



Doctoral Thesis in Chemical Engineering

Recovery of Rare Earth Elements from an Apatite Concentrate

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KTH Royal Institute of technology

School of Engineering Sciences in Chemistry, Biotechnology
and Health

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To My Love

Rana

Abstract

Rare earth elements (REE) are a group of 17 elements including lanthanides, yttrium and scandium; which are found in a variety of classes of minerals worldwide. The criticality of the application, lack of high grade and economically feasible REE resources and a monopolistic supply situation has raised significant attention in recovery of these metals from low grade ores and waste materials. In this thesis, the recovery of REE from an apatite concentrate, containing 0.5 mass% of REE, within the nitrophosphate route of fertilizer production has been investigated. Most of the REE ($\geq 95\%$) content can be recovered into a phosphate precipitate with almost 30 mass% REE. Different processes have been developed to convert the REE phosphate precipitate into a more soluble form to obtain a solution suitable for further REE purification and individual separation. It has been shown that after reprecipitation of the REE phosphate concentrate as REE sodium double sulphate and then transformation into a REE hydroxide concentrate, a solution containing 45g/L REE free of Ca, Fe and P can be obtained. The results suggest that the apatite waste after processing of iron ore have the potential to be a very important source for REE in Europe and that the economy is strongly supported by the simultaneous extraction of phosphorous.

The potential of using hollow fiber supported liquid membrane (HFSLM) extraction in individual and group separation of REE has been investigated. A hollow fiber supported liquid membrane plant in pilot scale has been operated according to the three main configurations: standard hollow fiber supported liquid membrane technology (HFSLM); hollow fiber renewal liquid membrane technology (HFRSLM) and emulsion pertraction technology (EPT). The standard HFSLM operation is more selective than HFRSLM and EPT, while higher metal transport rate is observed in EPT followed by HFRSLM and HFSLM. The HFRLM configuration helps to maintain the performance of the liquid membrane.

Keywords: Rare earth elements, precipitation, nitrophosphate process, hollow fiber supported liquid membrane extraction.

Sammanfattning

De 15 lantaniderna tillsammans med yttrium och skandium benämns här som sällsynta jordartsmetaller, "rare earth elements" (REE). Inom ramen för detta avhandlingsarbete har processer för återvinning av REE från ett apatitkoncentrat innehållandes 0,5 vikts% REE utvecklats. Apatitkoncentratet är en restprodukt/avfall vid produktion av järn från järnmalm. Arbetet har utgått från en process för produktion av gödselmedel från apatitkoncentratet och en metod har utvecklats för att utvinna REE inom denna process. Större delen av REE-innehållet (>95%) kan erhållas i en fällning bestående av nära 30 vikts% REE i fosfatform. Olika processer har tagits fram för att omvandla REE-fosfatfällningen till en mer löslig fast fas för att i ett nästa steg kunna erhålla en lösning som lämpar sig för ytterligare REE-rening och i slutändan individuell separation. Som ett sista steg har individuell separation och separation av REE i grupp från den initiala REE-lösningen undersökts och potentialen för att använda vätskemembranextraktion för detta ändamål har studerats. En anläggning för vätskemembranextraktion med hjälp av ihåliga porösa fibrer (HFSLM) i pilotskala har konstruerats. Standard HFSLM innebär att man fyller de porösa fiberväggarna med en organfas innehållande ett organiskt lösningsmedel och en extraktant. På utsidan och på insidan av fibrerna strömmar två vattenbaserade lösningar. Genom val av extraktant och genom att kontrollera förhållandena i då båda vattenfaserna kan man få REE att transporteras från den ena vattenlösningen genom fiberväggarna till den andra vattenlösningen. Pilotanläggningen har opererats enligt tre konfigurationer: standard HFSLM; HFSLM med en organfas dispergerad i den ena vattenbaserade lösningen (HFRSLM) och en teknik där den ena vattenbaserade lösningen är dispergerad i en organfas (EPT). HFSLM-metoden visade sig vara mer selektiv än HFRSLM och EPT medan en ökad metalltransport observerades för EPT följt av HFRSLM och HFSLM. HFRLM-konfigurationen visade sig behålla prestandan hos membranet bäst över tid.

Arbetet har utförts både på en grundläggande och tillämpad nivå med en ingenjörsmässig ansats. Studien har resulterat i olika metoder för att extrahera REE från apatitkoncentratet. Tillsammans utgör de ett underlag för att åstadkomma en ekonomiskt och miljömässigt hållbar extraktion av dessa metaller från den bärande malmen hela vägen till individuell separation av de olika REE. Resultaten visar att apatitkoncentratet kan vara en viktig potentiell källa för REE i Europa. Ekonomin kring den föreslagna processen stöds starkt av en simultan extraktion av fosfor.

List of appended papers

- I. Recovery of rare earth elements from nitrophosphoric acid solutions**
Mahmood Alemrajabi, Åke C. Rasmuson, Kivanc Korkmaz, Kerstin Forsberg
Hydrometallurgy, 169 (2017) 253-262,
<https://doi.org/10.1016/j.hydromet.2017.01.008>
- II. Upgrading of a rare earth phosphate concentrate within the nitrophosphate process**
Mahmood Alemrajabi, Åke C. Rasmuson, Kivanc Korkmaz, Kerstin Forsberg
Journal of Cleaner Production, 198 (2018) 551-563,
<https://doi.org/10.1016/j.jclepro.2018.06.242>
- III. Processing of a rare earth phosphate concentrate obtained in the nitrophosphate process of fertilizer production**
Mahmood Alemrajabi, Åke C. Rasmuson, Kivanc Korkmaz, Kerstin Forsberg
Submitted (2018)
- IV. Separation of rare earth elements using hollow fiber supported liquid membrane extraction in pilot scale**
Mahmood Alemrajabi, Jonas Ricknell, Sakarias Samak, Joaquin Martinez De La Cruz, Kerstin Forsberg, Åke C. Rasmuson
Submitted (2018)

Papers not included in the thesis

- V. **Recoveries of Valuable Metals from Spent Nickel Metal Hydride Vehicle Batteries via Sulfation, Selective Roasting, and Water Leaching**
Kivanc Korkmaz, Mahmood Alemrajabi, Åke Rasmuson, Kerstin Forsberg
Sustainable Metallurgy, 4 (2018) 1-13,
<https://doi.org/10.1007/s40831-018-0169-1>
- VI. **Mathematical modelling of hollow fibers supported liquid membranes for separation of rare earth metals**
J. Martínez, M. Alemrajabi, R. Rodriguez, K. Forsberg, Å. Rasmuson
(2018), in preparation.
- VII. **Sustainable hydrometallurgical recovery of valuable elements from spent nickel-metal hydride HEV batteries**
Kivanc Korkmaz, Mahmood Alemrajabi, Åke Rasmuson, Kerstin Forsberg
(2018), Submitted
- VIII. **Separation of Valuable Elements from spent HEV NiMH Battery leach Liquor via Anti Solvent Crystallization**
Kivanc Korkmaz, Mahmood Alemrajabi, Åke Rasmuson, Kerstin Forsberg
(2018), in preparation.

Conference presentations based on this thesis

- IX. Recovery of REE from an apatite concentrate in the nitrophosphate process of fertilizer production**
Mahmood Alemrajabi, Kerstin Forsberg, Åke C. Rasmuson
Proceedings and oral presentation, Beneficiation of phosphates VII, May 2015, Melbourne- Australia
- X. Isolation of rare earth elements phosphate precipitates in the nitrophosphate process for manufacturing of fertilizer**
Mahmood Alemrajabi, Kerstin Forsberg, Kivanc Korkmaz, Åke C. Rasmuson
Proceedings and oral presentation, Sep 2016, IMPC 2016, XXVIII International Mineral Processing Congress Proceedings, Quebec city- Canada
- XI. Dephosphorization and impurity removal from a rare earth phosphate concentrate**
Mahmood Alemrajabi, Kerstin Forsberg, Kivanc Korkmaz, Åke C. Rasmuson
Proceedings and oral presentation, May 2017, European Rare Earth Resources (ERES)- Santorini-Greece
- XII. Recovery of phosphorous and rare earth elements from an apatite concentrate.**
Mahmood Alemrajabi, Kerstin Forsberg, Åke C. Rasmuson
Proceedings and oral presentation, August 2018, Extraction 2018, Ottawa- Canada

Author's contributions to the appended papers

The contribution of Mahmood Alemrajabi to all the appended papers are as following.

- I. Design and plan the experiments. All the experimental work, analysis and evaluation of the results. Writing the first draft of the paper. All the authors reviewed and modified the paper.
- II. Design and plan the experiments. All the experimental work, analysis and evaluation of the results. Writing the first draft of the paper. All the authors reviewed and modified the paper.
- III. Design and plan the experiments. All the experimental work, analysis and evaluation of the results. Writing the first draft of the paper. All the authors reviewed and modified the paper.
- IV. Design and plan the experiments. Major part of the experimental work and analysis. Data evaluation and writing the first version of the paper. All the modifications and improvements in the pilot plant. The pilot plant was initially built by IVL in collaboration with KTH. All the authors reviewed and modified the paper.

Abbreviations

REE	Rare Earth Elements
Ln	Lanthanide
NP process	Nitrophosphate Process
NP solution	NitroPhosphoric solution
CNTH	Calcium Nitrate Tetra Hydrate
XRD	X-Ray Diffraction
ICP-OES	Inductively Coupled Plasma – Optic Emission Spectroscopy
CTPA	Clean Technology of Phosphoric Acid
SEM-EDS	Scanning Electron Microscopy- Energy Dispersive x-ray Spectroscopy
HF	Hollow Fiber
SLM	Supported Liquid Membrane
RLM	Renewal Liquid Membrane
EPT	Emulsion Pertraction Technology
FTSLM	Flat sheet Supported Liquid Membrane
D2HEPA	Di(2-ethylhexyl) phosphoric acid (CAS: 289-07-7)
EHEHPA	2-ethylhexylphosphonic acid mono-2-ethyl hexyl ester (CAS: 14802-03-0)
IHP	Improved Hard Process
DH	DiHydrate
HH	HemiHydrate
AH	AnHydrate
WPPA	Wet Process Phosphoric Acid
PG	PhosphoGypsum
ML	Mother Liquor
TBP	TriButyl Phosphate (CAS: 126-73-8)

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1. Introduction

Rare earth elements (REE) play an important role in many new technologies and high-tech products such as permanent magnets, high strength alloys, catalysts, etc. Although REE minerals are spread all around the earth crust, exploited REE deposits can only be found in a few countries where 95-97% of the world trade in REE come under the domination of China. REE are considered as strategic elements for European countries mainly due to criticality of the applications, a monopolistic supply situation, and lack of high grade and economically feasible REE reserves. Thus, recovery of REE from secondary sources, end-of-life products and landfill mining of industrial waste or residues has gained increasing attention. Generally, phosphate rocks contain 0.05 mass% REE on average [1]. After processing the apatite ore, an apatite concentrate normally with higher concentration of REE (~ 0.5-1 mass%) can be obtained. By taking into account the world phosphate rock production that is estimated to be 250 million tones yearly, apatite concentrates can be considered as a potential new REE source [1]. On the other hand, phosphate rocks are the main source of phosphorous which is widely used in agriculture, but it is a non-renewable source. The rapid increase in the world population and the consequent rise in consumption have rendered fertilizers an integral part of the food chain.

Since the concentration of REE in the apatite concentrate is low, it is not economical to design a process only for REE extraction and their separation process should be integrated within common processes of phosphate beneficiation. In the phosphate beneficiation methods, the phosphorus content of apatite is commonly turned into phosphoric acid by leaching the ore with different acids such as nitric acid, hydrochloric acid and sulfuric acid. The wet process of phosphoric acid production and the nitrophosphate process of fertilizer production are the main two processes that have been extensively adopted industrially. In the wet process of phosphoric acid production, which is the most common method of phosphate beneficiation, the apatite is first digested with sulfuric acid that produces sparingly soluble sulphate salts and thus allowing the calcium and other impurities to be separated from the phosphoric acid directly by filtration [2]. REE phosphates have very low solubility in phosphoric acid and therefore a large part of the REE will be present in the phosphogypsum

solid phase. As reported by different authors, 20-30 % of REE remain in the phosphoric acid and 70-80 % are absorbed by phosphogypsum [3, 4]. The recovery of REE from phosphogypsum is a complicated and uneconomical process that makes this route unattractive from a REE recovery point of view [5, 6].

The nitrophosphate process of fertilizer production is a viable alternative since both the phosphorous and the REE can be effectively recovered from the apatite concentrate. In the nitrophosphate process of fertilizer production the apatite is first digested in nitric acid and then the major part of the Ca is separated as $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ by cooling crystallization from the nitrophosphoric (NP) acid solution. Thereafter, the REE are precipitated as phosphates by partial neutralization of the nitrophosphoric acid mother liquor (ML) to a pH of ~ 1.8 by addition of ammonia. The NP acid solution after isolation of REE is further neutralized and then turns into a multi nutrient fertilizer after addition of K salt.

So far, few studies have concerned the recovery of REE from the nitrophosphate process and in there no attempts to reveal the details have been made. The results have shown that the calcium concentration and final pH in the partial neutralization are the key factors that control the concentration of REEs in the precipitate. Furthermore, the recovered REE from the nitrophosphate process are present in a REE phosphate concentrate relatively poor in REE concentration, incorporate impurities such as iron and contains considerable amount of P and Ca. As one of the objectives, this study bridges the gap that exist in further processing of the REE phosphate concentrate. Different processes have been developed to further purify and deliver the right feed quality for further individual separation of REE. These processes include partial dissolution of the REE phosphate concentrate in nitric acid, thermal treatment with sodium hydroxide and sodium double sulphate precipitation with and without alkaline conversion, followed by selective dissolution in different acids.

One of the greatest challenges in REE separation processes, is the individual separation of these elements from each other mainly due to their chemical similarity. Today the individual separation of REE is carried out by solvent extraction using mixer-settlers where sometimes up to hundreds of mixer-settler units are required to separate all the individual REE [7, 8]. The liquid-liquid extraction with hollow fiber supported liquid membranes (HFSLM) is an attractive alternative over mixer-settler contactors where simultaneous extraction and stripping is operated in one module. In

HFSLM, a hollow fiber module is used where the organic phase is immobilized via the capillary force inside the pores. The membrane separates the aqueous feed and the strip phase flowing on either the lumen or shell side respectively. The polymeric support only provides a structural support for the organic phase (solvent) and does not play any role in the separation [9]. As a part of this thesis, the behavior of different REE in an up-scaled version of a HFSLM extraction process and the parameters that affect the selectivity and the transport rate of the REE including the initial feed concentration and pH, configuration of HFSLM and operating mode have been investigated. The membrane stability is a major barrier for commercial application of supported liquid membrane extraction. Dissolution of the carrier in the aqueous phase, formation of micro emulsion due to lateral shear forces and gel formation are the main reasons for the membrane instability. This study has brought new insights into the behavior of REE in HFSLM extraction systems, and possible mechanism to explain the membrane instability and gel formation threshold in case of using D2HEPA as the carrier.

The lanthanides (Ce-Lu) are f-block elements and lanthanum, yttrium and scandium are d-block elements. Commonly these elements occur as trivalent ions. However, cerium, terbium and praseodymium can also occur in tetravalent state and europium, samarium and ytterbium can occur in divalent state [11]. The coordination numbers of lanthanides are high, typically between 6 and 12. The ionic radii is the key parameter to

understand the Ln^{3+} coordination chemistry and small changes in atomic radii greatly effects the chemical properties of REE. Across the lanthanide series (Ce-Lu) the electrons are placed in the 4f shell. The lanthanide contraction is due to the poor shielding of nuclear charge by the electrons in the 4f shell. This shell has little effect on bonding and the significant difference between two lanthanides is often only their atomic or ionic radius. The radii of the lanthanide trivalent ions (for coordination number 8) decreases steadily from 116 pm for La^{3+} to 98 pm for Lu^{3+} [12]. The ionic radius of yttrium is similar to those of the elements from dysprosium onwards. Yttrium often interpolates in a sequence of properties in the neighborhood of dysprosium, holmium or erbium. However, in some cases yttrium shows more similarities towards other of the REE, e.g. in the sequence of stability constants with some chelating agents [11]. Whether the properties of Y is more like the lighter or heavier of the lanthanides depend on the level of covalent character of the chemical bonds. The REE have a strong tendency to form complexes in aqueous solution throughout a wide range of temperature and pressure [13, 14].

Due to their chemical similarity, the rare earth elements are difficult to separate from each other. Based on their separability, they are divided into the light rare earth element group (La to Eu) and the heavy group (Gd to Lu plus Y). In another classification these elements are categorized in light REE (La, Ce, Pr, Nd and Sm), middle REE (Eu, Gd, Tb and Dy) and heavy REE (Ho, Er, Tm, Yb, Lu and Y) [11]. The lanthanide contraction results in more similar sizes of the lanthanides (series 6) and the transition metals in series 5, which makes the separation of these elements more difficult. Many properties change in a constant direction from lanthanum to lutetium, even though the rate of change may not be as regular as the ionic radii. In general La (III) and Ce (III) shows a larger difference in most properties than does any other adjacent pair.

The chemistry of the group falls between that of the alkaline earth elements and that of iron and aluminum. The oxides are basic and are little hydrolyzed even in slightly acidic solution. The temperature at which a rare earth salt containing oxygen as well as a given anion (e.g. sulphate, nitrate, acetate) is converted into an oxide or a basic salt of lower solubility decreases with decreasing basicity of the trivalent cation [10].

Apart from the unstable Pm (half-life 2.623 y) of which traces occur in uranium ores, the lanthanides are actually not rare. Cerium (66 ppm in the earth's crust) is the twenty-sixth most abundant of all elements. REE have

earned their reputation for being rare because they rarely exist in easy-processing resources. There are over 200 minerals known to contain lanthanides but the only two of commercial importance are monazite (REEPO_4), a mixed Ce, La, Nd, Sm and Th phosphate, and bastnasite, a La, Ce and Y fluorocarbonate (REECO_3F). These two minerals account for 95% of the current sources for light rare earth elements [11]. The primary mineral containing heavy REE is xenotime, a YPO_4 mineral which lately is also used industrially for the extraction of rare earth elements [11].

2.1.2 Applications of the REE

Numerous technological items that many are quite familiar with in modern life critically depend on rare earth elements and the importance of REE in the current modern world can hardly be exaggerated. There are several applications including many "green" technologies that depend on REE, including wind turbines, low-energy light bulbs and hybrid car batteries. Due to e.g. the unique spectroscopic and magnetic properties of the rare earth elements they are needed for a wide variety of products such as catalysts, rechargeable batteries, mobile phones, plasma televisions, disk drives, metal alloys, HT-superconductors, glass polishing agents, permeant magnets, pigments, nuclear control rods, photographic filters, lasers, tracing geochemical processes within the earth, and catalytic converters [15]. Table (1) summarizes REE applications.

Table 1. Overview of REE applications. The information is extracted from [11, 16, 17, 10, 18, 19].

Element	Symbol	Z	Application
Scandium	Sc	21	Alloying metal for aluminum used in aerospace framework, metal halide bulbs, Sc^{40} used as tracing agents in refinery crackers, mercury-vapor lamps
Yttrium	Y	39	Alloys, color televisions and monitors, camera lenses, microwave and radar applications, lasers, HT-superconductor, Yttrium-aluminum garnet, phosphors for lamps and displays
Lanthanum	La	57	Misch metal alloy, NiMH batteries, fluid catalytic cracking, special optical glasses, superconductor, phosphors, battery electrodes

Cerium	Ce	58	Polishing compound, Fluid catalytic cracking, catalytic converter, component in special glass, alloys, pigment, chromium plating, incandescent gas mantles, Hydrocarbon catalysts in self-cleaning ovens, activator in yttrium-silicon phosphors
Praseodymium	Pr	59	Misch metal, alloying element with magnesium, pigment for glass and enamel, Praseodymium-doped glass, fluoride-glass optical fibers
Neodymium	Nd	60	permanent magnets, dopant in yttrium-aluminum garnet (YAG) lasers,
Promethium	Pm	61	X-rays and radioactivity in measuring instruments
Samarium	Sm	62	Magnets, Kagan's reagent in reduction of water, reducing or coupling agent in organic synthesis
Europium	Eu	63	Phosphors, genetic screening tests
Gadolinium	Gd	64	shielding of nuclear reactors, neutron radiography, alloying elements, magnetic resonance imaging (MRI)
Terbium	Tb	65	luminescent materials, crystal stabilizer for solid-oxide fuel cells
Dysprosium	Dy	66	additive to NdFeB-magnets, dysprosium oxide-nickel cermet in cooling nuclear-reactor rods, dopant in BaTiO ₃ for small dimension capacitor, transducers
Holmium	Ho	67	magnetic flux concentrator, Neutron absorbance to control nuclear chain reactions, microwave equipment, medical and dental applications, dopant in yttrium-aluminum garnet

Erbium	Er	68	photographic filter, Glass colorant in eye glasses, Safety goggles for welders and glassblowers, optical fibers, Laser industry, special nuclear-fuel rods, alloying elements with vanadium
Thulium	Tm	69	dopant in YAG, thulium-doped holmium lasers,
Ytterbium	Yb	70	strengthening of steel, doping of phosphorceramic capacitors, industrial catalyst
Lutetium	Lu	71	β -emitter, so-called-bubble memory for computer memory, scintillation crystals for positron emission scanners

2.2.Critical raw materials

The European commission has placed REE as critical elements as defined based on supply risk and economic importance. As it is shown in Fig. (2), the heavy and light REE were reported to have the highest supply risk among 54 other materials [20, 21]. Among REE; Nd, Dy, Tb, Eu and Y face higher supply risk due to their importance to clean energy [22]

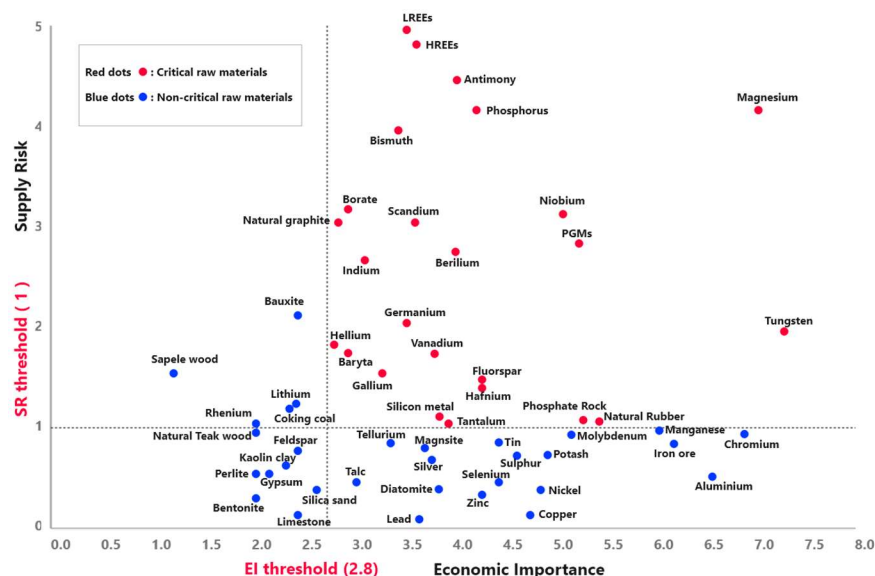


Figure 2. Economic importance (EI) and supply risk results (SR) of 2017 criticality assessment, the red dots show the critical raw material while blue dots show the non-critical raw materials. The red dots are located within the criticality zone of the graph (adopted from [20]).

The significant growth in demands for REE as well as the scarcity of supplies has drawn significant interests into methods of recovering REE from low-grade ores [15]. In addition, today about 97% of all rare earths are produced in China that exposes a great supply risk over the REE market [19]. Furthermore, the REE processing in China could be improved from environmental aspects. Thus, the environmental concern for the production of REE has become a target over the years for many countries. These concerns have opened and prompted new research into developing cleaner processes in recovery of these elements from alternative and local secondary resources.

It is common to say that phosphate is a non-renewable compound vital for plant growth to meet the need for feeding the growing populations. As is reported in the 2017 list of critical materials for the EU, phosphate rock is a new member to this list as compared to 2014 [20]. Phosphate rock is practically the only raw material for phosphate fertilizers. The primary source is sedimentary rocks which is a phosphate originating from seawater and bones. Magmatic or igneous phosphate rocks are also another

important source of phosphorous. Phosphate rocks contains calcium phosphate as apatite, mainly fluorapatite and are mined in almost 30 countries and phosphate fertilizers are produced in all the continents (26 countries in Europe, 13 in America, 9 in Africa and 13 in Asia and 2 in Australia) [23].

As one of the main sources for phosphorus, apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$) minerals are used to produce phosphate containing fertilizer and phosphoric acid where their consumption is estimated to be 250 million tons of phosphate rock yearly [1]. These minerals also contain considerable amount of REE ($\sim 0.05 - 1 \text{ mass\%}$ and exceptionally even $2-4 \text{ mass\%}$) and are considered as an important secondary source of REE with a great economical potential for the recovery of these metal within the common processes of phosphate beneficiation [1, 18]. Rare earth in the world's annual production of phosphate rock accounts for ~ 125000 tones which account for the major part of the current total need for these elements. In phosphate rock, REE are mostly present in the form of isomorphous substitution for Ca and deposit as REE-francolite which can be easily leached by mineral acids [1]. The REE could also be present in minority as monazite, xenotime, allanite and carbonate which are more challenging to be leached with mineral acids [1].

2.3. Phosphate beneficiation and recovery of REE

The presence of phosphorus and REE but also radioactive elements such uranium and thorium makes phosphate rocks very valuable economically and very challenging to handle from an environmental point of view. Different processes have been invented to make use of phosphate rocks. approximately 90% of mined phosphorous is used in fertilizers which almost equally is divided into superphosphates, ammonium phosphates, and compound fertilizers (nitrophosphate and NPK fertilizers). The first step towards production of many ammonium phosphates is to make phosphoric acid from phosphate rock which can be either obtained from the wet acid process or from a thermal process. The nitrophosphate route is another alternative for phosphate beneficiation which concerns the acidulation of apatite with nitric acid to produce compound fertilizers.

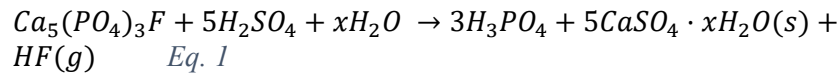
If REE are not recovered during phosphate mineral processing and beneficiation, they mostly end up in the fertilizer and eventually they are spread on farm lands, making it impossible to ever recover them. It can be fairly assumed that 71% of the world phosphate rock mined is consumed in the wet process, 5% is consumed in the thermal process, 13% in

production of direct fertilizers like single super phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), 10% in the nitrophosphate process, 5% for elemental phosphorus production and 0.5% concerns direct applications of the rock. There is also a great potential of REE recovery not only from phosphate rocks but also from other mining streams such as waste clay slurry and flotation tailings [18].

The recovery of REE from apatite concentrate is greatly dependent on the type of phosphate beneficiation route. In the H_2SO_4 process, the main challenge is the recovery of REE from phosphoric acid and phosphogypsum which contain a low concentration of REE while in the nitric acid process REE entirely transfer into the leach solution and the recovery is focused on REE extraction from this leach solution. In the thermal process the REE are diluted and present in the crystal lattice of the calcium silicate phases ($\text{CaO} \cdot \text{SiO}_2$) which make it very uneconomical to recover them. In the following sections an overview on the recovery of REE from the common processes of phosphate beneficiations is given.

2.3.1 Wet processing

Phosphoric acid as an important intermediate chemical product used for manufacturing different chemicals. The main application of the phosphoric acid is the production of fertilizers, detergent and animal feed which is expected to rise steadily [3, 24]. In the wet process, the phosphorus content of apatite is turned into phosphoric acid by acidulation of the ore with sulfuric acid. Sulfuric acid is the only acid that produces insoluble salt and thus allowing the phosphoric acid to be separated directly by filtration. The main reaction in the wet process can be written as in Eq. (1).



In the acidulation reactor depending on the temperature, sulfuric acid and phosphoric acid concentration; the calcium sulfate could be either dihydrate (DH), hemihydrate (HH) or anhydrate (AH) [25]. There are different processing alternatives within the wet process including the dihydrate process, hemihydrate process and recrystallization processes. The main difference between these processes are in properties of the produced phosphogypsum and phosphoric acid as well as further treatment of the phosphogypsum to recover the incorporated phosphorous [26]. The schematic process diagram of the dihydrate process is shown in Fig. (3).

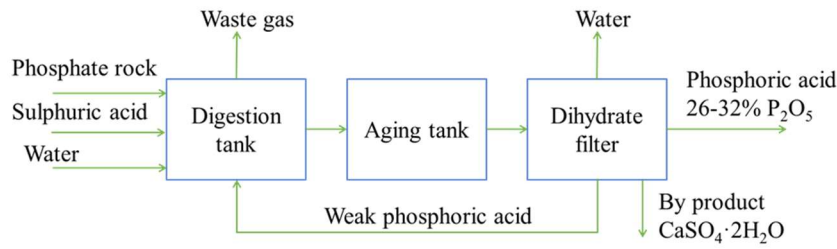


Figure 3. Dihydrate process for phosphoric acid production.

The application of produced acid from common wet processes like the dihydrate process or hemihydrate process is limited by the presence of impurities like cadmium and radium. In addition, the produced gypsum contains significant amount of impurities like rare earth elements, arsenic and cadmium, which restrict the use of the byproduct gypsum as well. The production of concentrated phosphoric acid with low cadmium amount and calcium sulphate hemihydrate with lower uptake of phosphorus, cadmium and radium is available through the clean technology of phosphoric acid (CTPA) production. The main difference between CTPA production and the wet process is existence of a predigesting step of the apatite in concentrated phosphoric acid in CTPA production [24, 27]. Fig. (4) shows the process scheme of CTPA production.

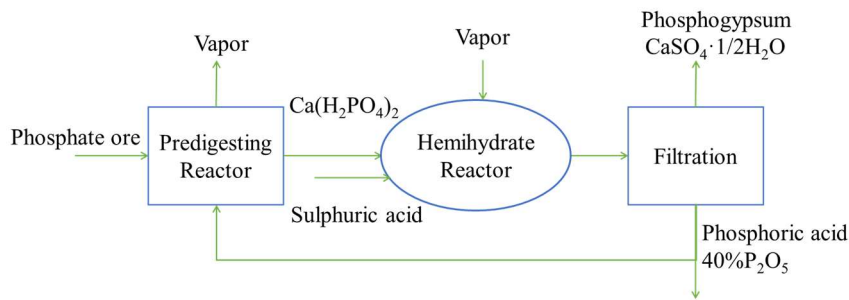
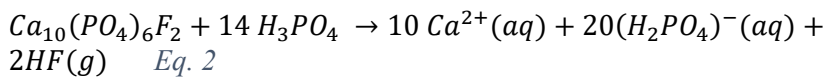


Figure 4. Process scheme of clean process of phosphoric acid production.

The predigesting step is governed by the following reaction (Eq. (2))



The conditions of the predigesting reactor are controlled by the solubility of $\text{Ca}(\text{H}_2\text{PO}_4)$ in phosphoric acid, which is dependent on the concentration of phosphoric acid and temperature [24].

2.3.1.1 *Isolation of rare earth elements from the wet process*

The REE in the wet process phosphoric acid are present in the complexes with phosphate ions. REE phosphates have very low solubility in phosphoric acid and therefore a large part of the REE will be present in the phosphogypsum solid phase. As reported by different authors, 20-30 % of REE remain in phosphoric acid and 70-80 % are absorbed by phosphogypsum [4, 3, 2]. Leaching the phosphate rocks at elevated temperatures like in the hemihydrate process leads to further incorporation of REE in phosphogypsum (up to 95%) due to retrograde solubility of REE phosphate [32, 33, 34]. Jarosinski et al. (1993) reported that during the acidulation of Phalaborwa phosphate with sulphuric acid, 70 % of the REE was found in the solid phase in the dihydrate process and in the HH process almost all REE enter the calcium sulphate stream [28]. Fava et al. (1987) reported that the amount of REE which is incorporated with phosphogypsum generally is in the range of 80% to 95%. [29]. Habashi, (1985) observed that less REE is incorporated in phosphogypsum if the digestion reaction happens at lower temperature and in less concentrated sulphuric acid [2]. In most cases, the concentration of REE in phosphodihydrate is less than in phosphohemihydrate [30]. The incorporation of HREE with phosphogypsum is less than LREE and therefore high content of the most valuable lanthanides in wet processing phosphoric acid makes it quite interesting for REE recovery [31].

The easiest and perhaps the most economical way to recover REE from apatite in wet processing is to extract them from the phosphoric acid. By increasing the leaching efficiency of REE during the acidulation of phosphate rock with sulfuric acid, more REE can be directly separated from phosphoric acid. The leaching efficiency of REE and phosphorus in wet processing is influenced by two phenomena; the blinding effect and incorporation in gypsum crystals by mainly isomorphous substitution for calcium ions. In ore blinding, simultaneous formation of a huge amount of calcium sulphate with dissolution of apatite leads to a coating of undissolved apatite with calcium sulphate that hinders further dissolution of the ore particles and thus greatly reduces the leaching efficiency. The parameters that control the efficiency of REE leaching are phosphoric acid concentration, the stoichiometric ratio of sulphuric acid to CaO ,

liquid/solid ratio of phosphoric acid to phosphate ore, temperature and additives [4]. The appropriate concentration of sulphuric acid not only increase the crystallinity of calcium sulphate and enhances the leaching efficiency of REE but also reduces the loss of phosphorus with calcium sulphate crystals (substitution of SO_4^{2-} by HPO_4^{2-} in the calcium sulphate crystal). The efficiency of REE leaching decreases with increasing the temperature [4]. Recently Rychkov et al. (2018) conducted a study to recover REE by treatment of PG from a copper smelting plant and showed that the REE can be leached out effectively (> 70%) using sulfuric acid after activation of the PG by mechanical grinding, ultrasonic impact and sorption by resins [35].

Leaching of phosphate rocks prior to addition of sulfuric acid (clean technology of phosphoric acid production) is a practical alternative for separation of these elements in a single phase either from leaching solution or residues. In this method, the crystallization of PG occurs after separation of REE which significantly reduces the incorporation of REE with PG crystals and produce high quality gypsum and cleaner phosphoric acid [3, 24]. However, by the addition of a pre-leaching step, the recirculation of phosphoric acid in the process significantly increase the processing volumes and the respective energy demands [24, 27]. This method is more suitable when the REE are present as an independent mineral inclusion in the phosphate rock which hardly dissolve in common mineral acid and thus can be enriched in leach residues [1].

2.3.1.2 *Recovery of REE from phosphoric acid*

The core techniques in recovery of REE from phosphoric acid involve different methods such as precipitation by evaporation [2, 31, 36], and by reagent addition with seeds [1, 37, 38], and without [1, 39, 40, 27]; and solvent extraction [1, 41, 4, 42, 43].

In general, the precipitation by evaporation methods of REE recovery from phosphoric acid suffer from high energy demand, high pressure and the need to use a temperature resistant apparatus, while the seeding method have the drawbacks of passivation and high processing cost of the seeds. The precipitation methods are limited due to large amount of reagent consumption, interference with the production of phosphoric acid and low REE content in the precipitate. The solvent extraction recovery of REE from phosphoric acid suffers from loss of phosphorous, co-extraction of calcium and uranium, large amount of extraction agent and washing solution, low recovery of LREE, and harsh working environment.

2.3.1.3 *Recovery of REE from phosphogypsum*

The main byproduct of WPPA is phosphogypsum. Phosphogypsum has various uses mainly in agriculture, construction and as a chemical raw material. Huge phosphogypsum stockpiles around the world (annual global production of 100–280 million tons) with considerable concentration of REE (the average concentration of REE in phosphogypsum is 0.4 mass%) [2] has raised significant attention to recover REE from this secondary source. As an example, in Poland, the apatite phosphogypsum is the most promising source of rare earth elements [28]. However, it is shown by Kulczycka et al. (2016) in a case study of the Wizow chemical plant that the technologies involved in REE recovery have higher negative impacts on the environment than just piling the phosphogypsum [44]. Later, it was mentioned that the recovery of REE from phosphogypsum stockpiles is only profitable if it is coupled with the right market for phosphogypsum applications [45]. Nowadays only 15% of generated gypsum is recovered for applications in gypsum board, agriculture and cement industries [46]. The low cost of the rare-earth products from Chinese manufacturers and the wide availability of these products on the world market have long reduced the industry's interest in the problem of REE recovery from phosphogypsum. However, the present deficit and the already risen costs are changing the attitude toward this problem. The recovery of REE from phosphogypsum will be significantly improved by development of an integrated processing technology combining the REE recovery with purification of phosphogypsum to remove detrimental impurities. [47].

The methods to recover REE from phosphogypsum are strongly dependent on the phase of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$, the age of the phosphogypsum stockpile and the REE phases in phosphogypsum (either as an independent phase or incorporated in the phosphogypsum crystal lattice). The processes involved in separation of REE from phosphogypsum are leaching using mineral acids [48, 49, 2, 30] followed by extraction of REE via precipitation, solvent extraction and ion exchange methods [1, 2, 46, 6, 28, 50, 36, 51, 52]. In general, the recovery of REE from phosphogypsum is a complicated and uneconomical process that makes these routes unattractive from a REE recovery point of view.

2.3.2 *Thermal processes*

In the dry process, the elemental phosphorus is produced as an intermediate by providing a large amount of heat in an electric furnace,

blast furnace or in a rotary kiln. The phosphate ore such as apatite is reduced in presence of silica and carbon to phosphorous according to Eq. (3). The P_4 is then oxidized to form P_2O_5 and absorbed by water to produce phosphoric acid (Eq. (4)).

This process has a meager contribution to the production of phosphoric acid because the required amount of energy makes the process economically unfavorable. However, since the produced acid contains fewer impurities compared to the other processes, it has applications in production of phosphoric acid for detergents and food additives.

The electric furnace and the kiln-based phosphoric acid process are both thermal processes that can be used to produce high quality phosphoric acid from relatively low-grade phosphate ores. In 1960, Lapple found that a rotary kiln had the ability to replace the energy supplied by electricity in the electric furnace process with energy generated by carbon. This concept was advanced by many researchers, but all failed because of melting problems that Dr. Hard later overcame in 1981. The process employs a rotary kiln reactor and was proven in pilot plant testing. In 2003, Joseph A. Megy restarted R&D on the Hard Process and made additional discoveries that led to the Improved Hard Process (IHP), and today design of a semi-commercial demonstration plant is in progress [53, 54]. The schematic of the improved hard process is shown in Fig. (5).

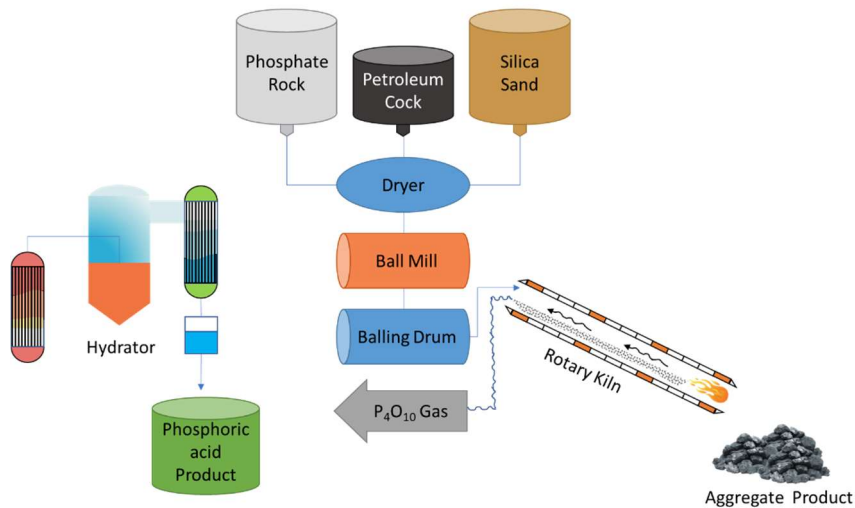
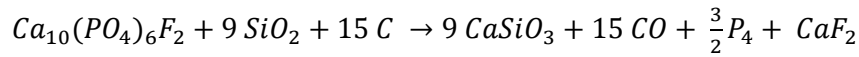
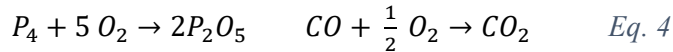


Figure 5. The thermal process of phosphoric acid production -improved hard process (adopted from [53]).

In the IHP process, the ground apatite with green petroleum coke and silica is formed into pellets in a balling drum (pelletization). Fines and oversize are returned to the balling drum and product sized pellets are fed to the ported kiln. Air is heated by burning natural gas and blown counter-currently to the flow of material in the kiln. The P_2O_5 gas is liberated and passes to the hydrator where it is absorbed in water (recycled phosphoric acid) to form phosphoric acid. Gases leaving the hydrator are further scrubbed in a venturi scrubber and mist eliminator to recover product not absorbed in the hydrator. Vent gases are then scrubbed with lime slurry, and then pass to a flue gas desulfurization unit for final cleaning. The heat source comes from a direct-fired rotary kiln reactor. The rotary kiln can operate simultaneously with reducing zone in the bed of solid and oxidation zone in the gas which results in perfect heat integration between the oxidation and reduction zones. The pellets (preheated to 300 °C) are introduced to the kiln countercurrent to hot gases. When the pellets are reaching the reduction temperature, phosphorous and carbon monoxide evolve and as they reach the gas phase, they are oxidized to P_2O_5 and CO_2 . The kiln temperature is 1450-1500 °C. The spent pellets leaving the kiln have a temperature of 1200 to 1400 °C. The chemistry of the process can be simplified as below in Eq. (3) and Eq. (4) [55, 56].



Eq. 3



By the delivery of the phosphorous rich gas to the hydration process, super phosphoric acid production with the concentration of 68-75% P_2O_5 is achieved. By-products can be used as inert spent pellets with low environmental impacts as aggregate, backfill for mine and fill material for infrastructure work.

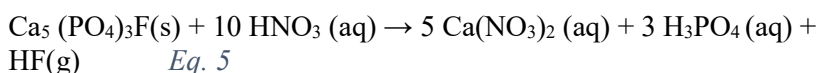
This process is not desirable from a REE recovery point of view since the content of REE is diluted in the slags (< 0.3-0.7 mass% based on mass balance) and all these elements are incorporated into the crystal lattice of the calcium silicate phases ($CaO \cdot SiO_2$) and require very severe acidic conditions to be dissolved and isolated. Habashi (1985) isolated REE from a slag containing 0.7mass% REE obtained during the manufacture of elemental P in an electric furnace. A REE recovery of 60% was reported

after leaching the slag with concentrated nitric acid followed by TBP extraction [2].

2.3.3 Nitrophosphate (NP) process

Nitrophosphate fertilizers are nitrogen and phosphorous containing fertilizers that are produced by nitric acid digestion of phosphate rock. Depending on the methods to remove calcium nitrate various NP processes are employed such as the commonly used Odda process, the mixed acid process, the calcium phosphate process and the carbonitric process. The invention of the most significant industrial NP process called Odda dates back to 1929 when Erling B. Johnson, Odda, Norway introduced this method to avoid dilution of super phosphates with sulphate ions [23]. The process was industrially developed by Norsk Hydro 1938. Approximately 10% of the world's phosphate fertilizer is now produced by the Odda NP process.

The Odda NP process starts with digestion of the phosphate rock in concentrated nitric acid. The use of concentrated nitric acid reduces the amount of water in the processing. The overall acidulation reaction takes place at a temperature of about 50-70 °C under 2 h of residence time in a stirred tank as it is given in Eq. (5).



The acidulation temperature range is designed in a way to assure complete digestion while to prevent corrosion. The reaction is normally carried out with an excess of 10-20% nitric acid of 60 mass%. The kinetics of this reaction has been studied extensively [57]. Acidulation of phosphate rock releases small amount of nitrogen oxides (NO_x), water vapour, hydrogen fluoride and silicon tetra fluoride which are vented to a scrubbing system. The acid-insoluble materials are then removed by hydro-cyclones, washed and filtered before disposal.

Most of the NP processes include removal of calcium nitrate. Calcium is a non-nutrient in NPK fertilizer and seen as a diluent. Calcium nitrate is removed from the digestion solution in order to increase the nutrient content as well as to reach the appropriate $\text{CaO:P}_2\text{O}_5$ ratio. Additionally, to avoid precipitation of water-insoluble di-calcium phosphate during the neutralization of the NP acid with ammonia and obtain a product with good thermal stability for transportation, the removal of calcium nitrate is

necessary. This is achieved by cooling crystallization down to $-5 - 0\text{ }^{\circ}\text{C}$ [58] at which $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (calcium nitrate tetrahydrate (CNTH)) is the most stable hydrated form of $\text{Ca}(\text{NO}_3)_2$ [59]. The separation of calcium nitrate and the phase equilibria in the system of $\text{CaO} - \text{P}_2\text{O}_5 - \text{N}_2\text{O}_5 - \text{H}_2\text{O}$ over a wide temperature range from $0\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$ has been studied [60]. CNTH crystallization starts at $23\text{ }^{\circ}\text{C}$ and the solubility decreases rapidly by decreasing the temperature. More than 60% of the CNTH can be crystallized at $20\text{ }^{\circ}\text{C}$ and 80-85% is removed at $-5\text{ }^{\circ}\text{C}$. The overall nutrient concentration and the $\text{N}:\text{P}_2\text{O}_5$ molar ratio of the final NPK are the main factors that determine the minimum amount of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ which has to be removed. Depending on the amount of Ca which has been removed, 50-90% water-soluble P_2O_5 can be produced while $> 99\%$ of P accounts for citrate-soluble $\text{P}_2\text{O}_5\%$. The best range for the $\text{CaO}:\text{P}_2\text{O}_5$ ratio is 0.3–1 [61]. The calcium nitrate by-product can be either used in production of calcium nitrate fertilizers or be converted into ammonium nitrate solution and calcium carbonate.

After cooling crystallization of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, by considering the initial concentration of fluoride and cadmium in the nitrophosphoric acid solution, defluorination and decadmiation processes may be needed to increase the quality of the produced fertilizer [62, 63, 64].

The leach solution after cooling crystallization contain nitric acid, phosphoric acid, hydrofluoric acid, calcium, magnesium, aluminum, and some other impurities like iron, silicon, suspended insoluble quartz and REE. The NP process continues with neutralization of the nitrophosphoric acid solution by the addition of gaseous ammonia under strict pH control (adjustment of N/P ratio). During the ammonization of the NP acid, the dissolved Ca is precipitated as fluoride and phosphate phases and most of the nitrate and phosphate ions remain in the solution. Normally, ammonium nitrate is added to adjust the N/P ratio. Ammoniation of the NP acid is extremely exothermic where the temperature of the mother liquor is kept between $120\text{--}130\text{ }^{\circ}\text{C}$. During neutralization, a great part of water content is evaporated and then the slurry is further concentrated by using reduced pressure or atmospheric evaporators. The evolved ammonia gas during evaporation is recovered by scrubbing with acidic ammonium nitrate solution or by direct condensation. Thereafter, granulation and further evaporation of water content take place in a drum granulator (spherodizer) after addition of a K salt (KCl , KNO_3 or K_2SO_4) to the slurry having a water content of ca. 15-20%. Towards the final NPK product, the granules are passed through screening, crushing, cooling and coating units [23, 65].

The energy consumption for production of fertilizer from the NP process is 5.5GJ/t of P_2O_5 while this number for production of phosphoric acid (54% P_2O_5) using the wet process is 10.8 and 12.9 GJ/t of P_2O_5 for the hemihydrate and dihydrate route respectively [23].

2.3.3.1 *Recovery of REE within the NP process*

A review of literature shows that, although numerous researchers have reported details of the process [23, 58, 61], there are only very few reports on the recovery of REE within the nitrophosphate process and none of them have investigated the details of the process by considering the industrial values of the NP process. The rare earth elements are dissolved in the nitrophosphoric acid solution in the digestion of the apatite and the leaching efficiency has been investigated [66, 67, 68, 69]. The highest recovery of REE was reported in 5 mol/L nitric acid, at 60 °C, solid liquid ratio of 1:6 g/mL and after 120 minutes of leaching. It has been shown that the leaching efficiency of REE is higher (> 95%) in apatite as compared to other phosphate rocks such as phosphorite (80-92%). The leaching of REE is also higher when the REE are present in apatite lattice as a substitution for Ca as compared to the cases where REE present as separate phases such monazite. Because of high solubilization of REE, the recovery of these metals in NP process is superior to that in wet processing. The recovery of REE from nitrophosphoric acid solutions has been achieved by crystallization/precipitation, solvent extraction and ion exchange methods [1].

The REE can effectively be separated from NP acid by precipitation through heating the NP acid up to 200-210 °C under 20 atm pressure [34]. Habashi, (1985) investigated the precipitation of REE from a NP acid after defluorination and calcium nitrate cooling crystallization down to -5 °C and adjustment of the free nitric acid to <2% by addition of NH_4OH [2]. This study showed that REE phosphates can be precipitated out after heating the respective NP acid solution up to 200 °C for 1 h. The formed crystals contained 41.1 mass% REE and the REE recovery was 95.2 %. The REE isolation via crystallization method is not industrially adopted due to high energy consumption, complexity of the process and corrosion.

Habashi, (1985) showed that the lanthanides can be recovered from the authentic leach solution after crystallization of $Ca(NO_3)_2 \cdot 4H_2O$ and defluorination then adjusting the pH to between 0.3-1.4 by NH_4OH at 70°C-90°C [2]. It was shown that the recovery of REE and their concentration in the obtained precipitate as phosphates is a function of pH

and calcium concentration. Al-Shawi et al. (2002) studied the separation of REE from nitrophosphoric acid solutions in Norsk Hydro's rare earth recovery plant by precipitation with ammonia at a pH of 1.8. They reported that the co-precipitation of REE with separated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is negligible but no attempt was made to report the degree of REE co-precipitation and loss of phosphorous [70]. Andropov et al. (2016) obtained a REE phosphate hydrate precipitate with 24-26 mass% REE by neutralization of the NP acid using ammonia gas to pH 1.8-2. The NP acid solution containing 6-7g/L REE, 400-500g/L phosphoric acid, 80-120 g/L nitric acid and 50-80 g/L of calcium was prepared after dissolution of apatite in nitric acid followed by cooling crystallization. The REE precipitate were further purified by solvent extraction with tributyl phosphate (TBP) after dissolution in nitric acid [71]. Ionic exchange method was also used for further purification of a REE phosphate concentrate which was obtained through partial neutralization of NP acid solution after leaching the Khibiny apatite concentrate with nitric acid [40].

Fig. (6) shows schematically the process of recovery of REE by precipitation integrated within the nitrophosphate process of fertilizer production. Neutralization of the NP acid solution with ammonia to a pH of 1.8-2 shows a great potential for REE recovery which weakly interfere with the main process of fertilizer production while all the reagents are already consumed in the fertilizer production. The quality of the REE phosphate concentrate is strongly dependent both on NP acid composition and precipitation conditions.

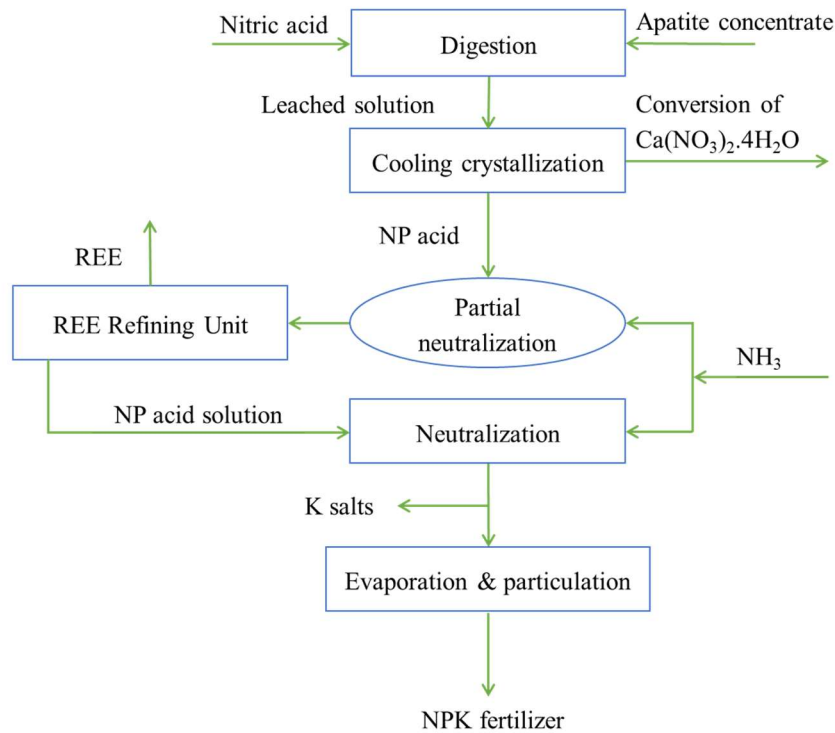


Figure 6. Nitrophosphate process with integrated REE recovery (reproduced from paper II).

Different type of acidic and neutral extractants have been used for solvent extraction of REE from NP and nitric acid solutions. Depending on the type of extractant used, the efficiency of REE extraction is a function of NP acid solution pH, REE concentration and presence of impurities like Fe. The neutral extractant like TBP and TOPO (trioctylphosphine oxide) are preferable over acidic extractants such as D2HEPA and EHEHPA due to the high acidity of the NP acid solution [7, 72, 73, 74, 75, 43]. Decomposition of the apatite with nitric acid followed by solvent extraction with a neutral extractant such as TBP has been proposed as the most viable industrial process for the recovery of REE from phosphate rocks. This process is claimed to have been adopted industrially in Russia. However, in this method a salting out component of nitrate should be added to the NP acid to enhance the extraction [72] which might change the composition of the NP acid significantly. In addition, usually low quality REE concentrates are obtained by precipitation of REE from

stripping solutions due to co-extraction of Ca. The REE concentrate should be further treated to increase the REE content. In using acidic extractant, the acidity of the NP acid should be reduced to enhance the REE extraction while it has been shown that, once the acidity is reduced to less than 0.3 mol/L, the REE are precipitated before being extracted by extractant [72]. Additionally, due to low concentration of REE in the NP acid (~ 2-6 g/L), the require organic inventory for effective separation of REE is very big and the pollution of NP acid with organic matter risk the quality of the produced fertilizer. In addition, the harsh solvent extraction working environment has raised great attempts to reduce the contribution of this method in REE recovery routes.

Habashi (1985) proposed a flowchart for recovery of REE from NP acid using TBP as the extractant. The leaching solution of apatite in nitric acid was first neutralized with NH_3 to pH 0.2 and then the REE was extracted using TBP followed by water stripping [2]. The REE were precipitated out from the stripping solution through neutralization with NH_3 . Appreciable co-extraction of Ca and P with REE and consequent precipitation of calcium phosphate in the stripping solution reduce the solubilization of REE due to co-precipitation. Similarly, TBP was used to separate REE from defluorinated NP acid solution obtained by leaching Abu Tartur phosphate rock with nitric acid and neutralization to pH 1. The stripped REE^{3+} and Ca^{2+} were then precipitated after addition of excess oxalic acid and ignited to 950 °C to produce a REE concentrate containing 96% CaO and 2.7 Ln_2O_3 [69]. The factors influencing the extraction of REE from NP acid solution using TBP such as TBP concentration, pH, contact time, temperature and aqueous/organic phase ratio were investigated in a study by Jorjani et al. (2012). Hot water was employed to scrub the loaded organic from Ca and P followed by precipitation stripping using oxalic acid and the optimum condition in terms of acid concentration, contact time and phase ratio was reported. At optimum condition, a REE oxide concentrate containing 86 mass% REE with a total recovery of ~ 80% was obtained [76].

2.4.Precipitation

Precipitation is generally defined as reactive crystallization [77, 78]. Processes where solid phases are involved are usually more complex than those that only involve homogeneous gases and liquids [79].

Supersaturation is the driving force for crystallization and is defined for $\text{A(aq)} + \text{B(aq)} \leftrightarrow \text{AB (s)}$ as in Eq. (6):

$$S=[A][B]/K_{sp} \quad \text{Eq. 6}$$

Where A and B are components forming the solid precipitate $AB(s)$ and K_{sp} is the solubility product of the precipitating solid phase, $K_{sp} = [A]_{eq}[B]_{eq}$. Thus, to determine the supersaturation the solubility of the desired solid phase must be determined. The solubility of a solid phase is both a function of temperature and composition of the solution. For nanocrystalline precipitates smaller than $10\ \mu\text{m}$, the solubility is a function of crystal size and smaller crystals have higher solubility. Supersaturation control is of great importance in controlling the properties of the solid product, namely composition, crystallinity, morphology, particle size and purity.

When a solid phase is formed from solution the different phenomena nucleation, crystal growth and aggregation are involved. Nucleation signifies the formation of new crystals. Nucleation is divided into primary and secondary. Primary nucleation is due to the merging of molecular clusters or embryos to crystal nuclei. Foreign particles (e.g. dust particles) can catalyze the primary nucleation. Secondary nucleation occurs by mechanisms that needs the presence of crystals in the solution. In a crystallization system, the collision between crystals or with the equipment is the most important mechanism of secondary nucleation.

In a solution, the ions that can form the solid phase tend to combine and form clusters consisting of 10-1000 molecules per cluster. Formation of clusters is the result of aggregation-polymerization of the solute species and trigger primary nucleation. For sparingly soluble substances, the primary nucleation often takes place at a relatively high supersaturation level. For highly soluble compounds, the primary nucleation may take place at low relative supersaturation level.

The change in Gibbs free energy (ΔG) associated with the process of formation of a spherical nucleus of radius r is equal to the sum of the volume excess free energy (ΔG_v) and the surface free energy (ΔG_s). As can be seen from Fig. (7), ΔG versus size passes through a maximum corresponding to the critical radius. In homogeneous nucleation, a nucleus is formed when the size of formed clusters exceeds the critical size (r_c). The critical nucleus size is a function of the supersaturation, temperature and interfacial tension. As the supersaturation increases the critical nucleus size decreases and the nucleation rate increases. The critical nuclei size, r_c , is in the order of 40 to 200 Å.

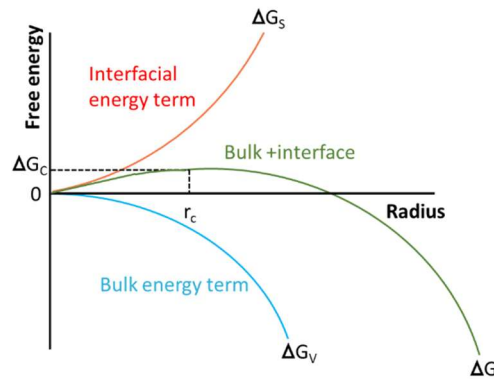


Figure 7. The behavior of free energy of change associated with the formation of a nucleus (adopted from [96]).

The growth of a crystal is due to the incorporation of molecules and molecular clusters into the crystal lattice. This incorporation happens primarily at kinks and steps on the crystal surface. Two subsequent mass transfer processes can be considered for crystal growth. First is the film diffusion, i.e., molecules diffuse from the solution bulk to the crystal surface. The second is surface integration where at this step, the molecules diffuse over the surface and are incorporated into the crystal lattice. The surface integration is often rate limiting step for weakly soluble substances and the growth rate can be assumed to be independent of hydrodynamic conditions [79].

In hydrometallurgy most often obtaining well grown precipitates are preferred and therefore when designing a precipitation system, the operating condition should be adjusted in a way that the supersaturation is kept inside the metastable zone (controlled by growth rate) while the precipitates are recycled to provide necessary seeds [78]. The metastable zone stands for the supersaturation interval where the primary nucleation is insignificant and secondary nucleation and growth prevail. The size of the metastable zone can be affected by a number of factors such as temperature, solution purity, presence of additives and hydrodynamics. Methods for the control of supersaturation include pH-control, metal complex formation and dissociation, dilution, redox reaction or via a dissolution reaction; a supersaturation-controlled precipitation strategy can be found by employing these methods [79, 78].

In precipitation processes, often a less stable phase initially precipitates due to favorable kinetics and then, given the time, converts into the stable form. This is in accordance to Ostwald's step rule "the least stable phase nucleates first as long as homogeneous nucleation determines the rate" [79]. Phase transformations in solution may take only a few minutes or it may take several years. Temperature and pH are the two important parameters that influence dissolution-recrystallization processes. Because of low temperature and/or high supersaturation, the formed precipitates can be amorphous but can then convert to crystalline solids upon aging [79].

2.5. Individual REE separation using HFSLM

Individual separation of REE from each other is one of the greatest challenges in REE separation processes mainly owing to their chemical similarity. The individual separation of REE is usually carried out industrially by solvent extraction using mixer-settlers [7, 8]. The liquid - liquid extraction using supported liquid membrane (SLM) is an attractive alternative over mixer-settler contactors. By SLM extraction simultaneous extraction and stripping is operated in one module. In SLM, a thin membrane where the organic phase is immobilized via capillary force, separates the aqueous feed and the strip phase. The polymeric support only provides a structural support for the organic phase (solvent) and does not play any role in the separation [9].

Compared to solvent extraction using mixer-settlers, in SLM, extraction and stripping is operated in one and the same unit, with a very high surface area for mass transport per unit volume of equipment, and the solvent inventory is much lower. Thus, the capital and operating cost, size of the unit and the respective energy consumption can be much lower. As opposed to a normal liquid-liquid extraction process being an equilibrium staged process, SLM is a mass transport governed unit operation driven by a hydrogen ion concentration difference rather than a REE concentration difference by which the REE can actually be transported from low to high concentration over the membrane. The low solvent inventory and solvent loss allows for using economically expensive and tailor-made extractants. High selectivity and no limitation caused by poor loading, solvent flooding and entrainment are other important advantages of SLM processes. In addition, the working environment of SLM extraction is indeed less challenging as compared to conventional mixer-settler solvent extraction plants [80, 81, 9, 82, 83].

Despite the numerous advantages, this technology has not yet been adopted industrially mainly due to membrane instability and gel formation beside the complexity and difficulty in scale-up [84]. In addition, the membrane module life time is finite and require regular replacement that imposes a great cost [80, 81, 9, 82, 83].

2.5.1 D2HEPA as carrier

The chemistry of REE solvent extraction using different solvent extractants and typical configurations has been studied by numerous researchers [7, 11, 8]. Di(2-ethylhexyl) phosphoric acid ((C₈H₁₇O)₂PO₂H) denoted as D2HEPA, DEHPA and HDEHP with the trade name of P204 is one of the most versatile alkyl phosphoric acid solvent used for REE extraction as group and individual with many advantages over other commonly used solvents. These advantages are chemical stability, generally good kinetics of extraction, good loading and stripping characteristics, low solubility in the aqueous phases and availability in commercial quantities [85, 8]. In general, cationic exchangers extractants show higher selectivity for REE extraction as compared to neutral and anionic extractant [75]. The overall reaction for extraction of rare earth elements using D2HEPA as an acidic extractant (cation exchanger) can be expressed as Eq. (7) where M stands for REE and A is the extractant which donates the organic anion [7].



Each molecule of REE is generally extracted in a complex with three molecules of D2HEPA dimers and releases three protons in a coupled transport.

Generally, the real case is more complicated and other stoichiometries are also reported especially in high concentration of counter anions [86, 87, 8, 85]. Mohammadi et al. (2015) showed that in solvent extraction of REE from dilute hydrochloric acid solution using D2HEPA diluted in kerosene, 1-2 hydrogen ion/REE ion for Nd (III) and 2-3 hydrogen ions for Y(III) and Dy (III) respectively are released which suggests that at least part of the REE are extracted as chloride complexes and complexation involves not only D2HEPA dimers but also monomers and to some extent aggregated REE species [88]. The relationships between metal concentrations in the organic phase and aqueous phase are described through equilibrium constants as shown in Eq. (8).

$$K_{eq} = \frac{[M(HA_2)_3][H^+]^3}{[M^{3+}][H_2A_2]^3} \quad Eq. 8$$

The Equilibrium constants for complexation of REE^{3+} with D2HEPA in different aqueous medium and diluents are reported by a number of investigators [85, 89, 8, 90, 91, 92, 92, 93, 94, 95]. The reported values normally show great discrepancies since they are calculated at different feed and organic range of concentration and aqueous phase pH that might change the extraction stoichiometry. Regardless of the K_{eq} values, the ratio of reported equilibrium constants and the respective separation factors between different REE are almost the same.

D2HEPA is also a suitable extractant for primary separation of REE from the original leach solution. This is mainly due to the ability of D2HEPA to separate REE from common impurities such as Fe, Ca, which stems from the difference in transport kinetics as well as between the distribution coefficients of REE and common impurities [96]. In addition, D2HEPA is used for concentrating the REE from dilute solution which attributes to the high distribution coefficients of REE [97, 98]. The difficulty in stripping the REE from loaded extractant especially in the case of heavy REE is a barrier of using this extractant. From Eq (8) it is evident that higher pH in the feed solution facilitates the extraction while the stripping (back-extraction) is prompted by high proton concentration. D2HEPA extracts lanthanides with higher efficiency from hydrochloric and sulfuric acid medium as compared to nitric acid [11].

2.5.2 Supported liquid membrane extraction

Understanding of the metal transport mechanism in SLM extraction is of great importance for determination and optimization of the industrial parameters that influence the selectivity of this process.

Fig. (8) shows the transport mechanism of M^{3+} cations of REE across a membrane using D2HEPA as the carrier. The extraction chemistry of SLM are basically the same as that in liquid-liquid extraction but the transport process is governed by both kinetic and equilibrium parameters [99]. Several mass transfer processes are involved in transportation of metals from feed to the receiver phase (stripping solution) through the supported liquid membrane phase. In general, the proton gradient between the feed and strip solution is the main driving force for the counter transport of M^{3+} . In the first step, the metal ions diffuse from the feed bulk to the feed-organic interface where the complexation reaction of metal ions with the

extractant takes place and respectively the protons are released and diffuse into the feed bulk. In the next step, the metal-organic complexes ($M(HA_2)_3$) diffuse through the liquid membrane from the feed-organic interface to the stripping-organic interface. Thereafter, upon reaching the strip interface, the decomplexation reaction occurs where the carriers (transportation shuttles for M^{3+}) are regenerated after binding with protons and M^{3+} are released. After decomplexation, the carriers (A_2H_2) diffuse back across the membrane. The process ends by the diffusion of M^{3+} from the stripping-organic interface towards the stripping solution bulk through the boundary layer of the stripping-membrane side. The hydrogen ions diffusion coefficient is normally much larger than the diffusion coefficient of metal ions in the aqueous phases and therefore the resistance against its mass transfer is not a limiting step [100].

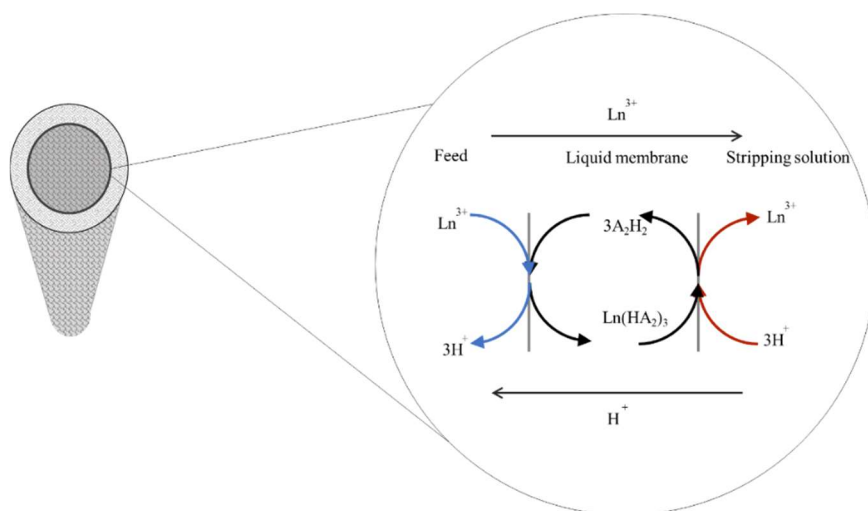


Figure 8. Transport mechanism of REE through a HFSLM using D2HEPA as the carrier.

High selectivity in LM is one of the advantages over solvent extraction processes which plays an important role in individual separation of REE. The selectivity of REE extraction in SLM is a function of pH, metal concentration in the feed, carrier concentration, diluent type and SLM operating configuration.

2.5.3 Configurations of SLM

Flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM) are the most common configurations of SLMs. In FSSLMs a flat microporous solid support impregnated with organic solvent is clamped between two compartments by which the feed and stripping solution are being separated. FSSLM are more likely to be used for research purposes in lab scale experiments due to low surface area to volume ratio and long run stability problems while HFSLM has gained industrial attention and can provide much larger interfacial surface area and higher stability for a longer time. In HFSLM, the extraction of solute species is carried out in a hollow fiber module consisting of a nonporous shell where many small, thin and porous hollow fibers are packed inside [9]. The organic phase is inside the fiber walls.

HFSLM contactors has adopted different configurations including hollow fiber renewal liquid membrane (HFRLM) and emulsion pertraction technology (EPT) which can be run either in batch or continuous mode. Fig. (9) schematically shows the aqueous-organic interfaces across a fiber pore in different configurations of HFSLM. The main purposes of new configurations are improving the efficiency of the SLM processes with long-term stability [80]. Fig. (9) shows the aqueous-organic interfaces in different configurations of HFSLM.

In standard HFSLM the pore membrane is impregnated with an organic solvent and the feed and strip solutions flow outside the fibre. The solute is extracted into the organic phase and then diffuse through the pores from feed side to strip side. At the strip-organic interface the solute is back extracted into the strip solution.

EPT or pseudo emulsion based hollow fibre strip dispersion is an attractive alternative for HFSLM. In this configuration the stripping solution are dispersed in an organic phase through high speed shear mechanical agitators (homogenizers) and a large surface area is provided on the strip side. Due to hydrophobicity of the membrane, the strip droplets cannot penetrate the pores and the emulsion does not need to be very stable. The feed solution flows inside the lumens and stripping-organic emulsion counter currently flows in the shell side. EPT are not restricted by the main deficiencies of emulsion liquid membranes which are membrane leakage and emulsion swelling [81], however; the lack of long term stability, extra emulsification and de-emulsification steps and higher inventory of the organic solvent in comparison with HFRLM and HFSLM are the

shortcomings of this configuration [80]. The principles behind this configuration basically follow emulsion liquid membrane (ELM) and supported dispersion liquid membranes [101]. EPT with hollow fiber contactors was introduced as a clean alternative to perform separation and recovery of different metals such as Zn, Cr, Hg, Fe, etc. present in low concentrations in aqueous industrial effluents [102, 103, 104, 105, 106, 107] as well as in the remediation of polluted ground water from heavy metals and organic matters [108, 109, 110].

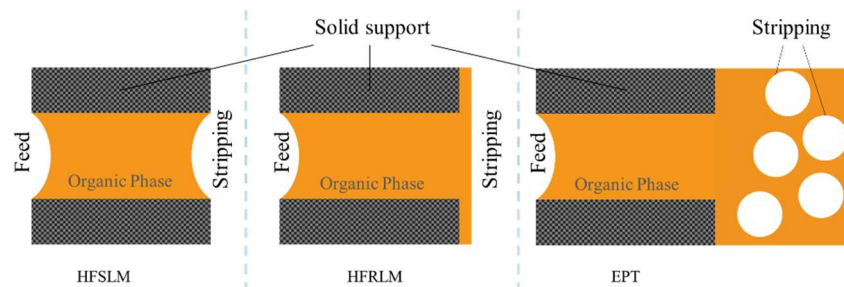


Figure 9. Aqueous-organic interface across a pore in different configurations of HFSLM.

HFRLM is a new technique which has been suggested based on surface renewal theory and takes the advantages of both fibre membrane extraction and liquid film permeation. In this technique the hydrophobic pores are first filled with organic solvent and then feed is pumped on the shell side while the uniformly dispersed stripping-organic solution or feed-organic solution (in HFRLM the organic phase is dispersed in the aqueous phase) flows inside the lumen building up a thin organic layer at lumen-pores interface and lumen walls. Peeled off organic from the stripping-organic and feed-organic interface due to shear forces caused by moving fluids are compensated constantly during the process by the organic droplet dispersed in the adjacent aqueous phase. The main advantages of HFRLM are long term stability, large mass transfer area, accelerated mass transfer and easy operation [111]. As compared to EPT, this configuration requires less organic inventory but providing less surface area on the stripping side [80]. The same concept has also been applied on flat sheet membranes to improve the membrane life time and stability [112]. Numerous researchers have studied HFRLM as a technique to improve the stability of SLM and investigated the parameters that affect the selectivity and transport rates through the membrane [111, 113, 114, 115, 116, 117, 118].

2.5.4 SLM instability problems

The membrane stability is a major barrier for commercial application of supported liquid membrane extraction. The stability of SLMs has been reported by different investigators empirically over the period of a couple of hours to months. The decay in mass flux and permeability, rapid increase in pH or loss of selectivity are the main indications of membrane instability. The loss of liquid membrane phase (carrier and solvent) which is immobilized in the pores is the main reason that causes the membrane instability and different mechanisms have been proposed to explain this loss [84]. The pressure difference over a certain limit between the two sides of the liquid membrane phase can push out the organic phase out of pores. The pressure difference over the membrane should be kept below the minimum transmembrane pressure required to replace any membrane phase with aqueous phases. Wetting the support pores by the aqueous phase is another proposed mechanism to explain the membrane instability. This mechanism is supported by the decrease in surface tension and contact angle of the organic phase after complexation with the metals which facilitate the replacement of the organic phase with aqueous phase. The blocking of the pores due to spontaneous formation of microemulsions or gelatinous precipitates could also lower the mass flux in SLM systems. Presence of an osmotic pressure gradient over the membrane is also proposed as a mechanism for displacement of the organic phase with water. All the aforementioned mechanisms might partly contribute in SLM instability; however, some of them are seriously doubted to have any effect. The dissolution of carrier and extractant in the feed and strip solution beside the emulsification of liquid membrane phase due to lateral shear forces are considered as the main mechanism of SLM degradation [84, 119, 83].

Gel formation is one of the important limitations of using D2HEPA as the carrier in SLM that leads to significant decay in mass transfer and membrane clog. In extraction system with rare earth elements, the concentration of metals in the aqueous phase is limited by the formation of a gelatinous third phase mainly due to high concentration of metals in the organic phase. The formation of these polymers is a function of carrier concentration, metal concentration and pH of aqueous phase [120]. The gel formation in the organic phase occurs when the metal loading is high. This is a very undesirable phenomena mainly due to associated viscosity and phase separation problems that cause the deficiency of the extraction and even can stop the process [121, 122]. In the case of using D2HEPA as

carrier, the gel occurrence is favored by increasing the metal concentration and pH in the feed and decreasing the carrier concentration in the membrane phase. To decrease overloading (any gel formation) more extractant can be added to the diluent. However this is only possible to a certain extent since too high concentration of extractant will give a very high viscosity of the organic phase.

3. *Experimental*

All the experimental procedures and used experimental apparatuses have been described in detail in the appended papers. In paper I, the experimental plan was sought to investigate the behavior of REE during leaching of apatite in nitric acid, cooling crystallization of CNTH and the parameters that effect the precipitation of REE during partial neutralization of NP acid using ammonium hydroxide. In Paper II, The potential of upgrading the REE phosphate precipitates as well as removing the impurities were assessed by selective dissolution and re-precipitation as double sulphate under optimum conditions. In paper III, further treatment of the REE phosphate precipitates were investigated with the focus on dephosphorization with thermal treatment and alkaline conversion to enhance the dissolution of REE. In paper IV, the individual and group separation of REE were studied by HFSLM extraction in pilot scale.

3.1. *Materials*

All the chemicals in this study were of laboratory grade and used without further purification. The apatite concentrate used in this study is a fluorapatite delivered by LKAB (Luossavaara-Kiirunavaara AB). The apatite concentrate is obtained by processing the tailings deposits at Kiruna by flotation. The tailings contain 4-8 mass% P_2O_5 and 1200-1300 mg/kg REE, and the deposit amounts to about 43 Mtons [123]. The apatite concentrate obtained by flotation contains 90 mass% fluorapatite, 6% dolomite and 4% calcite and REE to a concentration of 4000-5000 $\mu\text{g/g}$. The REE were reported to be present mainly as mineral inclusions in apatite and partly in allanite and liberated monazite [67]. The apatite is currently considered as a waste product in the processing of iron ore.

3.2. *Characterization Techniques*

Throughout this study, the apparent pH of different solutions was measured by using a Thermo Scientific Orion ROSS Ultra electrode, which was calibrated by standard solutions at pH 2, 4 and 7 at 25 °C. The main characterization techniques used in this study were ICP-OES, Powder XRD and SEM-EDX. For Powder XRD analysis, a Siemens, Model D5000 diffractometer equipped with an X-ray tube for $\text{CuK}\alpha$ radiation has been used to characterize all the solid samples. Powder XRD patterns were recorded from 5° to 90° with a $\theta/2\theta$ diffractometer. The phases were then identified by comparison with data in the International Center for Diffraction Data (ICDD)-Powder Diffraction Files. Depending

on the important peaks, the appropriate 2θ range was opted for data presentation. SEM-EDS analysis was performed using a Hitachi S-4800.

3.2.1 ICP-OES

Inductively coupled plasma optical spectroscopy (ICP-OES) is an analytical technique for detection of chemical elements in various type of samples (mostly water dissolved). This technique involves a plasma and a spectrometer. As it is shown schematically in Fig. (10), samples to be analyzed are pumped by a peristaltic pump through a nebulizer where it mixes with argon gas to form mist and then are sent to a spray chamber. The produced aerosol is then passed through an argon plasma. The plasma is generated by a high frequency alternate current flow produced by a radio frequency generator into a cooled induction coil. Then the ionization occurs due to collision between the argon atom and the electrons, forming a stable plasma. The plasma temperature is 6000-7000 K and it reaches even up to 10000 K in the induction zone. In the torch desolvation, atomization and ionizations of the sample occur. As thermal energy is absorbed by electrons, they reach a higher "excited" state and as they drop back to ground level, the absorbed energy is released as light (photons). The emission spectrum characteristics are unique for each element and is measured with a spectrometer. The concentrations can be calculated by measuring the light intensity on the wavelength and comparing with the calibration samples.

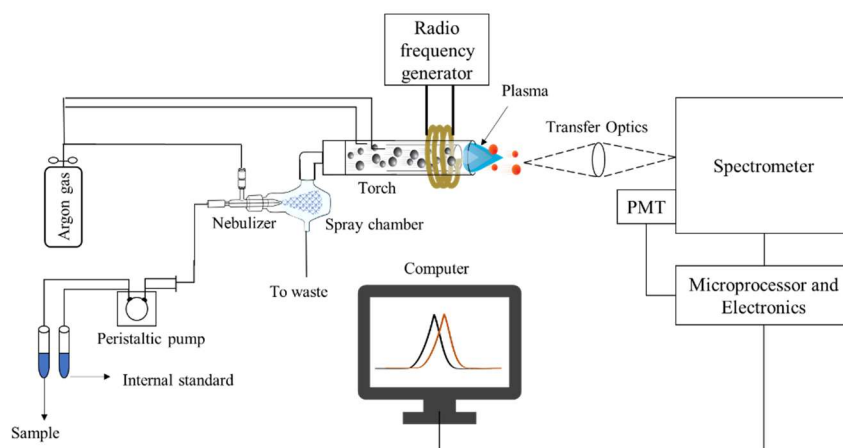


Figure 10. Schematic of ICP-OES in axial mode view with the use of internal standard.

ICP-OES (Thermo Fisher iCAP 7000-dual mode) with auto-sampler (ASX-520) was used to determine the elemental composition of the aqueous phases. To measure the composition of the solid samples, they were dried at appropriate temperature for 24 h and then dissolved completely in a mixture of nitric acid, hydrochloric acid and perchloric acid with the molar ratio of 10:30:1 at elevated temperatures and then were diluted with deionized water. For the ICP-OES analysis, the wavelengths were carefully selected to avoid overlapping and to reduce the background effects. The best lines' wavelength and measuring modes for analyzing the elements that were commonly measured in this study are reported in Table (2). In some cases, Hafnium in concentration of 10-15 mg/L was used as an internal standard. Qualification samples of known concentration were placed between samples to measure the accuracy of the results. Wash samples were placed between samples to reduce sample contamination. All samples were diluted 10 to 100 times with 5% (v/v) nitric acid and stored in HDPE bottles before analysis. The dilution ratio was selected in a way to measure all the concentration below 50 mg/L and preferentially between 1-10 mg/L. Normally standards of different concentration were used ranging from 0.1 mg/L to 500 mg/L depending on elements and the concentration range.

Table 2. Selected ICP lines for the commonly measured elements.

Element	Lines (nm)	View mode
Sc	335.373	Axial-Radial
	361.384	Axial
Y	360.073	Axial
La	333,749	Axial
Ce	404.076	Axial
Pr	390.844	Axial
Nd	430.358	Axial
Sm	442.434	Axial
Eu	381.967	Axial-Radial
Gd	310.050	Axial
Dy	353.170	Axial
Sm	442.434	Axial
Er	326.478	Axial
Ca	183.801	Axial
	315.887	Radial
P	214.914	Axial
Fe	259.940	Axial
	240.488	Axial

Al	167.079	Axial
Si	251.611	Axial
	212.412	Axial
S	180.731	Axial
	182.034	Radial
Na	589.592	Axial-Radial

4. Speciation calculations

The distribution of an element amongst chemical species in a system is referred to as chemical speciation. To predict the behavior of an element in a system, knowing the full chemical speciation is essential and it is not generally possible to perform a speciation analysis by analytical chemistry methods for complex systems [124]. There are several programs to calculate the chemical speciation in solutions with or without solids present, e.g. PHREEQC, MINEQL, EQ3/6, Visual MINTEQ and Medusa.

In this study, the chemical speciation calculations under conditions similar to those in performed experiments were investigated by the Hydra-Medusa speciation software [125]. The stability constants for the governing equilibrium reactions reported in the Medusa database (Hydra) were used, being valid at 25 °C and zero ionic strength. The mass balance equations were provided based on the studied systems. The activity coefficients must be calculated at the ionic strength of the solution. As an example the ionic strength of the NP acid solution obtained after the cooling crystallization was estimated to be in the range 3-3.6 mol/L. Numerous methods have been suggested for calculating activity coefficient at moderate and high ionic strengths [126, 127, 128] but in general, activity coefficients are less predictable at high ionic strength. In the speciation calculation done by the Medusa software, the equilibrium constants in the input file were given for zero ionic strength (standard conditions) and the activity coefficients at the actual ionic strength were calculated according to an approximation of the model by Helgeson et al. (1981) [126]. The total number of stability constants used in this study were more than 300. Some of the stability constants for the governing equilibrium reactions of Ca(II), Y(III), Ce(III) and (IV) and Fe(III) are reported in Table (3).

Table 3. Stability constants for some of the governing equilibrium reactions of Ca(II), Y(III), Ce(III)-(IV) and Fe(III) at $I = 0$ and 25 °C.

Reaction	log K
$Ca^{2+} + 2NO_3^- \leftrightarrow Ca(NO_3)_2$	0.6
$Ca^{2+} + F^- \leftrightarrow CaF^+$	0.94
$2H^+ + Ca^{2+} + PO_4^{3-} \leftrightarrow CaH_2PO_4^+$	20.96
$H^+ + Ca^{2+} + PO_4^{3-} \leftrightarrow CaHPO_4$	15.08
$Ca^{2+} + NO_3^- \leftrightarrow Ca(NO_3)^+$	0.50
$Ca^{2+} + PO_4^{3-} \leftrightarrow CaPO_4^-$	6.46
$Ca^{2+} \leftrightarrow 2H^+ + Ca(OH)_2(s)$	-22.8
$Ca^{2+} \leftrightarrow 2H^+ + CaO(s)$	-32.79

$2H^+ + Ce^{3+} + PO_4^{3-} \leftrightarrow Ce(H_2PO_4)^+$	22.16
$Ce^{3+} + NO_3^- \leftrightarrow CeNO_3^{2+}$	0.69
$2H^+ + Y^{3+} + PO_4^{3-} \leftrightarrow Y(H_2PO_4)^+$	22.37
$3Ca^{2+} + 2PO_4^{3-} \leftrightarrow Ca_3(PO_4)_2(s)$	28.92
$Ca^{2+} + 2F^- \leftrightarrow CaF_2(s)$	10.60
$H^+ + Ca^{2+} + PO_4^{3-} \leftrightarrow CaHPO_4 \cdot 2H_2O(s)$	18.99
$5Ca^{2+} + 3PO_4^{3-} \leftrightarrow Ca_5(PO_4)_3OH(s)$	40.46
$Ce^{3+} + PO_4^{3-} \leftrightarrow CePO_4(s)$	26.27
$Ce^{3+} \leftrightarrow 3H^+ + Ce(OH)_3(s)$	-19.9
$Ce^{4+} \leftrightarrow 4H^+ + CeO_2(s)$	4
$Y^{3+} + PO_4^{3-} \leftrightarrow YPO_4(s)$	25.02
$Y^{3+} \leftrightarrow 3H^+ + Y(OH)_3(s)$	-26.0
$2H^+ + Fe^{3+} + PO_4^{3-} \leftrightarrow FeH_2PO_4^{2+}$	24.98
$H^+ + Fe^{3+} + PO_4^{3-} \leftrightarrow FeHPO_4^+$	17.78
$Fe^{3+} + PO_4^{3-} \leftrightarrow FePO_4 \cdot 2H_2O(s)$	26.40
$Fe^{3+} \leftrightarrow 3H^+ + Fe(OH)_3(s)$	-4.891
$2Fe^{3+} \leftrightarrow 6H^+ + Fe_2O_3(s)$	-0.408

5. Key results and discussions

This chapter provides a selection of results and discussion chosen from appended paper I-IV and some unpublished data. To reference the repeatability, the experimental results were reported as average and for repeated experiments error bars showing the deviation from the average were added.

5.1. Apatite concentrate characterization

The composition of the apatite concentrate delivered by LKAB is reported in table (4). The particle size of the grinded material was typically less than 500 μm with a specific surface area of 0.1752 m^2/g .

Table 4. Apatite concentrate elemental composition (paper I).

Component	Mass%	Component	mg/kg	Component	mg/kg
Ca	34.86	La	632	Total HREE	1208
P	16.13	Ce	1183	Total LREE	3308
Fe	0.81	Pr	218	Total REE	4516
Cd	0.0001	Nd	886		
Cr	0.0005	Sm	162		
Cu	0.002	Eu	25		
Pb	0.001	Gd	202		
As	0.032	Tb	26		
Si	0.14	Dy	158		
Na	0.11	Ho	32		
F	~2-3	Tm	13		
Mg	0.2	Yb	65		
Mn	0.1	Lu	6		

This source is appropriate for production of fertilizer and phosphoric acid due to the high P content, and very low concentration of undesirable heavy elements such as (Cd, Cr, Cu, Pb and As) as well as radioactive elements (Th and U).

The value of REE per ton of apatite concentrate is estimated to be between 100-120 US\$ out of which 32% attributes to LREE, 35% to MREE and 33 to HREE [129, 130]. Fig. (11) shows the value distribution of different REE (as REE oxide with purity > 99%) per kg of apatite concentrate.

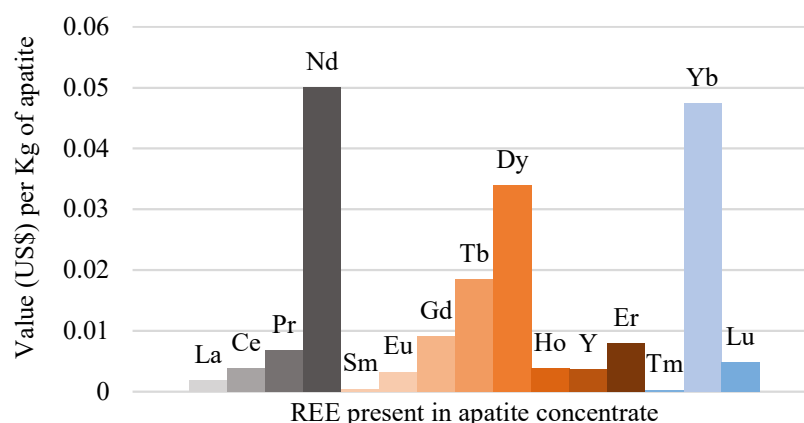
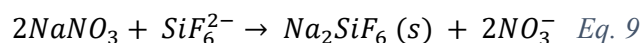


Figure 11. The value of REE as pure oxide per kg of LKAB apatite concentrate.

As alternative waste sources in Sweden to the apatite, the phosphogypsum stack at the island of Gråen, and the Åkulla deposit processed by Boliden (an apatite concentrate with ~ 3000 ppm REE out of which 81% is light REE and 19% is heavy REE) have been considered. However, in comparison with LKAB apatite, these sources not only exist in lower amount, contain lower amounts of REE with lower HREE/LREE ratio, but also the REE are present either incorporated with phosphogypsum or in a monazite phase in case of the Åkulla deposit. Recovery of REE from these phases requires strong acidic conditions. It will be difficult to design an economically sustainable process, and consequently these sources were deemed as less attractive from a REE recovery point of view.

5.2. Leaching and cooling crystallization

After leaching the apatite with 10M nitric acid in 10-20% excess (Eq. (9)), 2h of residence time, at 60-70 °C, the leaching yield of REE, Ca, P and iron were over 99%. The leaching residue was ~ 1 mass%. During leaching of apatite with nitric acid, a major part of F is volatilized as HF and SiF₄, which must be recovered in industrial installations. The remaining part was removed by the addition of NaNO₃ in excess over the stoichiometric requirement which was effective in precipitation of sodium fluorosilicate according to



Sodium fluorosilicate can be a starting material for the preparation of cryolite, Na_3AlF_6 , an important reagent in the electrolytic production of aluminum [69, 131].

To adjust the calcium concentration in the NP acid, calcium nitrate tetrahydrate crystals were then removed by cooling crystallization to -2°C to -5°C . 25 mg of CNTH seed per kg of digestion liquor was added at 20°C and 2 h of residence time was sufficient to reach the equilibrium at -2°C where 66% of the Ca initially present in the leach liqueur was removed. The ratio of $\text{CaO}:\text{P}_2\text{O}_5$ governs the amount of CNTH that should be crystallized out or the final cooling temperature. This ratio is normally kept between 0.3-1. Rare earth ions may replace calcium ions heterovalently in solid phases [36] that might reduce the total recovery of these elements. However, during the cooling crystallization of calcium nitrate tetrahydrate, more than 99 % of REE ended up in the nitrophosphoric acid liquor while only 1% co-precipitated with the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals. The coprecipitation of light REE was higher as compared to heavy ones owing to the fact that the radii of the light REE trivalent ions such as Ce(III), La(III) and Nd(III) is closer to that of Ca(II) compared to heavy REE like Y(III) and Dy(III) [12].

The general composition of nitrophosphoric acid solution for the processing of the LKAB apatite concentrate is shown in table (5). The free HNO_3 concentration in the NP acid solution may vary depending on the amount of excess acid used during leaching. It is normally about 10-12 mass% if 10% excess acid is used.

Table 5. Nitrophosphoric acid solution characteristics.

Characteristics	~	Unit
$\text{CaO}/\text{P}_2\text{O}_5$	0.7- 0.9	mol/mol
Ca/P	0.5-0.6	mass/mass
Ca	4-5	g/L
P	8-10	g/L
Free HNO_3/P	0.9-1	mol/mol
F/P	0-0.2	mass/mass
H_3PO_4	27-29	mass%
HNO_3	16-18	mass%
CNTH	26-28	mass%
H_2O	25-26	mass%
REE	2.5	g/L
Fe	2	g/L

5.3. Partial neutralization

By partial neutralization of NP acid using either ammonia gas or ammonium hydroxide, the REE can be precipitated as phosphates (REE phosphate concentrate). Precipitation of REE from NP acid is the main step of REE isolation from the apatite concentrate. Numerous parameters control the quality of the REE phosphate precipitates in terms of REE, Ca and P content in the precipitate, solid phases and impurity level. The right quality of REE phosphate concentrate significantly influences the economy of the whole REE recovery process and reduce the burden of the subsequent upgrading and purification steps. The key industry-relevant parameters that affect the recovery of REE from NP acid solution are Ca/P ratio, temperature, pH, Fe concentration in the NP acid solution, residence time, REE concentration and composition of the NP acid solution, and neutralizing agent either as gaseous ammonia or ammonium hydroxide. The result of REE precipitation in a typical case of neutralization of NP acid with ammonium hydroxide (25mass%) at 25 °C is depicted in Fig. (12).

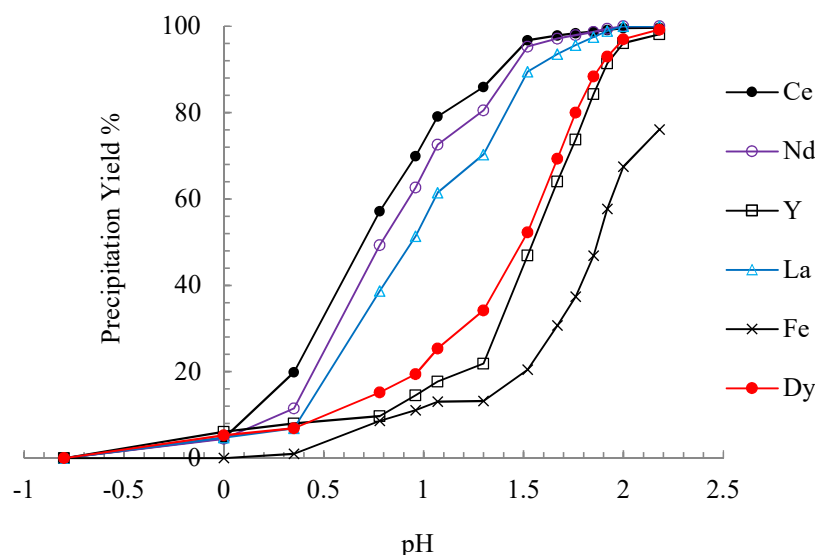


Figure 12. Precipitation of REE at different pH of NP acid, neutralization agent: ammonium hydroxide, 25 °C, residence time 2 h (paper I).

At higher pH, by deprotonation of phosphoric acid, the REE mainly precipitate as REEPO_4 [132, 32, 133]. All the REE starts to precipitate at negative pH values, but the main precipitation take place in the pH range

of 0.4 to 1.5 after 2 h of residence time, except for yttrium and dysprosium that precipitate from pH 1 to 1.8 (Y and Dy belong to the heavy REE while La, Ce and Nd are light REE). By the neutralization to the pH of 1.8, 95% of the total REE are precipitated. The major amount of iron (more than 60 mass % of the total amount) are precipitated in the pH range of 1.7 to 2. To reach pH 1.8, ~ 80 g of ammonia gas or 300 gr of ammonium hydroxide (25%) are required per kg of NP acid solution.

By the increase in end pH of the partial neutralization, the REE precipitation yield increases, but in general because of an increased calcium precipitation, the REE concentration in the precipitate decreases (See Fig. (13)).

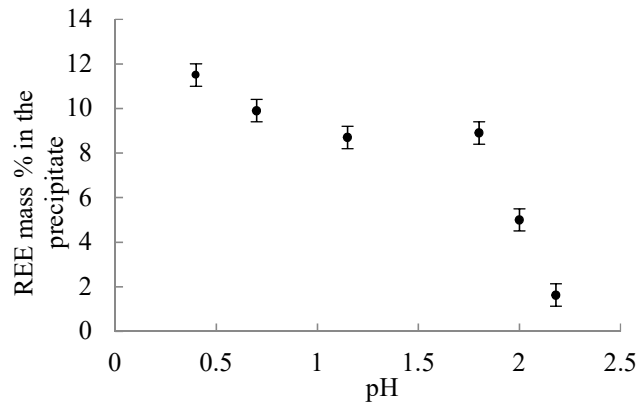


Figure 13. The influence of pH on the REE content in the precipitate, $0.93 < \frac{CaO}{P_2O_5} (\frac{mol}{mol}) < 1.15$, 25 ° C (paper I).

As it is shown in Fig. (13), the REE concentration remained essentially the same (8-10% by mass of REE) in the precipitate obtained at pH values between 0.5 and 1.8. By continuing the partial neutralization to a pH above 2, a great reduction in REE concentration is observed since the $CaHPO_4 \cdot 2H_2O$ precipitates at pH values above 2 (in accordance with data reported by [2]). By filtering off the precipitate at pH 1.8, REE precipitate with a yield of 95% and a REE concentration of 9 mass % is obtained. A higher Ca removal in the cooling crystallization, gives higher concentration of REE in the precipitate obtained during the partial neutralization. On the other hand, the REE starts to precipitate at lower pH values when the calcium concentration is higher since REE co-precipitate with the sparingly soluble calcium orthophosphates such as

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2$ [134, 135, 136]. The precipitation of REE at lower pH with significant amount of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ leads to a great loss in valuable phosphorus that affects the further purification of REE and decreases the efficiency of NPK fertilizer production markedly. Longer residence time favors the precipitation yield of REE and iron, especially in the range from 10 min to 24 h and less so from 24 h to 72 h.

Neutralization temperature significantly changes the behaviour of REE, Fe and Ca and is a very important parameter for controlling the selective precipitation of REE against Fe and Ca. Under equal residence time, the precipitation yields and the REE concentration is higher at 60 °C compared to 25 °C. This is mainly due to higher crystal growth rate at higher temperatures and retrograde solubility of REEPO_4 [32, 33]. At longer residence time (more than 24 h), the temperature dependency of precipitation yield is negligible and the concentration of REE in the precipitate remains unchanged. However, the precipitate obtained at higher temperature contains more iron.

Addition of seeds enhances the production of well grown crystals at lower supersaturation which might lead to lower level of impurity in the precipitating phase. The separation of REE in the nitrophosphate process is performed in a continuous crystallizer where the feed upon entering into the crystallizer directly come into contact with a slurry of precipitated REE. The result of seeding experiments showed higher REE precipitation yield as well as REE content in the precipitates when seeds were added. The same REE precipitation yield was observed after 24h in the seeded experiment compared to the experiment with no seeding and 72h of residence time. The obtained crystals in the seeded precipitation contain almost 50% more REE at a pH of 0.8 (12.5 mass%) compared to the experiments with the same conditions but with no seeding. However, a slight increase in REE concentration in the precipitate was observed by performing the seeded precipitation at 60 °C, but the precipitation of iron ions at lower pH values contaminates the precipitate. No improvement was observed in seeding the process with pure REE phosphates crystals instead of authentic REE phosphate concentrate.

5.3.1 Analysis of REE phosphate concentrate

Depending on how the precipitation is operated in the NP process (cooling crystallization end temperature, final pH and temperature of the partial neutralization step) in the nitrophosphate process, the recovery of REE and

the amount of coprecipitated calcium and iron in the phosphate concentrate will vary. Normally the REE phosphate concentrates mainly consist of 7–15% total REE, 10–16% phosphorus, 4–10% calcium and 1–10% iron. As an example, Table (6) shows the composition of a REE concentrate obtained at 25 °C, pH: 1.13 and a CaO:P₂O₅ ratio of 1.15.

Table 6. Elemental composition of the REE precipitate, 25 °C, pH: 1.13 and CaO:P₂O₅ ratio of 1.15 (paper I).

Element	Ca	P	Fe	Ce	La	Nd	Y	Dy	Sm	Gd	Er	Na	Si
Mass%	7.9	13.7	0.82	4.3	1.6	2.4	1	0.3	0.6	0.4	0.1	0.1	0.1

In Fig. (14), a SEM image of the precipitate obtained in an experiment with a final pH of 1.13 ± 0.1 is shown. EDS results measured as a point analysis revealed that the main phase (darker areas in the picture) contains a mixture of Ca, light REE (La, Ce, Nd), Y and Dy together with phosphorous. Furthermore, some points (lighter areas in the the picture) contain high concentration of fluoride and light REE and Ca which could be a sign of that a part of the REE are precipitated as a fluorite solid phase (CaF₂) which has been reported previously by Forsberg et al. (2014) [68] that during the precipitation of REE by adding ammonium hydroxide to a more diluted nitric acid leach solution of apatite, the REEF₃ co-precipitates with calcium as (CaF₂)_{0.85}(REEF₃)_{0.15}.

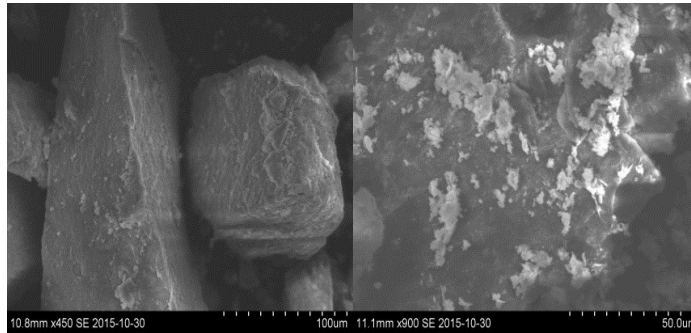


Figure 14. SEM micrograph of obtained precipitate at a pH of 1.13 ± 0.1 .

The crystal structures of the different precipitates were characterized by powder XRD. The solid phases were mainly amorphous, and the main components were found to be CaHPO₄·2H₂O and Ca₅(PO₄)₃OH. REE have

coprecipitated with calcium phosphate as $\text{REE}_n \text{Ca}_m (\text{PO}_4)_{(3n+2m)/3}$ as well as in the form of a rhabdophane type solid phase $\text{REEPO}_4 \cdot n\text{H}_2\text{O}$. Iron was also identified to precipitate mainly as $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. REE precipitate in the solid phase was further investigated by analyzing the synthetic precipitate obtained from the partial neutralization of a synthesized nitrophosphoric acid solution with the same concentration of REE (Ce, Y, Nd, La, Dy), PO_4^{3-} , NO_3^- , and NH_4^+ but with no calcium and other impurities at a pH of 1.2. The presence of calcium and other impurities beside the difference in total ionic strength of synthetic and actual solution may change the composition of REE precipitate. The REE were found in the forms of $\text{CePO}_4 \cdot \text{H}_2\text{O}$, $\text{YPO}_4 \cdot 0.8\text{H}_2\text{O}$, $\text{NdPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ and $\text{Dy}_2(\text{HPO}_4)_3$.

5.3.2 The effect of iron on the quality of the REE phosphate precipitate

The concentration of Fe in the NP acid has a great influence on the quality of the REE phosphate concentrate. The precipitate obtained at higher temperature contains more iron. For instance, as is shown in Fig. (15), in precipitation with ammonium hydroxide, at 60 °C the concentration of iron in the precipitate at pH 1 is 5.1 mass% while it is 0.7 mass% at pH 1.15 and 25 °C. This is probably because the oxidation of Fe(II) to Fe(III) in nitric acid solution is more favored at higher temperatures [137] and the solubility of Fe(III) as $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ($K_{\text{SP}} = 26.4$) is much lower than that of Fe(II) and this lead to precipitation as $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ($K_{\text{SP}} = 36$) [125].

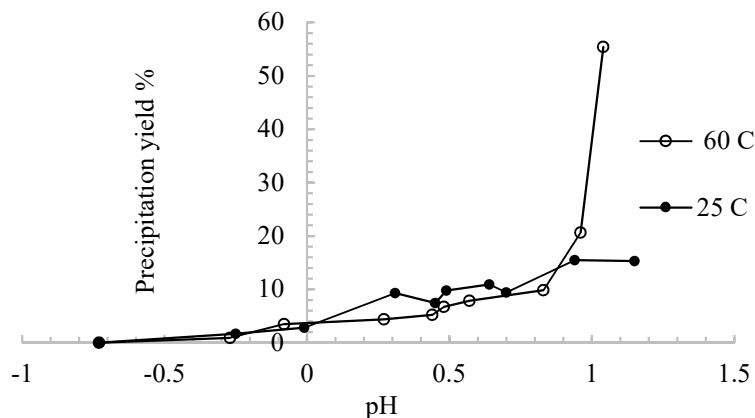


Figure 15. Influence of temperature on the precipitation yield of iron, $\text{CaO}:\text{P}_2\text{O}_5$ ratio of 0.75mol/mol (paper I).

Normally in the industry, the feed to the NP process consists of a mixture of different phosphate rocks and consequently the composition of the NP acid could vary. Iron concentration in the NP acid has great influence on the composition of the REE phosphate concentrate and thus the iron concentration should be adjusted in a way to reduce its impacts on the REE isolation process.

To further study the effect of iron on the precipitation of REE, the precipitation of REE and iron were investigated under the conditions which extra amount of iron as iron nitrate was added to the NP acid solution (increasing the iron concentration from 2.5 g/L to 8.9 g/L). The neutralization was performed using ammonium hydroxide at 80 °C. The precipitation yields of REE and iron; and the REE concentrate cake size and composition were followed. The REE cake size was defined as the ratio of dry REE phosphate concentrate mass over the starting NP acid solution mass. The dry cake is obtained by washing the precipitates after filtration with deionized water and drying at 80 °C for 24h.

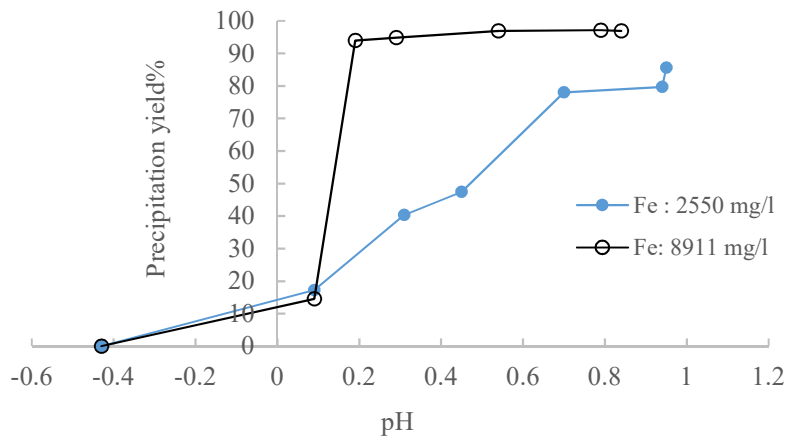


Figure 16. The influence of iron initial concentration in the NP acid solution on the precipitation yield of iron at different pH values, $T = 80\text{ }^{\circ}\text{C}$, residence time: 24h, Ca/P mass/mass = 0.55, neutralization agent: ammonium hydroxide 25 %.

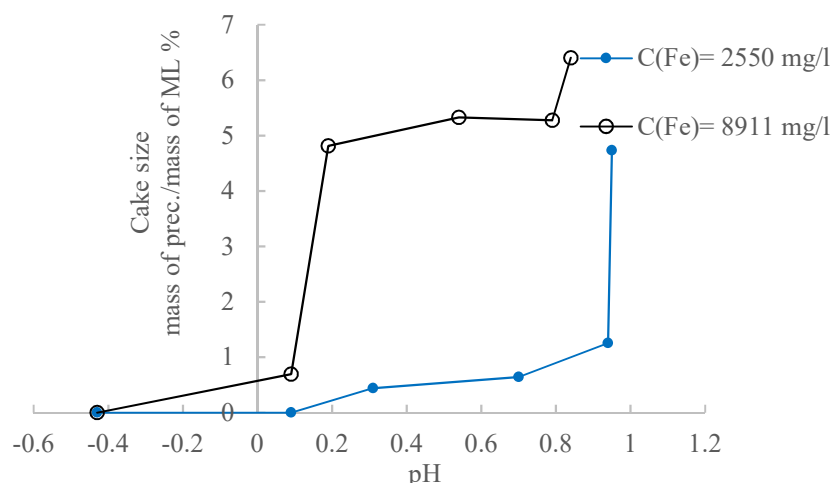


Figure 17. The influence of initial Fe concentration on the REE phosphate concentrate cake size, $T = 80\text{ }^{\circ}\text{C}$, residence time: 24h, Ca/P mass/mass = 0.55, neutralization agent: ammonium hydroxide 25 %.

As it is expected and shown in Fig. (16), by increasing the Fe concentration in the NP acid solution, the Fe precipitation yield increases. The increase in Fe precipitation yield at elevated Fe concentration in the NP acid, had little effect on the precipitation yield of REE however it significantly reduces the quality of the REE precipitates as the cake size increases as shown in Fig. (17). The precipitation yield of REE was slightly higher in the case of higher Fe concentration confirming the fact that part of the REE coprecipitate with Fe containing phases. However, based on mass balance and powder XRD analysis, the extra precipitated mass for the elevated iron concentration case is mainly attributed to precipitation of extra added iron as $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}(\text{H}_2\text{PO}_4)_3$. Therefore, it can be concluded that the effect of iron concentration on precipitation of REE and the REE concentrate cake size is negligible at $80\text{ }^{\circ}\text{C}$ using ammonium hydroxide as the neutralization agent. The NP acid water content at the end of neutralization is about 35-40%.

5.4. REE phosphate concentrate upgrading

As described earlier, depending on how the REE precipitation process is operated in the nitrophosphate process, the recovery of REE and the amount of coprecipitated calcium and iron in the phosphate concentrate will vary, and this will influence the further processing of the concentrate.

Upgrading of the REE concentrates is essential from different aspects, the primary REE concentrate is not only relatively poor in REE concentration and incorporate impurities such as iron, but also it contains significant amounts of P and Ca which must be recycled back and used in the final fertilizer product. On the other hand, the REE are present in such phases that requires strong acidic conditions to be solubilized. Therefore, to enhance the dissolution of REE and obtain a pregnant solution appropriate to use as a feed for further REE purification and individual separation, removal of phosphorous and impurities are necessary.

For the sake of REE phosphate concentrate upgrading and purification, numerous methods have been used in this study (paper II and III). These methods involve mainly: i. selective dissolution, ii. leaching in sulphuric-phosphoric acid solution followed by double sulphate precipitation, iii. thermal treatment, and iv. alkaline transformation. In Fig. (18) all the investigated methods are summarized. A brief explanation of each process is later given in the subsections.

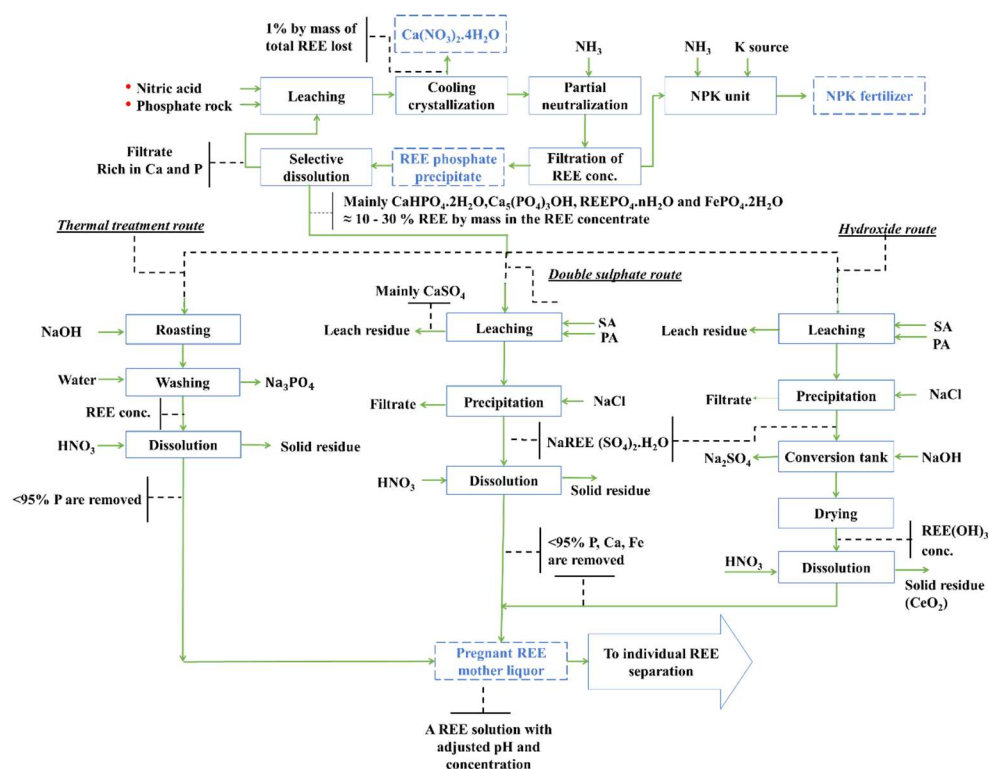


Figure 18. Recovery of REE within the NP process and methods for upgrading the obtained REE phosphate concentrate.

5.4.1 Selective dissolution

The difference in solubility of REE phosphates [32] and calcium phosphates [134, 138, 139], present in the REE phosphate concentrate, provides a possibility of calcium removal and phosphorous recovery from the REE phosphate concentrate by selective dissolution. The filtrate is a solution rich in Ca and P and can be recycled back to the leaching step. It is shown that the concentration of REE in the precipitate obtained after neutralization of the nitrophosphoric acid with ammonia could effectively be increased by a simple partial dissolution in nitric acid. The results from the dissolution in nitric acid at a pH of 2.4 and liquid/solid ratio of 100 mL/g showed a substantial increase in total REE concentration in a precipitate where it increased from 10.5 mass% to 29.5 mass%, and most of the calcium present as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved.

5.4.2 Sodium REE double sulphate route

Addition of sulfuric acid into phosphoric acid increases the solubility of REE phosphates significantly. As the concentration of sulfuric acid increases, the solubility of REE increases due to formation of REE sulfate complexes. The maximum solubility is found to be when the sulfuric acid concentration is between 10-15 mass % in 30-36 mass% of phosphoric acid. As an example, the solubility in terms of the total concentration of Ce and Y in the aqueous phase in 36 % phosphoric acid is almost 1 and 20 mmol/L respectively, while in 36% phosphoric acid - 15% sulfuric acid, the aqueous phase contains in total 152 and 505 mmol/L of Ce and Y respectively. The solid REE phase in equilibrium with the aqueous phase under this condition is REE phosphate monohydrate. The solubility of REE phosphates in phosphoric-sulfuric acid is favored by lower temperatures. By contrast in presence of sodium, the increase of sulfuric acid concentration in phosphoric-sulfuric acid solution decreases the solubility of REE due to formation of poorly soluble $\text{NaREE}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ [140, 39, 141].

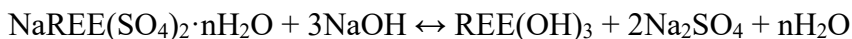
By taking advantage of high solubility of REE phosphates in phosphoric acid in presence of sulfuric acid, the REE phosphate concentrates were dissolved in a phosphoric-sulfuric acid solution (36%-15%). The powder-XRD spectrum of the leach residues illustrated that calcium sulfate anhydrate was the dominant phase with minor incorporation of REE. Selective dissolution of the calcium content of the REE phosphate concentrate prior to dissolution in phosphoric- sulfuric acid increased the dissolution yield of REE at liquid/solid ratio of 10 g/g from 89.4% to 96% for LREE and from 98.5% to 99% for HREE. After addition of a sodium salt to the phosphoric-sulfuric acid, the REE were precipitated as sodium double sulfates. The precipitation yield for light REE (Ce, La, Nd, Sm, Gd and Pr) were higher compared to HREE (Y, Dy and Er) since the solubility of LREE sodium double sulphates are considerably lower than that for heavy REE. The HREE remaining after separation of $\text{NaREE}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ are recovered by partial neutralization of the filtrate with ammonia at a pH of 2.3. To ease the further purification and individual separation of REE, the sodium REE double sulfate concentrate should be solubilized. By dissolution of the concentrate in nitric acid at pH 1, a solution containing 3g/L REE were obtained out of which 50% were the HREE with a dissolution yield of 30%, while the dissolution yield of LREE was 13%.

As is shown in Fig (18) for the sodium REE double sulphate route, the REE are extracted as a phosphate concentrate which is then re-dissolved and the REE are precipitated as double sulphates. The process can handle feed of varying composition in terms of e.g. REE/Ca ratio or concentration of impurities such as iron. In general, the process is more effective in the case of processing concentrates with higher REE and lower Ca concentration. However, the precipitation of REE as double sulphates is selective and it was shown than 95% of the Ca, Fe and P are removed by the proposed process.

Direct material and energy cost for processing 1 kg of REE phosphate concentrate in this process can be estimated to 3–5 US\$ (the value of REE per kg of REE phosphate concentrate is estimated to be 10-12 US\$). High phosphorous recovery and impurity removal are the main advantages of this process while low solubility of the double sulphate concentrate in mild acidic conditions and high cost are the main shortcomings.

5.4.3 Hydroxide route

As explained earlier, by reprecipitation of the REE phosphate concentrate in the form of sodium REE double sulfates, the REE and more specifically LREE can be effectively isolated from Ca, P and Fe in acidic media. The sodium REE double sulphate cake can be converted to hydroxides by caustic soda not only to improve the solubility, but also it opens up a possibility to separate the bulk of trivalent rare earth elements from Ce^{4+} . Cerium is the most likely to oxidize into its tetravalent state and considering its properties, separation is viable from the rest of trivalent REE by selective dissolution. In alkaline solution, the trivalent cerium can be oxidized into its tetravalent state by either purging oxygen during REE hydroxide precipitation or by drying the REE hydroxide in presence of air [11, 142]. The schematic of the proposed process is shown in Fig. (18) labeled as the hydroxide route. In this process, like in the sodium REE double sulphate route, first the REE phosphate concentrate converts into a sodium REE double sulphate concentrate and then are transformed into a hydroxide concentrate using 20% sodium hydroxide solution in 10% excess at ambient temperature as described in Eq. (10). The hydroxide concentrate is then dried at 160 °C to oxidize the Ce to its tetravalent state. The total conversion yield of REE from phosphate to double sulphate and then to hydroxide was 90-95%.



Eq. 10

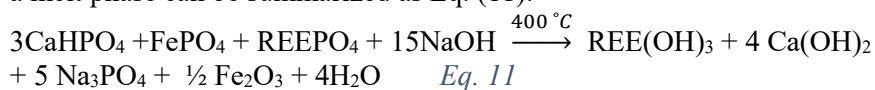
Solid characterization of the REE hydroxide concentrate showed that cerium is present as Ce (IV) and Ce (III) whilst other rare earths are present as trivalent hydroxides. Na and S are also present in the REE hydroxide concentrate (~ 3mass% S and 6 mass% Na) which are bound to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. The minor detected amount of P was mainly owing to presence of $\text{Ce}(\text{HPO}_4)_2 \cdot 0.33\text{H}_2\text{O}$ and $\text{Na}_4(\text{P}_2\text{S}_6)(\text{H}_2\text{O})_6$. The REE hydroxide concentrate was selectively dissolved in HNO_3 at a slurry concentration of 100g/L and 80 °C. The REE were effectively dissolved at pH < 7 in agreement with REE hydroxide solubility. At the pH of 1.56, a solution containing 43g/L REE with the main constituents being La, Nd, Dy and Y that accounted for almost 90% of total dissolved REE with an average dissolution yield of 92% was obtained. Cerium accounted for almost 10% of the total dissolved fraction with the dissolution yield of 45%. Low Ce dissolution yield confirms the fact that Ce is partly present as tetravalent Ce which has lower solubility as compared to its trivalent state ($K_{\text{SP}} \text{Ce}(\text{OH})_4 \sim 10^{-54}$, $K_{\text{SP}} \text{Ce}(\text{OH})_3 \sim 10^{-2}$) [143]. Hence, dissolution at the pH values > 2 gives the best compromise between the total REE dissolution and Ce (IV) separation from the REE bulk.

The main advantages of the hydroxide process are high phosphorous recovery and impurity removal beside obtaining a highly soluble REE hydroxide cake. However, this process is rather costly and the direct material and energy cost for processing 1kg of REE phosphate concentrate is estimated 5-7US\$.

5.4.4 Thermal treatment

Alkaline cracking by thermal treatment with sodium hydroxide at (400-500 °C) is an effective dephosphorization method for common REE phosphate bearing minerals such as monazite. This process is more energy efficient compared to the thermal decomposition of monazite minerals at ~ 1400 °C [144, 145]. As is plotted in Fig. (18), in the thermal treatment route, the REE phosphate concentrate were first thermally treated with sodium hydroxide and then the formed sodium phosphate was solubilized by water leaching. Thereafter, the thermally treated and washed REE concentrate was solubilized by acid leaching and the REE- rich solution

was sent to the REE separation unit. The main reaction that takes place in a melt phase can be summarized as Eq. (11).



After washing the thermally treated mass with water for 3h at 25 °C and a S/L ratio of 100 g/L, more than 98% of reacted P was leached out. In the water leaching step, less than 0.1 % of total REE and Fe were leached, and the final pH was between 12-13. The powder XRD analysis of the salts obtained by evaporation of filtrate in the washing step showed Na_3PO_4 as the main solid phase.

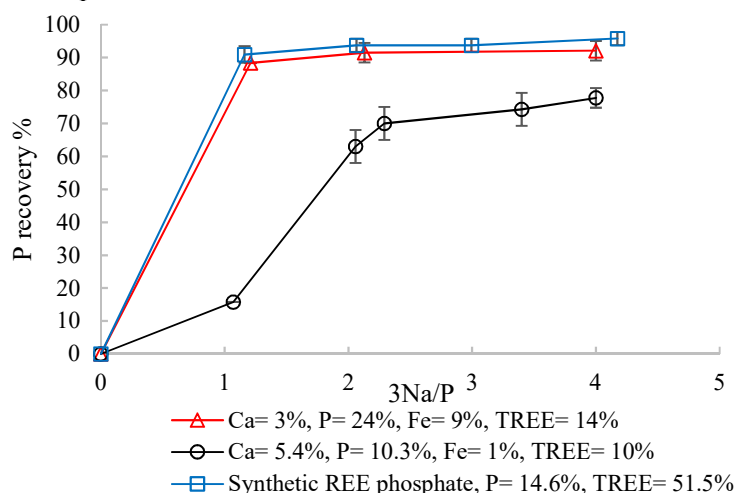


Figure 19. The influence of NaOH dosage on dephosphorization of the REE concentrate, temperature= 400 °C, residence time= 24h (paper III).

In Fig. (19) the effect of NaOH dosing on P recovery from different REE phosphate concentrates was investigated. Considering 3 mols of Na for each mole of P present in the concentrates, $3\text{Na}/\text{P} = 1$ references the stoichiometric amount of sodium. As the amount of excess NaOH increases so does the percentage of P removal by water leaching. By investigating the composition of the different REE concentrates, it can be concluded that the dephosphorization is higher in the precipitate with lower calcium content. This can possibly be explained by that mixed Ca and REE phases, e.g. $\text{REE}_m\text{Ca}_n(\text{PO}_4)_{3m+2n/3}$ and CaHPO_4 are less likely to dephosphorize at the condition of the experiment than $\text{REE}(\text{PO}_4) \cdot n\text{H}_2\text{O}$ and $\text{REEPO}_4 \cdot \text{H}_2\text{O}$. The largest fraction of leachable P was obtained after

thermal treatment at 400 °C as compared to 300 °C and 500 °C. Lower P removal after roasting at 300 °C can result from insufficient heat to form a complete melt phase since the melting point of NaOH is ~ 320 °C. The small decrease in P removal at 500 °C compared to 400 °C, could also be the consequence of too fast sample dry-out for the reaction to reach completion. The thermal treatment time was another parameter to optimize the dephosphorization and continuation of the thermal treatment at 400 °C longer than 4h had no effect on the total fraction of leachable P while 2 h was not enough.

The roasted synthetic REE phosphate concentrate after water leaching mainly consisted of both rare earth oxide and hydroxide. This observation can be explained by the fact that the transformation of different REE hydroxide to oxide takes place at various temperatures ranging from 250-500 °C [146]. REE oxides were also identified as another dominant phase in the form of $(\text{Ce}_{0.9}\text{La}_{0.1})\text{O}_{1.95}$ and $\text{La}_{0.5}\text{Nd}_{0.5}\text{YO}_3$. Cerium was present both in its tetravalent state in oxide form $((\text{Ce}_{0.9}\text{La}_{0.1})\text{O}_{1.95}$ and $(\text{Ce}_{0.95}\text{Y}_{0.05})\text{O}_{1.975}$) and trivalent state in hydroxide form $(\text{Ce}(\text{OH})_3)$. Minor amounts of Na and P were left in the REE oxide concentrate which were identified to be incorporated in Na_2CeO_3 and $\text{Ce}(\text{HPO}_4) \cdot 0.33\text{H}_2\text{O}$.

In thermal treatment of REE phosphate concentrates enriched in Ca, the REE were mostly present as oxides. However Ce was identified incorporated with Ca and P as $(\text{Ce}_{0.8}\text{Ca}_{0.2})\text{O}_{1.8}$ and $\text{Ce}(\text{HPO}_4)_2 \cdot 0.33\text{H}_2\text{O}$. The main iron containing phases were Fe_2O_3 and CaFeO_4 . The undephosphorized phase was identified as $\text{Ce}(\text{HPO}_4) \cdot 0.33\text{H}_2\text{O}$ and $\text{Ca}_3\text{Ce}(\text{PO}_4)_4$. As it is illustrated in Eq. (11) at 400 °C, the REE are first transformed into hydroxides and then partly are dehydrated and consequently a major portion of REE end up as oxides in the roasted mass.

To solubilize the REE and deliver a suitable feed solution for further processing, the REE phosphate concentrate after thermal treatment was selectively dissolved in nitric acid at a slurry concentration of 33g/L and 25 °C. The results showed that the calcium dissolution started at pH 7 and about 85 % of the calcium was found in the aqueous phase at pH 1. The REE were leached at $\text{pH} < 1.5$ and at $\text{pH} \sim -0.4$ about 30% of the LREE and 56 % of HREE were found in the aqueous phase. The iron content of the REE oxide concentrate started to dissolve around pH 2 and a complete dissolution was obtained around pH -0.4. A solution containing 1 g/L REE, 2 g/L Fe was attained at pH 1. The reasons for the low dissolution yield of

the REE are: the presence of REE as oxides which need higher acidity to be dissolved, and the release of phosphorous from calcium and sodium phosphate phases after dissolution at high pH values between 9-10.5, produces a buffer solution that prevents the REE hydroxides to be dissolved.

Efficient phosphorus recovery and low cost of processing (0.5-1.5 US\$ per kg of REE phosphate concentrate) are the main advantages of thermal treatment while low solubility of the thermally treated REE concentrate in mild acidic conditions and poor impurity removal are the disadvantages.

5.5. REE separation using HFSLM

Individual and group separation of REE is the most challenging step among all the unit operations involved in isolation of these metals from phosphate rock until delivering individual REE streams. In this chapter, the behavior of different REE in up-scaled HFSLM extraction processes and the parameters that affect the selectivity of the process including the initial feed concentration and pH have been investigated. In addition, the effect of running the HFSLM in different configurations on the membrane stability, mass transfer rate and process selectivity are studied and possible scenarios to explain the instability are given. Furthermore, the gel formation threshold in HFSLM systems as a function of organic loading capacity is specified. The results of this section are covered more in details in paper IV.

5.5.1 HFSLM pilot plant

As it is depicted in Fig. (18), the pregnant mother liquor after processing the REE phosphate concentrate can be used as the feed for HFSLM units and the feed composition has been sought to resemble the concentration of REE after dissolving the REE hydroxide precipitate obtained after the recovery of REE from the LKAB apatite concentrate in the nitrophosphate process. The carrier and stripping concentration were chosen in a way to obtain the highest possible selectivity and productivity based on similar studies in the literature [97]. D2HEPA diluted in Kerosene (10 (v/v)% equals to ~ 0.35 M) was chosen as the extractant and 3M HCl solution as the strip solution was used. It has also been shown that using HCl slightly improves the stripping yield as compared to other types of acid at comparable stripping conditions [112, 147].

The pilot plant (Fig. (20)) consisted of one stripping tank, the membrane module which is a hollow fiber membrane and two feed tanks. The membrane module was a microporous hollow fiber unit (3MTM Liqui-CelTM, 4X13 in., X-50 PP fibers) containing ca. 30,000 microporous hydrophobic fibers made of polypropylene providing an effective surface area of 8m². The 30 L stripping tank was equipped with an overhead stirrer to obtain a uniform concentration in the whole tank and the stripping liquid was always recirculated. The fluids were pumped by means of two peristaltic pumps. The pressures of the lumen and shell side were adjusted to apply slightly higher pressure on the nonwetting side (~ 0.2 bar) which is the shell side in HFRLM and HFSLM and lumen side in EPT. The synthetic feed solutions with various total volume of 70 to 200 L were prepared by dissolving an appropriate amount of REE oxide and adjusted in the range of 100 to 800 mg/L for different REE. The pH of the feed solution was adjusted by addition of concentrated HCl.

The HFSLM experiments were carried out in two operating modes (semi-continuous and recirculation) under different configurations of SLM (HFSLM, HFRLM and EPT). The schematic of the pilot plant operated in semi-continuous mode is depicted in Fig. (20) where the stripping solution was passed through the lumen side of the membrane and the feed was passed through the shell side in a countercurrent flow. During the process, the feed with constant initial conditions was passed through the membrane and as the first tank was emptied (one pass), the flow was reversed from the second tank to the first tank. Multiple passes through one membrane could resemble multiple membranes in series or a longer membrane of the same specifications. Recirculation or batch mode was another operating mode used in this study where the outlet streams of both sides of the module were recycled back to the respective reservoir tanks.

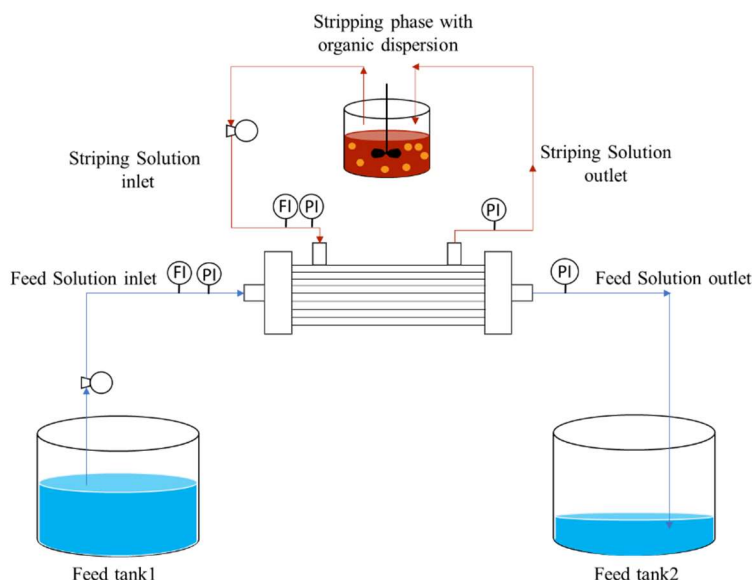


Figure 20. HFRLM in semi-continuous operating mode (paper IV).

Prior to each experiment the membrane module was carefully washed and then impregnated with 10 (v/v) % D2HEPA in kerosene to fill the membrane pores. In the HFRLM experiments, the stirred mixture of liquid membrane and stripping solution at volume ratio of the aqueous to organic (A/O) 25 was pumped through the lumen side while feed solution passed through the shell side of the module. The same procedure was repeated for HFSLM but with no addition of organic phase in the stripping solution. In EPT experiments, the feed flowed inside the lumen and the emulsion formed by dispersing the aqueous stripping solution into the organic phase with aqueous/organic (v/v) ratio of 1.5, was passed through the shell side.

5.5.2 Separation of heavy REE from light REE

The first stage in individual separation of REE is to isolate HREE from LREE. In Fig. (21) the result of passing a solution containing both light-, heavy- and middle REE through HFRLM, in semi-continuous mode is shown. The feed was passed through the membrane several times until all the heavy REE had been extracted (under 5 passes showed in Fig (21)) and then the stripping solution was changed with a fresh one and then the extraction was continued until all the LREE was extracted.

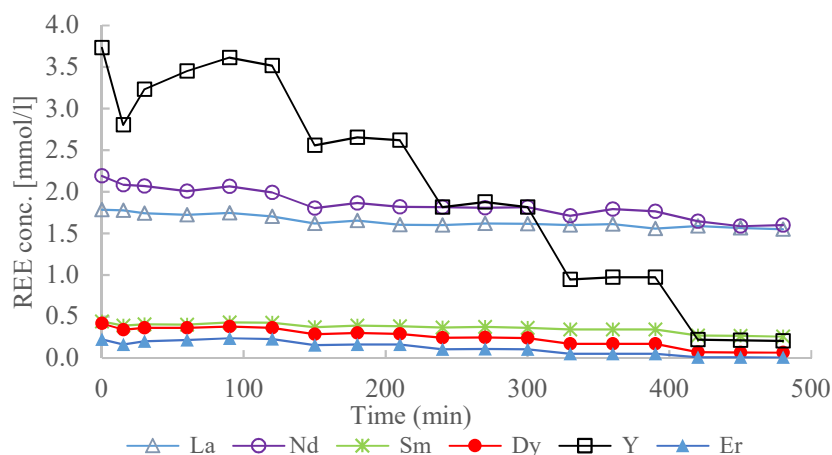


Figure 21. The concentration profile for feed outlet at different experimental time, HFRLM, semi-continuous mode, the concentrations at time zero show the initial feed concentration (paper IV).

As it can be inferred from the equilibrium constants of REE in D2HEPA, first the heavy REE were extracted followed by middle and LREE in accordance with their K_{eq} ($Er > Y > Dy > Sm > Nd > La$). Almost 100% of the HREE (Y, Dy and Er) has been extracted after 5 passes through the membrane but the main part of the LREE (La and Nd) is left in the feed. In addition, the major part of Sm which is considered as one of the middle REE, also remained in the feed while Dy as another middle REE was totally extracted into the membrane phase. By passing the metals through the liquid membrane the feed pH was decreased from 2.31 to the pH of 1.84 after 5 passes which was in accordance with the transfer of approximately 3 protons per metal. To further purify the stripping solution from the co-extracted light and middle REE, the stripping solution must pass through yet another membrane after pH adjustment.

The total molar flux was higher in a short period after the feed was put in contact with the liquid membrane phase and then it decreased to a constant value. During this period the extraction selectivity was also lower. During this period (accumulation period) the resistance against mass transfer increases until the concentration profiles within the liquid membrane are built up. By completion of the accumulation period, the diffusion film become constant which is equal to the membrane thickness plus the renewal layer thickness. The effect of metal concentrations in the bulk on

total molar flux is relatively small since the organic loading is high at the feed-organic interface and very low at the stripping-organic interface and consequently the total mass flux can be assumed to be fairly constant after the accumulation period until the HREE were almost extracted completely and the LREE extraction started. Total accumulation of metals in the liquid membrane phase after 5 passes was calculated to be 2.6% and mostly accounted for Er and Y.

The mass flux through the membrane was significantly higher in the case of LREE transfer as compared to HREE even though the concentration of REE in the liquid membrane phase is higher at the feed-organic interface in case of HREE transport. The average total molar flux in HREE transport over the first two hours was 0.051 mmol/m².min while this number is 0.20 mmol/m².min for LREE transport. This is because the stripping is favored when the equilibrium constant is smaller which is the case for LREE. Additionally, as it reported by Dolezal et al. (2000) for the same SLM solution as in this study, by increasing atomic number of the lanthanides, the permeability through the SLM solution decreases mainly due to stronger bonding and higher stability of HREE-organic complexes [148].

5.5.3 Selectivity and productivity in HFSLM

In SLM, the selectivity can't be solely described by equilibrium constants and is also a function of diffusion coefficients, feed concentration, feed pH and stripping concentration and pH [100]. The effect of feed pH and initial concentration as the most important parameters on the selectivity were investigated. In Fig. (22), the effect of initial feed pH on the molar fraction of yttrium in the stripping solution as a representation of REE extraction selectivity is shown. For simplicity, the results have been shown only for Y and plotted during the first two hours of processing time in a single pass to subside the effect of feed concentration depletion. The results showed that by the increase in H⁺ concentration in the feed (decrease in the pH), the molar fraction of Y in the stripping solution was increased. The average molar fraction of Y was increased from 60% to 73% while the molar fraction of Dy and Nd decreased respectively as the pH was decreased from 1.74 to 1.5. The higher selectivity of the process towards the metals with bigger K_{eq} under more acidic conditions can be explained by the fact that higher H⁺ concentration reduces the complexation reaction at the feed-organic interface and respectively the organic loading is decreased. Thus, the REE with bigger K_{eq} have bigger contribution in the loaded organic

and the competition between the HREE and LREE is reduced and the process selectivity towards HREE is improved.

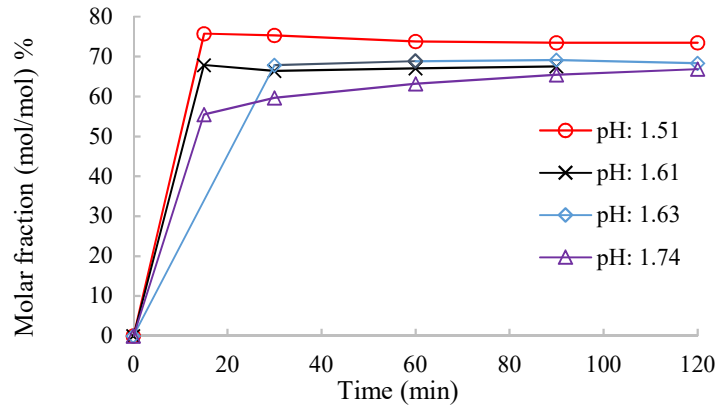


Figure 22. The influence of feed pH on the process selectivity of HFRLM extraction. HFRLM, semi-continuous mode. The lines are showing Y mol% in the stripping solution. Carrier: $[D2HEPA]=0.3$ mol/L in kerosene, stripping solution $[HCl]=3$ mol/L, $[REE]_{total} \sim 4.8 - 5.5$ mmol/L (paper IV).

Initial concentration of metals in the feed has a great influence on the selectivity of REE extraction using the HFSLM process. The initial feed concentration usually is not a changeable parameter but in the case of a network of membranes or in a multistage process where stripping solution of a membrane is used as a feed solution in another membrane, adjusting the concentration level can play an important role for controlling the selectivity. As it is displayed in Fig. (23), the selectivity is higher for higher level of initial concentration. To compare the selectivity of Y against Dy, as total concentration of REE was increased (the molar ratios between the metals are constant in both cases), the Y molar fraction in the stripping was enhanced while for Dy and LREE the molar fraction was reduced. The increase in the process selectivity by increasing the metal concentration in the feed leads to a higher loading of carriers in the liquid membrane phase which reduce the extraction of metals with lower K_{eq} .

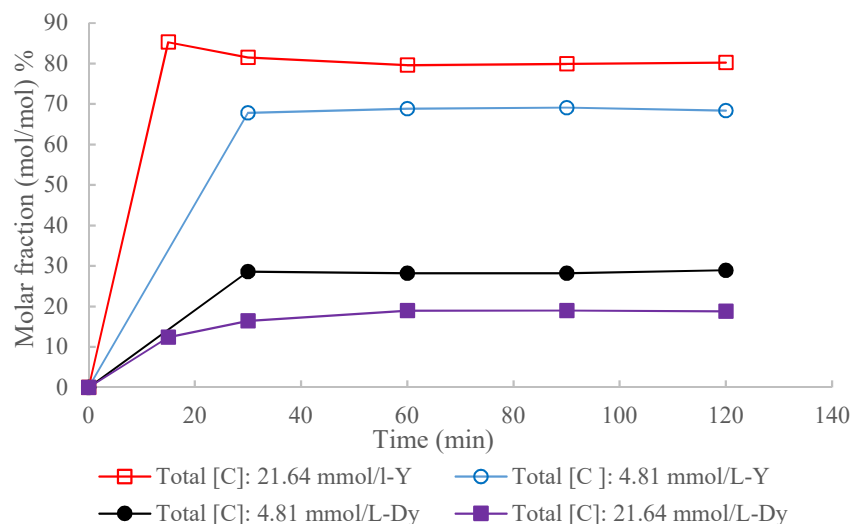


Figure 23. The effect of feed initial concentration on the molar fraction of Y and Dy in the stripping solution. HFRLM, semi-continuous mode. Carrier: $[D2HEPA] = 0.3 \text{ mol/L}$ in kerosene, stripping solution $[HCl] = 3M$, Feed $pH=1.63$ (paper IV).

The influence of different HFSLM configurations on the selectivity and total molar flux across the liquid membrane was investigated (See Fig. (24) and Fig. (25)) under similar experimental conditions. The average Y molar fraction in the stripping solution at different time intervals depicted in Fig. (24) showed that normal HFSLM was the most selective SLM configuration towards extraction of HREE as compared to LREE followed by HFRLM and EPT while the total transport rate of metals was higher in EPT followed by HFRLM and HFSLM.

Higher mass transfer in EPT configuration is owing to the large surface area on the stripping side provided by the presence of the emulsion on the stripping side which reduces the mass transfer resistance caused by the diffusional boundary layer in the stripping phase and the decomplexation reaction. The higher mass transfer in HFRLM as compared to HFSLM attributes to continued formation of micro droplet at the renewal layer and its simultaneous coalescence which produce a large surface area at the stripping interface. Additionally, in HFRLM, extensive mixing of two phases at the stripping-organic interface enhances the mass transfer.

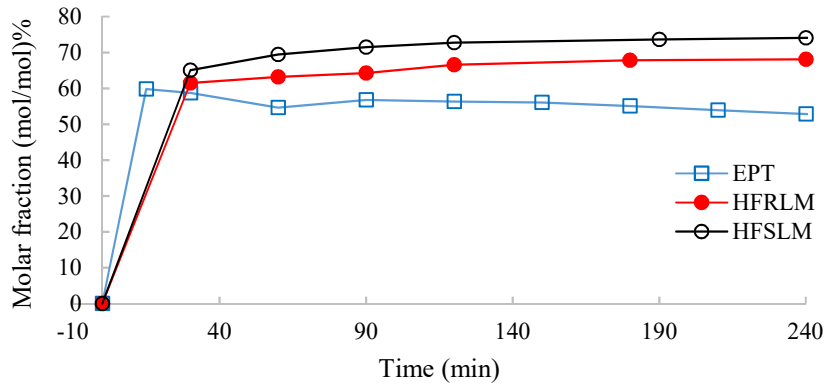


Figure 24. The effect of membrane configuration on the selectivity of the HFSLM extraction of REE. All the configurations were operated in batch mode and the experimental conditions were similar. The lines show the molar fraction of yttrium in the stripping solution (Paper IV).

Selectivity is weakly influenced by SLM configurations. More specifically, the selectivity of REE extraction in HFRLM and HFSLM are only slightly different. As it has been plotted in Fig. (24), the selectivity of HREE was in the order of HFSLM>HFRLM>EPT. The higher selectivity of HFSLM towards HREE as compared to HFRLM membrane could be due to shorter accumulation period where the process is less selective. Furthermore, the stripping is less favored in HFSLM and the concentration of metals that has been built up in the membrane phase is higher and accordingly the metals should compete more for carriers which favors the selectivity. The same reasonings can explain the higher selectivity of HFRLM as compared to EPT. In general, the increase of selectivity is the result of the lower concentration of unbound carrier in the liquid membrane phase.

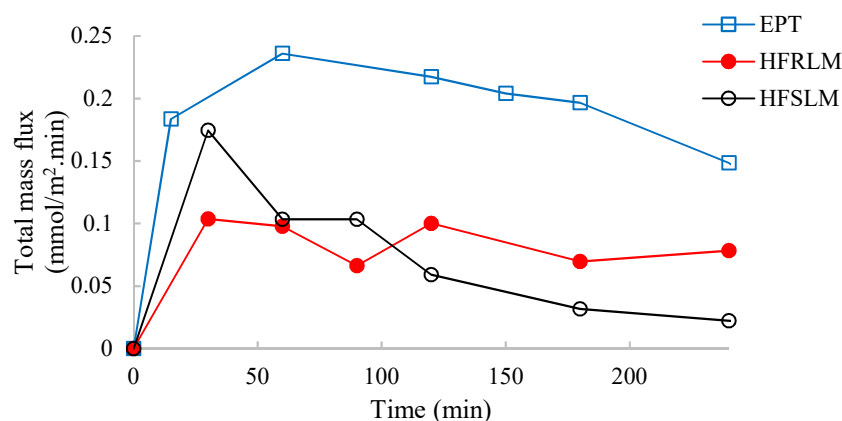


Figure 25. The effect of membrane configuration on total molar flux in HFSLM extraction of REE. All the configurations were operated in recirculation mode and the experimental conditions were similar (Paper IV).

5.5.4 Membrane stability

Undoubtedly, membrane instability is the main shortcoming in using HFSLM for industrial applications. In Fig (26), the stability of the HFRLM was investigated against the HFSLM process by comparing the total REE molar flux across the liquid membrane under similar experimental conditions over 24 hours of operating time.

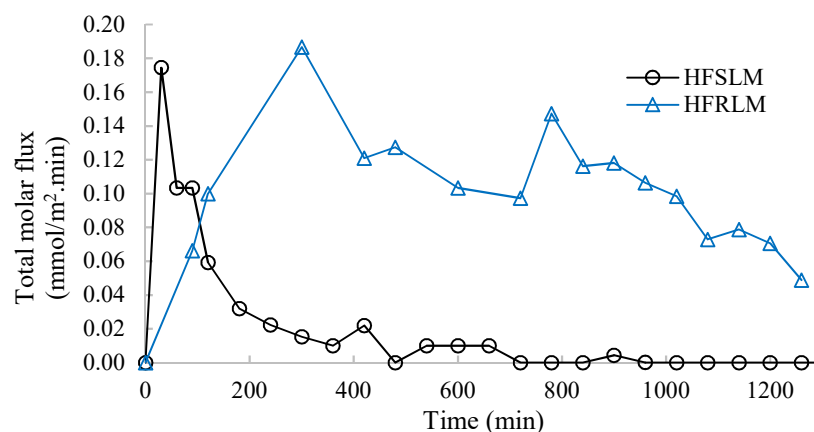


Figure 26. Total flux in HFRLM and HFSLM, batch mode (Paper IV).

During the first hour, the molar fluxes in both configurations were higher and then decreased steadily for HFSLM and completely stopped after 8 hours while the molar flux in RLM remained approximately constant for the first 10 hours and was then decreased due to the feed depletion. After the decay in SLM mass transfer, the H^+ transfer was also stopped and the pH in the exhausted feed after 8 hours remained constant. This observation confirms the stability of HFRLM against the addition of small amount of liquid membrane phase in the stripping solution. The additional organic phase in the lumen side fluid is needed only for the renewal and continuity of the organic layer where this layer automatically and continuously replenishes the loss of membrane.

The membrane instability is caused by a number of different reasons. The partial miscibility of the organic phase in the adjacent phases is inevitable what shortens the liquid membrane workability [81]. The dissolution of D2HEPA is higher at lower acidities and it is further dissolved at the feed-organic interface than the stripping-organic interface. The dissolution of the organic phase could not be the only reason for membrane instability in SLM since it cannot explain the complete mass decay in SLM in a short period of time. Exceeding the break through pressure can also expel the trapped organic out of pores and cause membrane instability. But in practice, the pressure difference applied were substantially smaller than the break through pressure. More influential, the formation of emulsion induced by lateral shear forces and local deformation of the liquid membrane meniscus in the pores was suggested as one of the main reasons of HFSLM instability [84]. However, this hypothesis cannot solely explain the decay in HFSLM mass transfer since if the formed micro droplets leave the surface of pores, the thickness of the liquid membrane will be decreased and therefore the mass transfer is increased due to higher diffusion coefficient of metals in aqueous phase as compared to metal-organic complexes in the liquid membrane. But if we assume that the micro emulsion drops coexisting with aqueous phases are piled up at the aqueous-organic interfaces and coat some of interface area (Fig. (27)- left side), for the metals to be transported from aqueous bulk to stripping bulk, they must overcome four more resistances against mass transfer caused by complexation and decomplexation at the droplets surfaces on both sides of the membrane. Because the decomplexation reaction at the feed side and complexation at the stripping side is very limited, the mass transfer is then reduced significantly. This hypothesis is not able to explain the complete decay in mass transfer.

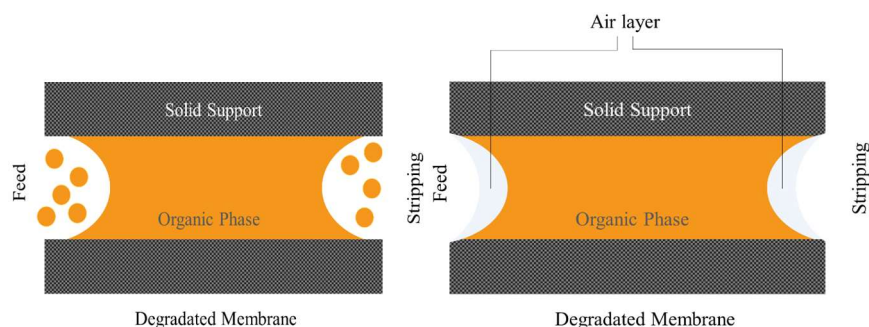


Figure 27. Suggested mechanism for HFSLM instability. Micro emulsions droplets accumulated inside the pores' neck of HFSLM (left picture) and formation of air layer at the pore interfaces (right picture).

Formation of a thin air layer inside the pores at the aqueous-organic interface (Fig (27)-right side) could also be regarded as a hypothesis to explain the decay in mass transfer of HFSLM. As the formed microdroplets leave the surface of the pores, some space inside the pore's neck is available and owing to hydrophobicity of the air microdroplets, an air layer can be formed inside the aqueous phases. Formation of this layer can totally block the pores and consequently the mass transfer is stopped completely.

5.5.5 Gelation

Formation of gel is one of the main shortcomings of using D2HEPA in extraction processes of REE. The organic phase overloading is the main reason for gel occurrence [149]. The gelation conditions should be carefully identified to achieve a threshold for the process parameters such as feed pH, metal concentration and carrier concentration. The formation of gel in HFSLM is more probable at the feed-organic interface where the organic loading is the highest. The formed gel in the feed tanks is shown in Fig. (28). A series of experiments were conducted to study the gel formation under the conditions resembling the feed-organic interface in HFRLM where small amount of organic phase was put in contact with much larger aqueous phase volumes at different REE concentrations (Er, Y, Dy, Nd and La) and pH to reach the equilibrium.



Figure 28. The gel formed in the feed tanks.

The gel observation tests showed that the gel was formed at the organic loading over 46% for Nd, 38% for Y, 46% for Dy and 65% for Er. Fig. (29) shows the organic loading at the feed-organic interface (Z axis) in a HFSLM extraction system of Y at different feed pH and concentration. The organic phase was assumed to be in equilibrium with the feed bulk and the resistance in the aqueous boundary layer on the feed side was neglected. In accordance with D2HEPA extraction chemistry, by the increase in pH and metal concentration, the organic loading was increased. The black horizontal plate shows the organic loading percentage where the gel formation was observed for Y. Therefore, by keeping the feed condition in the area where the organic loading is below this plate the gel formation is avoided. The intercept between the gelation plate and organic loading surface illustrates the operating line where the highest possible organic loading and consequently mass transfer rate without gel observation can be achieved.

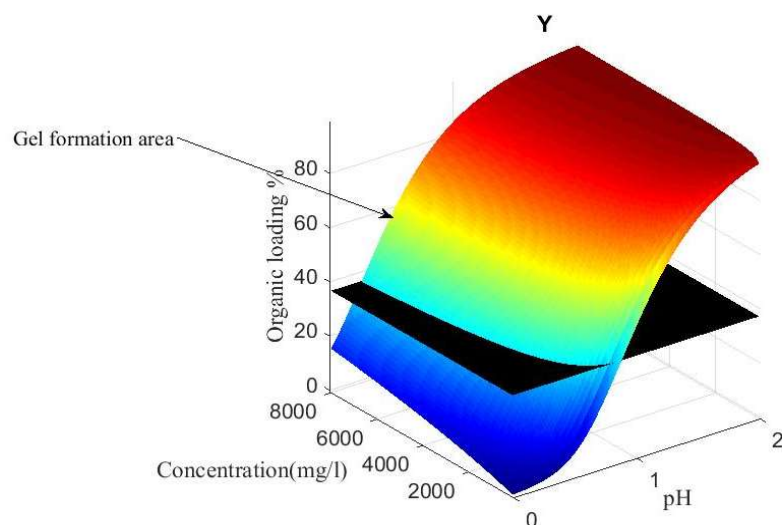


Figure 29. The organic loading at the feed-organic interface in HFSLM system. The black horizontal plate shows the organic loading where gelation occurs.

The absence of gel formation at the feed-organic interface in SLM experiments even in those experiments where theoretically the organic loading was higher than the gelation loading threshold of D2HEPA, contradicts the gel observation tests. This discrepancy can be explained by reduced organic loading caused by the local pH decrease at the feed-organic interface and the establishment of the concentration in the feed-organic interface far from the equilibrium due to fast stripping. Furthermore, [122] reported that the organogel of terbium-D2HEPA were irreversibly destroyed by a mechanical load showing the behavior of solid brittle bodies. Based on this observation, the formation of gel at the feed-organic interface can be suppressed by shear forces present at the interface.

6. Conclusions

The work presented in this thesis has focused on the recovery of REE from an apatite concentrate within the nitrophosphate process of fertilizer production. It provides an insight into the behavior of REE isolation from nitrophosphoric acid solution and tries to provide environmentally friendly, economic and industrially-driven solutions to the existing challenges. Based on the results presented in this thesis, the following main conclusions are drawn.

- The REE can be effectively separated from nitrophosphoric acid solution after cooling crystallization of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ by using ammonium hydroxide or ammonia gas as precipitating agent.
- The calcium concentration and final pH in the partial neutralization are the key factors that control the concentration of REE in the REE phosphate precipitate. Higher calcium elimination in the preceding cooling crystallization leads to a precipitate with higher REE concentration. The optimum pH for termination of the partial neutralization was found to be 1.8, where there is little loss of phosphorous and it gives the best compromise between the quantitative REE recovery and REE content in the precipitate.
- The REE phosphate precipitate mainly consists of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and REE are present both in coprecipitation with calcium phosphate as $\text{REE}_n\text{Ca}_m(\text{PO}_4)_{(3n+2m)/3}$ and as a rhabdophane type solid phase $\text{REEPO}_4 \cdot n\text{H}_2\text{O}$.
- The concentration of REE in the precipitate can effectively be increased by a partial dissolution in nitric acid. Dissolution in nitric acid at a pH of 2.4 and liquid/solid ratio of 100 mL/g gives a substantial increase in total REE concentration in the precipitate from 10.5 mass% to 29.5 mass%, and most of the calcium is dissolved. The main phases that have been dissolved are $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.
- Re-precipitation of the REE phosphate concentrate as a sodium REE double sulphate concentrate was found to be an efficient method for impurity removal. The REE phosphate concentrate can be dissolved in a mixture of phosphoric and sulfuric acid (36 mass% phosphoric acid - 15mass% sulfuric acid, liquid/solid ratio of 10g/g) with a dissolution yield of ~ 99 % for the REE where Ca is reprecipitated as calcium sulphate. The addition of sodium ions

to the leach solution leads to the precipitation of REE as sodium double sulfates and a concentrate consisting of 29.4 mass% TREE, free of iron and phosphorous is obtained. However, the low solubility of double sulphates concentrates, and low precipitation yield of HREE is an issue for further dissolution and individual separation of REE.

- By reacting with caustic soda, the sodium REE double sulphate concentrate is effectively transformed into a REE hydroxide concentrate where further dissolving the REE hydroxide concentrate in nitric acid at a pH of 1.6, a solution containing 45g/L REE free of Ca, Fe and P can be obtained. This solution can then be taken as feed to further downstream separation by liquid-liquid extraction, membrane extraction or chromatography.
- Phosphorous can also be removed from the rare earth phosphate concentrate by water leaching after thermal treatment with NaOH at 400 °C. $\text{REE}_m\text{Ca}_n(\text{PO}_4)_{3m+2n/3}$ and CaHPO_4 are less likely to dephosphorize at the condition of the experiment than $\text{REE}(\text{PO}_4) \cdot n\text{H}_2\text{O}$ and $\text{FePO}_4 \cdot \text{H}_2\text{O}$. The recovery of REE to the aqueous phase under mild acidic conditions is limited by the presence of remaining phosphate and by formation of REE oxide phases.
- In individual separation of REE using a hollow fiber supported liquid membrane with D2HEPA as the extract, the initial pH and REE concentration in the feed has a great influence on the selectivity of the process. High separation factors are favored by low concentration of the extractant in the organic phase and high concentration of extractable REE in the aqueous feed phase.
- HFSLM is more selective as compared to HFRLM and EPT while higher metal transport is observed in EPT followed by HFRLM and HFSLM.
- Formation of gel due to extractant overloading at the feed-organic interface appears to be one of the main shortcomings of using D2HEPA as the carrier. The gel is formed when the extractant is highly loaded but the limit depends on the particular REE: above ~ 46% for Nd, 38% for Y, 46% for Dy and 65% for Er.

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