Innovative recovery strategies of rare earth and other critical metals from electric and electronic waste

/ Julia Hobohm & Kerstin Kuchta

Institute of Environmental Technology and Energy Economics, Technical University of Hamburg-Harburg.

Abstract

Critical metals (CM) which include rare earth metals (REM) are essential and important for the production of electrical and electronic equipment. An increasing demand for green and information technology products could lead to a scarcity of these resources in future and a dependency on a very few supply countries. Currently the extraction of CM from ores is energy intensive and involves severe environmental risks due to the toxic chemicals involved in the mining. An alternative source for CM is Waste Electrical and Electronic Equipment (WEEE). Through the currently applied recycling processes of this complex waste stream REM are lost completely. Moreover, inadequate recycling approaches in developing countries are causing severe sanitary and environmental damages. Hence, it is essential to develop effective and ecologically sound systems, including concerted collection, pre-treatment and refining processes for an utmost efficient recovery. Due to these manifold challenges the recovery of CM from WEEE cannot be solved on a national level. Experts from all process phases have to create an interdisciplinary, transnational alliance in the pan-European context.

Resumen

Los Metales Críticos (CM) que incluyen a los Metales Tierras Raras (REM) son esenciales e importantes para la producción de equipos eléctricos y electrónicos. El incremento de la demanda de tecnologías verdes y de innovación podría conducir a una futura escases de estos recursos y a la dependencia de suministro por parte de muy pocos países. Actualmente la extracción de CM desde el mineral requiere un consumo excesivo de energía y representa severos riesgos ambientales debido a los químicos tóxicos involucrados en su extracción. Una Fuente alternativa de CM son los Residuos de Aparatos Eléctricos y Electrónicos (WEEE). A través del proceso de reciclaje aplicado actualmente a estos desechos tan complejos estamos perdiendo completamente el flujo de REM. Sobre todo, el método inadecuado de reciclaje utilizado en los países en desarrollo esta provocando severos danos sanitarios y ambientales.

Por lo tanto es esencial desarrollar sistemas efectivos y ecológicos, incluyendo una colección centralizada, pre-tratamiento y refinación para lograr una mayor eficiencia en la recuperación. Debido a estos múltiples desafíos , la recuperación de CM a partir de WEEE no puede ser resuelta a nivel nacional. Expertos de todas las áreas de procesos deben crear una alianza interdisciplinaria y transnacional en el contexto pan-Europeo.

Key-words: *Waste electrical and electronic equipment (WEEE), rare earth metals (REM), critical metals, interdisciplinary approach, network, sustainable recovery, recycling, bio-metallurgy, sanitary and environmental hazard, risk assessment, technology.*

1. Background

Raw Materials Initiative strategy document the European Commission proposed a number of targeted measures for promoting investment in extractive industries in Europe. Critical metals (CM) which include rare earth metals (REM) are integral composites in electrical and electronic equipment (EEE) in the area of steadily growing future technologies like green technologies (GT) or information and communication technologies (ICT). REMs are rarely available in commercially viable concentrations, the high complexity of the ores and their low REM concentration, mining, extraction and refinement of REM is a complex and energy-intensive process, entail severe negative environmental impacts, involving strong acids and radioactive materials resulting in the production of large amounts of hazardous wastes.

Europe is one of the world's largest consumers of REMs but holds no own primary production. The largest REM deposits are located in China (European Union critical raw material report, 2014) . The increasing worldwide demand (*Fig. 1*) is facing a crucial scarcity resulting in significantly rising prices, involving a severe risk for the supply guaranty since the export of these materials may be limited at any time.

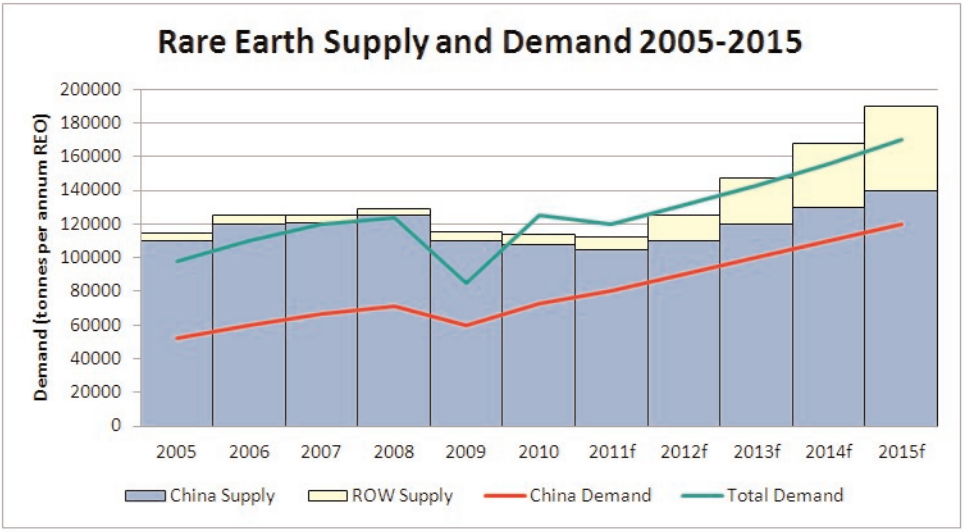

Fig. 1. Rare earth supply and demand 2005-2015 (Panneflek, 2015)

As supplying alternative, one of the most important material streams containing CM is Waste Electrical and Electronic Equipment. WEEE is a non-homogeneous and complex waste mixture that contains high Neodymium and Yttrium concentration

The losses of REM are up to 100 %. The applied recycling processes need to be adjusted (recycling processes mainly focus on base and precious metals) to achieve a CM-rich output stream as precondition for an efficient recovery of these materials. Changes in the production way considering reductions e.g. of lead, cadmium and mercury will result in simplified recycling processes and less hazardous waste.

Appropriate regulations and a significant harmonisation of policy basis on innovation and sustainability are therefore necessary to promote sustainable developments in production and recycling of WEEE on a European scale, beholding the solution of many conflicts and for the mobilisation of synergies between environment, economy and society (3-pillar-model) which cause positive effects on economic and/or social goals.

Today, different European countries undergo individual approaches to investigate and enhance single steps of the total recovery process. Research activities, carried out in parallel in different European countries, are certainly less effective than coordinated actions. The manifold challenges require experts from all steps of recycling and recovery to form interdisciplinary, transnational networks including e.g. engineers, chemists, biologists and toxicologists, an intense involvement of Young Researchers is one key factor for successful long-term achievements in this field of research. The Action's objective is the creation of a network made up of both the scientific community and industrial representatives from different European countries and scientific disciplines to develop interdisciplinary and effective WEEE recovery processes by bridging the individual cultural and educational backgrounds.

However, the scientific knowledge can only be completely exploited and valorised if authorities and industries are involved in these activities. Thus, an early inclusion of these parties is an essential part of the strategy of this Action.

2. Current state of knowledge

Waste electrical and electronic equipment (WEEE) is a chemically and physically specific form of municipal and industrial waste as it covers both valuables (e.g. non-precious metals: iron, steel, copper, aluminium, etc.; precious metals: gold, silver, palladium, platinum, etc.; critical metals: yttrium, neodymium, europium, etc.; plastics) and hazardous substances (e.g. lead-containing glass, mercury, cadmium, batteries, flame retardants, chlorofluorocarbons and other coolants with hazardous potential and environmental impact) (*Robinson, 2009; Tsydenova and Bengtsson, 2011*).

A number of legislative documents refer to the restriction of hazardous substances in EEE, Energy using Products Directive and WEEE Directive have been drafted and implemented in the EU. The strategic target of these legislations is to increase the recycling of EEE products by obliging producers to decrease the content of hazardous materials and implementation of an extended producer's responsibility covering the whole life cycle of EEE (OECD, 2001, Barba-Gutierrez et al., 2008).

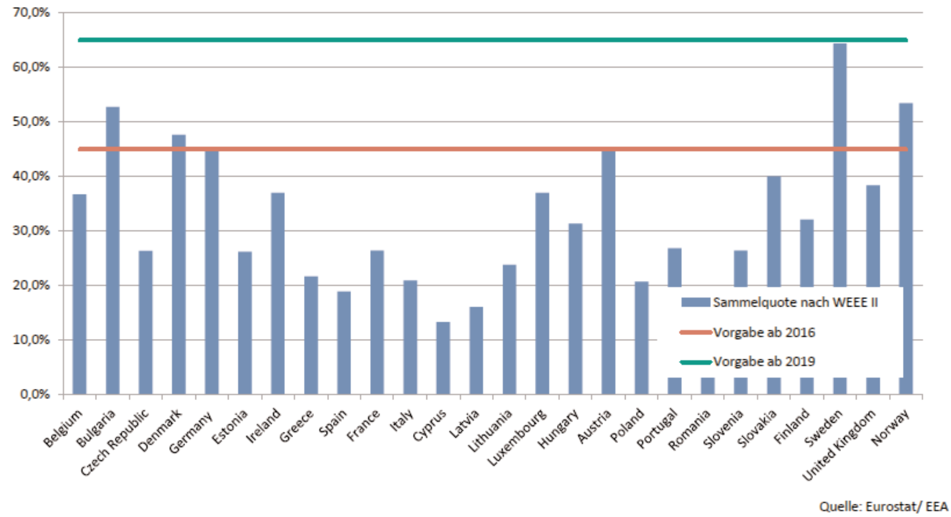

Fig. 2. The collection rate by WEEE II of the different countries and the target as from 2016 and 2019 (Sperlich, 2014)

According to annual WEEE collection target, 45 % of average annual weight of EEE placed on the market in preceding 3 years has been set for the period of 2016-2018. Likewise, annual WEEE collection targets from 2019 onwards have been established to 65 % (WEEE recast directive, 2014), (*Fig. 2*). By 2020, it is estimated that the total volume of WEEE will increase to 12 million tons.

WEEE Directive aims to provide:

- EU Member States with tools to fight illegal exports of waste more effectively

- Force exporters to test and provide documents on the nature of their shipments

- Highly complex streams waste, it must be collected separately and treated carefully to enable eco-friendly and safe recovery and disposal.

Considerable amounts of WEEE consist of information technology (IT) hardware products which have a relatively high economic value:

- Batteries from notebooks and smartphones show relevant concentrations of the CM cobalt. Recycling processes for cobalt from a range of IT products have already been established.
- For lithium-ion batteries and nickel metal hydride batteries has been opened a pyro metallurgical plant with an input capacity of 7,000 tons batteries per year.
- Tantalum is another example from the large group of metals which still exhibit end-of-life recycling rates.

However, a major challenge for the recycling industry is the enhancement of collection and systematic separation of the batteries in preparation for the refining processes described. Further studies deal with highly specific recycling processes in the field of water purification, ferrosilicon and wastes from the aluminium production:

- Recovering of REMs from red mud; a solid waste generated during the aluminium production. The methods are been applied in laboratory scale, the red mud was roasted and REMs were leached by HCl before scandium and other rare earth oxides were separated from the liquid.
- Technological conditions of smelting rare-earth ferrosilicon by two thermal methods to generate a pre-alloy for the production of ductile graphite iron

Beside to the research there is an economic aspect. Significant cost savings can be achieved, if these metals can be reintroduced into the manufacturer's supply chain by saving primary resources.

Although, recycling and reuse of outdated electronic products is strongly encouraged, only 9% is collected and recovered for recycling. Because of the rising market volume of WEEE it has to be startet to recycle *(Fig. 4*). However the recycling rate of REM is less than 1% worldwide (*Schueler et al., 2011*). For metals like copper, chromium and gold the recycling rates are higher than 50% of the input material. Unfortunately, critical metals are not recovered from WEEE and approximately 50-80% WEEE is being exported to developing countries and remaining 20-50% end up in electronic waste shredder without pre-separation and appropriate treatment (*Binnemans et al., 2013; Kücüker and Kuchta, 2012*).

These limited recycling rates are mainly due to uncoordinated and diffuse research and application approaches in the individual European countries. Most of the activities are focusing only on the optimisation of single steps in the whole WEEE management system.

3. Applications and Properties of Rare Earths in Luminescent Materials

Yttrium, europium, and lanthanum are commonly used in luminescent materials, such as the backlights of modern displays. These are particularly interesting in terms of possible substitution from a recycling and resource efficiency standpoint. Backlighting solutions in the form of CCFL lamps (CCFL = Cold-Cathode Fluorescent Lamp) are already in use in desktop monitors, notebooks, scanners, and other flat screen displays. In typical liquid crystal displays (LCD) of televisions, the amount of luminescent materials used is around 7 milligrams per square centimetre of cold-cathode lamp (mg/cmCCFL), meaning a total amount of between 3 and 15 grams per typical LCD screen. The rare earths that can be recovered from these applications include primarily yttrium (accounting for around 14 percent of the total) and lanthanum and europium.

As *table 1* shows, the rare earths that can be recovered from these applications include primarily yttrium (accounting for around 14 percent of the total) and lanthanum and europium.

Element	Weight amount [mg RE/mg powder]	Weight % in powder
Yttrium	0.05 – 0.52	13.81
Lanthanum	0.01 – 0.1	3.41
Europium	0.001 – 0.02	0.9

Table 1. Rare Earth concentration in backlight of screens

Yttrium and lanthanum are used to form a host lattice in oxide (Y_2O_3, La_2O_3) or phosphate form (YPO_4, $LaPO_4$), white powders that do not respond to exposure to electrons or UV photons by emitting light. The process of including europium (Eu) or terbium (Tb) in these host lattices is called doping. When UV light from a mercury discharge hits these luminescent elements, they are excited to emit light at a defined wavelength. This stimulation process can be direct or work on the activator via the ions of the host lattice. In addition to europium and terbium, other rate earths, such as samarium, praseodymium, erbium, dysprosium, thulium, and cerium can function as such activators. The rare earth ions emit light because the electrons in the 4f orbitals (Tb^{3+}4f8; Gd^{3+}4f7; Eu^{3+}4f7) are first excited and then return to their original state. The f orbitals are screened by the higher-energy 5d orbitals, which means that there is only minimal interaction between the rare earth ion and its chemical environs (the host lattice) (*Blasse & Grabmeier, 1994*). Electrons can be excited to a higher level on the 4f orbital (*Sastri, 2003*) and then emit a discrete wavelength of light when they return to the energetically more favourable original state. The wavelength of the emitted light is directly dependent on the energy difference between the two states. As a result, the electrons emit a specific spectrum in the form of a number of lines that is characteristic for each element, called the emission spectrum of the element [*Atkins & de Paula, 2006*]. The spectra of many rare earth ions are marked by their characteristically narrow range. Broader spectra, so-called band emission, are emitted only when using Eu^{2+} and Ce^{3+} [*Uhlich, 2009*].

This unique behaviour is caused by the fact that the electrons do not relax in the f-Orbitals, but rather engage in f-d transitions . The energetic state of the 4f5d band can be influenced specifically by the choice of host lattice. Depending on the chosen host lattice for the Ce^{3+} or Eu^{2+} ions, certain covalent interactions happen between the activator and the host lattice in addition to crystal field splitting. These specific interactions have a direct impact on the energetic state of the bands and therefore the colour of the emitted light.

4. REEE in Magnets

The strongest magnetic materials available, with energy products (BHmax) ranging from 225 to 415 kJ/m^3, are made of an alloy of neodymium, iron and boron (NdFeB) (*Hilzinger and Rodewald, 2012*). In this alloy, Nd is the key REM employed with smaller quantities of praseodymium (Pr), dysprosium (Dy) or terbium (Tb). Pr is often used as a substitute for Nd in its pure form or as a mixture with Nd (called didymium) generally to decrease cost and to improve the corrosion resistance of the magnet (*Dent, 2012*). Pr can be substituted Nd up to an extent of 25 weight percent (wt%) as at higher levels the properties of the magnet would suffer (*Oakdene 2010*). *Table 2* gives the composition (by wt %) of typical

Reference	Nd	Pr	Dy	Co	B	Others e.g. V, Nb, Al, Ga	Fe
(Westphal und Kuchta 2013a)	16-27	1-7	0-3				Rest
(IEC DIN IEC 60404-8-1)	28-35	0-10		0-15	1-2	0-1	Rest

Table 2. : Composition of sintered NdFeB-magnets (Westphal and Kuchta, 2013a), (DIN IEC 60404-8-1)

NdFeB magnets. The average REM content is up to 31 wt % (*Buchert et al. 2012*).
Magnetic materials have become a key component in a large variety of electrical and electronic equipment (EEE) and have also gained a significant commercial importance.

NdFeB-magnets have improved the performance of EEE both in reduction of weight and in enhancing their performance characteristics. Due to the high energy density of the permanent magnet, engines or loudspeakers can be designed much smaller, providing the same performance. Large quantities of NdFeB magnets are used in the manufacturing of consumer electronics, such as smartphones, tablets, cameras, sensors and mobile phones. All these devices include components that utilized permanent magnets, such as the vibratory motor in a mobile phone or voice coil actuators (VCA) in computers (*Gutfleisch et al. 2011*). The demand for all applications is expected to grow in the short and medium term considerably. The data presented in Table 3 show the relevant components of certain types of ICT electronics as well as the content (within brackets the content ranges) and the concentrations of Nd per device.

Device	Nd concentration in [mg/kg]	Nd concentration in [mg/kg]	Number of samples including NdFeB magnet vs total number of samples
PC*	5180 (2470 - 9950)	520	9/9
Hard disk drive	4280 (1890 - 8600)	7620	12/12
CD-ROM, DVD	885 (570-1330)	1010	8/8
Laptop*	2650 (2190 - 2970)	90	4/4
Hard disk drive	1440 (1050 – 1680)	10800	4/4
CD-ROM	255 (230 – 280)	1330	5/5
Mobile phone*	65 (30 – 120)	780	20/20
In-Ear phones**	90 (40 - 130)	6730	9/10
On-Ear phones**	310 (240 – 390)	1820	5/10
LCD-television***	4330 (1015-9060)	400	9/20

*Table 3. : Content [mg_Nd per unit] and concentration [mg_Nd/kg_unit] applied in certain types of EEE (Westphal and Kuchta 2013**; Hobohm and Kuchta, 2012***)*

5. Conclusion

The term “rare earths” covers 17 chemically related metallic elements, including yttrium, lanthanum, and europium. Extracting these rare earths from the source ores requires substantial amounts of chemicals in the process, including sulphuric acids. In electronic devices, rare earths are used primarily for backlit displays (e.g. in CCFL) and magnets. So, WEEE is promising as a secondary resource for these REM. Although REM concentrations in electronic appliances are very low, these metals have a high economic and environmental relevance compared to other substances present at much higher levels such as iron, copper or plastics. In addition the advantage of WEEE are the short lifespan and high number of sales of EEE. Electronics such as mobile phones reach the end of their life after a few years. The recycling of REE contained in WEEE can serve as a short-term solution to the current demand.

6. Anex

List of European projects related to REM recycling:

- **CWIT;** Countering WEEE Illegal Trade, (2013-09-01 to 2015-08-31).
- **REECOVER;** Recovery of Rare Earth Elements from magnetic waste in the WEEE recycling industry, (2013-12-01 to2016-11-30)
- **HYDROWEE;** Innovative hydrometallurgical processes to recover metals from WEEE, (2009-03-01 to 2012-02-29).
- **BIOLIX;** Bio-hydrometallurgical beneficiation of non-ferrous, (2012-10-01 to 2015-09-30).
- **REMANENCE;** Rare Earth Magnet Recovery for Environmental and Resource Protection, (2013-01-01 to 2016-06-30.
- **RECYVAL-NANO;** Development of recovery processes for recycling of valuable components from FPDs, (2012-12-01 to 2016-11-30.
- **RECLAIM;** Reclamation of Gallium, Indium and Rare-Earth Elements from Photovoltaics, Solid-State Lighting and Electronics Waste, (2013-01-01 to 2016-12-31).

National / Bilateral

- **BIOREEs,** Biotechnological Approach for Recovery of Rare Earth Elements and Precious Metals from E-Waste, Project No: 113Y011, 2014-2017.
- **RePro,** Closed loop and recycling of CM, (UBA FKZ 3711 95 318).
- **UPGRADE,** Integrated approaches for the recovery of trace metals and an improved added value of WEEE, (BMBF 033R087
- **Bo2W,** Global recycling of strategic metals, (BMBF 033R097).
- **REWIN,** Improving resource efficiency for the production and recycling of electronic products by adoption of waste tracking system.

7. References

Atkins P., de Paula, J. (2006). Physikalische Chemie. Weinheim: Wiley-VCH.

Barba-Gutierrez Y, Adenso-Diaz B, Hoppa M. (2008) An analysis of some environmental consequences of European electrical and electronic waste regulation. Resources Conservation and Recycling;52: 481–95.

Blasse, G., & Grabmeier, B. (1994). Luminescent Materials. Springer Berlin.

Binnemans, K., Jones, P. T., Blanpain, B., Gerven, T. V., Yang, Y., Walton, A., Buchert M. (2013) Recycling of rare earths: a critical review. Journal of Cleaner Production, 51: 1-22.

Buchert, M.; Manhart, A.; Bleher, D.; Pingel, D. (2012): Recycling critical raw materials from waste electronic equipment. Commissioned by the North Rhine-Westphalia State Agency for Nature, Environment and Consumer Protection. Hg. v. Öko-Institut. Darmstadt.

Dent, P. C. (2012): Rare Earth Elements and Permanent Magnets. In: Journal of Applied Physics, 111, article 07A721.

DIN CEN/TS 16171 (2012) Sludge, treated biowaste and soil – Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS).

European Commission (2014) Report on Critical Raw Materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials (http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-report-on-critical-raw-materials_en.pdf)

Gutfleisch O.; Willard M.A.; Brück E., Chen C. H., Sankar S.G., Liu J.P. (2011) Magnetic Materials and Devices for the 21st Century: Stronger, Lighter, and More Energy Efficient. Advanced Materials & Process 23: 821–842.

Hilzinger, R., Rodewald, W. (2012): Magnetic materials. Fundamentals, products, properties and applications. Erlangen, DE: Publicis.

Hobohm, J., Kuchta, K. (2012) Recover Potential *of Rare Earth Metals in Displays; Oral Presentation, Symposium of Urban Mining, Bergamo, Italy, 21.-23. Mai 2012*

Kücüker, M. A., Kuchta, K. (2012) Biosorption with Algae as a Green Technology for Recovery of Rare Earth Metals from E-waste. Istanbul, Turkey: Presented at the International conference on Recycling and Reuse, 4-6 June.

Oakdene H. (2010) Lanthanide Resources and Alternatives. Sustainable products and services, Clean technologies, Ressource efficiency. Unter Mitarbeit von H. Kara, A. Chapman, T. Crichton, P. Willis und N. Morley. Hg. v. Department for Business Innovation and Skills Department for Transportation. Oakdene Hollins Research & Consulting.

Organization for Economic Co-operation and Development, OECD (2001) Extended producer responsibility: a guidance manual for governments. Paris: OECD.

Panneflek E. (2015) Why Investing in Rare Earth Elements? http://www.pgm-blog.com/why-investing-in-rare-earth-elements/ (10.06.2015)

Robinson B. (2009) E-waste: an assessment of global production and environmental impacts. Science of the Total Environment, 408: 183–191.

Sastri, V. (2003). Modem Aspects of Rare Earths and their Complexes. Elsevier.

Schueler D., Buchert M., Liu R., Dittrich S., Merz C. (2011) Study on Rare Earths and Their Recycling- Final Report for The Greens/EFA Group. Darmstadt: Öko-Institut e.V.

Sperlich K. (2014) Chancen der Novelle ElektroG zur Stärkung der Ressourcenschonung. Rheinland Pfalz, UBA.

Tsydenova O., Bengtsson M. (2011) Chemical hazards associated with treatment of waste electrical and electronic equipment. Waste Management, 31: 45–58.

Uhlich D. (2009) Kristallographische und spektroskopische Untersuchungen an Eu3+-dotierten Molybdaten als potentiale Konverter für LEDs. Osnabrück: Universität Osnabrück Fachbereich Chemie/Biologie .

Westphal L., Kuchta, K. (2013) Permanent magnets from small waste electrical and electronic equipment (WEEE). Sardinia 2013, 14th International Waste Management and Landfill Symposium. University of Padova. Cossu, R. Sardinien, 30.09.2013.

WEEE Recast Directive update, (2014) http://eponline.com/articles/2014/04/28/weee-recast-directive-update.asp>