

Development of a solvometallurgical process for the separation of trivalent yttrium and europium

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Abstract

Non-aqueous solvent extraction is a method for separation of metals using a more polar phase with a limited water content. Ethylene glycol (+LiCl) as the more polar phase for the separation of yttrium and europium, two rare earths abundantly found in fluorescent phosphors, is promising since it offers better separation compared to the aqueous alternatives. Hence, a solvometallurgical process has been developed, using ethylene glycol (+LiCl) as the more polar phase and Cyanex 923 diluted in GS190 as the less polar phase. A three-stage counter-current extraction process extracted more than 99% of the yttrium, while co-extraction of europium was limited to 7%. A two-stage counter-current scrubbing step removed the co-extracted europium. Eventually yttrium could be recovered by precipitation stripping with an aqueous oxalic acid solution. The advantages of the developed process, besides the remarkable selectivity towards heavy rare earths, are the reduction of the waste water generation and the use of relatively cheap and green solvents.

Furthermore, other (green) solvents that potentially could be used as more polar phase such as propylene glycol, PEG-200 and dimethyl sulfoxide were tested, as well as mixtures of ethylene glycol and co-solvents. The system using DMSO (+LiCl) shows results similar to the ethylene glycol (+LiCl) system and is equally promising.

Samenvatting

Zeldzame aarden zijn metalen die men vaak terug kan vinden in hoog-technologische apparatuur en consumentenelektronica, bijvoorbeeld in fluorescentielampen. Ze worden vaak 'kritiek' genoemd omdat er enerzijds een onevenwicht bestaat tussen de samenstelling van de ertsen en de toepassing van de verschillende zeldzame aarden in verscheidene producten. Anderzijds is er ook een onevenwicht op geografisch vlak doordat China een quasi-monopolie heeft op de productie van zeldzame aarden. Het recupereren van zeldzame aarden vanuit bepaalde afvalstromen zou een (duurzame) manier kunnen zijn om deze problemen gedeeltelijk te omzeilen.

Deze masterthesis concentreert zich op de ontwikkeling van een proces voor de scheiding van yttrium en europium, twee zeldzame aarden die in relatief hoge concentraties in lampfosforen voorkomen. De scheiding wordt bewerkstelligd door solventextractie, waarbij gebruik gemaakt wordt van twee onmengbare fasen: een meer polaire en een minder polaire fase. Beide zeldzame aarden bevinden zich oorspronkelijk in de meer polaire fase. De minder polaire fase bevat een extractant molecule, Cyanex 923, dat een grotere affiniteit vertoont voor yttrium dan voor europium. Conventionele solventextractie maakt gebruik van water als meer polaire fase. Voor deze masterthesis is er echter gekozen om het gebruik van water te beperken en een solvometallurgische aanpak te volgen. Deze techniek is veelbelovend op het vlak van het verminderen van de productie van afvalwater en het verbruik van chemicaliën enerzijds, en het verhogen van de efficiëntie van het scheidingsproces anderzijds. Een niet-waterig solventextractie systeem waarbij ethyleenglycol (+ LiCl) als meer polaire fase gebruikt wordt bleek efficiënter te zijn dan de extractie vanuit waterige oplossing.

Vertrekkende vanuit dit systeem werden verschillende parameters geoptimaliseerd zodat yttrium volledig zou worden geëxtraheerd naar de minder polaire fase, en de extractie van europium tot een minimum beperkt zou worden. Deze parameters waren de concentratie van LiCl, de concentratie van het extractant, de volumeverhouding van de twee fasen en het aantal vereiste extractiestappen. Omdat toch een beperkte hoeveelheid europium in de minder polaire fase terecht kwam, moesten extra stappen geïntroduceerd worden om europium selectief en volledig vanuit de minder polaire fase te verwijderen. Hiervoor werd een wasoplossing van yttrium en LiCl in ethyleenglycol

in contact gebracht met de verontreinigde minder polaire fase, zodat een uitwisseling van europium vanuit de minder polaire fase met yttrium vanuit de wasoplossing plaatsvond. Uiteindelijk kon zuiver yttriumoxalaat neergeslagen worden door de gezuiverde minder polaire fase te strippen met een waterige oxaalzuuroplossing. Yttriumoxalaat zou vervolgens nog kunnen worden omgezet in het commercieel verhandelbare yttriumoxide door het te calcineren. De raffinaatfractie die overblijft na de extractie bevat bijna uitsluitend europium, dat op gelijkaardige wijze kan gerecupereerd worden als europiumoxalaat, na een extractie van dit raffinaat met de minder polaire fase. De raffinaatfractie die ontstaat tijdens het wassen zou kunnen terugvloeien naar de meer polaire voedingsoplossing in het extractiestadium, mits het compenseren van het verschil in concentratie van de zeldzame aarden.

Summary

Rare-earth elements are critical metals, which are frequently found in a variety of technologically advanced equipment and consumer electronics, such as phosphors for in fluorescent lamps. The criticality of these elements is based on the imbalance between the rare-earth ore composition compared to the use of the different rare earths in various high-volume applications. Besides, there is also a geographical imbalance, with China having a virtual monopoly on rare-earth production. A (sustainable) way to partially circumvent these problems is to recover the rare earths from waste streams, such as end-of-life fluorescent lamps.

This master thesis focusses on the development of a process to separate yttrium and europium, which are the two main rare earths that can be found in fluorescent lamp phosphors. The separation is performed using solvent extraction, which uses two immiscible liquids: a more polar and a less polar phase. Originally, both rare earth are found in the more polar phase. The less polar phase contains the extractant molecule, Cyanex 923, which shows greater affinity for yttrium compared to europium. Conventional solvent extraction uses water as more polar phase. However, for this master thesis a solvometallurgical approach has been chosen, since this shows great potential in lowering the production of waste water and chemicals, while increasing the efficiency of the process. A non-aqueous solvent extraction system in which ethylene glycol (+LiCl) is used as the more polar phase instead of water has proven to be more efficient than its aqueous counterpart.

Subsequently, the parameters of this system were further optimized to ensure full extraction of yttrium, while europium co-extraction had to be limited. These parameters were the concentration of LiCl, the concentration of the extractant, the phase ratio and the required number of stages. Since there was still a certain amount of europium extracted to the less polar phase, a few scrubbing stages were needed, to fully remove all europium from the impure less polar phase. Therefore, an ethylene glycol scrub solution containing yttrium and LiCl was contacted with the contaminated loaded less polar phase, in order to exchange europium from the less polar phase for yttrium from the more polar scrub solution. Eventually, pure yttrium oxalate was obtained through precipitation stripping of the yttrium rich less polar phase with an aqueous oxalic acid solution. If desired, the europium rich raffinate fraction acquired after the solvent

extraction stages can be extracted using fresh less polar organic, after which europium could be recovered by stripping with an oxalic acid solution. The scrub raffinate, which still contains both yttrium (from the scrub feed) and europium (scrubbed from the less polar phase), could flow back to the solvent extraction feed, after making up for the differences in rare-earth concentrations.

Thesis outline

The development of a separation process for the yttrium/europium pair using ethylene glycol (+LiCl) as more polar phase and Cyanex 923 extractant in GS190 Shell diluent as less polar phase was studied in this master thesis.

Chapter 1 discusses why the development of this process is of great importance and highlights its purpose for the circular economy. First, there is the statement of the problem (balance problem and supply risk) followed by the solutions and opportunities (valorization of various waste streams and possible applications).

Chapter 2 focusses on the technique of solvent extraction, the chemistry behind it and eventually discusses solvometallurgy and its advantages as well. The engineering aspects are only briefly discussed, since it was unfortunately not possible to test the developed flow sheet with the lab-scale mixer-settlers.

Chapter 3 discusses the instrumentation that has been used. Here, total reflection X-ray fluorescence spectroscopy (TXRF), rolling-ball viscometry and Karl Fischer titration are explained in more detail.

Chapter 4 summarizes the materials that were used, including the viscosity and water content of various feed solutions.

Chapter 5 explains the different techniques and methods used to optimize the flow sheet parameters.

Chapter 6 gives an overview of the measures (personal and collective) that had to be taken to ensure safe working in the lab.

In Chapter 7, the results are presented and discussed. The optimization of the process parameters are presented, as well as some side experiments using different feed solvents and studying the extraction of elements frequently associated with lamp phosphors and cathode ray tube phosphors. Eventually, a flow sheet is proposed.

The conclusions are presented in Chapter 8. Also the outlook and future experiments are discussed.

Chapter 9 is the list of references.

List of abbreviations and symbols

%E	Percentage extraction
%Sc	Percentage scrubbing
%St	Percentage stripping
A:O	Aqueous over organic phase ratio
AN	Acetonitrile
BAM	Blue phosphor in fluorescent lamps, BaMgAl ₁₀ O ₁₇ :Eu ²⁺
C	Coulomb
C923	Cyanex 923
CAT	Green phosphor in fluorescent lamps, (Ce,Tb)MgAl ₁₁ O ₁₉
CBT	Green phosphor in fluorescent lamps, GdMgB ₅ O ₁₀ :Ce ³⁺ ,Tb ³⁺
CCES	Counter-current extraction simulation
CCSS	Counter-current scrubbing simulation
cP	Centipoise
CRT	Cathode ray tube
D	Distribution ratio
D2EHPA	di-(2-ethylhexyl)phosphoric acid
DMSO	Dimethyl sulfoxide
EG	Ethylene glycol
GTL	Gas-to-liquid
HALO	Halophosphate phosphor, (Sr,Ca) ₁₀ (PO ₄) ₆ (Cl,F) ₂ :Sb ³⁺ ,Mn ²⁺
HREE	Heavy rare-earth element
keV	Kiloelectron volt
kV	Kilovolt
LAP	Green phosphor in fluorescent lamps, LaPO ₄ :Ce ³⁺ ,Tb ³⁺
LED	Light-emitting diode
LO	Loaded organic
LP	Less polar phase
LREE	Light rare-earth element
M	Molar (mol/liter)
MeOH	Methanol
MP	More polar phase
MSA	Methanesulfonic acid

OA	Oxalic acid
PC	Propylene carbonate
PEG	Polyethylene glycol
PG	1,2-propanediol
ppm	Parts per million
R	Universal gas constant (8.314 J/(K mol))
REE	Rare-earth element
REO	Rare-earth oxide
rpm	Rotations per minute
SF	Separation factor (see also: α)
SX	Solvent extraction
t	Time
T	Temperature
TXRF	Total reflection X-ray fluorescence
UV	Ultraviolet
vol%	Volume percent
W	Watt
wt%	Weight percent
YAG	Yttrium-aluminium garnet
YOX	Red phosphor in fluorescent lamps, $Y_2O_3:Eu^{3+}$
α	Separation factor (see also: SF)
η	Dynamic viscosity
ν	Kinematic viscosity

1. General introduction: relevance of this study

Rare-earth elements (REEs) are omnipresent in our modern, day-to-day environment: at home, at work and outside. The hard disk drives in laptops contain several grams of neodymium-iron-boron permanent magnets (NdFeB magnets), a material which revolutionized electronics industry and allowed for further miniaturization. They can contain praseodymium, neodymium, gadolinium and dysprosium. Inside the fluorescent lamps at home and in the offices, rare-earth phosphors can be found, mainly comprising yttrium, europium, terbium, gadolinium, cerium and lanthanum. Also renewable energy and green technology consume large amounts of REEs, wind turbines and hybrid or electric cars in particular, which contain large NdFeB magnets.

Although the applications for which they are used are important and ubiquitous, the broad public does not know what rare-earth elements are. These consist of a group of 17 different elements: scandium, yttrium and the lanthanide series. These elements share a lot of chemical properties, and are thus frequently found together in the ore minerals. Notable exception is the radioactive promethium, which does not occur (or very rarely, as a decay product of uranium-238) in nature. Historically, these chemical similarities caused problems when identifying single rare-earth elements, hindering proper separation of the elements. This was and still is an important issue and is hence also a central part of this master thesis.

1.1. Balance problem and supply risks

In nature, rare-earth elements (REEs) are found as a mixture of elements in different ratios depending on the type of ore. Although they are not to be considered scarce when looking at the average composition of earth's crust (e.g. gold and tin are even rarer), there is only a limited number of ores for which REE extraction is economically and technically viable. These can be divided in two groups: ores rich in light rare-earth elements (LREE), *i.e.* bastnäsite and monazite, and ores rich in heavy rare-earth elements (HREE), *i.e.* xenotime and ion-adsorption clays. In general, the natural abundance of REEs decreases with increasing atomic number Z . Besides, elements with an even atomic number Z are more abundant than elements with an odd atomic number, which is known as the Oddo-Harkins rule. This reflects clearly in the different

ores, where cerium is the most abundant element for the LREE ores, while yttrium has the largest share in the HREE ores.^{1,2}

Ideally, the global production of each rare-earth element matches its global demand, avoiding any surplus or shortage and resulting in the optimum market price for each element. Unfortunately, the balance between the market demand and the natural abundance of REEs in ores is a major issue. This is called the *balance problem* (or *balancing problem*). For instance, for the LREEs the market is driven by the demand for neodymium, which is used in neodymium-iron-boron magnets (NdFeB magnets). However, neodymium is much scarcer compared to other LREEs, and especially compared to cerium. Since a minimum of REE ore needs to be processed and separated in order to get a sufficient amount of high purity neodymium for high-tech applications, cerium and some other REEs will be produced in larger amounts than required by the REE market. As a consequence, this overproduction is stockpiled, driving the cost up for all of the rare earths.^{1,2}

Up to the 1960s, this composition versus market imbalance was not a big issue, since REEs were consumed as mixtures, not as pure single elements. For example, mischmetal was an alloy of LREEs used in for instance lighter flints. One of the first applications to use pure REEs was red cathode ray tube phosphors, $\text{YVO}_4:\text{Eu}^{3+}$ and later $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$. From the 1960s up to the early 1970s, europium became the most critical REE, because of its low natural abundance and its high demand. The production was also confined geographically to one mine in particular, the Mountain Pass mine in California. Later, in the 1970s and 1980, samarium was the most critical REE, since it was used in samarium-cobalt permanent magnets (SmCo magnets), which had an unprecedentedly high energy density and high coercivity (i.e. resistance to demagnetization). However, the scarcity of both samarium and cobalt were an obstacle for mass-production and implementation of these magnets. Therefore, NdFeB magnets rapidly replaced SmCo magnets after 1985. Up to today, neodymium plays the leading role in the LREE market. The HREE market on the other hand is driven by the demand for dysprosium, which is added to NdFeB magnets to increase the high-temperature and demagnetization resistance. For the HREEs however, the balance problem is less of an issue since they are produced in much smaller quantities. Besides

neodymium and dysprosium, also yttrium, europium and terbium are considered as critical REEs.¹

The natural occurrence of REEs is not only unevenly distributed over the periodic table of elements, there is also an unequal distribution on geographical level. The European Commission's 2017 report on the critical materials for the European Union (EU) mentioned that China accounted for 95% of the global production of both LREEs (Sc excluded) and HREEs (Y included).³ China can secure its dominant position on the REE market through export policies and quota, and guarantees domestic industries with cheaper and preferential access by levying export taxes.⁴ The rare-earth crisis of 2010-2011, with dramatic and global REO price increases, can be seen as the direct result of China's rare-earth policies. Also, all of the REEs consumed in the EU had to be imported, with China accounting for 40% of the imports, the United States 34% and Russia 25%. This underscores that also politics play an important role in the provision of solutions for the rare-earth criticality, besides economic and ecological concerns.

Therefore, action schemes and criticality assessments were put up by many governments, including the European Union (EU). The EU composed a list of critical raw materials, which is graphically represented in *Figure 1.1*. This not only serves for the identification of much needed investments that help to alleviate the reliance on imports and for the negotiation of equitable trade deals, but also points out the direction for the development of research and innovation actions, as implemented in the EU 2030 Agenda on Sustainable Development.³ This criticality assessment is based on both the economic importance (importance of application in EU end-use, substitutability of the material) and the supply risk (global supply, risk of disruption, import reliance) of the material.⁵ A material exceeding the predetermined threshold on both of these aspects is categorized as a critical raw material. This list of critical raw materials however is just a snapshot of the criticality today. The volatile resource market, the fast changing technologies and the unstable global politics can shift the focus on other materials very quickly. A further point of criticism lies in the bundling of the LREEs and HREEs. As discussed earlier, not all of the REEs are as critical. For the moment, only yttrium, europium, terbium, dysprosium and neodymium are to be considered as critical.

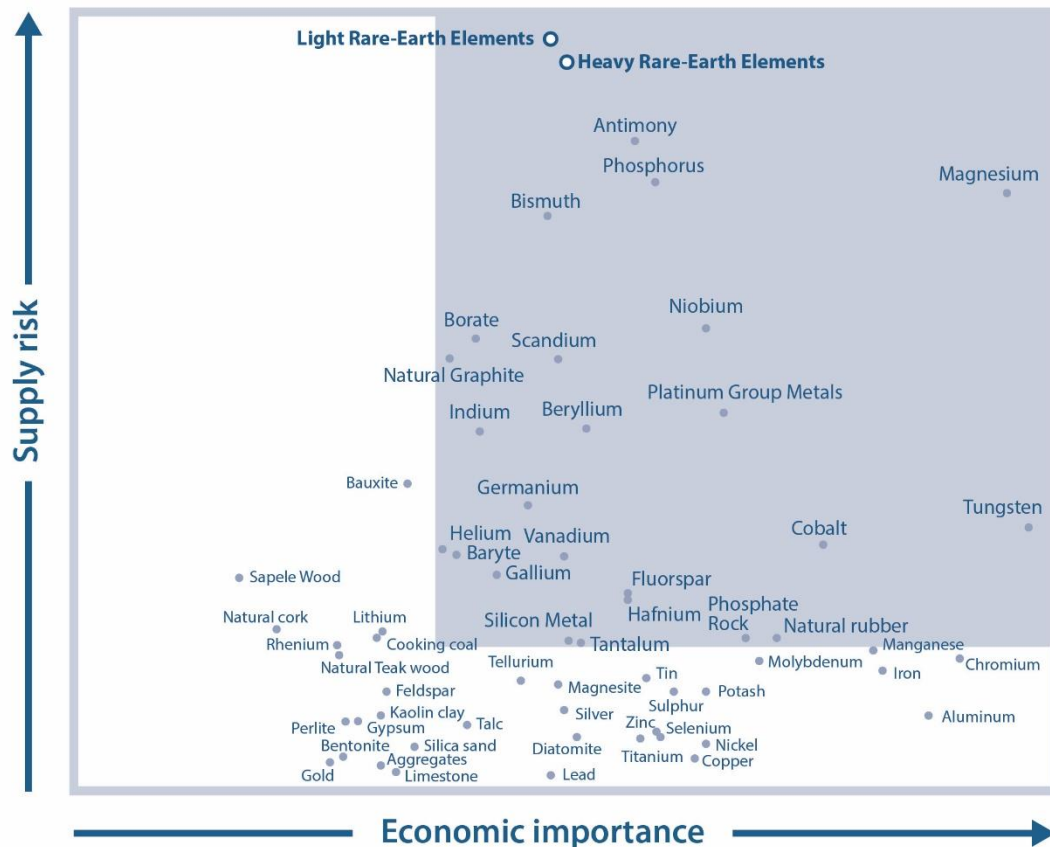


Figure 1.1 Criticality assessment of non-energy and non-agricultural raw materials for the EU, European Commission 2017. The criticality of the raw materials is measured as a function of two main parameters: economic importance and supply risk. Credit figure: P. McGuinness. ⁵

In general, several options can be discussed to provide new policies, mitigating the REE criticality problem and/or the balance problem:^{1,4,6}

- Opening new mines for primary rare-earth oxides (REOs) production and mining of other types of REE deposits;
- More efficient use of REEs (read: reducing) in technological components and other products;
- Substitution of REEs in key applications;
- Closing the REEs materials loop:
 - Direct recycling of (pre-consumer) manufacturing REE residues;
 - Urban mining of post-consumer end-of-life products;
 - Landfill mining of historic urban waste and industrial tailings containing REEs.

The first two options are rather straightforward, but will only have an effect on short to medium term. On long term, also these new mines will run out of (economically) mineable ores, even when less of the REEs are used for the same application. As to the mining of different REE deposits, this might also temporarily alleviate the supply shortages and even the balance problem (by mixing REE concentrates in such a way that the mixture composition reflects the market demand). Possible REE stocks may be extracted from minerals such as eudialyte, gadolinite, etc.¹ Also, the phosphate rocks from apatite mines (production of fertiliser) contain small amounts of REEs. The major drawback of these “new” deposits are their low REO grade.

Substitution of critical REEs with less critical REEs, non-critical REEs or even non-REEs is a third option. This could partially mitigate both the balance problem and the supply risk. However, substitution is often impossible or it leads to products with poor performance. Substitution can also be seen in a broader sense of the word: instead of substituting the chemical compounds, substitution of the entire system can also be a possibility.⁴ Such a trend can be seen on the lighting market, where rare-earth containing fluorescent lamps are being replaced by light-emitting diodes (LED) technology.^{1,7} Although some inorganic LEDs still contain yttrium and cerium ($Y_3Al_5O_{12}$ or YAG, doped with 0.003% Ce^{3+}), many LEDs do not use any rare earths at all. This alleviates partially both the supply risk and the balance problem temporarily, although also new problems arise concerning the balance problem. The replacement of fluorescent lamps by LEDs might cause the markets for europium, yttrium and terbium to decline in the coming five to ten years. New and upcoming applications are already available for yttrium (speciality ceramics) and terbium (substitution of dysprosium in NdFeB magnets). However, oversupply is looming for europium, which does not have any significant application besides fluorescent lighting and fluorescent safety markers. However, the global production of europium is much smaller than the production of cerium, making the oversupply of europium less significant compared to cerium overproduction.

Eventually, a circular economy seems to provide a good solution to many problems associated with the rare-earth supply risk and the balance problem. This approach will be discussed and illustrated in the next section with research performed on the recovery of yttrium and europium from fluorescent lamps and cathode ray tubes.

1.2. Recycling of yttrium and europium

1.2.1. Fluorescent lamps

Although there is large variety in possible shapes and sizes, the structure and functioning of a fluorescent lamp can easily be simplified and explained using *Figure 1.2*. Typically, a fluorescent lamp is a sealed glass tube, containing inert gas or working under vacuum conditions.^{8,9} An AC current through the tungsten cathode filament causes emission of electrons, which interact with mercury.¹⁰ When falling back to the ground state, mercury emits UV light (254 nm), that can be absorbed on its turn by the lamp phosphors coated inside the glass tube^{11,12}. Depending on the type of phosphor, the energy is released back as red, blue or green visible light. The relative percentages in the phosphor mix will determine the colour rendering of the white light. *Table 1.1* shows the typical composition of fluorescent lamp phosphors based on REEs. Furthermore fluorescent lamps may also contain large amounts of a broad-band white emitting halophosphate phosphor $(\text{Sr,Ca})_{10}(\text{PO}_4)_6(\text{Cl,F})_2:\text{Sb}^{3+},\text{Mn}^{2+}$, which does not contain REEs. In between the glass and the phosphor layer, an alumina (Al_2O_3) or silica (SiO_2) barrier layer is applied, to protect the glass tube from attack by mercury vapour.^{7,13}

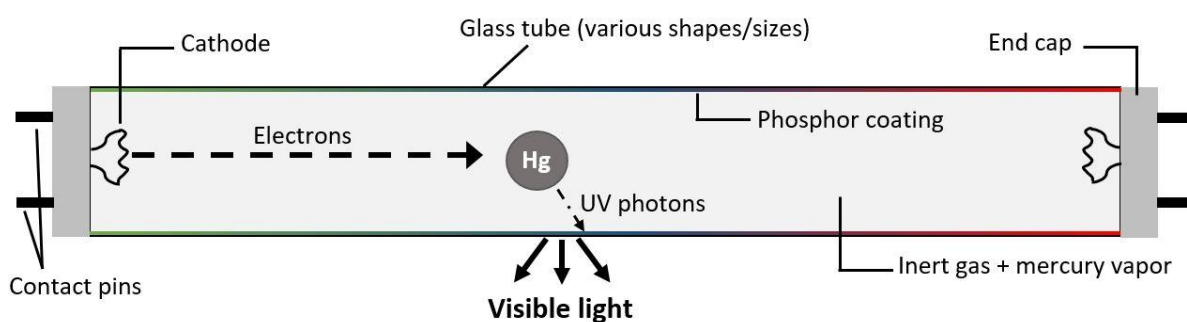


Figure 1.2 A schematic representation of a fluorescent lamp. This figure has been redrawn according to Wu et al. (2014).⁸

Table 1.1 Non-exhaustive list of common REE-based phosphors and typical composition found in lamp phosphor waste.¹³

Phosphor type	Possible compound types	Share of total REE phosphor mass (wt%)
Red	$Y_2O_3:Eu^{3+}$ (YOX)	20
Blue	$BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) $(Sr,Ca,Ba)_5(PO_4)_3Cl:Eu^{2+}$ (chloroapatite)	5
Green	$LaPO_4:Ce^{3+},Tb^{3+}$ (LAP) $(Ce,Tb)MgAl_{11}O_{19}$ (CAT) $GdMgB_5O_{10}:Ce^{3+},Tb^{3+}$ (CBT)	6–7
White	$(Sr,Ca)_{10}(PO_4)_6(Cl,F)_2:Sb^{3+},Mn^{2+}$ (HALO)	40–50

In most countries, a very extensive and efficient recycling program already exists for fluorescent lamps, albeit primarily to avoid the release of mercury into the environment.⁷ Each lamp contains a few milligrams of it, depending on the type and the power of the lamp. A typical 40 W fluorescent lamp contains 4 to 6 g of phosphor powder, accounting for 2-3 wt% of the total mass of the lamp.¹⁴ These lamp phosphors are normally either landfilled or stockpiled. However, the phosphors contain up to 27.9 wt% of REOs comprising critical (Y, Eu, Tb) and less-critical (La, Ce, Gd) elements.^{6,15} The red phosphor (YOX) is the most valuable fraction since it contains about 80 wt% of the rare earths in fluorescent lamps. These are two critical rare earths, yttrium and europium, as can be seen in *Table 1.1*.¹³ For this reason, fluorescent lamps rank second on the ERECON priority list for recycling of REE-containing waste, while they rank first if you only consider rare-earth phosphor based products.⁴

There are several ways to reuse or recycle the waste lamp phosphors. First, the phosphor mixture can be directly reused in new lamps after recovering them from the glass, metal and plastic scrap from end-of-life lamps. Though, there are several hindrances to this method:⁷

- Different blends of phosphors are used by different manufacturers and in different lamp types. The phosphors thus need to be recuperated by lamp type. If different lamp phosphor mixes are blended, inferior products are obtained.

- The recovery of the phosphors is not always straightforward. For linear fluorescent lamps processing is relatively easy: the end caps are cut off, after which the phosphor is blown out. Non-linear fluorescent lamps (i.e. bended tubes) and compact fluorescent lamps (see *Figure 1.3*) have to be crushed and sieved (dry or wet sieving). The finest fraction left is the phosphor powder. The phosphor powder obtained after crushing and sieving still contains a considerable amount of fine glass and binder material (alumina or silica) contamination.
- Overall, the recovered phosphor powders are most likely deteriorated by frequent exposure to high-energy UV light. Also, a considerable amount mercury tends to accumulate in the phosphor coating during the lamp's lifetime.

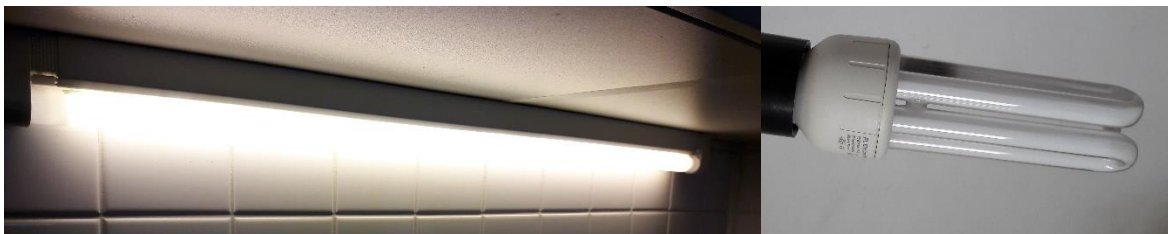


Figure 1.3 A linear fluorescent lamp (left) and a compact fluorescent lamp (right).

Secondly, recyclers can try to separate the phosphor mixture into its different components using physicochemical separation techniques.^{6,7} However, the limited purity of the recovered phosphors, the deterioration of the lamp phosphors during use, the contamination of the phosphors with mercury, the differences in phosphor types used in different fluorescent lamp types and changes in phosphor particle size during separation would all result in the production of lamps of inferior quality. Only in the case that fluorescent lamp producers can recycle their own lamps, this approach can be applied to recycle the phosphors.⁶

Finally, most research focusses on recovery of the rare earths, obtaining high-purity rare-earth oxides. There are however still problems with regard to selective dissolution and leaching efficiency. As to selectivity, the differences in difficulty to dissolve each phosphor can be used as an advantage.^{7,8} Many researchers have shown already the feasibility of the developed technologies. This has led to the application of some of these processes in industry, albeit relatively limited.

Generally, the recycling process starts with the physical treatment of the waste. In the case of linear fluorescent lamps, the phosphors can be blown out after removing the end caps. For other types of lamps, the phosphor is recovered through crushing and sieving of the lamp material. The residue obtained after crushing is separated into a metal, glass and powder fraction. The mercury contained in the lamp can be recovered by heating the powder fraction in vacuum environment up to 800 °C, after which it can be recovered through condensation or filtration. In case the contaminated lamp powder is present in a wet process stream, the mercury can be removed by leading the solution through a column filled with a chelating resin which binds mercury selectively. Eventually, a powder is obtained that not only contains the fluorescent phosphors, but also a large fraction of glass (up to 50% of the collected powder) and binder material (alumina or silica).^{7,8,16}

As to the chemical dissolution of the rare earths from the solid phosphor waste, an operation commonly called *leaching* in extractive metallurgy, several possible approaches exist, mainly based on the ability of certain phosphors to dissolve more readily at milder conditions than the other phosphors, as was stated earlier. Traditionally, the powder is first treated with dilute acid (HCl) at room temperature, at which point the halophosphate (HALO) is dissolved. More acidic conditions are necessary to dissolve $Y_2O_3:Eu^{3+}$ (YOX). Hot acid leaching with sulfuric acid is needed to recover LAP, while CAT and BAM only scarcely dissolved.¹³ To regain the latter two, strongly alkaline conditions and high temperatures or alkali fusion (NaOH, 900 °C or Na_2CO_3 , 1000 °C) can be applied.⁸ The main problem of this traditional method is the ease with which the relatively invaluable HALO is dissolved, consuming large amounts of acid and contaminating the valuable REEs-containing leachate fractions, thus complicating further processing.¹³

New recycling schemes often focus primarily on the recovery of yttrium and europium from YOX, since it takes up the largest share of value in the lamp phosphor waste and is easily dissolved at mild conditions.^{9,14} Several hydrometallurgical methods have been described, most of which are targeting quantitative dissolution of yttrium and europium only.^{15,17,18} Interestingly, some of these processes can recover yttrium and europium as a pure mixed oxide. For example, Dupont and Binnemans (2015) showed that YOX can be selectively dissolved in a functionalized ionic liquid (betainium

bis(trifluoromethylsulfonyl)imide or [Hbet][Tf₂N]), then stripped with solid oxalic acid and finally calcined to obtain pure YOX.¹³

A limited number of authors also investigated the possibility to separate europium and yttrium using solvent extraction from aqueous solutions. De Carolis *et al.* (2015) redissolved a mixed yttrium and europium oxide, obtained after leaching lamp phosphor waste with 6 M HCl and subsequent precipitation with oxalic acid.⁹ The rare-earth oxalate precipitate was oxidized during redissolution using an acidic solution of KMnO₄, rather than using the energy consuming calcination. Extraction was performed with a phosphonic acid (PC-88A) in kerosene. Adjustment of pH of the aqueous solution to 1.45 was necessary. Extraction efficiency for yttrium was not mentioned, but for europium, co-extraction was mentioned to be 23.2%. Innocenzi *et al.* (2018) used di-(2-ethylhexyl)phosphoric acid (D2EHPA) as the extractant for the separation of the rare earths (including terbium, cerium and lanthanum) from an aqueous sulfate medium at pH 0.5.¹⁹ Yttrium could be separated from the rest, with only terbium being co-extracted. After six *stages* (a stage is one extraction contact between 2 phases reaching equilibrium, *vide infra*), 47% of yttrium was extracted, together with 7% of terbium and 4% of cerium. Tunsu *et al.* (2016) also investigated solvent extraction for the separation of yttrium and europium from an aqueous leachate.²⁰ The leaching procedure, was part of earlier work by the authors.^{14,21,22} This procedure consisted of a decontamination step, removing mercury, a leaching step using 2 M HNO₃ to selectively extract yttrium and europium, a solvent extraction step, to remove unwanted impurities and a stripping step with 4 M HCl, generating an aqueous solution enriched with yttrium and europium. Separation of yttrium and europium by solvent extraction from this solution was performed with Cyanex 572 (1 M), which is a phosphorous-based chelating extractant with undisclosed composition.²³ Ten stages were needed for full extraction of yttrium. Co-extraction of europium was limited. Subsequently, europium was extracted from yttrium-depleted aqueous phase in one stage using the same extractant. Direct stripping of europium from the yttrium-depleted aqueous phase due to the presence of sodium (from pH adjustment with NaOH), which would co-precipitate. The yttrium and europium oxide obtained after precipitation with oxalic acid and subsequent calcination had a purity of about 99.8% and 91.6% respectively.

Other methods for the recovery of yttrium and europium are based on the reduction of trivalent europium to divalent europium, which is then easily separated from yttrium and other REEs. This reduction can be performed by addition of zinc powder or by photochemical reduction.^{24,25}

1.2.2. Cathode ray tubes (CRTs)

Since the advent of flat panel display devices, the demand for cathode ray tube (CRT) units, such as television screens and computer monitors, has declined dramatically. At present, the CRT technology is obsolete, with most of the CRT units being taken out of service. However, the electronic waste generated from this out-dated technology still poses some issues today because the glass screens contain a considerable amount of lead. Therefore, it has to be considered as hazardous waste, since improper disposal could lead to lead contamination of the environment. Millions of CRT units have been stockpiled during the last decades, awaiting proper recovery of the (toxic) components.

Besides, similar to fluorescent lamps, colour CRT units also contain rare earth phosphors, coated at the back-side of the screen. Here, only yttrium and europium are present as the red phosphor $Y_2O_2S:Eu^{3+}$, an oxysulfide. Older devices might still contain $YVO_4:Eu^{3+}$.⁶ The green and blue phosphors however, $ZnS:Cu$ and $ZnS:Ag$ respectively, do not contain any REEs. Each CRT display contains between 1 to 7 g of phosphor powder, for which an example of the composition is given in *Table 1.2*.^{26–30}

Table 1.2 Composition of phosphor powder obtained from computer monitors, according to Resende and Morais (2010). (in wt%)²⁶

Zn	S	Y	Si	Pb	Al	Ba	Eu
31.4	17.4	17.0	10.4	7.5	4.6	2.2	0.76

According to Tian *et al.* (2016), between 2001 and 2013 about 2,400 million CRT units have been discarded.³⁰ This is potentially an interesting secondary source of yttrium and europium, accounting for a reserve of 2,856 tonnes and 128 tonnes respectively if there is 7 g of phosphors per screen and based on the abovementioned figures and *Table 1.2*. Also in Europe, recovery of REEs from scrap CRTs and removal or

stabilization of hazardous materials ranks high in the priority list: the ERECON 2014 report had put it on fourth place in the priority list for recycling REE-based phosphors.⁴

As to the existing recovery techniques, only the disassembly, which is partly manual, is commercialized. Once the plastics, printed circuit boards and base metals are recovered, a conical shaped glass tube remains, which is the cathode ray tube (CRT) as depicted in *Figure 1.4*. It is the essential part in any television and computer monitor of this kind and takes also about 60% of the total weight. The glass tube consists out a glass front panel, *i.e.* the screen, a glass neck enveloping the electron gun and a glass funnel connecting the neck and the screen. Both the neck and the funnel glass contain PbO, while the screen glass contains BaO. Because of their density, lead and barium are added to absorb the ionizing radiation emitted inside the tube, thus preventing the escape of harmful radiation.^{31,32}

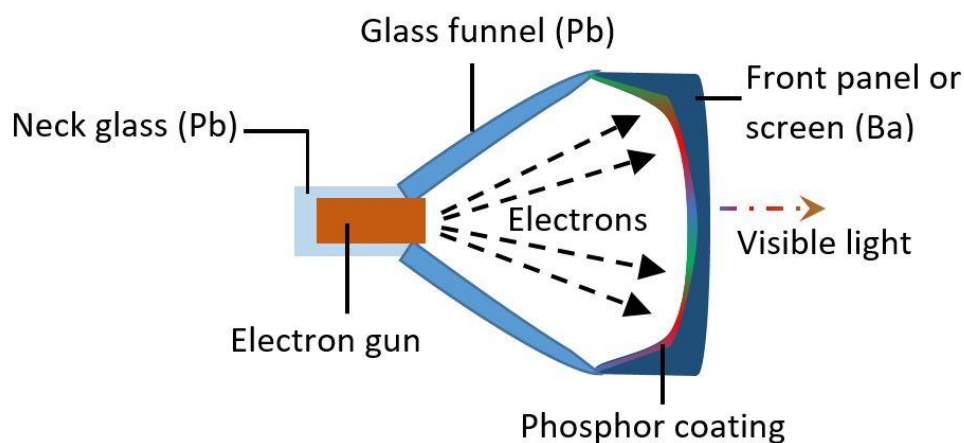


Figure 1.4 Schematic presentation of a cathode ray tube (CRT).

On one hand, research is focussed on the removal of lead from the CRT glass cones, since it is important to safely remove the lead from the glass or at least stabilize it. Recycling processes can either be closed-loop processes, generating new leaded glass for CRTs, or processes envisaging new applications such as ceramics, road filler and concrete bricks.³² Of course, for applications which could come into contact with humans the lead content should be reduced considerably. The different techniques and flow sheets developed to achieve this are beyond the scope of this work and will not be discussed.

On the other hand there is the processing of the phosphors, which is of considerable importance as a secondary source of yttrium and europium (*vide supra*). After cutting open the CRT at the screen-funnel interphase, the luminescent phosphors can be brushed out carefully. These phosphor powders might contain impurities such as silicates, lead and barium from the glass, zinc from the blue and green phosphors and aluminium from a film which holds the luminescent phosphor coating.²⁸ The presence of these impurities results in the need for selective separation techniques.

In contrast to the fluorescent lamps, not so much research has been performed on the recovery of rare-earth phosphors from CRTs. All of the publications mainly focus on the recovery of the rare earths from the solid phosphor waste by leaching rather than the separation of rare earths. Dexpert-Ghys *et al.* (2009) tested an oxidative alkaline process (NaOH+NaOCl) and an acidic process (dilute HNO₃), both of which are combined with a roasting step. They recovered a solid (Y,Eu)₂O₃ residue, which had a photoluminescence efficiency of 30% compared to virgin (Y,Eu)₂O₃. Disadvantage of this procedure is the generation of SO₂ gas during the roasting of ZnS to ZnO.²⁸ Yin *et al.* (2016) also recovered the red phosphor solid with a reported yield of 99.5% and purity higher than 99%. Their method consists of a leaching step using HCl+H₂O₂, a precipitation step using oxalic acid (recovering yttrium and europium oxalate) and a calcination step, which results in the final product. They reported that mechanical stirring was necessary during the leaching step to avoid formation of the toxic H₂S. This process thus avoids formation of harmful gasses such as the aforementioned H₂S and SO₂.²⁹ Tian *et al.* (2016) used H₂SO₄ as a leaching agent to recover yttrium and europium in the leachate liquor.³⁰ Again, formation of the toxic H₂S is avoided by the use of an oxidizing agent, H₂O₂. Eventually, 98.76% of yttrium and 100% of europium was recovered, as well as 45% of zinc and 80% of aluminium. The separation of the REEs and the purification (*e.g.* by solvent extraction) was not investigated by any of the authors, although some of them briefly mention the possibility.

1.2.3. Applications for yttrium and europium

Demand for fluorescent phosphors, used in lighting applications, is said to be stabilizing or even declining in the coming years. This is caused by the growing popularity of light-emitting diode (LED) technology. The declining demand for

fluorescent lamps and, ultimately, possibly also for yttrium and europium can cause the balance problem to shift. However, besides their use in fluorescent phosphors, europium and yttrium are applied in a variation of different applications. Some of these applications might see a rise in demand for the coming years, making it worthwhile to recover yttrium and europium from a rich secondary source, such as the fluorescent phosphors. Most of the applications however ask for high purity rare-earths in order to attain full performance. Exactly this is why the separation of europium and yttrium is very interesting and should be addressed.

Once yttrium and europium are recovered, they can be reused in different applications. Besides in fluorescent lamps and CRTs, yttrium can also be used (in smaller quantities) in the yellow phosphors in inorganic LEDs.⁷ Furthermore, a wide array of specialised ceramics containing yttrium have been developed. Yttria-stabilized zirconia for instance, which is a high-strength and high-toughness material, frequently used for medical applications (dentistry). Also, these alloys can be deposited as improved thermal barrier coatings in as improved thermal barrier coatings in gas turbines and jet engines, where there is need for materials that withstand thermal expansion stresses and oxidative environments at elevated temperatures.³³⁻³⁵ Similarly, yttrium-aluminium alloys can be used in medical applications (e.g. implants) since they are biocompatible and corrosion resistant.^{36,37} Because they are light-weight, they also have potential in automobile, aircraft and aerospace industries.^{38,39} Yttrium-iron garnets ($Y_3Fe_5O_{12}$) belong to the group of magnetic oxides and are frequently used in microwave technology.⁴⁰ Neodymium-doped yttrium-aluminium garnet (Nd:YAG) is a ceramic used in lasers, which are applied in the medical world. Furthermore, yttrium is also used in clean energy technology: solid-oxide fuel cells use yttrium in their electrolyte.⁴ Lastly, yttrium is also found in $YBa_2Cu_3O_7$ superconductors, with a critical temperature as high as 92 K.⁴¹ Europium is less in demand than yttrium, but is also less abundant. Besides being used in lamp phosphors, europium can also be used in alternative yellow phosphors in LEDs. Furthermore, it is also used in fluorescent markers, e.g. on banknotes.⁴²

2. Solvent extraction

For thousands of years humans have extracted metals such as gold, silver, copper, iron, lead, tin and mercury from rich ores using pyrometallurgy, a technique based on the conversion of metal-bearing minerals using high temperatures.⁴³ However, during the industrial expansion the rich ores were depleted at fast rates, causing the need to process lower grade minerals. Besides, other metals which are difficult to extract using the traditional pyrometallurgical techniques demanded the development of new technology. In the 19th century, given the increased availability of pure (organic) chemicals, the development of new mineralogy processing techniques such as froth flotation and above all solvent extraction proved useful to mitigate the resource problems.^{43,44} It was not until the 1940s though that solvent extraction gained worldwide popularity, mainly caused by the efforts during the Manhattan Project. Up to today, the *extractive metallurgy* (all operations concerning extraction and purification, from leaching of the ore through the recovery of the pure metal) has been evolving. Now, *hydrometallurgy* (treatment of mixed metal, low grade ore with aqueous solutions) and *pyrometallurgy* are the main extraction processes used in industry. However, more sustainable extractive methods are being developed, limiting the waste generation and the use or emission of harmful chemicals. *Solvometallurgy* is one of the most promising techniques amongst these upcoming technologies.⁴³ It is similar to hydrometallurgy, but it limits the water content of the solutions used during the process, decreasing the generation of waste water drastically.

As a consequence, the physical and chemical fundamentals of solvent extraction as presented in this section are presented in such a way that it will be applicable to both aqueous and non-aqueous solvent extraction. More detailed information on solvometallurgy is provided as well. Eventually, the engineering aspects are discussed in the third part of this section.

2.1. Solvent extraction: fundamentals and terminology

Solvent extraction is only a part of the entire extractive metallurgical process. Generally, it is preceded by the dissolution of the metals from the solid ore, which is called leaching. Subsequently, the metals in the pregnant leach solution are separated and purified during solvent extraction, after which they are recovered by e.g.

electrowinning. This part focusses on the chemistry of solvent extraction, which is greatly influenced by these preceding and following steps. Furthermore, the solvent extraction of rare earths is investigated in more detail.

2.1.1. Definition of solvent extraction and terminology

Solvent extraction is a separation and purification technique which can be used for inorganic species (metals) or organic compounds (e.g. medicinal molecules in pharmaceutical industry).⁴⁴ According to the International Union of Pure and Applied Chemistry (IUPAC), solvent extraction can be defined as follows:

“The process of transferring a substance from any matrix to an appropriate liquid phase. If the substance is initially present as a solute in an immiscible liquid phase the process is synonymous with liquid-liquid extraction.”⁴⁵

The matrix in which the extractable species is found can thus be solid or liquid. In the former case this is called *leaching* (or *solid-liquid extraction*), the latter, as clearly explained in the IUPAC definition, is *liquid-liquid extraction*. However, in literature the term *solvent extraction* is often used synonymously to liquid-liquid extraction, which is also the case throughout this work. IUPAC considers this acceptable if there is no confusion possible with extraction from solid phases due to the given context.

Specific solvent extraction terminology has to be introduced as well. *Figure 2.1* gives an overview of the vocabulary used to indicate the constituents at different phases of solvent extraction.^{46,47}

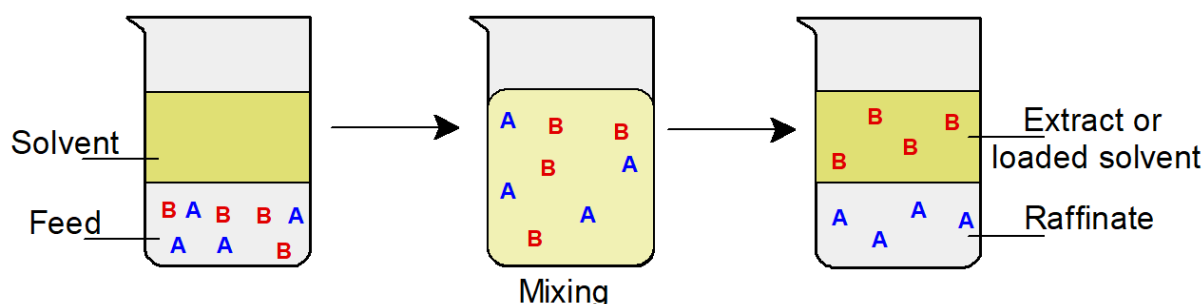


Figure 2.1 Schematic representation of the solvent extraction process.

The process starts with the *feed*, consisting of the more polar phase (e.g. water, DMSO,...) in which the extractable metals are dissolved. In hydrometallurgy, the term aqueous phase is used, for the obvious reason that the feed is in that case an aqueous solution of metal ions. The feed is either the pure pregnant leachate or redissolved metal precipitate (obtained after leaching) in polar solvent. The *solvent* (also called organic phase), which is a less polar (organic) phase, usually of lower density, contains either pure *extractant* (if liquid) or a solution of the extractant with a *diluent* (non-polar organic solvent). Such a diluent is needed to lower the viscosity of the extractant and should be virtually immiscible with the more polar phase. Of course, the diluent significantly influences the extraction behaviour of the system, due to its ability to retain both the extractant and extracted metal complex species. The interaction between diluent and extracted species influences the distribution ratio of the metal and can change the separation factor between two metals.⁴⁸ Ideally, a diluent should be inert (no degradation or side-reactions) and should have a low volatility (avoids losses) and a low flashpoint. Another practicality of the setup of an extraction experiment is choosing the volume ratio of the two phases, *i.e. phase ratio*. A larger volume of the less polar phase compared to the polar phase will result in more metal being extracted because of the higher availability of extractant. However, this also creates a less concentrated solution, which is unfavourable for the subsequent processing. A *salting-out agent* can be added to the feed solution, increasing the distribution ratio or the separation factor of two difficult-to-separate metal ions and reducing the miscibility of the two phases. Such a salting-out agent is a salt that usually contains the same anion to which the extractable metal is coordinated and a non-extractable cation.⁴⁶ Its effect on the distribution of metals is caused by the reduction of the amount of free solvent molecules in the feed which are now ordered around the ions from the salt. The higher the charge density of these ions, the stronger the salting-out effect. This reduction of solvation increases the activity of the rare-earth ions, enhancing extraction.⁴⁹

Subsequently, the extraction experiment or process takes place. The phases are agitated, dispersing them in one another and thus increasing the surface area. As a result, the extraction rate is increased, and the equilibrium, at which the rate becomes zero and thus the net transfer of species between the two phases reaches zero too, is reached faster.⁴⁸

On lab scale, the extraction can be performed in batch scale by stirring a certain amount of feed and solvent for a certain time in vials or beakers or by shaking the two phases in a separatory funnel. Also a continuous process can be attained by using mixer-settlers (see 2.3 *Solvent extraction: equipment and engineering aspects*), which is commonly used in industrial application as well.

Eventually, after reaching equilibrium the two phases settle naturally or by centrifugation. The more polar solution at this stage is called the *raffinate*. It contains the metal species that were intended to stay in this polar phase (**A**, see *Figure 2.1*) and might also hold some of the targeted but non-extracted species (**B**). The organic phase at equilibrium, called *extract*, *loaded solvent*, or *loaded organic*, has retained the extracted species (**B**) and could contain some co-extracted impurities. The two phases obtained after extraction should be clear and no third phase may appear at the liquid-liquid interphase. The formation of such phase can be caused by limited solubility of the extracted metal complex in the less polar phase or by differences in density between a metal complex-rich and metal complex-poor solution of the less polar phase.⁴⁸ In that case, a *modifier* has to be added to the initial solvent, usually an aliphatic alcohol (e.g. *n*-decanol), which improves the solubility of the extracted complex. The amount of modifier added to the solvent should be kept at a minimum (1-10 vol%), because it also interacts with the non-complexed extractant, limiting its availability for the reaction.

Often, a single extraction step as explained above is not enough to remove all of the desired metal ions from the polar phase: an extraction process can require several *stages* or *contacts*. One stage is completed once equilibrium concentrations in both phases are reached. By contacting the raffinate obtained after the first stage with new solvent and/or contacting the solvent with a new feed solution, further extraction of the desired element can be achieved. Such a process can occur *counter-current* or *cross-current*, as indicated in *Figure 2.2*. Cross-current extractions are rarely used in industry because a large number of product streams are generated, with each successive stream containing less of the desired solute.⁴⁴

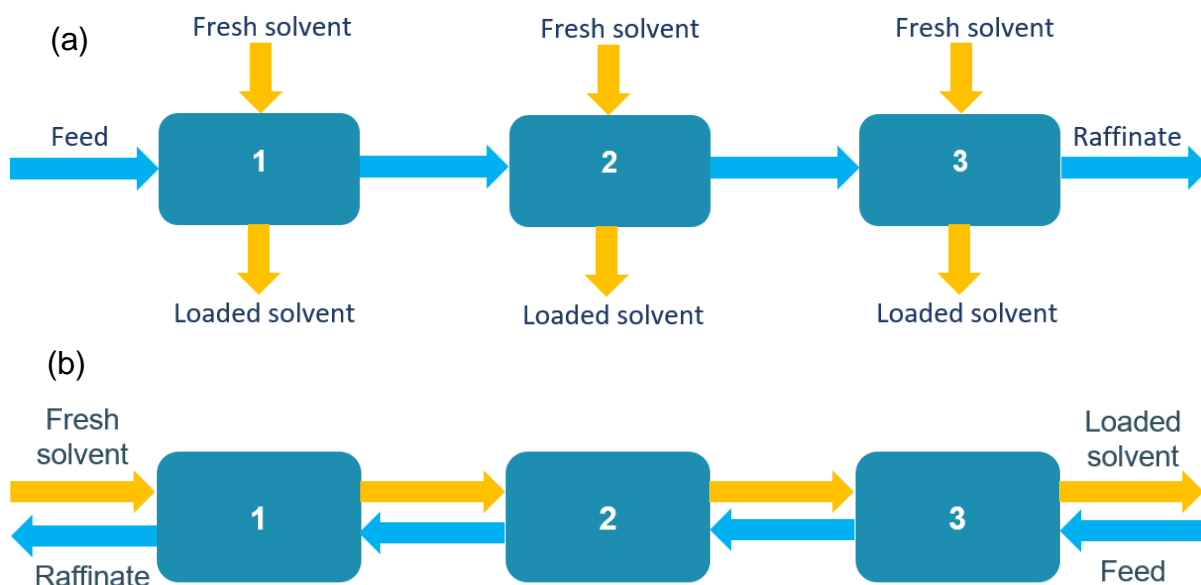


Figure 2.2 Schematic depiction of (a) a three-stage cross-current solvent extraction process and (b) a three-stage counter-current solvent extraction process.

On top of that, other metals can be co-extracted, which results in the need of *scrubbing* or selective *stripping*. Scrubbing is performed to remove impurities from the loaded organic phase by extraction with a dilute acid solution or by exchange of the impurity with the target element. If the desired metal compound can be selectively recovered during stripping, the scrubbing step can be left out. The strip solution used to back-extract the metal complex can consist of more concentrated acid solutions (e.g. 1 – 5 M HCl) or a precipitating agent (*precipitation stripping*).

2.1.2. Chemistry of solvent extraction and thermodynamics

Some background on the principles of thermodynamics and (coordination) chemistry that govern solvent extraction is essential, since it helps to explain the behaviour of metal complexes in media of different polarity. The difference in stability of the metal complex formed in the more polar and less polar phase is the driving force of the reaction. First topic in this discussion is the extraction equilibrium.^{46,48} The chemical composition of the two phases can be described as the distribution of a substance over the two phases. For example, for a certain solute M, the distribution or equilibrium constant K for the extraction can be written as:

$$K = \exp\left(\frac{\Delta\mu^\circ}{RT}\right) = \frac{(\bar{M})}{(M)} \quad (\text{Eq. 1})$$

In *Eq. 1*, the distribution constant is a function of $\Delta\mu^\circ$, the change in standard chemical potential, which is a measure of the driving force for interfacial mass transfer of M. (\bar{M}) is the activity of M in the loaded organic, (M) is the activity of M in the raffinate.⁴⁶

Depending on the counter anion present in the feed, different types of extractants can be chosen and different chemical reactions occur.^{50,51} Good inner-sphere ligands, such as chloride, can generate charge-neutral metal salts.⁵⁰ In this case, one can choose a neutral reagent that solvates the metal salt, *i.e.* a *solvating* or *neutral extractant*. The mechanism is presented in *Eq. 2*. The species marked with a line on top are the species present in the less polar top phase, the other species are found in the more polar phase. X indicates an anion directly coordinated to the metal, forming a complex. R is the (neutral) extractant containing on one side functional groups which can coordinate around the metal complex while the other end is hydrophobic, which enables dissolution in the less polar solution.

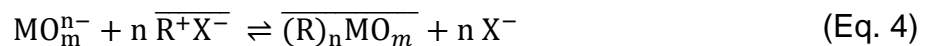


If the counter anion is a weak inner sphere ligand, such as sulfate, the metal occurs as a metal cation.⁵⁰ In this case, an *acidic* or *cationic extractant* should be used. This mechanism is presented in *Eq. 3*. Here, R can be an organic acid or a chelating molecule. It is clear that in this situation, the reaction depends on the initial acidity. Each acidic extractant has a pH range at which the extraction of a certain metal is optimal. This pH range can be presented by $\text{pH}_{1/2}$, which is the feed pH at which the solvent loading of a specific metal reaches 50%. This can be seen as the “strength” or efficiency of the extractant. Extractants having lower $\text{pH}_{1/2}$ values can be considered as stronger extractants. $\text{pH}_{1/2}$ also depends on the kind of metal that has to be extracted. Selective extraction can be attained by choosing the initial pH and extractant carefully. This selectivity can be based on the coordination chemistry of the metal. For example, in the case of extraction of M^{2+} ($M = 3d$ transition metal) with phosphinic, phosphonic and phosphoric acid extractants, hydrogen bonds between four coordinating extractants/ligands form 8-membered rings, hence stretching the O-M-O bond to angles greater than 90° . This could contribute to the selective extraction of the

base metals that adopt tetrahedral coordination geometries, *i.e.* Zn > Cu > Mn > Co > Ni as order of stability, contrary to the Irving-Williams series.⁵⁰



Finally, *Eq. 4* shows the mechanism in the case the metal species occurs as a negatively charged oxide. A *basic* or *anionic extractant* can be used, for example an organic quaternary ammonium salt. Loading and stripping are influenced by the counterion concentration $[X^-]$, which is called *anion-swing process*.⁵⁰ Also a neutral extractant can be used when an acidic feed solution can protonate the extractant. In this situation pH plays an important role in loading (low pH) and stripping (high pH), which is the *pH-swing process*.⁵⁰ If high chloride concentrations occur in the feed, the metal species can also be present in the chlorometalate form $(MCl)_m^{n-}$.⁵⁰ In contrast to acidic extractants, basic extractants do not enter the inner coordination sphere.⁵⁰ This makes it difficult to have high selectivity, since there is no way to take advantage of the preference of a metal for a certain coordination geometry. However, the transfer of a metalate anion into the solvent requires removal of most or all of the coordinated solvent molecules, which is harder for small and highly charged anions. Selective separation based on charge density is called the *Hofmeister bias* and can work well when separating platinum-group metal (PGM) chlorometalates.⁵⁰



Consequently, for these three extraction reactions, the equilibrium constant K can be written as:

$$K = \frac{[\overline{MX}_n \cdot mS]}{[MX_n][S]^m} \times F \quad (\text{Eq. 5})$$

$$K = \frac{[\overline{MR}_n][H^+]^n}{[M^{n+}][\overline{RH}]^n} \times F \quad (\text{Eq. 6})$$

$$K = \frac{[\overline{(R)_nMO_m}][X^-]^n}{[MO_m^{n-}][\overline{R^+X^-}]^n} \times F \quad (\text{Eq. 7})$$

Here, the factor F represents the ratio of the molar activity constants of the reaction product to the molar activity constants of the reactants.⁴⁶

However, Eq. 5-Eq. 7 are not practical to use in routine calculations. Since it is easier to measure only the total metal concentration, another more practical definition is applied. This is the *distribution ratio* (D), as shown in Eq. 8. Here, $[\bar{M}]$ represents the total concentration of a metal in the loaded organic, while $[M]$ is the total concentration in the raffinate.⁴⁶

$$D = \frac{[\bar{M}]}{[M]} \quad (\text{Eq. 8})$$

This expression is often applied to represent the efficiency of extraction, with high distribution ratios corresponding to high efficiencies. It is frequently used in fundamental extraction studies. For process development however, the efficiency of the extraction is often displayed as *percentage extraction* ($\%E$) as presented in Eq. 9. Here, V_{LP} is the volume of the less polar phase, while V_{MP} is the volume of the more polar phase.^{44,48}

$$\%E = \frac{V_{LP}[\bar{M}]}{V_{MP}[M] + V_{LP}[\bar{M}]} \times 100 \quad (\text{Eq. 9})$$

The selectivity of the solvent extraction can be expressed by the ratio of the distribution ratio of metal A (D_A) to the distribution ratio of metal B (D_B), as presented in Eq. 10. This is called the *separation factor* (α).^{46,48}

$$\alpha = \frac{D_A}{D_B} \quad (\text{Eq. 10})$$

By definition, this should be a value larger than one, so $D_A > D_B$. Larger separation factors indicate better separation.

2.1.3. Rare earths extraction chemistry

The rare earths are characterized by their similar external electronic structure. For the lanthanide series, from lanthanum to lutetium, the electrons gradually fill the 4f orbitals. These electrons are effectively shielded from the environment by the 5d and 6s shells. For all lanthanide ions the trivalent state is the most stable, which is why the chemical properties of the lanthanides remain remarkably constant. From lanthanum to lutetium, the increasing nuclear charge easily contracts the 4f electrons, causing the atomic radius and the basicity to decrease slowly throughout the series. This gradual decrease

is called the lanthanide contraction and is the reason why the different lanthanides show different behaviour during extraction. Yet it is very difficult to separate neighbouring elements, since this change in basicity is so small between these elements. Since separation factors between adjacent elements often approach unity, a larger amount of extraction stages is needed.⁴⁸

Also scandium and yttrium are quite similar to the lanthanides because they have an analogous electron configuration: [Ar] 3d¹4s² and [Kr] 4d¹5s² respectively. Scandium is considered a LREE, yttrium a HREE. Also these elements are trivalent. Exceptions to the trivalent state are cerium(IV), europium(II) and ytterbium(II), which are also stable due to their empty, half-filled or fully filled 4f shells, i.e. 4f⁰, 4f⁷ and 4f¹⁴ respectively.⁴⁸ Often, these elements are reduced in order to easily remove them, since this charge difference greatly influences their extraction behaviour. Once removed this makes the separation of other REEs, if present, much easier.

The reaction mechanism of REE-extraction widely varies throughout literature, mainly because of differences in process parameters (*vide infra*). This section will mainly focus on aqueous solvent extraction using solvating extractants, since this fits best with the subject of this master thesis and can be compared with non-aqueous solvent extraction (see 2.2.3 *Non-aqueous solvent extraction: state-of-the-art*). In general, it is assumed that the extraction mechanism is given by Eq. 11.^{48,53,54} Here, M³⁺ is the lanthanide ion, which is surrounded by a hydration shell. X⁻ is the counter anion (e.g. nitrate, chloride, etc.). The neutral extractant molecule L can only extract the lanthanide as a neutral salt species and has to remove the coordinated water before it can extract the lanthanide. Because water is strongly bonded to the lanthanide cation, extraction with a solvating extractant is often inefficient compared to other types of extractants and compared to non-aqueous systems, certainly in chloride systems.^{55,56} The extraction mechanism varies depending on the type of lanthanide, the type of counter anion and the type and concentration of the extractant: the amount of extractant molecules coordinated to the lanthanide can be 2, 3 or 4.^{48,54,57}



2.2. Non-aqueous solvent extraction and solvometallurgy

Solvometallurgy is the extraction of metals using non-aqueous solutions.⁴³ The term 'non-aqueous' does not mean that the solution is anhydrous, but it is used to indicate that a certain solution has a low water content. This technique can be applied in all metallurgical unit operations: solvent leaching, non-aqueous solvent extraction and metal recovery by precipitation or electrowinning from non-aqueous media. It is analogous to hydrometallurgy, yet this novel approach can offer a wide range of new possibilities and advantages. Therefore, the comparison of both solvometallurgy and hydrometallurgy will be addressed in this section. It is important to view solvometallurgy in the context of sustainability: the alternative solvents that are applied must be so-called *green solvents*. These solvents are usually safe to work with, non-toxic, and have a low environmental impact (e.g. bio-based, biodegradable, stable, recyclable). The criteria to which green solvents should comply with will be discussed in this section as well. Eventually, the focus will shift on what is already known about solvent extraction of REEs from ethylene glycol.

2.2.1. Comparison with hydrometallurgy

Solvometallurgy is in many ways similar to hydrometallurgy. Both approaches can be used during various metallurgical unit processes: leaching, solvent extraction, precipitation and electrolysis. For solvent extraction in particular, the aqueous phase used in hydrometallurgy is replaced by a non-aqueous phase. This non-aqueous phase can be an ionic liquid, a deep-eutectic solvent (DES), an inorganic liquid (e.g. concentrated sulfuric acid, super-critical carbon dioxide, etc.) or a molecular organic solvent.⁴³

A few advantages can be summed up for non-aqueous solvent extraction. Certainly in the field of liquid-liquid extraction of REEs, often many tens or even hundreds of stages are needed to separate two adjacent rare earths from aqueous solutions.⁵⁸ The extraction mechanism from non-aqueous solvents might be different, resulting in more efficient and selective processes. These differences can arise due to a different solvation in the non-aqueous solvent compared to the aqueous environment. Also other parameters may play a role, such as the polarity of the solvent, the dielectric constant and the Gutmann acceptor and donor number.⁵⁹⁻⁶¹ Yet, the effects of the

more polar phase on the extraction mechanism and on the extraction efficiency are still largely unknown. Additional advantage on the ecological side of the comparison is the limited generation of waste water during the non-aqueous process. Also, acidic extractants are often used for the aqueous solvent extraction of REEs. Extractions with these reagents request pH adjustment, causing consumption of large amounts of chemicals as well. Besides, loading of the organic phase containing these extractants cannot be too high, since this would result in gel formation.⁵⁸ In case of neutral extractants, extraction can only be performed from aqueous nitrate solutions, since extraction from chloride solutions seems to be inefficient.^{55,58} This is a disadvantage for aqueous solvent extraction, since HNO₃ is more expensive than HCl and treatment of nitrate-containing waste is more difficult.^{58,60}

There are still a few challenges left that need to be addressed for non-aqueous solvent extraction. First and most importantly, a suitable solvent pair has to be chosen to perform the extraction. Five conditions have to be fulfilled:^{43,59}

1. After mixing, the solvents must form two immiscible phases with a low mutual solubility.
2. The phases should separate fast after mixing.
3. The extractant and the extracted metal complex should be soluble in the less polar phase. The solubility of these species in the more polar phase should be limited.
4. The starting metal compounds and salts should be soluble in the more polar phase.
5. The metal compounds should not react with the organic solvents.

The main issue is the first condition, due to the mutual miscibility of many organic solvents. For the selection of a suitable solvent system, the mixotropic series are a very useful tool. This series ranks the solvents based on their polarity. The further two solvents are separated in this list, the lower their mutual solubility. Also reported miscibility data and the Hildebrand solubility parameter δ can be helpful during this selection. Yet, the theoretical data does not always reflect reality, since this is based on pure solvents. For instance, upon addition of the extractant to the less polar phase, a previously immiscible solvent pair can become partially miscible. Also, addition of a

salt to a pair of (partially) miscible solvents may induce phase separation. Secondly, the price and costs also influence the solvent choice. Thirdly, some solvents might be toxic, volatile, flammable or even explosive. Therefore, these solvents must be avoided (see: 2.2.2 *Green solvents*).⁴³

There is still some research to be done in the field of solvometallurgy, in order for the industrial world to implement it in their processes, besides the conventional extractive metallurgical techniques. Even then, solvometallurgy is to be seen as complementary to the other metallurgical approaches.⁴³ Of course, the solvometallurgical technique will only be applied for a specific processing stage in a certain case if it proves to be superior to hydrometallurgy and/or pyrometallurgy, or if the traditional techniques prove to be inefficient (e.g. low-grade ores, tailings and process residues). The integration of different extractive metallurgical techniques into a single flow sheet (leaching-extraction-valorization) is important to reach an optimally running process, where both economic and ecological aspects are taken into account.

2.2.2. Green solvents

The sustainability of the process should already be a priority during the selection of a suitable solvent pair for non-aqueous solvent extraction. Preferably, a so-called *green solvent* should be selected for solvometallurgical processes.⁴³ Several solvent-selection guides for industrial applications exist, although these are often only focussing on the chemical and pharmaceutical industries rather than the extractive metallurgy. Solvents are categorized by grading them on different factors (e.g. environmental impact, health, safety, waste, life cycle analysis (LCA) score, etc.) and transforming this information through mathematical calculation.^{62–65} Important industrial solvent-selection tools have been composed by Pfizer and GSK.^{63,66} Both subdivide the solvents in three groups (the so-called “traffic light”): the “green” solvents are solvents that are “preferred”. If none of these preferred solvents are suitable for the process, then the list of “useable” solvents can be checked (orange light). Lastly, there is a list of “undesirable” solvents (red light), which should be avoided and replaced by solvents from previous two lists. As an example, a concise overview of the Pfizer solvent-selection guide is given in *Table 2.1.*, which can of course be expanded for any solvent. Depending on the framework used to assess the solvents, one selection guide

might contradict another for a specific solvent. This is especially true for solvents in the green and yellow list, where specific factors or calculation methods might result in different categorization. Less uncertainty exist over the red-list solvents.

Table 2.1 Solvent-selection guide based on Pfizer solvent-selection tool.^{43,67}

Preferred	Usable	Undesireable
water	heptane	pentane
methanol	dimethyl sulfoxide (DMSO)	hexane
ethanol	ethylene glycol (EG)	dichloromethane
polyethylene glycol (PEG)	acetonitrile	chloroform
propylene glycol (PG)	acetic acid	pyridine
(biodegradable) GTL solvents	methanesulfonic acid (MSA)	benzene

It is important to highlight the relatively unknown gas-to-liquid (GTL) solvents, which are frequently used as a diluent in solvent extraction. GTL solvents mainly consist of *iso*-paraffins and normal paraffins (and a very small amount of cyclic paraffins). These are produced through the Fischer-Tropsch process, starting from natural gas. A broad range of GTL solvents is commercially available. For example, GS190 is a GTL solvent provided by Shell. Due to the very low content in aromatics and naphthenics, these solvents show good biodegradability. Other advantages are low volatility and low ecotoxicity.^{43,68}

2.2.3. Non-aqueous solvent extraction: state-of-the-art

Little research has been done on non-aqueous solvent extraction using two immiscible molecular organic solvents. Larsen and Trevorrow studied the separation of $ZrCl_4$ and $HfCl_4$ using isoamyl ether and acetonitrile, which would otherwise hydrolyze in aqueous environment.⁶⁹ Matsui *et al.* have investigated non-aqueous solvent extraction of zinc and cadmium from a bromide solution of ethylene glycol, using trioctylphosphine oxide as an extractant and toluene as diluent.⁷⁰ The same group continued their research, this time on the non-aqueous liquid-liquid extraction of zinc, cadmium and cobalt from a chloride solution of ethylene glycol and propylene glycol, using tri-*n*-octylamine and an alkyl ammonium extractant in toluene.⁷¹

More recently, Batchu *et al.* investigated non-aqueous solvent extraction of rare-earth nitrates from ethylene glycol, using the commercial solvating extractant Cyanex 923 in *n*-dodecane.⁵⁹ Cyanex 923 is a commercial mixture of trialkylphosphine oxides with *n*-hexyl and *n*-octyl chains. The main benefit over pure trioctylphosphine oxide (TOPO), which is the main component in Cyanex 923 and is shown in *Figure 2.3*, are its miscibility in all common hydrocarbon diluents and the fact that it is a liquid at room temperature.⁷² Large separation factors were observed between the LREE and HREE group, to the extent that this extraction system performed better in the separation of HREEs and LREEs than a system with an aqueous phase. The same authors continued this study by replacing nitrate with chloride.⁶⁰ Also this system could separate the REEs more efficiently than aqueous systems. For the ethylene glycol (+LiCl) system, Cyanex 923 was again chosen as extractant. Other extractants, such as Cyanex 272 (acidic), bis(2-ethylhexyl)amine (basic), Cyphos IL 101 (basic) and Aliquat 336 (basic), showed no or negligible extraction of rare earths from ethylene glycol. The benefit of chloride systems is the lower cost of HCl compared to HNO₃. Besides, nitrate-containing waste is more difficult to process.

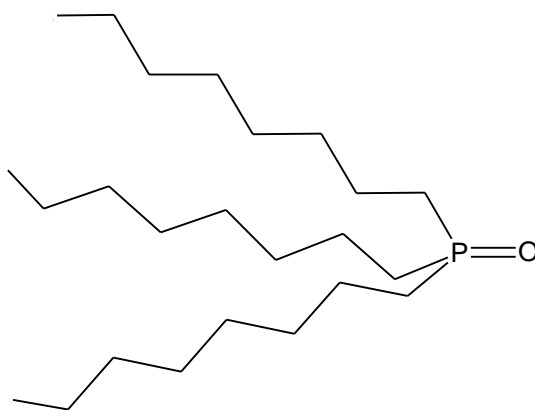
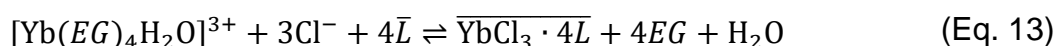
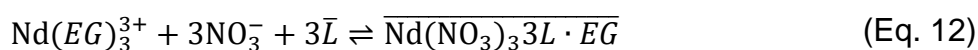


Figure 2.3 Molecular structure of trioctylphosphine oxide (TOPO), main component in Cyanex 923.

For the system in which ethylene glycol (+LiCl) was the more polar phase and Cyanex 923 in *n*-dodecane (+ 10 vol% 1-decanol) was the less polar phase, solubility studies reported by Batchu *et al.* showed that: (1) the solubility of Cyanex 923 and *n*-dodecane in the ethylene glycol is very low, (2) the solubility or co-extraction of ethylene glycol in the less polar phase was 46.3 g/L, while upon addition of 2 M LiCl, the solubility of

ethylene glycol dropped to 29.7 g/L. Loading the ethylene glycol phase with rare-earth salts further decreased the solubility. To compare, the solubility of water in the same less polar phase was 24.6 g/L when 2 M LiCl was added.⁶⁰

The differences in efficiency and selectivity for non-aqueous solvent extraction from ethylene glycol compared to the aqueous systems are most likely caused by differences in extraction mechanism. This mechanism is shown in *Eq. 12* for extraction of Nd(III) from an ethylene glycol (+LiNO₃) solution and in *Eq. 13* for the extraction of Yb(III) from an ethylene glycol (+LiCl) solution.^{59,60} Here, *L* is the extractant Cyanex 923. Ethylene glycol has largely replaced the hydration shell around both REEs due to preferential solvation. This solvation shell is different in the two equations, which might be caused by a lower water content and better quality data in the case of *Eq. 13*, according to the authors. Notice that a neutral extractant, such as Cyanex 923, extracts the rare earth in its salt form. Also, the amount of extractant molecules coordinated around the REE differs in the two systems. This is probably caused by the type of counter anion, the type of rare earth (ionic radius) involved and the concentration of the rare-earths, as was also the case for aqueous solvent extraction (see 2.1.3 *Rare earths extraction chemistry*).



2.3. Solvent extraction: equipment and engineering aspects

In industry, solvent extraction is performed in a continuous process using equipment called *contactors*. Several types of contactors exist, such as pulsed column systems, centrifugal contactors and mixer-settlers.⁴⁴ Each of these devices has its advantages and disadvantages and depending on the process characteristics and requirements one or the other is chosen. Important factors that drive this choice are technical (e.g. efficient extraction, good dispersion for optimal mass transfer, adjustability of the flows, height and footprint of installation) and economic (set-up, operating and maintenance costs, solvent inventory, throughput). For this work, focus will be on the mixer-settler contactors. One mixer-settler device will account for one stage and is build up out of a mixer compartment and a settling tank, as seen in

Figure 2.4. For a process involving multiple stages, a battery of mixer-settlers can be used. The volume of the mixer tank should be large enough for the two phases to reach (near-) equilibrium and the settler tank should be large enough for the two phases to disengage. The impeller present in the mixer chamber can be used both to mix and to pump the two phases from one stage to the next. The advantage of mixer-settlers are their high efficiency due to good contacting, their ability to handle a wide range of viscosities, their limited head-space, their operating flexibility, the ease to scale-up processes and the low maintenance costs. Some disadvantages are the high power costs, the large footprint of the installation and the high solvent inventory (a lot of solvent containing valuable resources is held up).⁴⁴

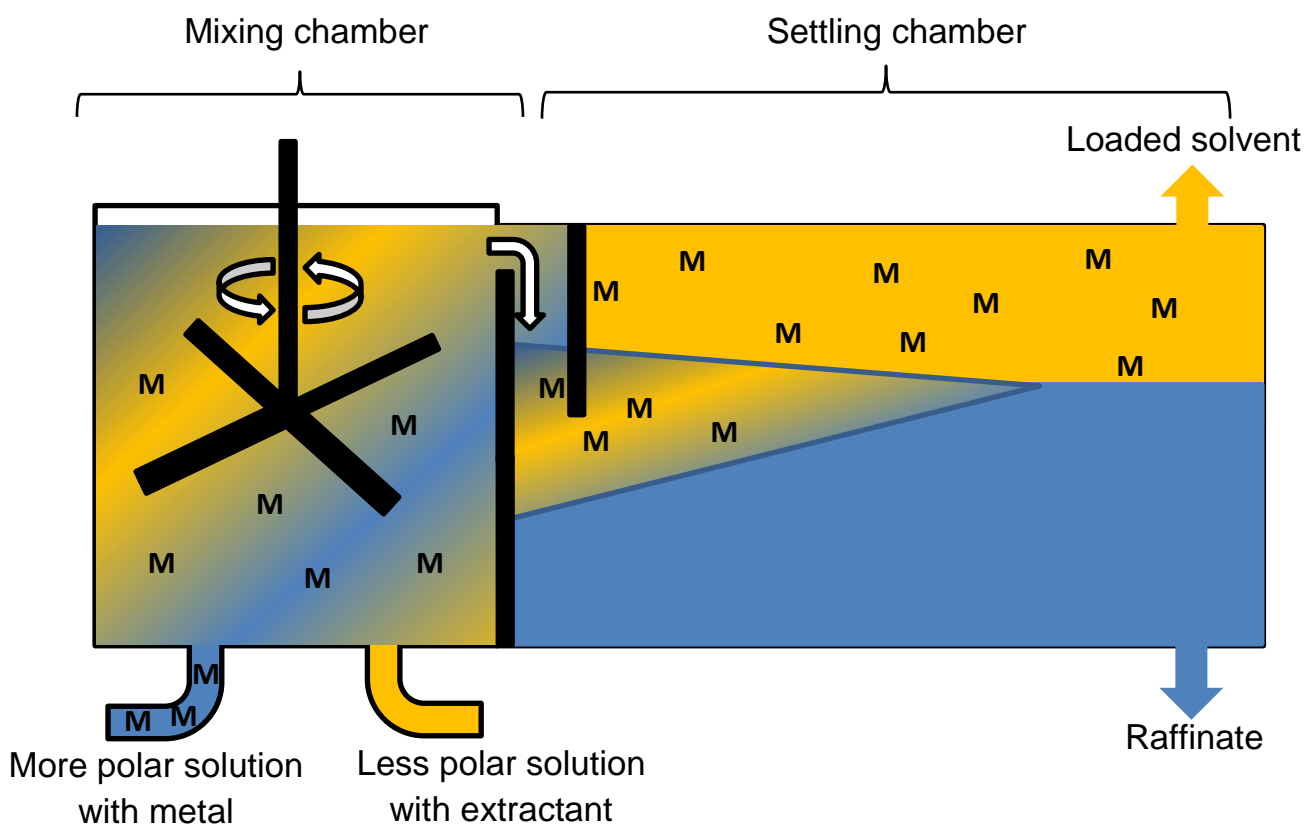


Figure 2.4 Cross-section of a mixer-settler.

3. Instrumentation

3.1. Total reflection X-ray fluorescence (TXRF)

Total reflection X-ray fluorescence (TXRF) is analytical quantification technique used to determine the concentration of metal ions, which is based on the measurement of secondary X-ray emissions (fluorescence) that are characteristic for a specific element. Metal concentration measurements in ethylene glycol solutions were performed on a Bruker S2 Picofox TXRF spectrometer. It is equipped with a molybdenum X-ray source and operated at a voltage of 50 kV.

The basic principle involved in the TXRF method can be described as follows. X-rays are generated by collision of accelerated electrons on a specific anodic material. These X-rays are then used to irradiate sample material, exciting the inner shell electrons (K and L) and expelling them as a consequence. Because this electronic structure is unstable, an electron from a higher orbital fills the gap, releasing the difference in energy between its old and new position as secondary radiation. Since the energy levels of the electronic orbitals are characteristic for each element, identification of the elements can be performed based on the energy of the released photons. In addition, the intensity of the fluorescence can be related to the quantity of each element. For this purpose, addition of an internal standard is required: a known amount of an element that is not present in the sample is added. The internal standard element has a fluorescence peak with an energy close to the elements to be quantified, to increase the accuracy of the measurement. Furthermore, amount of the standard element added should be close to the concentration of the analyte.⁷³

The term 'total reflection' refers to the limited transmission of the primary X-ray beam into the carrier material, used to support the sample. This limited penetration can be achieved by adapting a very low angle of incidence, smaller than the critical angle of the carrier material. For silicon, this is 0.1°. The detector is placed perpendicular to the sample carrier, at a distance of 0.5 mm, avoiding influence of the primary radiation on the results.⁷⁴

3.2. Rolling-ball viscometry

Viscosity is a measure for the resistance against deformation of a fluid by shear-stress (or tensile stress). In this master thesis, the dynamic viscosity (η) was measured rather than the kinematic viscosity (ν). The dynamic viscosity is defined as the ratio of shear stress (total force per unit of surface) to the rate of deformation, and is commonly expressed in centipoise (cP).

The viscosity measurements were performed using an Anton Paar LOVIS 2000 ME rolling-ball viscometer. A gold-coated stainless steel ball rolls through a borosilicate glass capillary which is filled with the liquid sample. The capillary is inclined at an angle of 70° . The viscosity can then be determined by measuring the time needed for the ball to travel a certain distance. During the measurement, the ball experiences three forces: gravity, the buoyancy force and the viscous force, as is illustrated in *Figure 3.1*. For identical angles (θ), the rolling time of the ball increases with viscosity.⁷⁵

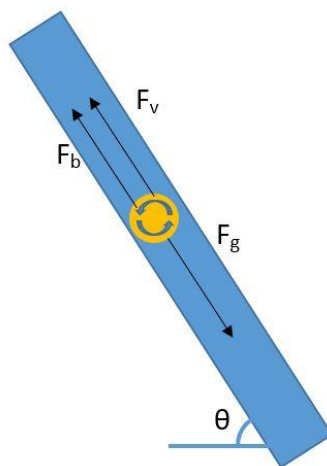


Figure 3.1 Schematic representation of the working principle of a rolling-ball viscometer. The capillary with the liquid sample are represented as a blue box. The gold-coated ball is a yellow circle. F_g is the effective portion of the gravitational force, F_b is the effective portion of the buoyancy force, F_v is the viscous force and θ is the angle of the capillary.

3.3. Karl Fischer titration

The determination of the water content of solvents was performed by coulometric Karl Fischer titration using a Mettler-Toledo DL39 titrator. The titration is based on the reaction of iodine with water. A mixture of I₂, SO₂, imidazole and solvent (e.g. methanol) is commercially sold as anolyte (*vide infra*). The Mettler-Toledo DL39 titrator uses Honeywell Hydranal Coulomat AG, a methanol solution with non-disclosed composition.^{76,77}

For the coulometric Karl Fischer determination of water, the reaction, is given in *Eq. 14*. Here, the iodine is generated by anodic oxidation in the coulometric cell ($2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}^-$), which is in contrast with volumetric Karl Fischer analysis. This oxidation reaction occurs at the generator electrode (in the anolyte), which can be seen in *Figure 3.2*. The reduction reaction happens inside the generator electrode at the cathode (in the catholyte). Here, hydrogen ions are reduced to hydrogen gas. An ammonium salt is present in the catholyte to supply hydrogen ions for the reaction ($2[\text{RN}]\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{RN}$). Close to the generator electrode, there is the measuring electrode, which monitors the potential of the sample solution.⁷⁷



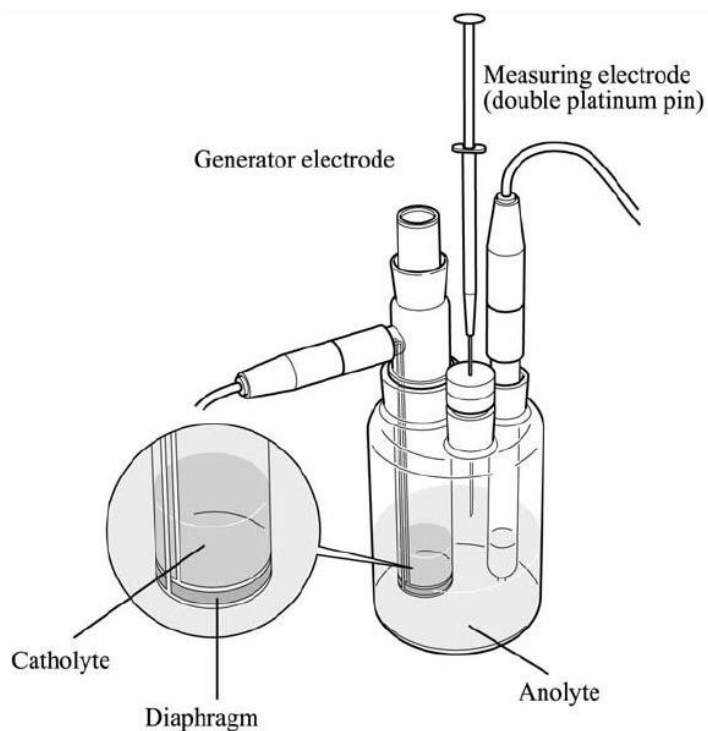


Figure 3.2 Schematic overview of a Karl Fischer titrator. Figure obtained from Mettler Toledo brochure.⁷⁷

As to the stoichiometry of the reaction, one water molecule consumes one iodine molecule, that on its turn released two electrons at the anode upon formation. Current and time are accurately measured by the Karl Fischer titrator, which allows to calculate the electrical current in coulomb (C) used to generate iodine. This current directly depends on the consumption of iodine and thus the water content.⁷⁷

4. Materials

4.1. General

Ethylene glycol (99.9%), propylene glycol ($\geq 99\%$) and PEG-200 (untested) were purchased from Acros Organics NV (Geel, Belgium); 1-decanol (99%) from Advocado Research Chemicals Ltd (Heysham, UK); GS190 GTL solvent was provided by Shell (Rotterdam, Netherlands); Cyanex 923 (93% trialkyl phosphine oxides) by Cytec Industries (Canada); *n*-dodecane ($>99\%$) was purchased from Merck (Darmstadt, Germany); $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (99.8%) from Sigma-Aldrich (Diegem, Belgium); $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (99.9%) from Alfa Aesar (Karlsruhe, Germany); zinc chloride (98%) from BDH Laboratory Supplies (Poole, UK); anhydrous lithium chloride (100%) and ethanol abs. (99.99%) from Fischer Scientific (Geel, Belgium); hydrochloric acid (37%), dimethyl sulfoxide (99.9%) from VRW Chemicals (Haasrode, Belgium); oxalic acid ($\geq 99\%$) from Sigma-Aldrich (Diegem, Belgium); methanesulfonic acid ($\geq 99.5\%$) and propylene carbonate ($>99.7\%$) from Carl Roth GmbH Co. KG (Karlsruhe, Germany); nitric acid (65%) and acetonitrile ($>99.5\%$) from Chem-Lab nv (Zedelgem, Belgium); The silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). The gallium standard (1000 ppm in 2-5% HNO_3) was purchased from Chem-Lab NV (Zedelgem, Belgium). The surfactant Triton 100-X was obtained from Merck KGaA (Darmstadt, Germany). For all dilutions, unless stated differently, ultrapure water (18.2 M Ω cm) was used, obtained using a Sartorius Arium Pro Ultrapure Water System.

4.2. Properties of the feed solutions

Table 4.1 Overview of the properties of the feed solution. Concentrations for the feed solutions are approximately $[Y] = 11.1 \text{ g/L}$; $[Eu] = 1.5 \text{ g/L}$; $[LiCl] = 2 \text{ M}$. For the DMSO feed, $[LiCl] = 1 \text{ M}$. For the EG scrub feed: $[Y] = 11.1 \text{ g/L}$; $[Eu] = 0 \text{ g/L}$ and $[LiCl] = 1 \text{ M}$. For rolling ball viscosity measurement: $T = 25 \text{ }^\circ\text{C}$, inclination angle $\theta = 70^\circ$.

Solution	Dynamic viscosity (mPa s)	Water content (wt%)
EG feed	76	1.54
EG scrub feed	40	1.54
PG feed	251	1.84
PEG-200 feed	1592	2.68
DMSO feed *	9.4	1.60
EG/PG feed	153	1.94
EG/PEG-200 feed	253	2.12
EG/DMSO feed *	55	1.72
EG/H ₂ O feed	6.6	-
EG/MeOH feed	14	1.80

* Due to a slow side reaction of DMSO with Karl Fisher reagents, the water content of DMSO solutions cannot be considered accurate.

5. Methods

5.1. Bench-scale solvent extraction

The lab-scale, single-contact solvent extraction experiments are carried out in clear glass vials with mechanical stirring or shaking using a Burrel Wrist-Action Shaker. The extraction, scrubbing and stripping experiments take 1 hour to complete and are carried out at room temperature. Afterwards, samples are centrifuged at 4000 rpm for 3 minutes using a Thermo Scientific Heraeus Labofuge 200 centrifuge for vials up to 4 mL or using a Megafuge 1.0 Eppendorf centrifuge for larger volumes.

The composition of the two phases during an extraction experiment can vary in each experiment, but generally the used parameters can be described as follows:

- The feed solution is an ethylene glycol (EG) solution of about 11.1 g/L yttrium (Y(III)) and 1.5 g/L europium (Eu(III)), which are added as $YCl_3 \cdot 6H_2O$ and $EuCl_3 \cdot 6H_2O$. This corresponds to a molar ratio of $Y/Eu = 100/8$, which is representative for the composition of fluorescent phosphors. Also 2 M LiCl is added as salting-out agent, unless stated differently.
- The solvent is a solution of the extractant Cyanex 923 with the Shell GS190 solvent (a GTL solvent). In a first screening experiment, *n*-dodecane was used as diluent instead, but this had no influence on the extraction as it has similar characteristics as the GTL solvents. As to the concentration of Cyanex 923, 1 M was used in most experiments, unless defined differently. Also 10 vol% 1-decanol was added as modifier, since the formation of three phases was observed in a preliminary extraction test in absence of modifier.

For the scrubbing and stripping experiments, a loaded organic was generated on a larger scale, which is discussed in the section *7.10 Scrubbing and stripping experiments*. The exact composition of the strip and scrub feed solutions are mentioned in this section as well. The handling (mechanical stirring or shaking and centrifugation) is the same as in the case of the extraction experiments.

The measurement of the (equilibrium) metal concentration in the raffinate is performed with TXRF (*vide supra*). The concentration in the loaded organic can be calculated using the mass balance shown in *Eq. 15*. Here, $[\bar{M}]_f$ is the equilibrium concentration of

the metal in the loaded organic, $[M]_i$ is the initial feed concentration, $[M]_f$ is the measured equilibrium concentration in the raffinate and V_{MP} and V_{LP} are the volumes of the more polar phase and the less polar phase respectively.

$$[\bar{M}]_f = ([M]_i - [M]_f) * (V_{MP}/V_{LP}) \quad (\text{Eq. 15})$$

With this information, the percentage extraction %E, the distribution ratio D and the separation factor can be calculated according to *Eq. 8 – 10* in section 2.1.2 *Chemistry of solvent extraction and thermodynamics*. For scrubbing and stripping, percentage scrubbing (%Sc) and percentage stripping (%St) are defined as presented in *Eq. 16*. Here, $[\bar{M}]_i$ is the initial metal concentration in the loaded organic, $[\bar{M}]_{f2}$ is the metal concentration in the scrubbed or stripped loaded organic after reaching equilibrium,

$$\%Sc \text{ or } \%St = (([\bar{M}]_i - [\bar{M}]_{f2}) / [\bar{M}]_i) \times (V_{MP}/V_{LP}) \times 100 \quad (\text{Eq. 16})$$

In the case of precipitation stripping (using oxalic acid), the precipitate after equilibrium was redissolved in concentrated HCl. The concentration of the metal in the HCl solution is then measured, so that %St can be calculated as well.

5.2. McCabe-Thiele approach

A McCabe-Thiele diagram is used to visualize the theoretical number of stages required for a counter-current extraction process, for a specific phase ratio. *Figure 5.1* shows such a diagram for a metal M. The equilibrium line OA is the extraction isotherm for this metal, which can be constructed by conducting extraction experiments using a range of phase ratios (in this master thesis, A:O = 7:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5, 1:7) and by plotting the resulting equilibrium concentrations of M in both phases. Besides the distribution isotherm, this diagram also consists of an operating line BC, the slope of which is determined by the phase ratio, *i.e.* the volume of the more polar phase to the volume of the less polar phase (V_A/V_O). Ideally, a small volume of solvent to a larger volume of feed is chosen. The reason for this is twofold: (1) less of the (rather expensive) extractant is needed; (2) a higher solute concentration in the loaded organic solvent is desirable. The feed line is a last component of the diagram. This is a vertical line indicating the feed concentration of the extractable species. The

intersection of this feed line with the operating line, is the starting point of drawing the first stage in the McCabe-Thiele diagram. From here, a horizontal line is drawn, until it intersects with the extraction isotherm. Then, a vertical line originating from this intersection is drawn down to the operating line, from which this procedure is repeated until the origin with coordinates (0,0) is reached. One couple of vertical and horizontal lines represents one (theoretical) stage. An intersection on the operating line between for example stage 2 and 3 will give the concentration $[M]_3$ in the more polar phase and the concentration $[\bar{M}]_2$ in the less polar phase between stage 2 and 3. An intersection of the diagram on the extraction isotherm gives the concentration of the loaded solvent and the raffinate flowing out of each respective stage.

A similar approach can be used to estimate the number of stages for a scrubbing or stripping experiment. In such cases, the abscissa value is the metal concentration in the less polar phase and the ordinate value reflects the concentration in the more polar phase.

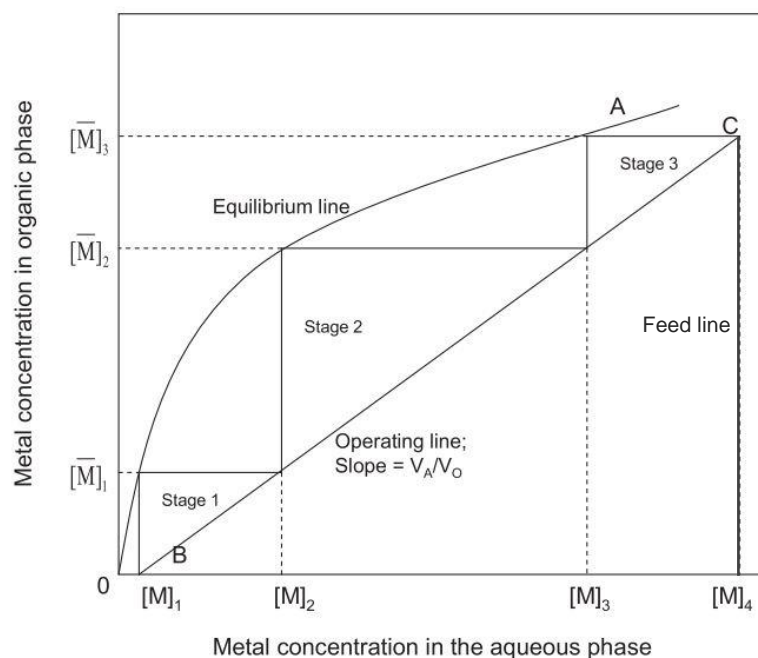


Figure 5.1 Schematic representation of a McCabe-Thiele diagram for a counter-current solvent extraction process. Figure obtained from Xie et al. (2014).⁵⁸

5.3. Counter-current extraction simulation (CCES)

CCES is a lab scale simulation of a continuous multistage counter-current extraction process. In general, a three-stage counter-current extraction can be represented by *Figure 2.2 b* in section 2.1.1 *Definition of solvent extraction and terminology*. In this process the direction of the flow of the more polar phase (feed) is opposite to the direction of the flow of the less polar phase (solvent). From right to left, the fresh solvent is contacted with a low-concentrated feed solution and proceeds to the next stages, where the metal concentration of the feed, with which it is contacted, increases in every stage.

Practical, the three- or two-stage lab-scale extraction simulation, as presented in *Figure 5.2* for a three-stage simulation, is performed in batch scale using 100 mL or 50 mL separatory funnels. Each box in this scheme represents a batch extraction in a separatory funnel. After each extraction, the ethylene glycol feed or Cyanex 923 solvent are either withdrawn or transferred to the next batch extraction. Once the exact feed and solvent volumes are added, the separatory funnels are stoppered and attached to the Burrel Wrist-Action Shaker. The extraction is performed at 500 rpm for 15 minutes. The extraction time of 15 minutes is significantly lower than the 1 h for the single-contact bench-scale extraction as presented in 5.1 *Bench-scale solvent extraction*. However, since equilibrium is usually reached very fast (under 5 minutes) and since prolonged equilibrium time does not affect the extraction efficiency, this should have no influence on the results.⁵⁹

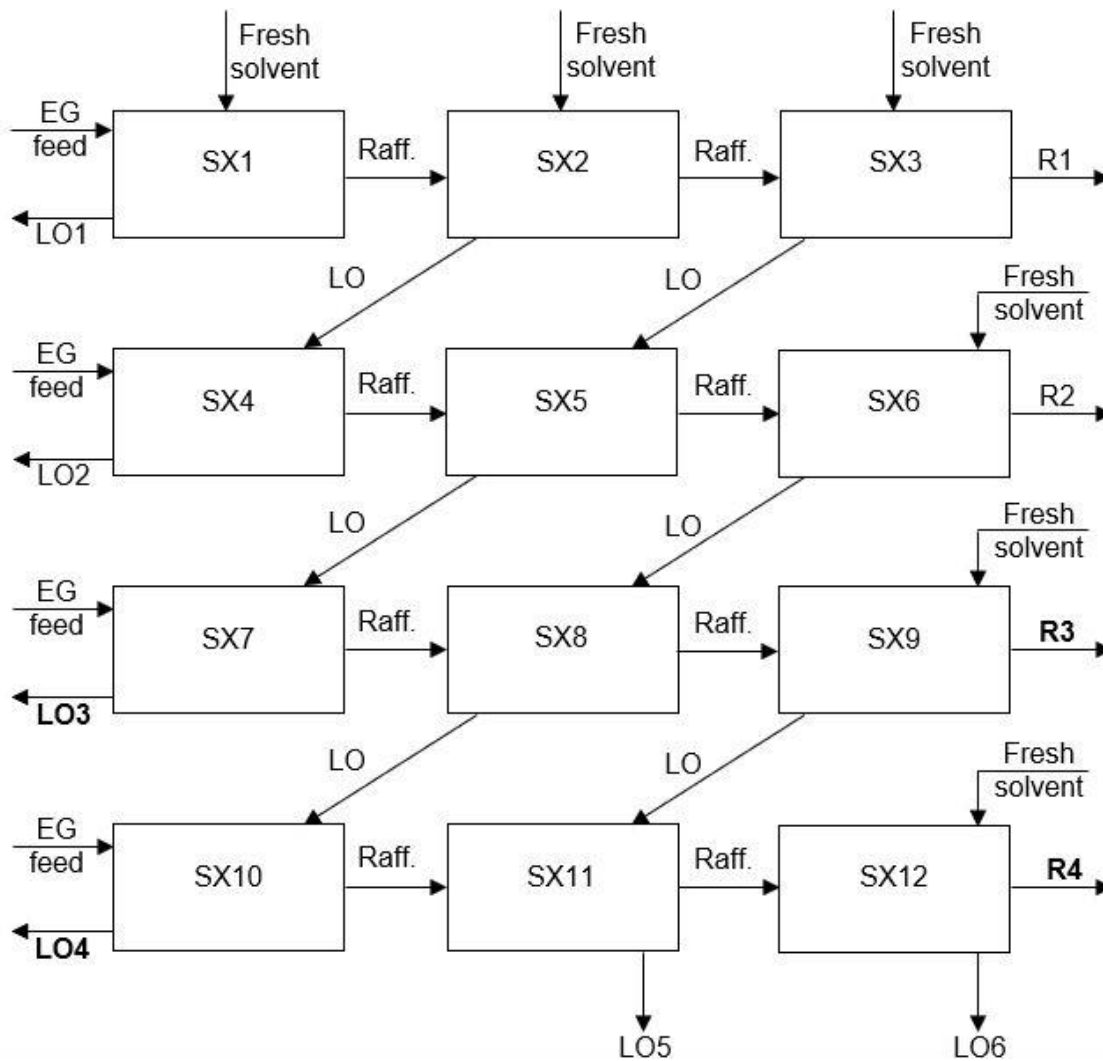


Figure 5.2 Scheme for a three stage counter-current extraction simulation. Extractions were performed as ordered in the figure, from SX1 (solvent extraction 1) to SX12 (solvent extraction 12). The abbreviations used here can be defined as follows: EG feed = ethylene glycol feed; Raff. or R = ethylene glycol raffinate; LO = loaded organic phase.

Some more explanation to the CCES experiments should be given though. *Figure 5.3* gives a simplified overview of a typical three-stage counter-current extraction simulation scheme. The red arrows indicate the flow of the solvent, which is in accordance to the principle described above, *i.e.* it is in a direction opposite to the feed/raffinate flow. Fresh solvent is contacted with depleted raffinate, while the loaded organic is contacted with the rich feed. According to Injarean *et al.*, the steady-state should be approached after a number of cycles, so that the liquids in the funnels resemble the streams in an actual continuous counter-current extraction.⁷⁸ Eventually, in the case of the three-stage CCES presented in *Figure 5.2*, the loaded organic

fractions LO3 and LO4 and the raffinate fractions R3 and R4 contain metal concentrations representative the actual counter-current process.

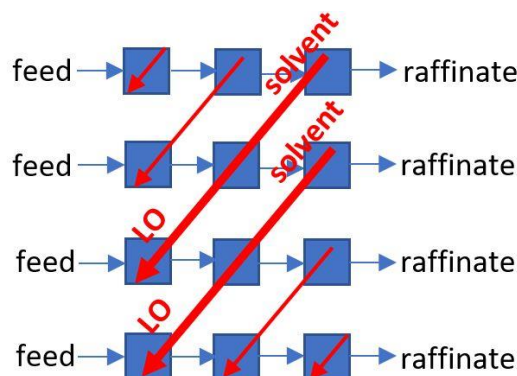


Figure 5.3 Schematic overview of the explanation of the three-stage CCES. LO = loaded organic.

5.4. TXRF sample preparation and method

For the TXRF measurement, samples were taken from the more polar phase. The sample dilutions were generally prepared in two steps. First, the sample from the more polar phase is diluted 10 times with a 5% HNO₃ solution. Then, this was further diluted 5 times (to a total dilution of 50 times) using a Triton X-100 solution, which is a surfactant, and addition of 100 µL of 500 ppm or 1000 ppm gallium standard. Of course, this procedure changed depending on the metal concentrations in the more polar phase. Ideally, the concentration of the analyte in the dilution should be between 50 ppm and 200 ppm and the internal standard concentration should be as close as possible to the concentration of the analyte.

Gallium is a typical internal standard for TXRF, due to the central position of its fluorescence peak in the energy spectrum. The closer the energy of the fluorescence peak of the internal standard element to that of the analyte, the higher the accuracy of the quantitative measurement over a broad concentration range.^{73,74} For both europium (E = 5.849 keV) and yttrium (E = 14.958 keV), the gallium fluorescence peak (E = 9.251 keV) lies close enough to give reliable results.

Subsequently, 2 µL of sample dilution was spotted on SERVA-pretreated quartz glass carriers and eventually dried for 30 minutes at 60 °C. Each sample is measured for 300 seconds, using a Bruker S2 Picofox TXRF spectrometer.

6. Health, Safety and Environment (HSE)

When working in the laboratory it is of utmost importance to familiarize yourself with the possible risks involved when using chemicals or certain devices/procedures and the necessary precautions to take. Therefore, a risk assessment is made on forehand, which gives an overview of the planned experiment, the hazards accompanying the used chemicals, the precautions to take when working with these chemicals, the risks and precautions to be taken when using certain devices or equipment. Moreover, continuous application of the *Code of Good Practice for Safety in the Lab* is important: awareness of the risks and taking appropriate measures to ensure safety for yourself and all co-workers.⁷⁹ Personal protection is mandatory: a laboratory coat, safety glasses and appropriate gloves should be worn.

As to the chemicals, the Cyanex 923 extractant (E3) is corrosive and can cause serious burns and eye damage. Besides it is very toxic to the aquatic environment. So it is of utmost importance to ensure proper disposal of waste streams containing this substance. Hydrochloric acid (37%), nitric acid (65%) and methanesulfonic acid ($\geq 99.5\%$) (all E3) also cause severe burns eye damage. Certainly for hydrochloric acid, it is important to work in the fume hood, since HCl vapours evolve from the solution already at room temperature. Nitric acid on the other hand is oxidative and should be kept away from unstable organics and disposed as oxidative waste (category 5). Acetonitrile and ethanol (both E3) are both flammable, and should be kept away from fire, sparks and hot surfaces.

Emission of chemical waste into the environment should be avoided by collecting all solvents or mixtures in the appropriate waste containers. Organic solvents, such as ethylene glycol, mixtures of Cyanex 923 in GS190 solvent and methanesulfonic acid are to be collected in category 3 (non-halogenated organic solvents). Hydrochloric acid should be treated as category 1 waste (inorganic acids). Nitric acid is a category 5 chemical (oxidative).

Before using devices equipped with X-ray sources, the training on “Radiation protection for open and sealed sources” was followed. The possible dangers have been explained: X-rays can penetrate easily through the human body and through meters of air. This radiation might cause damage to the DNA, which increases the risk for cancer and mutations.

7. Separation of yttrium and europium from ethylene glycol (+ LiCl) by Cyanex 923

7.1. Introduction

The goal of the first series of experiments that were conducted, was to obtain an optimized conceptual flow sheet for the separation of trivalent yttrium and trivalent europium. First, the solvent extraction process was optimized. This was performed by using a non-aqueous system with on one hand an ethylene glycol feed containing rare-earth chloride salts ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$) and LiCl, and on the other hand the solvent which consisted of a Shell gas-to-liquid (GTL) diluent GS190 and the extractant. From literature, it was found that Cyanex 923 (C923) was a suitable extractant when separating heavy rare-earth elements (HREEs) from light rare-earth elements (LREEs) when using ethylene glycol (+LiCl) as feed solvent.⁶⁰ In this case, Y behaves as a HREE positioned between Dy and Ho, while Eu is positioned earlier in the lanthanides series, between Sm and Gd. Parameters to be optimized were the extractant concentration, the LiCl concentration and co-solvents. Also, instead of ethylene glycol, a feed consisting of propylene glycol, PEG-200 or dimethyl sulfoxide (DMSO) was tested. Besides, the non-aqueous approach was compared with an aqueous extraction experiment. In a side-experiment, it was attempted to simulate real waste streams by adding elements to the feed solution that are commonly found in CRT and fluorescent lamp waste besides yttrium and europium.

For the optimization of the scrubbing and stripping steps, several approaches were tested. For the scrubbing of europium from the loaded organic phase, ethylene glycol was used, with varying concentrations of LiCl and YCl_3 . For the stripping experiments, HCl, oxalic acid (OA) and methanesulfonic acid (MSA) were chosen for investigation.

Subsequently, preparations were made to upscale the separation process using the obtained optimized extraction, scrubbing and stripping data. A McCabe-Thiele diagram was constructed for both extraction and scrubbing, which allowed to optimize the phase ratio and to determine the number of extraction stages needed. In a next step, counter-current extraction simulations were performed to confirm the parameters of the developed process. Eventually, based on these simulations a process flow sheet is presented.

7.2. Screening experiments: influence of Cyanex 923 concentration

In the first two screening experiments, the influence of the extractant concentration was studied. Cyanex 923 (C923), which is a phosphine oxide, has been chosen as extractant. In the first experiment, ethylene glycol (EG) was used to dissolve the yttrium and europium chloride hexahydrate salts, as well as lithium chloride (LiCl). The diluent chosen for this first screening experiment was *n*-dodecane, which is very similar to the GS190 GTL-solvent used in most of the other experiments. Therefore, experimental results will not deviate greatly.

First, an extraction without a modifier (1-decanol) was attempted. However, for the extraction test having 0.5 M of C923, three-phase formation occurred, which is vaguely visible in *Figure 7.1*. For this reason, the extraction was repeated successfully with addition of 1-decanol as modifier (10 vol%, *i.e.* 100 μ L of a total volume of 1 mL). As to the mixing, a wrist-action shaker device was used, shaking all samples for 1 hour at 500 rpm. The data obtained for this first experiment are shown in *Table 7.1*.

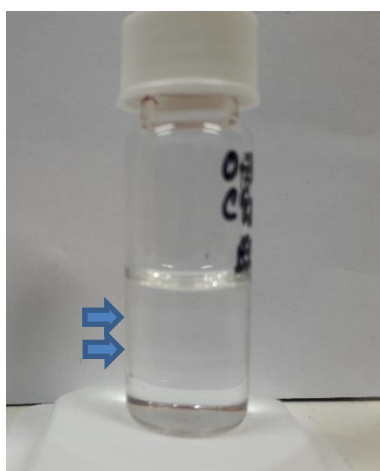


Figure 7.1 Sample after extraction with 0.5 M C923 in *n*-dodecane and ethylene glycol feed with $[Y] = 1.4$ g/L; $[Eu] = 10.9$ g/L and $[LiCl] = 2$ M. The blue arrows indicate the liquid-liquid interphases.

Table 7.1 TXRF results of EG raffinate after extraction with C923. Extraction efficiency (%E), distribution ratio (*D*) for Eu(III) and Y(III) and the separation factor (*SF* or $\alpha = D_Y / D_{Eu}$) are given as a function of [C923].

[C923], M	%E, Y	%E, Eu	<i>D</i> , Y	<i>D</i> , Eu	SF
0.1	13.8	5.81	0.20	0.06	3.3
0.2	16.9	0.83	0.16	0.008	19
0.3	34.7	6.34	0.53	0.07	7.6
0.5	54.3	8.70	1.19	0.10	12
0.7	64.5	4.56	1.82	0.05	38
0.8	74.5	4.03	2.92	0.04	69
1	84.5	14.0	5.45	0.16	33

Evidently, the higher the concentration of the extractant, the higher the percentage extraction for both yttrium and europium. At 1 M of Cyanex 923, about 85% of yttrium has been extracted, while 14% of europium was co-extracted. The separation factor between both rare-earths is 33, which is lower than in the case for 0.8 M. This can however be an experimental or analytical error. It is chosen to work further with 1 M Cyanex 923, since it provides good values to work further with and to optimize. This test was also repeated with the Shell GTL-solvent GS190, as seen in 7.3 *Influence of Cyanex 923 concentration and comparison with aqueous extraction*.

7.3. Influence of Cyanex 923 concentration and comparison with aqueous extraction

To see the advantages of non-aqueous solvent extraction over aqueous solvent extraction, a comparative experiment on the influence of C923 concentration with EG feed versus aqueous feed has been performed. The results of this experiment can be found in *Figure 7.2 (a) and (b)* and *Table 7.2*. The experiment performed with EG feed is in fact identical to the experiment mentioned earlier, in 7.2 *Screening experiments: influence of Cyanex 923 concentration*. However, the diluent chosen to dissolve the Cyanex 923 extractant now is the Shell GS190 diluent.

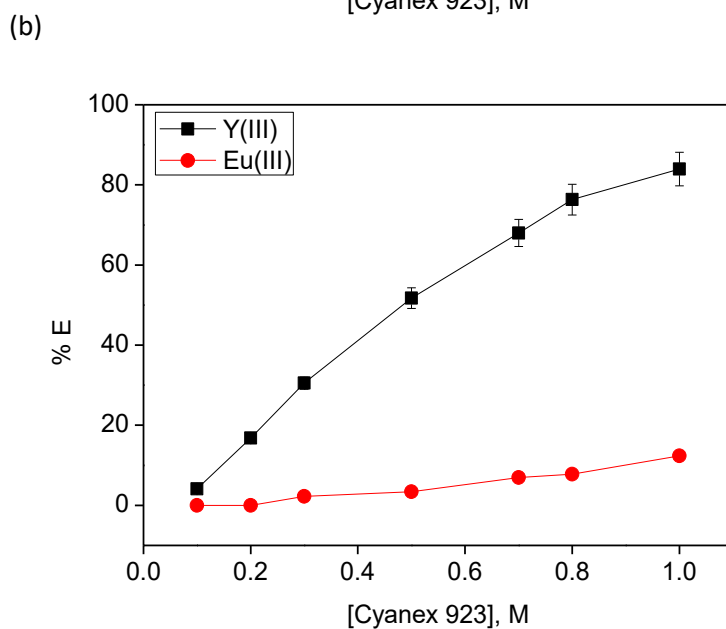
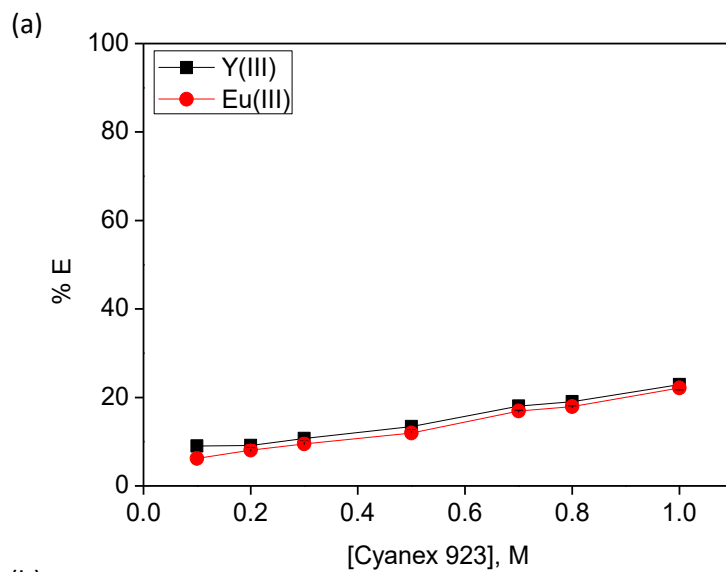


Figure 7.2 Influence of Cyanex 923 on the separation of yttrium and europium in (a) aqueous extraction (error bars not visible) and (b) non-aqueous extraction (EG). Conditions: $t = 1$ h; room temperature; phase ratio more-polar:less-polar phase = 1:1; feed concentrations: $[Y] = 10.5$ g/L; $[Eu] = 1.3$ g/L and $[Y] = 11.4$ g/L; $[Eu] = 1.4$ g/L for EG feed and aqueous feed respectively; $[LiCl] = 2$ M.

Table 7.2 TXRF results of H₂O raffinate and EG raffinate after extraction with C923. Distribution ratio (*D*) for Eu(III) and Y(III) and the separation factor (*SF* or $\alpha = D_Y / D_{Eu}$) are given as a function of [C923].

[C 923], M	Aqueous			Ethylene glycol		
	<i>D</i> , Y	<i>D</i> , Eu	<i>SF</i>	<i>D</i> , Y	<i>D</i> , Eu	<i>SF</i>
0.1	0.10	0.07	1.4	0.04	0.00	-
0.2	0.10	0.09	1.1	0.20	0.00	-
0.3	0.12	0.11	1.1	0.44	0.02	22
0.5	0.15	0.14	1.1	1.07	0.04	27
0.7	0.22	0.20	1.1	2.13	0.08	27
0.8	0.23	0.22	1.0	3.22	0.07	46
1	0.29	0.28	1.0	5.62	0.24	23

Two major differences between the aqueous and non-aqueous systems are observed: (1) the extraction efficiencies for both europium and yttrium are very low (< 25%) in the aqueous extraction systems, compared to the non-aqueous extraction system; (2) both extraction curves in aqueous extraction almost overlap (α almost equal to 1), the extraction of europium is as 'efficient' as the extraction of yttrium in aqueous environment, while for non-aqueous extraction, yttrium is easily extracted and europium is left in the raffinate. The first observation can be explained by the preference of the solvating extractant Cyanex 923 to extract the metals as metal cations coordinated to an anion (salt extraction). In aqueous solutions, the water molecules are strongly bonded to the REE and no chloride is present in the inner coordination sphere, which causes inefficient extraction from aqueous solutions.^{55,56} In addition, the solvent molecules coordinating to the REE have to be fully or partly replaced by Cyanex 923 molecules. This exchange is easier when using an ethylene glycol feed compared to the aqueous feed, since the energy required to remove the solvation sphere around the metal ion (solvation energy) is lower in the case of the ethylene glycol feed. The second observation can be explained by a recent study by Batchu *et al.*, where it was found that HREEs are extracted more efficiently than LREE from ethylene glycol feeds.⁵⁹ This is mainly caused by a difference in charge density of rare-earth ions: heavier rare-earths have a smaller ionic radius and thus a higher charge density. Hence, the extractants bind these HREEs stronger, resulting in higher extraction efficiency and higher separation factors. In the case of aqueous feed

solution, this difference is less pronounced due to the poor extraction of both REEs from water with Cyanex 923.

Since this master thesis focusses on process development, limited attention has been given to the extraction mechanism. However, the number of Cyanex 923 molecules that extract yttrium was estimated through a loading experiment, using a highly concentrated yttrium feed (26.8 g/L) and 4 M LiCl. This was contacted with a solvent containing 1 M Cyanex 923. After equilibrium was reached, the loaded organic was separated from the raffinate and reused in a second extraction with fresh concentrated feed, in order to reach saturation of the solvent (*i.e.* maximum amount of yttrium the solvent can take). Calculation of the amount of yttrium that was extracted showed that three Cyanex 923 molecules are used for every yttrium species extracted, which suggests a mechanism as was presented in *Eq. 12*, 2.2.3 *Non-aqueous solvent extraction: state-of-the-art*. Yet, more information is needed to confirm this assumption.

7.4. Influence of lithium chloride concentration

A salting-out agent is an electrolyte containing the anion of the extractable species and a non-extractable cation, which aids extraction by improving phase separation and/or the distribution ratio. In this case, lithium chloride was used because of its good solubility in EG.⁶⁰ To see the effect of its concentration, an experiment was performed with LiCl concentration varying between 0 and 4 M. The results can be found in *Figure 7.3* and *Table 7.3*.

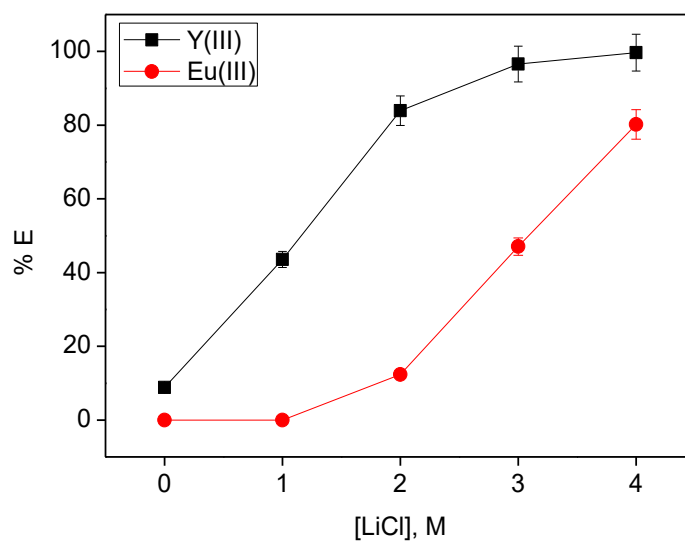


Figure 7.3 Influence of LiCl concentration on the separation of yttrium and europium. Conditions: $t = 1$ h; room temperature; phase ratio EG:C923 = 1:1; feed (EG) concentrations: [Y] = 11.6 g/L, [Eu] = 1.2 g/L for 0 M LiCl; [Y] = 10.3 g/L, [Eu] = 1.2 g/L for 1 M LiCl; [Y] = 11.8 g/L, [Eu] = 1.2 g/L for 2 M LiCl; [Y] = 10.0 g/L, [Eu] = 1.2 g/L for 3 M LiCl; [Y] = 10.5 g/L, [Eu] = 1.2 g/L for 4 M LiCl; [C923] = 1 M.

Table 7.3 TXRF results of EG raffinate after extraction with C923. Distribution ratio (D) for Eu(III) and Y(III) and the separation factor (SF or $\alpha = D_Y / D_{Eu}$) are given as a function of [LiCl].

[LiCl], M	D, Y	D, Eu	SF
0	0.10	0.00	-
1	0.77	0.00	-
2	4.11	0.10	41
3	28.19	0.89	32
4	325.12	4.04	80

The co-extraction of europium is negligible up to [LiCl] = 2 M, while the extraction efficiency for yttrium increases rapidly with increasing LiCl concentrations. Between [LiCl] = 2 M and 4 M, the europium extraction efficiency increases at the same pace as it did for yttrium between 0 M and 2 M. Meanwhile, extraction efficiency of yttrium approaches 100% at [LiCl] = 4 M. Maintaining [LiCl] = 2 M might be the best option, since europium co-extraction is limited at this concentration, although the separation factor at [LiCl] = 4 M is much higher. In fact, for process development, the percentage extraction is more informative than results based on distribution ratios.⁴⁴

7.5. Influence of co-solvents in the feed

Experiments with a mixed ethylene glycol – co-solvent feed have been performed, mixing these selected solvents in a 1:1 ratio with ethylene glycol: water (ultra-pure), methanol (MeOH), acetonitrile (AN), PEG-200, dimethyl sulfoxide (DMSO), propylene carbonate (PC) and PG. This addition should improve mass transfer in some cases, for example by lowering the viscosity (of course this is not the case for addition of PEG-200 and PG). A list of viscosities of the different feeds can be found in section 4.2 *Properties of the feed solutions*, as well as the water content of each feed. Also, differences in solvation might alter the extraction mechanism. All the selected solvents were miscible with the EG feed (which contained $[Y] = 22.2 \text{ g/L}$; $[Eu] = 3 \text{ g/L}$; $[\text{LiCl}] = 4 \text{ M}$), except for AN and PC, as shown in *Figure 7.4*. Consequently, extraction was not performed with the latter two systems. The results for these experiments can be found in *Figure 7.5* and *Table 7.4*.

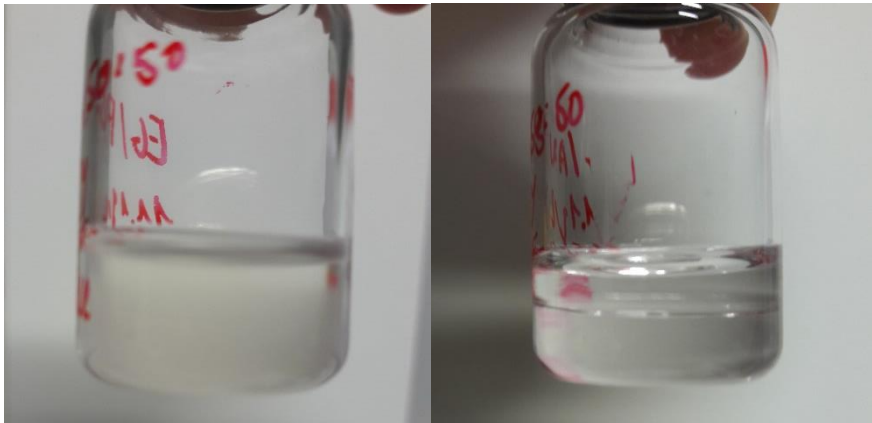


Figure 7.4 The EG/PC (left) and EG/AN (right) feed mixtures do not mix, but phase-separate. This phase separation was better visible for EG/AN than for EG/PC, where transition between the two phases seemed to be more gradual. In both cases, the bottom layer is cloudy. Extra info on densities of the pure solvents: $\rho(\text{EG}) = 1.11 \text{ g/cm}^3$; $\rho(\text{AN}) = 0.81 \text{ g/cm}^3$; $\rho(\text{PC}) = 1.2 \text{ g/cm}^3$.

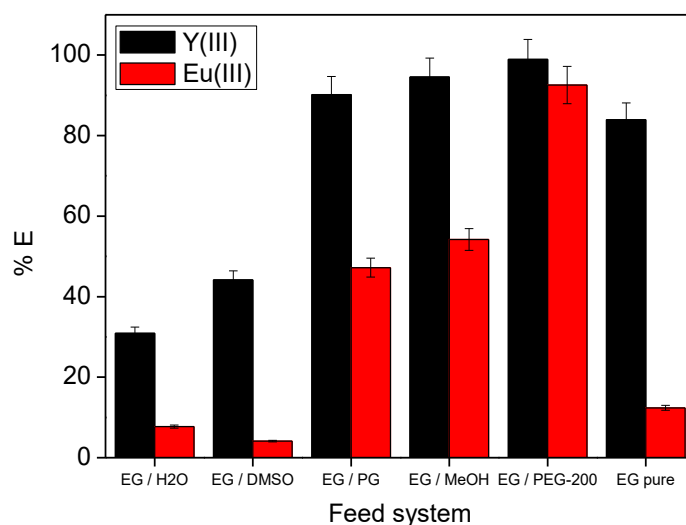


Figure 7.5 Influence of co-solvents in the feed system on the separation of yttrium and europium. Conditions: $t = 1$ h; room temperature; phase ratio more-polar:less-polar phase = 1:1; $[LiCl] = 2$ M; $[C923] = 1$ M; EG/co-solvent = 1:1.

Table 7.4 TXRF results of EG/cosolvent raffinate after extraction with C923. Distribution ratio (D) for Eu(III) and Y(III) and the separation factor (SF or $\alpha = D_Y / D_{Eu}$) are given as a function of feed system.

Feed system	D, Y	D, Eu	SF
EG / H ₂ O	0.45	0.08	5.6
EG / DMSO	0.79	0.04	20
EG / PG	9.20	0.89	10
EG / MeOH	17.31	1.18	15
EG / PEG-200	93.60	12.45	7.5
EG pure	5.51	0.14	39

As can be seen from *Figure 7.5*, both EG/water and EG/DMSO resulted in lower extraction efficiencies. However, the separation factor for the DMSO system was still larger than in all other systems studied during this experiment. For PG and methanol, the percentage extraction was far higher, while quite some europium was co-extracted (about 50%). Surprisingly, PEG-200, although more viscous than EG, resulted in the highest extraction efficiencies for both yttrium and europium, which hence led to a low separation factor. The explanation for this might be found in the preferential solvation of the rare-earth cations with one or the other solvent. For instance, Johansson *et al.* found that in the case of DMSO versus water, the rare-earth cation preferentially coordinates with DMSO.⁸⁰ It is not certain if the rare-earth cations are preferentially solvated by DMSO over EG. Further investigations are needed, but it is certain that an

EG/DMSO mixture lowers extraction of a HREE such as yttrium compared to pure EG. The type of complex formed (REE-salt complexes are extracted more efficiently), the energy needed to remove the solvation shell, the solubility of the formed complexes in both more and less polar phase, the properties of the feed solvents (dielectric constants, polarity, Gutmann donor and acceptor number) all contribute to the extraction mechanism and thus the extraction efficiencies of different REEs.^{60,61,80} Since non-aqueous solvent extraction is an underexposed topic, still a lot of research has to be done on the influence of the more polar phase in solvent extraction.

7.6. Investigation of other feed systems for yttrium/europium separation

Since one of the main advantages of solvometallurgy is the possibility to (re)use green solvents, it is worthwhile to study the separation behaviour of yttrium and europium from other feed solvents as well. As already mentioned in 2.2.2 *Green solvents*, EG is to be considered as a *useable* solvent, although sometimes it is also classified as a *preferred* solvent.⁴³ One of the reasons why ethylene glycol can be called a green solvent is due to the possibility to produce it from renewable resources.^{81–83} It is interesting to test other feed systems based on green solvents, such as propylene glycol (PG), poly(ethylene glycol) with an average molar mass of 200 g/mol (PEG-200) and dimethyl sulfoxide (DMSO).

7.6.1. Propylene glycol (propane-1,2-diol, PG)

Propylene glycol (PG) is to be considered a green solvent for the same reasons as ethylene glycol. Similar concentrations for yttrium, europium and LiCl were dissolved in PG: 10.5 g/L, 1.3 g/L and 2 M respectively. Compared to EG, the dissolution of the rare-earth chloride salts and LiCl at room temperature took longer than expected: about 24 hours. After complete dissolution, the viscosity of the PG feed was noticeably higher than the viscosity of the EG feed (see 4.2 *Properties of the feed solutions*). The effect of the concentration of Cyanex 923 extractant was tested on this PG feed. Also here, 10 vol% of 1-decanol modifier was needed to avoid the formation of three phases. The results for this experiment can be found in *Figure 7.6* and *Table 7.5*.

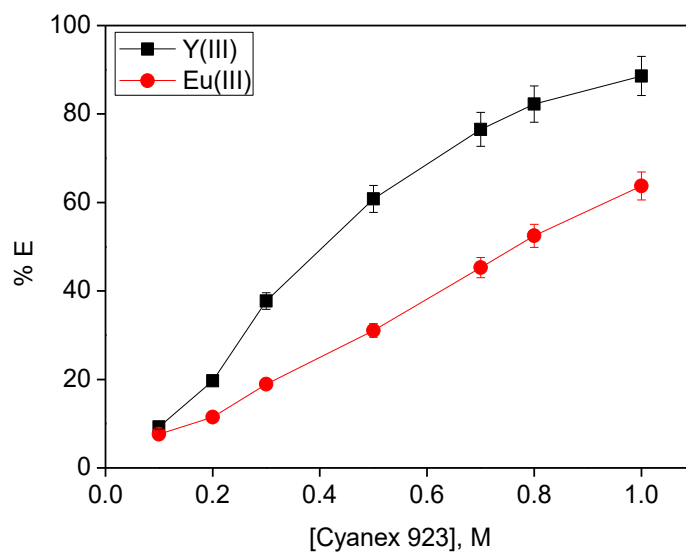


Figure 7.6 Influence of Cyanex 923 concentration on the separation of yttrium and europium. Conditions: $t = 1$ h; room temperature; phase ratio PG:C923 = 1:1; feed (PG) concentrations: $[Y] = 10.5$ g/L; $[Eu] = 1.3$ g/L; $[LiCl] = 2$ M.

Table 7.5 TXRF results of PG raffinate after extraction with C923. Distribution ratio (D) for Eu(III) and Y(III) and the separation factor (SF or $\alpha = D_Y / D_{Eu}$) are given as a function of [C923].

[C 923], M	D, Y	D, Eu	SF
0.1	0.10	0.08	1.3
0.2	0.25	0.13	1.9
0.3	0.61	0.23	2.7
0.5	1.55	0.45	3.4
0.7	3.26	0.83	3.9
0.8	4.63	1.10	4.2
1	7.77	1.76	4.4

For both the system with EG and PG feed, the extraction efficiency of yttrium increased at a rate of about 10% per 0.1 M of extractant. Eventually, an extraction efficiency of 88 % was obtained for yttrium in the case of the PG feed system (84% for EG). However, co-extraction of europium was limited in the experiment with EG up to 0.8 M of C923, whereas for the PG experiment already 50% of europium has been co-extracted at the same concentration of C923. This also reflects in the separation factors, which are at 69 for EG and 4 for PG at $[C923] = 0.8$ M. It can be concluded that, while with EG extraction of HREEs is easier than for the LREEs, extraction of LREEs from a PG feed is efficient as well. Either way, in the case of this approach, one

should choose to continue with the EG system, because of the higher selectivity. Even though PG shows good extraction efficiency, it is incapable of separating europium and yttrium to the extent that would make it useful. Yet, PG seems promising due to the aforementioned high efficiency and the separation of other metals or REEs from a PG feed might be better feasible.

7.6.2. PEG-200

Similarly, an extraction experiment using a poly(ethylene glycol), PEG-200, is presented. This solvent has a low flammability and it is non-toxic, biodegradable, non-volatile and relatively inexpensive.^{84–86} However, a major disadvantage for solvent extraction is the high viscosity of PEG-200, leading to slower kinetics. For the experiments with PEG-200, the extractant concentration was once again used as a variable. Yttrium, europium and LiCl concentrations were 11.6 g/L, 1.6 g/L and 2 M respectively. Here as well, 10 vol% 1-decanol had to be added to the less-polar phase as a modifier. The results are presented in *Figure 7.7* and *Table 7.6*.

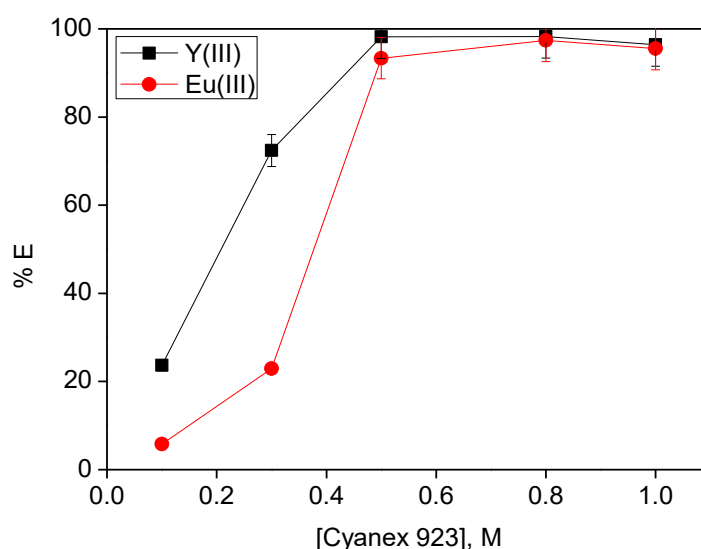


Figure 7.7 Influence of Cyanex 923 on the separation of yttrium and europium in PEG-200. Conditions: $t = 1$ h; room temperature; phase ratio PEG-200:C923 = 1:1; PEG-200 feed concentrations: $[Y] = 11.6$ g/L; $[Eu] = 1.6$ g/L; $[LiCl] = 2$ M.

Table 7.6 TXRF results of PEG-200 raffinate after extraction with C923. Distribution ratio (D) for Eu(III) and Y(III) and the separation factor (SF or $\alpha = D_Y / D_{Eu}$) are given as a function of [C923].

[C 923], M	D, Y	D, Eu	SF
0.1	0.3	0.06	5.2
0.3	2.6	0.30	8.7
0.5	54.6	14.04	3.9
0.8	57.3	37.67	1.5
1	26.6	21.31	1.2

Compared to the EG system, the solvent extraction with PEG-200 does not result in good separation of yttrium and europium. However, it is remarkable that already at lower concentrations of Cyanex 923, the extraction of yttrium and europium is very high: 72.4% and 22.9% respectively at 0.3 M of extractant. This is also to point where the separation of both REEs is optimal, albeit at lower yttrium extraction compared to the EG system. From 0.5 M of extractant on, both yttrium and europium are (almost) completely extracted. The ease with which both REEs are extracted from PEG-200 is possibly caused by the preferential solvation of the REEs with PEG-200. This solvent molecule can wrap itself around the metal by interaction of its electron-donating ether and hydroxyl functionalities, creating a chelating effect. Because of this, the entire REE-PEG complex is probably extracted towards the less-polar phase, which would explain the high extraction efficiencies.

7.6.3. Dimethyl sulfoxide (DMSO)

DMSO is not considered as a “preferred” solvent by the Pfizer solvent-selection guide.⁴³ There are plenty of publications though referring to DMSO as a “green” solvent.^{62,63,87,88} DMSO might provide interesting results for solvent extraction using Cyanex 923 as extractant in GS190 GTL diluent.

Similar to previous series of experiments with the EG/GS190 system, the optimization of the solvent extraction started with the examination of the influence of extractant concentration. An initial screening experiment was set up to determine if good phase separation can be obtained, or in other words whether or not a modifier should be added to the solvent. DMSO feed and solvent consisting of GS190 and varying concentrations of Cyanex 923 were tested in a 1:1 ratio (1 mL : 1 mL). The samples were shaken by hand for 2 minutes. After centrifugation, a clear phase separation was

obtained, i.e. there was no cloudiness nor formation of a third phase. Consequently, no modifier had to be added to the less-polar phase. Also an experiment to test if volume changes occur (due to partial miscibility) was necessary. Therefore, two tests were performed at low LiCl concentrations (since LiCl already enhances phase separation): (1) 3 mL DMSO feed containing the REE chloride salts and 0.5 M LiCl plus 3 mL of 1 M Cyanex 923 solution in GS190 diluent, (2) 3 mL of DMSO feed containing the REE chloride salts and 1 M LiCl plus 3 mL of 1 M Cyanex 923 solution in GS190 diluent. In both cases, the samples were shaken at 500 rpm using a wrist-action shaker, for 5 minutes. After centrifugation, it was clear that no volume change had taken place, even at these lower LiCl concentrations. Consequently, no phase-inducer (e.g. addition of H₂O would minimize the volume change) needs to be added when performing the solvent extraction experiment.

Then, a proper extraction experiment was set up, varying the extractant concentration between 0.1 M and 1 M. The feed concentrations for yttrium, europium and LiCl were 11.4 g/L, 1.4 g/L and 2 M respectively. The results can be found in *Figure 7.8* and *Table 7.7*.

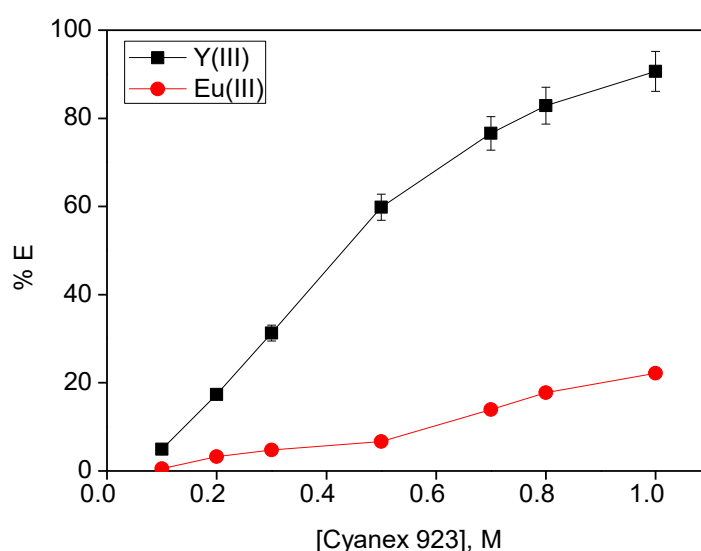


Figure 7.8 Influence of Cyanex 923 on the separation of yttrium and europium in DMSO. Conditions: $t = 1$ h; room temperature; phase ratio DMSO:C923 = 1:1; DMSO feed concentrations: $[Y] = 11.4$ g/L; $[Eu] = 1.4$ g/L; $[LiCl] = 2$ M.

Table 7.7 TXRF results of DMSO raffinate after extraction with C923. Distribution ratio (D) for Eu(III) and Y(III) and the separation factor (SF or $\alpha = D_Y / D_{Eu}$) are given as a function of [C923].

[C 923], M	D, Y	D, Eu	SF
0.1	0.05	0.005	1.2
0.2	0.21	0.03	3.3
0.3	0.46	0.05	5.1
0.5	1.49	0.07	15
0.7	3.3	0.16	14
0.8	4.8	0.22	14
1	9.7	0.28	16

Compared to similar results for the EG experiments (*Figure 7.2*), extraction efficiency for both yttrium and europium have slightly increased. This resulted in a lower separation factor: 16 for DMSO at 1 M of Cyanex 923, compared to about 33 for EG at 1 M of Cyanex 923. The differences in solvation (e.g. ethylene glycol is a bidentate ligand, DMSO is monodentate), combined with changes in the salting-out effect of LiCl due to a difference in dielectric constant, could cause solvent extraction with a DMSO feed to be slightly less selective. Overall, the separation of yttrium and europium is still good, which is something unexpected: the pure EG and pure DMSO systems both result in good extraction of HREEs, while a mixture of these solvents extracts yttrium poorly (< 50%), as seen in *7.5 Influence of co-solvents in the feed*. This remarkable observation is worth further investigation. Also, further optimization of the DMSO system is needed, since the high extraction efficiencies show that this system is promising as well.

7.7. Influence of commonly associated elements

As was already made clear in the first chapter (*1 General introduction: relevance of this study*), the two most important waste streams in which significant amounts of yttrium and europium are found, are lamp phosphors and cathode ray tube (CRT) phosphors. Prior to the experiment, data on the relative composition of real waste streams needed to be collected, in order to get a clear view on the proportion of yttrium and europium compared to the other associated elements. Based on information found in the literature, a few commonly associated elements could be identified and included in two preliminary extraction tests.^{21,30,89–92} It is clear that the results reported in literature significantly deviate from each other. Zinc was found to be the main

associated element in CRTs phosphors, while terbium, gadolinium, cerium and lanthanum were also found in the lamp phosphors. For CRTs, all references show that the concentration of zinc is almost always twice that of yttrium. There is less agreement to be found in the literature values for the composition of the lamp phosphors, so we used the values given by Innocenzi *et al.*⁹⁰ For lamp phosphors, it was chosen to only add gadolinium and terbium. Of course, in real lamp phosphor waste lanthanum, cerium and other metals such as Ca, Fe, Sb or Mn will also be present in solution. The experiments will be split up in these two parts, with the concentrations chosen as mentioned in *Table 7.8*.

Table 7.8 Overview of the metal concentrations used during the experiments for the study on the influence of the commonly associated elements in both CRTs and lamp phosphor waste.

	Elements	Concentrations (in g/L)
CRTs phosphors	yttrium	11.1
	europium	1.52
	zinc	22.2
Lamp phosphors	yttrium	11.1
	europium	1.52
	gadolinium	0.35
	terbium	0.10

For the (Y, Eu, Zn) experiment, the concentration of Cyanex 923 extractant was varied again. The feed solution contained 2 M LiCl and the concentrations of the metals is given in *Table 7.8*. The results for this experiment can be found in *Figure 7.9* and *Table 7.9*.

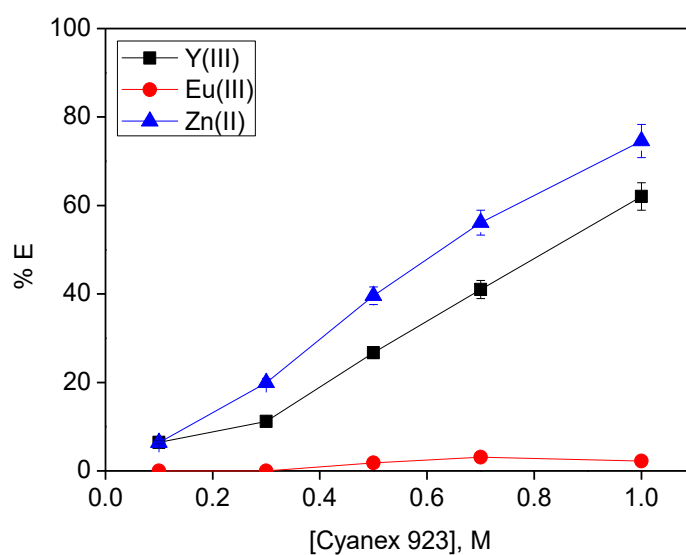


Figure 7.9 Influence of Cyanex 923 on the separation of yttrium and europium in presence of zinc. Conditions: $t = 1$ h; room temperature; phase ratio EG:C923 = 1:1; feed concentrations: $[Y] = 11.0$ g/L; $[Eu] = 1.4$ g/L; $[Zn] = 20.6$ g/L; $[LiCl] = 2$ M.

Table 7.9 TXRF results of EG raffinate after extraction with C923. Distribution ratio (D) for Eu(III), Y(III) and Zn(II) and the separation factor α are given as a function of [C923].

[C923], M	D, Y	D, Eu	D, Zn	SF (Y,Eu)	SF (Y,Zn)
0.1	0.07	0.00	0.07	-	1.0
0.3	0.13	0.00	0.25	-	1.9
0.5	0.36	0.02	0.66	18	1.8
0.7	0.69	0.03	1.28	23	1.9
1	1.64	0.02	2.93	82	1.8

From these data, it can be observed that both yttrium and zinc are extracted very well, with zinc being extracted with higher efficiency than yttrium. This is in contrast to europium co-extraction, which is almost non-existing. Zinc extraction probably inhibits europium co-extraction, so that the mutual separation factor of yttrium and europium increases greatly. It is clear that the presence of zinc in the loaded organic phase makes recovery of pure yttrium difficult, unless either zinc is removed prior to yttrium/europium separation using a different extractant (selective for Zn) or zinc is selectively removed after extraction by a suitable scrubbing agent. By further

optimization it is fully feasible to apply the present process for the selective recovery of rare earths and zinc from CRT phosphors.

For the (Y, Eu, Gd, Tb) experiment, the results can be found in *Figure 7.10* and *Table 7.10*.

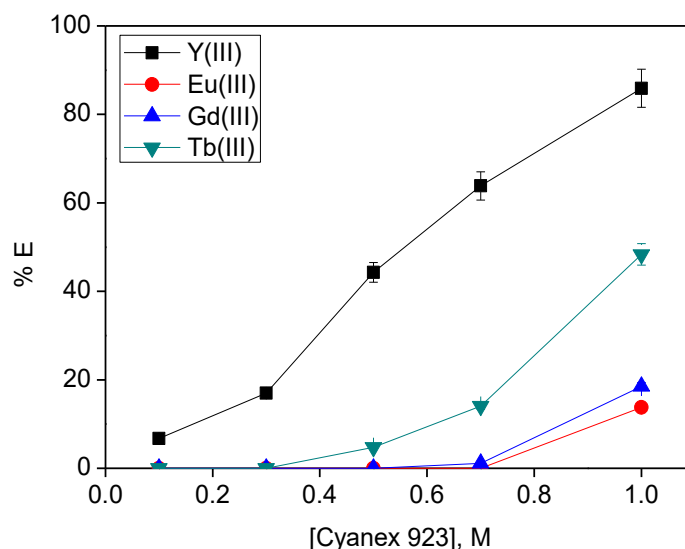


Figure 7.10 Influence of Cyanex 923 on the separation of yttrium and europium in presence of zinc. Conditions: $t = 1$ h; room temperature; phase ratio EG:C923 = 1:1; feed concentrations: $[Y] = 11.0$ g/L; $[Eu] = 1.4$ g/L; $[Gd] = 0.29$ g/L; $[Tb] = 0.12$ g/L; $[LiCl] = 2$ M.

Table 7.10 TXRF results of EG raffinate after extraction with C923. Distribution ratio (D) for Eu(III), Y(III), Gd(III) and Tb(III) and the separation factor (SF or $\alpha = D_Y / D_{REE}$) are given as a function of [C923].

[C923], M	D, Y	D, Eu	D, Gd	D, Tb	SF (Y,Eu)	SF (Y,Gd)	SF (Y,Tb)
0.1	0.07	0.00	0.00	0.00	-	-	-
0.3	0.20	0.00	0.00	0.00	-	-	-
0.5	0.80	0.00	0.00	0.05	-	-	16
0.7	1.77	0.00	0.01	0.16	-	177	11
1	6.10	0.16	0.23	0.93	38	27	6.6

As can be seen from *Table 7.10*, the addition of gadolinium and terbium does not influence the extraction of yttrium and europium greatly. However, co-extraction of gadolinium and (especially) terbium is considerable, since these elements can be positioned in between europium and yttrium in terms of extraction behavior.⁵⁹ Finally, it is also surprising that the values for the separation factor for gadolinium and terbium

are diverging so much: 177 for gadolinium and 11 for terbium at 0.7 M of C923. Presumably, the extraction behavior of yttrium in this case is positioned closer to that of terbium. To continue further with this system, yttrium has to be extracted selectively using 0.5 M C923, which needs several stages to fully recover yttrium. Afterwards, Gd and Tb should be removed, which needs optimization of several process parameters.

7.8. Influence of the phase ratio on yttrium extraction

In a last optimization step of the solvent extraction process, a range of phase ratios was screened. The results of these experiments can be presented as an extraction isotherm: the concentration of the extractable element in the less polar (C923) phase is plotted as a function of the concentration of the same element in the more polar (EG) phase at equilibrium. This can be used to construct a McCabe-Thiele diagram (see 5.2 *McCabe-Thiele approach*), which allows to further optimize the phase ratio and the number of stages theoretically needed to get full extraction of yttrium.

For the phase ratio experiment, phase ratios of EG:C923 = 7:1 up to 1:7 were tested. The results are summarized as an extraction isotherm in a McCabe-Thiele diagram in *Figure 7.11*. The data used to construct the extraction isotherm can be found in *Table 7.11*, as well as the concentrations of europium in the raffinate and loaded organic phase and the percentage extraction.

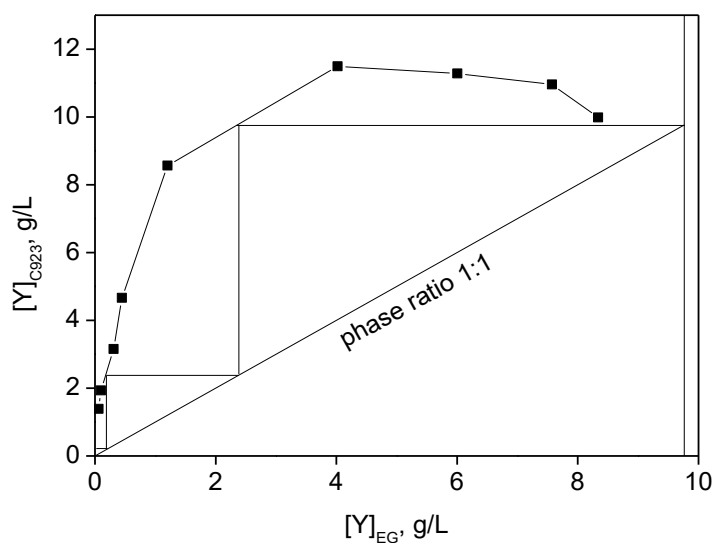


Figure 7.11 McCabe-Thiele diagram for the extraction of yttrium. Conditions: $t = 1$ h; room temp.; feed concentrations: $[Y] = 9.8$ g/L; $[Eu] = 1.1$ g/L; $[LiCl] = 2$ M.

Table 7.11 Yttrium and europium concentration in the EG and C923 phase and percentage extraction (%E) as a function of phase ratio.

Phase ratio (EG:C923)	[Y] _{EG} , g/L	[Y] _{C923} , g/L	[Eu] _{EG} , g/L	[Eu] _{C923} , g/L	%E, Y	%E, Eu
7:1	8.3	10.0	1.1	0.0	14.6	0.0
5:1	7.6	11.0	1.1	0.0	22.4	0.0
3:1	6.0	11.3	1.1	0.0	38.5	0.0
2:1	4.0	11.5	1.1	0.0	58.8	2.7
1:1	1.2	8.6	1.0	0.2	87.7	13.5
1:2	0.4	4.7	0.6	0.3	95.4	45.8
1:3	0.3	3.2	0.4	0.2	96.8	60.5
1:5	0.1	1.9	0.3	0.2	99.0	71.1
1:7	0.1	1.4	0.3	0.1	99.4	77.0

As can be seen in the McCabe-Thiele diagram, three theoretical extraction stages are needed to achieve almost 100% extraction of yttrium. Based on these results, a 1:1 phase ratio was chosen as the optimized value. No meaningful result could be obtained for an EG/C923 phase ratio of 2:1, since the intersection of the feed line and the operating line (initial feed concentration, on the right hand side of *Figure 7.11*) is situated above the curve, so no theoretical stages can be drawn for this. A 1:2 EG/C923 phase ratio would result in two theoretical stages. However, two times the amount of C923 phase is needed in this case, which can be economically less interesting. Also, it would result in a less concentrated loaded organic phase.

7.9. Counter-current extraction simulation (CCES)

Based on McCabe-Thiele diagram predictions (*Figure 7.11*), a three-stage counter-current extraction simulation scheme is constructed and tested. This is a first step towards upscaling and will prove the feasibility of the process.

The first CCES will be performed according to the scheme shown in 5.3 *Counter-current extraction simulation (CCES)*, *Figure 5.2*. As to the experimental setup, separatory funnels (100 mL) were shaken using a wrist-action shaker. The feed solution contained 10.4 g/L of yttrium, 1.3 g/L of europium and 2 M LiCl. The solvent consisted of 1 M Cyanex 923 and 10 vol% 1-decanol, dissolved in the Shell GTL-

diluent GS190. Eventually, the REEs concentrations in the LO3 and 4 fractions and the concentrations in the R3 and 4 fractions (as presented in 5.3 Counter-current extraction simulation (CCES)) are representative to those obtained in a three stage counter-current extraction process. The results derived from TXRF measurement of R4 are shown in Table 7.12.

Table 7.12 Results of the three-stage counter-current extraction simulation studies of yttrium extraction by C923. Extraction efficiency (%E) and concentrations of Y, Eu in the raffinate and loaded organic phase (after equilibrium) are given for each of the experiments. EG:C923 = 1:1.

Raffinate (g/L)		Loaded organic (g/L)		%E	
Y	Eu	Y	Eu	Y	Eu
0.0	0.5	10.4	0.9	100	63.3

Feed concentration: [Y] = 10.4 g/L; [Eu] = 1.3 g/L.

As expected, the extraction percentage for yttrium reached 100%. However, the co-extraction of europium was significant, attaining a value of 63% – 68%. An excess of Cyanex 923 extractant could be the reason for the significant co-extraction of europium.

Consequently, another approach should be considered based on this CCES: to lower the co-extraction of europium, the amount of Cyanex 923 that is available should be lowered. This can be achieved by lowering the concentration of the extractant or by changing the phase ratio. The latter has been chosen, because it has the advantage of increasing the concentrations of the REEs in the loaded organic phase. Therefore, a second CCES experiment was conducted, with a phase ratio of EG:C923 = 1.5:1. Also for this experiment a three-stage counter-current approach was chosen. The feed solution contained 11.6 g/L of yttrium, 1.4 g/L of europium and 2 M LiCl. The results are presented in Table 7.13.

Table 7.13 Results of the three-stage counter-current extraction simulation studies of yttrium extraction by C923. Extraction efficiency (%E) and concentrations of Y, Eu in the raffinate and loaded organic phase (after equilibrium) are given for each of the experiments. EG:C923 = 1.5:1.

Raffinate (g/L)		Loaded organic (g/L)		%E	
Y	Eu	Y	Eu	Y	Eu
0.07	1.3	17.3	0.1	99.4	7.0

Feed concentration: [Y] = 11.6 g/L; [Eu] = 1.4 g/L.

Compared to the first CCES with EG:C923 = 1:1, europium co-extraction is significantly lower, while the extraction percentage for yttrium is still about 100%. In conclusion, this CCES with EG:C923 = 1.5:1 and counting three stages might be a good option for the separation of yttrium and europium. A fourth stage should be added to extract all the yttrium. The remaining europium can be scrubbed from the organic phase as mentioned in 7.10 *Scrubbing and stripping experiments*.

A third CCES was performed using EG:C923 = 2:1 as phase ratio, this time simulating a two-stage counter-current extraction. The feed solution contained 10.4 g/L of yttrium, 1.3 g/L of europium and 2 M LiCl. The results are presented in *Table 7.14*.

Table 7.14 Results of the two-stage counter-current extraction simulation studies of yttrium extraction by C923. Extraction efficiency (%E) and concentrations of Y, Eu in the raffinate and loaded organic phase (after equilibrium) are given for each of the experiments. EG:C923 = 2:1.

Raffinate (g/L)		Loaded organic (g/L)		%E	
Y	Eu	Y	Eu	Y	Eu
1.9	1.1	17.9	0.0	82.8	0.0

Feed concentration: [Y] = 10.4 g/L; [Eu] = 1.3 g/L.

By limiting the amount of the extractant through fine-tuning of the phase ratio, the co-extraction of europium is eliminated. However, also the extraction efficiency of yttrium decreased, to around 80%, which could indicate the need for a three-stage counter-current extraction.

Overall, the approach in which the phase ratio was changed to 2:1 is far better than the 1:1 phase ratio three-stage counter-current extraction, since the co-extraction of europium was limited. A three-stage counter-current extraction for the last approach might be considered, to remove yttrium completely from the EG phase. Eventually however, it was chosen to proceed with EG:C923 = 1.5:1, although a three-stage counter-current extraction with a 2:1 phase ratio is likely to deliver better results (lower europium co-extraction).

7.10. Scrubbing and stripping experiments

Intrinsically, scrubbing and stripping have the same principle: removing rare earths from the organic phase to obtain an (aqueous) solution of REEs or to recover REEs as a precipitate. Yet, scrubbing focusses on the selective removal of co-extracted impurities (europium in this case) while stripping targets full recovery of the all extracted metals.

To generate loaded organic phase for the scrubbing and stripping studies, two larger-scale extractions were performed. In the first larger-scale extraction, 100 mL of feed containing 11.5 g/L of yttrium and 1.3 g/L of europium was contacted with 100 mL of solvent containing 1 M of Cyanex 923 and 10 vol% of 1-decanol for one hour at room temperature. The second larger-scale extraction was performed at a 250 mL:250 mL scale, with the feed containing 10.7 g/L yttrium and 1.3 g/L europium. The solvent was identical. The results of these extractions and the corresponding concentrations of the generated loaded organic phases can be found in *Table 7.15*. Which loaded organic has been used in which experiments will be mentioned beneath each table with scrubbing and stripping results.

Table 7.15 TXRF results of EG feed after extraction with C923. Extraction efficiency (%E), distribution ratio (D) for Eu(III) and Y(III) and the separation factor (SF or $\alpha = D_Y / D_{Eu}$) are given as a function of [C923]. LO = loaded organic.

Phase volume	%E, Y	%E, Eu	D, Y	D, Eu	[Y] _{Lo} , g/L	[Eu] _{Lo} , g/L
100 mL : 100 mL	88.0	19.4	7.29	0.24	10.1	0.24
250 mL : 250 mL	88.2	19.1	7.45	0.22	9.5	0.24

For the scrubbing experiments ethylene glycol scrub solutions were tested, which offer the possibility of recycling the scrub raffinate for reuse during the extraction. The principle idea was to make use of the preferential extraction of yttrium compared to europium. When a scrub feed solution containing yttrium is contacted with the loaded organic, co-extracted europium from this organic phase can be exchanged with yttrium

from the scrub solution since yttrium has more affinity for Cyanex 923. Various lithium chloride concentrations were tested as well as scrub solutions containing no yttrium, for the sake of comparison. The parameters used during these experiments are listed below. Notice that the phase ratio of the scrub solution to the loaded organic is 1:3. This way, the possibility that yttrium is stripped is diminished, while a more concentrated europium solution can be obtained. Also, the yttrium added to the scrub solution in the final process is a part of the yttrium that is recovered at the end of the process. The 1:3 phase ratio makes sure that only a small fraction of the recovered yttrium is recycled again in the process for scrubbing. The results of the bench-scale scrubbing experiments can be found in *Table 7.16*.

Table 7.16 *Scrubbing of europium from loaded Cyanex 923 using various scrub solutions. Scrubbing efficiency (%Sc) and concentrations of Y (III), Eu(III) in the scrub raffinate and scrubbed organic phase are given for each of the experiments.*

EG scrub solution	Scrub raffinate (g/L)		Scrubbed organic (g/L)		%Sc	
	Y	Eu	Y	Eu	Y	Eu
0 M LiCl, 11.3 g/L Y	21.2	1.06	6.8	0.00	32.7	100
1 M LiCl, 10.9 g/L Y 1:3	9.2	0.73	10.6	0.00	-	99.2
1 M LiCl, 10.9 g/L Y 1:2 *	8.9	0.49	10.1	0.00	-	100
2 M LiCl, 10.5 g/L Y	3.2	0.49	12.5	0.08	-	63.7
0 M LiCl 1:3	14.0	0.86	5.4	0.00	46.4	100
0 M LiCl 1:1 *	7.0	0.28	2.5	0.00	74.0	100
1 M LiCl	4.2	0.69	8.7	0.04	13.1	90.7
2 M LiCl	1.2	0.36	9.7	0.38	3.98	46.7

* Phase ratio EG:C923 = 1:3, except for the indicated experiments, where the phase ratio is explicitly given. The original concentrations in the loaded organic phase are: [Y] = 10.1 g/L, [Eu] = 0.24 g/L, except for the indicated experiments: [Y] = 9.5 g/L, [Eu] = 0.24 g/L.

Three conclusions can be drawn from these results. First, it is obvious that higher concentrations of LiCl in the scrub solution result in a lower scrubbing efficiency, and thus a higher concentration of yttrium and europium in the less-polar phase (*i.e.*

scrubbed organic in *Table 7.16*), a trend which was also seen in *Figure 7.3*. Secondly, the experiment with 1 M LiCl and $[Y] = 10.9$ g/L shows to be the most efficient system to remove almost all europium from the loaded organic solvent to the scrub solution, without removing yttrium from the loaded organic solvent. Instead, about 1 g/L of yttrium is taken up from the scrub solution into the C923 phase. The remaining scrub raffinate, containing still about 9.24 g/L yttrium and 0.73 g/L europium, can be added to the fresh feed which has to be extracted (after adjusting REE and LiCl concentration). The scrubbed organic phase, containing almost pure yttrium, can undergo a second scrubbing stage, to fully remove all europium. If the phase ratio is changed to EG:C923 = 1:2, an even better result is obtained, removing all europium in one contact. However, this results in a more dilute process stream, which makes this approach less attractive.

For the stripping experiments, a first possibility is to strip yttrium with acidic solutions. It was chosen to work with aqueous solutions of hydrochloric acid (0 M – 3 M) and methane sulfonic acid (MSA, 1 M and 2 M). A second possibility is precipitation stripping, using aqueous solutions of oxalic acid. The K_{sp} for europium and yttrium oxalate in water are 4.2×10^{-32} and 5.1×10^{-30} respectively.⁹³ Also solutions of oxalic acid in EG were tested, since oxalic acid exhibited good solubility in EG. The main idea behind stripping with oxalic acid is the formation of an insoluble rare-earth oxalate precipitate, which can be dried and eventually calcined further down the process, obtaining rare-earth oxides (REOs). These REOs are the main commercial form of REEs for various end-use applications. The results of the stripping experiments with abovementioned strip solutions can be found in *Table 7.17*.

An important side-note to the experiments testing HCl strip solutions: for distilled water and HCl solutions with concentrations from 0.001 M to 0.05 M, a white precipitate had formed, which accumulated on the interphase of the completely settled phases. In these cases, the pH of the aqueous phase might have been too high, resulting in hydrolysis of yttrium and thus formation of $Y(OH)_3$ precipitate. As a consequence, no sensible results could be reported for these concentrations.

Another observation: for the stripping experiments with oxalic acid, a white precipitate could clearly be seen for the aqueous strip solution, while no precipitate had formed in the EG strip solutions. This result suggests that yttrium oxalate is soluble in EG. This hypothesis was tested by adding oxalic acid to an yttrium feed solution in EG, and indeed no precipitation was observed. Hence, the approach using an ethylene glycol solution of oxalic acid could not be continued, although this can be useful for dissolution of rare-earth oxalates.

Table 7.17 Stripping of yttrium and europium using different stripping agents. Stripping efficiency (%St) and concentrations of Y(III) and Eu(III) in the strip raffinate and stripped organic phase are given. D. water = deionized water and OA = oxalic acid. A:O = 1:1.

Strip solution	Strip raffinate (g/L)		Stripped organic (g/L)		%St	
	Y	Eu	Y	Eu	Y	Eu
0.1 M HCl	7.8	0.25	2.3	0.00	77.7	100
0.5 M HCl	8.4	0.26	1.7	0.00	83.7	100
1 M HCl	8.5	0.26	1.6	0.00	84.1	100
2 M HCl	8.4	0.27	1.7	0.00	82.9	100
3 M HCl	8.4	0.25	1.7	0.00	83.0	100
1 M OA in H₂O, A:O = 1:1*	-	-	1.0	0.00	89.8	100
1 M OA in H₂O, A:O = 2:1*	-	-	0.0	0.00	100	100
0.1 M OA in EG	7.2	0.24	2.3	0.01	76.3	97.9
0.5 M OA in EG	7.5	0.29	2.0	0.00	79.2	100
1 M OA in EG	9.0	0.29	0.5	0.00	94.7	100
1 M MSA	9.1	0.29	0.2	0.00	96.5	100
2 M MSA	9.2	0.29	0.3	0.00	97.5	100

The original concentrations in the loaded organic phase are: [Y] = 9.5 g/L, [Eu] = 0.24 g/L.

* For the aqueous oxalic acid solutions, the values for the stripped organic and %E are based on the TXRF measurement of the oxalate precipitate, after dissolution with 3 mL of 37% HCl.

First, it is clear from the data in *Table 7.17* that yttrium could not be selectively stripped directly from the loaded organic phase. In all cases, europium is stripped quantitatively, while a lower stripping efficiency is encountered for yttrium. However, these solutions can be used to quantitatively strip yttrium if the loaded organic phase is contacted more

than once with these solutions. In combination with a scrubbing step, a pure yttrium solution or pure yttrium oxalate precipitate can be obtained, since it was shown that europium can be selectively scrubbed from the organic phase using an EG solution containing yttrium and LiCl (*vide supra*). Secondly, the aqueous oxalate stripping seems to provide the most interesting results. If the phase ratio of aqueous oxalic acid strip solution to the loaded organic is changed from 1:1 to 2:1, the percentage stripping increases to 100% for yttrium. Thirdly, HCl does not seem to be very efficient as a stripping agent. Increasing the acid concentration does not result in enhanced stripping efficiency. This is probably caused by the presence of chloride, which is also the counter anion used during extraction. Addition of extra chloride results in shift of the extraction reaction, as presented in Eq. 17, towards the extracted yttrium-Cyanex 923 complex (with R = C923). On the other hand, MSA is the most efficient acid to strip yttrium. This is a promising result, since MSA has quite some advantages over other acids. It is bio-degradable, it has low toxicity and low tendency to oxidize organic compounds.⁹⁴



Oxalic acid was chosen over other strip solutions, since it allows the quasi-direct recovery of yttrium as a REO.

Besides the experiment using an oxalic acid strip solution, also two experiments in which solid oxalic acid was applied directly to the loaded organic were performed. Three equivalents of oxalic acid were added to one equivalent of yttrium, present in the loaded organic. Both an experiment at room temperature and at 60 °C were performed while stirring the sludge. The amount of yttrium stripped during these experiments was determined by redissolving the oxalate precipitate with 37% HCl. However, this gave erroneous results. Instead, a qualitative test was performed. 2 µL of stripped loaded organic was spotted immediately on a TXRF carrier without dilution or internal standardization. This is called a *standardless* TXRF measurement. These analyses indicated that there was still yttrium left in the stripped organic phase. Direct addition of solid oxalic acid does not work as efficiently as an oxalic acid solution, probably because the rare-earth oxalate directly precipitates on top of fresh oxalic acid

particles, obstructing further precipitation of rare earths. Similar results were obtained if the amount of oxalic acid was increased to 5 or 10 times excess.

7.11. Influence of the phase ratio on europium scrubbing

Phase ratio experiments are needed to determine the optimum phase ratio and the number of stages for the scrubbing of europium. The scrub feed made for this experiment is an EG solution containing 11.8 g/L yttrium and 1 M LiCl, which was found to be the optimal composition in *Table 7.16*. The loaded organic used for this experiment contained 9.5 g/L yttrium and 0.31 g/L europium. More polar to less polar phase ratios between 7:1 and 1:7 were investigated.

Again, McCabe-Thiele diagrams were constructed. However, due to the odd shape of the isotherm, the McCabe-Thiele diagrams were not useful to determine the suitable phase ratio and number of stages. Therefore, the results in *Table 7.18* were used instead to make a decision on the phase ratio and the estimated number of stages needed.

Table 7.18 The yttrium and europium scrubbing efficiency and their concentration in the EG and C923 phase as a function of the phase ratio.

Phase ratio (EG:C923)	[Y] _{EG} , g/L	[Y] _{LO} , g/L	[Eu] _{EG} , g/L	[Eu] _{LO} , g/L	%Sc, Y	%Sc, Eu
7:1	6.2	49.0	0.04	0.00	0.0	99.9
5:1	6.4	36.9	0.06	0.02	0.0	94.6
3:1	6.5	25.5	0.09	0.04	0.0	88.5
2:1	6.7	19.8	0.14	0.03	0.0	89.5
1:1	6.6	14.7	0.28	0.03	0.0	90.2
1:2	7.0	11.9	0.55	0.03	0.0	89.2
1:3	7.0	11.1	0.76	0.06	0.0	81.9
1:5	6.7	10.5	1.17	0.07	0.0	76.1
1:7	6.2	10.3	1.47	0.10	0.0	68.3

A trade-off between the phase ratio and the scrubbing efficiency for europium should be found. Firstly, it is desirable to obtain a scrub raffinate that has a higher concentration of europium than the original loaded organic before scrubbing. This can be achieved by choosing a phase ratio with higher volume of less polar solvent compared to more polar solvent (EG:C923 between 1:2 and 1:7). Secondly, scrubbing

efficiency for europium should be high. For instance, at EG:C923 = 1:3, a scrubbing efficiency of about 82% is obtained, which is already a good value to work with. In this case, a three-stage counter-current experiment might be sufficient to remove all europium. However, this result is surprising since *Table 7.16* showed 99% scrubbing of europium at EG:C923 = 1:3 at similar conditions, which is significantly higher than the value found in the phase ratio experiment. The experiment at the same conditions has been repeated two times and it was found that the scrubbing of europium is about 91%. The cause for these deviations is unknown, so conclusions should be drawn with caution.

7.12. Counter-current scrubbing simulation (CCSS)

In a next phase of the counter-current simulation experiments, the co-extracted europium will have to be removed from the loaded organic by scrubbing. In *7.10 Scrubbing and stripping experiments* a scrubbing process was proposed, using an EG solution containing yttrium and 1 M LiCl. The phase ratio experiment in *7.11 Influence of the phase ratio on europium scrubbing* revealed three things: (1) a phase ratio of EG:C923 = 5:1 or 3:1 can be considered as optimal according to the McCabe-Thiele diagram, (2) the phase ratio EG:C923 = 1:3 is however a better choice because it has high scrubbing efficiency (about 82% of europium is scrubbed) and it generates a more concentrated EG process stream (0.76 g/L europium) which is economically advantageous, (3) the concentration of europium in the scrub raffinate (after equilibrium) fluctuates, probably due to an analytical error. Therefore, it was chosen to work with a phase ratio of EG:C923 = 1:3 and it was estimated that three stages would be sufficient to scrub all europium.

As to the experimental setup, the flow of the liquid streams in the counter-current scrubbing simulation (CCSS) is somewhat different compared to the flow in the CCES. The ethylene glycol feed and raffinate flows for CCES in *Figure 5.2* are replaced by loaded organic and scrubbed loaded organic flows respectively in CCSS, while the fresh solvent and loaded organic flows in CCES are replaced by scrub feed and scrub raffinate flows in CCSS. The scrub solution used during these experiments is an EG solution containing 12.0 g/L of yttrium and 1 M LiCl. As to the loaded organic, two representative batches of loaded organic obtained from the CCES with phase ratio EG:C923 = 1.5:1 (*vide supra*) were mixed and the total rare-earth content was

determined using the values from *Table 7.13* and taking the average for both batches, taking into account the volumes of each batch. The calculated concentration for yttrium is 17.3 g/L, for europium 0.16 g/L.

The results of the SR4 batch, which is the representative scrub raffinate fraction for a three-stage counter-current scrubbing process are summarized in *Table 7.19*.

Table 7.19 Results of the three-stage counter-current scrubbing simulation of europium. Scrubbing efficiency (%Sc) and concentrations of Y, Eu in the scrub raffinate and scrubbed organic phase (after equilibrium) are given for each of the experiments. Phase ratio EG:C923 = 1:3.

Scrub raffinate (g/L)		Scrubbed organic (g/L)		%Sc	
Y	Eu	Y	Eu	Y	Eu
21.1	0.48	14.3	0.00	25.0	100

Concentration in loaded organic: [Y] = 17.3 g/L; [Eu] = 0.16 g/L.

Two observations are to be made based on these results. Firstly, as expected, the scrubbing efficiency for europium is 100% after a three-stage counter current experiment. Secondly, and more importantly, yttrium also is transferred to the scrub raffinate. Even for SR1 (not shown in the table), which can be seen as a single-contact scrubbing experiment, a scrubbing efficiency of 16% for europium was measured, which was not anticipated. Either an experimental error or a difference in the concentration of the loaded organic obtained after CCES compared to loaded organic obtained after a single contact might be the cause. To illustrate the last presumption: the yttrium concentration in the loaded organic after CCES was 17.3 g/L, compared to about 10 g/L for the loaded organic obtained after one contact, as was used in the bench-scale scrubbing experiments. This hypothesis can be tested by recreating a loaded organic with about 17 g/L of yttrium and performing a one-contact scrubbing experiment, to see if the results are repeatable. If this is indeed the case, alterations have to be made to the scrubbing process. Changing the composition of the scrub feed from 1 M LiCl (and 11.1 g/L yttrium) to 2 M LiCl (and 11.1 g/L of yttrium) can avoid the scrubbing of yttrium into the more-polar phase, solving the problem. Only concern here is the low scrubbing efficiency for europium: about 64% in one contact with the 2 M LiCl scrub feed (see *Table 7.16*). If this is the case, a three-stage counter-current process might be just sufficient to have 100% scrubbing efficiency for europium.

To test the abovementioned hypothesis, four additional scrubbing tests were planned. In the first two experiments, a loaded organic phase containing 9.3 g/L yttrium and 0.2 g/L europium (obtained after single contact solvent extraction) and two different EG scrub solutions were used: one containing 12.5 g/L yttrium and 1 M LiCl (experiment A) and one containing 12.1 g/L yttrium and 2 M LiCl (experiment B). Besides, for the two other experiments a loaded organic phase with a high yttrium concentration (18.2 g/L) and a concentration of 0.1 g/L europium was generated, similar to the loaded organic obtained after a counter-current process simulation. This loaded organic was scrubbed with both the 1 M and 2 M LiCl scrub solutions as well (experiment C and D respectively). The yttrium and europium concentrations in the scrub raffinate after equilibrium was reached were measured. These data were then used to calculate the concentration of both REEs in the scrubbed organic as well as the scrubbing efficiency, as can be seen in *Table 7.20*.

Table 7.20 Results for the additional scrubbing tests. Scrubbing efficiency (%Sc) and concentrations of Y, Eu in the scrub raffinate and scrubbed organic phase are given for each of the experiments. The concentrations in the scrubbed organic are calculated according to the mass-balance. Phase ratio EG:C923 = 1:3.

Experiment	Scrub raffinate (g/L)		Scrubbed organic (g/L)		%Sc	
	Y	Eu	Y	Eu	Y	Eu
A	9.0	0.71	10.5	0.000	0	100
B	2.4	0.51	12.7	0.033	0	83.7
C	21.9	0.24	15.0	0.000	17.2	100
D	12.1	0.21	18.0	0.002	0.8	96

As expected, no yttrium was scrubbed from the loaded organic with a low yttrium concentration, while scrubbing efficiency is 100% when a scrub feed containing 1 M LiCl was used. For higher LiCl concentrations, less europium was scrubbed, in accordance with the findings in section 7.4 *Influence of lithium chloride concentration*. The results of experiment C and D confirm the findings from the counter-current scrubbing simulation. Indeed, a higher yttrium loading will result in scrubbing of yttrium. The cause of this surprising result still remains unclear. Supersaturation of the loaded organic might be a possible reason why yttrium (and europium) show increased transfer back towards the EG solution.

In accordance with these results, the parameters for the second CCSS experiment were fine-tuned. A two-stage scrubbing procedure was performed. The loaded solvent phase contained 17.3 g/L yttrium and 0.05 g/L europium. The scrub solution was an EG solution with 12.0 g/L yttrium and 2 M LiCl. The results for the representative scrub raffinate are given in *Table 7.21*. Complete scrubbing of europium was attained with the fine-tuned process. A limited amount of yttrium was scrubbed as well. Yet, the rather limited loss of yttrium is not a problem, since the scrub raffinate can be recovered as a feed stream for the extraction stages.

Table 7.21 Results of the two-stage counter-current scrubbing simulation of europium. Scrubbing efficiency (%Sc) and concentrations of Y, Eu in the scrub raffinate and scrubbed organic phase are given for each of the experiments. Phase ratio EG:C923 = 1:3.

Scrub raffinate (g/L)		Scrubbed organic (g/L)		%Sc	
Y	Eu*	Y	Eu*	Y	Eu
12.7	0.37	17.1	0.00	1.4	100

Concentration in loaded organic: [Y] = 17.3 g/L; [Eu] = 0.05 g/L.

*Measurement errors in europium concentrations led to deviating results for scrub raffinate. Standardless tests of the scrubbed loaded organic showed that europium was completely scrubbed.

7.13. Extraction of europium

After the extraction step, for which the parameters have been optimized by bench-scale experiments as described in previous sections, a loaded organic phase rich in yttrium and an ethylene glycol raffinate fraction rich in europium are obtained. The further processing of the former is described in section 7.10 *Scrubbing and stripping experiments*. The processing of the raffinate requires extra extraction steps, since stripping europium directly from the ethylene glycol phase is not possible. The same less polar phase as for the primary extraction of yttrium can be used, which is a solution of 1 M Cyanex 923 plus 10 vol% 1-decanol in GS190 Shell diluent. The concentration of europium in the raffinate is chosen to be about 1.3 g/L (see section 7.14 *Process flow sheet*). The actual concentration of europium in the feed that has been prepared for these experiments was 1.1 g/L. The phase ratio of the europium feed to Cyanex 923 phase was varied, to investigate the extraction efficiency for each phase ratio and to see how many stages are needed for the preferred phase ratio. The results are shown in *Table 7.22*.

Table 7.22 TXRF results of EG raffinate after extraction of europium with C923. The concentration of europium in the ethylene glycol and C923 phase after equilibrium, extraction efficiency (%E) and distribution ratio (D) are given as a function of phase ratio.

Phase ratio (EG:C923)	[Eu] _{EG} , g/L	[Eu] _{C923} , g/L	%E, Eu	D, Eu
1:3	0.1	0.3	87.8	7.19
1:2	0.2	0.4	81.2	4.32
1:1	0.4	0.8	68.2	2.14
2:1	0.6	1.1	50.4	1.02
3:1	0.7	1.4	41.3	0.70

Obviously, the lower the more polar to less polar phase ratio, the more Cyanex 923 available, the higher the extraction efficiency. If a more concentrated solution of europium is targeted, the phase ratios 2:1 and 3:1 should be chosen. However, more stages will be needed to fully extract europium. If the amount of stages is to be minimized, the lower phase ratios 1:3 and 1:2 have to be chosen, since extraction efficiency is already high after a single contact. A phase ratio of 1:1 can be a good trade-off between both. In this case, a McCabe-Thiele plot has been constructed for the 1:1 phase ratio, which indicated that 4 to 5 stages would be necessary to fully extract europium. The fact that more stages are needed again shows that europium is extracted less efficiently compared to yttrium. The loaded organic obtained in this process step should be further treated with an aqueous oxalic acid strip solution, as is discussed in *7.10 Scrubbing and stripping experiments*.

7.14. Process flow sheet

The overall process that has been developed during this master thesis is shown in *Figure 7.12*. Extraction is performed using a non-aqueous system with an ethylene glycol (+ 2 M LiCl) feed solution containing yttrium and europium in concentrations that are representative for fluorescent lamp phosphors (molar ratio yttrium:europium = 100:8). Together with a less polar phase containing 1 M Cyanex 923 plus 10 vol% 1-decanol in GS190 Shell diluent, the three-stage counter-current process results in efficient separation of these two rare earths. A limited amount of yttrium (less than 40 ppm) is still present in the raffinate, so there is an option to extend the process to four stages. The phase ratio is EG:C923 = 1.5:1. Co-extraction of europium is limited (7 – 8%) and can be removed by a two-stage counter-current scrubbing procedure, using an ethylene glycol solution of yttrium (from yttrium product obtained in this process) and LiCl. The scrub raffinate, containing yttrium, europium and 2 M LiCl can be directed back to the extraction feed, after making up for the differences in REE concentration. The scrubbed loaded organic, containing only yttrium, can be stripped several times with an aqueous solution of oxalic acid (1 M) to recover yttrium oxalate, which can be further calcined to yttrium oxide. Temperatures of 800 °C should be sufficient to ensure complete conversion.¹⁴ Subsequently, the regenerated less polar phase can be reused in the extraction stages. Europium from the europium-rich raffinate obtained after the extraction can be recovered after a secondary extraction of the raffinate with Cyanex 923 and stripping of the europium-rich loaded organic with an aqueous solution of oxalic acid. To ensure high purity of europium, the yttrium extraction process should count 4 stages.

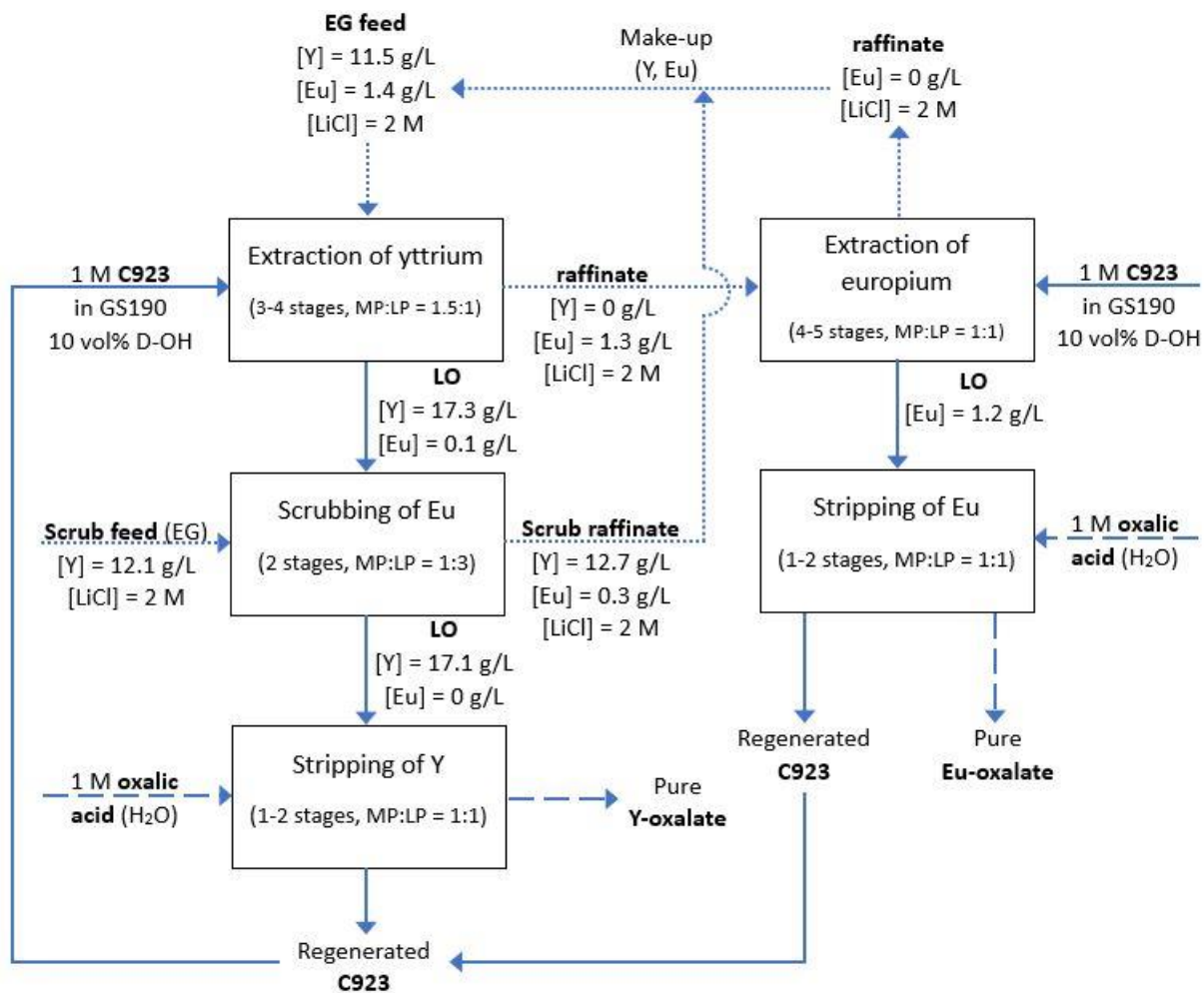


Figure 7.12 Flow sheet for the separation of yttrium and europium from ethylene glycol solution by Cyanex 923 (C923). D-OH = 1-decanol, EG = ethylene glycol, LO = loaded organic, LP = less polar phase, MP = more polar phase.

In conclusion, this process seems to be efficient in separating yttrium and europium, using a limited number of stages and a limited amount of water and chemicals. Overall, the solvometallurgical process has several advantages compared to state-of-the-art hydrometallurgical process. For instance, Tunsu *et al.* used an acidic extractant, Cyanex 572, to separate yttrium (18 g/L) and europium (1 g/L), which were present in a chloride aqueous feed.²⁰ NaOH had to be consumed to adjust the pH of this feed solution prior to extraction. Furthermore, 10 stages were needed for the extraction process, which is 2 to 3 times more compared to the non-aqueous process developed in this master thesis. Finally, the hydrometallurgical process ended up with acidic aqueous solutions, which still had to be treated. In the solvometallurgical approach, most of the streams can be recycled within the process, limiting waste generation, consumption of chemicals and environmental impact.

8. Conclusions and outlook

A non-aqueous solvent extraction process was developed for the separation of yttrium and europium using ethylene glycol (+LiCl) as more polar phase and Cyanex 923 in GS190 Shell diluent as less polar phase. Higher efficiencies and separation factors were found for this approach compared to aqueous extraction under the same conditions. Besides ethylene glycol, also DMSO (+LiCl) seemed to be a promising non-aqueous system. However, this system needs to be studied into more detail. Both propylene glycol and PEG-200 seemed to be not suitable to properly separate yttrium and europium.

After optimization of the parameters (extractant concentration, LiCl concentration, phase ratio, number of stages, *etc.*), counter-current extraction and scrubbing simulations have been used to further fine-tune the conceptual process. These counter-current experiments helped to prove that the developed process is feasible. After full extraction of yttrium using 3 – 4 extraction stages, the co-extracted europium could be removed in 2 scrubbing stages. Both yttrium and europium can be recovered as rare-earth oxalates. However, lab-scale mixer-settler studies still need to be performed, as this will exactly simulate industrial process conditions.

Future investigation is needed to unravel the extraction mechanism for non-aqueous systems and the influence that different feed solvents might have on separation or extraction efficiency of two metals. If the effects of for instance solvent polarity or solvation energy on the extraction are known, targeted improvements and rational design of extraction processes might become more straightforward.

Furthermore, liquid-liquid extraction is just one step in the entire metallurgical process. This emphasizes the need to bridge the gap between leaching and non-aqueous solvent extraction. The leaching step itself can be both aqueous and non-aqueous, and results in mixture of europium and yttrium oxides. Since these oxides do not dissolve in ethylene glycol, mineral acids such as HCl, HNO₃ or H₂SO₄ will have to be used to dissolve the oxides before adding them to the non-aqueous feed solution. Once the effects of the addition of acid to ethylene glycol has been investigated, the developed process can be integrated in a full-scale metallurgical process.

9. References

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