THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Hydrometallurgical Recovery of Rare Earth Elements from Fluorescent Lamp Waste Fractions

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Gothenburg, Sweden, 2016

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CRISTIAN TUNSU
ISBN 978-91-7597-434-7

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Doktorsavhandlingar vid Chalmers tekniska högskola
Ny Serie Nr. 4115
ISSN 0346-718X

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Cover: Scanning Electron Microscopy picture of one of the fluorescent lamp waste phosphors fractions investigated (5000x magnification)

Printed by:
Chalmers Reproservice
Gothenburg, Sweden, 2016

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ABSTRACT

Recovery and reuse of materials is important for a circular economy. In recent years the recovery of critical metals from end-of-life products has received increased attention. Various streams, e.g. permanent magnets, nickel metal hydride batteries and fluorescent lamps are considered targets for the recovery of rare earth elements (REEs). The last can be a source of up to six different REEs: europium and yttrium (primarily), as well as lanthanum, cerium, terbium and gadolinium (secondarily).

Because fluorescent lamps use mercury to generate light, a decontamination step needs to be carried out prior to processing discarded products for REEs recovery. This is often carried out using thermal treatment (up to 800 °C) but this method has some drawbacks, e.g. energy consumption and the fact that it is not best suited for waste streams containing high amounts of moisture.

Hydrometallurgical methods for the decontamination of fluorescent lamp waste fractions and subsequent recovery of the REEs contained are presented in this study. A selective leaching process followed by separation of metals using solvent extraction was developed. Mercury was leached in a first stage using iodine in potassium iodide solutions. Further processing of the mercury in solution was investigated using various techniques, e.g. ion exchange, reduction and solvent extraction. In a second leaching step, impurity metals, e.g. calcium, barium, etc., were selectively leached from the REEs with nitric acid solution by making use of their fast dissolution kinetics. Further leaching, carried out with more concentrated acidic solutions for longer time, led to the dissolution of the REEs. Partial leaching selectivity between yttrium + europium and the other four REEs was achieved by controlling the leaching time, acid concentration and temperature.

A group separation of the REE ions in solution was carried out using solvent extraction with Cyanex 923, a commercial mix of trialkyl phosphine oxides. Testing of the process at laboratory pilot scale in mixer-settlers showed promising results, leading to a final product consisting of a yttrium/europium-rich solution. Over 99% of the REEs present in lamp leachates were extracted and stripped, respectively, in a mixer-settler system comprised of three extraction stages and four stripping stages. The metals were then further separated using Cyanex 572, a novel phosphorus-based chelating extractant aimed at the separation of individual REEs. Selective separation of yttrium and europium was achieved by controlling the equilibrium pH (pH_{eq}) during extraction. Yttrium was extracted at $pH_{eq} = 0$ and europium at $pH_{eq} = 1$. Rare earth oxides were prepared via oxalic acid precipitation and thermal treatment of the obtained oxalates at 800 °C. A mixed REE oxide (99.96% REEs, with 94.61% yttrium, 5.09% europium and 0.26% others) was synthetized from the strip product after extraction with Cyanex 923. Yttrium oxide (99.82%) and europium oxide (91.6%) were synthetized from the strip products after extraction with Cyanex 572.

KEYWORDS: fluorescent lamp waste, rare earth elements, recycling, waste treatment, leaching, solvent extraction, Cyanex 923, Cyanex 572.

LIST OF PUBLICATIONS

This thesis is based on the work contained in the following publications, referred to by Roman numerals in the text:

Publication I

Tunsu, C., Ekberg, C., Retegan, T., 2014. Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury. Hydrometallurgy 144-145, 91-98.

Contribution: main author, all experimental work, processing and interpretation of data.

Publication II

Tunsu, C., Ekberg, C., Foreman, M., Retegan, T., 2014. Studies on the Solvent Extraction of Rare Earth Metals from Fluorescent Lamp Waste Using Cyanex 923. Solvent Extraction and Ion Exchange 32, 650-668.

Contribution: main author, all experimental work, processing and interpretation of data.

Publication III

Tunsu, C., Ekberg, C., Foreman, M., Retegan, T., 2015. Investigations regarding the wet decontamination of fluorescent lamp waste using iodine in potassium iodide solutions. Waste Management 36, 289-296.

Contribution: main author, all experimental work, processing and interpretation of data.

Publication IV

Tunsu, C., Petranikova, M., Ekberg, C., Retegan, T., 2016. A hydrometallurgical process for the recovery of rare earth elements from fluorescent lamp waste fractions. Separation and Purification Technology 161, 172–186

Contribution: main author, majority of the experimental work, processing and interpretation of data.

Publication V

Tunsu, C., Lapp, J.B., Ekberg, C., Retegan, T. Selective separation of yttrium and europium using Cyanex 572 for applications in fluorescent lamp waste processing. Hydrometallurgy, decision pending.

Contribution: main author, experimental work, processing and interpretation of data.

Other publications that were not included in this thesis

Tunsu, C., Petranikova, M., Gergorić, M., Ekberg, C., Retegan, T., 2015. Reclaiming rare earth elements from end-of-life products: A review of the perspectives for urban mining using hydrometallurgical unit operations. Hydrometallurgy 156, 239-258.

Contribution: main author.

Tunsu, C., Retegan, T., 2016. Chapter 6: Hydrometallurgical processes for the recovery of metals from WEEE, in: Chagnes, A., Cote, G., Ekberg, C., Nilsson, M, Retegan, T. (Eds.), WEEE Recycling: Research, Development, and Policies. Elsevier, 139-175.

Contribution: main author.

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ABBREVIATIONS AND DEFINITIONS

The following abbreviations and definitions are used throughout this thesis:

°C	Degrees Celsius
>	More than
<	Less than
% wt.	Percentage weight total
% vol.	Volumetric percentage
%E	Percentage extracted
$\alpha_{A/B}$	Separation factor between A and B
ΔH^0	Enthalpy change at standard state
ΔS^0	Entropy change at standard state
approx.	Approximately
aq	aqueous
BAM	$BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor
CAT	$(Ce,Tb)MgAl_{11}O_{19}$ phosphor
CFL	Compact fluorescent lamp
CRT	Cathode ray tube
$CyMe_4BTBP$	6,6’-bis(5,5,8,8-tetramethyl-5,6,7,8- tetrahydro-benzo-[1,2,4-]triazin-3-yl)-[2,20]bipyridine
D	Distribution ratio
D2EHPA	Bis-2-ethylhexyl phosphoric acid
e.g.	For example; such as
g	Gram(s)
h	Hour(s)
HDD	Hard disk drive
HEHEHP	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
I_2/KI	iodine in potassium iodide (solution)
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
K	Degrees Kelvin
kg	Kilogram(s)
L	Litre(s)
Lanthanides	The 15 elements ^{57}La to ^{71}Lu, inclusive
Lanthanoids	The 14 elements ^{58}Ce to ^{71}Lu, inclusive (the lanthanides without ^{57}La)
LAP	$LaPO_4:Ce^{3+},Tb^{3+}$ phosphor
LED	Light emitting diode
M	Molar concentration (mol/L)
MPa	Megapascal
min	Minute(s)
mL	millilitre(s)

NiMH	Nickel metal hydride
O:A	Organic:aqueous (phase ratio)
org	Organic
pH_{eq}	Equilibrium pH
Phosphor	Compound capable of luminescence
ppb	Parts per billion
REEs	Rare earth elements (the lanthanides, ^{39}Y and ^{21}Sc)
rpm	Revolutions per minute
s	Solid
SEM/EDS	Scanning Electron Microscopy/Energy Dispersive Spectroscopy
S/L	Solid to liquid (ratio)
TBP	Tri-n-Butyl Phosphate
TPH	TetraPropyleneHydrogenated
TRPO	TrialkylPhosphine Oxides; Cyanex 923
UN	United Nations
US	United States
UV	Ultraviolet
vpm	Vibrations per minute
vs.	Versus
w/v	Weight/Volume
XRD	X-Ray Diffraction
YOX	$Y_2O_3:Eu^{3+}$ phosphor

1. INTRODUCTION

Recycling and re-use of materials are important parts in circular economies. The increasing demand of raw materials required by industries is a challenge that needs to be addressed. This demand often leads to excessive mining and exploitation of natural deposits, as well as generation of secondary streams during resource processing. These considerations have led to an increased interest in recycling, especially for scarce materials such as the rare earth elements (REEs).

The REEs are presently regarded as being some of the most critical materials (European Commission, 2011; UN Environment Programme and UN University, 2009; US Department of Energy, 2011). The European Commission declared REEs to have the highest supply risk among non-energy, non-agricultural raw materials twice, in 2010 and 2014 (European Commission, 2010; 2014). There are several reasons for this, the most important ones being related to geological distribution of REEs, difficult and complex separation of individual elements, high demand and political factors.

The fact that REE-containing minerals rarely occur in concentrated forms makes exploitation of this group of elements difficult (Gupta and Krishnamurthy, 2005). Their geological occurrence, together with either the uranium or thorium decay chains, makes the processing of REEs challenging in many countries due to radiotoxicity (Kilbourn, 1994). Moreover, REEs have similar chemical properties, which translates into separation and purification difficulties. Production of REEs is often associated with environmental issues due to the numerous hydrometallurgical separation stages needed to achieve the high degrees of purity required in certain applications. This often leads to high amounts of secondary waste.

The REEs have a wide variety of applications, ranging from simple ones, e.g. polishing agents, to more advanced ones, e.g. laser repeaters for high speed and high distance data transfer (USGS, 2002). Some of these applications are characterized by high specificity; the REEs needed having no efficient substitutes with similar properties. Most importantly, REEs are essential in future sustainable technologies. Neodymium, dysprosium, europium, yttrium and terbium, the five most critical REEs (US Department of Energy, 2011), are used in green energy applications e.g.:

- neodymium and dysprosium in permanent magnets, which are used in wind turbines, hard disk drives (HDDs), speakers, headphones and others;
- europium, yttrium and terbium, together with lanthanum, cerium and gadolinium, in phosphors in low-energy fluorescent lamps;
- neodymium, yttrium, cerium, lanthanum and praseodymium in nickel metal hydride (NiMH) batteries for electric transportation.

Because of their large variety of applications, REEs are in high demand. A recent concern was their limited availability on the market. The closing of Mountain Pass mine in the US in the early 2000s allowed China to gain over 90% of the REE market share, although the country possesses less than half of the global deposits (Xie et al., 2014). This has led to significant price fluctuations over the past decade, as well as export quotas.

All these aforementioned factors have focused attention towards a better processing of various end-of-life products and industrial waste streams for the recovery of the contained REEs. Permanent magnets in HDDs, NiMH batteries and fluorescent lamps are the most targeted products due to their abundance on the market and relatively high REE content (Tunsu et al., 2015).

Up to six REEs are found in the composition of the phosphors powder of modern fluorescent lamps: cerium, europium, gadolinium, lanthanum, terbium, and yttrium. Mercury is an essential component in these appliances, being required for photon emission (Chang et al., 2009). Its presence requires special collection and treatment of end-of-life fluorescent lamps. Moreover, mercury interferes with the further processing, requiring removal from the stream prior to the recovery of the contained REEs. Hydrometallurgical methods e.g. leaching, solvent extraction, ion exchange and precipitation are most suited for the recovery of REEs and have been studied in recent years for potential processing of fluorescent lamp waste (Tunsu et al., 2015). Despite the research, large-scale applications to recover REEs are uncommon. In 2011 the global average functional recycling rates of REEs and mercury from end-of-life products were reported to be less than 1% and 1-10%, respectively (UN Environment Programme, 2011). This is because some of the efforts in this field were only carried out at bench scale, sometimes using clean lamps, carefully treated and/or decontaminated material, or pure samples that imitate the composition of phosphors powder. Many of the proposed processes were not tested using higher amounts of real, chemically complex and mercury-contaminated waste. Description of full processes that use contaminated fluorescent lamp waste fractions as input feed and separate solid REE compounds as final products are scarce. For this reason, improving and/or developing industrial processes that remove mercury from phosphors powder fractions and individually recover the contained REEs is of great importance.

1.1. Goal and driving forces

The goal of this research is the development of a robust process for recovery of REEs contained in the phosphors powder of fluorescent lamp waste fractions. Emphasis has been placed on:

- developing a wet-based mercury decontamination process as an alternative to the traditional, energy intensive, thermal treatment to remove the mercury in the waste. Thermal treatment can be an issue for waste fractions obtained via wet-sieving processes (described in section 2.4) (Binnemans et al., 2013) e.g. some of the waste samples investigated in this thesis;
- separation and recovery of REEs from the waste using a hydrometallurgical approach based on selective leaching, solvent extraction and precipitation. Preparation of solid REEs oxides was desired;
- scaling-up the developed process up to laboratory pilot scale, based on leaching reactors and counter-current mixer-settler contactors.

These were deemed important because, at the beginning of the present decade, large scale treatment of real fluorescent lamp waste was scarcely described in the literature, especially complete processes that address all steps e.g. decontamination, selective leaching, individual REEs separation and oxide production.

The development of effective recycling processes cannot entirely replace mining, especially considering the increasing demand for raw materials. However, processing of end-of-life products e.g. fluorescent lamps can provide additional sources of REEs in addition to known natural deposits and can increase the global availability of these elements. The driving forces can be grouped into three categories, as shown in Table 1: material supply, environmental benefits and economic issues (Tunsu et al., 2015).

Table 1 – Some of the driving forces behind the development of processes for the decontamination and recovery of REEs from fluorescent lamp waste. Adapted from Tunsu et al., 2015.

Sector	*Benefits*
Environmental	Limit the spreading of radioactive isotopes e.g. uranium and thorium during REEs ore mining and processing. Prevent the spreading of toxic chemicals e.g. mercury in the environment. Reduce landfill areas both when it comes to mining tailings and disposal of discarded products or fractions from discarded products. Clean landscapes. Reduce exploitation by reducing mining. Conserve natural deposits.
Material supply	Materials can be recycled back into production cycles (for the same or different applications). Increase the availability of certain compounds (also due to the fact that the concentrations of REEs are higher in discarded products compared to some ores).
Economic	Reduce the costs of raw materials by creating additional supply.

2. BACKGROUND AND THEORY

2.1. Rare earth elements

The REEs group, also referred to as *rare earth metals* or *rare earths* comprises the 14 lanthanoids (cerium to lutetium), lanthanum, yttrium and scandium (Greenwood and Earnshaw, 1998). This group is often divided into two groups; light REEs and heavy REEs. The former, also referred to as the cerium group, comprises the first seven lanthanides, up to europium (Greenwood and Earnshaw, 1998; Tyler, 2004). The rest of the lanthanides and yttrium, which has an ionic radius between those of dysprosium and holmium, form the heavy REEs group, also referred to as the yttrium group. Although not that well defined, an intermediate group containing REEs of intermediate atomic mass and ionic radius, known as medium REEs, is sometimes mentioned in the literature (Tyler, 2004).

Although the name implies otherwise, REEs are relatively abundant in the Earth's crust, with light REEs e.g. lanthanum, cerium and neodymium being more common than lead. Thulium and lutetium are the scarcest REEs but even these are one hundred times more abundant than gold (USGS, 2002). The main issue is their geological distribution. Rare earths are encountered together with other members of the group and seldom form concentrated ore bodies. Due to the fact that they have similar chemical properties, their individual separation is challenging. Obtaining high purity REEs requires complex chemical processing e.g. a large number of solvent extraction separation and stripping stages.

The slow decrease in ionic radii along the lanthanide series, known as the lanthanide contraction, allows individual element separation (McLennan, 1994). This decrease leads to increased strength of cation-anion, ion-dipole and ion-induced dipole interactions, meaning that heavier REEs will form stronger complexes with hard donor extractant molecules (Nash, 1993). The tetrad effect (Peppard et al., 1969) was noticed in various extraction systems when plotting the logarithm of certain physical chemical parameters vs. the corresponding atomic number. Four breakpoints, explained by the stabilization energy related to the inter-electron repulsion energy of the 4f electrons, were noted; lanthanum–cerium–praseodymium–neodymium, promethium–samarium–europium–gadolinium, gadolinium–terbium–dysprosium–holmium, and erbium–thulium–ytterbium–lutetium. The breakpoint in the middle of the series is due to the stabilized half-filled $4f^7$ electron configuration of gadolinium.

As mentioned in the introduction section, REEs are essential in a wide variety of technological applications, some characterized by high specificity (Table 2).

Table 2 – Some applications of REEs (US Department of Energy, 2011; USEPA, 2012; USGS, 2002).

Element	*Applications*
Scandium	Metal alloys for the aerospace industry, nuclear applications, lighting.
Yttrium	Phosphors, metal alloys, lasers, temperature sensors, ceramics, yttrium iron garnet (transmitter and transducer of acoustic energy), yttrium aluminium garnet (simulated diamond).
Lanthanum	Carbon arc lamps. automotive catalysts, catalysts for petroleum refining, glasses, phosphors, batteries, lasers, X-ray films.
Cerium	Lighter flints, polishing powders, component and decolourizer in glasses, carbon-arc lighting, catalyst in petroleum refining, metallurgical and nuclear applications.
Praseodymium	Carbon arc lights, glass and enamel colorants, magnets (improved corrosion resistance), search lights, airport signal lenses, photographic filters.
Neodymium	Magnets, lasers, glass colorant (welder goggles), fluid-fracking catalysts, colorant for enamels.
Promethium	Beta radiation source, fluid-fracking catalyst, portable X-ray sources.
Samarium	Magnets, reactor control rods, guidance and control systems, electric motors, carbon arc lamps, lasers, infrared absorbing glass.
Europium	Phosphors, lasers, glass additive, targeting and weapons systems, communication devices.
Gadolinium	Phosphors, glass additives, magnetic resonance imaging contrast agent, gadolinium yttrium garnets (microwave applications), alloys, magnetocaloric materials, burnable neutron poison in nuclear fuel.
Terbium	Phosphors, magnets, guidance and control systems, targeting and weapons systems, electric motors.
Dysprosium	Magnets, lasers, nuclear sector, alloys.
Holmium	Industrial magnets, nuclear applications.
Erbium	Lasers, glass colorant, nuclear and metallurgical uses.
Thulium	Radiation source in portable X-ray equipment, potentially useful as an energy source (^{171}Tm), ferrites (ceramic magnetic materials) used in microwave equipment, doping fibre lasers, high power magnets.
Ytterbium	Portable X-ray devices (radiation source), lasers, fibre-optic cables, improving the grain refinement, strength and other mechanical properties of stainless steel.
Lutetium	Catalysts in cracking, alkylation, hydrogenation, and polymerization, X-ray phosphors.

2.2. Mercury

Mercury is a toxic element for living organisms and the environment (Clifton II, 2007). However, due to its physical and chemical properties, mercury is used in several applications, a common example being fluorescent lamps (Chang et al., 2009). One of the properties of mercury is the rapid increase in vapour pressure and concentration in air with an increase in temperature (Table 3) (OSHA, 1987). Because of this, one of the methods used to recover mercury from contaminated materials is thermal treatment. An alternative is a wet process, in which mercury is leached from the material using suitable leaching agents. The speciation of mercury e.g. elemental mercury and/or ionic species (Hg^{+}; Hg^{2+}), as well as other factors e.g. strong adsorption of mercury in the material, presence of moisture etc., strongly influence the type of suitable decontamination processes and, in the case of leaching, the choice of leaching agent. For fluorescent lamps, this aspect is further addressed in section 2.4.

Table 3 – Vapour pressure-saturation concentration of mercury at various temperatures (OSHA, 1987).

Temperature (°C)	*Vapour Pressure (Torr)*	*Mercury concentration in air (μg/m^3)*
0	0.000185	2.18
10	0.000490	5.88
20	0.001201	13.2
24	0.001691	18.3
28	0.002359	25.2
30	0.002777	29.5
32	0.003261	34.4
36	0.004471	46.6
40	0.006079	62.6

2.3. Fluorescent lamps

One of the applications of REEs is the production of phosphors – substances capable of luminescence (Cuif et al., 2005). Phosphors are used in products such as cathode ray tubes (CRTs), light emitting diode (LED) lamps, plasma display panels, field emission displays (large format and billboard displays), fluorescent lamps (general service fluorescent lamps, compact fluorescent lamps (CFLs), cold cathode fluorescent lamps), and electronic products that use LED or fluorescent lamp backlight illumination (flat screen televisions, computer screens, etc.).

In recent decades, fluorescent lamps have experienced increased usage due to the advantages compared to incandescent bulbs, political and marketing campaigns, and energy-related environmental considerations. Fluorescent lamps consume about 75% less energy to produce the same light output as an incandescent bulb and have up to ten times longer life expectancy (US Department of Energy, 2010).

A schematic representation of a typical fluorescent lamp and the principle of operation are presented in Figure 1. A glass tube, which can have different shapes and sizes, is filled with an inert gas e.g. argon. The inside of the glass is coated with a thin layer of phosphors powder. Mercury is a vital component in all fluorescent lamps and it is added in elemental form during manufacturing. Invisible ultraviolet (UV) photons are generated when mercury atoms interact with electrons emitted by the cathode. The phosphors absorb the UV energy, re-emitting it as visible light.

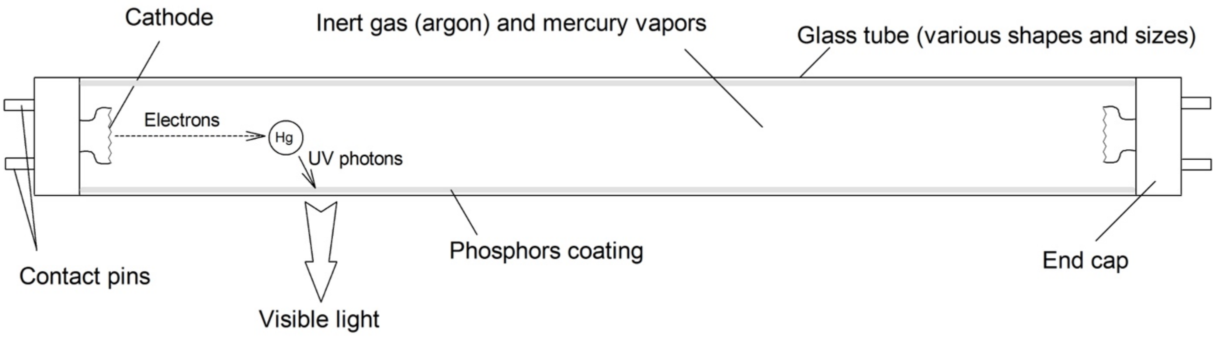


Figure 1 – Schematic representation and operation principle of a typical fluorescent lamp.

Modern fluorescent lamps use various mixes of red, green and blue REE-containing phosphors to produce the desired light output (Table 4) (Cuif et al., 2005; Ronda et al., 1998; Song et al., 2013; US Department of Energy, 2009). These lamps are known as *tri-phosphors* fluorescent lamps or *tri-band* lamps. Europium and yttrium account for the vast majority of the content of REEs in lamps, being present together in the red phosphor. Europium is also used in blue phosphors. All green phosphors contain terbium, alongside other REEs e.g. cerium, gadolinium and lanthanum.

Table 4 – Some of the REE-based phosphors used in fluorescent lamps (Cuif et al., 2005; Ronda et al., 1998; Song et al., 2013; US Department of Energy, 2009).

Phosphor type	*Possible compounds*	*Typical amount in tri-band lamps*
Red	$Y_2O_3:Eu^{3+}$ (YOX)*	55% (contains mostly yttrium; 4–10% europium)
Blue	$BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) $(Sr,Ca,Ba)_5(PO_4)_3Cl:Eu^{2+}$	10% (contains <5% europium)
Green	$CeMgAl_{10}O_{17}:Tb^{3+}$ $LaPO_4:Ce^{3+},Tb^{3+}$(LAP) $(Ce,Tb)MgAl_{11}O_{19}$ (CAT) $(Ce,Gd,Tb)MgB_5O_{10}$	35% (contains approx. 10% terbium)

* The colon symbol specifies doped compounds, in this case yttrium oxide doped with europium.

Typically, the phosphors powder accounts for 2% wt. of a typical 40 W fluorescent lamp, which is in the range of 4-6 g (Raposo et al., 2003). Rare earths-free phosphors are sometimes used, especially in cheaper lamps, and are regarded as impurities from a recycling point of view (Dupont and Binnemans, 2015). Halophosphors fall into this category e.g. $(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2:Sb^{3+},Mn^{2+}$.

The type of lamp, the manufacturer, and the year of manufacture influence the amounts of mercury in fluorescent lamps. The average mercury content in fluorescent lamps decreased from 48.2 mg in 1985 to 8.3 mg in 2001 (NEMA, 2005). At the beginning of this century the European Union set a limit of 5 mg mercury/CFL (The European Parliment and the Council of the European Union, 2003). Despite this, lamps containing mercury above this limit are still found on the market. Mercury contents in the range of 1.6-27 mg/lamp were quantified in 15 different types of CFLs, with 40% of the investigated samples failing to pass the aforementioned requirement (dos Santos et al., 2010). Unfortunately, mercury is required in fluorescent lighting and its replacement with a substitute with similar properties is not energy-feasible. Such a lamp would consume three times more energy to generate a similar light output as a mercury-based one (NEMA, 2005).

During lamp operation mercury is adsorbed mainly in the phosphor powder and in smaller amounts in the glass, end caps and electrodes (Dang et al., 1999; Doughty et al., 1995; Rey-Raap and Gallardo, 2012; Thaler et al., 1995). The concentration of mercury in the phosphors powder of end-of-life lamps can in some cases be 40-fold higher compared to the powder of new lamps of the same type (Raposo et al., 2003). It has been reported that 85% of the mercury in CFLs binds to the phosphor powder and about 13% to the glass (Rey-Raap and Gallardo, 2012). Elemental mercury (Hg^0), Hg^+ and Hg^{2+} species were measured in fluorescent lamp waste, with the first two species found to be predominant over divalent mercury (Raposo et al., 2003).

2.4. Industrial processing of fluorescent lamps

The presence of mercury classifies end-of-life fluorescent lamps as hazardous waste. Special collection and treatment to reduce the mercury content of the waste under a defined threshold is required under the legislation of many countries.

An initial processing step to separate various macro-fractions e.g. glass, aluminium end caps, phosphors, plastics, electronics etc., and to address mercury contamination is typically carried out by lamp processers (Binnemans et al., 2013). Linear fluorescent lamps can be processed using the end-cut method, in which the ends of the glass tubes are mechanically cut and the phosphors powder is blown out. The clear advantage is the recovery of relatively clean phosphors fractions, but this method is not able to handle a large number of lamps in a given time and it is not suited for lamps with more complex construction e.g. CFLs.

Another common practice, which overcomes these disadvantages, is crushing and shredding, followed by separation of macro-fractions using techniques such as dry/wet sieving or Eddy current separation. In this case, separation of clean phosphors is impossible to achieve due to very fine glass particles being generated during crushing. Glass can amount up to 50% wt. of the collected phosphors fractions (Binnemans et al., 2013). Other shredded lamp components e.g. plastics, electrode fragments etc. can also contaminate the collected phosphors.

Thermal treatment (distillation), chemical leaching and stabilization are the three options for handling mercury in fluorescent lamps (Durao et al., 2008). Distillation makes use of the rapid volatilization of mercury with increasing temperature (Table 3) and decomposition of mercury compounds to elemental mercury at elevated temperatures. High temperatures (800 °C) are needed for complete decontamination, however, due to the strong adsorption of mercury in the glass matrix (Raposo et al., 2003). The use of reducing agents, e.g. sodium borohydride and citric acid, can lower the temperatures needed for mercury desorption by up to 30% (Durao et al., 2008) but, despite this, distillation is an energy-intensive process. Moreover, special equipment is needed for this, e.g. perfectly sealed distillation units that operate under negative pressure in order to prevent the escape of mercury vapours (Chang et al., 2009). The method is not best applicable for waste obtained via wet-sieving processes due to the high amounts of moisture present in such streams (Binnemans et al., 2013). An alternative is hydrometallurgical processing, which involves the chemical leaching of mercury from the waste, followed by its further recovery from solution using selective adsorbents, electrochemical methods or solvent extraction. Strong oxidizing solutions, e.g. hypochlorite and nitric acid, are efficient for leaching mercury from the phosphors powder (Sobral et al., 2004).

Chemical stabilization can be used to contain elemental mercury by oxidation to yield more stable and less volatile Hg^+ and Hg^{2+} species. Although mercury is not completely removed from the stream, the method allows for safer storing and processing of fractions. Removal of mercury from the phosphors powder fractions is indicated for subsequent recovery of REEs, however, to prevent the spread of mercury in various process steps, e.g. leaching, solvent extraction, striping, refining etc. Stabilization via wet processes can affect the further treatment of fractions. Distillation of mercury becomes more complicated because of the moisture present in the material. Additional energy input will be required to evaporate water. Also, higher temperatures are needed for the desorption of the mercury compounds in higher oxidation states that form during chemical stabilization (Raposo et al., 2003). Because of these drawbacks, finding selective hydrometallurgical processes for mercury removal is important as an alternative to the thermal treatment of wet, stabilized, fluorescent lamp waste phosphors fractions.

2.5. Hydrometallurgical unit operations

When it comes to recovery and separation of individual REEs, hydrometallurgical processing is the method of choice. Low grade and chemically complex streams can effectively be processed using hydrometallurgy, leading to high purity products. Applications of pyrometallurgy in the processing of end-of-life products containing REEs typically leads to the accumulation of the REEs in the slag phases in low concentration, making their economic recovery more difficult (Binnemans et al., 2013).

Hydrometallurgical recovery of metals from solid streams requires two main steps:

- Leaching, in which the soluble fraction contained in a solid phase is removed as a solution. This step dissolves the metals of interest and, depending on conditions, other undesired constituents present in the material;
- Separation of the metals of interest from each other and/or from undesired elements present in solution using e.g. solvent extraction, ion exchange and/or precipitation.

Additional processing steps, e.g. pre-concentration of metal ions in solution, refining and purification of separated feeds, complement these two main steps. A simplified representation of a typical hydrometallurgical process for the separation of REEs is presented in Figure 2 (Tunsu et al., 2015).

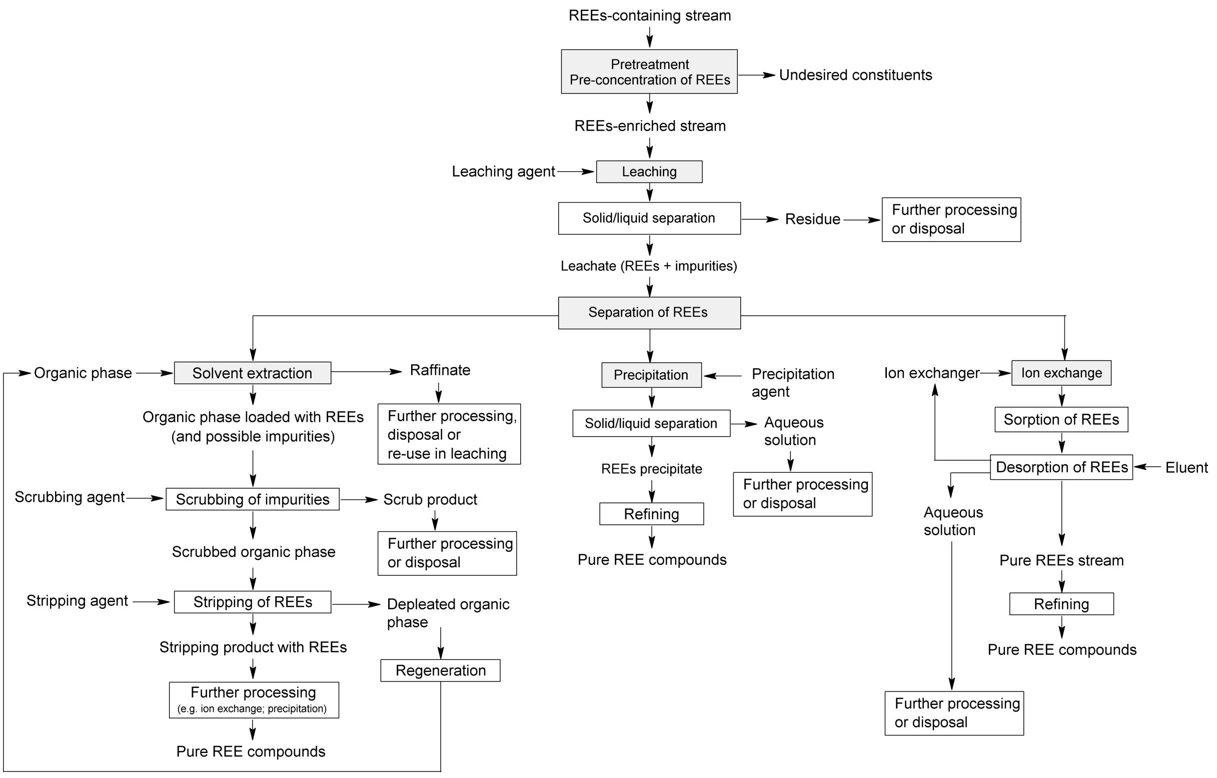

REEs-containing stream
Pretreatment
Pre-concentration of REEs
Undesired constituents
REEs-enriched stream
Leaching agent
Leaching
Solid/liquid separation
Residue
Further processing or disposal
Leachate (REEs + impurities)
Separation of REEs
Organic phase
Solvent extraction
Raffinate
Organic phase loaded with REEs (and possible impurities)
Further processing, disposal or re-use in leaching
Scrubbing agent
Scrubbing of impurities
Scrub product
Scrubbed organic phase
Further processing or disposal
Stripping agent
Stripping of REEs
Depleated organic phase
Stripping product with REEs
Regeneration
Further processing (e.g. ion exchange; precipitation)
Pure REE compounds
Precipitation
Precipitation agent
Solid/liquid separation
Aqueous solution
REEs precipitate
Further processing or disposal
Refining
Pure REE compounds
Ion exchanger
Ion exchange
Sorption of REEs
Desorption of REEs
Eluent
Aqueous solution
Pure REEs stream
Refining
Pure REE compounds
Further processing or disposal

Figure 2 – A simplified flowsheet based on pre-treatment, leaching, solvent extraction, ion exchange and precipitation for the separation of REEs from solid streams (Tunsu et al., 2015).

2.5.1. Leaching

Water, acid, base or salt solutions are used for leaching, depending on the solubility and the chemical form in which the metals of interest are present in the stream. The efficiency of the process is affected by leaching agent concentration, temperature, contact time, stirring, solid-to-liquid ratio and pre-treatment methods, e.g. crushing and grinding. The distribution of soluble compounds in the material, possible adsorption in the matrix, entrapment of soluble compounds in less soluble or insoluble particles, and slow reactions between the soluble constituents and the leaching agent affect the leaching kinetics (Rao, 2006). From an economical point of view, fast kinetics are desired, but slower kinetics can sometimes be beneficial, e.g. for selective leaching.

The choice of leaching agent is highly important as it influences not only the leaching process but also the further recovery of metals from solution. In a solvent extraction process the nature of the aqueous phase (the leachate) and the presence of certain ions in the system can limit the choice of organic solvents and affect the separation efficiency.

2.5.2. Solvent extraction

In a solvent extraction process the compounds of interest are partitioned between two immiscible liquid phases; an aqueous and an organic phase (Cox and Rydberg, 2004). A schematic representation of a solvent extraction process for REEs is presented in Figure 3.

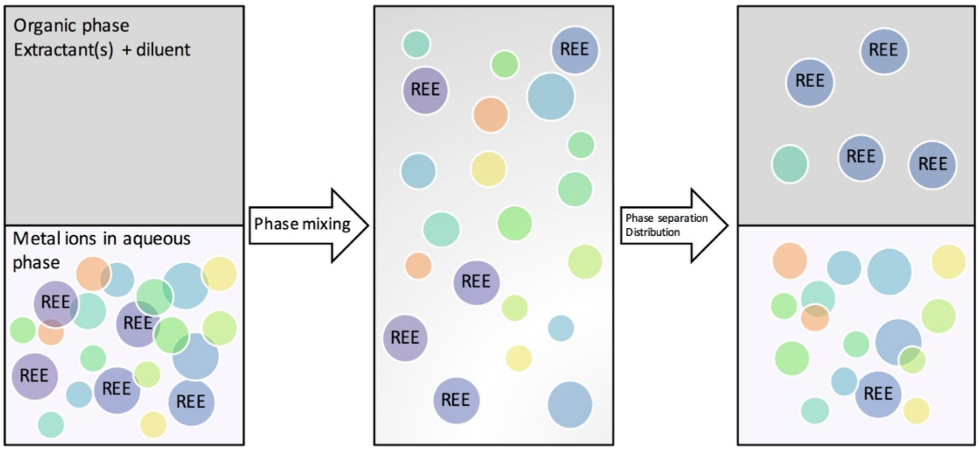


Figure 3 – Schematic representation of a solvent extraction process for REEs. The metals, initially present as soluble ions in an aqueous phase, are partitioned between the aforementioned aqueous phase and an organic phase containing one or more specific extractants dissolved in an adequate diluent.

The distribution ratio (D), defined as the ratio between the total concentration of an element in the organic phase and the total concentration of the same element in the aqueous phase, characterizes the extraction process (Equation 1).

$$D_A = \frac{[A]_{org}}{[A]_{aq}} \qquad (1)$$

The distribution ratio can be used to calculate the percentage extracted (Equation 2); and the separation factor, which characterizes the degree to which two solutes, *A* and *B*, can be separated (Equation 3).

$$\%E = \frac{100*D}{\frac{V_{aq}}{V_{org}}+D} \qquad (2),$$

where V_{org} and V_{aq} are the volumes of organic and aqueous phases, respectively.

$$\alpha_{A/B} = \frac{D_A}{D_B} \qquad (3)$$

The extracted metal ions are subsequently recovered by contacting the organic phase after extraction with a clean aqueous solution, called a stripping agent. The elements of interest will partition between these two phases; a process called stripping or back-extraction. Scrubbing (removal of unwanted co-extracted species) is carried out in a similar manner. A common practice to recover the REE ions in strip products is precipitation with oxalic acid, followed by thermal treatment of the obtained oxalates to produce oxides.

Five main extraction systems have been described (Cox, 2004):

- extraction of almost purely covalent inorganic compounds by non-solvating solvents.
- extraction of neutral coordinatively saturated complexes formed between metal ions and lipophilic organic acids (chelate extraction).
- extraction using solvating extractants, which replace the water of hydration in the complexes formed between the metal ions and the counter-ions present in the aqueous phase (solvate extraction).
- ion pair extraction (anion/cation exchange).
- extraction of metal complexes that do not fit into any of the previous categories (e.g. clathrate compounds).

For the extraction of REEs, chelating and solvating extractants play an important role.

The choice of diluent has an important role in the extraction process, affecting the distribution ratios and separation factors between metal ions extracted with different, or the same extraction mechanism. The extraction of a complex is a function of two steps (Löfström Engdahl et al., 2010):

- the collapsing of the cavity containing the complex in the aqueous phase, followed by the transfer from the aqueous phase;
- breaking the bonds between the water molecules that solvate the complex, followed by creation of a cavity in the organic phase and dissolving of the complex.

The diluent influences not only the attractive energies between the extracted species and the organic phase, but also the energy required for cavity formation.

2.5.2.1. Cyanex 923 extractant

Cyanex 923 is a commercially available solvating-type extractant. It has an average molecular weight of 348 g/mol and it is a mixture of four trialkylphosphine oxides (TRPO) (Table 5). (Dziwinski and Szymanowski, 1998).

Table 5 – Chemical composition of Cyanex 923 (Dziwinski and Szymanowski, 1998).

Compound	*General formula*	*Amount*
Trioctylphosphine oxide	R_3PO*	14%
Dioctylmonohexylphosphine oxide	$R_2R'PO$**	42%
Dihexylmonooctylphosphine oxide	RR'_2PO	31%
Trihexylphosphine oxide	$R_3'PO$	8%

*R denotes n-octyl: $CH_3–(CH_2)_7–$

**R' denotes n-hexyl: $CH_3– (CH_2)_5–$

The principle for the extraction of a metal ion with a solvating extractant is described by Equation 4 (Cox, 2004).

$$M^{z+}{}_{(aq)} + z\,X^{-}{}_{(aq)} + b\,B_{(org)} \leftrightarrow MX_zB_{b\,(org)} \qquad (4)$$

The metals in the aqueous phase (M^{z+}) form complexes with the counter-ions present (X^-). The remaining coordination sites are occupied by water. Due to their water content, these complexes have very low distribution coefficients. In the presence of a solvating extractant, the water molecules are replaced by the organic extractant molecules. More lipophilic complexes are formed, enhancing their extraction into the organic phase.

Three TRPO molecules were found to bind to lanthanides and yttrium in nitric acid media (Reddy et al., 1998) (Equation 5). Chloride complexes of mercury are also extracted by Cyanex 923 (Meera et al., 2001) (Equation 6).

$$M^{3+}{}_{(aq)} + 3\,NO_3^{-}{}_{(aq)} + 3\,TRPO_{(org)} \leftrightarrow M(NO_3)_3TRPO_{3\,(org)} \qquad (5)$$

$$Hg^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} + 3\,TRPO_{(org)} \leftrightarrow HgCl_2TRPO_{3\,(org)} \qquad (6)$$

2.5.2.2. Cyanex 572 extractant

Cyanex 572 is a novel phosphorus-based chelating extractant tailored for individual separation of REEs. Its exact composition has not been disclosed but it is mentioned to be a mixture of phosphinic and phosphonic acids (Cytec, 2014). The separation factors between adjacent elements are similar to those of phosphonic acids commonly used in REE separations e.g. EHEHPA, but extraction occurs at higher pH and stripping requires less concentrated acids. The extraction mechanism, as stated in the extractant sheet, is presented in Equation 7.

$$REE^{3+}{}_{(aq)} + 3HA_{(org)} \leftrightarrow REEA_{3\ (org)} + 3\ H^{+}{}_{(aq)} \qquad (7)$$

Usually, the mechanism is more complex, with the dimer form of the extractant being involved in the extraction (Equation 8; Xie et al., 2014).

$$REE^{3+}{}_{(aq)} + 3\ (HA)_{2\ (org)} \leftrightarrow REE(HA_2)_{3\ (org)} + 3\ H^{+}{}_{(aq)} \qquad (8),$$

where $(HA)_2$ is the dimer form of the extractant.

Since protons are involved in the equilibrium reaction, the distribution of metal ions between the aqueous and the organic phase will be pH-dependent. Equations 7 and 8 show that extraction of REEs is favoured by increases in pH in the aqueous phase. The opposite process (stripping) is favoured by decreases in pH, thus an increased acidity of the aqueous phase. Separation of REEs is achieved by controlling the equilibrium pH (pH_{eq}) during extraction.

2.6. Hydrometallurgical recovery of REEs from fluorescent lamps

A number of scientific studies directed towards the recovery of REEs from fluorescent lamps have been published and are presented below. Some of these address certain steps of hydrometallurgical processing e.g. leaching or testing of extractants, while others focus on combined leaching and/or solvent extraction to recover REEs. While some studies use real phosphors fractions collected from end-of-life lamps, part of the experimental work was also performed using pure commercial phosphors, carefully cleaned lamps that are broken under controlled conditions, and even artificial mixtures intended to simulate phosphors powder. Most studies do not use mercury-contaminated material as feed.

Due to the chemical structure of the REE phosphors used in fluorescent lighting (Table 4), efficient leaching requires the use of acidic solutions to bring the REEs into solution. The chemical processes for this can be written according to Equations 9-11.

Red phosphor: $Y_2O_3{:}Eu^{3+} + 6\ H^+ \rightarrow 2\ Y^{3+} + Eu^{3+} + 3\ H_2O$ (9)

Blue phosphor: $BaMgAl_{10}O_{17}{:}Eu^{2+} + 34\ H^+ \rightarrow Ba^{2+} + Mg^{2+} + 10\ Al^{3+} + Eu^{2+} + 17\ H_2O$ (10)

Green phosphor: $CeMgAl_{10}O_{17}{:}Tb^{3+} + 34\ H^+ \rightarrow Ce^{2+} + Mg^{2+} + 10\ Al^{3+} + Tb^{3+} + 17\ H_2O$ (11)

Acids will also leach other impurity metals in the stream, notably calcium (Equation 12).

$$(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2{:}Sb^{3+},Mn^{2+} + 18\ H^+ \rightarrow 10\ (Sr,Ca)^{2+} + 6\ H_3PO_4 + 2\ (Cl,F)^- + Sb^{3+} + Mn^{2+} \quad (12)$$

Separation of REEs, either as a group or individually, is carried out using solvent extraction. Precipitation with oxalic acid is also used to recover REEs, either directly from leachates or from the stripping products of solvent extraction (Equation 13). The latter approach leads to higher product purity due to co-precipitation of impurity metals with the REEs when the leachate is directly subjected to oxalic acid treatment.

$$2REE^{3+}_{(aq)} + 3C_2O_4{}^{2-}{}_{(aq)} \rightarrow REE_2(C_2O_4)_{3\ (s)} \quad (13)$$

Efficient leaching of all REEs in lamp phosphors is an energy- and reagent-intensive process, as has been reported by Zhang et al. (2013). Notably, the solubility of the LAP, CAT and BAM phosphors (Table 4) is low in acids at ambient conditions. A conversion step, similar to the one used for leaching of REEs from monazite ore, can be employed. Alkali fusion of these low-soluble REE phosphors can be carried out with sodium hydroxide at 800 °C. This will lead to more soluble europium, cerium and terbium oxides, according to Equations 14 and 15.

$$Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19} + NaOH + O_2 \rightarrow NaAlO_2 + MgO + CeO_2 + Tb_4O_7 + H_2O \quad (14)$$

$$BaMgAl_{10}O_{17}{:}Eu^{2+} + NaOH + O_2 + CO_2 \rightarrow NaAlO_2 + BaCO_3 + MgO + Eu_2O_3 + H_2O \quad (15)$$

A multi-step leaching process for fluorescent lamp waste has been described by Otto and Wojtalewicz-Kasprzak (2011). Dissolution of the halophosphors can be done with hydrochloric acid at ambient temperatures (<30 °C). Hydrochloric acid at 60-90 °C is then used to dissolve easily soluble REE phosphors such as YOX. Sulphuric acid at 120-230 °C is used to leach the REE phosphates. Alkali fusion with hydroxides, followed by acid leaching is finally carried out to dissolve the remaining REE compounds.

Sulphuric acid was suggested to reduce the amounts of calcium, barium and lead that leach together with the REEs from fluorescent lamp waste (De Michelis et al., 2011). This will form insoluble calcium, barium and lead sulphates but it has the disadvantage of co-precipitation of REEs. Direct precipitation of yttrium was carried out from the leachate using oxalic acid. Yttrium oxalates with purities in the range 90-95% were obtained. Reducing the amount of impurity metals (notably zinc and calcium) in sulphuric acid based leachates of lamp phosphors and mixtures of lamp-CRT phosphors was investigated with sodium sulphide, after a pH adjustment step with sodium hydroxide in the range 2-3 (Innocenzi et al., 2013). Significant losses of yttrium were reported during the pH adjustment step (78% for lamp phosphors leachate and 30% for the mixed phosphors leachate) due to the formation of amorphous compounds of calcium, silicon and yttrium. Yttrium losses were also reported for the sodium sulphide treatment step, with a maximum of 20% yttrium being co-precipitated in the lamp leachate.

Solvent extraction was applied for separation of pure commercial YOX, BAM and CAT phosphors in an aqueous phase consisting of potassium sodium tartrate and sodium carbonate (Mei et al., 2009). The extractant 2-thenoyltrifluoroacetone dissolved in heptane extracted BAM at alkaline pH. This is due to the chelating adsorption of 2-thenoyltrifluoroacetone with the Eu^{2+} ions, which makes the particles hydrophobic. CAT is extracted with chloroform containing added 1-pentanol, due to homo-aggregation.

A comparison between the extraction of REEs in lamp phosphors using tri-n-butyl phosphate (TBP) complexes with nitric acid and water at atmospheric pressure and under supercritical conditions (carbon dioxide) has been carried out (Shimizu et al., 2005). Testing at atmospheric pressure led to 37.4% extraction efficiency for yttrium, 36.8% for europium and <3% for lanthanum, cerium and terbium. Under supercritical conditions (15 MPa, 333 K) the extraction efficiencies for yttrium and europium were >99% while those for lanthanum, cerium and terbium were <7%.

Further investigations on the extraction of oxides of REEs used in fluorescent lamps using supercritical carbon dioxide modified with TBP-nitric acid adducts were carried out (Baek et al., 2016). Different types of adducts were prepared and characterized, and the phase-equilibrium behaviour for each adduct in supercritical carbon dioxide was studied. The water, acid and TBP contents of the adducts is very important for the extraction of REEs. More acidic adducts lead to excess acid and water that condensates, lowering the extraction efficiency of REEs. Best adducts are prepared from dehydrated nitric acid and TBP, ensuring minimum content of excess water and only enough acid to facilitate the formation of extractable REE nitrate complexes. Highest extraction efficiencies of selected REEs were achieved using a $TBP(HNO_3)_{1.7}(H_2O)_{0.6}$ adduct at 34.5 MPa and 338 K: >99% for yttrium and europium, 92.1% for terbium and only 0.12% for cerium.

Separation of europium, terbium and yttrium from nitric acid media with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP) in kerosene for applications in fluorescent lamp processing has been studied (Nakamura et al., 2007). Simulations in a counter-current mixer-settler cascade (15 extraction stages to separate yttrium from europium and terbium, followed by 10 extraction stages to separate europium from terbium) gave recoveries of 97.8% for yttrium, 58.1% for terbium and 52.8% for europium. The purities in this case were 98.1%, 85.7% and 100%, respectively.

Conversion of europium and yttrium in sulphuric acid leachates of lamp phosphors to thiocyanates, followed by extraction with trimethyl-benzylammonium chloride has been described (Rabah, 2008). The two REEs were extracted with >96% efficiency, followed by stripping with 1 M nitric acid, selective separation of the nitrates in ethanol, and hydrogen thermal reduction at 850 °C and 1575 °C to obtain metallic europium and yttrium, respectively. The separation factor between the two REEs was 9.4.

In recent years, ionic liquid extraction has received increased attention. These compounds are regarded as alternatives to conventional solvents due to negligible vapour pressure, flame resistance and the absence in their composition of elements such as phosphorous (Cevasco and Chiappe, 2014; Yang et al., 2013).

Selective and quantitative recovery of REEs from nitric and sulphuric acid leachates of lamp phosphors was achieved at pH 3 using N,N-dioctyldiglycol amic acid in the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Yang et al., 2013). The system showed drawbacks during stripping with sulphuric acid, with 1.4% of the ionic liquid being lost. A decline in extraction efficiency after five extraction cycles was also noted.

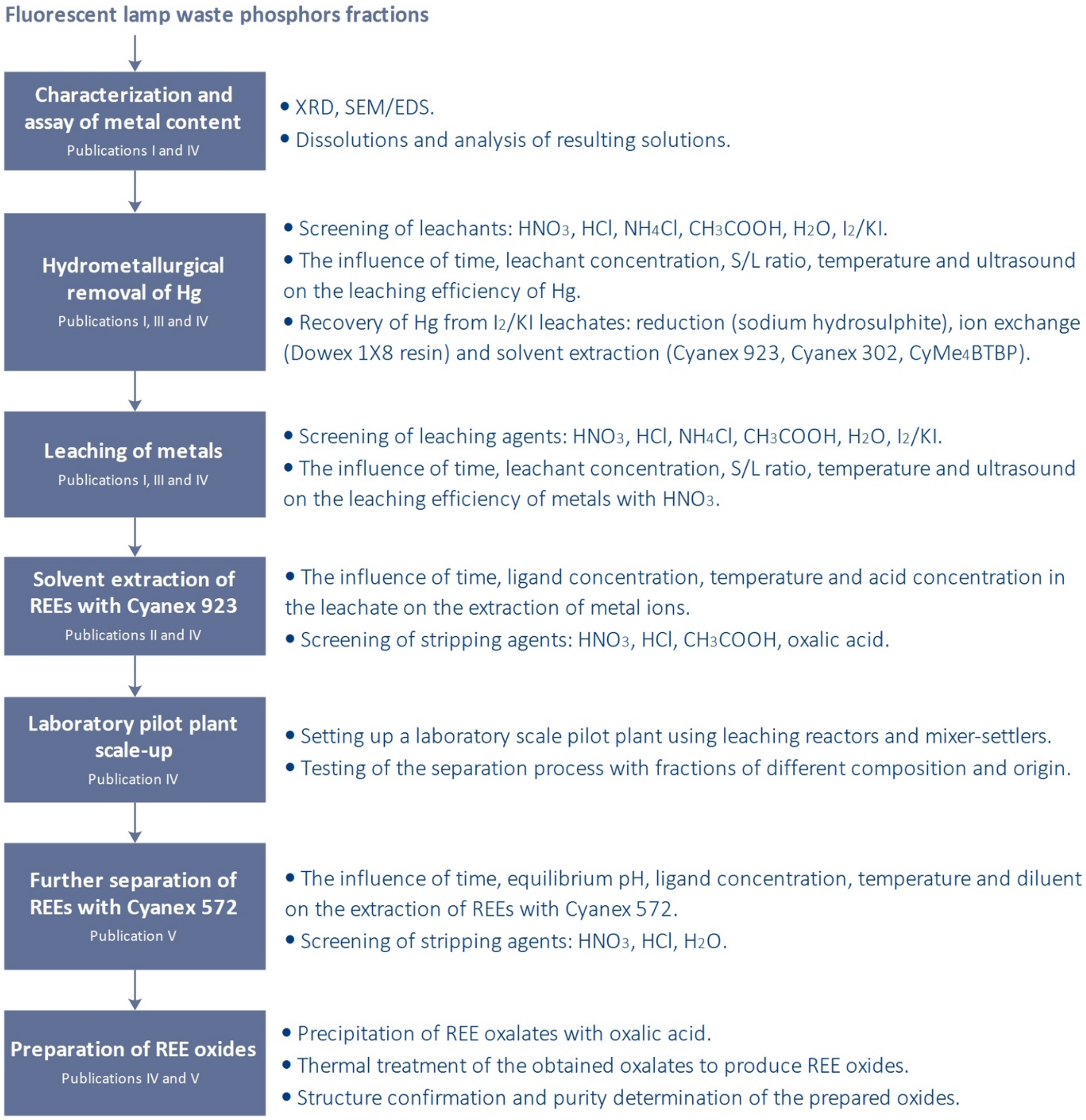
Applications of the ionic liquid betainium bis(trifluoromethylsulfonyl)imide on simulated fluorescent lamp phosphors powder showed that it is possible to separate YOX from BAM, LAP and halophosphors (Dupont and Binnemans, 2015). YOX is dissolved into the ionic liquid, from where it can be recovered by precipitation with oxalic acid.

Bifunctional ionic liquid extractants prepared from Aliquat 336, bis-2-ethylhexyl phosphoric acid (HDEHP) and HEHEHP were applied for the recovery of REEs from simulated tri-band phosphor powder (Yang et al., 2012). Their efficiency was better than HDEHP and TBP but lower Cyanex 923.

3. EXPERIMENTAL

3.1. Overview of the experimental work

The experimental work carried out is presented in Figure 4 and is based on the five publications stated in the *Publication list* at the beginning of the thesis.


Fluorescent lamp waste phosphors fractions
Characterization and assay of metal content
Publications I and IV

- XRD, SEM/EDS.
- Dissolutions and analysis of resulting solutions.

Hydrometallurgical removal of Hg
Publications I, III and IV

- Screening of leachants: HNO_3, HCl, NH_4Cl, CH_3COOH, H_2O, I_2/KI.
- The influence of time, leachant concentration, S/L ratio, temperature and ultrasound on the leaching efficiency of Hg.
- Recovery of Hg from I_2/KI leachates: reduction (sodium hydrosulphite), ion exchange (Dowex 1X8 resin) and solvent extraction (Cyanex 923, Cyanex 302, $CyMe_4BTBP$).

Leaching of metals
Publications I, III and IV

- Screening of leaching agents: HNO_3, HCl, NH_4Cl, CH_3COOH, H_2O, I_2/KI.
- The influence of time, leachant concentration, S/L ratio, temperature and ultrasound on the leaching efficiency of metals with HNO_3.

Solvent extraction of REEs with Cyanex 923
Publications II and IV

- The influence of time, ligand concentration, temperature and acid concentration in the leachate on the extraction of metal ions.
- Screening of stripping agents: HNO_3, HCl, CH_3COOH, oxalic acid.

Laboratory pilot plant scale-up
Publication IV

- Setting up a laboratory scale pilot plant using leaching reactors and mixer-settlers.
- Testing of the separation process with fractions of different composition and origin.

Further separation of REEs with Cyanex 572
Publication V

- The influence of time, equilibrium pH, ligand concentration, temperature and diluent on the extraction of REEs with Cyanex 572.
- Screening of stripping agents: HNO_3, HCl, H_2O.

Preparation of REE oxides
Publications IV and V

- Precipitation of REE oxalates with oxalic acid.
- Thermal treatment of the obtained oxalates to produce REE oxides.
- Structure confirmation and purity determination of the prepared oxides.

Figure 4 – A simplified overview of the experimental work presented in this thesis.

The investigations were grouped into seven blocks:

- Characterization of the waste fractions (Publications I and IV).
- Hydrometallurgical removal of mercury (Publications I, III and IV).
- Bench scale leaching of REEs and other metals in the samples (Publications I, III and IV).

- Group batch extraction of REEs with Cyanex 923 (Publications II and IV).
- Testing of the leaching and separation processes at laboratory pilot scale (Publication IV).
- Further separation of individual REEs with Cyanex 572 (Publication V).
- Preparation of REE oxides using oxalic acid precipitation followed by thermal treatment of obtained oxalates (Publications IV and V).

Details about the experimental parameters are given in each respective publication and in each figure and table caption in this thesis. A short summary of the work done in each block is presented in the following subsections.

3.2. General information about the fluorescent lamp waste fractions used

Various real fluorescent lamp waste fractions that contain phosphors were used in the experiments. Details regarding the type and origin of the investigated fractions are given in Publications I and IV and are summarized in Table 6.

Table 6 – Types of fluorescent lamp waste fractions investigated.

Sample origin (type of process)	*Additional details about the process generating the sample*	*Sample characteristics*	*Publication no. investigating the sample**	*Sample name used in the publication*	*Sample name used in this thesis*
Wet process	Crushing of large batches of various types of lamps under controlled conditions, followed by (partial) separation of macro-fractions e.g. metals, glass etc. Mercury is stabilized using hypochlorite oxidation.	Wet sludge that is mercury-contaminated. Contains glass as major impurity, fibres and other non-soluble fractions. Various fractions of this type, with different REEs, glass and moisture content were investigated.	I	-	IV, V
			II	-	IV
			III	-	IV
			IV	III	III
Wet process	Water-based process for treatment of end-of-life fluorescent lamps. The resulting phosphors fraction was thermally treated to remove mercury.	Dry, fine powder that does not contain mercury. Contains approx. 50% wt. glass and other non-soluble fractions.	IV	II	II
Dry process	No details provided by the supplier.	Mix of phosphors from new lamps and production waste. Dry, fine powder that is mercury-contaminated. Contains approx. 40% wt. glass and other non-soluble fractions.	IV	I	I

* according to the publication list presented at the beginning of the thesis.

Emphasis was placed on studying waste samples originating from wet processes, in which mercury was stabilized using oxidative reagents and is still present in the streams. This is because of the processing challenges associated with this type of waste, as previously mentioned in section 2.4. Drying of the material was carried out at ambient conditions in order to determine the moisture content and to facilitate parts of the investigations. Homogenization of the samples was performed by thorough mixing. Some of the investigated samples are presented in Figure 5.

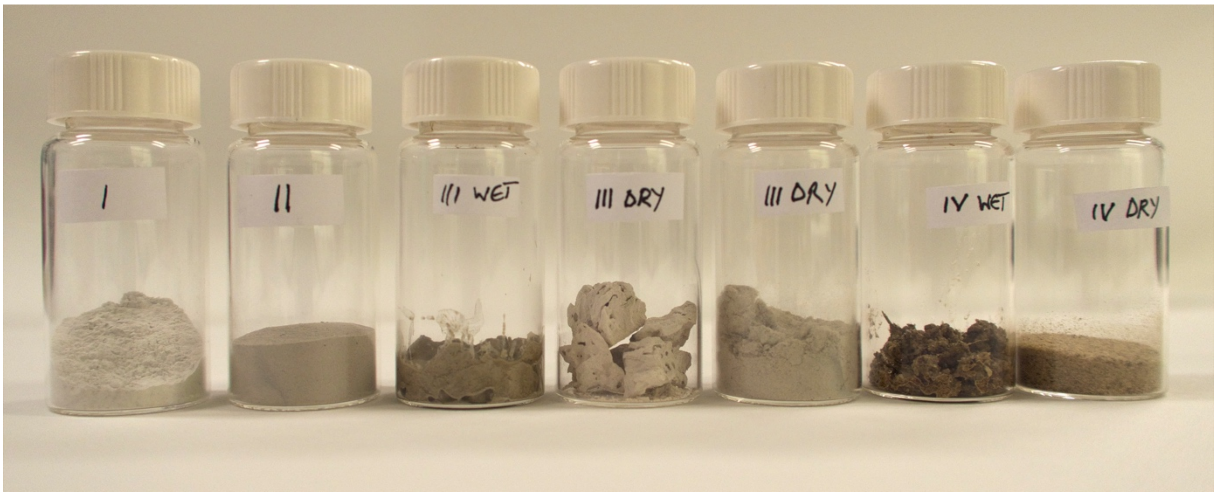


Figure 5 – Samples used in the present study. Additional details for each sample are provided in Table 6.

3.3. Chemicals and techniques

The inorganic reagents used were of analytical grade purity or higher. All inorganic solutions were prepared using pure water (MilliQ, Millipore, >18 MΩ/cm). Pure water was also used in some experiments as leaching agent, stripping agent and to wash residues after leaching. The investigations were carried out at ambient conditions (usually approx. 21 °C), with the exception of the experiments that addressed the influence of temperature. All organic solvents (extractants and diluents) were used as supplied by the manufacturer, with no additional purification. Dilutions of the inorganic aliquots collected for analysis were made using 0.5-1 M nitric acid solution, prepared from concentrated stock solution (65%, Suprapur, Merck) and pure water. Where needed, solutions were filtered using either polypropylene syringe filters (0.45 µm, VWR) and syringes, or glass fibre filters.

Phase mixing for solvent extraction batch experiments using volumes <10 mL was performed in glass vials secured with lids. The vials were placed in a closed thermostatic sample holder connected to a cooling/heating water bath and fixed to a shaking machine (IKA Vibrax VXR Basic) set at >1500 vibrations per minute (vpm). For larger volumes, phase mixing was performed in separation funnels using manual shaking. Kinetic experiments were initially carried out to estimate the phase contact time required for equilibrium. Generally, after phase mixing, the samples were centrifuged to ensure complete phase separation.

Most investigations were made in triplicate tests in order to account for uncertainties and material inhomogeneity.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (iCAP 6500, Thermo Fischer) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (iCAP Q, Thermo Fischer) were used to obtain qualitative and quantitative elemental information.

3.4. Characterization of waste fractions

Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) (FEI Quanta 200F/Oxford Inca 300 EDS System) was used to magnify the samples investigated, to obtain qualitative data and to determine the occurrence and distribution of the components. X-Ray Diffraction (XRD) (Siemens Diffraktometer D5000) was used to obtain structural information about the major components. Additional information about these techniques is provided in Appendix 1.

To determine the soluble metals content in the waste, as well as in the residues collected during leaching, dissolution of the material in aqua regia (3:1 mixture of concentrated hydrochloric and nitric acid) at elevated temperature was carried out, followed by analysis of the obtained solutions using ICP-OES. Aqua regia dissolution was determined to be among the best methods for elemental analysis of fluorescent lamp shredder waste (Hobohm et al., 2016). This method showed highest leaching values for REEs among different reagent mixtures, including nitric/perchloric/hydrofluoric acid mixture, various mixtures of nitric and hydrochloric acids, sulphuric and hydrochloric acids, nitric acid and hydrogen peroxide, nitric acid only, and hydrochloric acid only. The only REE for which dissolution was favoured by another leaching system was terbium, which was leached in slightly higher amounts (+14%) by a sulphuric:hydrochloric acid mixture (5:1.5 volumetric ratio). However, at the same time, this latter system led to poor dissolution of elements such as mercury, lead, iron, aluminium and others. The formation of insoluble sulphates accounts for some of these poor leaching results.

3.5. Hydrometallurgical removal of mercury

Water, ammonium chloride, nitric, hydrochloric and acetic acid (Publication I), as well as iodine in potassium iodide (I_2/KI) solutions (Publications III and IV) have been investigated as possible leaching agents for mercury. The influence of parameters such as leaching time, leaching agent concentration, solid to liquid (S/L) ratio and temperature on the leaching efficiency of mercury has been studied, notably for the nitric acid and I_2/KI systems. Since the latter showed selectivity for mercury, possible recovery routes for mercury in I_2/KI lamp waste leachates were investigated: reduction with sodium hydrosulphite, ion exchange with Dowex 1X8 resin, and solvent extraction with Cyanex 923, bis(2,4,4-trimethyl-pentyl) monothiophosphinic acid (Cyanex 302) and 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo-[1,2,4-]triazin-3-yl)-[2,20]bipyridine ($CyMe_4BTBP$).

3.6. Leaching of metals

The leaching behaviour of metals in the waste was studied using various solutions: water, ammonium chloride, nitric, hydrochloric and acetic acid (Publications I and IV), and I_2/KI (Publication III). Various parameters were investigated, the emphasis being placed on the nitric acid system e.g. leaching time (up to 96 h), leaching agent concentration (0.5-4 M), S/L ratio (10-30% w/v), temperature (20 °C, 60 °C) and ultrasound. The focus was the six REEs present in the samples but attention was also paid to leaching of impurity metals, with the goal of developing a selective leaching process (Publication IV). After leaching of mercury with I_2/KI solution, the resulting residue was washed and further leached with 1 M nitric acid solution at ambient conditions using short contact times (0-60 min). A 10 min leaching time was deemed sufficient to remove a large amount of impurity metals, notably calcium. Subsequent leaching, carried out with 2 M nitric acid at ambient conditions, was used for up to 30 h to study the dissolution of REEs. Most of the yttrium and europium in the waste was dissolved within 24 h, alongside traces of cerium, lanthanum, gadolinium and terbium. The bulk of these last four REEs was left in the final residue, together with other low soluble/insoluble components e.g. alumina and glass.

3.7. Solvent extraction of REEs with Cyanex 923

Batch extraction of metal ions in nitric acid-based leachates of fluorescent lamp waste with Cyanex 923 dissolved in Solvent 70, a commercial kerosene with low aromatic content, was extensively studied in Publication II. The investigations targeted the influence of various parameters on the extraction e.g. time (0-20 min), ligand concentration in the organic phase (0.24-2.35 M), acid concentration in the aqueous phase (0.005-4.1 M) and temperature (23-60 °C). Stripping of the metal ions extracted was carried out with nitric (0.1-4 M), hydrochloric (0.1-4 M), acetic (25% vol.) and oxalic acid (0.5 M) solutions.

3.8. Testing of the process in laboratory pilot scale

The leaching and solvent extraction process with Cyanex 923 was further tested in laboratory pilot scale using batches of 0.5 kg waste, as described in Publication IV. Mercury-contaminated fractions and fractions that were thermally decontaminated were tested. Leaching was tested in 5 L leaching reactors with propeller stirring set at 400 revolutions per minute (rpm). Mercury in the contaminated waste was leached with 0.025/0.075 M I_2/KI solution for 4.5 h, using a S/L ratio of 25% w/v. Leaching of impurity metals, and the bulk of RREs, with nitric acid was studied as a one step process (22 h), as well as a two-step selective leaching process (10 min, followed by 22 h), using S/L ratios of 10% w/v. Extraction of REE ions in the obtained leachates was done in a counter-current mixer settler-system comprised of three extraction chambers and four stripping chambers (120 mL each; polyvinylidene difluoride construction) (Figure 6).

Additional information about mixer-settlers is provided in Appendix 2. The organic:aqueous (O:A) phase ratio used for both extraction and stripping was 2:1. The flow rates for the aqueous and organic feeds were 2.5 and 5 mL/min, respectively, and the mixing speed in the mixing chambers was 700 rpm. Extraction was studied with 35% and 50% vol. Cyanex 923 in Solvent 70. Stripping was studied using 2 M and 4 M hydrochloric acid solutions.

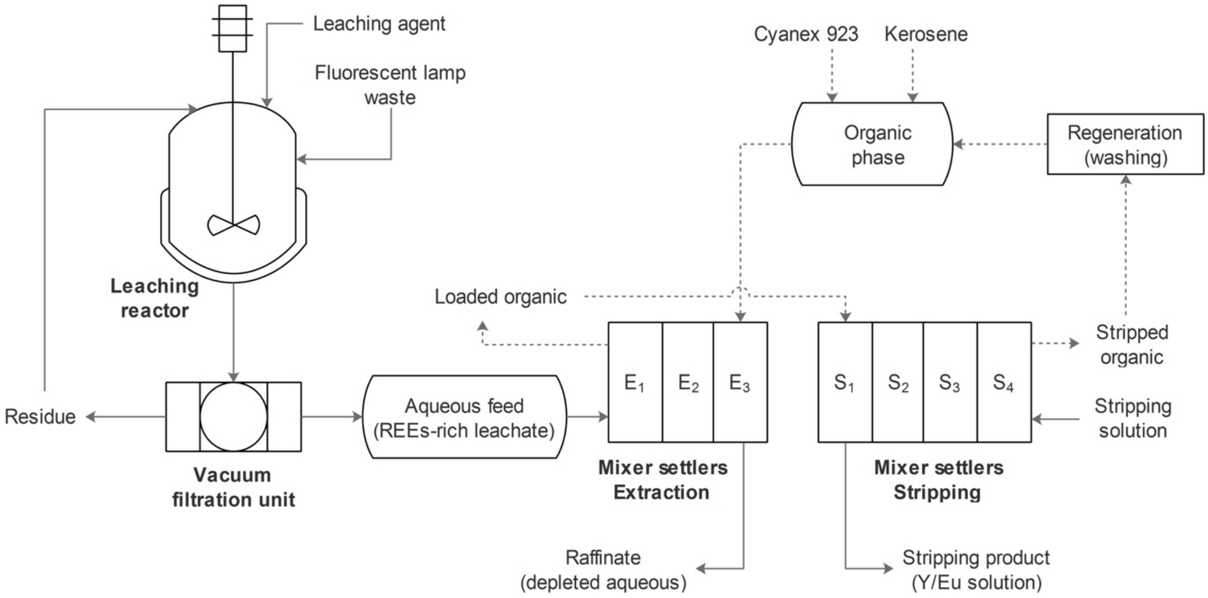

Leaching agent
Fluorescent lamp waste
Leaching reactor
Residue
Vacuum filtration unit
Aqueous feed (REEs-rich leachate)
Cyanex 923
Kerosene
Organic phase
Regeneration (washing)
Loaded organic
E1
E2
E3
S1
S2
S3
S4
Stripped organic
Stripping solution
Mixer settlers Extraction
Mixer settlers Stripping
Raffinate (depleted aqueous)
Stripping product (Y/Eu solution)

Figure 6 – Laboratory pilot scale setup for the separation of REEs from fluorescent lamp waste fractions. The dashed lines represent the flow of organic streams.

3.9. Further separation of REEs with Cyanex 572

Further separation of the REEs in the stripping products collected after the solvent extraction with Cyanex 923 in mixer settlers was carried out with Cyanex 572 (Publication V). The focus was the separation of yttrium and europium, the bulk REEs in solution. The effects of various parameters were studied; phase contact time (0–30 min), equilibrium pH (pH_{eq}= -0.35–1.15), ligand concentration (0.75-2 M), diluent (long chain alcohols, aliphatic and aromatic diluents) and temperature (25-65 °C). Stripping was investigated with water and hydrochloric and nitric acid solutions (0.1-6 M). Separation of yttrium was carried out on a larger scale in ten successive batch extraction stages with 1 M Cyanex 572 in Solvent 70 at pH_{eq} = 0 using a O:A phase ratio of 1. Europium was subsequently extracted in one stage at pH_{eq} = 1. Stripping of the extracted metal ions from their respective organic phases was carried out in one stage with 3 M hydrochloric acid using a O:A phase ratio of 1.

3.10. Preparation of REE oxides

The REEs in the various strip products after solvent extraction with Cyanex 923 and Cyanex 572 were precipitated by addition of oxalic acid (Publications IV and V). The precipitates were washed with pure water and dried at ambient temperature. The oxalates were heated for two hours at 800 °C in an oven, in air atmosphere. The structure of the formed compounds was determined using XRD. The purity of the compounds was determined by dissolutions into concentrated nitric acid (65%, Suprapur, Merck), followed by analysis of the obtained solutions with ICP-OES and ICP-MS.

4. RESULTS AND DISCUSSIONS

4.1. Characterization of waste fractions

All samples contained a significant amount of glass and other non-soluble fractions that were generated during lamp crushing. Even for some of the fractions rich in REEs the content of such impurities reached 40-50% dry wt. Glass accounted for the vast majority of the impurities. Metallic (aluminium end caps, electrode remains) and plastic parts and even packaging residues (small carton pieces) were observed in coarser fractions like the one studied in Publication I. The glass particles varied greatly in size, ranging from over 1000 µm (in coarse fractions) to less than 25 µm. Sieving of the more REE-concentrated fractions through meshes of different size showed that the bulk of the material (up to 83 % dry wt.) consists of particles <25 µm. The phosphors particles are also concentrated in this fraction, making isolation of the fluorescent powder inefficient using simple fractionation techniques.

SEM/EDS imaging showed that the phosphors particles vary in size. They can be smaller than 2 µm and have a tendency to form larger aggregates consisting of multiple small particles (Figure 7).

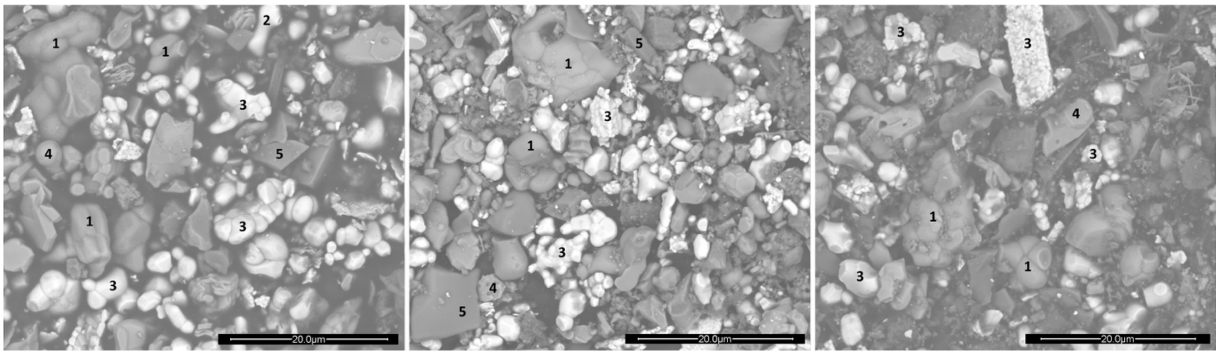


Figure 7 – SEM magnification of three samples (5000 x), as presented in Publication IV. From left to right: samples I, II and III, respectively (referenced in Table 6 in this thesis). Particle numbers are indicated as follows: 1 – calcium halophosphate, 2 – LAP, 3 – YOX, 4 – CAT, and 5 – glass.

For one of the fractions that had been thermally treated to remove mercury (sample II), the presence of such aggregates was lower compared to non-heated samples. Also, the thermal treatment resulted in cracking of some phosphor particles. Not surprisingly, this was shown to affect the leaching behaviour, leading to a slightly increased leaching efficiency of metals due to larger surface area contact with the solution. Yttrium was found to co-exist with europium in distinct particles as YOX but europium was also found independent of yttrium. Halophosphor, LAP and CAT particles were also detected. Mercury was found spread throughout the material, being present in the phosphors and on glass particles. This confirms its absorption onto lamp components during usage of the lamp, a phenomenon discussed in several publications (Dang et al., 1999; Doughty et al., 1995; Raposo et al., 2003; Thaler et al., 1995).

The soluble metal content in the various fractions investigated is presented in Table 7.

Table 7 - Soluble content for several metals in the dried waste fractions, determined using aqua regia digestion at elevated temperature, followed by measurements of the obtained solutions using ICP-OES. Compiled data from Publications I and IV. The error represents the standard deviation of three sample replicates; nd = not detected.

Element		*Unit*	*Sample number (according to Table 6) and metal content*				
			I	*II*	*III*	*IV**	*V***
REEs	Eu	g/kg	10.5 ± 0.3	10.8 ± 0.3	10.9 ± 0.3	0.4 ± 0.03	4.7 ± 0.2
	Y		164.7 ± 3.3	162.3 ± 3.9	174.7 ± 2.1	6.8 ± 0.3	94.8 ± 4.6
	Ce	mg/kg	700 ± 28	678 ± 44	1060 ± 61	382 ± 23	2015 ± 145
	Gd		766 ± 10	978 ± 35	2043 ± 68	244 ± 17	1937 ± 81
	La		773 ± 46	609 ± 68	412 ± 64	339 ± 25	1400 ± 215
	Tb		427 ± 16	416 ± 22	661 ± 32	158 ± 10	904 ± 44
Others	Al	g/kg	7.5 ± 0.1	7.7 ± 0.3	9.3 ± 0.2	1.1 ± 0.1	14.3 ± 0.7
	Ba		4.7 ± 0.2	4.5 ± 0.1	7.1 ± 0.6	2.3 ± 0.2	10.5 ± 0.4
	Ca		135.0 ± 3.9	87.8 ± 0.7	93.1 ± 1.8	70.0 ± 1.8	88.3 ± 5.4
	Fe		4.5 ± 0.1	7.2 ± 0.1	6.0 ± 0.3	3.3 ± 0.4	5.2 ± 0.4
	Mg		2.8	1.1	2.5	2.1 ± 0.1	2.0 ± 0.1
	Mn		4.4 ± 0.2	3.3 ± 0.1	3.5 ± 0.1	0.8 ± 0.1	3.1 ± 0.2
	Na		1.7	2.3	2.4 ± 0.1		
	Sb		1.6	1.2	1.1		
	Sr		1.8 ± 0.1	3.1 ± 0.1	4.8		
	B	mg/kg	466 ± 10	1531 ± 19	2462± 71		
	Cd		253 ± 9	40	207 ± 5	40 ± 2	274 ± 16
	Cr		56 ± 2	36 ± 2	57 ± 1	25 ± 21	30 ± 2
	Cu		70 ± 3	220 ± 4	359 ± 9	513 ± 61	548 ± 38
	Hg		112 ± 2	nd	227 ± 5	724 ± 70	367 ± 26
	K		490 ± 18	619 ± 20	600 ± 17	508 ± 3	946 ± 43
	Mo		nd	61 ± 1	37 ± 1	148 ± 7	263 ± 19
	Ni		39 ± 1	133 ± 3	236 ± 4	159 ± 168	181 ± 16
	Pb		137 ± 5	310 ± 7	548 ± 13	344 ± 91	743 ± 41
	Si		445 ± 17	268 ± 8	134 ± 6		
	Sn		11 ± 1	43 ± 1	203 ± 3	83 ± 20	227 ± 18
	Ti		472 ± 13	468 ± 4	489 ± 6		
	W		136 ± 19	435 ± 17	441 ± 8	666 ± 33	905 ± 69
	Zn		409 ± 15	193 ± 12	1299 ± 41	1234 ± 114	1690 ± 117
	Zr		7 ± 1	20 ± 1	20 ± 1		

* Coarse fraction containing large amounts of glass and other impurities.

** Fraction derived from sample IV, after partial separation of impurities (sieving).

Yttrium was the dominant REE in all samples, followed by europium. In the REE-rich fractions e.g. samples I-III, these two elements accounted for approx. 98% of all REEs in the streams. The other four REEs, cerium, lanthanum, gadolinium and terbium, were also detected. Among these, only terbium and possibly gadolinium are regarded as having potential recovery importance. This is because cerium and lanthanum are typically obtained in sufficient quantities during the processing of ores containing heavy REEs and are not regarded as being critical (USEPA, 2012). The cost, energy demand and environmental burdens of alkali conversion to facilitate the effective dissolution of cerium, lanthanum, gadolinium and terbium, coupled with their separation and purification costs, directed attention in this study towards the recovery of yttrium and europium alone. Nonetheless, the leaching and extraction behaviours of these other four REEs were also studied alongside yttrium and europium and are also reported.

The XRD analysis confirmed the presence of yttrium and europium as yttrium europium oxide. These observations were in agreement with already published data on the status of REEs contained in spent fluorescent lamp waste (Belardi et al., 2014). Similar XRD patterns were noted between the different samples, suggesting that the initial treatment, either thermal or wet, does not alter the crystal structure of the major components.

Other impurity metals were detected in the samples. These originate from the phosphors (Table 4), remaining electrode material, end caps, electronic board fragments generated during crushing etc. Calcium is the impurity metal that is present in the largest amounts, being a major component of halophosphors. Other notable impurity metals were aluminium, barium and iron.

4.2. Hydrometallurgical removal of mercury

Leaching of mercury was studied with water, ammonium chloride, nitric, hydrochloric and acetic acid (Publication I) and I_2/KI solutions (Publications III and IV). Water gave the poorest leaching efficiency, with 0.3 ± 0.1% of the mercury being leached during 168 h from sample IV (Figure 8).

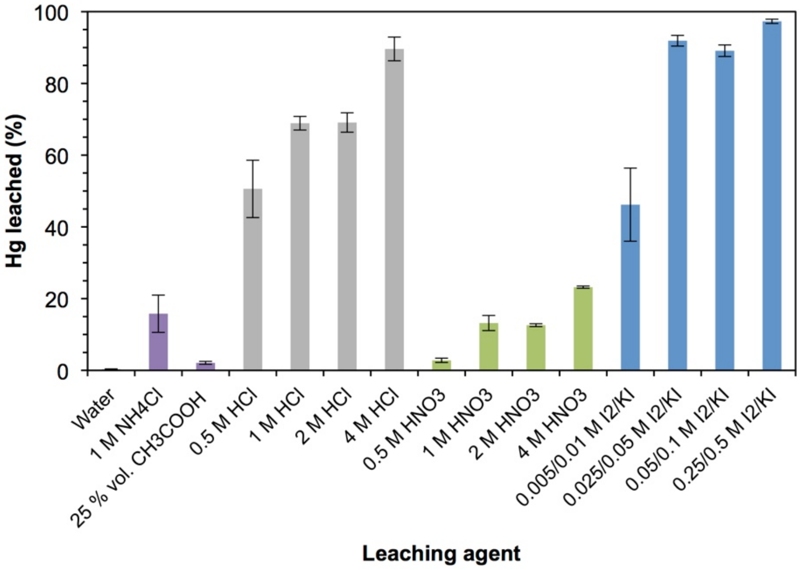


Figure 8 – Comparisons between the leaching efficiencies for mercury from sample IV using various leaching agents, as described in Publication III. Leaching conditions for water, ammonium chloride, acetic, hydrochloric and nitric acid solutions: 20 ± 1 °C, 168 h, S/L ratio of 10% w/v, magnetic stirring 200 ± 50 rpm. Leaching conditions for I_2/KI solutions: 21 °C, 2 h leaching time, S/L ratio of 10% w/v, magnetic stirring 300 rpm. The error represents the standard deviation of a triplicate test.

Under similar conditions, 2.1 ± 0.4% of the mercury was leached with 25% vol. acetic acid, and 15.8 ± 5.2% with 1 M ammonium chloride. This indicates the presence of mercury as compounds with low water solubility e.g. elemental mercury, oxides, mercury (I) chloride etc. and/or strong absorption in the glass and phosphorus powder. Nitric and hydrochloric acid solutions led to better leaching efficiencies, most notably for the latter (Figure 8).

Increased acid concentration and increased temperature/ultrasound improved the efficiency of the process, as described in Publication I. The main issue is that these acidic solutions will also leach the REEs, notably yttrium and europium, as further discussed in section 4.3. Therefore, a selective leaching agent for mercury is desired in order to prevent the contamination of subsequent REE-containing streams. Iodine in potassium iodide was found to have very good selectivity for mercury, with almost no REEs being leached alongside. Leaching of calcium and antimony was also under 1%. No leaching of aluminium, cadmium, chromium, iron, lead, tin or zinc was noticed. Only low amounts of barium, copper, magnesium and nickel (each under 2% of their initial content) were dissolved.

Leaching of mercury with I_2/KI occurs via two main chemical processes (Foust, 1993):

- oxidation of mercury and its compounds to divalent mercury (Hg^{2+});
- reaction of the previously oxidized species with the iodide ions (I^-) to form HgI_4^{2-} ions.

The very strong complexes formed by the divalent mercury ions with iodide ions ($\beta_4=5.6 \times 10^{29}$) and the high solubility of the HgI_4^{2-} ion (Clever et al., 1985) leads to the efficient mobilization of mercury from the matrix. Leaching of elemental mercury, mercuric sulphide, mercuric oxide and adsorbed mercury occurs according to Equations 16-19 (Mattigod et al., 2009).

$$Hg + I_2 + 2\,I^- \rightarrow HgI_4^{2-} \tag{16}$$

$$HgS + 4\,I_2 + 3\,H_2O \rightarrow HgI_4^{2-} + SO_4^{2-} + 6\,H^+ + 4\,I^- \tag{17}$$

$$HgO + 4\,I^- + 2\,H^+ \rightarrow HgI_4^{2-} + H_2O \tag{18}$$

$$Hg\text{-}X_{2\,(s)} + 2\,K^+ + 4\,I^- \rightarrow 2\,KX + HgI_4^{2-} \tag{19}$$

The leaching efficiency of mercury was found to increase with increased I_2/KI concentrations (Figure 8) and a 0.025/0.05 M solution was enough to achieve removal of more than 90% of the mercury. Complete decontamination was not achieved, possibly due to very strong adsorption of mercury in the glass cullet (Jang et al., 2005). The leaching behaviour of mercury over time is presented in Figure 9, suggesting a minimum leaching time of two hours for this type of waste under the tested conditions.

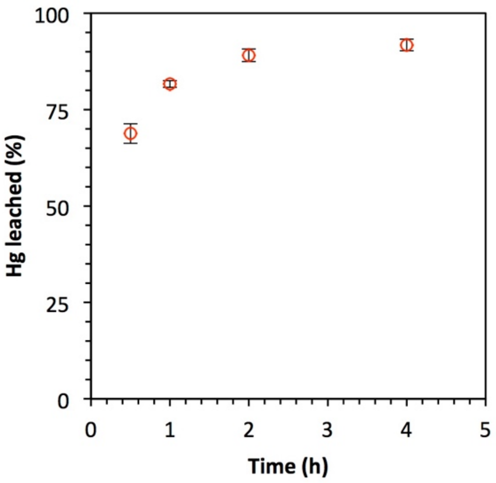


Figure 9 – Leaching behaviour of mercury from sample IV using 0.05/0.1 M I_2/KI solution, according to Publication IV (21 °C, up to 4 h leaching time, S/L ratio of 10% w/v, 300 rpm magnetic stirring). The uncertainty bars represent the standard deviation of a triplicate test.

Increases of the S/L ratio led to slight decreases in leaching efficiency (Figure 10).

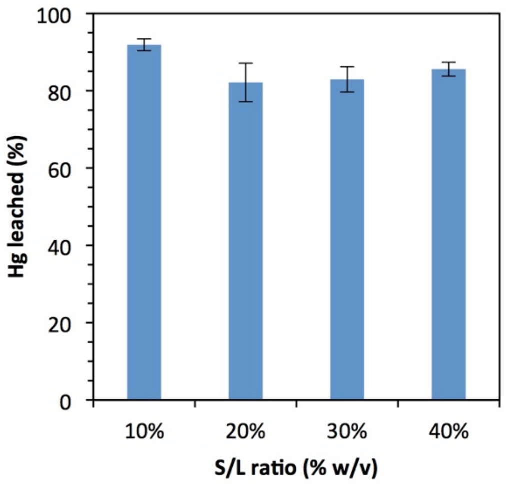


Figure 10 – Leached percentages of mercury from sample IV using 0.025/0.05 M I_2/KI solution and different S/L ratios, according to Publication IV (21°C, 2 h leaching time, 300 rpm magnetic stirring). The uncertainty bars represent the standard deviation of a triplicate test.

Due to the oxidizing nature of the solution, thiol-based adsorbents are not suited to the recovery of mercury in the leachate, due to oxidation to disulphide (Equation 20).

$$2\ \text{-SH} \rightarrow \text{-S-S-} + 2\ H^+ \qquad (20)$$

Anionic exchange using Dowex 1X8 resin (chloride form) led to complete removal of mercury from solution. The iodine dissolved in potassium iodide, present as a tri-iodide species (Equation 21) (Mattigod et al., 2009), was removed alongside (Figure 11).

$$I_2 + I^- = I_3^- \tag{21}$$

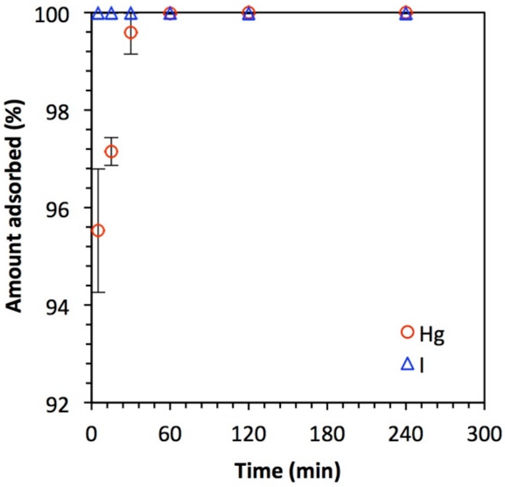


Figure 11 – Kinetics for removal of mercury and iodine from I_2/KI based leachates using Dowex 1X8 resin (chloride form), as presented in Publication III. The initial mercury content in solution was 24.5 mg/L. 25 mL of leachate was treated with 2.5 g Dowex 1X8 resin for up to 4 h at 21 °C, under magnetic stirring (500 rpm). The uncertainty bars represent the standard deviation of a triplicate test.

This prevents the reuse of the resulting solution for further leaching of mercury. The advantage is that the obtained stream can be disposed of as non-hazardous industrial wastewater or can be used as a solvent for the preparation of new I_2/KI leachant.

An alternative is the addition of a reducing agent e.g. sodium hydrosulphite to precipitate the mercury in the leachate. Complete reduction of mercury was achieved by adding sodium hydrosulphite to a leachate containing 149 mg/L mercury using a S/L ratio of 2.5%. Approximately 99.5% of the mercury was reduced when using a S/L ratio of 0.5%. Similar to the Dowex 1X8 treatment, this makes the resulting solution impossible to reuse for further mercury leaching due to reduction of oxidizing iodine species. It does however make the recovery of metallic mercury easier to achieve, e.g. isolation of the residue, followed by thermal treatment.

A third alternative to recover mercury from I_2/KI leachates is solvent extraction. Extractants such as Cyanex 302 and Cyanex 923 have previously been studied for mercury recovery from chloride media (Francis and Reddy, 2003; Meera et al., 2001).

Mercury was extracted from iodine leachates with great efficiency in one stage ($D \geq 500$) with both Cyanex 302 and Cyanex 923 in Solvent 70, respectively. When using $CyMe_4BTBP$ in nitrobenzene, an average distribution ratio of 42.1 ± 11.1 was calculated based on three investigated replicates. One of the advantages of solvent extraction is the fact that the resulting solution retains some of its oxidizing characteristics, making its reuse for further mercury leaching possible.

Leaching of mercury from other types of contaminated samples (I and III) with I_2/KI solution was also tested in Publication IV and the findings are in agreement with the aforementioned data (Table 8).

Table 8 – Leached percentages for mercury from samples I and III after 2 h with 0.025/0.05 M I_2/KI solution at 21 °C, according to Publication IV.

Sample	Hg content (mg/kg dry waste)	S/L ratio (% w/v)	Hg leached (%)
I	112 ± 2	20	93.4
		40	91.9
III	227 ± 5	20	93.1
		40	90.5

A clear advantage for this mercury leaching process is the use of simple, commercially available, chemical reagents. Thermal treatment of fluorescent lamp waste fractions has large energy requirements, given the fact that temperatures as high as 800 °C are needed to achieve complete decontamination. For wet samples the energy input will be higher. The hydrometallurgical process developed here can be an alternative to thermal treatment and has a considerably lower energy requirement. Because the residue obtained after the I_2/KI leaching step is meant to be processed hydrometallurgically to recover the contained REEs, there will be an overlap between the space and equipment requirements for these two steps. Decontamination in this case can be carried out in a leaching tank, the largest amount of the energy input going into agitation and the pumping of feeds. Further treatment of the residue e.g. REEs leaching can be carried out using the same equipment, after removal of the I_2/KI leachate. The initial investment in equipment, especially as this is the same equipment needed in the subsequent treatment of the residue for REEs recovery, will be lower compared to dedicated equipment for thermal desorption.

The treatment of the contaminated I_2/KI leachate follows a simple approach and, depending on the process chosen, does not require complicated equipment e.g. a column (if ion exchange is used) or a reduction tank (if $Na_2S_2O_4$ treatment is preferred). Both iodine and mercury are removed from the leachate, allowing for the resulting wastewater to be reused further in the process, e.g. for the washing of residues or preparing new leaching agent, thus equilibrating the water balance.

Since decontamination is not 100% efficient using I_2/KI leaching, the method is suitable if the amounts of mercury left in the residue after decontamination are below the requirements set by legislation. This is very important when taking safety and environmental aspects into consideration.

4.3. Leaching of metals

Water, ammonium chloride, acetic, nitric and hydrochloric acid solutions were screened as potential leaching agents for the REEs in the waste (Publication I). Only the acidic solutions led to noticeable leaching of REEs.

Little over 50% of the europium and 75% of the yttrium was leached from sample IV with 25% vol. acetic acid (168 h, ambient temperature, S/L ratio of 10% w/v) (Figure 12).

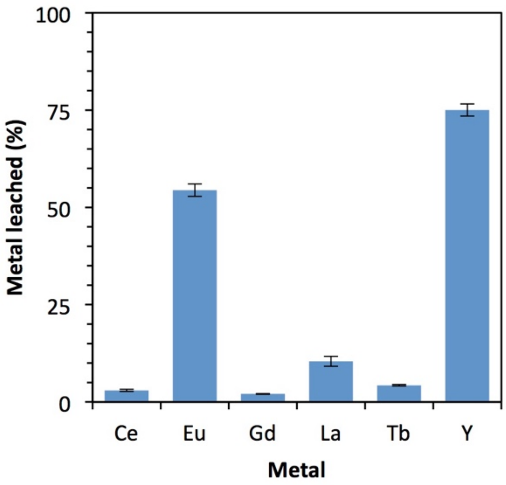


Figure 12 – Leaching of REEs from sample IV using 25% vol. acetic acid solution (20 ± 1°C, 168 h, S/L ratio of 10% w/v, 200 ± 50 rpm magnetic stirring). The uncertainty bars represent the standard deviation of a triplicate test.

Small amounts of the other REEs (2-10%) were leached alongside. Nitric and hydrochloric acid proved to be very effective at leaching yttrium and europium under similar conditions (Figure 13).

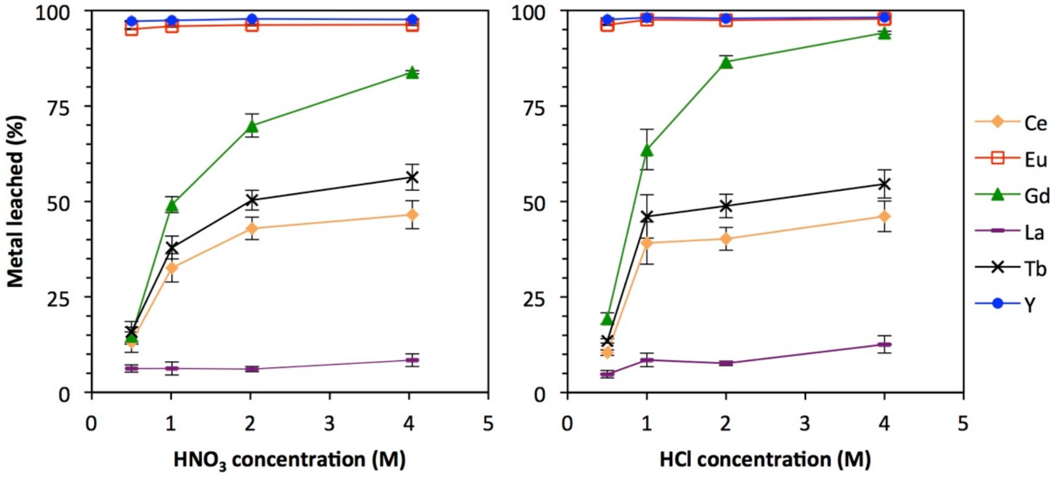


Figure 13 – Leached percentages of REEs using nitric and hydrochloric acid solutions of various concentrations (20 ± 1 °C, 168 h, S/L ratio of 10% w/v, 200 ± 50 rpm magnetic stirring). The uncertainty bars represent the standard deviation of a triplicate test.

Acid concentration was found to play a more important role in the leaching of cerium, gadolinium, lanthanum and terbium. While leaching efficiencies >95% were reached for yttrium and europium even with diluted solutions, the effective dissolution of the green phosphors was found to increase with acid concentration. This is due to the significantly increased solubility of YOX phosphor compared to LAP and CAT phosphors.

Nitric acid was chosen for further study. The leaching behaviour of REEs from sample IV with nitric acid solutions of various concentrations is presented in Figure 14.

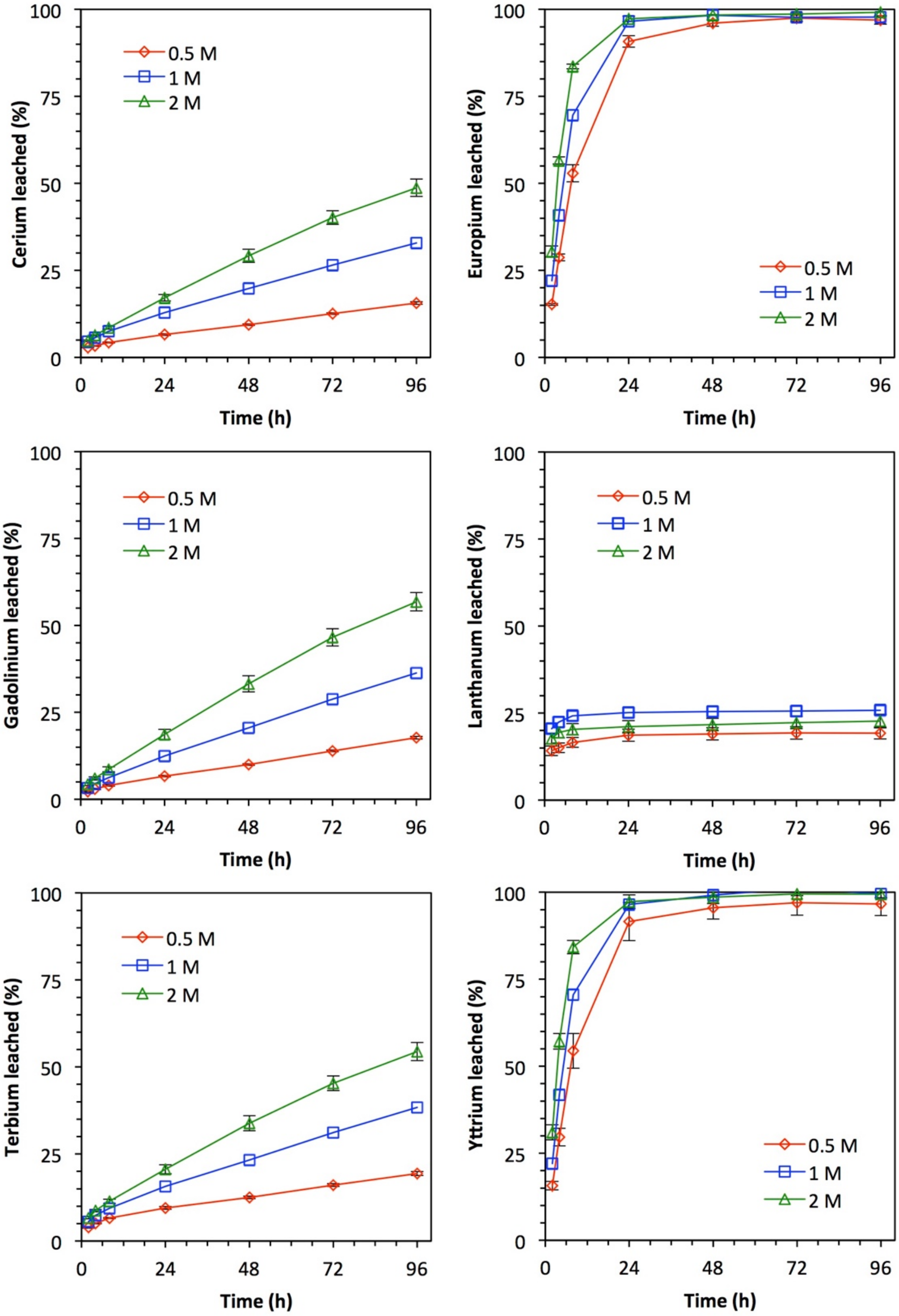


Figure 14 – Leaching behaviour of REEs from sample IV using nitric acid solutions of various concentrations (20 ± 1°C, S/L ratio of 10% w/v, 100 rpm magnetic stirring). The uncertainty bars represent the standard deviation of a triplicate test.

Leaching of cerium, gadolinium and terbium occurred slowly over time, without reaching equilibrium under the investigated conditions. Similarities in the leaching patterns were noticed due to the fact that these elements are usually encountered together in green phosphors. Yttrium and europium are leached much faster, with equilibrium being reached after about 24 h These differences in leaching behaviour can be exploited to achieve partial selectivity between yttrium + europium and the other four REEs, facilitating their subsequent separation, e.g. less separation stages are required for solvent extraction. An increased leaching efficiency for cerium, gadolinium, lanthanum and terbium was observed when increasing temperature and when using ultrasound (Figure 15).

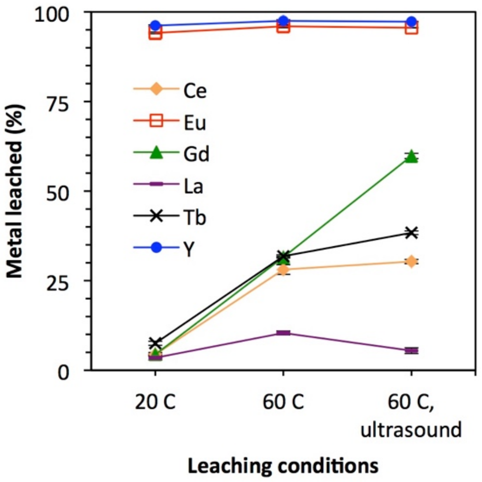


Figure 15 – Leached percentages of REEs from sample IV using 1 M nitric acid solution under various conditions: 20 ± 1 °C and 60 ± 2 °C and ultrasound assisted digestion at 60 ± 2 °C, respectively (6 h leaching time using a S/L ratio of 10% w/v and manual shaking, followed by 24 h resting at 20 ± 1 °C). The uncertainty bars represent the standard deviation of a triplicate test.

The recovery of these elements from the residue remaining after leaching of yttrium and europium can thus be carried out in a subsequent leaching step using more concentrated solutions at elevated temperature. Alternatively, alkali fusion followed by acid dissolution can be used, as suggested by Zhang et al. (2013) (Equations 14 and 15).

Since a consumption of protons occurs during the leaching of REEs (Equation 9-11), acid concentration is an important parameter in this process. The presence of calcium-based halophosphors in the waste fractions poses problems during leaching by increasing acid consumption and limiting the S/L ratio. Leaching of calcium with acidic solutions occurs significantly faster than REEs, leading to fast consumption of protons (Figure 16).

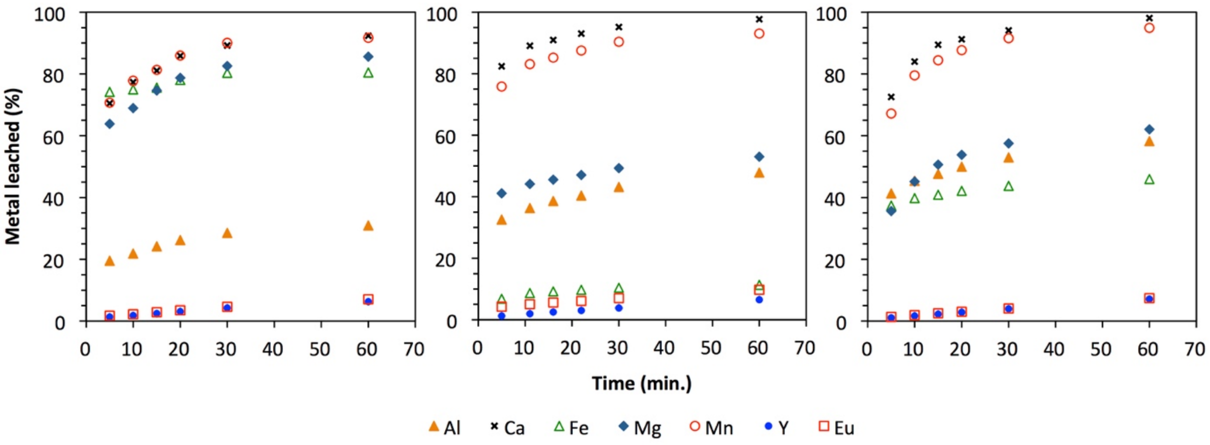


Figure 16 – Leaching behaviour of several metals present in larger amounts in samples I-III with 1 M nitric acid at 21 °C and S/L ratio of 10% w/v. From left to right: samples I, II and III, respectively.

According to Equation 12, 18 moles H^+ are consumed during leaching of one mole halophosphate (Dupont and Binnemans, 2015). Leaching of calcium and other impurity metals in the halophosphors alongside REEs also leads to increased metal concentration in the leachate and, depending on pH changes, possible precipitation issues during solvent extraction. Leaching with sulphuric acid avoids calcium, barium and lead dissolution due to the formation of insoluble sulphates. Nonetheless, this was shown to lead to co-precipitation of REEs, and therefore losses of potential recyclable material (De Michelis et al., 2011; Innocenzi et al., 2013).

The difference in leaching behaviour of calcium and other impurities can be used to selectively leach these elements. This will lower the impurity metal concentrations in the REEs leachates, as discussed in Publication IV. For the more concentrated waste fractions e.g. samples I-III, a 10-15 min leaching time with 1 M nitric acid at ambient temperature and S/L ratio of 10% w/v was deemed sufficient to leach calcium with 80-90% efficiency (Figure 16). The losses of yttrium and europium were below 2-3%, with the exception of sample II, which was thermally pre-treated to remove mercury. An almost 2-fold increase in the leaching of yttrium and europium was noted for this sample. This was attributed to the breaking of the particles of phosphor aggregates and cracking of particles upon heating, which in turn leads to faster dissolution due to larger surface area contact with the leaching agent.

Other soluble impurity metals that leached in sufficient amounts from samples I-III during the first 15 min were barium (up to 70% efficiency), antimony (up to 77% efficiency), strontium (up to 92% efficiency), cadmium (up to 88% efficiency), silicon (up to 80% efficiency), tin (up to 72% efficiency), lead (up to 78% efficiency), copper (up to 67% efficiency) and zinc (up to 88% efficiency). The dissolution behaviour of most of these elements was similar to that of calcium, manganese or magnesium (faster leaching within the first 10-15 min, followed by slower dissolution after this point). Aluminium was found to have lower dissolution efficiencies, partially due to the chemical stability of alumina used as a barrier level in fluorescent lamps (one of the sources of aluminium).

The REEs left in the residue after leaching of the bulk calcium from samples I-III (Figure 17) were found to have a similar leaching behaviour to that observed during leaching of sample IV (Figure 14). Again, leaching of yttrium and europium occurred almost concomitantly over approx. one day, and was significantly faster than for the other four REEs. The same slight increase in leaching efficiency of metals from sample II (thermally pre-treated) was also observed.

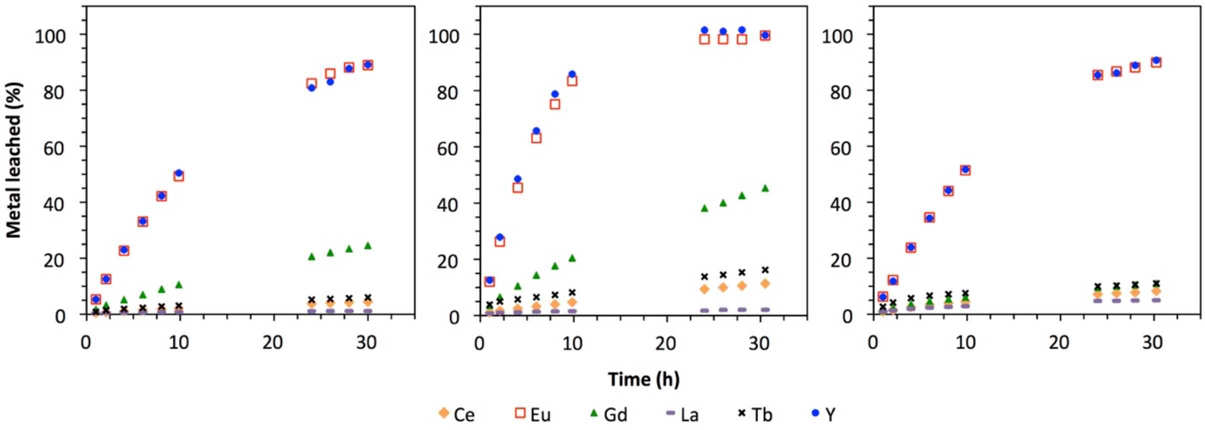


Figure 17 – Leaching behaviour of REEs from samples I-III after prior leaching of impurity metals. First leaching step: 1 M nitric acid for 10 min at 21 °C and S/L ratio of 10% w/v. Second leaching step for REEs (presented here): 2 M nitric acid at 21 °C and S/L ratio of 10% w/v. From left to right: samples I, II and III, respectively.

Two approaches were compared for the leaching of REE-concentrated waste fractions, with the goal of dissolving as much of the yttrium and europium and as little of the other four REEs:

1. Leaching of the waste in a single step with nitric acid solution. This will dissolve most metals, leading to a complex solution rich in calcium and yttrium. The main advantages are that only one leaching step is performed and one liquid stream is obtained (reduced volumes of secondary wastes). The disadvantages are a higher metal load in solution, possible precipitation issues during solvent extraction and lower grade final product.
2. Selective leaching of calcium, barium and other impurity metals, followed by further leaching of the residue to dissolve the REEs. The advantages for this are less impurities in solution (higher grade final product) and less issues with the solvent extraction step. The disadvantages are minor losses of REEs during the first leaching step and the need to process two solution streams (secondary wastes).

Table 9 shows a comparison between the concentrations of metals in the REE-rich solutions obtained using these two approaches. A clear reduction of impurity metals in solution was noted in the case of a two-step leaching process.

A multi-step leaching approach also has the advantage of reducing the unwanted anionic species in the REE-rich solution. In this case the largest amount of anionic species will end up in the calcium-rich leachate. The halophosphate phosphors make a high contribution to this, with six phosphate ions and two chloride and fluoride ions, respectively, being released per dissolved halophosphate molecule (Equation 12). Since the bulk of the REEs are in oxide form (YOX, BAM, CAT), the presence of unwanted anionic species in the REE-rich leachate will be low. The LAP phosphor is a source of phosphate anions, but the amount present in the waste is relatively low, as is its solubility under the tested conditions.

Table 9 – Comparisons between the concentrations of some metals in the REE-rich solutions obtained by (1) a single step leaching of REEs with 3 M nitric acid for 24 h using a S/L ratio of 10% w/v, and (2) a two-step leaching, as follows: i) partial leaching of impurities with 1 M nitric acid for 10 min, using a S/L ratio of 10% w/v, followed by ii) leaching of REEs in the remaining residue with 2 M nitric acid for 24 h using a S/L ratio of 10% w/v.

Approach	*Sample*	*Element concentration in the REE-rich solution (g/L) and changes in concentration using two-step leaching (%)*							
		Al	*Ba*	*Ca*	*Fe*	*Mg*	*Mn*	*Eu*	*Y*
(1)	I	0.19	0.43	12.91	0.34	0.22	0.42	0.96	15.25
	II	0.23	0.39	8.31	0.17	0.06	0.26	1.01	15.49
	III	0.33	1.69	9.22	0.32	0.15	0.30	1.02	17.07
(2)	I	0.09 (-53%)	0.06 (-86%)	1.53 (-88%)	0.03 (-91%)	0.04 (-82%)	0.05 (-88%)	1.37 (+43%)	20.88 (+37%)
	II	0.13 (-44%)	0.13 (-67%)	0.39 (-95%)	0.06 (-65%)	0.05 (-17%)	0.01 (-96%)	1.40 (+39%)	22.29 (+44%)
	III	0.11 (-67%)	0.85 (-50%)	0.56 (-94%)	0.10 (-69%)	0.07 (-53%)	0.03 (-90%)	1.34 (+31%)	21.83 (+28%)

4.4. Solvent extraction of REEs with Cyanex 923

The extraction of REEs with Cyanex 923 was found to reach equilibrium within one min (Figure 18).

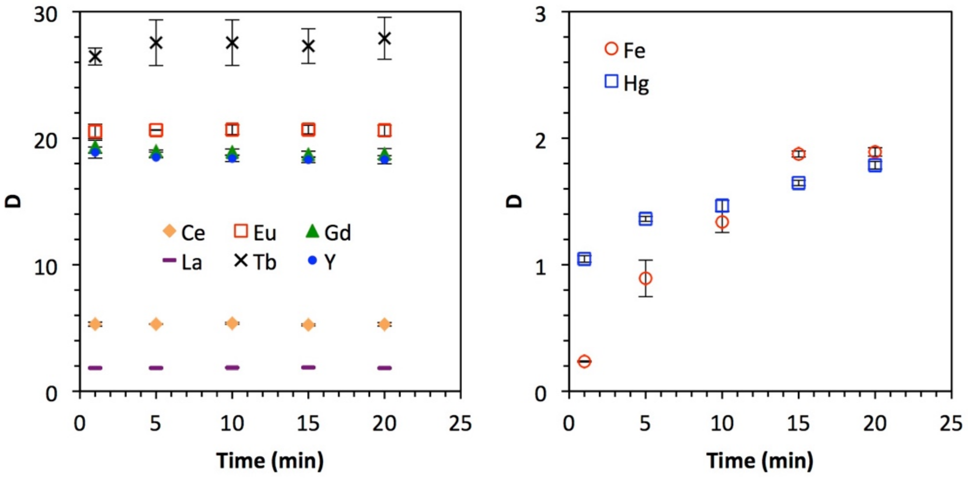


Figure 18 – Kinetics of the extraction process for REEs, iron and mercury using 0.7 M Cyanex 923 in Solvent 70, according to Publication II. The aqueous phase was obtained by leaching 20 g sample IV with 200 mL 2 M nitric acid solution for 48 h at 60 ± 2 °C (final nitric acid concentration was 1.7 M). The extraction was carried out at 23 ± 1 °C and 1750 vpm, using a phase ratio of 1. The uncertainty bars represent the standard deviation of a triplicate test.

The distribution ratios of lanthanides generally increased with decreases in ionic radius. Gadolinium showed distribution ratios lower than those of europium, despite having smaller ionic radius (Greenwood and Earnshaw, 1998). Similar behaviour has been observed in other solvent extraction systems and this is explained by the half-filled electron shell of gadolinium(III) ($4f^7$) (Nilsson et al., 2006). Iron and mercury ions were also extracted but the kinetics were significantly slower (Figure 18). Equilibrium was attained after 10-15 min for iron, while extraction of mercury occurred continuously for the duration of the investigated time. A short contact time between the two phases can be used in order to achieve partial separation of the REEs from these two undesired elements. Chloride ions in solution are responsible for the extraction of mercury (Equation 6). No extraction of mercury was observed from nitric acid solution containing only pure REEs, mercury and iron nitrates. For this reason, a decontamination step prior to the solvent extraction of REEs is advised in order to prevent the spreading of mercury in subsequent process streams.

The acidity of the aqueous phase plays an important role in the extraction of REE ions (Figure 19).

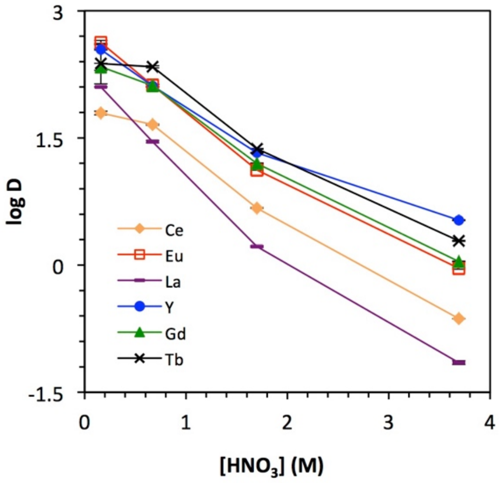


Figure 19 – Extraction of REEs from fluorescent lamp leachates of various acidity using 0.7 M Cyanex 923 in Solvent 70, according to Publication II. The aqueous phases were obtained by leaching sample IV with 0.5 M, 1 M, 2 M and 4 M nitric acid solutions for 168 h at 20 ± 1 °C, using a S/L ratio of 10% w/v (final nitric acid concentrations in the leachates were 0.16 M, 0.67 M, 1.7 M and 3.69 M, respectively). The extraction was carried out at 23 ± 1 °C, using a phase ratio of 1. Initial nitric acid concentrations in the leachates are plotted on the x-axis, not the equilibrium values. The uncertainty bars represent the standard deviation of a triplicate test.

A decrease in extraction efficiency was observed with an increase in acidity, due to competition of protons with the REE ions for the extractant molecules. The data in Figure 19 refers to the initial concentrations of nitric acid in the aqueous phases investigated, not to the actual equilibrium concentrations, which are expected to be lower. This is because Cyanex 923 is capable of extracting nitric acid, according to Equation 22.

$$x\,H^{+}_{(aq)} + x\,NO_{3\,(aq)}^{-} + y\,TRPO_{(org)} \leftrightarrow yTRPO\cdot xHNO_{3\,(org)} \qquad (22)$$

It was stated that probable Cyanex 923-nitric acid complexes can be of the type 2:1, 1:1 and 1:2 (Ansari et al., 2004). Figure 19 is meant to be a representation of how extraction is influenced by the acidity in the aqueous phase during the first stage of an extraction process.

The distribution ratios of nitric acid increase with increases in Cyanex 923 concentration in the organic phase (Figure 20; equilibrium data).

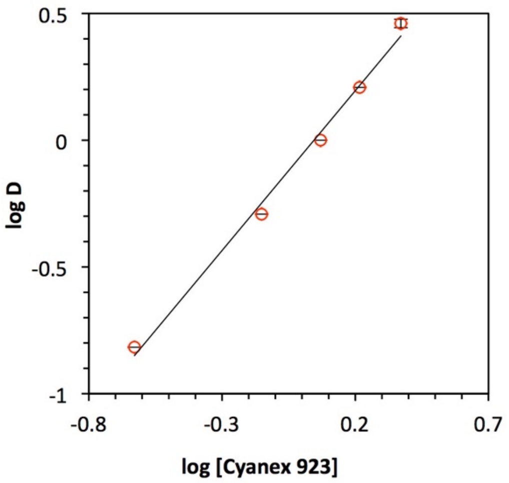


Figure 20 – Extraction of nitric acid from a real fluorescent lamp waste leachate at various Cyanex 923 concentrations, according to Publication II. The aqueous phase was obtained by leaching 20 g sample IV with 200 mL 2 M nitric acid solution for 48 h, at 60 ± 2 °C (final nitric acid concentration was 1.7 M). The organic phase consisted of 0.24 M, 0.7 M, 1.18 M, and 1.65 M Cyanex 923 in Solvent 70 and undiluted Cyanex 923 (2.35 M), respectively. The extraction was carried out for 10 min at 23 ± 1 °C and 1750 vpm, using a phase ratio of 1.

Upon extraction, the pH of the aqueous phase will increase. This can lead to hydrolysis of metals ions and formation of insoluble precipitates, which are undesired in any solvent extraction process. For this reason, the presence of large amounts of calcium in lamp waste leachates can hinder the extraction process if the pH increase is high enough. Use of a two-step leaching process for the waste is indicated to avoid dissolving the bulk of the calcium together with the REEs.

The extraction of REEs was found to decrease with an increase in temperature (Figure 21).

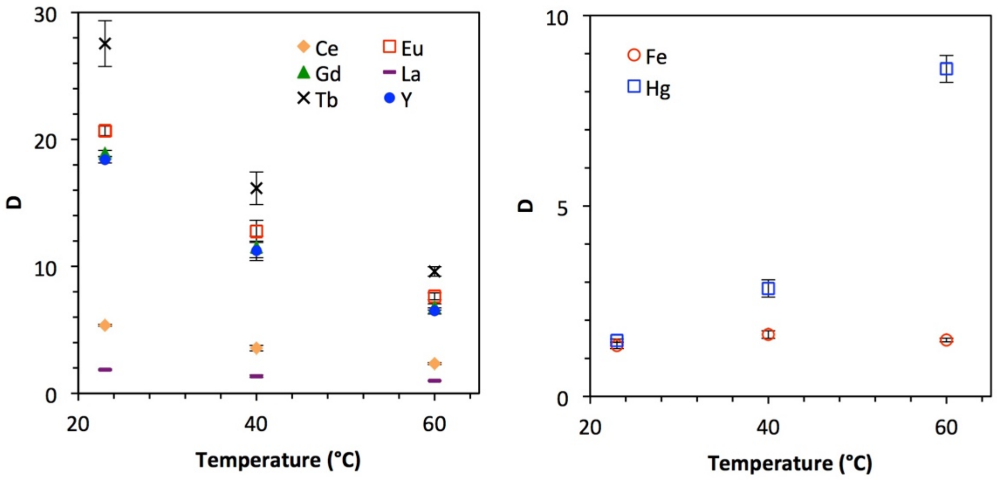


Figure 21 – The influence of temperature on the extraction process for REEs, according to Publication II. The aqueous phase was obtained by leaching 20 g sample IV with 200 mL 2 M nitric acid solution for 48 h at 60 ± 2 °C (final nitric acid concentration was 1.7 M). The extraction was carried out with 0.7 M Cyanex 923 in Solvent 70 for 10 min at 23 ± 1 °C, 40 ± 1 °C and 60 ± 1 °C, respectively, using a phase ratio of 1 and 1750 vpm. The uncertainty bars represent the standard deviation of a triplicate test.

It was concluded that the extraction of REEs is driven by changes in enthalpy. For all six REEs the enthalpy and entropy of extraction were found to be negative (Table 10).

Table 10 – Enthalpy and entropy of complexation in the extraction of REEs from a real fluorescent lamp waste leachate of sample IV using 0.7 M Cyanex 923 in Solvent 70, according to Publication II.

Element	*ΔG^o (23 °C; kJ/mol)*	*ΔH^o (kJ/mol)*	*ΔS^o (J/mol·K)*
Ce	-17.96 ± 0.03	-18.3 ± 0.4	-1 ± 1
Eu	-21.28 ± 0.04	-22.1 ± 0.5	-3 ± 2
Gd	-21.06 ± 0.03	-22.7 ± 0.5	-5 ± 2
La	-15.36 ± 0.06	-14 ± 0.4	5 ± 1
Tb	-21.98 ± 0.16	-23.3 ± 1	-5 ± 3
Y	-20.99 ± 0.03	-23.1 ± 0.5	-7 ± 2

Hydrochloric and nitric acid solutions, respectively, were found to effectively strip the extracted metals (Figure 22). The former was capable of selectively stripping the REEs from co-extracted iron and mercury. Nitric acid can be used for the scrubbing of co-extracted species, after stripping of REEs with hydrochloric acid. Acid extracted by Cyanex 923 can be scrubbed by washing the organic phase with water. This was observed by a pH drop in pure water to <1 upon washing, as noted in Publication IV.

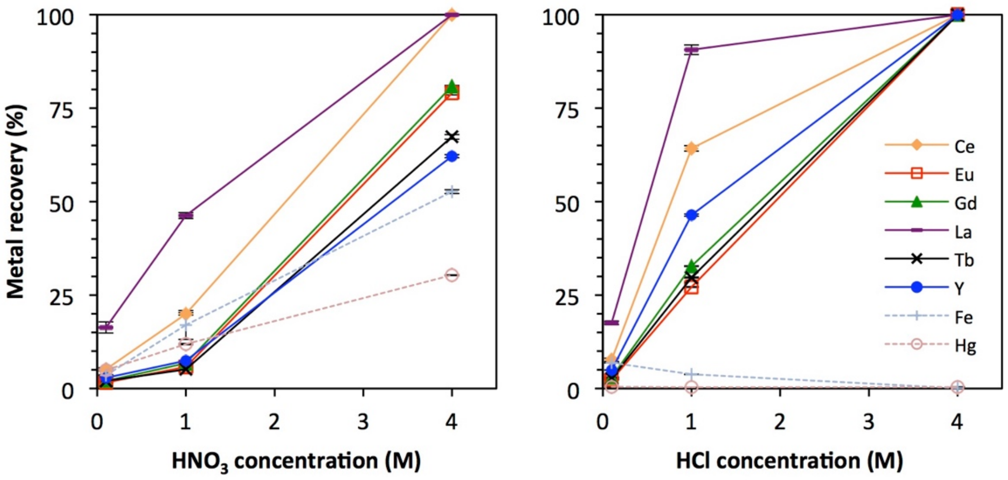


Figure 22 – Stripping of extracted metals using hydrochloric and nitric acid solutions, according to Publication II. An organic phase containing 0.7 M Cyanex 923 in Solvent 70 was loaded with metals by manually shaking it with a nitric acid-based leachate of sample IV for 10 min at 21 °C, using a phase ratio of 1. Stripping was performed at 22 ± 1 °C for 5 min, using a phase ratio of 1. The uncertainty bars represent the standard deviation of a triplicate test.

4.5. Testing of the process in laboratory pilot scale

Based on the aforementioned findings, the leaching and separation processes were tested in laboratory pilot scale using a leaching reactor with propeller stirring and a counter-current mixer-settler system, as described in Publication IV.

4.5.1. Processing of thermally-treated fractions

Leaching of metals from the mercury-free sample II was investigated using the two approaches discussed in section 4.3. This was to determine if the presence of large amounts of calcium alongside the REEs would hinder the solvent extraction separation process. The metal concentrations in the solutions obtained are presented in Table 11.

Table 11 – Concentrations of metals in the solutions obtained after leaching of sample II using i) a single-step for 22 h using 3 M nitric acid solution and ii) two-step leaching, first with 1 M solution for 10 min, followed by further treatment of the residue with 2 M solution for 22 h. All leaching experiments were carried out in ambient conditions.

Elements		*Leachate type and the concentrations of several metals in solution (mg/L)*		
		Single-step leaching (2 M acid; 22 h; S/L ratio 10% w/v)	*Two-step leaching; Ca-rich leachate (1 M acid; 10 min; S/L ratio 10% w/v)*	*Two-step leaching; REE-rich leachate (Resulting residue + 2 M acid; 22 h; S/L ratio 10% w/v)*
REEs	Ce	12.9	3.4	21.6
	Eu	966.6	70.7	1196
	Gd	29.0	4.1	55.2
	La	8.0	6.0	4.4
	Tb	10.6	4.4	14.1
	Y	15860.0	591.6	18020.0
Impurities	Al	213.8	137.7	102.0
	B	117.9	75.5	81.5
	Ba	278.1	314.6	78.3
	Ca	8143.0	7576.0	205.5
	Cd	3.8	4.5	0.2
	Cr	0.8	0.5	0.3
	Cu	18.6	8.8	11.3
	Fe	101.5	48.6	26.6
	K	66.8	53.0	20.4
	Mg	79.7	49.7	45.7
	Mn	208.6	257.0	4.5
	Mo	5.2	2.3	3.8
	Na	209.8	191.5	36.8
	Ni	7.3	2.3	6.6
	Pb	27.8	26.3	6.8
	Sb	131.9	100.3	38.0
	Si	122.0	164.9	60.3
	Sn	3.2	2.5	1.6
	Sr	250.0	213.9	100.3
	Ti	1.4	0.5	1.3
	W	21.3	5.9	17.5
	Zn	10.0	7.4	4.8
	Zr	1.5	0.8	3.5

The two REE-rich leachates, denoted as calcium-rich leachate and calcium-depleted leachate, were pumped into the counter-current mixer settler system described in Figure 6. The extraction and stripping behaviours of yttrium and europium are presented in Figure 23.

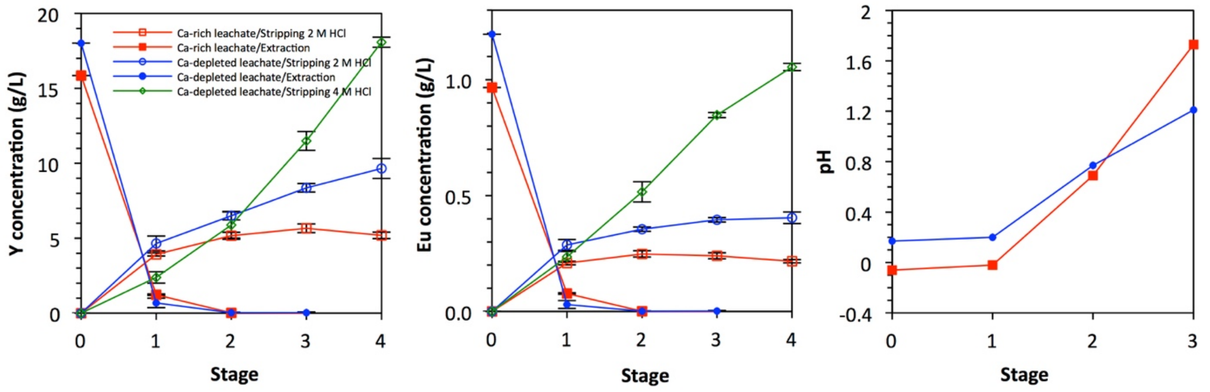


Figure 23 – Extraction/stripping behaviour of yttrium (left) and europium (middle) from different leachates of sample II in a mixer-settler system comprised of three extraction and four stripping chambers, respectively. The pH change of the aqueous phase during extraction is shown on the right. The extraction was carried out with 50% vol. Cyanex 923 in Solvent 70. Stripping was done with 2 M and 4 M hydrochloric acid, respectively. All O:A phase ratios were 2:1. The error represents the standard deviation of up to six samplings, up to one hour apart, during operation time.

The separation trial showed good stability over time, with only minor variations in metal concentrations between the collected samples. Similarities in the extraction and stripping behaviours of REEs between the two types of leachates were observed, the minor differences being due to increased content of REEs in the calcium-depleted leachate. Most of the REEs (>92%) were extracted in the first stage, followed by recovery of >99% after two stages. For the calcium-rich leachate, precipitation was observed to be most obvious after system shutdown overnight. Precipitation was strongest in chamber E3 and was connected to pH changes during extraction with Cyanex 923 (Figure 23). Since this was not an issue for the calcium-depleted leachate, it is advised to carry out leaching of REEs in two-steps, especially if the material contains high amounts of halophosphate powder. This will also lead to lower amounts of co-extracted species in solution. Iron, molybdenum, tin, titanium, tungsten and zirconium were co-extracted almost entirely alongside the REEs but they were not stripped by hydrochloric acid. Extraction of boron, lead and silicon was almost absent in the first stages but was noticeable in the third extraction chamber. Using two separation stages in this case will lead to higher product purity.

Stripping with 2 M hydrochloric acid was not completely effective at recovering all the extracted metals. This was achieved by increasing the acid concentration to 4 M. The metal content in the final strip products is presented in Table 12.

Table 12 – Concentration of impurity metals in the final strip product derived from sample II. The extraction and stripping were carried out with 50% vol. Cyanex 923 and 2 M hydrochloric acid, respectively. All O:A phase ratios were 2:1. The initial concentrations in the aqueous feed are shown in Table 6. The uncertainty bars represent the standard deviation of up to six samplings, up to one hour apart, during operation time; nd=not detected.

Feed	*Metals and their concentration in the final strip product (mg/L)*													
	Al	*B*	*Ba*	*Ca*	*Fe*	*Mn*	*Pb*	*Sb*	*Si*	*Sr*	*Ce*	*La*	*Gd*	*Tb*
Ca-rich leachate	3.1 ± 0.1	20.9 ± 1.0	1.4 ± 0.1	118.8 ± 8.5	0.1	4.1 ± 0.3	6.2 ± 0.7	0.6	18.0 ± 0.6	0.9	9.8 ± 0.5	6.6 ± 0.1	9.3 ± 0.5	2.8 ± 0.1
Ca-depleted leachate	1.4 ± 0.3	10.6 ± 1.7	0.7 ± 0.1	5.9 ± 1.6	nd	nd	1 ± 0.2	0.2	9.7 ± 0.9	0.4 ± 0.1	19.4 ± 1.1	4.4 ± 1.5	24.2 ± 0.5	6.2 ± 0.4

4.5.2. Processing of mercury-contaminated fractions

The separation process was also tested for sample III. Because this sample contains 227 ± 5 mg/kg mercury, a decontamination step was carried out with 0.025/0.075 M I_2/KI solution. The mercury leaching efficiency was >96% after 4.5 h (Figure 24). Equilibrium was achieved faster compared to the bench scale trials (within 45 min), a consequence of significantly better mixing and contact between the phases, e.g. propeller stirring vs. magnetic stirring.

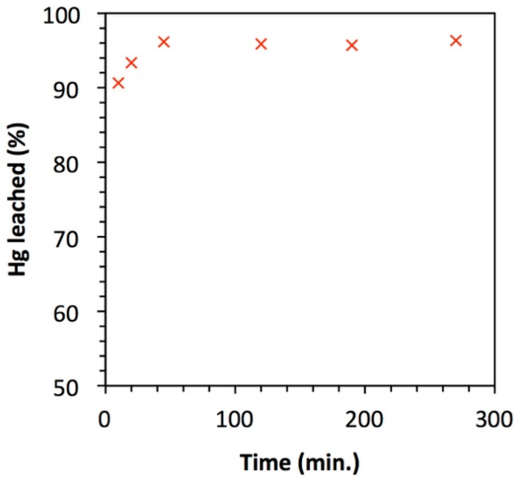


Figure 24 – Leaching of mercury from 500 g sample III with 0.025/0.075 M I_2/KI solution and a S/L ratio of 25% w/v.

In a subsequent leaching step some of the impurity metals were dissolved with 1 M nitric acid for 10 min in order to avoid any precipitation issues during solvent extraction. A solution containing 8.6 g/L calcium and 1.2 g/L barium as major impurities was obtained. This solution also contained 0.05 and 0.7 g/L europium and yttrium, respectively. In a final leaching step, the bulk of the REEs were leached with 2 M nitric acid. Extraction of REEs from this solution was carried out using 50% vol. Cyanex 923 but also with 35% vol. Cyanex 923. This was based on the previous observation that two stages should be sufficient to achieve separation of these two REEs when using 50% vol. extractant. Stripping was carried out with 4 M hydrochloric acid. The extraction and stripping behaviour of yttrium and europium is presented in Figure 25.

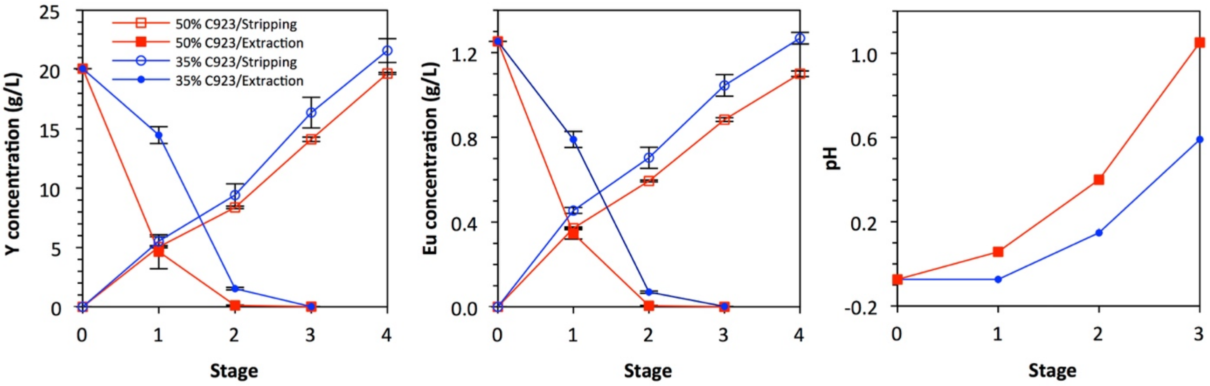


Figure 25 – Extraction/stripping behaviour of yttrium (left) and europium (middle) from a calcium-depleted leachate of sample III in a mixer-settler system comprised of three extraction and four stripping chambers, respectively. The pH change of the aqueous phase during extraction is shown on the right. The extraction was carried out with 35% and 50% vol. Cyanex 923 in Solvent 70, respectively. Stripping was performed with 4 M hydrochloric acid. All O:A phase ratios were 2:1. The uncertainty bars represent the standard deviation of up to three samplings, up to one hour apart, during operation time.

The concentration of metals in the aqueous feeds and in the stripping products is shown in Table 13. Similarities between the co-extraction of impurity elements in this leachate and the leachates of sample II were observed. The 35% vol. Cyanex 923 was more than sufficient to completely extract yttrium and europium. Using less concentrated organic phases also leads to higher strip product purity. Lower acid uptake during extraction will also occur, therefore resulting in an easier regeneration of the extractant. Phase separation was observed to be better at lower Cyanex 923 concentrations.

Table 13 – Concentrations of metals in the REE-rich leachates obtained after leaching sample III in laboratory pilot plant scale, as well as in the stripping products after extraction with 35% and 50% vol. Cyanex 923 in Solvent 70; nd = not detected.

Elements		*Solution type and the concentrations of several metals in solution (mg/L)*		
		REE-rich leachate	*Strip product (35% vol. Cyanex 923)*	*Strip product (50% vol. Cyanex 923)*
REEs	Ce	11.5	15.2 ± 1.8	15.0 ± 0.2
	Eu	1253.0	1268.5 ± 27.5	1100.3 ± 13.5
	Gd	28.4	29.4 ± 1.0	27.5 ± 0.0
	La	2.2	2.7 ± 0.4	2.5 ± 0.1
	Tb	9.2	8.6 ± 0.2	7.8 ± 0.1
	Y	20080.0	21605.0 ± 1005.0	19676.7 ± 81.8
Impurities	Al	61.5	1.3 ± 0.0	3.1 ± 0.3
	B	186.3	8.8 ± 1.3	16.1 ± 1.0
	Ba	387.8	4.3 ± 0.4	10.2 ± 1.7
	Ca	200.6	3.6 ± 0.3	5.8 ± 0.2
	Cd	0.6	nd	nd
	Cr	0.3	nd	nd
	Cu	14.3	nd	nd
	Fe	61.8	nd	nd
	K	13.3	nd	nd
	Mn	10.3	nd	0.4 ± 0.0
	Mo	0.6	nd	nd
	Na	9.8	nd	1.3 ± 0.0
	Ni	6.5	nd	0.3 ± 0.1
	Pb	9.8	1.5 ± 0.0	2.0 ± 0.4
	Sb	21.5	nd	0.4 ± 0.0
	Sn	0.8	nd	nd
	Sr	300.9	3.9 ± 0.3	6.8 ± 0.3
	Ti	1.2	nd	nd
	W	5.2	nd	nd
	Zn	8.5	nd	nd
	Zr	0.4	nd	nd

4.6. Further separation of REEs with Cyanex 572

The objective of these experiments, described in detail in Publication V, was to individually separate yttrium and europium, the predominant REEs in the stripping products obtained after extraction with Cyanex 923. The aqueous phases used originated from the mixer-settler tests discussed in the previous section.

Under the tested conditions, the extraction and stripping kinetics of REEs with Cyanex 572 were found to be slower compared to Cyanex 923 (Figure 26).

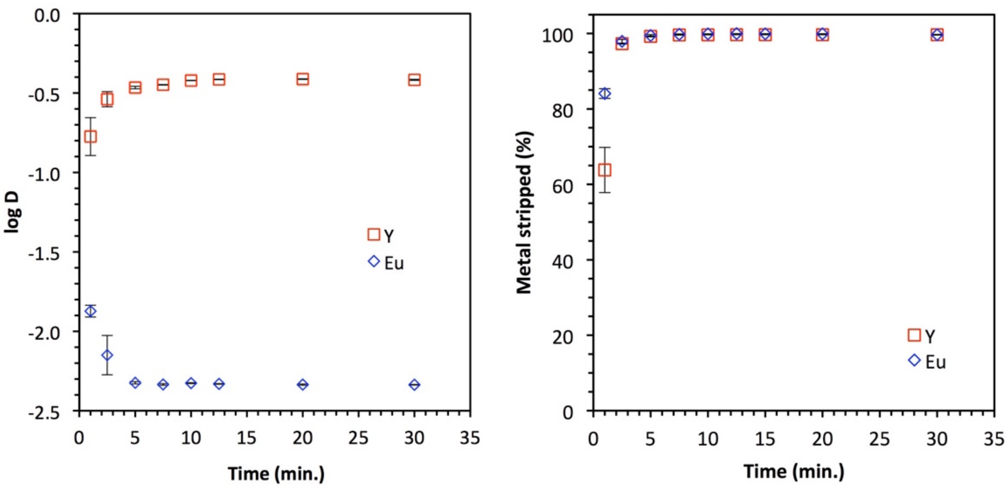


Figure 26 – Extraction (left) and striping (right) behaviour of europium and yttrium over 30 min. Extraction was carried out with 1 M Cyanex 572 in Solvent 70 at 21 ± 1 °C, using a phase ratio of 1. pH_{in} *= 0.7;* pH_{eq} *= -0.1. Stripping was carried out with 6 M hydrochloric acid at 21 ± 1 °C from a 1 M Cyanex 572 solution in Solvent 70 that was previously contacted with yttrium/europium feed. The uncertainty bars represent the standard deviation of a triplicate test.*

The Cyanex 572 system reached equilibrium within 12.5 min, significantly longer than the <1 min for Cyanex 923. Stripping equilibrium was achieved within 5 min, with over >99.9% of the europium and yttrium in the organic phase being back-extracted with a 6 M hydrochloric acid solution.

Equilibrium pH has significant importance, as Cyanex 572 is an acidic extractant (Equations 7 and 8). The extraction behaviour of yttrium and europium at various pH_{eq} is presented in Figure 27.

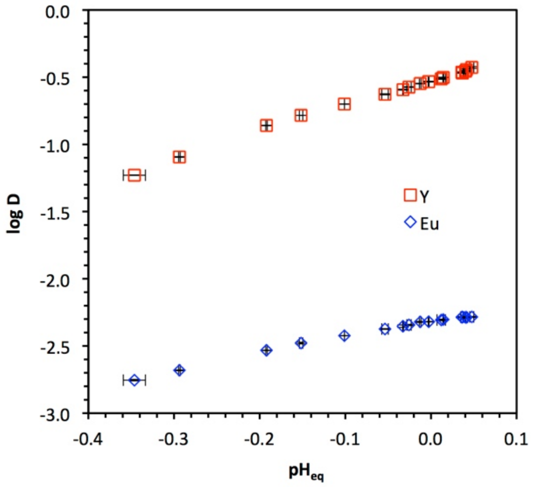


Figure 27 – Extraction behaviour of yttrium and europium at various pH_{eq}*. Extraction was carried out from aqueous phases of various pH values with 1 M Cyanex 572 in Solvent 70 at 21 ± 1 °C, using a phase ratio of 1. Initial concentrations of yttrium and europium in the aqueous phase were 18 g/L and 1 g/L, respectively. Phase contact time was 15 min. The uncertainty bars represent the standard deviation of a triplicate test.*

Yttrium can be separated from europium at around $pH_{eq} = 0$. This will require several separation stages as approx. 22% the total yttrium was extracted in one stage. At the same time, <0.5% of the europium was co-extracted. These amounts increase as pH_{eq} increases. A separation factor of 61 between yttrium and europium was attained at $pH_{eq} = 0$. Since phase disengagement did not pose any problems, being <15 seconds, and no third phase formation occurred. Phase modifiers were not used.

Increases in ligand concentration in the organic phase led to expected increases in distribution ratios of both REEs.

For Equation 7, the extraction constant K_{ex} can be written according to Equation 23.

$$K_{ex} = \frac{[REEA_{3\,(org)}] \cdot [H^{+}{}_{(aq)}]^{3}}{[REE^{3+}{}_{(aq)}] \cdot [HA_{\,(org)}]^{3}} \tag{23}$$

The distribution ratio of a REE is written according to Equation 24.

$$D = \frac{[REEA_{3(org)}]}{[REE^{3+}{}_{(aq)}]} \tag{24}$$

By inserting Equation 24 into Equation 23, Equation 25 is obtained:

$$logD = logK_{ex} + 3 \cdot log\frac{[H^{+}{}_{(aq)}]}{[HA_{(org)}]} \tag{25}$$

The decimal logarithm of the distribution ratios of REEs vs. the ratio between the concentration of protons and extractant at equilibrium were plotted (Figure 28).

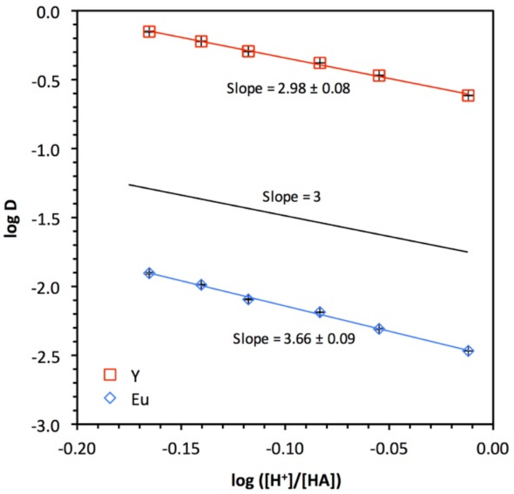


Figure 28 – Dependency of the extraction behaviour of europium and yttrium on Cyanex 572 concentration. Equilibrium values were plotted. Extraction was carried out with Cyanex 572 in Solvent 70 (0.75-2 M) at 21 ± 1 ℃, using an aqueous phase with pH_{in} = 0.8. Contact time was 15 min, and the phase ratio used was 1. The uncertainty bars represent the standard deviation of a triplicate test.

The slope of this linear dependency should be equal to 3 (the number of extractant molecules involved in the extraction of one REE ion), according to Equation 7. Yttrium showed a good correlation with this theoretical model. The slope for europium was higher, 3.66 ± 0.09. For slope analysis it is recommended that the extractant is in larger excess compared to the amount of metal ions extracted. This is to ensure that the free extractant concentrations at equilibrium do not vary significantly with loading. For the data presented here, the content of REEs in the aqueous phase can be approximated to 0.2 M. Even at distribution ratios <1, as is the case here, this requirement is not entirely satisfied for all points in the slope. This can be a reason for the observed deviations from the theoretical model. Hein (2014) reported a slope of 3.85 ± 0.06 for the extraction of europium with Cyanex 572 at trace levels (approx. 0.65 mM) from nitric acid media. Quinn et al. (2015) reported that deviations from linearity and a slope of 3 are likely due to the change in properties of the organic phase, especially at high extractant concentration e.g. formation of hydrogen-bonded aggregates.

The influence of various types of diluents on the extraction of yttrium was investigated (Table 14).

Table 14 – Diluents tested in the Cyanex 572 solvent extraction study.

Diluent category	*Commercial name/compound*	*Characteristics*
Aliphatic	Solvent 70	0.5% wt. aromatic content
	TetraPropyleneHydrogenated (TPH)	Similar to dodecane. Used in the PUREX process in La Hague.
	Isopar L	<0.01% wt. aromatic content
	Escaid 120	0.4% wt. aromatic content
Aromatic	Toluene	
	Nitrobenzene	
	Tertbutylbenzene	
	Solvesso 150	>99% wt. aromatic content
Alcohols	1-octanol	Long chain aliphatic alcohol

Best performance was obtained using aliphatic diluents. Very small differences were noted between aliphatic diluents such as TPH, Isopar L and Escaid 120 (Figure 29).

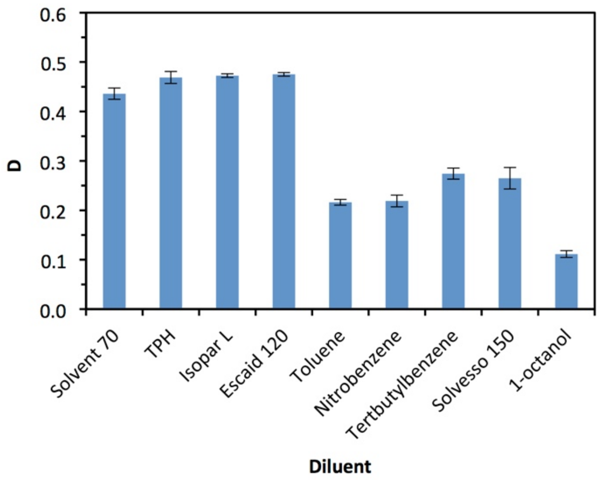


Figure 29 – Distribution ratios of yttrium with 1 M Cyanex 572 in various diluents. Extraction was carried out at 21 ± 1 °C, from an aqueous phase with pH_{in} = 0.8, using a phase ratio of 1. Phase contact time was 30 min. The uncertainty bars represent the standard deviation of a triplicate test.

A significant drop in distribution ratios (30-45%) was seen when substituting Isopar L with aromatic diluents. When using 1-octanol the distribution ratio dropped even more. In this system a third phase formation occurred at the organic-aqueous interface.

By increasing the temperature of the system, an increase in the distribution ratios of yttrium and europium was noted (Figure 30).

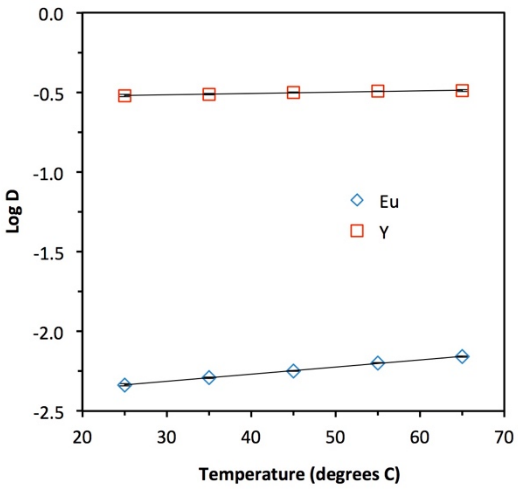


Figure 30 – Dependency of the extraction of europium and yttrium on temperatures in the range 25-65 °C (± 1 °C). Extraction was carried out with 1 M Cyanex 572 in Solvent 70. Contact time was 30 min, and the phase ratio was 1. The uncertainty bars represent the standard deviation of a triplicate test.

The increase in distribution ratios with increasing temperature was more significant for europium. This led to a decrease in separation factors, from $\alpha_{Y/Eu}$ = 65 to $\alpha_{Y/Eu}$ = 46, when the temperature increased from 25 to 65 °C. To achieve better separation and higher product purity it is therefore advised to carry out the extraction at lower temperatures.

Stripping of the extracted REEs can be carried out with mineral acids e.g. hydrochloric and nitric acid solutions (Figure 31).

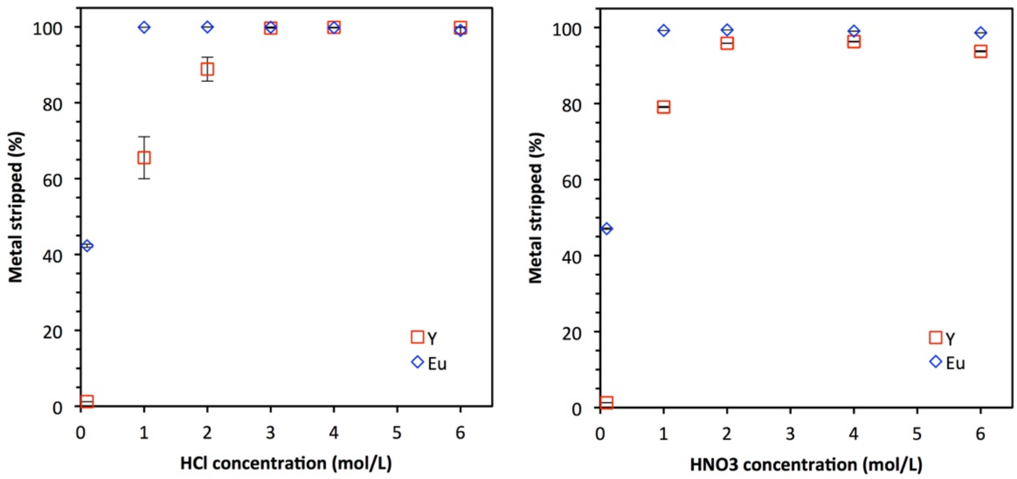


Figure 31 – Stripping behaviour of europium and yttrium in one stage with hydrochloric and nitric acid solutions of various concentrations. The organic phase was 1 M Cyanex 572 in Solvent 70 that was previously contacted with an aqueous solution containing 1 g/L europium and 18 g/L yttrium (pH_{in} =0.8; 15 min, with manual shaking at 21 ± 1 °C using a phase ratio of 1). Contact time during stripping was 15 min, at 21 ± 1 °C, using a phase ratio of 1. The uncertainty bars represent the standard deviation of a triplicate test.

One of the main advantages of Cyanex 572 over phosphonic acids is the fact that stripping requires less concentrated acids (Cytec, 2014). Hydrochloric acid solutions ≥3 M stripped all the REEs extracted in one stage when using O:A ratios of 1. Diluted acids (0.1 M) can be potentially used to scrub part of the co-extracted europium (42-47% efficiency) in order to achieve higher purity of potential yttrium products.

Using these results, the separation of yttrium from europium was further carried out from 1 L feed in ten successive batch extraction stages with 1 M Cyanex 572 (pH_{eq} in the range 0-0.1). More than 97% of the yttrium was extracted during the first seven stages, with >99.9% being recovered after the tenth stage. This separation more closely resembles an analytical procedure rather than a continuous counter-current process, as would be required industrially. Further stripping was carried out with 3 M hydrochloric acid to obtain a yttrium-concentrate meant for further processing, e.g. oxalic acid precipitation (further described in the next section).

The aqueous phase left after the extraction of yttrium contained the bulk of europium and traces of gadolinium, terbium, cerium, lanthanum and yttrium. Extraction of europium was subsequently carried out at $pH_{eq} = 1$, in one stage, according to Figure 32. The extracted europium was stripped with 3 M hydrochloric acid.

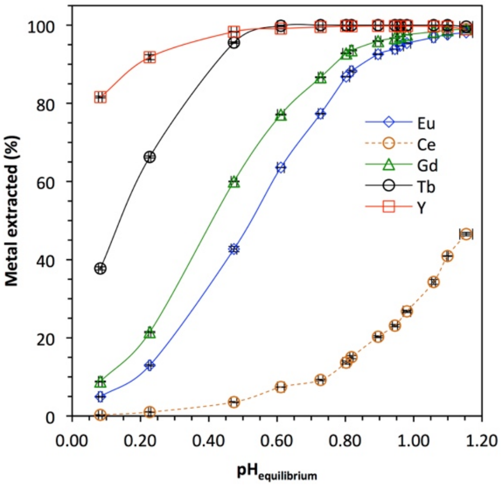


Figure 32 – Extraction dependency of europium and trace REEs on pH_{eq}, after extraction of bulk yttrium. Extraction was carried out with 1 M Cyanex 572 at 21 ± 1 °C, from aqueous phases of various pH, using a phase ratio of 1. Phase contact time was 15 min. The uncertainty bars represent the standard deviation of a triplicate test.

4.7. Preparation of REE oxides

Rare earth oxalates can be precipitated from solution using oxalic acid in accordance with Equation 13. The oxalates can be converted to oxides via thermal treatment in accordance with Equation 26.

$$2\ REE_2(C_2O_4)_{3\ (s)} + 3\ O_{2\ (g)} \rightarrow 2\ REE_2O_{3\ (s)} + 12CO_{2\ (g)} \tag{26}$$

Rare earth oxides were prepared from the yttrium/europium-rich stripping product obtained after solvent extraction with Cyanex 923 (Publication IV); and the yttrium stripping product and the europium stripping product obtained after solvent extraction with Cyanex 572 (Publication V). For the former, a mixed yttrium-europium oxide was obtained and the structure was confirmed by XRD measurements. The REEs content was 99.96% REEs: 94.61% yttrium, 5.09% europium and 0.26% the other four REEs. One fifth of the 0.04% impurity metals (mostly sodium, silicon, boron, calcium and barium) originated from the oxalic acid used for precipitation.

Scrubbing of the Cyanex 572 loaded with yttrium with 0.1 M hydrochloric acid prior to stripping of yttrium with 3 M acid led to an increase in purity of yttrium oxide from 99.77% (without scrubbing) to 99.82%. The major impurity in both cases was europium oxide (Table 15).

Table 15 – Metal content of the prepared yttrium and europium oxides, respectively (%). The assay was performed by dissolving the oxides in Suprapur nitric acid solution, followed by measurements of the obtained solutions using ICP-MS and ICP-OES.

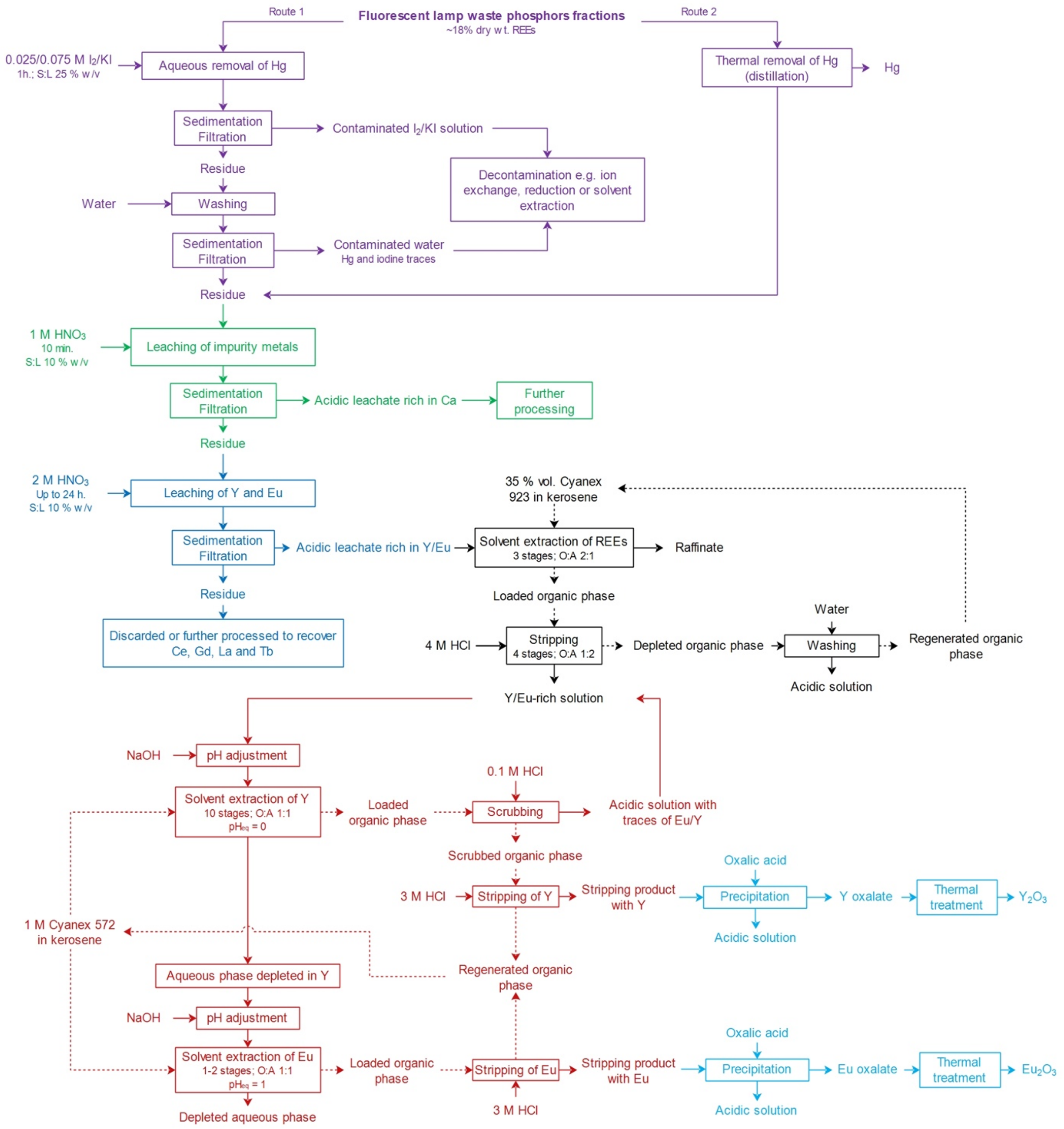
Metal	*Compound/preparation method and metal content (%)*			
	Y_2O_3; no scrubbing with 0.1 M HCl prior to stripping	*Y_2O_3; scrubbing with 0.1 M HCl prior to stripping*	*Eu_2O_3; direct precipitation from the aqueous phase after extraction of Y*	*Eu_2O_3; further extraction with Cyanex 572 after extraction of Y*
Al	<0.01	<0.01	nd	nd
B	<0.01	<0.01	0.09	0.02
Ba	<0.01	<0.01	0.13	nd
Ca	<0.01	<0.01	0.10	nd
Ce	nd	nd	1.87	0.38
Eu	0.13	0.08	82.81	91.60
Fe	<0.01	<0.01	0.01	nd
Gd	0.01	0.01	6.24	7.16
K	0.01	nd	0.41	nd
La	nd	nd	0.37	0.06
Na	0.03	0.02	6.15	0.04
Si	<0.01	<0.01	0.25	nd
Tb	0.02	0.02	0.41	0.46
Y	99.77	99.82	1.08	0.29
Zn	<0.01	<0.01	0.07	nd

For europium oxide, the obtained purity was lower (91.6%) due to the presence of the other four REEs in solution (notably gadolinium, which was present in a slightly higher amount in the feed used in this particular experiment (approx. 90 mg/L)). Minimization of these unwanted REEs can be achieved by having better control over selectivity during leaching. By optimizing the leaching conditions with respect to maximum dissolution of yttrium/europium and minimum dissolution of gadolinium/terbium/cerium/lanthanum, higher purities of europium oxides can be obtained using Cyanex 572. As discussed in sections 4.1 and 4.3, thermal treatment to remove mercury was shown to lead to increased leaching efficiency of these four REEs.

It is worth mentioning that if precipitation of europium is carried out from the raffinate directly after solvent extraction of yttrium, the obtained purity of europium oxide will be lower due to the co-precipitation of sodium (Table 15). High amounts of sodium from the sodium hydroxide used for pH adjustments were present in solution. In this case, further extraction of europium at higher pH, followed by its stripping, will lead to much higher product purity.

4.8. Proposed process flowsheet

A general flowsheet to process fluorescent lamp waste fractions like those investigated in the present study, based on the aforementioned observations, is presented in Figure 33.



Route 1
Fluorescent lamp waste phosphors fractions
~18% dry wt. REEs
Route 2
0.025/0.075 M I₂/KI
1h.; S:L 25 % w/v
Aqueous removal of Hg
Thermal removal of Hg (distillation)
Hg
Sedimentation Filtration
Contaminated I₂/KI solution
Residue
Decontamination e.g. ion exchange, reduction or solvent extraction
Water
Washing
Sedimentation Filtration
Contaminated water
Hg and iodine traces
Residue
1 M HNO₃
10 min.
S:L 10 % w/v
Leaching of impurity metals
Sedimentation Filtration
Acidic leachate rich in Ca
Further processing
Residue
2 M HNO₃
Up to 24 h.
S:L 10 % w/v
Leaching of Y and Eu
35 % vol. Cyanex 923 in kerosene
Sedimentation Filtration
Acidic leachate rich in Y/Eu
Solvent extraction of REEs
3 stages; O:A 2:1
Raffinate
Residue
Loaded organic phase
Water
Discarded or further processed to recover Ce, Gd, La and Tb
4 M HCl
Stripping
4 stages; O:A 1:2
Depleted organic phase
Washing
Regenerated organic phase
Acidic solution
Y/Eu-rich solution
NaOH
pH adjustment
0.1 M HCl
Solvent extraction of Y
10 stages; O:A 1:1
pHeq = 0
Loaded organic phase
Scrubbing
Acidic solution with traces of Eu/Y
Scrubbed organic phase
Oxalic acid
3 M HCl
Stripping of Y
Stripping product with Y
Precipitation
Y oxalate
Thermal treatment
Y₂O₃
1 M Cyanex 572 in kerosene
Acidic solution
Aqueous phase depleted in Y
Regenerated organic phase
NaOH
pH adjustment
Oxalic acid
Solvent extraction of Eu
1-2 stages; O:A 1:1
pHeq = 1
Loaded organic phase
Stripping of Eu
Stripping product with Eu
Precipitation
Eu oxalate
Thermal treatment
Eu₂O₃
Depleted aqueous phase
3 M HCl
Acidic solution

Figure 33 – Proposed flowsheet for the recovery of REEs from fluorescent lamp waste fractions containing phosphors. The process comprises removal of mercury (in purple colour), selective leaching of impurity metals (in green) and REEs (in dark blue), group solvent extraction of REEs with Cyanex 923 (in black), further separation of yttrium and europium with Cyanex 572 (in dark red), and preparation of REE oxides (in light blue).

The main targets are yttrium and europium. All hydrometallurgical steps in the process are carried out at ambient conditions. A decontamination step is first carried out to remove mercury and prevent its spread in subsequent process streams. This can be done thermally (the traditional route) or using the hydrometallurgical process based on the I_2/KI solutions presented in this thesis. After a washing step to remove residual iodine and soluble mercury, the bulk metals in the waste are leached selectively with nitric acid by taking advantage of their different leaching kinetics. Calcium, together with some of the other impurity metals, is dissolved after 10 – 15 minutes. A 1 M solution and a S/L ratio of 10% w/v are needed for samples containing in the range of 10% wt. calcium. The resulting residue is leached with 2 M nitric acid for 18 h or longer, using a S/L ratio of 10% w/v, to dissolve yttrium and europium, followed by a group separation of the REEs in this leachate using solvent extraction with commercial solvents. A 35% vol. Cyanex 923 solution in kerosene is sufficient to completely extract the REEs in three stages at O:A ratios of 2:1. Stripping with 4 M hydrochloric acid will lead to yttrium/europium-rich solutions. From here there are two possible paths; either precipitate a mixed REEs oxalate with oxalic acid or process this solution with Cyanex 572 to separate yttrium from europium at different pH_{eq} values. The separated streams are then treated with oxalic acid to precipitate REE oxalates, which are subsequently thermally treated at 800 °C to obtain oxides.

5. SUMMARY AND CONCLUSIONS

The goal of this study was to develop a hydrometallurgical process to recover REEs from fluorescent lamp waste phosphors fractions at ambient temperature. Mercury-contaminated real waste samples originating from lamp processing companies were investigated. The waste fractions studied had high chemical complexity, with many impurity metals present alongside cerium, europium, gadolinium, lanthanum, terbium and yttrium, the six REEs commonly found in such streams. On average, 17-18% dry wt. REEs were quantified in the most concentrated fractions, alongside >100 mg/kg mercury.

Because thermal treatment of the waste (a common method used today to remove mercury) is energy intensive and not always suitable for wet samples, an alternative hydrometallurgical decontamination process was proposed. Leaching of mercury with I_2/KI solutions at ambient temperatures was found to be selective over REEs. Mercury removal efficiencies of >90% were achieved using 0.025/0.05 M I_2/KI, and increases in efficiencies were noted with increases in leachant concentration. Ion exchange with Dowex 1X8 resin, reduction with sodium hydrosulphite and solvent extraction with Cyanex 302, Cyanex 923 and $CyMe_4BTBP$ were all efficient at recovering mercury from solution. The recovery rates of mercury from solution were often >99% when using these methods.

Impurity metals, notably calcium, which is the most prevalent impurity metal, were selectively leached prior to the leaching of REEs by taking advantage of their fast dissolution kinetics. A 10-15 min contact time with 1 M nitric acid was found to be sufficient to leach the bulk of calcium (80-90% leaching efficiency). This allows for higher final product purity and minimizes some of the issues that can occur in subsequent process steps, e.g. precipitation during solvent extraction.

Mineral acids, e.g. nitric and hydrochloric acid, were more effective at dissolving REEs compared to organic acids, e.g. acetic acid. Partial leaching selectivity between the six REEs in the samples was achieved by controlling the leaching time and temperature, and also making use of ultrasound-assisted digestion. Leaching of yttrium and europium did not pose a problem at ambient conditions. Leaching efficiencies >95% were noted for these two REEs over 24 h, even with diluted acids. This is due to the relatively easy dissolution of the YOX phosphor (yttrium-europium oxide) compared to LAP (cerium, terbium-doped lanthanum phosphate) and CAT (cerium, terbium-doped magnesium aluminate) phosphors. After dissolution of the YOX phosphor, further leaching of the remaining REEs can be carried out using concentrated acids and temperature/ultrasound, or by chemically converting the undissolved phosphors to more soluble oxides (alkali fusion).

Two commercial extractants, Cyanex 923 and Cyanex 572, were used to separate the REE ions in solution. The former was used for a group separation of the REEs from the other impurity metals in lamp leachates, while the latter was used to individually separate yttrium from europium. Leaching, followed by separation of REEs with Cyanex 923, was successfully tested in laboratory pilot scale using leaching reactors and counter-current mixer-settler systems. Selective leaching of metals was preferred over leaching of all metals in a single step. The latter led to lower stripping product purity and to precipitation during extraction due to pH changes and the presence of large amounts of impurity metals in solution. Over 99% of the REEs present in lamp leachates were extracted and stripped, respectively, in a mixer-settler system comprising three extraction stages with 35% vol. Cyanex 923 and four stripping stages with 4 M hydrochloric acid at O:A ratios 2:1.

The stripping product after extraction with Cyanex 923 was further processed with Cyanex 572, a novel reagent aimed at individual REEs separations. Yttrium was selectively separated from europium at $pH_{eq} = 0$ using ten successive batch extraction stages, followed by recovery of europium at $pH_{eq} = 1$ in one stage. Rare earth oxides were prepared by precipitating the REEs in the strip products with oxalic acid, followed by thermal treatment of the oxalates at 800 °C. A mixed REEs oxide (99.96% REEs, with 94.61% yttrium, 5.09% europium and 0.26% others), as well as yttrium oxide (99.82%) and europium oxide (91.6%) were synthetized.

7. FUTURE WORK

Additional studies are required to improve certain steps in the process. Particular areas requiring further development are described below.

1. Recovery of mercury from I_2/KI leachates using ion exchange and solvent extraction. The experiments presented in this study were a proof of concept and more insight is needed. Regeneration of the Dowex resin requires addressing, to avoid excessive consumption of ion exchanger. Also, the solvent extraction recovery of mercury requires more study to gain knowledge of the extraction systems. Alternatives of removing the mercury from the leachates without altering the oxidizing nature of the solution (the iodine speciation) would be beneficial, to ensure the reuse of this solution for further leaching.

2. Further optimization of the leaching process of metals with regard to the S/L ratio. This is needed in order to minimize the volumes of secondary waste generated e.g. the calcium-rich solution or the raffinate after solvent extraction with Cyanex 923.

3. Further optimization of the solvent extraction and stripping process with regard to the O:A ratio and acid consumption. Similar to the above, this would reduce the amounts of secondary waste generated. The use of less concentrated acid during stripping would also require less sodium hydroxide for pH adjustment during solvent extraction with Cyanex 572. Acid uptake by Cyanex 923 and its scrubbing with water also needs additional investigation.

4. Better control of selectivity during leaching. Minimizing the amounts of undesired constituents during leaching would translates into higher product purity. Less gadolinium and terbium leached alongside yttrium and europium would lead to higher purity of europium oxide.

5. Examine the use of Cyanex 572 to extract REEs from the yttrium/europium-rich leachate without first carrying out a group extraction of REEs with Cyanex 923. This would significantly simplify the separation process, minimize chemical consumption and lower the amounts of secondary waste generated.

8. ACKNOWLEDGMENTS

Formas, Energimyndigheten and Vinnova, Sweden, are acknowledged for financial support. The partners involved at various stages in this research are acknowledged for supplying guidance and waste samples: Nordic Recycling AB (a member of the Hans Andersson Group AB), CIT Recycling Development AB, MRT System International AB, MEAB Metallextraktion AB and IVL Svenska Miljöinstitutet.

Special thanks go to my supervisors, Teodora Retegan and Christian Ekberg, and all the other people who have guided me on the path I currently walk, helped me be where I am today and blessed me with their advice, knowledge, friendship and love.

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APPENDIX 1. ANALYTICAL AND INTRUMENTAL TECHNIQUES

ICP-OES

Inductively Coupled Plasma-Optical Emission Spectroscopy is an analytical measurement technique designed for element quantification at trace levels. The method is characterized by having low detection limits; lower than flame atomic absorption spectrometry but not as low as ICP-MS. Detection limits in the range of 1-50 μg/L (ppb) have been reported by the manufacturer for the instrument used in the experiments presented (iCAP 6500, Thermo Fischer). One of the advantages of this method is multi-element analysis, with no compromise of precision or detection limits.

The method requires the analytes to be in solution or as gas. To quantify elements in solids or sediments, a dissolution step must first be carried out. The resulting solution is injected in the plasma with a carrier gas, in this case argon, as aerosol. The sample is atomized in argon plasma at high temperatures. Upon de-excitation, photons with characteristic wavelength are emitted by the elements present. The intensity of the emitted photons, which is proportional to the amount of elements present, is detected. By using an external calibration, the elements present in the origial sample can be quantified.

SEM/EDS

Scanning Electron Microscopy/Energy Dispersive Spectroscopy is a technique used to magnify and analyse the appearance of materials, to obtain data about the elements present, and to determine the occurrence and distribution of components.

A focused beam of high-energy electrons is directed towards the target. Upon interaction with the sample, secondary electrons, backscattered electrons and X-rays are emitted. These electrons can give morphological information about the sample, while the X-rays that are characteristic to each element present in the sample can be used for elemental analysis.

XRD

Hull pointed out in 1919 that *'every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others'* (Hull, 1919). An X-ray beam hits the target and the intensity of the reflected beam is measured by a detector. This results in a spectrum in which the reflected intensities are plotted against the angles of reflection. Since the XRD pattern of a crystalline compound is like a fingerprint of that compound, this method can be applied for characterization and identification of polycrystalline phases.

A Siemens Diffraktometer D5000 system with copper radiation source and scintillation detector was used in this study. Components in the analysed samples were identified by search/match procedures using the DifracEVA software from Bruker.

APPENDIX 2. MIXER-SETLERS

Industrial solvent extraction of metals is often carried out using counter-current phase contactors e.g. mixer-settlers. In a counter-current separation process the phase volumes are constant. The schematics and principle of operation of a mixer-settler unit are presented in Figure 34.

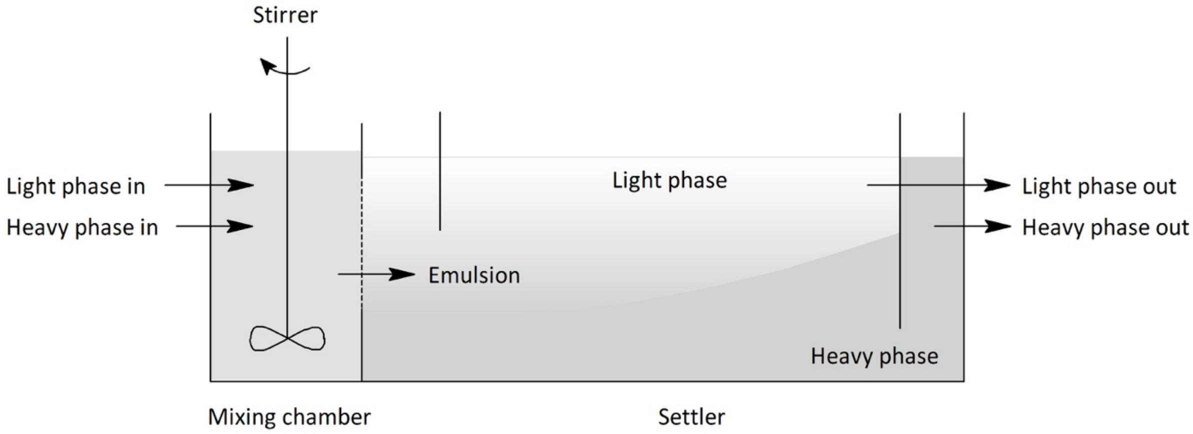
Stirrer
Light phase in
Heavy phase in
Light phase
Emulsion
Light phase out
Heavy phase out
Heavy phase
Mixing chamber
Settler

Figure 34 – Schematics and principle of operation of a mixer-settler unit.

As the name implies, the system comprises a part that achieves mixing of the aqueous and organic phases, e.g. a chamber with propeller-assisted mixing, and a part that allows for the mixed phases to separate. By combining multiple mixer-settler units together, multiple separation stages are achieved (Figure 35).

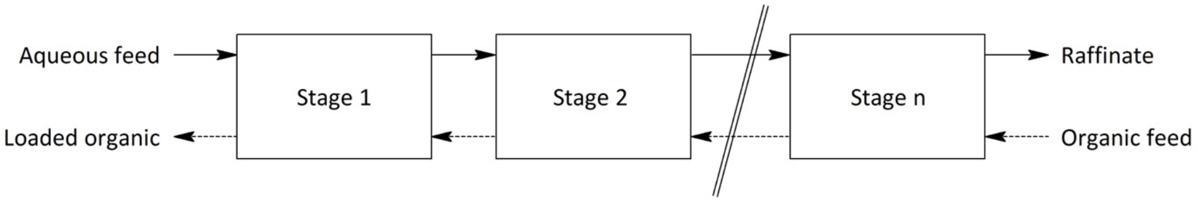
Aqueous feed
Loaded organic
Stage 1
Stage 2
Stage n
Raffinate
Organic feed

Figure 35 – Counter-current mixer-settler setup for separation of metal ions. Dashed arrows show the flow of the organic phase while continuous arrows show the flow of the aqueous phase. A similar setup was used in the present study for separation of REEs from fluorescent lamp waste leachates.

Multiple-stage separation is an important aspect when it comes to achieving high product purity. Individual separation of REEs with high purity often requires a high number of separation stages, due to the similarities in chemical properties. The aqueous and organic phases are fed in at opposite ends of the bank of contactors, which maximizes the driving force for extraction (the solute concentration difference between the two phases) (Cox and Rydberg, 2004).

Mixer-settlers have some advantages over other types of phase contactors used in industrial solvent extraction separations, e.g. pulse column (Ritcey, 2004), such as:

- High efficiency
- Simple construction
- Low maintenance
- Easy to scale up
- Good phase contact
- A wide range of flow ratios can be handled
- Well defined steps allow simple process calculations
- The process is easy to start and restart
- Stages can be added or removed easily.

Downsides relate to:

- Space requirements (sometimes a large floor area is needed)
- The need for large organic phase volumes (large holdups)
- The time it may take the system to reach steady state
- High energy consumption requirement for mixing and pumping the feeds in systems with a large number of stages.

The mixer-settler setup used for the group separation of REEs with Cyanex 923 (discussed in section 4.5) is presented in Figure 36.

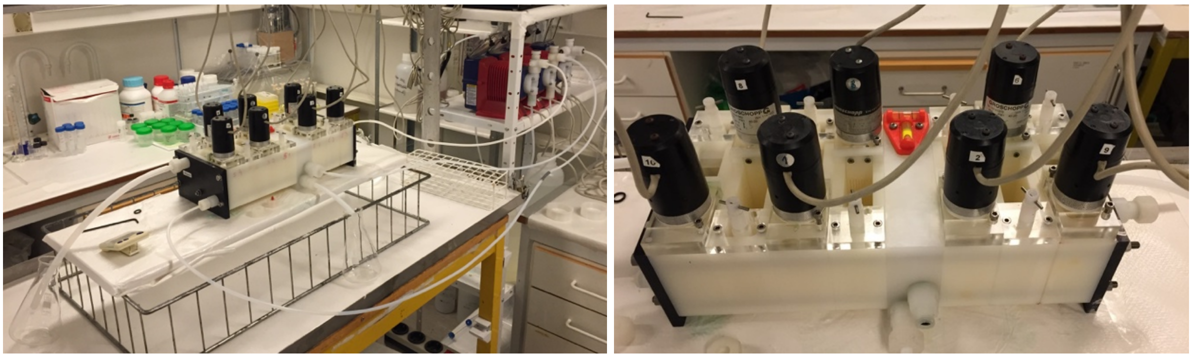

Figure 36 – The mixer-settler setup used for the group separation of REEs with Cyanex 923, discussed in section 4.5. The system consisted of three extraction units, which can be seen on the right in both pictures, and four stripping units, located on the left.