The separation of light lanthanoids through pertraction

T Daniels

orcid.org: 0000-0002-0002-9097-5885

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Supervisor:	Mnr DJ van der Westhuizen
Assistant supervisor:	Dr JT Nel

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PREFACE

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ABSTRACT

The light lanthanoid elements (57-60) are the most common of the f-block elements. These elements are plentiful and upon their discovery, the specified application of individual elements have grown alongside our ability to separate them. The growing demand for these elements is driven by their irreplaceability within modern society. Most noteworthy, by the modern green technologies associated with cerium and neodymium.

It is the occupation of the f-orbitals which separate these elements from the rest. These valence orbitals are shielded by the 5th orbital shell from the environment. This results in unique magnetic- and electronic properties but, by the same grace, these metals exhibit nearly identical chemical behaviours especially within the trivalent cationic state which they all adopt in aqueous media. Therefore, chemically separating them becomes inefficient. The many benefits of pertraction has seen to its rise as the hydrometallurgical separation process of the future. In this light the separation of the light lanthanoid elements through this process is evaluated during this investigation.

Within the light lanthanoid group, it is only cerium which is relatively stable in the tetravalent state and this has become the common starting point within their separation effort. In this study a green alternative to cerium oxidation is presented through hydrogen peroxide (H_2O_2). Initially an efficient, environmentally sound solvent extraction process was identified, followed by the novel liquid-liquid oxidation of cerium(III) to cerium(IV). This is shown through UV/Vis-spectroscopic analysis. The simultaneous optimization of extraction parameters for both oxidized and un-oxidized separation processes illustrates the effect of this species manipulation.

It is shown that within the oxidized system the extraction of cerium is supressed resulting in increased separation efficiency, and ultimately within the pertraction application, the oxidation process results in a decrease in metal transfer rate. In this continuous circulating batch application with a Hollow-Fibre membrane contactor, the mass transfer coefficients for each metal is calculated in order to evaluate pertraction as feasible separation process.

It is shown in this study that the separation of the LLn elements through pertraction is viable at the very least to effectively separate lanthanum and, with the novel oxidation process, also cerium from the valuable neodymium.

Key terms: *light lanthanoid elements, cerium oxidation, hydrogen peroxide, solvent extraction, pertraction*

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1 Introduction

1.1 Prologue

The four elements pertinent to this separation study form part of the Lanthanoid[1] (Ln) group. These fifteen f-block metals ranging from element 57 to 71, show very little chemical distinction, especially between neighbouring elements. This is no more so than when in an aqueous solution where they all typically adopt a trivalent cationic state. Herein lies the crux of this study.

1.1.1 Terminology

The Ln elements are often subdivided into three groups. The nomenclature used, refers to the naturally increasing atomic mass when moving across the group. Assignment of their constituencies however, is often done with regard to applicable chemical differences, or simply to ease differentiation between lighter and heavier elements within discussion.

The most distinct group, and the focus of this study, is called the light Lanthanoid (LLn) elements, i.e. 57 lanthanum (La), 58 cerium (Ce), 59 praseodymium (Pr) and 60 neodymium (Nd). This group's partition from the other Ln elements is due to the radioactive properties of 61 promethium (Pm).[2] All isotopes of Pm have half-lives of less than 20 years, producing isotopes of either Nd or 62 samarium (Sm) through decay.[3-5] The scarcity of natural Pm means that its only real source is nuclear fission. For this reason it is often omitted in discussion of the group.

The remaining ten Ln elements (62 – 71) do not contain any such natural dissimilarities, but are often classified as either Middle or Heavy Ln elements. Although the differences between neighbouring boundary elements are not as bespoke as that created by the "absence" of Pm, the terminology often adds comparative value when working with elements across the entire Ln group.

The common inclusion of 21 scandium (Sc) and 39 yttrium (Y) to the Ln group is due to their similar chemical characteristics and geological congenerism. These inclusions find particular applicability when referring to the group as Rare-Earth (RE) elements within a geological context. As with most discussions regarding the Ln elements, this descriptor forms the genesis of this thesis.

1.1.2 Rare-Earth Elements

1.1.2.1 History

The discovery of Ytterbite ore in Sweden[6; 7] led to the identification of Y by J. Gadolin[8] in the late 18th century. He named the oxide yttria. This discovery was soon followed by the identification of ceria, Ce oxide, by M. H. Klaproth[9], as well as J.J. Berzelius and W. Hisinger[10] in separate studies. Unbeknown to them, both these oxides contained several other Ln elements.

Almost 50 years later, C.G. Mosander[11] succeeded by isolating two substances from within the yttria, which he named erbia and terbia. It took another half century to identify all seven Ln elements contained within Gadolin's yttria by various researchers. These seven elements ranged from 65 terbium (Tb) to 71 lutetium (Lu).

As with yttria, the remaining Ln elements and Sc were identified within ceria. Mosander found that ceria contained La and didymium. As with erbia, didymium contained the remaining Ln elements from Pr through 64 gadolinium (Gd), save Pm. Almost two centuries had passed after the initial discovery of Ytterbite before Pm was ultimately added to the list of Ln elements soon after the Second World War.[12]

The phrase "Rare-Earth" elements originates from their relatively late discovery and subsequent delusion of scarcity. This descriptor has since its inception been proven to be an oxymoron, as the abundance of most of the Ln elements is greater than even those of the longer known platinum group or surrounding metals. [13-15]

1.1.2.2 Economy

Following suit with this misnomerism, the topic of Ln separation has of yet to dissipate since their initial beneficiation. The last two decades have seen a continuous increase in Ln application and more importantly, the use of increasingly purified Ln oxides has gained significant traction. By the end of the previous decade, the growing demand for purified Ln oxides and subsequent foot-hold in world economy has led to a substantial increase in market price and research activity.

In 2010 (published 2011) Du and Graedel[16] studied the ~ 60% increase in global RE production from 1995 to 2007. Considering that ~97% of RE products originated in China alone, this study posed to calculate the mass of Ln oxides residing as "in-use" RE products. Their aim was to identify RE products as a possible future alternative source for Ln oxides through recycling.

Herein they showed that ~85% of the total mass of RE oxides produced, consisted of the LLn elements and as such are the largest contributors to possible recyclable products. Furthermore, the total "in-use" stock at the time was roughly four times that produced in 2007, of which ~31% resided as Nd products. Herein the possibility of LLn recycling as potential offset for a growing supply shortage was elucidated.

By mid-2011, Moss *et al*.[17] reported supply risk predictions regarding critical metals in strategic energy technologies for the European-Joint Research Commission's Institute for Energy and Transport. Supported by annual surveys conducted from 2008 through 2010, wherein Nd was continuously earmarked with "high" supply risk classifications, Moss *et al*. reaffirmed this classification for the years to follow. Their sources included, among others, the United States - Department of Energy and National Resource Council and were based on future wind energy applications predicted up to 2030. Their deductions were supported by the United States Department of Energy [18] later that same year.

Both these studies compiled purified Ln oxide prices from Jan. 2001 to Dec. 2010, and periods of 2011 where possible. The data showed the dramatic increase in all RE oxide prices specifically between 2009 and 2011. This eventuality was due to yearly export quotas being enforced on Chinese RE oxides in order to cope with their own growing demand.

In the year that followed, Massari and Ruberti[19] looked at the irreplaceability of RE elements as strategic market resource. An overview of price fluctuations during the 2011 and early 2012 financial year demonstrated the fragility of these commodities' market value. Due to their singular origin, these prices are especially susceptible to political influences and international trade negotiations. From an economical perspective, the desperate need for continuous diversification and improvement of both supply and recycle processes were highlighted as vital.

By the end of 2012 Jordens *et al*.[20] had reviewed the beneficiation of RE bearing minerals. While identifying a variety of exploitable mineral sources, the focus of their review centred on the three principle source deposits; Bastnasite, Monazite and Xenotime. Apart from a lack of research on other deposit types, these ores were highlighted due to their dominance as principle Ln source and subsequent research activities. After an overview of RE-from-ore beneficiation processes, the study concluded by emphasising the need to develop well-defined processes for other deposits which could be exploited to offset a growing supply shortage.

Binnemans *et al*.[21] reviewed the RE products as potential future recyclables in a publication early in 2013. After an overview of Ln containing products and their expected life cycles, the positive feasibility of RE recycling as future economic stabiliser was concluded. The biggest challenge addressed herein, was the treatment of a wide variety of RE products. These ranged from large permanent magnets used in generating wind energy to smaller components used in electronics. Apart from large magnets which could be re-used directly after disassembly, the bulk of RE-containing products such as optical glass or electronic devices, end in slurries. These contain multiple elements of which the Ln concentrations are often relatively low. The recycling process is similar to the treatment of Ln source ores, after which separation and enrichment of individual species follow. Therefore the study was concluded by expressing the need to advance ore treatment and separation processes as this would also benefit future recycling.

Later that same year Rademaker *et al*.[22] predicted the potential yield from recycled Nd-containing magnets. The study followed Kingsnorth,[23] who demonstrated an expected annual application growth of up to 15% for this, the fastest growing Ln application at the time. Rademaker *et al*. demonstrated, however, that recycling of these products will only be economically feasible by mid- to late 2020s, since as of yet the supply of RE recyclables is too low.

Use of Ln elements is relatively new and novel applications are continuously being developed. Therefore, the market remains unsaturated with regard to most Ln containing products. Apart from the obvious advantage of supplementing primary supply, they ultimately emphasised that recycling of RE products will avoid over-production of LLn elements.

In 2015 Wang *et al*.[24] modelled and predicted RE production in China up to 2050. They concluded that maximum annual RE production would be achieved in 2020. The study culminates in Wang *et al*. indicating the global supply-demand gap which is sure to increase lest other countries, such as Australia and the U.S.A., re/initiate RE production programs.

In January 2016, however, the United States Department of the Interior and Geological Survey's Mineral Commodity Summaries[25] reported a decrease in annual RE production in the U.S.A. for the first time since 2012 but consequently showed an increase in import dependency for the first time during the same period. China's production remained unchanged from the previous year (2014) which left a supply gap that was quickly filled by Australia. The continually increasing prices led to illegal mining in China and the subsequent over-production culminated in a decrease in RE oxide prices by 2015.

The next annual summary,[26] released in January 2017, reported the suspension of RE production in the U.S.A. during 2015 and reported no commercial production for the year that followed. Consequently, another increase to import dependency was reported by the U.S.A. Chinese exports remained unchanged and none of the other countries showed any significant increase in production over the same period. This meant that illegal mining was offset by a growing demand, causing prices to stabilise.

The relative abundance of the LLn elements compared to that of the Middle and Heavy Ln elements is the reason for their substantially lower market price. The advantage, depending on one's viewpoint, is that the cost of LLn elements were the only ones to remain relatively unchanged from 2015 through 2016. From May to June 2017, Nd showed a 10% increase in price as illegalities were brought under control.

Although the growing global demand ensures the future of RE production, it quickly becomes clear that having a single source to satisfy this need is economically concerning. As was observed in 2009-2011, the impact of failing exports from China led to major effects in material price. Furthermore, the above mentioned studies clearly emphasise the global impact a shortage of Ln elements has on several sectors ranging from the hydrometallurgical- and petrochemical industry to renewable energy sectors.

1.1.2.3 Problems

Consideration of these economic impacts has led to a general consensus, briefly mentioned by Sholl and Lively[27], emphasising three aspects where research attention is sorely needed. These envelope the problems which are addressed in this M.Sc. study, and more:

(a) The development and re/initiation of RE production projects for unexploited Ln source minerals. As the global demand for RE products is forecast to continue to grow, it is imperative that global production follows suit. Since China's contribution to the total production is declining, the responsibility and opportunity shift to other countries, such as Brazil, Malaysia and South Africa.

(b) The improvement of current production processes. The hydrometallurgical production and purification of RE oxides are known to generate significant amounts of waste, while coping with large volumes of chemicals. These processes need improvement in both efficiency and environmental impact.

(c) The design and implementation of well-defined recycling processes for Ln containing products to ensure economic stability.

Over the following decade, RE production is sure to diversify in both geographical and geological origin. South Africa is just one of many countries to possess significant deposits ripe for beneficiation.[28]

1.1.2.4 Mineralogy

The need to diversify Ln sources is gaining traction as the production dominance of China continues to decline. As mentioned earlier, the focus of most discussions regarding RE containing ores is on three major minerals currently being exploited.

- Bastnasite is a Ce based fluorocarbonate (FCO_3^{3-}) which contains mostly LLn elements and, to a lesser extent, the Middle Ln elements; Sm through 66 dysprosium (Dy).
- Monazite and Xenotime are Ce and Y based phosphates (PO_4^{3-}), respectively. The former, like Bastnasite, is made up mostly of LLn elements while Xenotime is mined for its predominant heavy Ln disposition.

These mineral types are the main source of RE products because, among them they contain 95% of all earthbound RE elements.[29] Bastnasite consists of up to 75% RE oxides, the highest of the three. Monazite and Xenotime follow with 65% and 61%, respectively[30], and consequently these minerals have received significant research focus over recent years.

There are, however, hundreds more known scattered globally, a handful of which are ready for commercial extraction. It was to these sources that Jordens *et al.* [20] referred while emphasising source diversification. These deposits have variable RE content as well as RE distribution and, as with the three principle sources, are often found as accessory minerals in major deposits of unrelated elements, such as 26 iron (Fe) or 40 zirconium (Zr).

For instance, the earlier discussed Ytterbite ore found in Sweden, later renamed as Gadolinite, consists of Fe -, 4 beryllium (Be) -, 14 silicon (Si) - and Y oxides. Euxenite is a deposit found in the U.S.A. and mined for its high content of 22 titanium (Ti), 41 niobium (Nb) and 73 tantalum (Ta). In addition to these metals, Euxenite also contains significant amounts of Y, Ce, 90 thorium (Th) and 92 uranium (U). This trait is shared with several other minerals such as Uraninite or Samarskite. As Gadolin and others which came later proved, RE minerals always contain many other elements.

The economical attractiveness of such a diverse mineral is obvious but it is important to note the unavoidable beneficiation of RE and other elements. Whether these metals are targeted or not, they will always form one of the product streams when exploiting sources such as these. As was seen in 2015, overproduction can lead to major economic consequences. As a result of how these elements are formed, the LLn are especially susceptible.

In 1970 Cameron[31] reviewed the information on their abundance available at the time and the mechanisms involved in nucleosyntheses. When considering the solar abundance data presented herein, two crucial trends become clear. Simplified, they are:

(1) Lighter elements are more abundant than heavier elements. Lighter elements are formed in the core of a star while heavier elements are formed in supernovae. This speaks to the difference in energy required to form heavier elements during fusion and subsequently, their relative scarcity.

(2) Elements with even atomic numbers are more abundant than their odd atomic numbered neighbours. Odd atomic numbered elements are more likely to gain a neutron due to their increased neutron capture cross section.

Keeping these trends in mind, it is easy to see why ~85% of all Ln products consist of the LLn elements and why the abundance of Nd in the solar system is comparable to that of the lighter La. These tendencies translate almost effortlessly to crustal abundance illustrated in Figure 1-1.

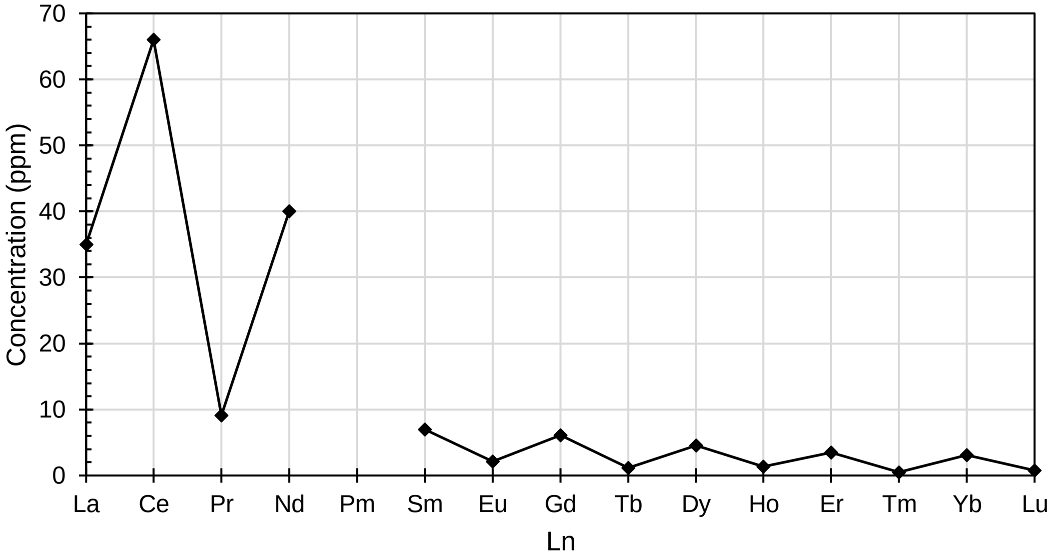

Figure 1-1: The crustal abundance of lanthanoid elements excluding Pm. Adapted from Cotton.[14]

The conservation of these tendencies is also observed when looking at the Ln distribution within the three principle source minerals as is shown in Table 1-1. With the exception of Xenotime, the LLn elements are dominant in all sources including alternative sources such as RE containing desert or beach sand[32]. It is also important to note the musketeeristic comradery i.e. where there is one, there will be all. Their consequent dispersion as a group is explained through natural occurrence while the conservation of elemental distribution within these sources, is attributed to their similar chemistry.

Table 1-1: Lanthanoid distribution in principle RE source minerals. Trace amounts are denoted (-). Adapted from Jordens *et al*.[20]

RE (%)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Monazite	17.5	43.7	5.0	17.5	4.9	0.2	6.0	0.3	0.9	0.1	-	-	0.1	-
Bastnasite	23.0	50.0	6.2	18.5	0.8	0.2	0.7	0.1	0.1	-	-	-	-	-
Xenotime	1.2	3.1	0.5	1.6	1.1	-	3.5	0.9	8.3	2.0	6.4	1.1	6.8	1.0

With regard to the four LLn elements, another important trend is observed, i.e. the intergroup ratio remains relatively unchanged within all sources. Accordingly, the Ce content is always roughly twice that of La and Nd and up to ten times that of Pr depending on the source. Although seldom, exceptions to this statement do exist due to extraneous factors. In RE containing Uraninite deposits for instance, the natural decay of U produces an excess of Nd and Sm. Alternatively, the La concentration herein is almost non-existent as Ce is formed when scattered neutrons are captured.

1.1.2.5 Focus

Considering the RE mineralogy discussed above, the focus of this and most RE studies on the LLn group is justified and can be summarised as follows:

- The LLn elements are present in all RE sources. For the most part, the LLn elements are also the dominant Ln species wherever RE minerals are found.

- Because of their dominance, the beneficiation of the LLn elements cannot be avoided when targeting any RE species.

- The extent of their dominance may vary depending on the specific source, but their intergroup distribution remains relatively unchanged.

For these reasons, research activity relating to this group can be generalised to benefit the exploitation of all source types. The involvement of these elements in all aspects of RE production, implies that improvement in their beneficiation and/or separation will surely mean the same for all Ln species.

1.1.3 Rare-Earth Research

There are three key points forming the objectives of global RE research which merit their reiteration here:

(1) The recyclability of RE containing products.

(2) The needed improvement of post-beneficiation process efficiency.

(3) The environmental impact of RE production.

These three aspects can effectively be reduced to form the core aim of global RE studies. The foundation of this study will analogously follow these constituent objectives.

1.1.3.1 Recyclability

From a chemical consideration at least, it is easily conceivable that the recyclability of any product is completely dependent on its purity. RE compounds are still dominant in global production as opposed to RE oxides and, in the case of the latter, often find application within other products. It is this internal application that brings with it austere mechanical recycling processes and intrinsically defines most Ln recyclables as a mixture of elements. These have variable Ln concentrations depending on the product identity.

Considering that the properties, i.e. use, of the contained Ln product and its efficiency as such, are dependent on the purity of the metal, an elementary need for improvement exists. Simply put: increased purification means a) increased resource distribution efficiency, b) increased product functionality and most importantly c) increased recyclability.

1.1.3.2 Process Efficiency

The efficiency of any given processing step can unambiguously be traced back to the ratio of 'resource amount available' to 'product amount delivered'. This is broadly coined the recovery of said process and directly affect production costs.

1.1.3.3 Environmental Impact

Any improvement in recovery or purity becomes meaningless if the environment wherein they are implemented cannot be sustained. Where possible, all investigatory choices are justified through environmental consideration.

1.1.4 Rare-Earth South-Africa

The Republic of South-Africa boasts several deposits with RE contents high enough to merit development.[33] These deposits are mostly similar to Monazite- or Bastnasite. As was stated in the mineralogical consideration, these resources are often found as accessory minerals which can complicate discrete classification. The beneficiation of these deposits are in some cases already underway,[34] although the Ln elements might not be targeted herein for commercial production. These potential products often end in storage mounds awaiting suitable separation processes.

1.1.4.1 Research Foundation

Under the auspices of the South-African Department of Science and Technology (DST), the Advanced Metals Initiative (AMI) was established in 2003 for the development of sustainable processing technologies. As part of this program, the Nuclear Energy Corporation of South Africa (NECSA) is at the head of South Africa's nuclear metals development. It is here that this purification study finds its place and funding as one of many investigations into RE development, particularly from Monazite.

1.1.4.2 Research Origin

The North-West University is home to the Chemical Resource Beneficiation (CRB) and the Membrane Technology group is one of several groups within this consortium. This group is currently working on the Proof of Feasibility project regarding the application of Pertraction (PX) as an alternative commercial metallurgical separation process. This study takes place within this group and as such will benefit from the advantageous accompaniment of this PX application.

1.2 Aim and Objective

The discussion thus far has laid claim to several aspects of this study summarised here:

- Research motivation is attributed to both global production need and economical dependency.
- The LLn focus is gained from the mineralogical consideration.
- Process focus is specified by the research foundation (NECSA).
- PX application is attributed to the research origin (CRB-Membrane Technology).

These form the construct of this study and the subsequent definition of the research aim.

1.2.1 Aim

The aim of this study is to evaluate the feasible post-beneficiation chemical separation of the LLn elements through pertraction, and with environmental aforethought, attempt to increase separation efficiency.

1.2.2 Objectives

This aim will be achieved through completion of the following objectives:

1. In order to address any problem, it must first be understood. The first objective therefore is completion of an extensive literature overview consisting of:

    a. LLn chemistry. Herein the aim is to identify exploitable chemical differences which could help in the separation effort.

    b. Solvent Extraction (SX) processes. Understanding the role and influence of all chemical factors is key to identifying not only the optimal process parameters, but also the most environmentally friendly option.

    c. PX application. The SX process will be facilitated through a membrane based application. Herein consideration is made of the method employed in order to understand the fundamental kinetic factor influencing this application method and how these are used to evaluate the separation of the LLn elements.

2. Identification of a suitable SX process must be followed by the investigation of influencing factors in order to not only optimize process efficiency but also to fully define the chemical separation process. Any possible chemical modification to effect increased separation is applied within this process.

3. SX process optimization will be followed by its application within a PX setup. Through consideration of the LLn mass flux during the process, the feasible use of PX as separation method for the LLn elements will be qualitatively evaluated.

1.3 Research Hypothesis

1.3.1 Solvent Extraction

The separation of Ln elements through SX is well known and commonly used. However, the chemical similarities of the LLn elements translate to very similar extraction profiles. For this reason commercial purification requires multiple process steps to achieve significant separation. The hypothesis to be investigated involves the chemical manipulation of any LLn species to effect increased purification with increased efficiency.

1.3.2 Pertraction

The use of membranes to facilitate SX has a host of advantages over conventional processes. This facet of investigation will focus on the application of a newly developed SX purification process via a Hollow-Fibre (HF) contactor module. Hereby the separation of these elements through PX will be evaluated and the effect of chemical manipulation on the separation process will be illustrated.

1.4 Research Profile

1.4.1 Chapter 2

In this literature chapter the reader is firstly familiarised with the chemistry of the LLn elements. Understanding the chemical characteristics of this group forms the basis to this investigation. It is within this context that the separation problem is founded and logically forms the investigatory starting point.

The SX process is widely known and applied as a hydrometallurgical separation process. Compilation of known processes is key to avoid redundant work while delivering an in-depth consideration of feasible LLn applications.

PX is relatively novel, but is quickly affirming its place in the future of separation processes. The reader is guided through the fundamentals of this application in order to understand the effect different parameters have and more importantly the numerous accompanying advantages.

1.4.2 Chapter 3

Herein the reader is guided through the materials which were used in this investigation. Furthermore, the methods employed as well as the analytical techniques used during this study are described. Hereby the replication of the results presented hereafter is made possible.

1.4.3 Chapter 4

In this chapter the liquid-liquid equilibrium (LLE) data obtained is used to identify an environmentally sound SX process. Herein the effective novel manipulation of Ce species is shown and exploited to achieve increased separation. Through simultaneous optimization by mono-variant analysis, the induced effect on the SX process is illustrated through comparison.

In this M.Sc. project, the application of PX is at the core. The optimal extraction condition achieved in the LLE study for both affected and unaffected processes will then be applied. The comparative study that follows, allows the evaluation of LLn separation through PX.

1.4.4 Chapter 5

Ultimately, the final step of the scientific process is covered herein. The evaluations of these two investigations will be summarised and discussed and concludes with possible future work.

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CHAPTER 2

CONTENT

2 Literature Study

2.1 Introduction

Completing the first objective in the aim of evaluating the feasible separation of LLn elements through PX, the reader is familiarized with the relevant literature in order to more comprehensively understand the research question asked, as well as the manner by which it is answered. Initially an overview of LLn chemistry is presented in order to understand the origin of the separation problem and further identify fundamental avenues in their chemical manipulation to supplement the separation efforts. Thereafter the fundamentals of the SX process are discussed and described, followed by consideration of the relevant PX application.

2.2 Lanthanoid Chemistry

When the chemistry of the Ln group is considered, it is quickly observed that their distinction as a group is rooted in their occupation of the 4f-orbitals. It is the unique properties of these orbitals which define every aspect of their individuality, from their isolated placement on the periodic table to the subtle differences governing their reactivity. In this section the chemistry of these elements within the context of a SX environment is explored.

2.2.1 Lanthanoid Periodicity

The arrangement of the elements is a conquest as old as their discovery and credit is given to the Russian chemist D.I. Mendeleev for the construct of modern day organization. Based on the publication of "The periodic law of chemical elements." in 1879, later republished by Knight[1], Mendeleev stated that: "when elements are ordered according to their atomic masses, their chemical behaviour is a periodic function of this ordering." This discovery effectively led to the modern day periodic tables and even more noteworthy, the predictability of the properties of yet unknown elements.

The periodic table of elements allows us to qualitatively predict the nature of elements through their relative placement, describing both chemical and physical properties. The Ln elements, do not enjoy the same bespoke placement in modern periodic tables. Together with the Actinoid (Ac) elements, these groups are separated from the rest, and while one explanation would suggest the conservative use of space, an alternative reasoning would rather propose the conservation of periodicity.

It is imaginable that with his passing in 1907, Mendeleev barely saw his final conquest as the slow discovery of the Ln elements was probably the most strenuous test to organizing the elements. Within what seemed to be a seamless periodic system, the frequency suddenly changes in the 6th period, from elements 57 to 71. While neighbouring elements often have similar properties, between the Ln elements the difference in properties becomes particularly small. So much so that by direct comparison of physical properties and trends in the periodic table, *Jensen*[2] suggested that Lu be appointed the first of the d-block elements in the 6th period rather than La, since it fits the periodic frequency better. On the other side of this proverbial wormhole, elements with almost identical properties to the previous period are found, elements such as 72 hafnium (Hf) which has almost twice as many electrons yet the same atomic radii as Zr (155 pm) or Ta which mimics Nb.

In order then to conserve the periodicity of the modern table of elements, the Ln and Ac groups were separated from the main group so that the similarities between elements such as Zr and Hf can easily be seen. A task which would otherwise be much more tedious. Within this consideration the optimal form of the periodic table is still debated, and several alternatives have been suggested in order to better capture the periodicity of all the elements.[3]

The culprits of this change in periodic frequency are the 4f-orbitals. Their increasing stability across the Ln group results in fifteen consecutive elements, each almost indistinguishable from the next. It is herein that their identification problem was founded and to understand the minute chemical difference, a closer look at these orbital occupations is needed.

2.2.2 Lanthanoid Orbital Occupation

For the earlier Ln elements, the 5d orbital subshells are energetically lower than the aforementioned unoccupied 4f-orbitals. This occasion yields the zeroth element in this series, La, which hold no f-electrons ([Xe] $4f^0 5d^1 6s^2$) in its ground state. The next element in line is Ce, and here the 4f-orbitals are sufficiently stabilized by the increased positive nuclear charge to facilitate the first occupation ([Xe] $4f^1 5d^1 6s^2$). Continuing along the group, the f-orbitals are stabilized even more. So much so that the following element, Pr, no longer uses the 5d-orbital and in its stead the 4f-orbital now contain three electrons ([Xe] $4f^3 6s^2$). Nd is the last element in the LLn subgroup, and similar to Pr, its electrons occupy the 6s- and 4f-orbitals only ([Xe] $4f^4 6s^2$).[4]

Apart from La and Ce, there are two other Ln elements which uses the 5d-orbitals in their ground state. As soon as the 4f-orbitals are half- and completely filled the 5d-orbitals once again become energetically viable. Consequently, Gd and Lu each contain one 5d-electron, similar to La and Ce. The remainder of the elements do not, and has configurations similar to that of Pr or Nd.

For this study the trivalent species are the most relevant. The reason being, in the aqueous solutions commonly used in SX, the trivalent ionic state is the most stable.[4] The configurations for these Ln^{3+} species and the ground state configurations can be seen in Table 2-1. By concentrating on these differences, the first foothold can be found to understand the differences between these elements, and by first considering a few similarities, a better understanding of these differences are gained.

Table 2-1: The ground state and trivalent electron configurations of the lanthanoid elements.

Ground State Configuration	$[Xe]\ 4f^{m-1}5d^{1}6s^{2}$														
			$[Xe]\ 4f^{m}6s^{2}$						$[Xe]\ 4f^{m}6s^{2}$						
Ln	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
m	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Trivalent Configuration	$[Xe]\ 4f^{m-1}$														

Friedman *et al.*[5] suggested through approximation of the radial wave function, that the 4f-orbitals are spatially contained within the already filled 5s- and 5p-orbitals. Across the Ln group then, consecutive electrons are added to orbitals inside the 5th orbital shell rather than the "usual" outlying valence orbitals. Furthermore, the containment of the 4f-orbitals within the 5th orbital shell renders them unavailable for interaction with ligand orbitals.

It is within this realization that the economic value of the Ln elements is found which merits some discussion. The protection of the 4f-orbitals by the outlying filled 5s- and 5p-orbitals means that their properties remain largely uninfluenced by the ligands with which they may be found. Hereby specific compound can be tailor made to cater for the environmental requirements of the Ln containing product without compromising its functionality.

For instance, the f-orbitals allows for a large number of unpaired electrons, and so too then a large magnetic moment. As explained by Cotton[4], because these orbitals are protected from the ligands, the usual diminishing effect known as quenching, is not observed here. This can be clearly seen in Figure 2-1, where the observed magnetic moment of $Ln(phen)_2(NO_3)_3$ is compared to the predicted magnetic moment calculated through the Russell-Saunders coupling scheme.

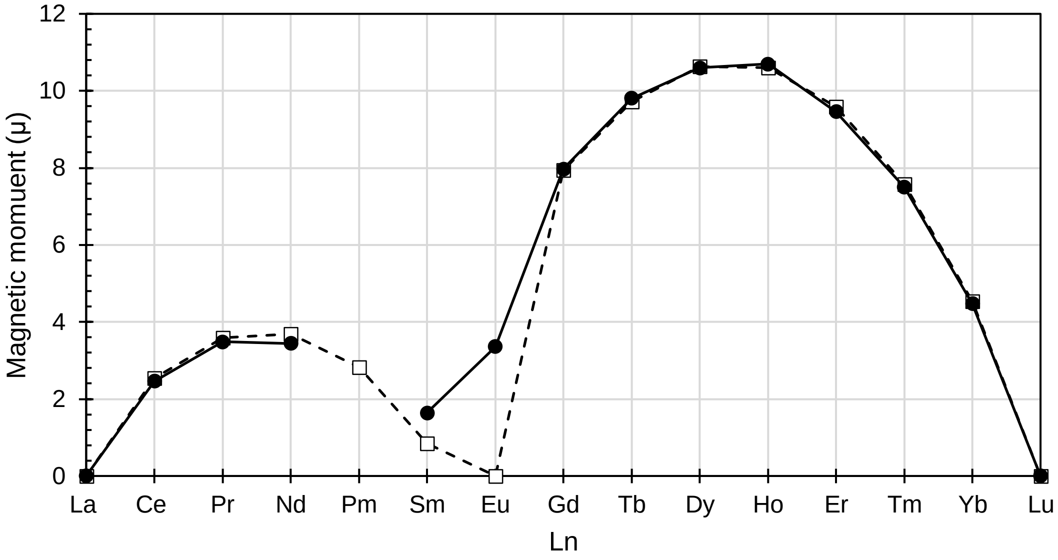

Figure 2-1: The magnetic moment (μ) of the lanthanoid elements observed (–●–) from $Ln(phen)_2(NO_3)_3$, and the calculated (–□–) through LS-coupling.[4]

The only real deviations appear at Sm and 63 europium (Eu) which, according to Cotton, are explained by low-lying excited states. That is why Nd, Dy and 67 holmium (Ho) are often used to produce permanent magnets. Similar to their magnetic properties, the electronic properties of the Ln elements also remain largely unaffected by their environment. It is unsurprising then, that the identification of these elements was made primarily from spectroscopic analysis rather than chemical reactions.[6] The properties of the LLn elements have led to a wide variety of applications and some of these are compiled in Table 2-2.

Irrespective of the various applications made possible by the unique properties of the f-orbitals, their protection does not bode well for the separation effort. This is especially so in the common trivalent cationic state. Once all the outlying 6s and 5d electrons have been removed to form the trivalent species, the attacking ligand is in all cases presented with nearly the same 5th orbital shell with which to interact. Therefore, irrespective of the amount of electrons occupying in 4f-orbitals, the chemical behaviour of these Ln elements is very similar. The only discernible differences stem from the size and therefore charge density of a specific element within this group.

Ellis *et al*.[7] clearly demonstrated the combination of both steric- and coordination energy effects stemming from their size through SX. The affinity of the extractant to the smaller, heavier Ln elements is clearly shown but ultimately because the differences between neighbouring Ln elements are so small, little separation was achieved.

Table 2-2: Applications of some of the LLn elements [[8-17]]

Ln/Sector	La	Ce	Pr	Nd
Ceramics/ Plastics	Colouring, Optics Dental Ceramics, Camera Lenses	Colouring, Polishing, Filter Glass, Goggles, Opacification Agent, Piezoelectric Ceramics	Colouring, Filter Glass, Goggles	Colouring, Filter Glass, Goggles
Emission/ Detection	OLED, Microwave Control, Phosphor Coating, Fluorescent Lights, Microscopic Tracer	Incandescent Lamps, Phosphor Coating, Fluorescent Lights, Carbon-Arc Lights		Lasers, Microwave Control
Magnetics		Permanent Magnets	Permanent Magnets	Permanent Magnets
Metallurgy	Alloys	Corrosion Inhibiter Mischmetal, Alloys	Alloys	Alloys
Electronics	Capacitors, Semiconductor, Data Storage, Batteries	Batteries	Solar Cells, Batteries	Data Storage, Batteries
Catalysis	Photo-catalyst	Fuel cells, Photo-catalyst, Emission Control		

When any chemical reaction is applied to a mixture of neighbouring Ln elements, the product mixture will always be the same, varying only by the slightest of differences in their orbital energies. Chemical separation then becomes a numbers game, repetition of the same mundane process in a cascade fashion until sufficient purities are obtained. Such is the case presented in this study.

2.2.3 Lanthanoid Energetics

It should follow then, that if the chemical and physical differences between the common trivalent ions are too minute, then selectively changing the properties of one of the elements could increase separation efficiency. The options within this endeavour, however, are limited as will be shown herein, and as is the theme of this section, these limitations are enforced within the 4f-orbitals.

In achieving their trivalent state some slight but interesting energy differences arise as consecutive electrons are removed from the ground state during the ionization process. It is herein that the possible deviation from the stable trivalent species is made possible. The dominant trend when observing the ionization energy of these elements (I^n_{Ln}), is governed by two fundamental changes when traversing the Ln group:

(1) The number of protons in the nucleus increases. Therefore the attraction force on valence electrons also increases, and so too the energy required to remove it.

(2) Each subsequent element has one more electron than the previous, balancing the charge of the additional proton in the nucleus. These electrons occupy the 4f-orbitals reducing the effective charge experienced by the 6s and 5d electrons known as shielding [18].

For the most part I^n_{Ln} increases steadily across the group for any given ionization step. This can be clearly seen in the first (I^1_{Ln}) and second (I^2_{Ln}) ionization energies[4] presented in Figures A1 and A2, and can be found in Appendix A. It is no coincidence that the only deviation from the smooth increase of I^1_{Ln} and I^2_{Ln}, occurs with the elements that contain a 5d-electron in their ground states. Through consideration of the effective charge[18] associated with these various electron configurations, these are briefly explained, and herein the natural dissection of the Ln and the LLn subgroup is seen.

Contrary to the dominant trend in I^1_{Ln} and I^2_{Ln}, a decrease in ionization energy is first observed from La to Pr. This is attributed to the increased shielding experienced by the valence 6s-electrons as additional shielding electrons are added to the underlying 4f-orbitals. Moreover, in Pr, the 5d-electron now accompanies the other 4f-electrons in an orbital shell even closer to the [Xe] core. This results in better shielding of the valence electron and the low I^1_{Pr}.

Furthermore, once the first 6s-electron is removed from La and Ce, the remaining 6s-electron is demoted to a 5d-orbital.[19] Although the f and d-orbitals are inherently shielded more by underlying orbital shells, they are no longer shielded by the 5d-electrons with which they now share an orbital shell. So in both cases, I^1_{Ln} and I^2_{Ln} decrease to minima at Pr before the expected trend is adopted.

The second deviation in both I^1_{Ln} and I^2_{Ln} appears when the 4f-orbitals are half filled. The half-filled orbitals are stabilised by the quantum mechanical exchange of electrons with the same spin[20].To maintain this symmetry, Gd contains a 5d-electron rather than an eighth 4f-electron. Its contribution to shielding the 6s-electrons is therefore less resulting in higher than expected values for I^1_{Gd} and I^2_{Gd}.

Lu is the last element where deviation from the norm is observed, although not as neatly as its predecessors. The use of the 5d-orbital by Lu is a result of the already filled 4f-orbitals rather than the fact that the 5d-orbital is more energetically stable than the 4f-orbitals as was previously the case. Consequently, while I^1_{Ln} entails the loss of a paired 6s-electron for all the Ln elements, for Lu it is the lone 5d-electron which is removed first. I^1_{Lu} is therefore much lower and comparable to that of the much lighter Pr. The deviation of I^2_{Lu} from the expected energy shows the difference between removing a lone 6s electron and a paired 6s electron.

The third ionization energies of the Ln elements (I^3_{Ln}) are presented in Figures 2-2, where the natural dissimilarities arising from their different configurations are seen in duplicate. As with the previous ionization steps, it is their individual electron configurations which govern the orbital stability and therefore the ease by which its configuration is changed.

At this point, Eu and 70 ytterbium (Yb) have half-filled ([Xe] $4f^7$) and completely filled ([Xe] $4f^{14}$) 4f-orbitals, respectively. As mentioned earlier, these orbitals are stabilised dramatically by quantum mechanical exchange and departure from these configurations requires vastly more energy. Similarly, the high I^3_{Sm} is a consequence of the same exchange interaction loss[21], while the increased spin angular momentum associated with the loss of the only paired electron explains the higher I^3_{Tm}.

For Tb on the other hand, a combination of the same effects results in a slightly lower energy requirement. According to Huang[22], Tb can possibly have either of the configurational forms. In either case, the removal of this electron happens more readily; the low energy required to remove it from the 5d-position was justified previously, while the removal from a 4f-position is just as undemanding because the symmetry achieved herein dominates the associated angular momentum increase[23].

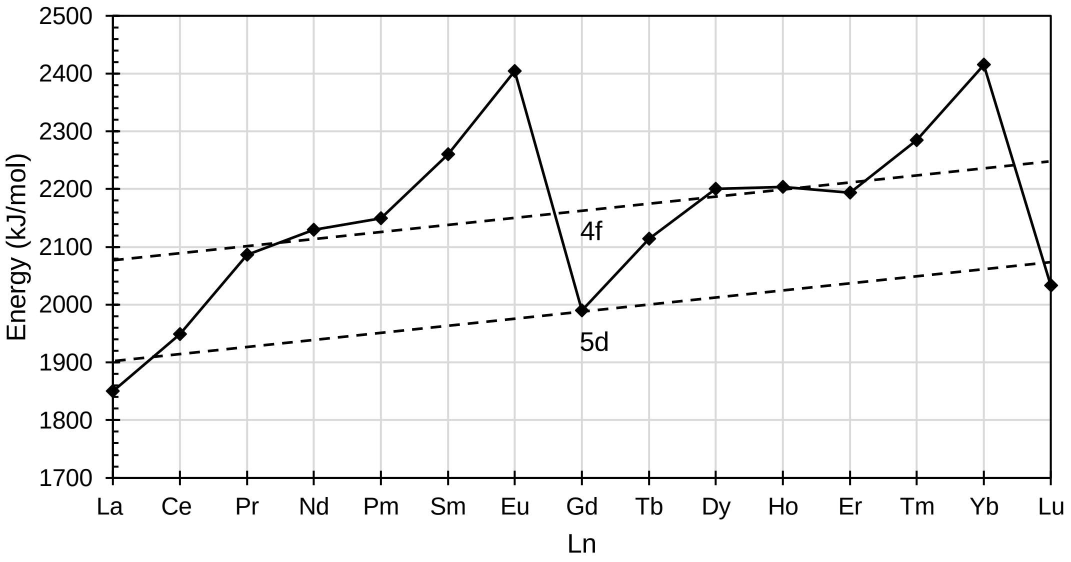

Figure 2-2: **The third ionization (*I^3_{Ln}*) energies of the lanthanoid elements. Adapted from Cotton.[4]**

Within the formation of the Ln^{3+} species the fundamental energies involved in species stability are shown. These are:

- Columbic repulsion energy,
- Exchange energy.

Hereby the interplay between these forces can be seen in the irregularities between Nd and Sm, and again between Dy and 68 erbium (Er). A combination of these effects governs the stability of electron configurations, whether in the ground- or trivalent state. Within this discussion the achievement of the stable trivalent state illuminates the fundamental differences between the Ln elements by considering their inter-atomic energetics. It is these energies which also open the possibility to their selective manipulation and ultimately, within the context of this study, effect tangible separation. As the orbital occupation and the energies therein govern the ionization process, so too does it govern the redox process.

2.2.4 Lanthanoid Redox Chemistry

In principle, selectively changing one of these Ln^{3+} ions comes down to the energetics within the individual orbital occupations. From the previous discussion, the stability of at least some additional species such as Eu^{2+} and Yb^{2+} can easily be predicted from their half and completely filled 4f-orbitals, respectively. It should follow clearly then that the addition of an electron to the 4f-orbitals of these trivalent species, i.e. the trends in reduction energy, will be inverted compared to the third ionization energy. Herein then lies the correlation between the ionization energy and the redox potentials. In Figures 2-3 the reduction potentials of the Ln^{3+} species alongside their third ionization energies are presented.

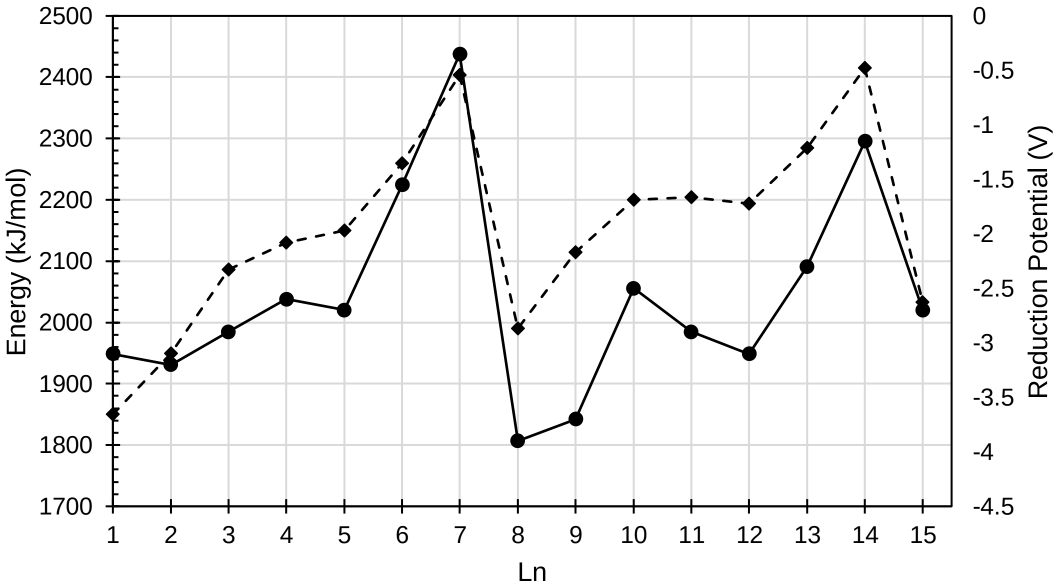

Figure 2-3: The relation between the third ionization (I^3_{Ln}) energies and reduction potential ($Ln^{3+} + e^- \rightarrow Ln^{2+}$) of the lanthanoid elements. (–♦–) ionization energy, adapted from Cotton.[4]; (–•–) calculated reduction potentials adapted from MacDonald *et al*.[24]

It is theoretically conceivable that all divalent species should be accessible given enough energy. It is the stability of these species, however, which drives the inherent tendency to revert back to the more stable trivalent state, resulting in strong reducing agents. For this reason, the only divalent species which were believed isolable for the better part of a century were Sm^{2+}, Eu^{2+} and Yb^{2+}[25] and became known as the classic divalent species. Herein a lively race was afoot to isolate the divalent forms of the remaining Ln elements. It was especially within organometallic chemistry where the reductive chemistry of the Ln elements flourished, and in 2013 MacDonald *et al*.[24] finally added the last four soluble species; Pr^{2+}, Gd^{2+}, Tb^{2+} and Lu^{2+} to the list.

This came more than 50 years after Corbett[26] had established the synthesis of dihalide (LnX_2) solids through high temperature reduction. But, as the energy required to achieve this divalent state is related to the stability of these species, it should be obvious that these elements would have the inherent tendency to revert back to the more stable configuration of the trivalent state[4]. Within this consideration then, the final and most intricate difference between the Ln species is observed.

In 1980 D. A. Johnson[21] attempted to assimilate these differences based on work by E.D. Cater[27] a few years earlier. Herein Johnson concluded that “the chemistry of the Ln elements differs significantly in reaction where the number of 4f-electrons changes, as opposed to those in which they are conserved.” This observation came after the thermodynamic properties of various divalent solids were considered – solids such as the dihalides by Corbett[26] (LnX_2), Cater’s oxides (LnO) and ultimately Johnson’s monosulphides (LnS).

Through observation of their sublimation and formation enthalpies, Cater concluded that this reduction is not in fact so straightforward. Considering the reduction potential of the trivalent species, it should be clear that the addition of an electron is an unfavourable process. It was found that in the solid state, the additional electron occupies a 5d-orbital rather than the 4f-position in all the Ln elements except Sm, Eu and Yb. Only once enough energy has been added to sublimate these solids into the free gaseous state is the expected divalent [Xe] $4f^m$ configuration adopted.

In the solid state then, it is only Sm, Eu and Yb which truly obtain their divalent 4f-configuration ($4f^m$). With the other Ln elements, the number of 4f-electrons remains unchanged from their trivalent state. For La, Ce, Gd and Lu, this divalent ([Xe] $4f^{m-1}5d^1$) configuration is justified within the previous discussions, but for the rest (Pr-Nd; Tb-Tm) this would imply an excited state. Johnson[21] therefore distinguished between his Ln monosulfides as either semi-conductors or metals. However, it was reactions with ammonium halides which were later used to comprehensively explore these occurrences. Hereby Taylor and Carter[28] observed the formation of Eu^{2+} and Sm^{2+} [$Ln^{2+}(X^{1-})_2$] compounds at high temperatures.

Most of the other Ln elements were seen to form salt-like solids [$Ln^{3+}(e^{-1})(X^{1-})_2$] with a delocalised electron promoted from the 4f-orbitals. The ease of this promotion is inherently linked to the stability of the configuration, and therefore the third ionization energy. It is not surprising then that the promotional energies observed by Cater[27], follow the same pattern as in Figure 2-2, and the dashed line imposed hereon would then indicate the different configurations. Those above the 4f-line act as metals ([Xe] $4f^m$), while those below are salts ([Xe] $4f^{m-1}5d^1$). In later studies, Yin *et al.*[29] observed similar promotions from monovalent species (Ln^+) through reactions with 1,3,5 – tri-tert-butyl benzene whereas Koyanagi *et al.*[19] succeeded using inorganic ligands NO_2 and O_2, respectively.

Within the organometallic chemistry then, it is often through use of larger multi-dentate ligands that this excited divalent state is stabilized. Even within the synthesis of the last divalent species by MacDonald et al.[24], the debate still persists as to their true configuration. They concluded from the stability of these various species that the excited state persists even within their soluble, isolable divalent species.

Nonetheless, herein the lanthanide reductive chemistry was established and the reduction of all the Ln^{3+} species have been proven possible[24]. But, while this "forced" chemistry sustains their growing application in organometallic chemistry, for this particular aqueous study it provides little more than understanding their energetics.

Although various footholds in the separation of neighbouring elements, Sm through Tb, could thus far be found, where the LLn are concerned some further exploration is required. Like the third ionization energies is related to the reduction of the Ln^{3+} species, so too the fourth ionization (I^4_{Ln}) energy is related to their oxidation. In Figure 2-4 this correlation is presented.

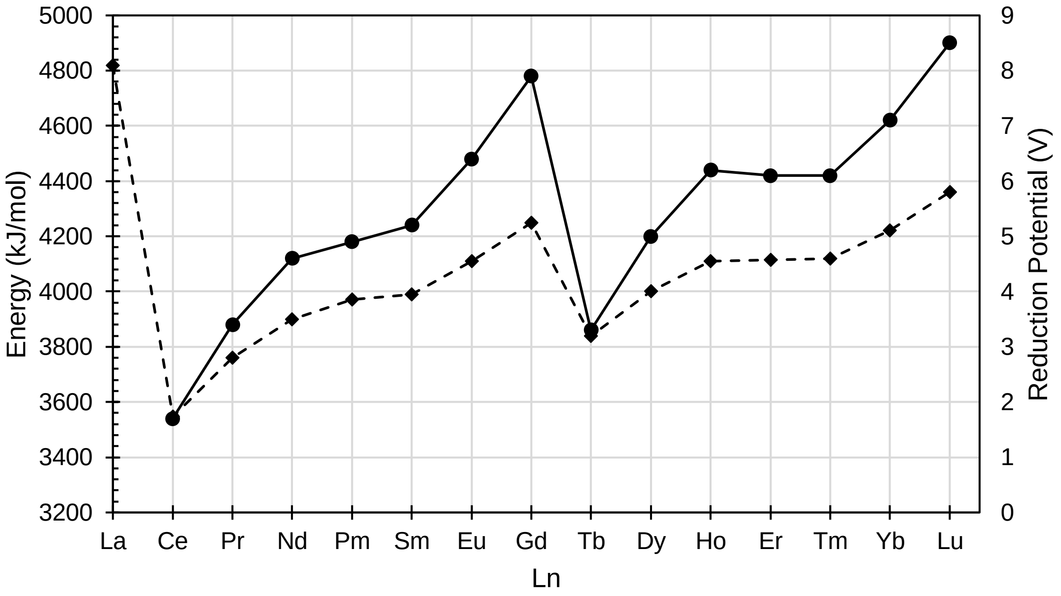

Figure 2-4: The relation between the fourth ionization (I^4_{Ln}) energies and reduction potential ($Ln^{4+} + e^- \rightarrow Ln^{3+}$) of the lanthanoid elements. (–♦–) ionization energy; (–•–) predicted reduction potentials. Adapted from Cotton[4]

The trends observed can be explained in a similar fashion to patterns in the reduction of the trivalent lanthanoid species. Due to the associated tetravalent charge however, the energies in question are vastly greater and the viable possibilities therefore even fewer. But, like Sm, Eu and Yb distinguish themselves in their reduction, so too does Ce, Pr and Tb with their oxidation. Unlike their reduction, however, it is only these three for which oxidation is practically viable.

Within this discussion, the inter-electronic energies arising from the various configurations are used to elucidate the chemistry of the Ln elements. The unique properties of the f-orbitals make for superior magnetic and electronic properties which drives research regarding their beneficiation. Furthermore, it is within these energetics that the selective manipulation of these elements is made possible. This has led to the development of some rich organolanthanide chemistry and ultimately the only viable foothold in this separation effort. Within the aqueous phase containing the LLn^{3+} elements, the only alternative ionic species which is relatively stable and energetically accessible is Ce^{4+}, and herein lies the first step in the separation of the LLn elements.

2.3 Lanthanoid Beneficiation

The commercial production of Ln elements however is more complicated than simply dealing with the intricacies of the LLn separation problem. Apart from having to deal with the specific compositions of the ore in question (Bastnasite, Monazite, Xenotime, etc.), these are commonly found as accessory minerals. Before their specific purification then, the LLn containing ores undergo several treatments of which a short overview is presented in Figure 2-5.

Comminution, as defined in Wills Mineral processing technologies[30], entails the progressive reduction of ore particle sizes (< 300 μm) through crushing and grinding. In the case of Ln ores, a ball mill is commonly used to achieve smaller particle sizes (< 100 μm).[17]

In the second stage, sizing is followed by another physical separation step. Commonly, screens are used to initially separate optimally sized particles. Certain particle sizes are allowed through, while larger particles are retained for further sizing. Particles which are too small for separation through screening are separated in a process called classification wherein separation occurs based on the particle velocity falling through a liquid medium.[30]

After screening, properties such as specific gravity, magnetism, or conductivity are exploited to separate the important minerals from the unwanted material (gangue). The physico-chemical separation by froth flotation requires the addition of a flotation reagent. Other processes such as gravimetric separation are much simpler and require no additives.

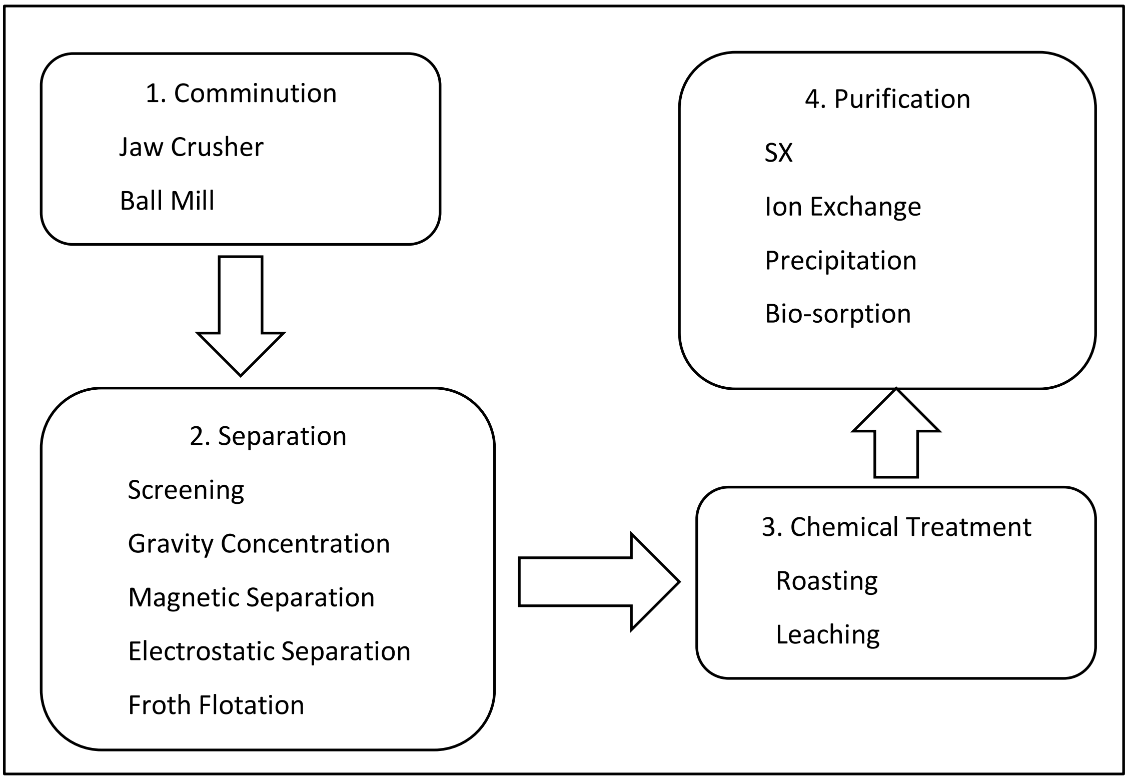

Figure 2-5: **Schematic representation of some common steps in the lanthanoid beneficiation process.**

Combinations of these stage 2 separation methods can be used so that groups of materials are separated in various stages. In beneficiation of Ln containing ores for example, a combination of froth flotation and gravity separation is used, while elsewhere magnetic separation is used alongside gravity separation to the same end.[17] Upon separation of mineral groups and impurities, the mineral slurry undergoes a dewatering phase. Herein the water-to-particle ratio is reduced through use of settlers, thermal dryers or filtration units.

From the concentrated mineral slurry, the elements of value are then freed from their crystal structures. As predicted in the accumulation of ionization energies in the formation of aqueous Ln^{3+} species, this step entails vast amounts of energy both chemical and thermal. A combination of these is often used, such as high temperature roasting in concentrated acids, so that the Ln elements are freed from their ore compound.

The composition of these ores, such as the fluorocarbonate Bastnasite or the phosphates from Monazite, and accessory minerals such as Th and U, impose vastly more intricate processes. Very little mention is made of the various end to end combinations and stages possible depending on the source ore. These were reviewed by Gupta *et al.*, Krishnamurthy *et al*, Kumari *et al*. and more recently Jha *et al*.[31-33; 16] The recycling effort has undergone similar research attention by Binnemans *et al*.[34], Sun *et al*.[35] Jiang *et al*.[36] and with recent focus on the Nd-containing magnets, Kumari *et al*.[37]

While these processes are well beyond the scope of this particular study, the first step in LLn separation is found herein. Upon, or possibly alongside, the removal of the addition elements (Th, U, S, F, etc), the third stage entails the precipitation of these minerals as oxalates, oxides, hydroxides, sodium sulphates or combinations hereof.[38] Hereafter the selective leaching of elements allows certain elemental groups to be removed for further purification. The oxidation of Ce^{3+} is often achieved herein and effectively exploited as such[39]. While selective dissolution of the trivalent species can be used to obtain high purity cerium, the leachate often still contain substantial amounts of the entire mixture. Based on the same solubility difference, the selective precipitation of Ce^{4+} promptly follows as explained by Morais *et al*.[40] and Abreu *et al*.[41] In these processes MnO_4^- is used as oxidizer to achieve the ceric tetravalent state which is co-precipitated in the process.

Throughout the beneficiation of LLn containing ores, numerous physical and chemical processes manage the various aspects accompanying the LLn elements before the final purification of the individual elements. The studies by Abreu[41] and Morais[40] provide a viable separation through selective oxidation of Ce. However, these are often employed for bulk separation, ultimately a mixture of these elements persists as a low-content by-product. For these a more concise purification system is needed.

2.4 Liquid-Liquid Equilibrium

Solvent extraction[42] (SX) is commonly used for the ultimate production step. Herein the target metal(s) are selectively extracted from an aqueous feed solution into an immiscible organic solvent. Hereby, groups of metals can be effectively separated, whether from each other or from unwanted impurities. The various processes employed to separate rare earths by SX were diligently reviewed from both the mineral source by Xie *et al*.[43] and in recycling processes by Yoon *et al*.[44] The SX process can manage large quantities of metal bearing aqueous solutions, but the waste streams generated are often of high acidic concentrations and large in volume. Conscientiously then, to offset these cons, in this study the use of an extraction system which does not require high acidic content is favoured.

A variety of organic compounds have been designed for this purpose and their use in as many process environments is well established.[45; 46] The functional design of these extractants as separators, is based on the coordination energy differences between individual elements or compounds. These define the equilibrium constant or affinity of each element towards a given extractant.

For ease of discussion consider the following general cationic extraction reaction. Herein a cationic metal (M^{n+}) in the aqueous phase coordinates with an organic acid (HA). The formed complex is only miscible in the organic phase, transferring the metal from the aqueous phase to the organic phase. This is accompanied by the transfer of protons to the aqueous phase whereby the charge balance is maintained.

$$M^{n+}{}_{(aq)} + mHA_{(org)} \leftrightarrow MA_{n(org)} + mH^{+}{}_{(aq)} \tag{2.1}$$

Depending on the aqueous matrix, the metal can sometimes be accompanied by an inorganic ligand.[47; 48] Investigations into these mechanisms of extraction can be intricate and a theoretical consideration of some main influences on the kinetics was presented by Geist *et al.* [49], wherein special mention was made of diffusion rates and aqueous matrixes.

Nonetheless, in this instance, the forward extraction reaction is driven by the increased pH of the aqueous feed. Within this context then, the manipulation of the metal cation effectively alters the reaction by which it is extracted and ultimately increases separation either through increased or decreased extraction. To quantify the value of a given extraction step, the following methods of evaluation are defined.

2.4.1 Distribution

The distribution (D_{LLn}) ratio of a metal species is a measure of the extractability within a given SX system. It is defined as the ratio of the metal concentration extracted into the organic phase ($[LLn]_O$) to the concentration of the metal remaining in the post-contact aqueous solution a.k.a. the raffinate ($[LLn]_R$)[42]:

$$D_{LLn} = \frac{[LLn]_O}{[LLn]_R} \tag{2.3}$$

The metal extracted into the organic phase ($[\mathrm{Ln}]_O$) is calculated through mass balance of the aqueous feed ($[LLn]_F$) and raffinate ($[LLn]_R$) so the Equation 2.3 becomes:

$$D_{LLn} = \frac{[LLn]_F - [LLn]_R}{[LLn]_R} \tag{2.4}$$

2.4.2 Separation

The separation factor (β) is a measure of the selectivity exhibited by a SX system towards one of two metals, and is calculated as the ratio of the distribution factors of the two metals[42]. In this study, the target metal is the more valuable Nd. Therefore, the separation factors calculated throughout this study (β_{LLn}) refer to the separation of that metal from Nd and is defined as:

$$\beta_{LLn} = \frac{D_{Nd}}{D_{LLn}} \tag{2.5}$$

2.4.3 Cerium Oxidation

In studies such as that by Singh *et al.* [50], where the extraction performance of various carboxylic acids was evaluated, or that of Lu and Liao[51], wherein a newly developed calix[4]arene was compared to its predecessors, the effect of the specific extractant was shown to have a definite effect. Within the context of separating neighbouring Ln elements however, it could be deemed superfluous since their inseparability persists.

Gupta *et al*. [52] focused on the effect of different acidic media (H_2SO_4, HNO_3, HCl and H_3PO_4) and the concentration thereof during extraction with a mixture of trialkyl phosphine oxides commonly known as Cyanex 923. Once again the effect of these various acids can be seen and while their investigation illuminated possible ways to separate say the LLn from the heavy Ln elements, the separation between neighbouring elements remains largely unaffected. To a similar result, the influence of various organic diluents was tested by El-Nadi[53] also using Cyanex 923.

The combination of two compounds often yields more extraction than the sum of its part. This is coined synergistic extraction.[42] This effect was clearly demonstrated by Sahu and Mishra[54] through observing the extraction of Ce by Cyanex 923, tri-n-octyl phosphine oxide (Cyanex 921) and a mixture of both. El-Nadi[55] showed the same effect using the same extraction system but with La and Nd. Quinn *et al*.[56] investigated the same effect during extraction of neighbouring elements Ce, Pr, Nd and Sm, as well as most of the heavier Ln elements. They illustrated clearly how the mixture of extractants effectively changes the extraction behaviour compared to the individual extractants. What also comes to light, however, is that the same effect is observed between neighbouring elements to relatively the same extent. Piled hereon are studies on the effect of temperature[57] and diluent[58] on various synergistic extraction systems.

As these studies show, there are any number of variables which could be effectively altered to manipulate the extraction performance of a given system, and while the description of these variables may be pertinent to the design and development of any separation process, their contribution to increase separation efficiency is often negligible. Luckily, the Ln elements are no strangers to this purification process and no less so is the incorporation of Ce oxidation.

In 1949 Warf[59] addressed the strong oxidizing properties of Ce^{4+} by observing the extraction of Ce^{4+} by tributyl phosphate (TBP). Oxidation was achieved through electrical oxidation with bromates in high nitric acid solutions. Herein the longevity of the Ce(IV) species within the phosphorous extractant complex was highlighted and feasible extractability was concluded. In 1961, Butler and Ketchen[60] examined the separation of Ce and Y from Pm and Eu in acidic nitric acid media using di-(2-ethyl hexyl) phosphoric acid. The oxidation of Ce^{3+} with $KMnO_4$, increased separation. The majority of this study however covered the effects of the radioactive fission by-products.

These earlier studies show the extractability of the Ce^{4+} species, and in doing so, various oxidation techniques had to be employed both electrical and chemical. As was mentioned earlier in Chapter 2.3: Lanthanoid Beneficiation, the oxidation of Ce^{3+} is of late also often achieved in stages preceding the purification step. However, like the oxidation of Warf[59] or Butler and Ketchen[60], high acidic concentrations are also required to achieve and maintain the tetravalent species. Preston[61] clearly showed the dependence of the Ce^{4+} species stability on the concentration of nitric acid used in the dissolution of CeO_2.

The latest in a series of similar individual studies found during this literature investigation, was published in late 2016.[62] Herein Formiga and de Morais evaluated various oxidizing agents within the conventional

SX environments and effectively encompassed current liquid oxidation methods. As with this M.Sc. project, they focused on the separation possibilities using liquid-liquid separation and forego separation of cerium through precipitation because these often require additional purification for both resulting phases. Ultimately they concluded the feasible selective extraction and consequent purification of cerium through oxidation. In this study we pose to build on these foregoing studies through the introduction of a greener alternative to cerium oxidation.

Hydrogen peroxide (H_2O_2) is known for its functional malleability and is used in both oxidation and reduction of different cerium species. As early as 1963, Czapski *et al*.[63] investigated the kinetics of Ce(IV) reduction with H_2O_2 and H_2O. Sworski *et al*.[64] followed in 1971 by investigating the influence of acidity. Ultimately in 2006 Yu *et al.*[65] explained the phase stability of Ce species in aqueous solutions containing O_2 and H_2O_2 as oxidizers. Herein it is shown that at high acidic conditions, H_2O_2 reduces Ce(IV) to Ce(III) and conversely, oxidation from Ce(III) to Ce(IV) is achieved within near basic conditions. The latter is used during coating of cerium as corrosion inhibiter for various metals.[66]

While the exact mechanism by which this oxidation is achieved is not of importance to this study, the focus is rather on the advantages posed by its use. Not only is H_2O_2 capable of achieving the required species manipulation of Ce, it does so without generating by-products that would otherwise contaminate the stream. Therefore, the post-process treatment of chemical leftovers is not necessary as is the case with conventional oxidizers such as $AgNO_3$, $KMnO_4$ $(NH_4)_2S_2O_8$, $Na_2S_2O_8$ and $K_2S_2O_8$ used by Formiga and de Morais[62] or NH_4NO_3 and $NaBrO_3$ by El-Nadi[67] and El-Hefni[68], respectively. Moreover, it negates the need for highly acidic solutions within this process.

The premise suggested hereby informs the novelty of this study, which is to investigate the feasibility of H_2O_2 as a pre-oxidizing agent in the liquid-liquid separation of the LLn elements. Within this pursuit is the simplistic aim of observing the difference in extraction between an extraction system which has undergone oxidation with H_2O_2, and one that has not.

2.5 Pertraction

The overview of LLn separation through liquid-liquid extraction presented thus far focused on the various parameters involved within the purification process. These are largely chemical although several statistical factors can have a substantial effect. While continuous research into these variables sustains the chemical optimization, the physical application of this process is also of importance. In this section, a membrane module will be used to facilitate the separation process. i.e. PX.

In SX, the aqueous and organic phases have to be in contact regardless of the application, whether through columns, mixer-settler or membrane based. Herein then the intrinsic need to maximize the interfacial area between these phases exist. The use of a membrane to bring the liquid phases into contact has gained significant traction through achieving exactly this.[69]

There are several other advantages in using membrane contactors as opposed to conventional methods. Some of these merit reiteration here.

(a) Because the phases are separated by the membrane, problems arising within conventional applications, such as emulsification are effectively negated. For the same reason, density differences between the phases are no longer a requirement.

(b) The organic diluents which are often used are highly volatile. By enclosure within the PX system, the risk of using these diluents is minimized. Furthermore, the contactors contain no moving part making for an overall more manageable system.

(c) Design parameters are simpler than conventional methods leading to simpler scale-up methods and due to the known interfacial area, the performance is also easier to predict.

Rout and Sanrangi[70] compared SX and PX with extraction systems wherein only Ce was present, and observed the increased efficiency of the PX application. A comprehensive overview of this application was published by Gabelman and Hwang[71], and more relevantly an overview of various strategies pertaining to the separation of RE elements using membranes was published by Chen *et al*.[72]

Upon these justifications and studies, this study concludes with the PX application and centres on the effects observed through chemical manipulation. It should be noted that it is not within the scope of this study to design the PX process for application purposes but only to evaluate the feasible use thereof as separation method for the LLn elements. Furthermore, from the studies mentioned in the previous paragraph, it is clear that various methods of application can be applied, and that each requires due consideration.

In the membrane module to be used in this study, schematically represented in Figure 2-6, threads of porous HF tubes are suspended between inlets containing one of two liquid phases. The other liquid phase is contained within the casing surrounding these HF tubes. Advantageously then, the liquid phases are separated by the membrane and the interfacial area is created at the opening of the pores in the membrane.

As the efficiency of SX step can be evaluated thermodynamically by the distribution ratio (D_{LLn}) and separation factors (β_{LLn}), so too the efficiency of a pertraction setup is measured by the kinetic rate of transfer between the two phases, specifically the difference in transfer rate between two elements. The rate of transfer, or flux, is dependent on the various rate determining steps (resistances) pertaining to the specific transfer from one phase to the other. What follows is a comprehensive discussion of these factors based on the specific method of application presented in Figure 2-6A.

2.5.1 Limitation and Assumptions

In this study a hydrophobic membrane will be used which implies that the HF tubes are wetted by the organic phase penetrating the pores of the membrane (Figure 2-6B). A slight overpressure ($P_{Aq} \sim 50kPa$) was maintained on the aqueous side, high enough so the organic filled pores would not drain into the aqueous shell side but low enough as not to displace the organic phase from the pores (breakthrough). According to Yun *et al.*[73], the extraction reaction occurs at the phase interface as is indicated in Figure 2-6C.

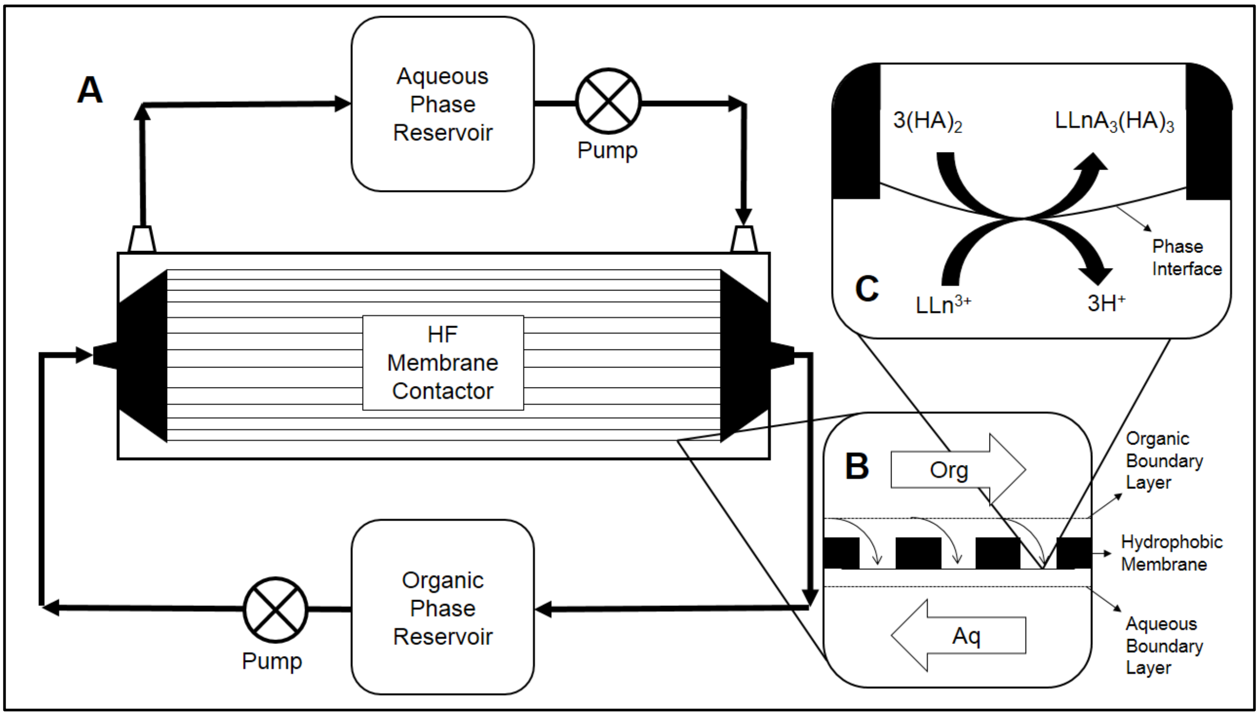

Figure 2-6: Schematic representation of the counter-current circulating batch pertraction.

In efficient extraction processes which are logically aimed for, the forward extraction reaction is strongly favoured resulting in large distribution coefficients (D_{LLn}). Through this favoured extraction reaction, a discontinuation of the concentration profiles occurs in both phases near the membrane. That is, the concentration gradients, which drive the diffusion rates in either phase, are represented by the respective phase boundary layers. Several steps then govern the rate by which the metal species are transferred from the aqueous to the organic phase:

(i) The rate by which the metal ion migrates across the aqueous boundary layer to the phase interface.

(ii) The rate by which the extractant migrates across the organic boundary layer to the membrane.

(iii) The rate by which the extractant moves through the membrane to the phase interface.

(iv) The extraction reaction rate.

(v) The rate by which the coordinated complex moves back through the pores.

(vi) The rate by which the coordinated complex migrates across the organic boundary layer.

Gabelman *et al.*[71] explained that in systems with high D_{LLn}, step 4 is almost instantaneous compared to the other steps and can be neglected. Also, the counter-current application insures that the extractant was always in excess relative to the metal concentration at any point during the experiment. Therefore, it can be further assumed that by the time a metal species arrives at the phase interface, an extractant with which to coordinate, will already be present. Therefore, the resistance from steps 2 and 3 is also insignificant. Furthermore, in a high D_{LLn} system, steps 4 and 5 can be assumed negligible due to the obvious affinity of the coordinated complex to the organic diluent.[71] As a result, within this pertraction setup, the rate determining step and the driving force behind the entire process, is most likely the aqueous metal concentration gradient. Calculations regarding the mass transfer rate were therefore done regarding this phase only.

There are a few further assumptions which merit mentioning here: [71; 74]

- Isothermal and steady state conditions are applicable.
- Extraction equilibrium is achieved at the phase interface.
- The contactor and its constituent fibres are uniform in pore size and wetting characteristics.
- The shape of the phase interface does not influence the mass transfer rate.
- The membrane is completely filled by the organic phase.

2.5.2 Theoretical Consideration

Using fixed volumes of the respective phases the experimental approach (Chapter 3), the concentration integers ($[LLn]$ $(\frac{mol}{l})$) can be directly converted to mass through fundamental calculations ($LLn\ (mol) = [LLn] \times 1l$). To further ease notation, cerium (Ce) will be used as LLn representative throughout this consideration.

As explained by Chen *et al.*[75], a single stage process such as this suffers from equilibrium limitations, i.e. the contactor is often too short for extraction equilibrium to be achieved within a single pass. This is overcome through the circulating batch application or otherwise, by coupling contactors in series. In effect then, the length of the contactor is increased to such an extent that the extraction equilibrium can be achieved (Figure 2-7) and represents a single process stage for this specific membrane contactor.

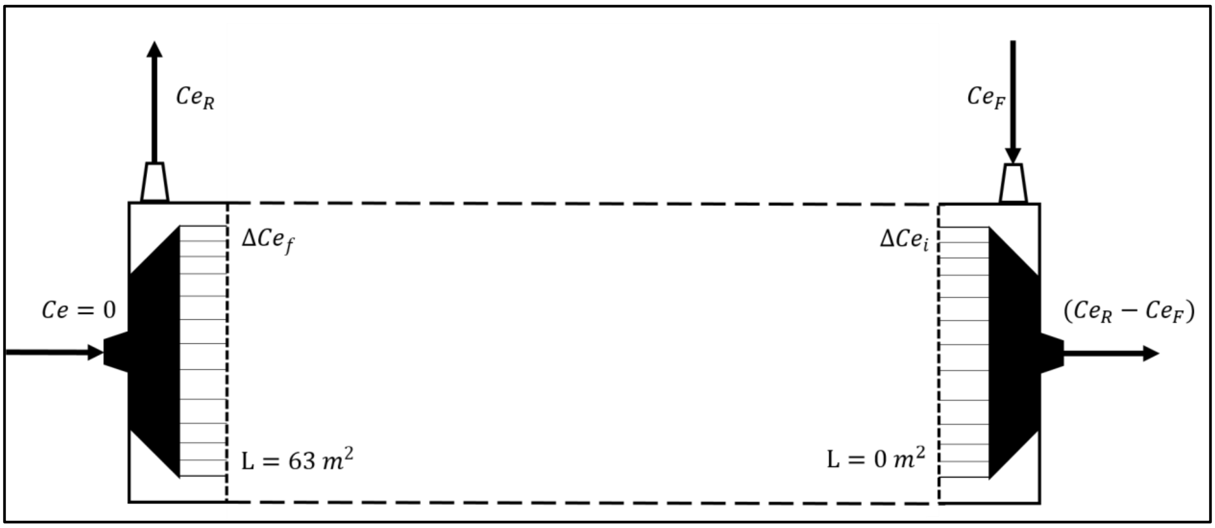

Figure 2-7: **Theoretical representation of continuous batch application through a single contactor.**

Effectively, the area (L) of contactor used, is related to the time (t) of circulation and can be determined from the aqueous flow rate ($\tilde{v}_{Aq}$) and known interfacial area (α = 1.4 m^2) per contactor:

$$L\ (m^2) = \tilde{v}_{Aq} \times t \times \alpha \tag{2.5}$$

Similar to the distribution coefficient defined in the LLE study, the single stage distribution coefficient (D_{Ce}) was determined through mass balance as the ratio of mass extracted into the organic phase ($Ce_R - Ce_F$) over the mass remaining in the aqueous raffinate (Ce_R).

$$D_{Ce} = \frac{(Ce_R - Ce_F)}{Ce_R} \tag{2.6}$$

Similarly, the single stage recovery (X_{Ce}) is the ratio of the same mass extracted over the mass initially available (Ce_F).

$$X_{Ce} = \frac{(Ce_R - Ce_F)}{Ce_F} \tag{2.7}$$

Assuming the organic phase contains no metal species at the onset ($t = 0$), the aqueous concentration gradients at the beginning (ΔCe_i) and end (ΔCe_f) of the stage can be determined through the following equations.

$$\Delta Ce_i = D_{Ce} \times Ce_F \tag{2.8}$$

$$\Delta Ce_f = (D_{Ce} + 1) \times Ce_R - Ce_F \tag{2.9}$$

The average concentration gradient over the entire stage is then determined by[71]:

$$\Delta Ce_{Ave} = \frac{(\Delta Ce_f - \Delta Ce_i)}{\ln(\frac{\Delta Ce_f}{\Delta Ce_i})} \tag{2.10}$$

Using Equations 2.6 - 2.9, Equation 2.10 can be reduced to:

$$\Delta Ce_{Ave} = \frac{[-D_{Ce} \times (Ce_F - Ce_R)\,]}{\ln[\,1 - X(1 + \frac{1}{D_{Ce}})]} \tag{2.11}$$

Using the flux equation[76],

$$Q_{Ce} = \alpha \Delta Ce_{Ave}\, k_{Ce} \tag{2.12}$$

the average mass transfer coefficient of Ce (k_{Ce}) (m/s) can be calculated through the mass transfer rate ($Q = \frac{d(Ce_F - Ce_R)}{dt}$) (mol/s). The same can be done for the remaining LLn metals (La, Pr and Nd), and a combination of these average mass transfer coefficient (k_{LLn}) constitute the overall mass transfer coefficient (k_{ov}) for this specific system. Hereby the transfer rate of specific elements in optimal extraction conditions are quantified and the effect of Ce oxidation can also be evaluated through comparison.

2.6 Conclusion

In this chapter limitations imposed on the separation of the LLn elements are discussed through consideration of the Ln chemistry. Although the unique properties of the f-orbitals make for some interesting occurrences, they limit the possibilities within their manipulation and more so the selectivity thereof. Herein we identify Ce as the only LLn element for which selective oxidation can be achieved relatively easily. Furthermore, the longevity of this species within the aqueous phase makes for its obvious candidacy.

The purification of the LLn elements has been extensively researched and within the SX context the incorporation of Ce oxidation is well known. Whether for better or worse, the oxidation invariably changes the mechanism by which this species is extracted. In a novel attempt, H_2O_2 will be used as oxidizer during this step. The justification hereof is grounded within the environmental consideration of possible oxidation techniques.

The evaluation of feasible LLn separation is posed within the context of PX and is ultimately the goal of this thesis. Hereby the numerous advantages associated by its use are exploited. By application within the same PX system, the effect of Ce pre-oxidation within the liquid-liquid equilibrium can also be used herein in an attempt to effect increased separation.

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CHAPTER 3

CONTENT

3 Materials and Methods

3.1 Introduction

The definitive test in the pursuit of the research aim, would surely pertain the physical application of a working separation process to a suitable PX setup. This process is defined within the SX context and logically, this study originates from this basis and progresses towards the application using a HF membrane contactor. Hereby the pertractibility of the LLn metals was evaluated. Within this chapter then, the materials used and methods employed to this end are iteratively and chronologically presented and discussed.

3.2 Materials

Stemming from the immiscibility of the two liquid phases involved in this study, the chemical materials used are divided into organic and aqueous phase materials, respectively.

3.2.1 Organic Phase Materials

The commercial extractants presented in Table 3-1 were used in preparation of organic phase solutions through appropriate dilution in Kerosene (UN1223) from Sigma-Aldrich (Pty) Ltd. Octan-1-ol (≥95%, 5wt%) from Fisher Scientific was added as a modifier to prevent emulsification and promote phase separation. All organic phase materials were used without further purification.

Table 3-1: Extractants used in preparation of organic solutions.

Abbreviation	Name		Assay	Supplier
	Commercial	**Scientific**		
		Amine Extractants		
Alm336	Alamine®336	Tri-C8-C10-alkyl amine		Cognis Corporation
Alq336	Aliquat®336	Tri-octyl-methyl ammonium chloride		Sigma- Aldrich (Pty) Ltd
UN2280	Uniquat™2280	N,N-Didecyl-N,N-dimethyl ammonium chloride	80%	HexaChem
		Phosphorous Extractants		
TBP	TBP	Tributyl phosphate	97%	Sigma-Aldrich (Pty) Ltd.

D2	D2EHPA	Bis(2-ethylhexyl) phosphate	≥95%	Merck Chemicals (Pty) Ltd.
Io801	Ionquest801	Mono (2-ethylhexyl) ester phosphoric acid	>95%	Rhonia Inc.
TOPO	TOPO	Tri-octyl phosphine oxide	90%	Sigma-Aldrich (Pty) Ltd.
Cy923	Cyanex®923	Tri-C8-C10-alkyl phosphine oxide		Cytec Industries Inc.
		Other Extractants		
MIBK	MIBK	4-Methyl-2-pentanone	>99.5%	Sigma-Aldrich (Pty) Ltd.
LIX	LIX®-84IC	1-(2-Hydroxy-5-tert-nonylphenyl)ethan-1-one oxime	60< wt.% >70	BASF South-Africa (Pty) Ltd.

3.2.2 Aqueous Phase Chemicals

The materials used in the preparation of the aqueous feed solutions are presented in Table 3-2.

Table 3-2: Materials used in preparation of aqueous feed solutions.

Formula	Name	Use	Assay	Supplier
		Acids		
H_2SO_4	Sulphuric Acid	Acid matrix preparation, pH control, phosphate leachate	98%	Merck Chemicals (Pty) Ltd.
HNO_3	Nitric Acid		55%	
HCl	Hydrochloric Acid		32%	
		Feed Solution Modifiers		
NaOH	Sodium Hydroxide	pH adjustment	99%	Rochelle Chemicals
Na_2SO_4	Sodium Sulphate	Anionic Matrix Control	>99%	
KCl	Potassium Chloride		>99.5%	Labchem (Pty) Ltd.
H_2O_2	Hydrogen Peroxide	Oxidizing Agent	30%	
		Light Lanthanoid Salts		

$LaPO_4.xH_2O$	Lanthanum Phosphate	Phosphate Feed Preparations	99%	Alfa Aesar.
$CePO_4$	Cerium Phosphate		99%	
Pr_6O_{11}	Praseodymium Oxide		99.9%	British Drug Houses (BDH) Ltd.
Nd_2O_3	Neodymium Oxide		99.999%	Cerac Inc.
		Light Lanthanoid Solutions		
La_2O_3,	Lanthanum Oxide	Oxide Feed Preparations	99.999% (5% HNO_3 matrix)	De Bruyns Spectroscopic Solutions (Ultraspec)
$Ce(NO_3)_2.H_2O$	Cerium Nitrate			
Pr_6O_{11}	Praseodymium Oxide			
Nd_2O_3	Neodymium Oxide			

3.3 Method

3.3.1 Apparatus

The aqueous metal concentrations were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The instrument used was the Agilent 5110 by Agilent Technologies. The calibration standards used herein were certified reference material (CRM) solutions obtained from De Bruyns Spectroscopic Solutions (Ultraspec). An Eppendorf Multipette® Xstream was used for all solution and sample preparations. A Metrohm 744 was used for pH measurement. A Specord® s600 UV/Vis spectrophotometer (measurements range: 200 - 1 000 nm) from AnalyticJena was used for spectroscopic analysis. Herein a Helma® cuvette of Suprasil Quartz was employed with a 10 mm path length. For the PX study a 1.4 m^2 Liqui-Cel® XF membrane contactor was acquired from 3M, a division of Membrana™.

3.3.2 Cerium Oxidation

The oxidation of Ce was analysed within the UV/Vis light range serving solely as qualitative support to ensure maximum formation of Ce(IV) species. Hereby then the un-oxidized LLn(III)-system and the oxidized LLn(IV)-system are distinguished. This optimization process was analysed through the following consideration:

The measured absorbance (A) of a sample at a specific wavelength (nm), is defined as the logarithm of the ratio of intensity of the incident radiation on the sample (P_0), divided by the intensity of the radiation transmitted by the sample (*P*), and is therefore without units.[1] According to the Beer-Lambert Law, (*A*) is related to (*b*), the path length of absorbance (cm) and (*c*) the molar concentration of the absorbing species (mol/L) through (*ε*), the molar extinction coefficient (L/mol.cm).

$$\mathrm{A} = \log\left(\frac{P_0}{P}\right) = (\varepsilon)(\mathrm{b})(\mathrm{c}) \tag{3.1}$$

In multi-element feed solutions, at any specific wavelength, the total absorbance observed is the sum of absorbance of the individual components.[2] From Equation 3.1, the absorbance of the un-oxidized LLn(III)-system becomes;

$$\mathrm{A}_{\mathrm{LLn(III)}} = \sum(\varepsilon_{LLn(III)})(\mathrm{b})([\mathrm{LLn(III)}]) \tag{3.2}$$

The same justification for a oxidized LLn(IV)-system yields,

$$\mathrm{A}_{\mathrm{LLn(IV)}} = (\varepsilon_{Ce(IV)})(\mathrm{b})([\mathrm{Ce(IV)}]) + \sum(\varepsilon_{LLn(III)})(\mathrm{b})([\mathrm{LLn(III)}]) \tag{3.3}$$

Calculating the difference in system absorbance (∆A)

$$\Delta\mathrm{A} = A_{LLn(IV)} - A_{LLn(III)} \tag{3.4}$$

$$\Delta\mathrm{A} = (\varepsilon_{\mathrm{Ce(IV)}})(\mathrm{b})([\mathrm{Ce(IV)}]) - (\varepsilon_{\mathrm{Ce(III)}})(\mathrm{b})([\mathrm{Ce(III)}]) \tag{3.5}$$

From Equation 3.5 it follows that the formation of Ce(IV) species is indicated through the positive change in absorbance while the decrease in Ce(III) species is shown by the negative change, granted respective wavelengths of absorbance for these species. Assuming adherence to the Beer-Lambert law,[3] at fixed total Ce concentration, this species transformation can hereby be tracked.

Note that this method is used solely to maximize the increasing [Ce(IV)] through variation of [OH^-] and [H_2O_2] rather than making further explicit deductions with regard to specific oxidation species concentrations. The effect of this proven oxidation was subsequently studied within the LLE and PX studies.

3.3.3 Liquid-Liquid Equilibrium

The SX equilibrium data presented in this section of the study was generated using standard batch shake-out tests. Herein equal volumes of freshly prepared aqueous and organic solutions ($\frac{V_{Aq}}{V_{Org}} = 1$) were placed in a single container. The mixture was then placed in a shaking incubator at standard temperature and pressure, and shaken at 200 rev/min for one hour.

The liquid barrier between the organic and aqueous phases was therefore minimized for sufficient time to ensure extraction equilibrium was achieved. Hereafter the mixture was transferred to a separation funnel and the phases were allowed to separate. The prepared aqueous feed and resulting raffinate samples were analysed using ICP to determine the metal concentrations. Hereby the extraction of these metals could be observed for a fixed set of extraction parameters.

3.3.4 Pertraction

The data presented in this section of the study was generated using circulating batch PX (Figure 2-6A). Herein equal volumes ($\frac{V_{Aq}}{V_{Org}} = 1$) of freshly prepared aqueous and organic solutions ($V = 0.001\, m^3$), as optimized in the LLE study, were allowed to equilibrate by counter-current circulation through the HF membrane contactor. The organic solution was pumped through the HF tubes (Lumin), while the aqueous solution was pumped though the outside casing (Shell) using positive displacement gear pumps. This was done at constant and equal flow-rates ($\tilde{v} = 5 \times 10^{-6}\ \frac{m^3}{s}$) for both phases ($\frac{\tilde{v}_{Aq}}{\tilde{v}_{Org}} = 1$), over a period ($t = 0 \rightarrow 9000\, s$) of two and a half hours. The aqueous solution was sampled before and periodically during the experiment and analysed using ICP to determine the change in metal concentrations.

3.4 Experimental Conditions

3.4.1 Screening Study

A comprehensive screening extraction study was initially done to identify a suitable extractant with which the pertraction study could be completed. The phase focus for this study was the aqueous, while the organic phase and therefore, the extractant used, became the consistent backdrop. To this end, ten individual extractants (Table 3-1) were initially chosen as representatives of various classes.

This variety was based on the consideration that the metal species to be extracted may vary depending on its residential acid and its concentration. They were therefore chosen to envelope these metal species possibilities and increase chances of identifying at least one suitable candidate. From the LLn sources listed, two individual yet analogous feed solution types were prepared:

(1) Phosphate Feed: As was mentioned earlier (Chapter 1.1.10; Research Origin), the beneficiation of the LLn elements (La, Ce, Pr and Nd) from a phosphate source is of particular importance to the research benefactor (NECSA). To promote collaborative and incorporative research with foregoing leaching studies[4], Ln salts were provided by NECSA in order to simulate leachate indicative of this source. Excess amounts of the individual LLn salts provided by NECSA were each allowed to saturate 1 M solutions of HNO_3, H_2SO_4, or HCl respectively. These were then filtered and the LLn concentration in the filtrate determined through ICP analysis. Through dilution of these leachate solutions with appropriate amounts of the relevant acid, a range of aqueous feed solutions were prepared. These solutions were limited to higher acidities due to the low solubility of the La- and especially Ce-phosphates.

(2) Oxide Feed: Based on the environmental consideration, in this study intrinsically lower acidic conditions were favoured. In order then to bypass the solubility problem presented by the LLn phosphate feed, LLn solutions were used in preparation of feed solutions at lower acidities. These were prepared by appropriate dilution of the acquired nitric acid based LLn solutions with the NaOH solution. These solutions were further supplemented with either sulphate or chloride salt in order to create respective anionic matrixes i.e. nitric, sulphate or chloride.

3.4.1.1 LLn Phosphate Screening Conditions

Aqueous: $[LLn_T]$ = 500 mg/L; [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1;

- $[HNO_3]$ = (0.5; 1; 2; 4; 6; 8) M
- $[H_2SO_4]$ = (0.5; 1; 2; 4; 6; 8) M
- [HCl] = (0.5; 1; 2; 4; 6; 8) M

Organic: Molar extractant to total metal ratio: $[E/LLn_T]$ = 4

3.4.1.2 LLn Oxide Screening Conditions

Aqueous: [Ce] = 200 mg/L

$[H^+]$ = (0.01; 0.05; 0.1; 0.3; 0.5) M

Organic: $[E/LLn_T]$ = 10

It should be noted that in the LLn oxide screening study, only cerium was present in the aqueous feed solutions. This decision was based on a) the high cost of the acquired solutions, b) the chemical similarities of the LLn metals and c) the simplistic aim of these screening studies. It goes without saying then that all positive results here would bear repeating in the presence of the other LLn elements for confirmation of the extraction performance.

3.4.2 Cerium Oxidation

3.4.2.1 Effect of Oxidizer Concentration $[H_2O_2]$

Individual batch feed solutions with varying added oxidizer concentrations (*$[H_2O_2]$ = 0; 0.005; 0.010; 0.020; 0.030; 0.040 M*) were prepared. Herein; the total metal concentration ($[LLn_T]$ = 500 mg/L), species ratio ([Ce]:[La]:[Pr]:[Nd] = 2:1:1:1) and [NaOH] = 0.0400 M remained fixed. The resulting UV/Vis absorbance was measured directly after preparation and the change in absorbance calculated.

3.4.2.2 Effect of pH Buffer Concentration [NaOH]

Individual batch feed solutions with varying added *[NaOH] = 0.0100; 0.0200; 0.0300; 0.0400; 0.0404; 0.0408 M* were prepared for both the LLn(III)-system and the LLn(IV)-system. Herein the total metal concentration ([LLn_T] = 500 mg/L) and species ratio ([Ce]:[La]:[Pr]:[Nd] = 2:1:1:1) remained fixed. In the LLn(IV)-system the oxidizer concentration ([H_2O_2] = 0.040 M) also remained constant. The resulting absorbance was measured directly after preparation and the difference in absorbance between systems calculated.

3.4.3 Liquid-Liquid Equilibrium

3.4.3.1 Effect of pH Buffer Concentration [NaOH]

A set of individual batch feed solutions were prepared for each of the LLn(III)- and LLn(IV)-systems. The variation of added *[NaOH] = 0.0000; 0.0100; 0.0200; 0.0300; 0.0400; 0.0404 M* within a set was identical for both systems. The SX conditions were as follows:

Aqueous: [LLn_T] = 500 mg/L; [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1;

LLn(III)-system: [H_2O_2] = 0.000 M.

LLn(IV)-system: [H_2O_2] = 0.040 M.

Organic: [E/LLn_T] = 10.

3.4.3.2 Effect of extractant Concentration [D2EHPA]

Subsequently, the [D2EHPA] concentration was varied within the organic phase using identical variation in extractant to metal ratios ([E/LLn_T]) for both LLn(III)- and LLn(IV)-systems. The SX conditions were as follows:

Aqueous: [LLn_T] = 500 mg/L; [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1

[NaOH] = 0.0400 M.

LLn(III)-system: [H_2O_2] = 0.000 M.

LLn(IV)-system: [H_2O_2] = 0.040 M.

Organic: [E/LLn_T] = (1; 2; 4; 6; 8; 10; 15; 20; 30; 50)

3.4.3.3 Effect of Strippant Concentration [HNO_3]

The final experiment illustrates the effect on back-extraction or stripping from the loaded organic phase. For this experiment, optimally loaded organic solutions were prepared for both LLn(III)- and LLn(IV)-systems. Loading conditions were as follows for the two experiments conducted:

Aqueous: [LLn_T] = 500 mg/L; [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1

[NaOH] = 0.0400 M.

LLn(III)-system: [H_2O_2] = 0.000 M.

LLn(IV)-system: [H_2O_2] = 0.040 M.

Organic: [E/LLn_T] = 30

These two sets of loaded organic solutions were then respectively contacted with identical HNO_3 solutions of varying concentrations.

Loaded Organic:

LLn(III)-system: [Ce]:[La]:[Pr]:[Nd] = 98.4%; 95.2%; 98.7%;99.0%

LLn(IV)-system: [Ce]:[La]:[Pr]:[Nd] = 97.7%; 93.9%; 98.2; 98.6%

Strippant: [HNO_3] = 0.001; 0.01; 0.05; 0.1; 0.5 M

3.4.4 Pertraction

The optimal conditions for extraction by D2EHPA were demonstrated for both the LLn(III)- and LLn(IV)-systems. The final step and ultimate goal of this study was the application of these respective extraction systems within a PX environment. In this section of the study, the optimal extraction conditions were used to evaluate the separation of these metals through a HF contactor. Additionally, the advantages of the novel liquid-liquid pre-oxidation of Ce by H_2O_2 is shown through a comparative application to the same PX system.

3.4.4.1 Comparative Extraction Study

The preparation of the aqueous and organic phases was done similar to those in the LLE study and the following optimal conditions were set for extraction using the circulating PX system.

Aqueous: [LLn_T] = 500 mg/L; [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1;

[NaOH] = 0.0400 M.

LLn(III)-system: [H_2O_2] = 0.000 M. (Feed pH: 3.81)

LLn(IV)-system: [H_2O_2] = 0.040 M. (Feed pH: 2.51)

Organic: [E/LLn_T] = 30

3.4.4.2 Comparative Stripping Study

For this experiment, the organic solutions obtained from the comparative extraction study were respectively contacted with strippant solutions using the same circulating PX system.

Organic:

LLn(III)-system: [Ce]:[La]:[Pr]:[Nd] = 95.1%; 88.5%; 96.7%; 97.2%

LLn(IV)-system: [Ce]:[La]:[Pr]:[Nd] = 96.5%; 89.9%; 97.5%; 98.1%

Strippant: [HNO_3] = 1 M.

LLn(III)-system: Strippant pH = -0.03

LLn(IV)-system: Strippant pH = -0.22

3.5 Bibliography

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CHAPTER 4

CONTENT

4 Separation Study

4.1 Introduction

Proving feasible separation of the LLn elements through PX firstly requires definition of the chemical separation process within the fundamental SX context. Although the PX of these elements are at hand within this investigation, both SX and PX also become the yardstick with which the effect of Ce oxidation with H_2O_2 is measured. To these ends then, the first objective was to identify a suitable extraction system with which these evaluations could be made. Upon identification of a suitable extraction system, and confirmation of its extraction capability, the oxidation of Ce with H_2O_2 was optimized using UV/Vis-spectroscopic analysis. Hereafter the effect of this novel environmentally friendly application of H_2O_2 as oxidizer was shown through simultaneous optimization of the respective oxidized and un-oxidized SX systems. Ultimately the physical application of the SX process was amended to include the use of a HF membrane module. Hereby PX as separating process for the LLn elements was evaluated, as is the goal of this MSc dissertation.

4.1.1 LLn Source Evaluation

In order to fully comprehend the results presented herein, a relevant consideration of the feed solutions is first called for. It should be clear that although the total metal concentration ($[LLn_T]$) and its elemental distribution were fixed in all aqueous solutions, the aqueous matrixes stemming from the two respective LLn sources were not equal. These were the LLn phosphate source and the LLn oxide source (Table 3-2), and preparation methods (Chapter 3.4.1) enabling their use in this study resulted in different aqueous matrixes. The differences between these feed solutions also surmise the environmental justification, but this does not include the implications of source choice towards foregoing beneficiation processes.

- The range prepared from the provided LLn phosphate salts consisted of ever increasing concentrations of acid ($[HNO_3/H_2SO_4/HCl]$) ranging from 0.5 to 8 M. This complicates considerations for any large scale operation. The disadvantages in maintaining a highly corrosive system, although sometimes unavoidable, are logically not desirable.

- This phosphate leachate is in contrast then to the acquired solutions prepared from the oxide source solutions. Herein the acidity ($[H^+]$) of solutions with fixed anionic concentrations, was decreased from 0.5 to 0.01 M through the addition of a NaOH pH buffer. This would presumably culminate in milder feed solutions with additional sodium content. However at low acidities, the liquid-liquid dominance required by the PX application is threatened by LLn hydrolysis [1-3] according to the reaction:

$$LLn^{n+} + mH_2O \leftrightarrow LLn(OH)_m^{n-m} + mH^+ \tag{4.1}$$

Considering both the operational and environmental implications of these sources though, the milder conditions resulting from the latter remain undeniably favoured.

- Lastly; although both these screening studies contained matrixes which were labelled either nitric-, sulphuric- or chloride-based, both sets contained anionic species not represented hereby. The concentration of these anions however remained constant and equal throughout the solutions within their respective studies, and were considered as follows:

  a. The LLn phosphate source solutions invariably contained phosphate (PO_4^{-3}) anions. These were however in such minority within the high acidic concentrations that they could safely be presumed irrelevant to the dominant coordination chemistry.

  b. Contrarily, the LLn oxide source solutions unavoidably contained nitrate (NO_3^-) anions. The concentration of these was by a factor ten greater than the pertinent metals. Arguably then, the addition of vast amounts of sulphate (SO_4^{2-}) or chloride (Cl^-) anions could be used to dominate the matrix, but this is economically counterproductive.

     It was therefore decided that the added [SO_4^{2-}] and [Cl^-] should merely equal the [NO_3^-] in order to constitute that given matrix. Through their equimolar presence then, the influence of these anions on a working nitric-based system could at least be observed, if any.

4.2 LLn Screening Study

The goal of this screening study was simply to identify a working extraction system for either of the two LLn (phosphate and oxide) sources from 10 different extractants (Table 3-1). In Figures 4-1 to 4-3, the extraction of Ce achieved from the LLn phosphate source in respective HNO_3, H_2SO_4 and HCl matrixes is presented. The extraction of the other LLn elements present (La, Pr and Nd) during this source specific screening study, was expectedly similar. These results are presented in Figures B1 to B9 and can be found in Appendix B. In the LLn oxide screening study, only Ce was present and its extraction from NO_3^- , SO_4^{2-} and Cl^- matrixes are presented in Figures 4-4 to 4-6.

While the aqueous feed solutions and their preparation require due consideration, the organic phase extraction system could be handled more consistently. Through appropriate dilution in large volumes of the kerosene based diluent, identical organic phase solutions containing a given extractant could be used for the entirety of a screening study.

Keeping with the process of single variable manipulation, the molar extractant to total metal ratio ([E/LLn_T]) was therefore fixed to ten times the concentration of the dominant metal species, [Ce] = 200 mg/L. This ensured that excess extractant was present for extraction while equalising the opportunities between extractants within respective screening studies. The results of the screening studies presented in Sections 4.2.1 and 4.2.2 are discussed in Section 4.2.3.

4.2.1 LLn Phosphate Screening

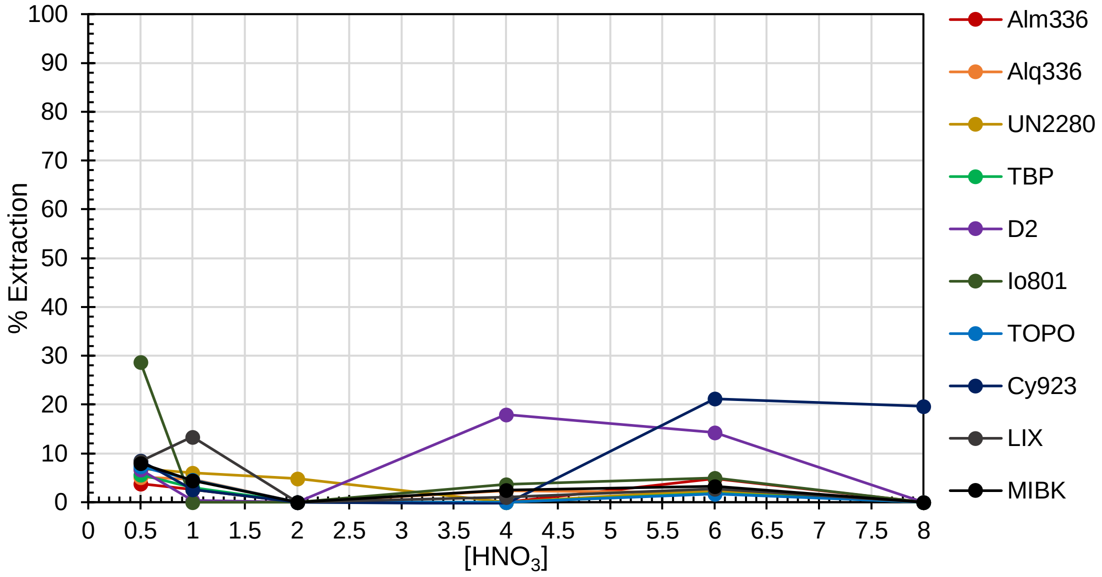

Figure 4-1: **The % Ce extracted from LLn phosphate feed solutions of various nitric acid concentrations. [LLn$_T$] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V$_{Org}$/V$_{Aq}$ = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

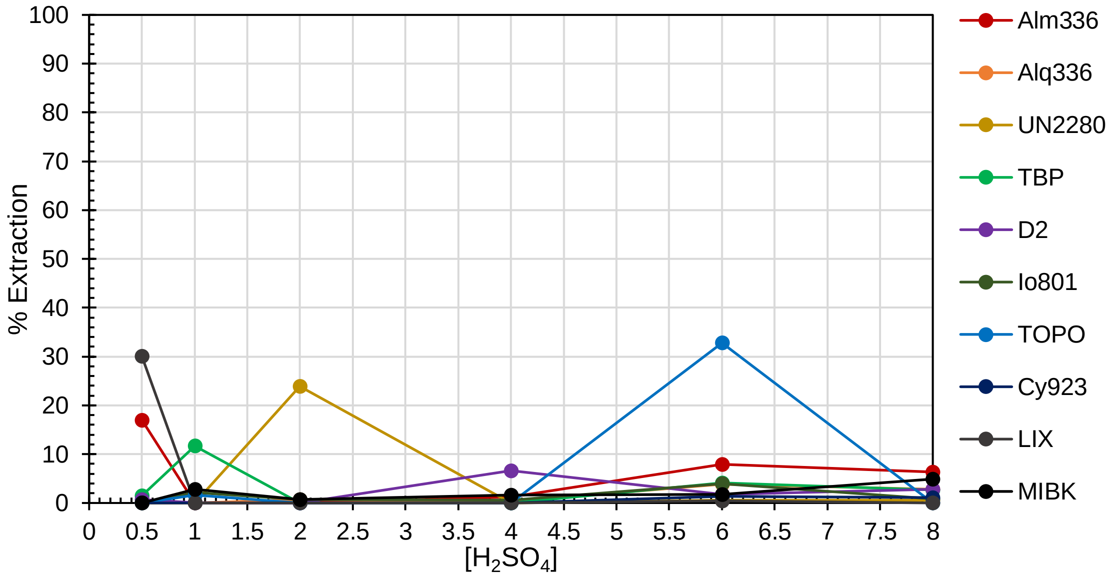

Figure 4-2: **The % Ce extracted from LLn phosphate feed solutions of various sulphuric acid concentrations. [LLn$_T$] = 500 mg/L.**
[Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V$_{Org}$/V$_{Aq}$ = 1. Diluent: Kerosene.
Modifier: 5wt% 1-Octanol.

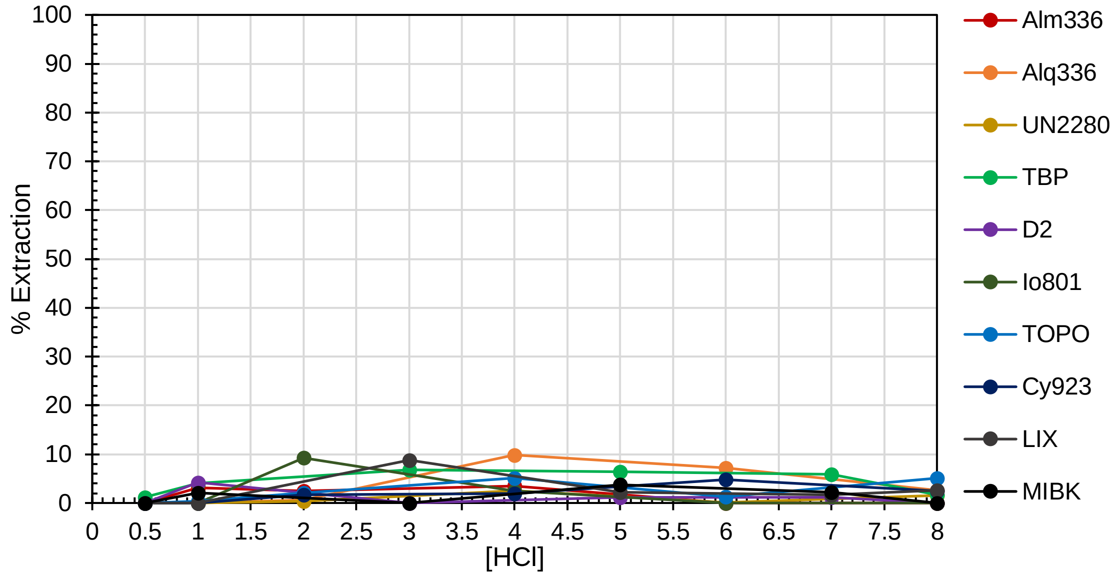

Figure 4-3: The % Ce extracted from LLn phosphate feed solutions of various hydrochloric acid concentrations. $[LLn_T]$ = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. $[E/LLn_T]$ = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

4.2.2 LLn Oxide Screening

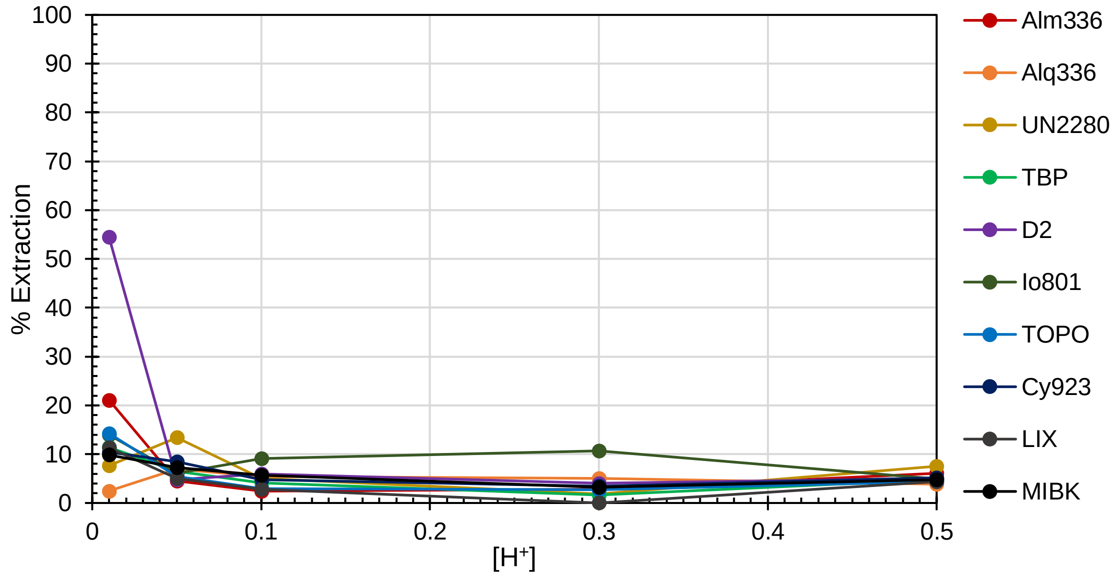

Figure 4-4: The % Ce extracted from LLn oxide feed solutions of various acidities and fixed anionic concentrations. [Ce] = 200 mg/L. $[NO_3^-]$ = 0.8 M. $[E/LLn_T]$ = 10. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

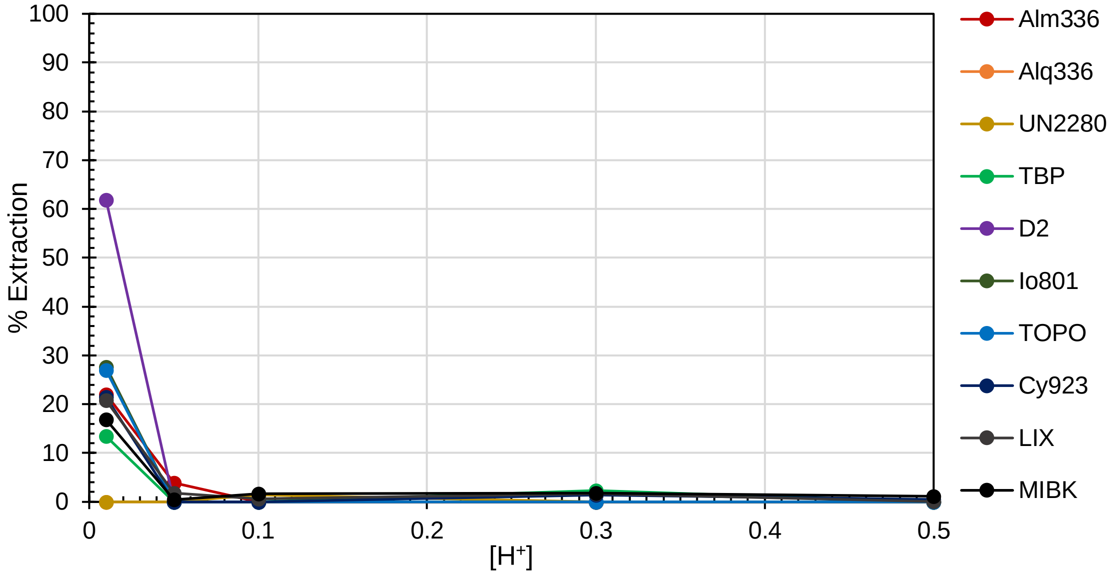

Figure 4-5: **The % Ce extracted from LLn oxide feed solutions of various acidities and fixed anionic concentrations. $[NO_3^-] = [SO_4^{2-}] = 0.8$ M. [Ce] = 200 mg/L. $[E/LLn_T] = 10$. $V_{Org}/V_{Aq} = 1$. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

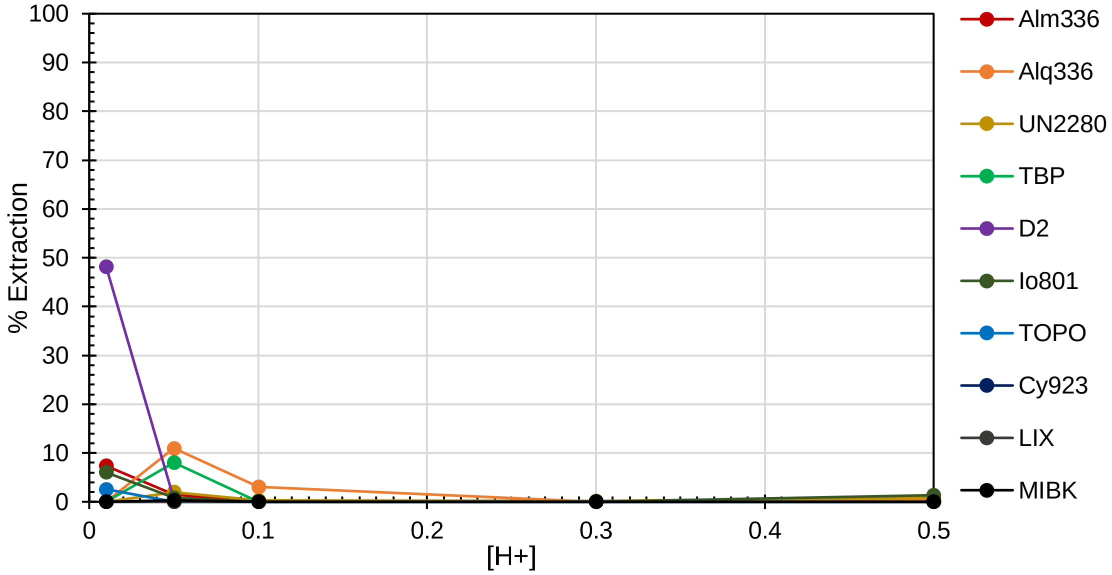

Figure 4-6: **The % Ce extracted from LLn oxide feed solutions of various acidities and fixed anionic concentrations. [Ce] = 200 mg/L. $[NO_3^-] = [Cl^-] = 0.8$ M. $[E/LLn_T] = 10$. $V_{Org}/V_{Aq} = 1$. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

4.2.3 Extraction Verification

From the equilibrium data generated in the LLn phosphate screening study in Chapter 4.2.1, several extractants appeared to achieve acceptable extraction (>20%) granted $[E/LLn_T] = 4$. None of these however were reproducible from the same conditions and were seen to approach zero as was the case for all the other conditions tested herein. From those extractants tested, no suitable candidate was therefore identified within the LLn phosphate screening study and hence not considered further.

From the LLn oxide screening study in Chapter 4.2.2, the best results were obtained when using D2EHPA. Demonstrating repeatability within itself, more than suitable extraction (>45 %) was achieved from all three anionic matrixes, each at the lowest acidic condition tested ($[H^+] = 0.01$ M). Additionally, the onset of LLn hydrolysis (Equation 4.1) was observed as a milky white suspension within these low acidic feed solutions.

The experimental sights were therefore refocused and the first step entailed the successful reproduction of this extraction performance in the presence of the remaining LLn metals La, Pr and Nd. This positive reproduction, although expected, required further consideration.

- The addition of the remaining LLn metals to the aqueous feed solution would lead to an increase in total metal concentration and therefore a decrease in the extractant to metal ratio ($[E/LLn_T] = 10$). During this extraction verification experiment then, the extractant concentration was also raised to maintain this ratio.

- Morais *et al.*[4] observed precipitation of trivalent LLn species at lower acidic concentrations ($[H^+] < 0.001$ M]), so the precipitation within the extraction range in question was expected. To maintain the liquid-liquid dominance of this research, a precipitation threshold of 15 ± 1.5 % was set for the remainder of this study. That is, aqueous feed solutions prepared wherein greater precipitation of any LLn species was observed, were omitted from the study.

  Furthermore, the onset of hydrolysis within this range complicates calculation of the acidic concentration ($[H^+]$). From Equation 4.1, it is seen from the various stages involved during the precipitation of LLn hydroxide species ($LLn(OH)_m^{n-m}$), that the addition of the NaOH buffer solution no longer yielded the neutralisation of free protons on a one-to-one basis. Therefore, the % extraction was presented as a function of the feed pH measured (pH_F) as altered by incremental NaOH addition.

- Within the SX context, the small amount of total precipitation allowed (≤ 75 mg/L) remained suspended within the aqueous phase. It is known from the cationic exchange mechanism (Equation 2.1) involved during D2EHPA extraction that the aqueous phase is acidified. This acidification would presumably aid in dissolving the precipitate making the metals available for extraction. This was confirmed through the absence of any precipitate in the resulting aqueous raffinate.

- The effect of the added SO_4^{2-} and Cl^- was observed to be minor. Respectively, their addition to the nitric acid matrix roughly yielded a 5% increase and decrease in extraction. These effects could easily be accredited to human error or analysis drift, but from the similarity of the LLn elements (see Chapter 2.2) it is known that even if these variations were a result of the addition of the anionic species, the effect on the separation of these elements would be just as slight. For the purposes of this study then any of these matrixes are presumably sufficient. The redundant addition of SO_4^{2-} and Cl^- was therefore neglected for the remainder of this study and only the nitric acid matrix was used.

Based on these considerations, the extraction of LLn elements from a nitric acid medium by D2EHPA was repeated. The preparation of these multi-element aqueous feed solutions was done analogously to those in the LLn oxide screening study, with the simple addendum of smaller increments of added [NaOH]: (0.0024; 0.003; 0.0036; 0.0037; 0.038) M when nearing apparent extraction/precipitation conditions. Hereby then the observed extraction performance of D2EHPA was confirmed, and is presented in Figure 4-7.

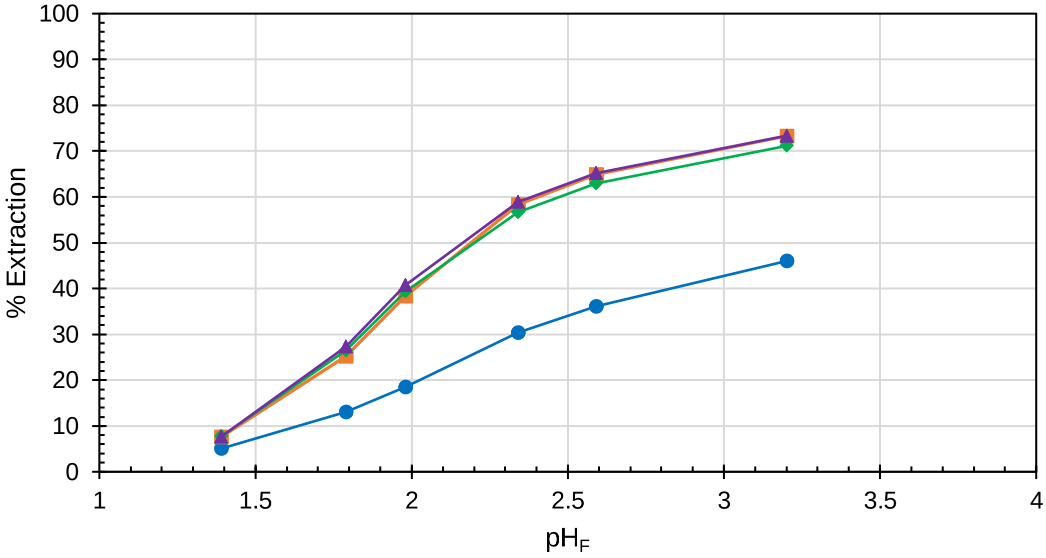

Figure 4-7: **Extraction verification of -●- La; -■- Ce; -◆- Pr; -▲- Nd from LLn oxide source solutions by D2EHPA as a function of the feed pH.**
$[LLn_T]$ = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. $[NO_3^-]$ = 0.8 M.
$[E/LLn_T]$ = 10. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

This clear illustration of the extraction capability of D2EHPA, meant that although far from optimized, a suitable organic extraction system had been identified. Hereby then, not only was the organic extraction system determined but also the aqueous feed. For the remainder of this investigation, only the LLn oxide source solutions were used in preparation of all LLn containing aqueous solutions.

Based on the common processes employed during the beneficiation of LLn source ores (Chapter 2.3), this was deemed the more fitting choice even though monazite type sources were considered. Furthermore, due to the solubility issue encountered during preparation of the LLn phosphate leachate, the extraction by D2EHPA at low acidities could not be reproduced and the lack of suitable results within the LLn phosphate screening study speaks for itself.

4.3 Cerium Oxidation

The identification of a working extraction system meant that the separation effort could then begin in earnest. Yu *et al*.[5] explains that Ce^{4+} becomes the more stable species over the same pH range in question during extraction, and is formed in the presence of H_2O_2. In order then to optimally observe the effect this oxidation process has on the D2EHPA extraction system, optimizing Ce oxidation was the first step. This was done by varying the [H_2O_2] and added [NaOH], respectively.

4.3.1 Absorbance Study

The analytical method that was used to optimize this oxidation process (Chapter 3.3.2), was calculating the difference in the UV/Vis-absorbance of two almost identical LLn containing aqueous feed solutions, as prepared for extraction. The only difference between these solutions was the presence of H_2O_2 in one. By preparing a series of these feed representatives, varying identically the increasing amounts of NaOH added to each series, the increasing pH and the presence of H_2O_2 yielded the oxidation of Ce(III) to Ce(IV) and a corresponding change in absorbance.

The oxidation process was qualitatively observed through the progressive change in colour of the H_2O_2 containing solutions from colourless to bright yellow. A picture of this colour change is shown in Figure: C1, and can be found in Appendix C. In order to interpret this absorbance change throughout the range measured (200 – 1000 nm), the identification of the various species was required.

Solutions of increasing total metal concentrations containing either individual LLn elements ([LLn_T] = (200, 500; 1000) mg/L), or a mixture of all four ([LLn_T] = (500, 1250; 2500) mg/L; [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1), were analysed. Hereby the various increasing absorbance peaks associated with each LLn species were identified within the single element solutions, and through comparison were earmarked within the mixture. Presented in Appendix C are the absorbance spectra of Ce, Pr and Nd in single element solutions in Figures C2 to C4, followed by their absorbance spectra in the mixed element solutions in Figure C5 and C6.

La expectedly exhibited no discernible absorbance peaks, at least not within the range measured since there are no 4f electron which can be excited to a higher state.[6] A strong absorbance peak associated with Ce(III) was observed within the UV-range (200 – 400 nm), centred around ~250 nm and entered the noise region. A similar observation was made by Ebendorff-Heidepriem *et al*.[7] Pr, also confirmed in literature,[6; 8] alongside Nd exhibited various much smaller absorbance bands at higher wavelengths within the visible (400 – 700 nm) and in the case of Nd, also in the near IR- range (> 700 nm).

In the multi-element solutions, we know that at any specific wavelength, the total absorbance observed is the sum of the absorbance bands of the individual components.[9] Through the difference in absorbance (ΔA) method used at fixed [LLn_T], the absorbance bands associated with any species will effectively culminate to zero unless a change in the magnitude of absorbance is found i.e. a change in oxidation state. Accordingly, the increase in [Ce(IV)] resulted in a positive absorbance change while the decrease in [Ce(III)] constituted a negative change at respective wavelengths (colourless to yellow). Either of these could therefore, be used to effectively maximize the oxidation process, but due to the proximity of the absorbance band associated with Ce(III) to the noise region, the analysis was focused on the increasing absorbance of Ce(IV) species.

4.3.2 Effect of H_2O_2 Concentration

The oxidation of Ce(III) to Ce(IV) is illustrated in Figure 4-8 with increasing [H_2O_2] and constant added [NaOH]. As the [H_2O_2] increased, a broad positive change in absorbance was observed at ~310 nm associated with Ce(IV). Similar associations were also made by Ebendorff-Heidepriem *et al.*,[7] Medalia and Byrne[10] and in Fundamentals of Analytical Chemistry by Skoog et al.[8] This increase in absorbance maximized at [H_2O_2] = 0.030 M with an almost identical absorbance change profile recorded when further increasing the [H_2O_2] to 0.040 M. This indicates that the oxidizer was in excess above 0.030 M yielding maximum amounts of Ce(IV) possible under these conditions.

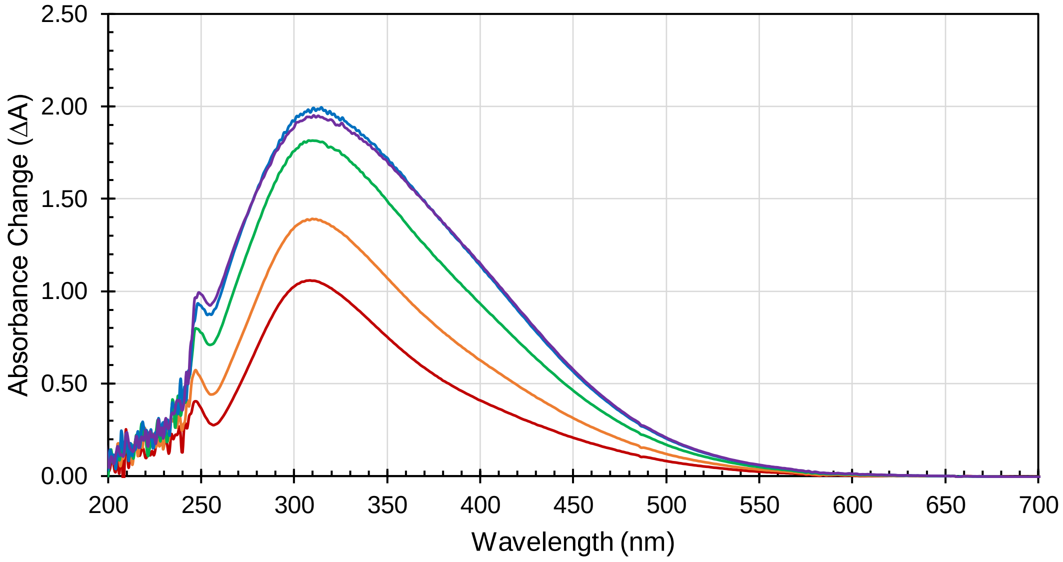

Figure 4-8: **Calculated change in UV/Vis-absorbance (ΔA) indicating the formation of Ce(IV) species in feed solutions with varying oxidizer concentrations [H_2O_2]: — 0.005 M; — 0.010 M; — 0.020 M; — 0.030 M; — 0.040 M. [LLn_T] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1 . [NaOH] = 0.0400 M.**

4.3.3 Effect of NaOH Buffer Concentration

In Figure 4-9 the influence of the added ^{-}OH groups on the oxidation of Ce(III) is presented. Herein, the added [NaOH] was increased while keeping the [H_2O_2] constant at excess 0.04 M. The increase in [NaOH] resulted in the same positive change in absorbance, and further supported the association with Ce(IV) species formation.

While the change in absorbance did not reach a maximum within this added [NaOH] range, a second gradual colour change was observed from yellow to dark orange at concentrations exceeding [NaOH] = 0.0400 M. Over time this change in colour dissipated slightly while an orange-brown precipitate eventually became visible. This is accredited to the formation of Ce(IV) oxide species as explained in the precipitation study by Scholes *et al*.[11] Furthermore, precipitation coincided with the absorbance changes profiles at these higher added [NaOH] becoming increasingly more jagged.

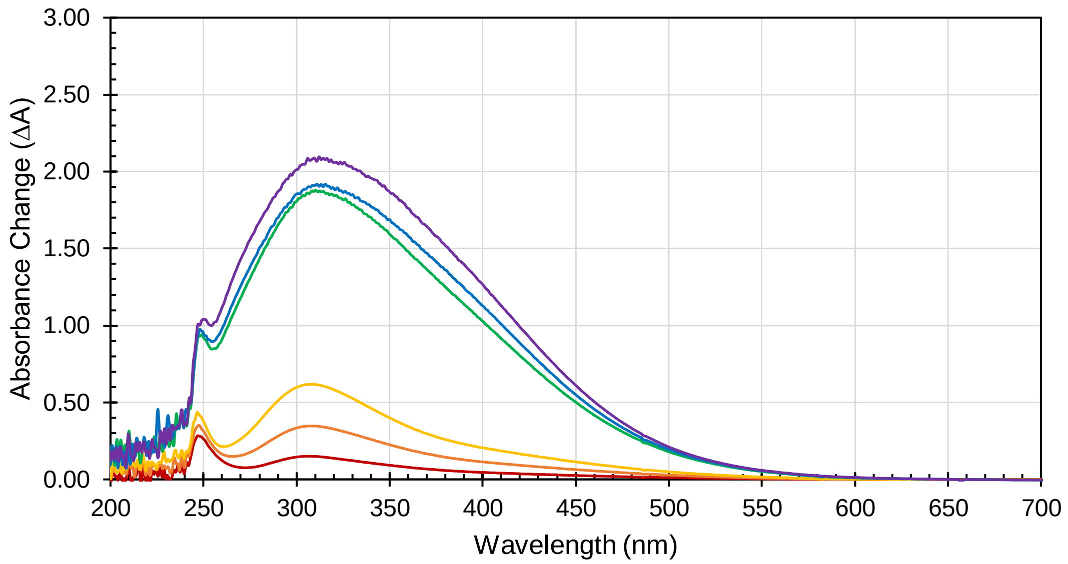

Figure 4-9: Calculated change in UV/Vis-absorbance (ΔA) indicating the dependence of Ce oxidation on added pH buffer concentration. [NaOH]: — 0.0100 M; — 0.0200 M; — 0.0300 M; — 0.0400 M;— 0.0404 M; — 0.0408 M.
$[LLn_T]$ = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. $[H_2O_2]$ = 0.040 M.

The addition of NaOH to increase the pH of the feed solution finds particular relavence within the extraction optimization study which follows, but it is this same addition which is also neccesary for oxidation. It should also be clear that both the extraction by D2EHPA and the oxidation with H_2O_2 are limited by the threshold as imposed by the precipitation of LLn species.

4.4 Liquid-Liquid Equilibrium Study

In this experimental section, simultaneous and identical optimization of the non-oxidized LLn(III)-system, and the optimally oxidized LLn(IV)-system was done. In all cases the only difference between these systems was the presence of H_2O_2 in the latter. The parameter variations were identical in both systems to show the influence of Ce oxidation with an excess (0.040 M) amount of oxidizer on a working D2EHPA extraction system.

The extraction of LLn elements with organophosphorus extractants such as D2EHPA has been well researched[12-21] allowing first for a more relevant description of LLn extraction to be made. Hereby the general cationic exchange mechanism presented in Equation 2.1 becomes more specific;

$$LLn^{3+}{}_{(aq)} + m(H_2A_2)_{(org)} \rightarrow LLnA_m(HA)_m + mH^{+}{}_{(aq)} \tag{4.2}$$

Herein the dimeric (H_2A_2) form of the monoprotic phosphorus acid (HA) is considered because it is more common in non-polar diluents[20]. Through logical consideration of charge balances, it can easily be conceded that m = 3 when considering dimer extraction. Furthermore, this mechanism assumes that only this dimeric form is involved during extraction; however, this is not always the case.

As early as 1978, Yoshiyuki *et al*.[12] observed lowering values of m depending on the organic diluent. Five years later Lundqvist *et al*.[22] suggested that involvement of some monomeric species rendered m closer to 2.5. More recently, Moreno *et al*.[13] and Xinghua *et al*.[23] addressed the non-integer stoichiometry in their respective studies; in the case of the former, by observing the extraction of Pr and Ho by D2EHPA from a nitric acid medium, almost identical to the one presented here.

They determined that in order to maintain charge balance, a nitrate ion is co-extracted as a $Ln(NO_3)A_2(HA)_3$ species, and from graphical analysis, this is logically shown to happen at higher equilibrium acidities and lower extractant concentrations ([D2EHPA] = 0.002 M). Furthermore, they conclude that when [D2EHPA] ≥ 0.005 M, $LnA_3(HA)_2$ species are formed. As first proposed by Lundqvist *et al.*,[22] both these observations then imply a more fitting description as;

$$LLn^{3+}{}_{(aq)} + \frac{(p+n)}{2}(H_2A_2)_{(org)} \leftrightarrow LLnA_p(HA)_{n\,(org)} + pH^{+}{}_{(aq)} \tag{4.3}$$

Note that this is not different from the reaction posed in Equation 4.2, rather therein *p* = *n*. Considering only the simpler case of Equation 4.2 for now, at equilibrium it follows that;

$$K_{eq} = \frac{[LLnA_m(HA)_m][H^{+}]^m}{[LLn^{3+}][H_2A_2]^m} \tag{4.4}$$

and in combination with the definition of the distribution coefficient in Equation 2.3, this becomes;

$$\log(K_{eq}) = \log(D_{LLn}) + m\log[H_2A_2] + mpH_{eq} \tag{4.5}$$

From the gradient of the graphs of $\log(D_{LLn})$ vs. either pH_{eq} or $\log(H_2A_2)$ the stoichiometric coefficient (*m*) can be determined. Similarly *p* and *n* from Equation 4.3 can be determined, although herein the respective slopes might not be equal ($\frac{\Delta\langle\log(D_{LLn})\rangle}{\Delta pH_{eq}} \neq \frac{\Delta\langle\log(D_{LLn})\rangle}{\Delta\langle\log([D2EHPA]_2)\rangle}$). However, due to the hydrolysis boundary and the method of oxidation in this study, this is easier said than done.

- The allowance of precipitation within the feed solution means that the pH at equilibrium is not the true representative which this slope analysis would require. Moreover, during variation of added [NaOH] in order to effect extraction, the oxidation process is also altered. So from one side of the measured range to the other, the transformation from one species to the other happens.

- Furthermore, the green nature of the oxidizer (H_2O_2) means that upon completion of the oxidation reaction, no reduced agent remains. The drawback, however, is that without this redox couple, Ce(IV) will inevitably revert back to the trivalent state through;

  $$4Ce^{4+} + 2H_2O \rightarrow O_2 + 4H^+ + 4Ce^{3+} \tag{4.6}$$

  So although Ce oxidation was maximized and every possible measure was taken to perform extraction as quickly as possible upon preparation, the LLn(IV)-system will always be a mixture of Ce(III) and Ce(IV). Therefore with regard to the LLn(IV)-system at least, no pertinent conclusion can be made to its specific extraction reaction.

Hereby then, extraction optimization starts by manipulation of pH_F, i.e. the optimal added [NaOH] to achieve maximum extraction and also maximum oxidation. Only hereafter can some mechanistic investigation be made through variation of the [D2EHPA].

4.4.1 Effect of NaOH Buffer Concentration

Considering the extraction reaction, the aim of this experiment was to get as close to the precipitation threshold as possible. The extraction data generated herein were carried out through identical variation of added [NaOH] measured as a function of pH_F. The % extraction achieved in the absence and presence of H_2O_2 is shown in Figure 4-10A and 4-10B, respectively.

Firstly; the addition of H_2O_2 to the D2EHPA extraction system (Figure 4-10B) yielded increasingly lower pH_F values with identical increases in added NaOH. From Equation 4.1 this can be explained by Ce(IV)'s increased capacity to accommodate OH^- ligands and earlier onset hydrolysis to form cerium hydroxide species ($Ce(OH)_m^{4-m}$) as opposed to its trivalent state[4]. It can be qualitatively observed that within either system, La could be removed relatively easily from Nd. Conversely, the extractions of Pr was near identical to Nd, and this will ultimately pose the largest challenge in a separation process such as this.

As the LLn(IV)-system approached the maximum [Ce(IV)] at $pH_F > 2.8$, slightly increased extraction of La, Pr, and Nd was observed in comparison to the LLn(III)-system. The extraction of Ce, however, decreased slightly. The addition of H_2O_2 to the extraction system could therefore be said to have had a suppressive effect on Ce extraction. This reads contrary to the findings of previous studies involving cerium oxidation, where it was shown that the oxidation of Ce generally results in increased extraction over the remaining trivalent counterparts.[24-27]

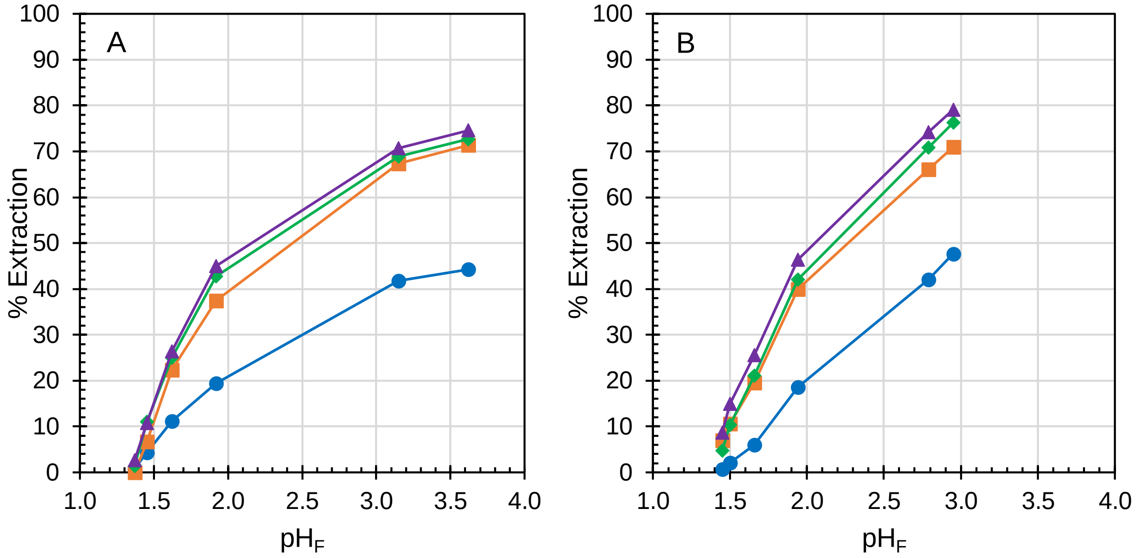

Figure 4-10: **The % extraction of the LLn elements, -●- La; -■- Ce; -◆- Pr; -▲- Nd, as a function of the feed pH, from (A) the LLn(III)-system ([H_2O_2] = 0.000 M), and (B) LLn(IV)-system ([H_2O_2] = 0.040 M). [LLn_T] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. Extractant: D2EHPA. [E/LLn_T] = 10. V_{Org}/V_{Aq} = 1.Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

The observed suppression of Ce extraction comes down to the affinity of the extractant to either the Ce(III) or Ce(IV) species. The decreased extraction of Ce can then be accredited to one of the following;

(1) If the extraction of Ce(IV) is in fact favoured over Ce(III) extraction then the manner by which Ce(IV) was extracted, affected the extraction of the remaining trivalent LLn metals. This would suggest that either

  (a) less extractant was needed for Ce(IV) extraction, which increased extractant availability for the remaining trivalent LLn elements, or

  (b) an anionic species that supresses trivalent LLn extraction was co-extracted with Ce(IV), or conversely one that was needed for trivalent LLn extraction was not co-extracted with Ce(IV).

Furthermore, for Ce(IV) favoured extraction systems, it has early on become common practice to use H_2O_2 as additive to the acidic stripping solution.[24] As mentioned earlier, within an acidic medium, this yields the reduction of Ce(IV) to Ce(III) and affects increased recovery from the loaded organic solution. Therefore, if H_2O_2 was in excess, the acidification of the aqueous phase could have caused back-extraction of Ce due to reduction.

(2) On the other hand, if Ce(III) was favourably extracted over Ce(IV), the net decrease in extraction is simply accredited to the decreased [Ce(III)] with increased oxidation. This also increased the extractant availability for trivalent LLn extractions.

Nevertheless, it should be noted that the addition of H_2O_2 to the D2EHPA extraction system had a direct effect on Ce only, and that this then in turn affected the entire system. Keep in mind that relatively low individual metal concentrations were used in this system with the largest being Ce ([Ce] = 0.0015 M). It follows from the [E/LLn_T] = 10, that the extractant concentration was also low ([D2EHPA] < 0.040 M). Moreover, the [Ce] within the aqueous system is twice that of the other LLn metals. Therefore, although the probability of Ce extraction was statistically favoured, through the suppression of the Ce extraction, the extraction of Nd, Pr and La was increased.

4.4.1.1 Distribution

This is more clearly demonstrated when looking at the change in D_{LLn}, presented in Figure 4-11A and 4-11B. Within a first qualitative assessment it can be stated that the trend exhibited by the LLn(III)-system (Figure 4-11A) seems to reach a plateau above pH_F = 3.15 consistent with a system that will eventually reach its maximum loading capacity. The effect does not fully come to fruition because of the precipitation threshold reached. Conversely, the LLn(IV)-system (Figure 4-11B) exhibited the opposite trend, i.e. as the oxidation process maximized towards higher extraction, the system behaved ever more like that of an empty organic phase.

As is then expected, D_{Ce} decreased slightly coinciding with an increased distribution for Nd, Pr and La. For these three metals, the individual differences in the species distribution (ΔD_{LLn}) between LLn(III)- and LLn(IV)-systems, increased across the group ($\Delta D_{Nd} > \Delta D_{Pr} > \Delta D_{La}$). This is akin to the natural selectivity of the LLn(III)-system and further supports the basis that extractant availability towards trivalent LLn species was increased by the oxidation of Ce.

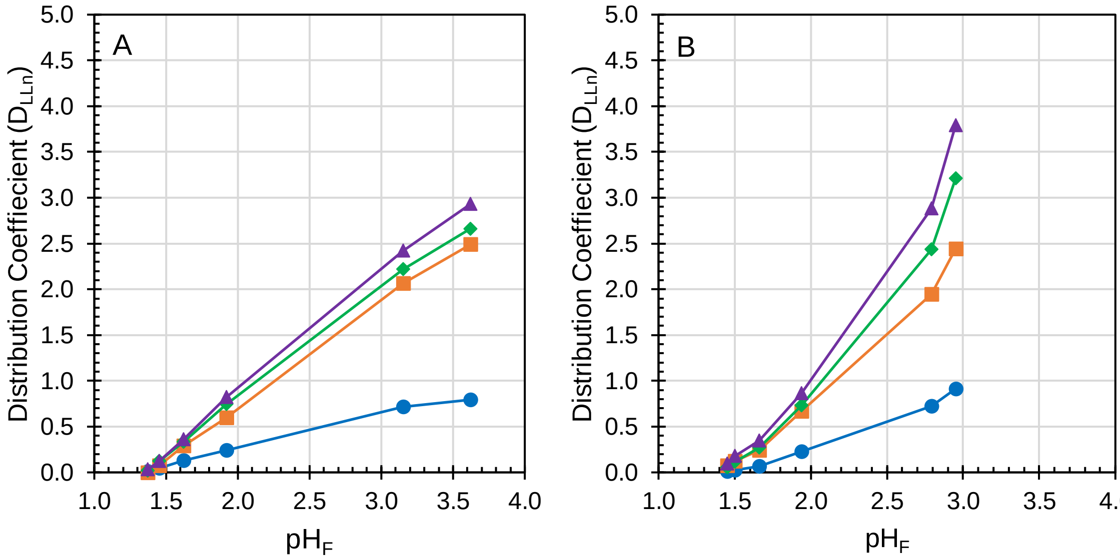

Figure 4-11: The change in species distribution ($D_{LLn} = [LLn]_{Org.}/[LLn]_{Aq.}$) of the LLn elements, -●- D_{La}; -■- D_{Ce}; -◆- D_{Pr}, -▲- D_{Nd}, as a function of the feed pH for (A) the LLn(III)-system ([H_2O_2] = 0.000 M), and (B) the LLn(IV)-system ([H_2O_2] = 0.040 M).

4.4.1.2 Separation

The distribution increase was greatest for the target metal Nd, and due to the manner by which the separation factor (β_{LLn}) is defined (Equation 2.5), in the LLn(IV)-system it yielded increased separation from Nd across the board. The change in β_{LLn} for either system can be seen in Figure 4-12 as a function of pH_F, and the effect is particularly important when considering Ce. Within the LLn(III)-system (Figure 4-12A), the separation of Ce from Nd (β_{Ce}) decreased continuously which could be ascribed to the organic phase seemingly nearing its maximum loading capacity, and the statistical probability favouring Ce. In the LLn(IV)-system (Figure 4-12B), β_{Ce} increased, albeit more slightly, and the net effect of adding H_2O_2 to this system almost seems to stabilize Ce separation throughout this feed pH range.

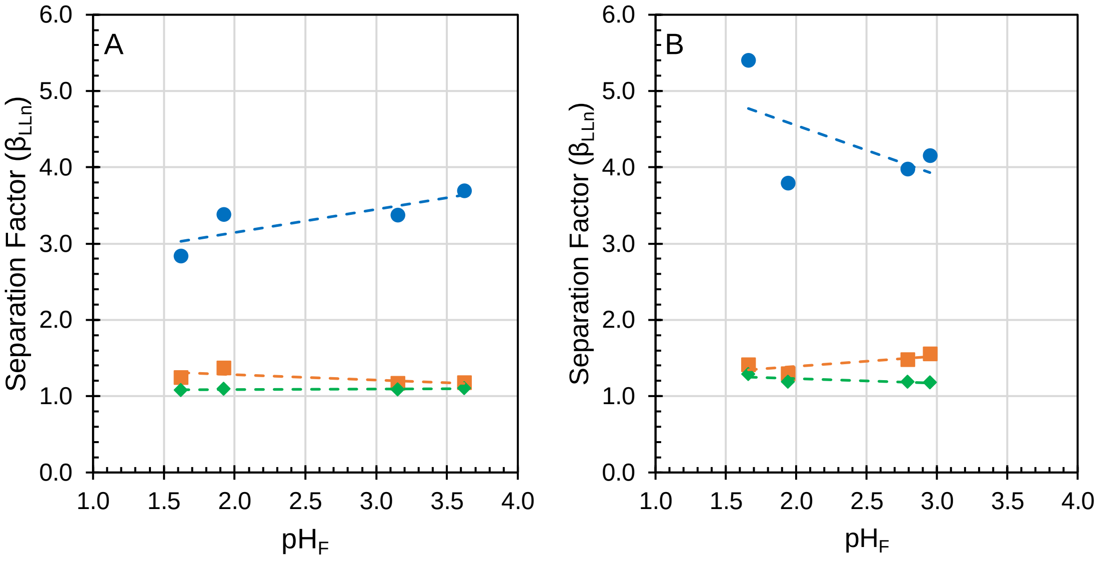

Figure 4-12: **The separation factor ($\beta_{LLn} = D_{Nd}/D_{LLn}$) of the LLn elements, ● β_{La}; ■ β_{Ce}; ♦ β_{Pr}. as a function of the feed pH, in (A) the LLn(III)-system ($[H_2O_2]$ = 0.000 M), and in (B) the LLn(IV)-system ($[H_2O_2]$ = 0.040 M).**

Thus far, it should be clear that the exceedingly low β_{Ce} in these systems was a result of statistical effects. Ce was the dominant species in this aqueous feed as was explained in the mineralogical consideration (Chapter 1.1.2.4) – this will most often be the case. Although the selectivity of D2EHPA increased across the LLn group, the Ce rich aqueous feed would inevitably lead to a Ce rich organic feed, which is redundant and is even further propagated through insufficient extractant availability.

The selective exchange of metals at equilibrium was similarly dominated by the statistics of the organic metal complex encountering a metal other than Ce. Therefore, to address this and to fully observe the effect of Ce oxidation, the extractant concentration would have to be increased. Similar to the absorbance study, the optimal added [NaOH] to ensure as little precipitation as possible, while still achieving sufficient extraction was found to be 0.0400 M, and was fixed for further experiments.

4.4.2 Effect of D2EHPA Concentration

With both the maximum oxidation ($[H_2O_2]$ = 0.04 M) and extraction (added [NaOH] = 0.0400 M) achieved while inside the precipitation threshold (15 ± 1.5 %), the identical variation of [D2EHPA] for both optimal systems can be seen in Figure 4-13 as a function of $[E/LLn_T]$. As the extractant concentration was increased, the probability of an extractant interacting with a metal other than Ce increased as well. Consequently, the chemistry which determines the order of selectivity began dominating over numerical favouritism.

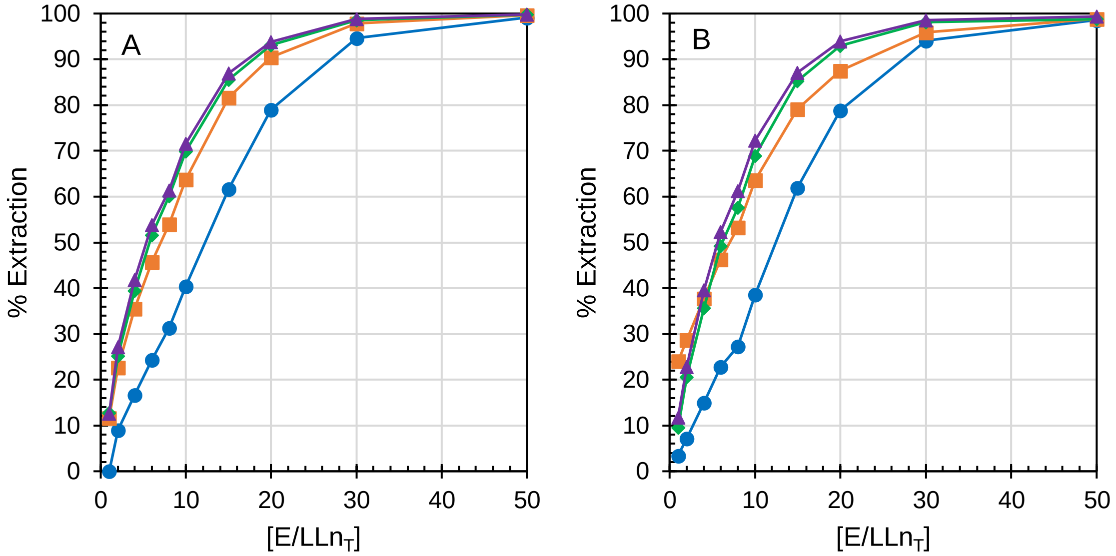

Figure 4-13: The % extraction of the LLn elements, -●- La; -■- Ce; -◆- Pr; -▲- Nd, from (A) the LLn(III)-system (pH_F = 3.6; $[H_2O_2]$ = 0.000 M) and (B) the LLn(IV)-system (pH_F = 2.72; $[H_2O_2]$ = 0.040 M), as a function of increasing extractant to total metal concentration $[E/LLn_T]$. $[LLn_T]$ = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. $[NO_3^-]$ = 0.8 M. [NaOH] = 0.0400 M. Extractant: D2EHPA. V_{Org}/V_{Aq} = 1. Diluent: Kerosene.Modifier: 5wt% 1-Octanol.

The resulting differences in extraction were slight which leads back neatly to the original problem statement. Even at high extractant concentrations ($[E/LLn_T]$ = 20) where the chemistry dominates, the separation in the LLn(III)-system (Figure 4-13A) remained small, and further increases to the extractant concentration ($[E/LLn_T] \geq 30$) only yielded the opposite statistics where nothing was left behind in the aqueous phase.

Looking now at the LLn(IV)-system in comparison (Figure 4-13B), at the onset ($[E/LLn_T]$ = 1), the method used here showed substantially increased extraction results for Ce. This is most likely due to too little acidification of the aqueous phase from the small amount of extractant. This caused some Ce to remain as precipitate within the raffinate which led to these discrepancies within the mass balance. As soon as sufficient extraction had been achieved, however, ($[E/Ln_T] \geq 6$) the expected trend was observed.

On the topic of accuracy, a quantitative assessment was subsequently made regarding the entire method employed for this LLE study. Through comparison of Figure 4-10 and Figure 4-13, the corresponding pH_F and $[E/LLn_T]$ values show an average difference in % extraction data of no more than 3.35% across both oxidation systems and constituent elements. Considering that the solutions used in generating these corresponding data sets, both aqueous and organic, were prepared especially for each experimental set, this margin of deviation confirms the repeatability of the method and accuracy of analysis.

Hereby then, previous deductions are supported. At the penultimate point ($[E/Ln_T] = 30$), where the chemical effects are presumed dominant, the extraction of Ce was almost equal to that of La. This confirms that the change in the extraction mechanism of Ce brought on by its oxidation, somehow favoured the extraction of the remaining trivalent LLn within the same system. To better understand this occurrence the distribution is once again at hand.

4.4.2.1 Distribution

From Equation 4.5 the dependence of the extraction reaction on the extractant concentration is illustrated in Figure 4-14. Note that in these graphs, as with the equation, the D2EHPA dimer is considered. The trend line gradient obtained for each system and constituent metals can be found in Table 4.1.

From the Equations 4.2 and 4.3 and the discussion surrounding these, it should be clear that the stoichiometric coefficient ($m = \frac{p+n}{2}$) of the extractant varies between 3 and 2.5. So, from the proximity of ($m = \frac{\langle \log(D_{LLn}) \rangle}{\langle \log([D2EHPA]_2) \rangle}$) to either of these values, the dominant mechanism can be deduced, i.e. if m approaches 3, extraction predominantly occurs in the formation of $LnA_3(HA)_3$ species, while deviation toward 2.5 would therefore presumably imply the increased formation of either $Ln(NO_3)A_2(HA)_3$ or $LnA_3(HA)_2$ species as suggested by Moreno *et al*.[13]

Looking at the LLn(III)-system (Figure 4-14A), it should firstly be mentioned that within these slopes the natural selectivity of D2EHPA can be explained. The ionic radii decreases across the Ln group, and due to the resulting increased charge density and electrostatic attraction, the stability of the extracted complex increases.[6] Furthermore, Ellis *et al*.[28] showed the increased strain energy of the larger LLn elements as opposed to the smaller heavy Ln elements within their specific computational system.

The steady increase in gradient m from La to Nd illustrates the decreasing strain and increasing stability of the multi-dentate ligand. So, while the smaller Nd can easily accommodate the three dimeric species, posed in Equation 4.2, the same cannot be said for the larger La. Hereby then the mechanism in Equation 4.3 becomes ever more likely resulting in a gradient midway between 2.5 and 3.

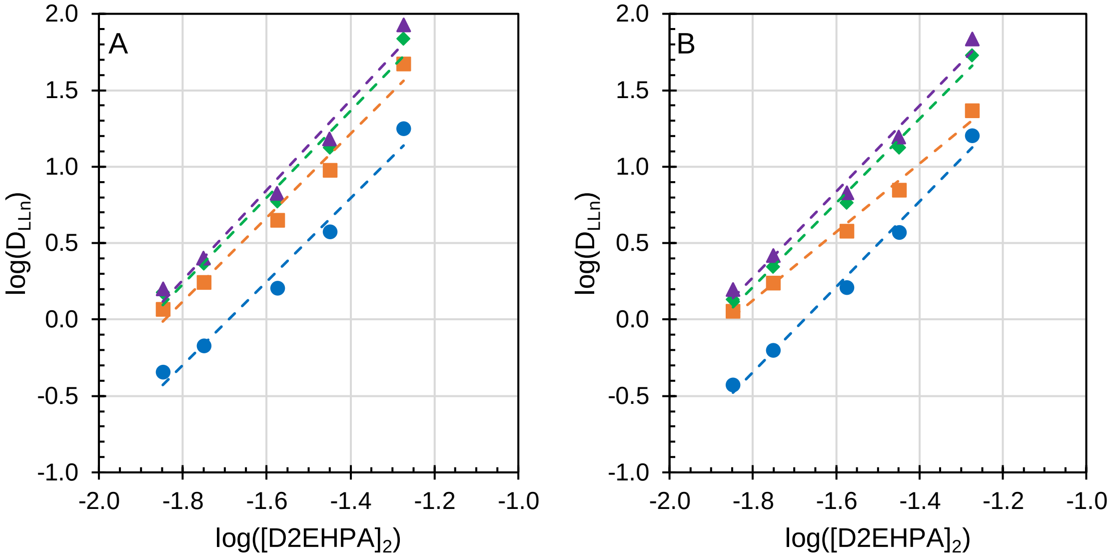

Figure 4-14: **The increasing distribution ($\log(D_{LLn})$) of the LLn elements, ● La; ■ Ce; ♦ Pr; ▲ Nd, from (A) the LLn(III)-system ($pH_F = 3.6$; $[H_2O_2] = 0.000$ M), and (B) the LLn(IV)-system ($pH_F = 2.72$; $[H_2O_2] = 0.040$ M), as a function of increasing extractant concentration ($\log[D2EHPA]_2$).**

In general the slopes obtained from the LLn(IV)-system (Figure 4-14B) are similar to those in the LLn(III)-system and the same general trends were observed. In this system however, Ce was optimally oxidized with H_2O_2 and the effect is significant. On the basis of selectivity, it can be clearly seen that the extraction of La, Pr, and Nd remained remarkably unscathed from the oxidation process. As was the case in the LLn(III)-system, the mechanism in Equation 4.2 is presumed dominant for Nd extraction, and becomes less so towards La.

Table 4-1: **The linear trend line gradient (*m*) and its R^2 value of the LLn elements as obtained from Figure 4-14.**

LLn	**LLn(III)-system**		**LLn(IV)-system**	
	m	**R^2**	***m***	**R^2**
La	2.73	0.976	2.79	0.989
Ce	2.74	0.978	2.24	0.989
Pr	2.84	0.977	2.75	0.991
Nd	2.94	0.977	2.81	0.988

In the case of Ce, a dramatically lower gradient was observed as a result of its oxidation with H_2O_2. Keeping in mind that the LLn(IV)-system did not contain only Ce(IV), but also Ce(III) species, this then represents the combination of both mechanisms. From the slope of 2.24 it can be surmised that the mechanism involved during Ce(IV) extraction is even further removed from the one given in Equation 4.2. That is if it was indeed Ce(IV) species which were extracted.

Using the same charge balance consideration made by Moreno *et al.*[13], the Ce(IV) species possibly extracted can be postulated. Similar to the mechanism in Equation 4.3, gradients closer to 2.5 indicated that *p* and *n* were still either 2 or 3, respectively, and extraction possibly occurred as the formation of $Ce(NO_3)_2A_2(HA)_3$ species. Otherwise, similar to Equation 4.2, if the stoichiometry approaches 2, it points to the possible formation of $Ce(NO_3)_2A_2(HA)_2$ species. Without the confirming slope analysis of the equilibrium pH, however, this remains conjecture. The implication of this oxidation process however is far more tangible.

4.4.2.2 Separation

The subsequent effect on separation is shown in Figure 4-15, where the separation factor was again calculated in terms of the target metal Nd (Equation 2.4). Nd has the largest extractant affinity, and with increased access to the extractant as [E/LLn$_T$] increased, this natural selectivity was exploited leading to increased separations. Consequently β_{Ce} in the LLn(III)-system (Figure 4-15A) increased from 1.3 to 1.8 when [E/LLn$_T$] increased from 4 to 30.

Within the context of this comparative study, this obtained selectivity can be viewed as the natural separation achievable using this SX system. In contrast, the incorporation of H_2O_2 within the same system yielded significantly greater separation. As can be seen from the LLn(IV)-system (Figure 4-15B) β_{Ce} increased substantially more to 2.9 throughout the same range.

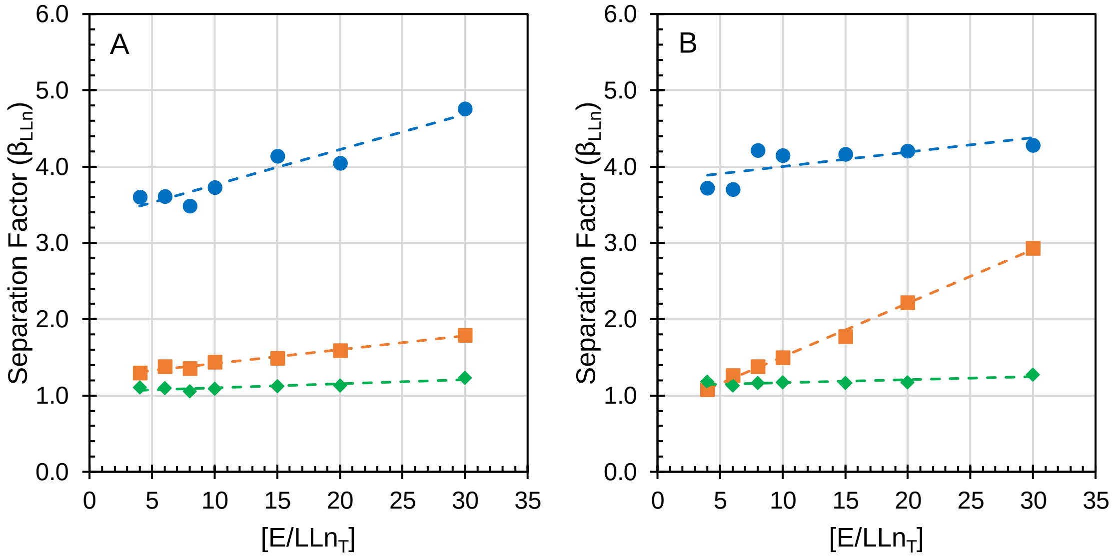

Figure 4-15: The separation factor ($\beta_{LLn} = D_{Nd}/D_{LLn}$) of the LLn elements, ● β_{La}; ■ β_{Ce}; ♦ α_{Pr}, in (A) the LLn(III)-system ($pH_F = 3.6$; $[H_2O_2] = 0.000$ M) and in (B) the LLn(IV)-system ($pH_F = 2.72$; $[H_2O_2] = 0.040$ M).

Herein lies a contradiction. From the distribution it was stated that the extractant affinity increased with decreasing size, yet the extraction of the smaller Ce(IV) was less than the logically bigger Ce(III). It was also observed that Ce(IV) extraction was far less dependent on the extractant concentration yet the separation increased due to apparent suppression of Ce extraction throughout the study. So the question begs; why is Ce extraction suppressed while all evidence indicates that it should occur more readily. Attempting to answer this question, the focus ultimately shifts to the recovery of these metals once they have been extracted.

4.4.3 Effect of Strippant Concentration [HNO_3]

During this LLE study, extraction was optimized using the mechanistic pH_F dependency. By increasing pH of the metal bearing feed solution, the forward extraction reaction was favoured. For stripping, the reverse was used where the loaded organic phase was contacted with increasingly acidic solutions to strip the metals back into a second aqueous phase. To minimize the chemicals involved, nitric acid (HNO_3) was used as the strippant representative, effectively forming nearly the same aqueous matrix from which the metals were first extracted.

The % stripping achieved with increasing [HNO_3], is shown in Figure 4-16. It is seen that the order of back-extraction was the reverse of extraction. This was expected since the metal with the highest extractant affinity should be the hardest to strip, and conversely, the metal with lower extractant affinity, would be recovered more easily. La exhibited the lowest extraction throughout this study, and as expected then, showed the easiest stripping.

Between the LLn(III)-system (Figure 4-16A) and LLn(IV)-system (Figure 4-16B) very small differences were observed. The LLn(III)-system once again serves as natural baseline for the system and it should be evident that La could be easily separated using this process step as well. Separation of the remaining LLn metals with this step is however almost non-existent, since the stripping profiles of Ce, Pr, and Nd were almost identical. This is again a consequence of the statistical probability favouring Ce. Within the LLn(IV)-system, the stripping profiles separated analogously to those considered during extraction.

It was previously observed that the Ce oxidation within this system resulted in increased extractant availability for the remaining LLn metals. The increased transfer to the organic phase can be seen in the increased dispersion of the LLn(IV)-stripping profiles. The chemical selectivity again started to dominate resulting in individually observed profiles. This is expected but these changes are far too slight to exploit towards actual separation within this process.

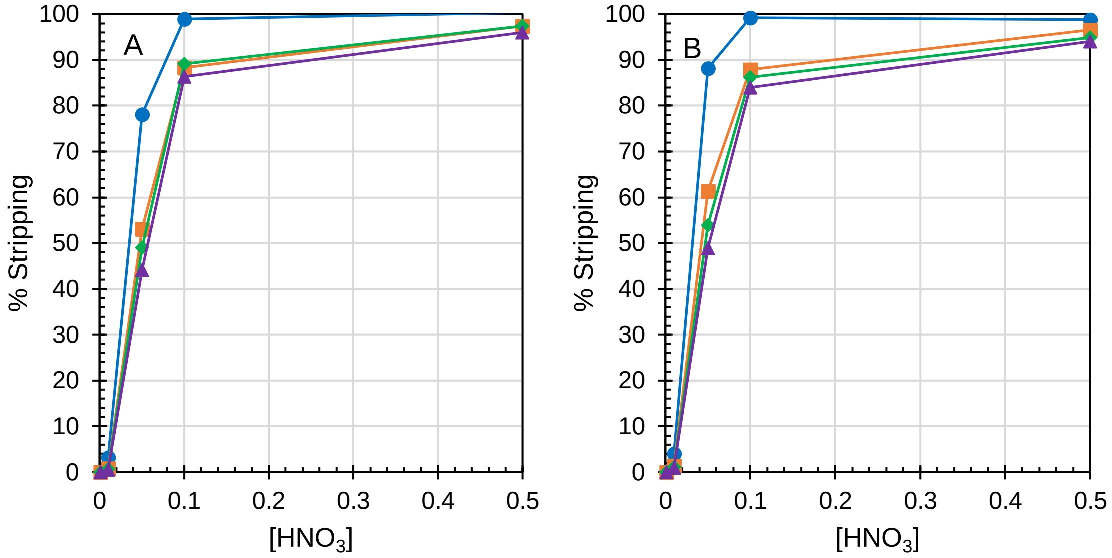

Figure 4-16: **The % back extraction of the LLn elements, -●- La; -■- Ce; -◆- Pr; -▲- Nd, from optimally loaded (A) LLn(III)-system ($[H_2O_2]$ = 0.000 M) and (B) LLn(IV)-system ($[H_2O_2]$ = 0.040 M), as a function of the strippant concentration $[HNO_3]$.**

Considering that the mechanism of Ce extraction presumably changed, the same should hold for stripping and herein the extraction preference is again in question.

- If it is assumed that Ce(IV) species are extracted preferably to Ce(III) according to its own mechanism, then it should be harder to strip Ce(IV) than Ce(III) which should result in its decreased stripping performance in the LLn(IV)-system.

- Conversely, if Ce(III) extraction is preferable, then stripping Ce from the LLn(IV)-system should be similar to the LLn(III)-system.

Through comparison it can be seen that the stripping performance of Ce remained virtually identical between the LLn(III)- and LLn(IV)-systems. Hereby it follows that Ce(III) extraction is favoured in this extraction system. Furthermore; throughout this study, very little discolouration of the organic phase was observed, and the colour change associated with oxidation slowly dissipated upon contact with the organic phase indicating reduction to Ce(III). This supports the statement that Ce(III) was preferentially extracted over Ce(IV).

4.5 Pertraction

In the LLE study, the extraction of the LLn elements by D2EHPA from a nitric acid medium was observed, and thereupon the chemical oxidation of Ce with H_2O_2 was shown to increase separation. In this last experimental section, the physical application of this separation process is amended to include the use of a HF membrane contactor. Hereby PX with this specific membrane module and application method as feasible separation process of the LLn elements was tested.

4.5.1 Comparative Extraction Study

Similar to the LLE study, the separation of these elements through circulating batch PX was done for both the LLn(III)-system and the LLn(IV)-system. In the latter, the liquid-liquid oxidation of Ce with H_2O_2 was achieved and comparatively, the benefits of adding this green oxidizer to a working LLn PX system are evident. In Figure 4-17, the % extraction achieved is presented as function of the time circulated.

The patterns in their extraction are familiar and observations made within the LLE study are effortlessly transferred to PX. In the LLn(III)-system (Figure 4-17A), the fundamental LLn separation problem is observed. Within this Ce dominant system, the % extraction of Ce is almost identical to that of Pr and Nd with La following close behind.

Within the context of circulating batch PX, the elapsed time becomes a measure of membrane contact area used (Equation 3.5) and as the number of circulations add up, nearly the same respective chemical equilibria are achieved in either system. This might infer some possibilities toward optimizing separation by altering the membrane length, but ultimately it is the rate by which each individual metal is transferred from the feed to the solvent over the same length of membrane which creates separation, as will be shown.

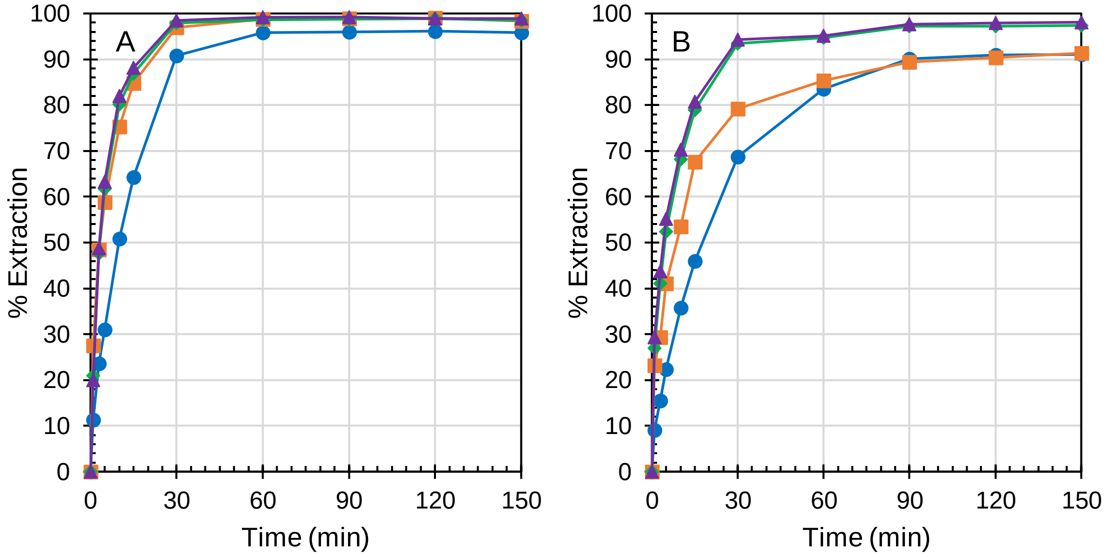

Figure 4-17: The circulating batch PX of the LLn elements, -●- La; -■- Ce; -◆- Pr; -▲- Nd, from (A) the LLn(III)-system ($[H_2O_2]$ = 0.000 M, pH_F = 3.81), and (B) LLn(IV)-system ($[H_2O_2]$ = 0.040 M, pH_F = 2.51). $[LLn_T]$ = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. Extractant: D2EHPA. $[E/LLn_T]$ = 30. V_{Org}/V_{Aq} = 1. $\tilde{v}_{Org}/\tilde{v}_{Aq}$ = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

4.5.2 Comparative Stripping Study

Before the quantitative assessment of mass transfer rates, however, the observed recovery of these metals from the resulting organic phases using the same PX setup is first discussed. The stripping profiles for both systems can be found in Figure 4-18, and herein it can be seen that back extraction using the same PX system is not nearly as effective as their initial extraction. In either stripping system, less than 90% of the metal originally extracted was recovered back into the aqueous phase over a circulation period of 150 min.

This slow metal transfer rate is a result of the hydrophobic membrane used in this PX setup. The extraction reaction (Equation 4.3) is now reversed, and the metal bearing feed is in the organic phase. This means that several more resistances hinder the rate of transfer between phases than for extraction. This can be overcome by using a hydrophilic membrane for the stripping process so that the pores of the membrane are wetted by the aqueous stripping phase. Hereby the rate of transfer will once again be mainly influenced by the diffusion gradient of the LLn complexes in the organic phase.[29]

The stripping profiles observed in the LLn(III)-system (Figure 4-18A) and the LLn(IV)-system (Figure 4-18B), are nearly identical. Moreover, apart from maybe La, the differences between individual LLn elements within either system are non-existent. The results obtained here imply that there is no discernible difference between these loaded organic systems. Similar to the observations made in the LLE study then, it follows that the same oxidative species were present during both stripping experiments, and that very little, if any, Ce(IV) species were extracted into the organic phase.

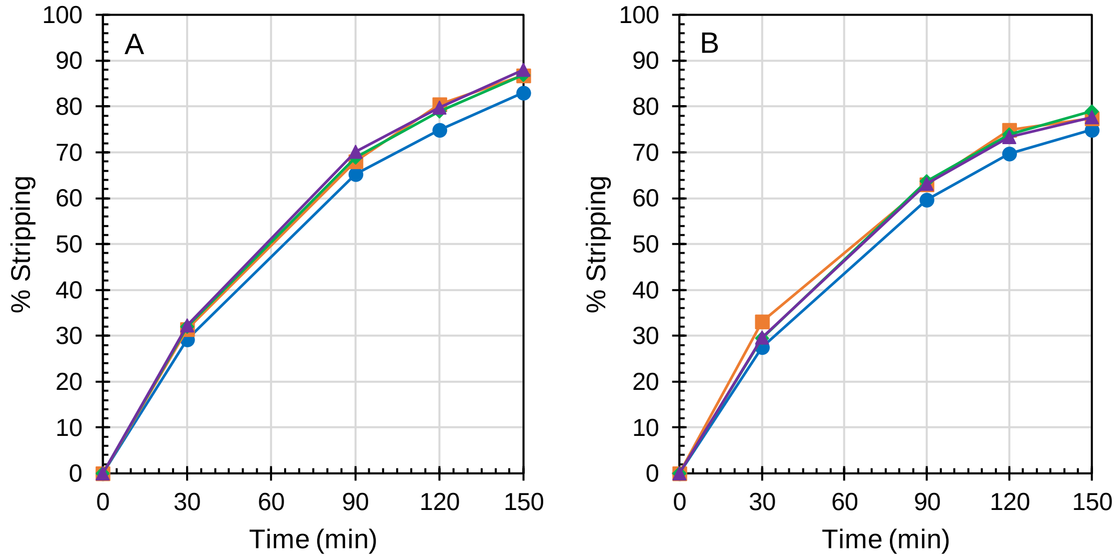

Figure 4-18: **Stripping the LLn elements -●- La; -■- Ce; -◆- Pr; -▲- Nd through circulating batch PX, from (A) the loaded LLn(III)-system (Strippant pH = -0.03), and (B) the loaded LLn(IV)-system (Strippant pH = -0.22).**

Within the context of this study the clear inefficiency of the stripping experiment merits no further deliberation, but an argument can be made for its relevance to the application method wherein the extraction and stripping steps are combined. During this application, the organic phase in the Lumin is replaced with an aqueous stripping solution after the membrane has been wetted by the organic phase. The aqueous feed solution and aqueous stripping solution are hereby separated by the organic filled membrane known as a Hollow-Fibre Supported Liquid Membrane (HFSLM). Two steps are hereby combined into a single membrane module.

In a series of individual publications, Wannachod e*t al.*[30], Wannachod e*t al*.[31] Wannachod e*t al*.[32] and Wannachod e*t al*.[33] fully investigated this application method also with regard to Ln separation. An identical Nd rich Ln source was used in all of these studies which implied application during late/final stage purification. For the most part, these studies focus on Nd using various extractants and mixtures thereof. It is obvious that using this application the consideration of the various resistances to metal transfer become much more complicated.

From the stripping profiles in Figure 4-18, it should be clear that the HFSLM application applied to this study will effectively reduce the cost of organic and membrane materials used in the process. It does not, however, affect the separation efficiency. Based on the stripping achieved in the LLE study (Chapter 4.4.3) and the clear similarities between the extractions via SX and PX, this stripping stage can in fact be used, at least as a viable option to separate La (scrubbing) from the rest of the LLn elements. As stated earlier, this can be done by using a hydrophilic membrane in a separate stage which merits its own investigation.

4.5.3 Comparative Mass Transfer

Among other concessions made within consideration of the used PX method (Chapter 2.5.1), it was presumed that the extraction reaction rate is very fast, and like all the transfer steps considered, contributes little toward the series of kinetic resistances which governs the rate of metal transfer (Q_{LLn}). In truth, the average mass transfer coefficients (k_{LLn}) calculated herein contains resistance presented by the aqueous diffusion rate, the extraction reaction rate, and in fact all the other resistances.[29]

Due to the relative size of these resistances they were assumed negligible during the derivation of Equation 2.12. Therefore calculating the magnitude of each component is not possible using this method. It does, however, allow for the qualitative assessment of PX as separation method for the LLn elements and equally as useful, it allows the measurement of change in overall transfer. Within this feasibility study these coefficients are therefore not only used to evaluate the separation process, but also become the final comparative measurement between the oxidized and un-oxidized systems.

Between the LLn(III)-system and LLn(IV)-system presented above in the comparative extraction study (Chapter 4.5.1), there is no difference with regard to metal concentration. Yet it can be seen in Figure 4-17 that there is a clear and obvious decrease in the rate of transfer of all metal species in the LLn(IV)-

system. The only differences which could therefore account for this change in transfer rate are the changes brought on by the oxidation process and therefore a decrease in the availability of extractable Ce species.

In Figure 4-19, the mass (mol) of individual LLn elements extracted over the first 15 min of circulation is presented for both systems. During this initial circulation period, it can be assumed that the concentration gradient is at a maximum. For both systems, the average mass flux (Q_{LLn}) over this period is represented by the slope of the dashed line through the origin.

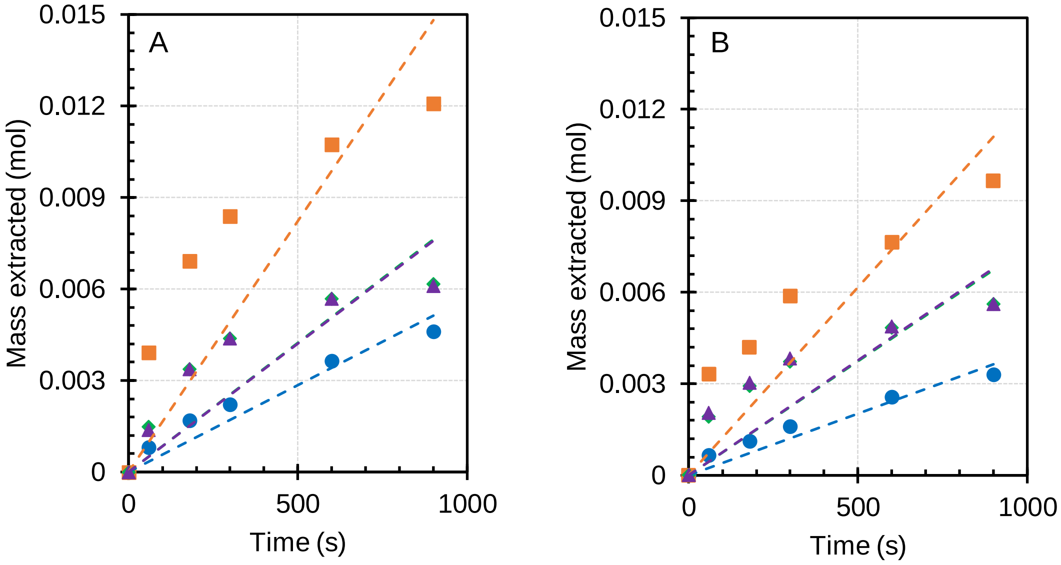

Figure 4-19: The mass extraction rate of the LLn elements, ● La; ■ Ce; ♦ Pr; ▲ Nd; in (A) the LLn(III)-system (pH_F = 3.81; [H_2O_2] = 0.000 M) and in (B) the LLn(IV)-system (pH_F = 2.51; [H_2O_2] = 0.040 M).

It can be seen in Figure 4-19 that the average transfer rate of Ce was much greater than that of either Nd, Pr or La, which is the result of the Ce rich aqueous phase. The transfer rate is dominated by the aqueous diffusion rate, and since the diffusion gradient increases with initial feed concentration, so too does the rate of transfer. The transfer rates of Nd, Pr and La, however, are more statistically comparable. As was seen throughout this dissertation, the behaviour of Pr and Nd is nearly identical, and analogue yet smaller La follows close behind. From the similarities of these elements (Chapter 2.2) it would be expected that had it not been for the high [Ce], its transfer rate would fit somewhere between La and Pr.

To gain more insight into the difference between the LLn(III)-system (Figure 4-19A) and the LLn(IV)-system (Figure 4-19B), the average mass transfer coefficients (k_{LLn}) of the individual elements provides more insight. These were calculated through Equation 2.12 using the observed transfer rate, and can be found in Table 4-2. It was previously stated that the differences between these systems can only be explained by the oxidation process and the subsequent result is seen on two fronts.

Table 4-2: The mass transfer coefficients (k_{LLn}) of the LLn elements as calculated from the average transfer rates in Figure 4-20.

LLn	**Mass transfer coefficient (k_{LLn} x 10^6)**		**Δk_{LLn} x 10^6**	**$\lambda_{LLn} = k_{LLn}/k_{Nd}$**	
	LLn(III)-system	**LLn(IV)-system**		**LLn(III)-system**	**LLn(IV)-system**
La	4.07	2.89	1.18	0.68	0.54
Ce	11.79	8.79	3.00	1.96	1.63
Pr	6.05	5.34	0.71	1.00	0.99
Nd	6.01	5.39	0.63	-	-

As a result of the oxidation process, the acidity of the LLn(IV)-system (pH_F =2.51) is lower than that of the LLn(III)-system (pH_F = 3.81), and through the thermodynamic equilibrium constant (K_{eq}) from Equation 4.4, this should lead to lower distribution values within this extraction system. The decreased extraction which is implied hereby, was not seen within the LLE study because the reduction of Ce (Equation 4.7)[5] counters the acidification through the oxidation of hydrogen.

$$Ce(OH)^{3+}{}_{(aq)} + H^{+} + e^{+} \rightarrow Ce^{3+} + H_2O \qquad (4.7)$$

Hereby the driving force behind the forward extraction reaction is maintained within the oxidized system in spite of the lower pH_F. In the LLE study this effect is masked but in the PX application this can be seen in the overall slower transfer in the LLn(IV)-system. From the chemical similarities between these elements discussed in Chapter 2.2, the resulting change reveals a clear pattern within the LLn group but the change observed for Ce (Δk_{Ce} x 10^6 = 3.00 m/s) is far removed from what this pattern might suggest (0.8 < Δk_{Ce} x 10^6 > 1.1).

In the LLE study it was concluded that it is in fact only the trivalent Ce species which are extracted, and this deduction is supported by the findings in this PX study. So in a system with mostly Ce(IV) species, extraction would presumably have to wait until reduction to Ce(III) occurred through either Equation 4.6 or 4.7. This implies that upon first contact between the liquid phases, the trivalent LLn species are first extracted, which includes Ce(III) species still present within the oxidized system. Only after sufficient acidification of the aqueous phase by these forgoing extractions, does the trivalent Ce species become more dominant and can then be extracted.

The rate of Ce extraction within the LLn(IV)-system is therefore not only dependent on the rate of reduction back to Ce(III) but also the rate of foregoing trivalent extraction whereby reduction is facilitated. This is the ultimate effect of the oxidation process and results in the large change in the k_{Ce}. It is the selectivity by which Ce transfer is altered which ultimately results in increased separation and therefore increased process efficiency. In PX applications, separation is achieved through the differences in transfer rates and the individual mass transfer coefficient ratio (λ_{LLn}) in Table 4-2 is a measure of the efficiency by which each metal can be separated from Nd under these particular PX conditions.

It can be seen herein that the transfer rate of Ce is twice that of Nd in the LLn(III)-system because there are twice as many Ce ions driving its concentration gradient. So for each unit of Nd transferred, twice the amount of Ce is transferred over the same membrane length and the result is the same mixture only in the organic phase. Through the oxidation of Ce with H_2O_2 the [Ce(III)] in the LLn(IV)-system is lowered reducing its effective concentration gradient. For every unit of Nd transferred herein, only 1.6 units of Ce is transferred over the same membrane length. Hereby separation of Ce was successfully increased. The transfer of La is much slower than that of Nd in either system affirming the ease by which it can be separated. This deduction was made as early as Chapter 4.4.1. Alternatively, the transfer of Pr remains almost identical in both system yielding no separation whatsoever.

4.6 Conclusion

In this chapter D2EHPA was initially identified as extractant candidate with which the separation of the LLn elements through PX was evaluated. Upon optimizing the novel Ce oxidation process with H_2O_2, its effect on this working separation process was illustrated though a comparative optimization of both oxidized and un-oxidized systems.

It was clearly shown that the addition of H_2O_2 to a representative extraction system at low [acidic], yielded the oxidation of Ce(III) to Ce(IV), and ultimately the preferred Ce(III) was easier to extract because of its much lower hydration enthalpy (ΔH = -3326kJ/mol) compared to Ce(IV) (ΔH = -6309kJ/mol).[6] Therefore, throughout the extraction process, Ce(IV) was most likely reduced back to Ce(III) before extraction occurred.

Lastly, the PX application was investigated. It was hereby shown that H_2O_2 can be effectively employed to induce Ce oxidation within a liquid-liquid PX system, and it was seen that this simple addition to a functioning PX system resulted in decreased Ce flux through the membrane leading to increased separation from Nd and a more efficient process. The process avoided precipitation and claimed a stake in the feasible separation of Ce through liquid-liquid processes.

The use of this pre-oxidized extraction system requires far more research as the multiple kinetics within this ever changing redox system complicates definition of the extraction mechanisms. It can however be said that this serves as a proof of concept towards possible increased separation and will set the basis for further research.

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CHAPTER 5

CONTENT

5 Evaluation

5.1 Introduction

This study focused on the separation of the LLn elements, specifically through the membrane facilitated SX process known as PX. As discussed in the economical consideration (Chapter 1.1.2.2), the driving force behind LLn separation research stems from the value of Nd and is defined herein as the target metal. Aiming (Chapter 1.2.1) to evaluate the PX as a viable separation process for these elements, three core objectives (Chapter 1.2.2) were identified.

The first of these objectives was the completion of a multifaceted literature review which is discussed hereafter in Chapter 5.2. The second objective entailed the identification and optimization of a suitable extraction system which could then be used in the third objective, the PX of the LLn elements. These two objectives are individually discussed in Chapter 5.3. Hereby the attainment of the aim is made possible, and the final evaluation is presented in Chapter 5.4 followed by recommendations in Chapter 5.5, and future work as suggested by this study in Chapter 5.6.

5.2 Literature Overview

The first objective was an extensive three-pronged literature study (Chapter 2) aiming to define the separation problem at hand. Herein the fundamental chemistry (Chapter 2.2) of the Ln elements was firstly considered in order to elucidate the basic similarities between these f-block elements. These similarities were shown through consideration of the individual orbital energetics and ultimately revealed a single viable option whereby separation could possibly be bettered i.e. the oxidation of Ce.

It was shown that the separation of the LLn elements through SX processes (Chapter 2.4) is well known and that the manipulation of Ce's oxidation state is often used to increase separation. Moreover, this is commonly applied in foregoing beneficiation or recycling processes (Chapter 2.3) such as roasting and leaching. Ultimately however, a mixture of these elements persists in effluent streams, often of low metal concentration. As was shown by the mineralogical consideration (Chapter 1.1.2.4) the elemental distribution of these streams is similar to the common source ores making this study applicable to LLn beneficiation and recycling processes in general.

Upon definition of the separation problem and identification of possible chemical manipulations, the specific PX application was considered. Herein the multiple advantages of the PX application over conventional SX methods were discussed, and it was concluded that within the planned application method (Chapter 3.3.4), using a sufficiently effective SX system, separation is predominantly based on the diffusion rate of the elements within the aqueous phase. Hereinafter a derivation of the mass flux equation (Equation 2.12) was presented whereby the observed mass transfer rate between liquid phases could be used to ultimately evaluate PX as viable separation process for LLn elements.

5.3 Separation Study

Experimental work (Chapter 4) using the presented materials and methods (Chapter 3), starts with the identification and confirmation of a working extraction system. Herein it was found that bis(2-ethylhexyl) phosphate (D2EHPA) was capable of extracting LLn elements advantageously from low acidic aqueous solutions. Hereby an environmentally friendly SX system was identified. Furthermore, the low acidic conditions necessary for extraction by D2EHPA allowed for the novel application of H_2O_2 as liquid oxidizer of Ce. The feasible application hereof was then shown through UV/Vis- spectroscopic analysis as a function of the H_2O_2 and H^+ concentrations. Hereby then an alternative extraction system was proposed and to illustrate the effect of this oxidation process, this system was simultaneously and identically investigated alongside the unaltered system.

5.3.1 Liquid-Liquid Equilibrium

Upon optimizing the oxidation process, a simultaneous comparative study was completed wherein the aqueous proton and organic extractant concentrations were used to maximize extraction within respective oxidized and un-oxidized systems. Herein the separation problem identified within the literature study was clearly visible in the un-oxidized LLn(III)-system. Of the three LLn elements (La, Ce and Pr) it is only La which could effectively be separated from Nd within this system. Due to the increased concentration of Ce, very little separation was achieved and as for Pr, its chemical similarity to Nd means separation was nearly non-existent.

Through consideration of the individual distribution ratios as a function of the extractant concentration, it was shown that extraction predominantly occurs according to the extraction mechanism posed in Equation 4.2. Hereby the selectivity of this extraction system to the individual LLn elements was explained and in comparison, the effect of Ce oxidation in the LLn(IV)-system was evident. The subsequent recovery of these elements from the loaded organic phase clarified not only the separation problem in the original LLn(III)-system, but also elucidated the achieved effect in the LLn(IV)-system.

It was found that the simple addition of H_2O_2 to the D2EHPA extraction system showed significantly better Ce separation by supressing its extraction within this system. During the recovery step, it was shown that very little, if any, Ce(IV) species were extracted and only once reduction to Ce(III) had occurred, was Ce extraction achieved. These findings therefore showed that the use of H_2O_2 as an environmentally friendly option to common oxidation techniques is not only viable but vastly beneficial to the separation of Ce from Nd.

Herein then both the LLn(III)-system and the LLn(IV)-system was optimized. In both systems the extraction was maximized at respective feed acidities (pH_F = 3.6 and 2.72), and using enough extractant (E/LLn_T =50) more than 99% could effectively be extracted. This would be necessary for the initial bulk separation of impurities. The D2EHPA extraction system was therefore highly effective in LLn extraction and suitable for the PX investigation which followed.

5.3.2 Pertraction

The membrane based application of both oxidized and un-oxidized systems using a HF contactor was then completed. Herein it was shown that within the LLn(III)-system, the separation problem pertaining to Ce and Pr at least, persisted even within PX. By comparison, in the LLn(IV)-system it was shown that the advantages of Ce oxidation with H_2O_2 translated effortlessly to the PX system and the separation of Ce was improved to a major extent. The observed mass flux rates of both systems were then used to qualitatively observe the change in mass transfer coefficients of individual species brought on by the oxidation process. Herein, the conclusions made within the LLE study were used to explain the marked decrease in the transfer rate of Ce whereby its separation from Nd was successfully achieved.

5.4 Evaluation

The completion of the objectives discussed above finally makes it possible to evaluate the separation of LLn element using the PX process. The first objective provided the relevant insight into Ln chemistry within context of hydrometallurgical separation processes SX and PX. Hereby the fundamental separation problem could be defined and understood, which in turn yielded the revelation as to why only Ce redox chemistry is commonly used to aid in LLn separation.

In the second objective the extraction system to be used in the PX process was defined using efficiency as sole criteria. Herein the difficulties of LLn separation was illustrated beautifully by the representative extraction system chosen, and a baseline was set whereby improvement was ultimately the goal. Although the chemical options available in this endeavour might be limited to Ce oxidation, as identified in the first objective, the manner by which Ce should be oxidized is still debated. A novel environmentally friendly option is presented herein through H_2O_2. Throughout this objective the effect of this oxidation process was measured against the aforementioned baseline in identical optimizations.

In the final objective these optimized systems could be applied in a PX setup so that the PX of the LLn elements could be evaluated, and so to the performance of H_2O_2 as oxidizing agent. The low acidic conditions required not only for extraction but also oxidation has yielded, through this study, a potential separation system for the LLn elements which is not only environmentally sound, but also highly efficient.

Ultimately it was the aim of this study to evaluate the PX process as viable separation process, and to this end the separation of the La, Ce and Pr from Nd through the applied method and material used, is hereafter considered individually:

- As was seen throughout this study, the separation of La is easily achieved in either the LLn(III)-system or the LLn(IV)-system. From the high separation factors and slower rates of transfer observed for La, this holds true whether through conventional SX or PX. This results from the increased affinity of the extraction system toward the other smaller and heavier LLn elements, which within a PX application, results in a much slower rate of transfer. Hereby then PX is a well suited process for the purification of La and from the observed results it can be said that both the extraction and recovery steps could be effectively used to this end.

- The Ce rich aqueous feed solution results in very little separation of Ce from Nd in the baseline LLn(III)-system. This statistical effect was observed within SX as well as the PX application since the diffusion gradient of metal species in the aqueous phase is dependent on their concentration. Only through the oxidation of Ce could separation be efficiently achieved by selectively varying the concentration of extractable Ce species. It was shown that the addition of H_2O_2 to the aqueous feed solution before pH control could be used to this end and results in increased separation of Ce from Nd in both SX and PX processes. From as inseparable as Pr to as separable as La, the extraction and therefore the transfer rate of Ce is slowed and can be effectively removed from Nd containing solutions using PX as separation method.

- Ultimately the chemical similarities of Pr and Nd means that their separation will invariably be tediously inefficient regardless of the separation method. Even when using PX, the extraction of these two metals are virtually identical. This could be concluded as early as the literature investigation, and since no viable chemical alternatives are available, as was the case with Ce, the separation effort here becomes mechanical in nature. On the basis that the affinity of the extraction system favours Nd over Pr it is conceivable that increasing the interfacial contact area could lead to increased separation. This is the advantage of PX over SX and hereby it remains the most viable separation process for even Pr.

Although the process design is beyond the scope of this study, it should follow logically that end-to-end stages of the PX process showed in this study could effectively be used to separate La, and incorporating H_2O_2 as oxidizer the same can be said about Ce. For Pr, however, the separation problem persists.

5.5 Recommendation

It is known that there are various extractants which could be effectively used in the extraction of the LLn elements. Considering that each of these requires its own working conditions, and the environmental impact thereof, it is recommended hereby that future separation efforts continue using D2EHPA or analogous phosphorous species as extractant. It was shown in this study that these cationic exchangers are highly efficient at low acidic conditions yielding a process which is cost efficient and safe to maintain. Boosting this environmental recommendation is the accompanied use of H_2O_2 as green oxidizer since it generates no by-product to clean, and works under the same low acidic conditions required for extraction.

Through this study it can also be recommended that PX is a viable separation process. For La and Ce this has been clearly shown and even though the separation of Pr remain frustratingly difficult, various possibilities for future improvement present themselves when the applied PX method is considered.

5.6 Future Work

In an effort to address the Pr-Nd separation problem discussed above, the development of a Spiral-Wound (SW) membrane contactor was ongoing throughout this M.Sc. project. Due to manufacturing issues, the development of this contactor could not be completed in time and therefore did not form part of this study. It does, however, remain a viable avenue of research for future work.

As part of her Hons BSc project in 2016, Miss. Anje Claassens investigated several commercial membranes with which the module could be constructed. Using a constructed containment cell, different membrane types were used to separate the liquid phases within respective cavities similar to conventional membrane contactors. Herein the effective contact area was identically limited for each membrane so that their mass transfer performance under identical extraction conditions could be compared directly. A photo of this setup can be seen in Figure D1 in Appendix D. Her findings suggested the use of the Celgaurd 2400 membrane.

Hereafter, the manufacturer of the SW-module (SolSep B.V.) provided various adhesive samples for their possible use in construction. These samples consisted of sections of the intended construction tubing whereon pieces of the identified membrane (Celgaurd2400) were glued with five different adhesives. These samples were placed in the organic diluent in order to evaluate their stability over a period of time. Hereby it was found that the third adhesive, described by Solsep only as “Epox”, was stable for up to 120h. Photos of these samples before and after testing are shown in Figures D2 and D3 and can be found in Appendix D.

Through these two studies, the construction of the SW-contactor, seen in Figures D4 to D6, was completed by the end of 2017. The photos seen herein were generously provided by Solsep B.V. Herein then a separate word of gratitude to Dolf Bruinsma and Solsep B.V. for their vested interest and support in this project. Unfortunately, during initial setup and testing of this module, an internal leak resulted in complete failure to separate the liquid phases. Degradation of the adhesives between membrane layers is the suspected cause. While disappointing for this study, this remains a possible topic for future research upon reconstruction of the module.

In general, there are a few aspects which merit further research attention. The complete design of a PX process requires a more detailed description. In this study, the [LLn] remains fixed in all feed solutions, yet with each consecutive step in the process this will change. Logically at very low [LLn], the extraction efficiency within the SX context will start to suffer so that smaller D_{LLn} values are obtained, and within the PX application the resulting low ΔLLn_{Ave} leads to slower mass transfer.

The recovery of these metals also merits much more research, specifically stripping using a hydrophilic membrane. In this study the recovery step using PX was generated with a hydrophobic membrane. The inefficiency of this application was evident although some chemical insight was gained. The recovery of these metals from the loaded organic phase would therefore merit its own research as an individual purification step or simultaneously in the HFSLM application briefly discussed in Chapter 4.5.

Furthermore, in the PX application used in this study, the respective phase flow rates were kept constant and equal in order to compare the respective oxidized and un-oxidized systems. Variation of these flow rates could be used to further investigate the multiple resistances involved, which in this study were assumed to be negligibly small during calculation of k_{LLn}. Hereby it follows that the much slower transfer rate of the Ce and La in the LLn(IV)-system can be exploited by varying the flow rate ratio ($\frac{V_{Aq}}{V_{Org}}$).

During the Ce oxidation study it was observed that the lifetime of the Ce(IV) species (indicated by the yellow colour) in solutions containing only Ce, is much shorter compared to that in solutions containing all four LLn elements. This suggests a redox couple with one of the other LLn metals. Some evidence of this was observed in the UV/Vis-spectroscopic analysis through small absorbance changes at wavelengths associated with Pr.

The location of these absorbance changes within the tail of the Ce(IV) peak renders these findings insufficient for concise deliberation. It would suggest, however, that Ce(IV) could be used in turn to oxidize Pr(III) to Pr(IV) in a chain like oxidation reaction. If true, this could be exploited to increase separation of Pr, as was done in this study with Ce. Testing this theory however, requires far more accurate analysis than was used here, possibly the absorbance within the IR region could be used for better discrimination between the metal species.

6 Appendixes

6.1 Appendix A

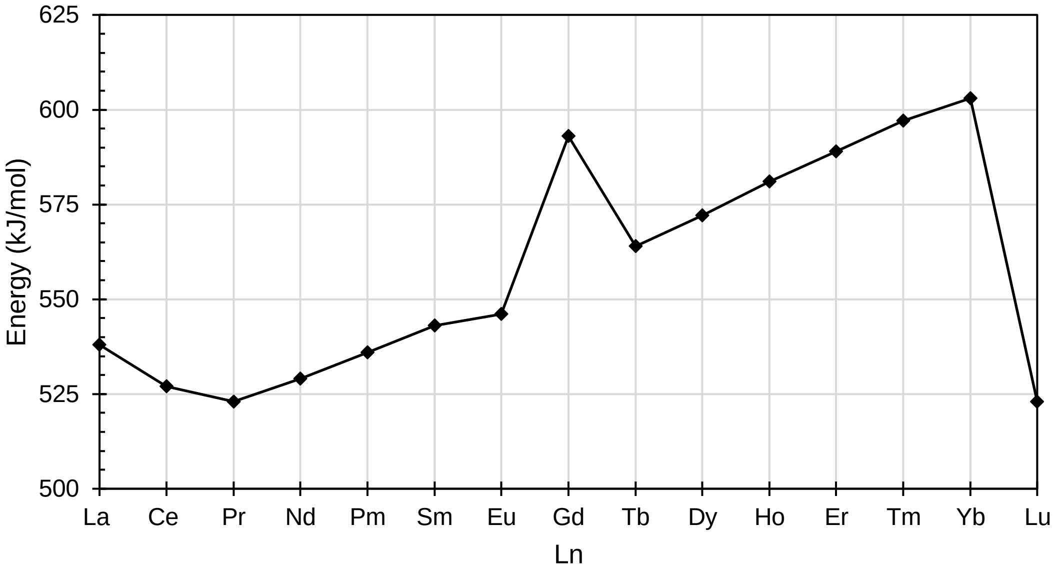

Figure A1: The first ionization (I^1_{Ln}) energies of the lanthanoid elements.

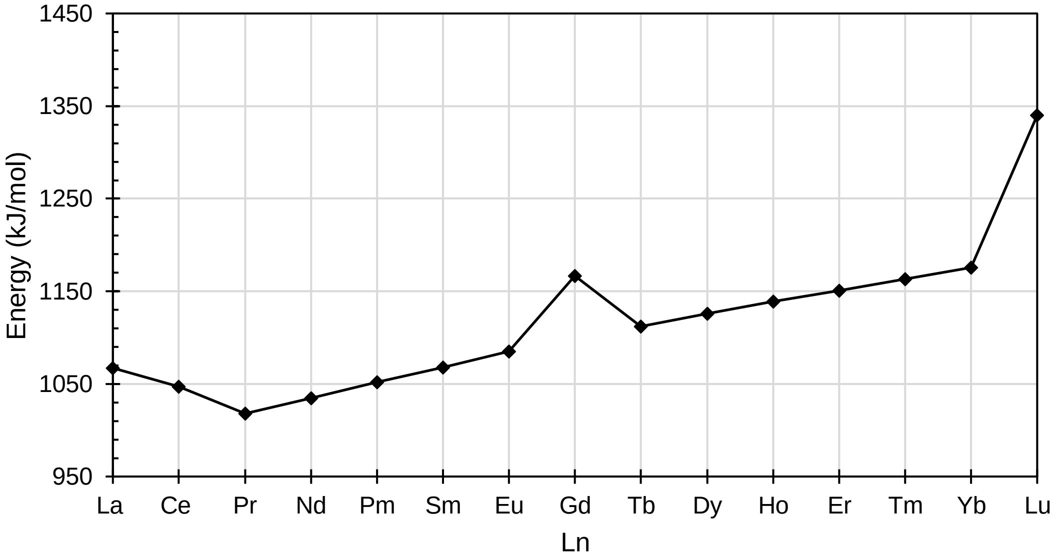

Figure A2: The second ionization (I^2_{Ln}) energies of the lanthanoid elements.

6.2 Appendix B

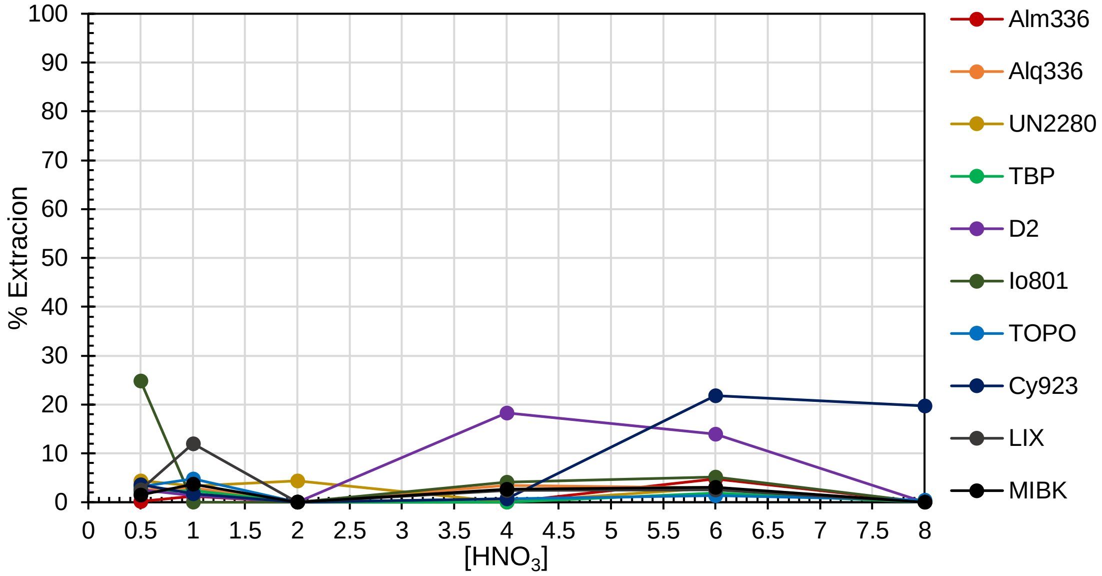

Figure B1: **The % La extracted from LLn phosphate feed solutions of various nitric acid concentrations. [LLn$_T$] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

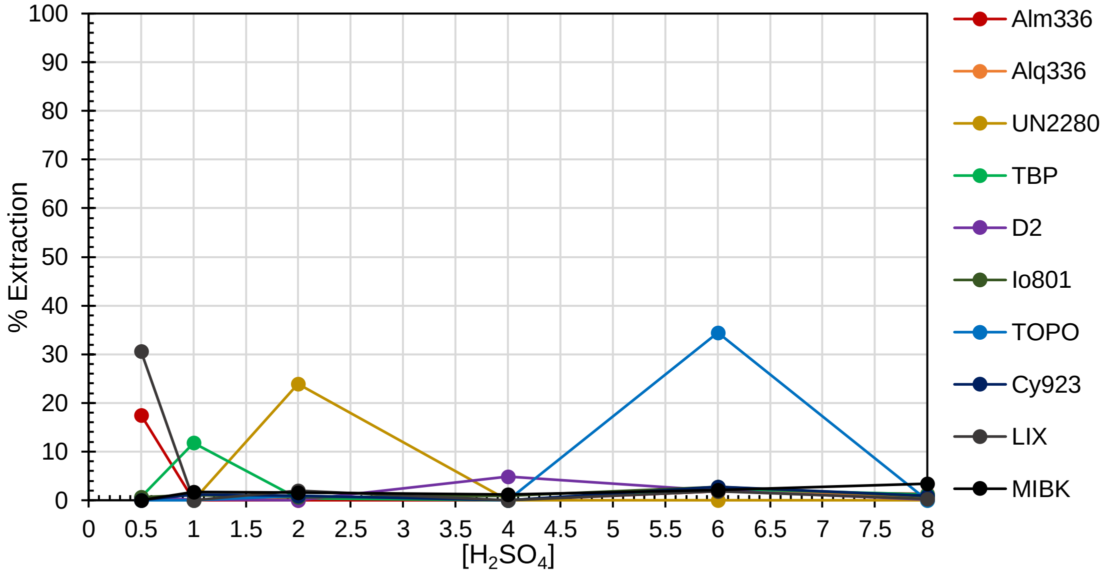

Figure B2: **The % La extracted from LLn phosphate feed solutions of various sulphuric acid concentrations. [LLn$_T$] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

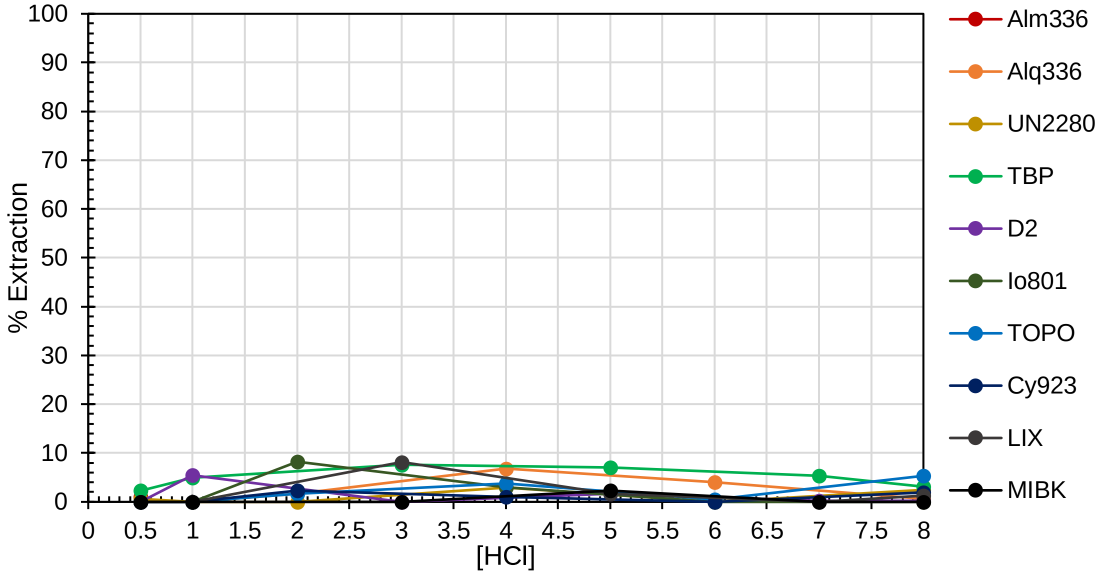

Figure B3: The % La extracted from LLn phosphate feed solutions of various hydrochloric acid concentrations. [LLn_T] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn_T] = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

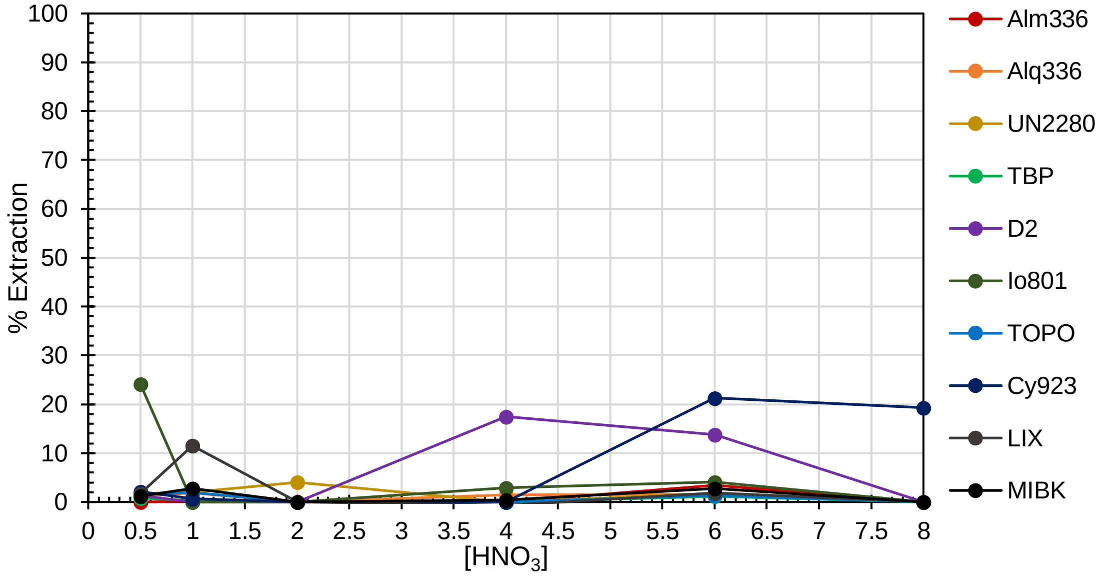

Figure B4: The % Pr extracted from LLn phosphate feed solutions of various nitric acid concentrations. [LLn_T] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn_T] = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

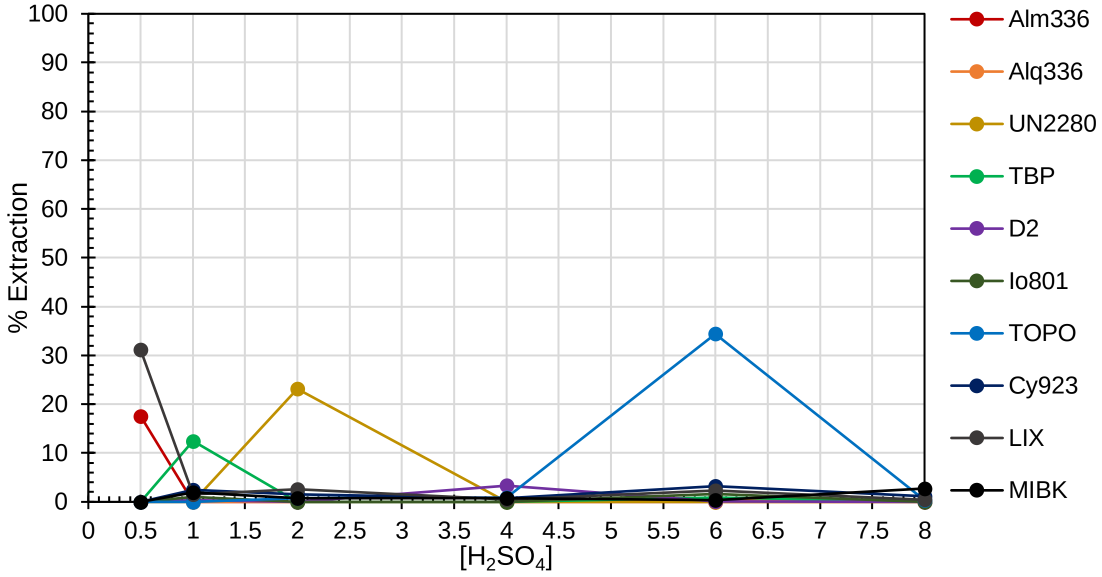

Figure B5: **The % Pr extracted from LLn phosphate feed solutions of various sulphuric acid concentrations. [LLn$_T$] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V$_{Org}$/V$_{Aq}$ = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

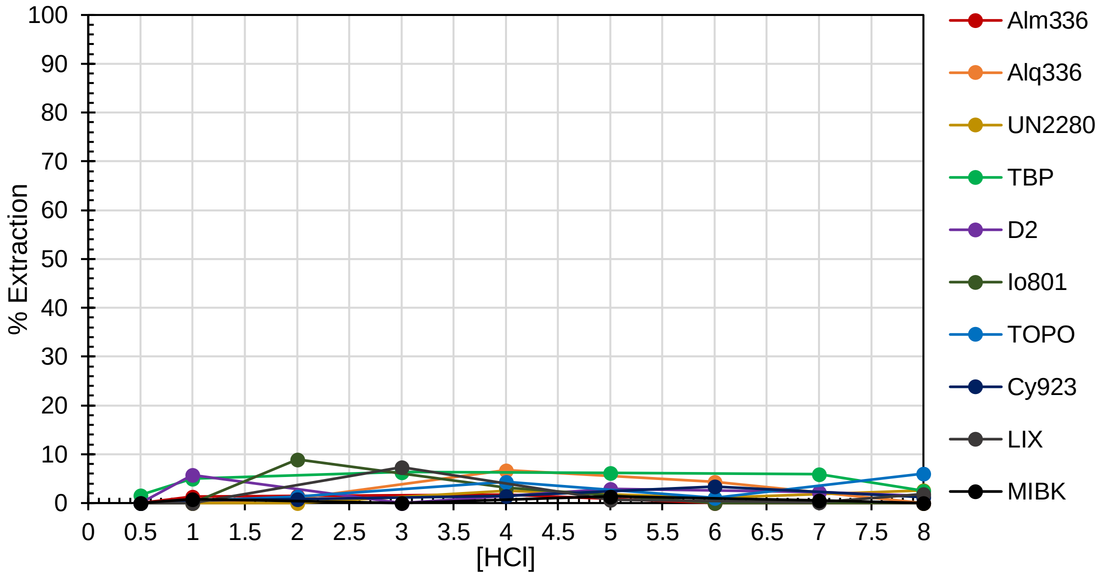

Figure B6: **The % Pr extracted from LLn phosphate feed solutions of various hydrochloric acid concentrations. [LLn$_T$] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V$_{Org}$/V$_{Aq}$ = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.**

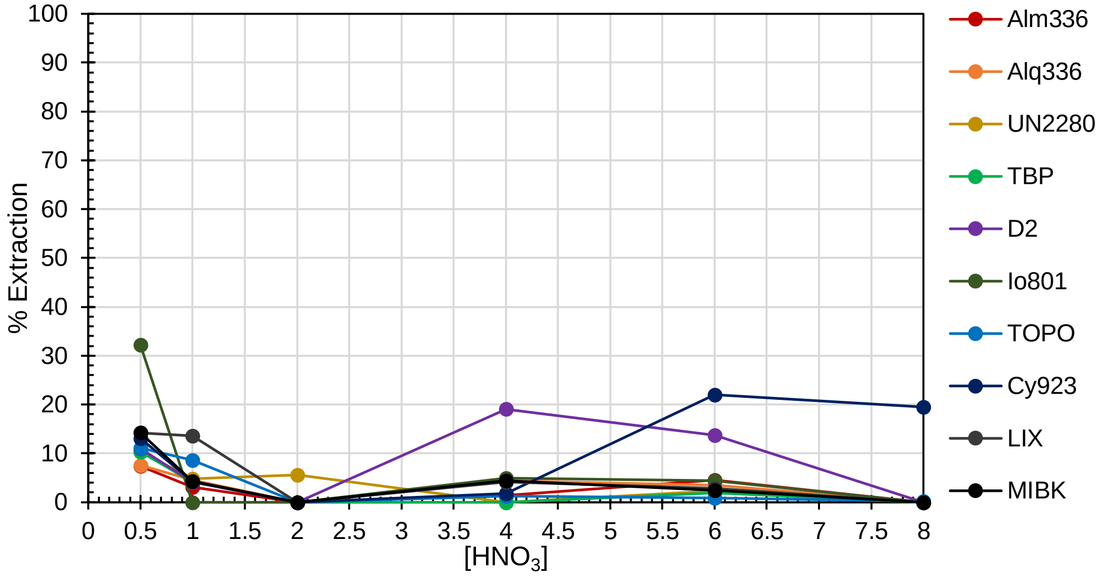

Figure B7: The % Nd extracted from LLn phosphate feed solutions of various nitric acid concentrations. [LLn$_T$] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

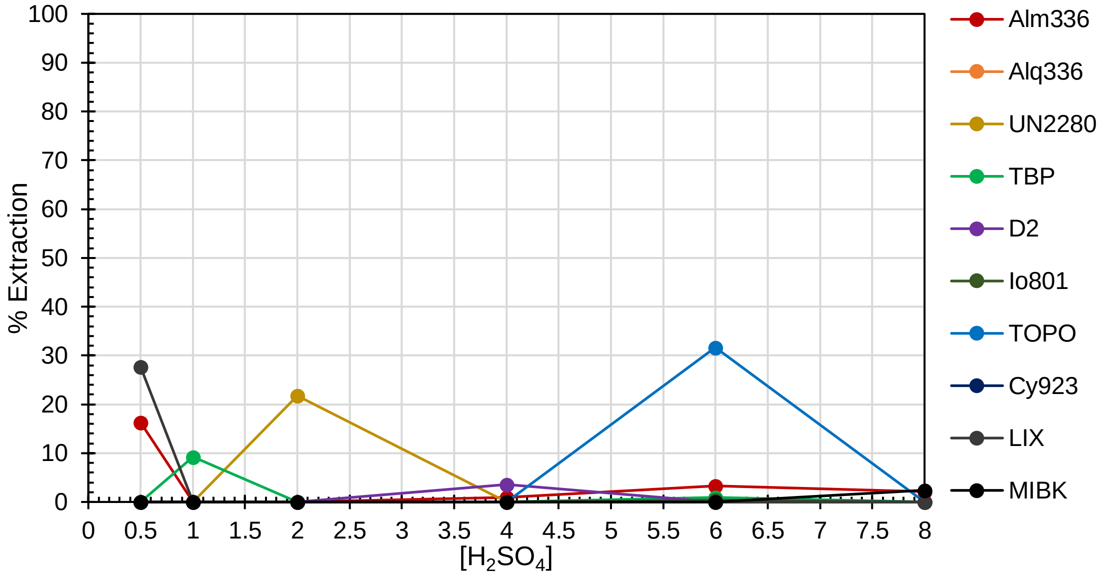

Figure B8: The % Nd extracted from LLn phosphate feed solutions of various sulphuric acid concentrations. [LLn$_T$] = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. [E/LLn$_T$] = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

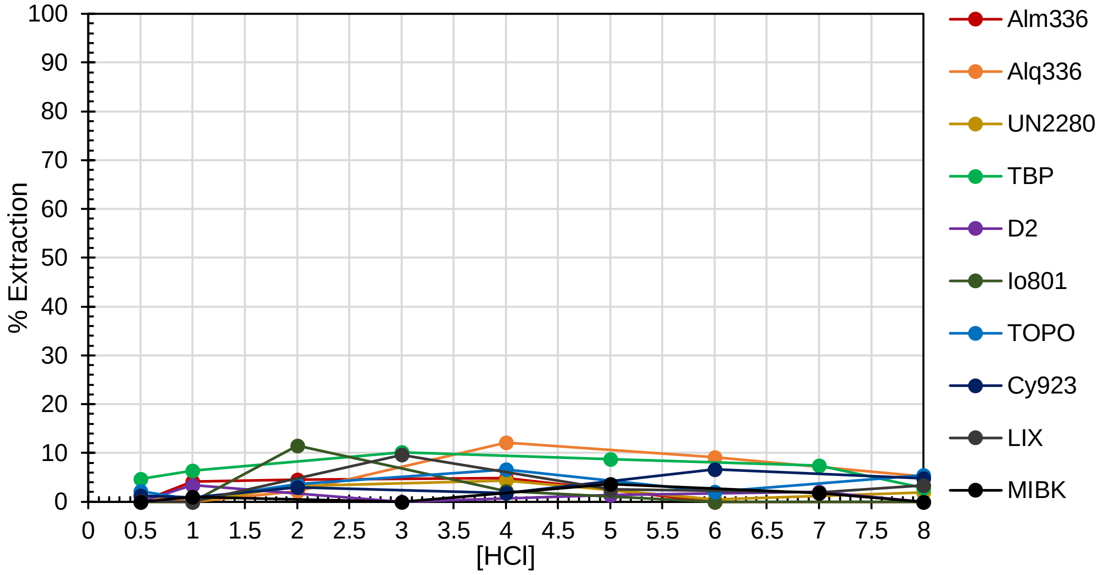

Figure B9: The % Nd extracted from LLn phosphate feed solutions of various hydrochloric acid concentrations. $[LLn_T]$ = 500 mg/L. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1. $[E/LLn_T]$ = 4. V_{Org}/V_{Aq} = 1. Diluent: Kerosene. Modifier: 5wt% 1-Octanol.

6.3 Appendix C

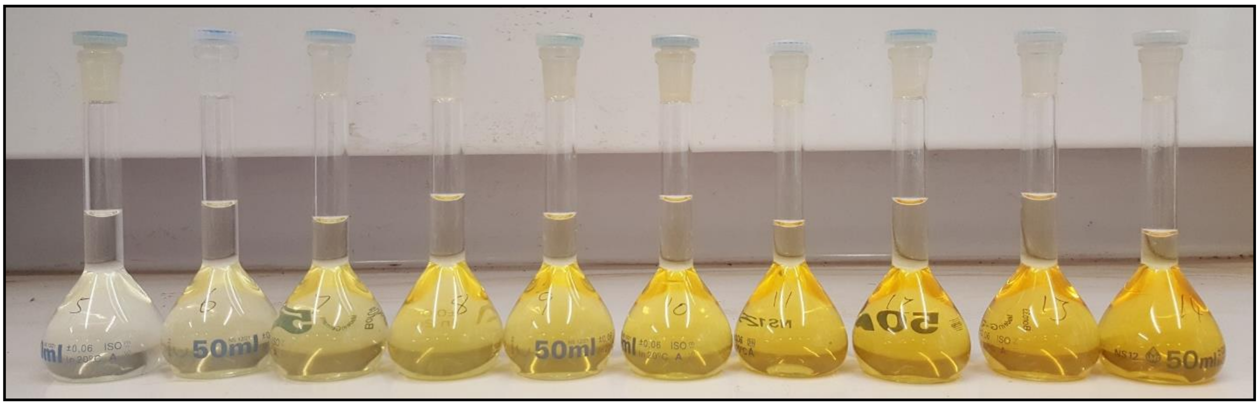

Figure C1: **The oxidation of Ce(III) to Ce(IV) as indicated by the colour change from colourless to bright yellow.**

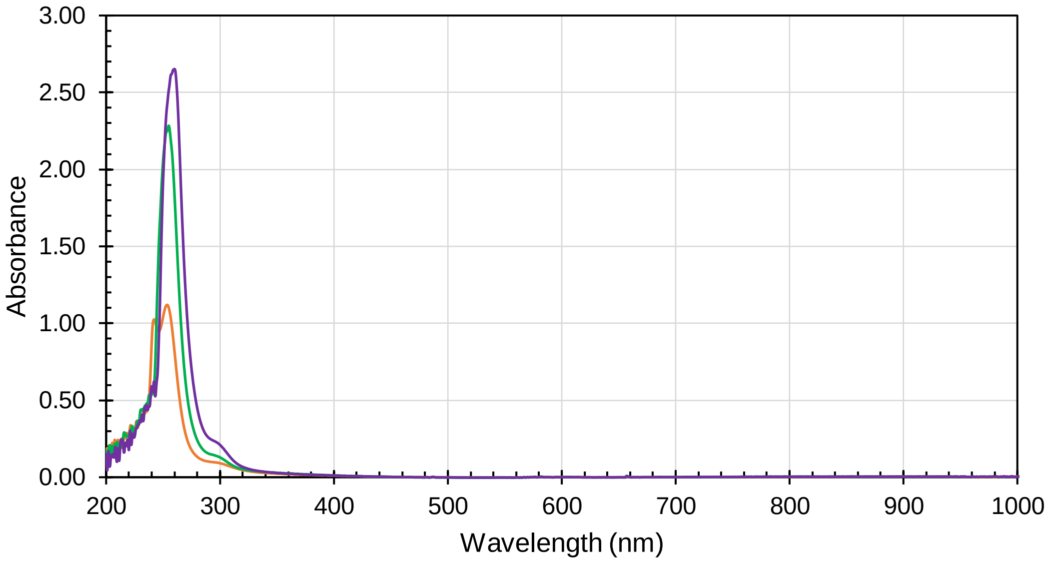

Figure C2: **The absorbance spectrum of — 200; — 500; — 1000 mg/L. Ce in the nitric acid feed solutions.**

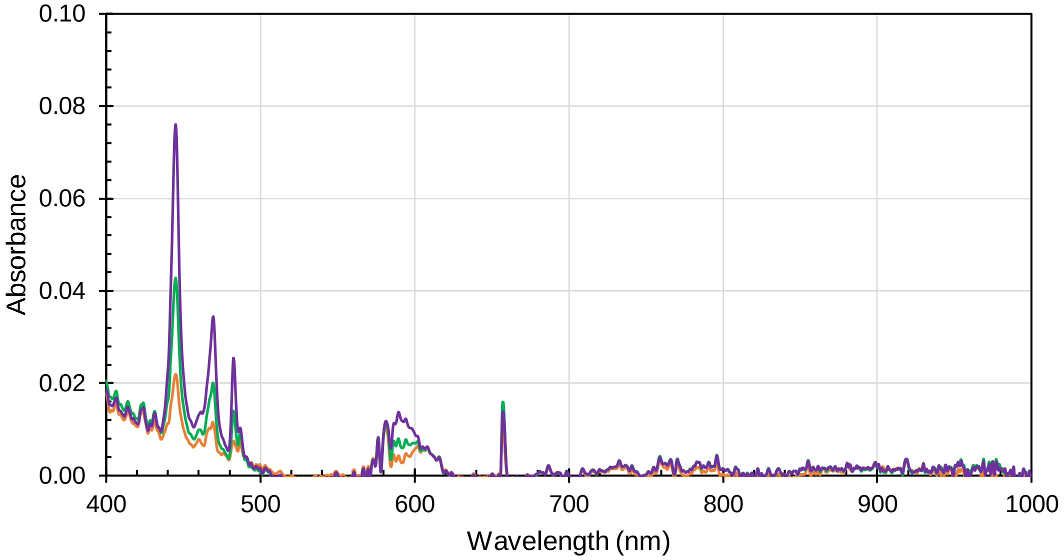

Figure C3: **The absorbance spectrum of — 200; — 500; — 1000 mg/L. Pr in the nitric acid feed solutions.**

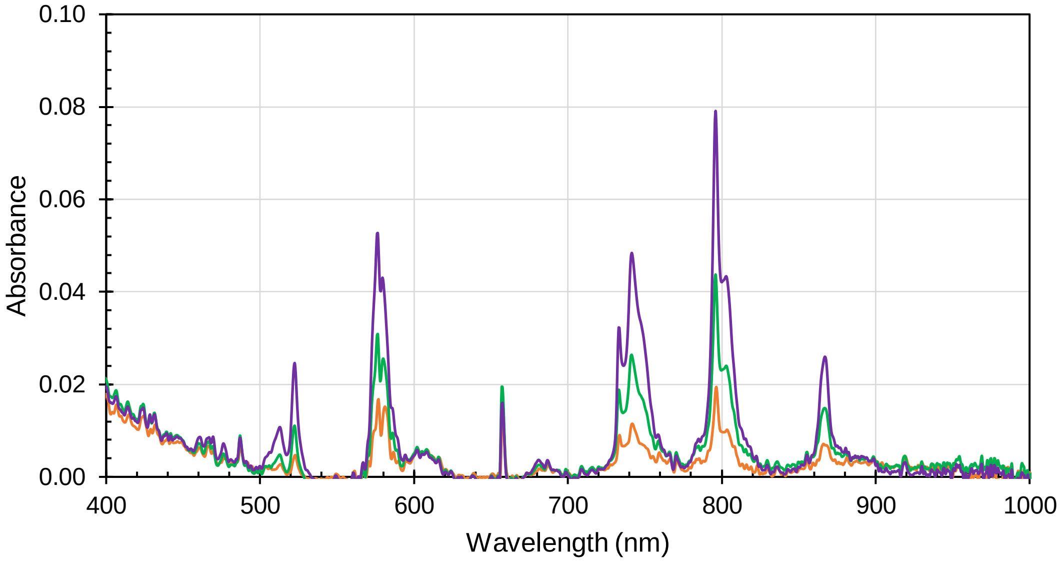

Figure C4: **The absorbance spectrum of — 200; — 500; — 1000 mg/L. Nd in the nitric acid feed solutions.**

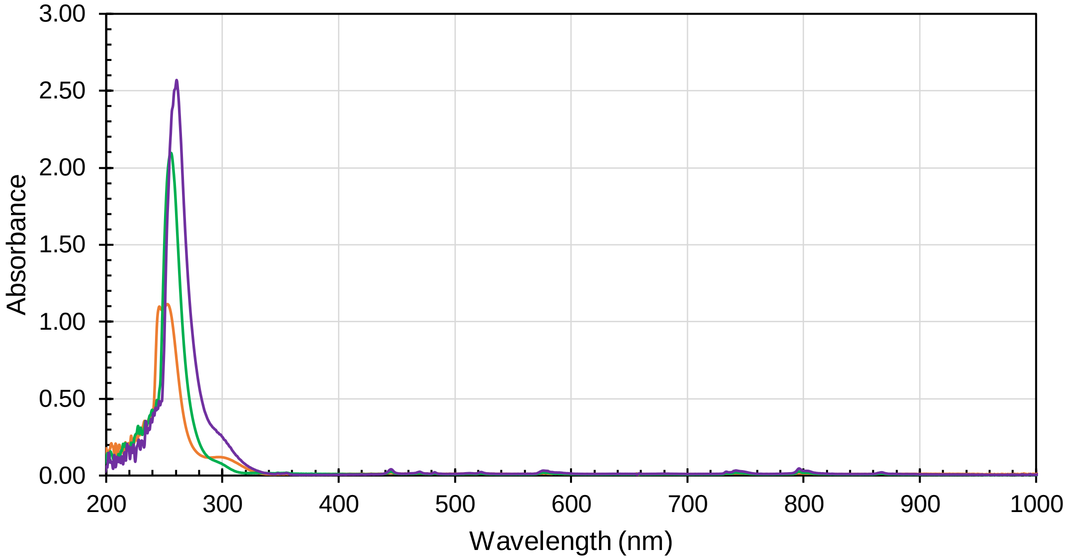

Figure C5: **The absorbance spectrum of — 500; — 1250; — 2500 mg/L. LLn mixture in the nitric acid feed solutions. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1**

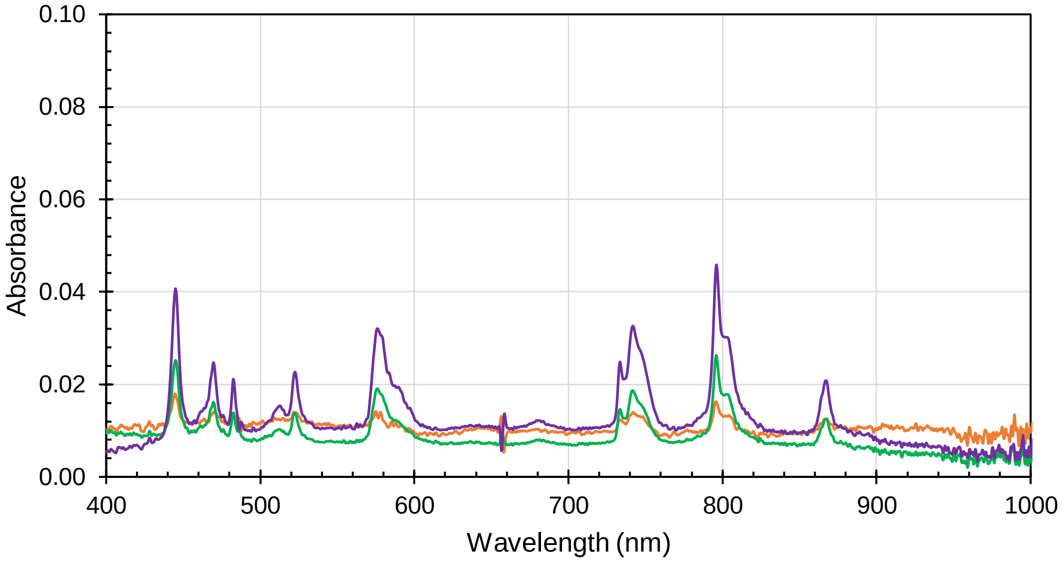

Figure C6: **The absorbance spectrum of — 500; — 1250; — 2500 mg/L. LLn mixture in the nitric acid feed solutions. [Ce]:[La]:[Pr]:[Nd] = 2:1:1:1**

6.4 Appendix D

Figure D1: **The containment cell PX setup used in testing various membrane types for construction of the SW-membrane module.**

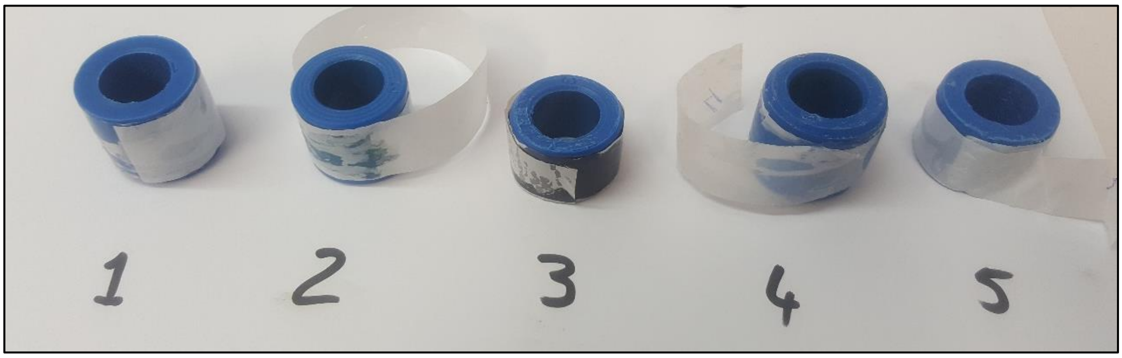

Figure D2: **The adhesive samples provided by Solsep B.V. for possible construction of the SW-membrane module.**

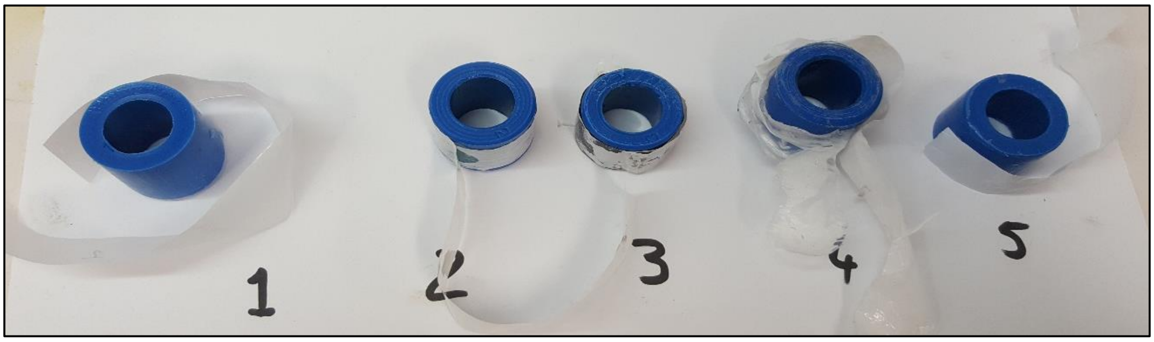

Figure D3: **The adhesive samples provided by Solsep B.V. for possible construction of the SW-membrane module after submergence within the organic diluent for 120h.**

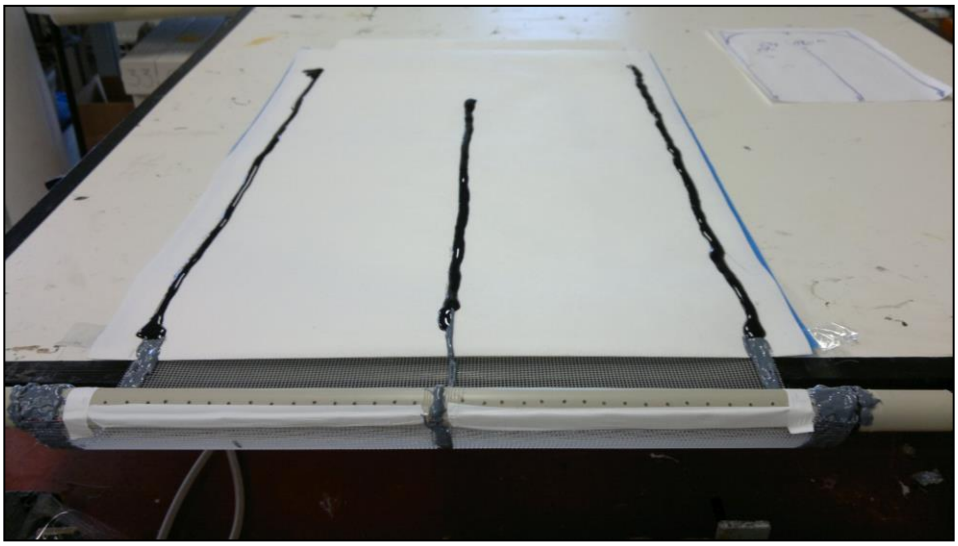

Figure D4: **Construction of the SW-module. Herein the black adhesive has been applied to the Celgaurd 2400 membrane before it is wound around the inner tube. Photo provided by Solsep B.V.**

Figure D5: **The inner (top) and outer (bottom) sections of the constructed SW-module. Photo provided by Solsep B.V.**

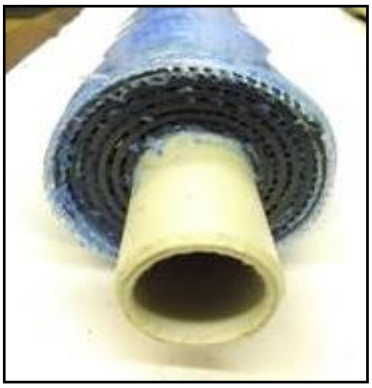

Figure D6: **The inner section of the SW-membrane removed from its casing after failure. Herein the origin of the name can be seen with the Celgaurd 2400 membrane wound around the inner tube and layers glued by the black adhesive. The discolouration of the membrane in this photo is due to the presence of organic phase Cobalt ions trapped within the pores of the membrane.**

LIST OF ABREVIATION

α	*Interfacial Area*
A	*Absorbance*
Ac	*Actinoid*
β_{LLn}	*Separation Factor*
D_{LLn}	*Distribution Ratio*
HF	*Hollow-Fibre*
HFSLM	*Hollow-Fibre Supported Liquid Membrane*
I^{n}_{LLn}	*Ionization energy*
K_{eq}	*Equilibrium Constant*
k_{LLn}	*Mass-transfer Coefficient*
LLE	*Liquid-Liquid Equilibrium*
Ln	*Lanthanoid*
LLn	*light Lanthanoid*
PX	*Pertraction*
RE	*Rare-Earth*
SX	*Solvent Extraction*
SW	*Spiral-Wound*
V	*Volume*
$\tilde{v}$	*Flow rate*
X	*Recovery*