily be a factor 5-10. Therefore a good separation of PCBs or other precious metal bearing fractions - from plastic fractions beforehand has a double advantage: the precious metals will be concentrated rather than diluted and more refining capacity will be available because of the lower plastic content.

Table 2: Average content in circuit boards from EEE.

	Ag (ppm)	Au (ppm)	Pd (ppm)	Cu (wt. %)
PC	1000	200	90	15-25
CRT monitor	280	15	10	10
LCD monitor	1100	123	14	20
Mobile phone	5540	980	285	25

Sampling

Materials are sampled and assayed to determine accurately the exact composition and precious metal content. It is a crucial step to enable correct settlement with customers, to enable optimum processing of the material and for operations monitoring. Continuous innovation of the in-house developed sampling and assaying processes is supported by automation and information management to achieve maximum accuracy. The entire procedure takes place in a secured area, following strictly regulated and controlled processes so human intervention and sampling risks are minimized.

Directly after arrival the moisture content is determined. PCB sampling involves shredding with a rotating knife mill to 4x4 cm taking a stream sample of about 400 kg that is further shredded to 7x7 mm pieces, collecting a 4 kg sample. In the final sample preparation the Loss of Ignition is determined. The remaining (inorganic) material is divided over 16 sample bags of 100 g each, which are sent to the assaying lab, to the customer, and a few are kept on file. The metals content is determined using state-of-the-art equipment and methods (XRF, AAS, OES and ICP-AES), combined with conventional fire assay and chemical procedures. The extensive experience allows extraction of the maximum amount of the elements from the most complex materials.

Smelter-refinery process

The integrated smelter has into two main routes: the precious metals operations and the base metals operations (figure 2). For most of the EEE materials the smelter is the first step. The smelter uses IsaSmelt submerged lance combustion technology and is equipped with extensive off gas emission control installation. Since its start in 1998 continuous optimization has resulted in a current capacity of 1000 t/day, while originally designed for 650 t/day. At about 1200 °C enriched air and fuel are injected through a lance in a liquid bath and cokes is added for reduction of the metals. Blowing air and fuel into the bath ensures rapid chemical reactions and good mixing as the solid feed material, the copper metal phase and the lead slag phase are stirred vigorously. The precious metals dissolve in the copper, while most other (special) metals are concentrated in the lead slag together with oxide compounds such as silica and alumina.

At the leach-electrowinning plant (built 2001-2003) the granulated copper is leached with sulphuric acid resulting in a CuSO₄ solution and a precious metal-rich residue. In the residue the precious metals content is 10x higher than in the copper feed material. The CuSO₄ solution is sent

to electrowinning for recovery of the copper as 99.99% pure cathodes.

The precious metals residue is further refined at the precious metals refinery, which was successfully and completely redesigned in 2008. All possible variations and ratios of Ag, Au and PGMs are one by one recovered as high purity metals (> 99.9% pure), using classical methods combined with unique in-house developed processes. The flexible capacity of the refinery provides unique flexibility on the ratio of precious metals in the feed. About 25% of the annual production of Ag and Au, and 65% of Pd and Pt originates from recyclables (= EEE materials plus catalysts).

The lead oxide slag from the smelter, containing Pb, Bi, Sn, Ni, In, Se, Sb, As, and some Cu, is further treated in the lead blast furnace together with Pb-containing raw materials. The furnace produces about 200-250 t/day of lead bullion (95% Pb) in which special metals and silver are collected. Besides bullion the blast furnace produces copper matte (\rightarrow smelter), nickel speiss (\rightarrow nickel refinery and any precious metals \rightarrow precious metal refinery) and slag, which is sold as a construction material. Refining of the bullion in the lead refinery, with the Harris process, yields - besides Pb - Bi, As, Sn, Sb and two residues. The Ag-residue is further treated in the precious metals refinery. The Te-In residue is further treated in the special metals refinery together with the Se-residue from the precious metals refinery [1].

The Umicore integrated process achieves high precious metal recoveries from complex EEE materials. Independent of the route the precious and special metals take through the flow sheet, in the end they are all separated from the carrier metal and recovered while substances of concern are converted into useful products (Pb, Sb, As) or captured and immobilized in an environmentally sound manner (Hg, Be, Cd).

Environmental Considerations

Off gas treatment

The Cu-smelter, the Pb blast furnace and the Pb refinery are equipped with heat recovery systems, which generate high pressure steam for internal use. The IsaSmelt process is equipped to cope with the complex mix of metals, organic resins and plastics as it is connected to an extensive off gas treatment installation. Dust is captured in an electrostatic precipitator and returned to the smelter, dioxins emissions are prevented, water used for quenching is treated in the water treatment plant and recirculated, the sulfuric gases are converted to sulfuric acid for use

in the plant and external sales. The gasses leaving the stack are continuously monitored for SO₂ and NO_x content, with direct feedback to the process operators. Diffuse dust emissions are prevented by intensive sprinkling of roads and stocks, dust-free handling procedures and covering conveyor belts. The continuous improvement of these measures results in very low emissions [9] and prevents any losses of precious metals dust.

Resource Efficiency

Reducing agent consumption and energy efficiency are important parameters and a reduced demand for primary resources and fossil fuels has also a positive impact on the conservation of resources. The carbon-containing materials in the EEE materials function as an alternative source of reducing agent and energy. Smelting of PCBs requires 1500 kJ/kg and further refining needs 6500 kJ/kg. The energy contained in the boards (9600 kJ/kg) released during smelting can easily fulfill this demand [2], allowing for partial replacement of fossil fuels and utilization of the excess heat for steam generation.

Furthermore the recovery of metals from EEE materials avoids the high CO₂ emissions associated with primary metals production. The CO₂ emission to produce precious metals from ore ranges between 9380 and 13954 t CO₂/t for PGMs compared to 3.4 t CO₂/t for Cu [10]. The primary production of the metal demand (4.7 million t/y) for EEE manufacturing accounts for an annual CO₂ emission of 23.4 million tonnes, almost 1/1000 of the world's CO₂ production [2]. The CO₂ emissions of the Umicore process when used to recover 75 000 tons of metal from 300 000 t of recyclables and smelter by-products is only 3.73 t CO₂/t metal produced compared to 17.1 t CO₂/t metal when using a primary production route. This single operation can thus prevent CO₂ emissions and lower the environmental footprint of the metals substantially. Would only relatively high-grade feed materials be taken into account the avoided emission is even larger!

Recovery of Metals from Batteries

Umicore Recycling Solutions operates the in-house developed Val'Eas® process with an annual capacity of 4000 t for treatment of Ni-metallhydride and Li-ion batteries from among others EEE devices, but also from hybrid and electric vehicles in an environmentally sound way. In this metallurgical process the main metals Co, Ni, Cu and Fe are first separated from the other battery materials in the smelter in Hofors, Sweden. The post combustion technol-

ogy (based on the use of a plasma gun) guarantees that all organic compounds are fully decomposed and that no harmful dioxins or volatile organic compounds (VOCs) are produced. The obtained alloy is further refined with a hydrometallurgical process in Olen, Belgium to obtain very high purity cobalt oxide and nickel salts, the source materials for battery cathode material. Final conversion to active cathode material for Lithium-ion cells is done in the Umicore Korea plant in Cheonan, S. Korea. For the nickel metalhydride batteries the Ni-compound is converted into nickel hydroxide at the JC Umicore plant in Jiangmen, China. In this way spent batteries are converted to new materials for battery applications, thus closing the material loop.

Feed Materials

Rechargeable Ni-metal hydride (NiMH) and Li-ion batteries and production scrap can be treated in the recycling process. Average compositions of batteries are given in table 3. Besides Ni and Co the NiMH batteries also contain a rare earth mischmetal, which is a mixture of lanthanum (La), cerium (Ce), praseodymium (Pr) and neodymium (Nd) [7]. In Li-ion batteries LiCoO₂ is used as cathode material, but other oxides such as LiNiO₂ or LiMnO₄ are used as well [8].

Table 3: Average composition of rechargeable batteries in wt. %.

	NiMH	Li-ion	Li-polymer
Misch metal	5.3	-	-
Electrolyte	10	-	-
Steel or Fe	25	35**	1
Plastic	8	10-20	3
Nickel	21.8*	1-2	2
Copper	-	7-8	16
LiCoO ₂	-	25-27	35
Carbon	-	10	15
Aluminium	-	35**	15
Others	17.4	12-18	23

* in NiOOH ** depending on use of Al or Fe can.

Recycling process

In the first step the spent batteries are charged to a smelter (figure 4), without further sorting, treatment or removal of the housing. During smelting at about 1500 °C the plastic casings and the polymers provide energy for the smelting process. Further, the graphite from the batteries as well as the carbon from the plastics is used as a reducing agent in the reaction zone to reduce all metal oxides to their metallic form, so a liquid alloy containing Co, Ni, Cu, Mn and Fe is formed. The Li and Al collect

in the Ca-Al-O slag, which is used in the cement or steel industry. Only any electrolyte present in the batteries is evaporated.

The temperature is closely controlled throughout the smelting process. Firstly to ensure that gaseous compounds formed during heating of the batteries can leave the battery in a controlled manner so the risk of potential explosion is minimized. Secondly to prevent the formation of any VOCs during the smelting and off gas treatment process. When exposing the plastics and polymers which contain organic material together with halogens, to high temperatures dioxins and furans can be created when the incompletely combusted gases have time to recombine at a temperature between 400 and 900 °C. To prevent the creation of VOCs the off gas from the smelter is further heated by a plasma gun to temperatures above 1200 °C to break all organic bonds, and kept under reducing conditions. As a result the halogens are present in their reduced form (HBr, HCl) instead of as molecules and hence more stable. When these reactions have taken place the temperature of the gas is instantaneously decreased from 1250 °C to below 350 °C, so that the carbon chains do not have time to re-combine, and above all, no halogens can be linked with carbon thus the formation of dioxins is avoided.

As most of the materials in the batteries are converted to useful products, (alloy, concrete additive) or employed for feedstock recycling (graphite) the recycling efficiency is ranging between 60 and 85% depending on the type of battery. This is well exceeding the recycling efficiency set by the EU Battery Directive (directive 2006/66/EC).

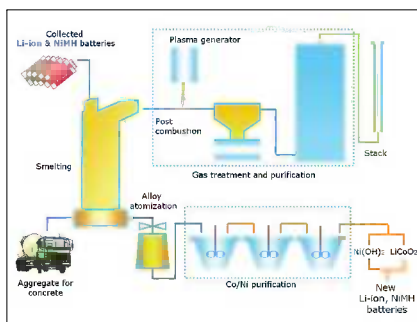


Figure 4: Flow sheet of the battery recycling process.

The alloy is refined using a classical hydrometallurgical

process. This second step already existed within Umicore. It is leached with sulphuric acid to remove Cu, followed by removal of Fe, Mn and Zn in the second step to obtain a NiSO₄ and a CoCl₂ solution. Both solutions are further purified in solvent extraction installations. The purified NiSO₄ solution is crystallized. One of the further treatments of NiSO₄ crystals is the transformation into spherical Ni(OH)₂ particles for application in rechargeable batteries. The pure CoCl₂ is oxidized in a dedicated in-house developed furnace. Precise control of the furnace conditions enables the production of a cobalt oxide (Co₃O₄) that meets the quality requirements for battery materials. Co₃O₄ is mixed with lithium-containing compounds and transformed into LiCoO₂, which is used as cathode material in new Li-ion and/or Li-polymer batteries.

Discussion and Conclusions

In the past ten years Umicore has changed from a traditional primary metals producer to a materials technology company, where state of the art, in-house developed metallurgical recycling processes are employed to recover precious and special metals from EEE materials in an environmentally sound manner, keeping metals in a closed loop.

EEE developments go quick and new devices appear on the market rapidly after each other. The highly flexible flow sheets combined with extensive expertise are key to dealing with these developments. Umicore uses Cu, Pb and Ni as collector metals and thus can extract many minor metals that metallurgically fit into these flows. Research is ongoing to further extend the range of feed materials (e.g. photovoltaic applications) and recovered special metals (e.g. Ga, Mo, Re, Li) anticipating on the changes in type and composition of future EoL products.

The combination of metals, toxics and halogenated organic substances in many EEE requires special installations and considerable investments to secure environmentally sound managed operations. However in developing and transition countries some E-scrap is treated 'industrially' in non-compliant smelters and hydrometallurgical plants, but most is treated in the 'informal sector' using highly inefficient open air incineration, leaching and amalgamation processes [11, 12, 13] to recover only Cu and Au [14]. This poses a threat to health and environment.

To achieve 'green recycling' of EEE metallurgical technology itself is often not the barrier. With economic incentives appropriate technological processes can be developed. But 'green recycling' is more! As long as the collection rates are low and the losses along the recycling

chain are high, both in developed and developing countries, 'green recycling' remains wishful thinking. To become a reality other societal, legislative and life cycle factors have to be addressed in a co-operative manner.

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