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**POLYTECHNIQUE MONTRÉAL**

affiliée à l'Université de Montréal

et

l'Université du Québec en Abitibi-Témiscamingue

**Rare earth elements pre-separation using carbonation and selective HCl  
leaching**

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

Génie Minéral

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Ce mémoire intitulé:

## **Rare earth elements pre-separation using carbonation and selective HCl leaching**

présenté par **Alexandru MURESANU**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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## DEDICATION

*I dedicate this thesis to my parents Doina Muresanu and Cristian Muresanu who have helped me tremendously in overcoming the challenges of higher education.*

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## RÉSUMÉ

Les éléments des terres rares (ETR) sont des éléments cruciaux pour le développement de nombreuses industries, incluant la gestion de l'énergie et la défense nationale. Ils sont considérés comme minéraux critiques et stratégiques dans plusieurs pays à travers le monde. Les ETRs sont omniprésents dans le monde moderne: de voitures électriques, ordinateurs, lasers jusqu'aux missiles, avions et de nombreuses autres utilisations. Les ETRs sont réputés comme difficiles à séparer en éléments individuels. Malgré le fait qu'ils soient stratégiques pour plusieurs pays dans le monde, la majorité de la séparation en ETRs individuels de haute pureté est réalisée en Chine en utilisant l'extraction par solvants, ce qui nécessite plusieurs centaines d'unités de mélangeurs/décanteurs. Il est donc important de découvrir de nouvelles techniques de séparation afin de proliférer la production d'ETR à travers le monde et diminuer le monopole que certains pays détiennent. Une étude précédente a montré que l'injection de  $\text{CO}_2$  en conditions supercritiques suivie d'une lixiviation au  $\text{HCl}$  permettrait potentiellement la pré-séparation des ETRs. En effet, certains oxydes de terres rares (OTRs) ont tendance à se carbonater en présence de  $\text{CO}_2$  en conditions supercritiques, tandis que d'autres ne le font pas. Une fois carbonatés, les ETR peuvent être sélectivement récupérés par lixiviation à l' $\text{HCl}$ , tandis que les OTRs non carbonatés restent insolubles. Cela séparerait hypothétiquement les ETR en deux groupes différents, réduisant significativement la difficulté de la séparation par extraction par solvants.

L'objectif principal de ce projet de recherche de maîtrise était d'étudier une nouvelle technique de pré-séparation pour les ETR utilisant la carbonatation (ou l'injection de  $\text{CO}_2$ ) des oxydes de terres rares (REOs) suivie d'une lixiviation sélective au  $\text{HCl}$ . Pour atteindre cet objectif, des expériences de carbonatation ont été réalisées sur différents matériaux contenant des ETR incluant du  $\text{Nd}_2\text{O}_3$  ou du  $\text{Pr}_6\text{O}_{11}$  individuels, des mélanges de ces oxydes ainsi que des OTR mélangés mécaniquement (en utilisant un ratio équimolaire et un ratio basé sur la composition de minerais d'ETR), des OTR co-précipités et des hydroxydes de terres rares co-précipités afin de mieux comprendre l'effet de la composition des matériaux contenant des ETR sur la carbonatation sélective de certains OTRs (du groupe A) mais pas d'autres (du groupe B). Différentes conditions opératoires ont aussi été testées pour améliorer les efficacités de pré-séparation de l'étape de carbonatation, utilisant divers pH (1,0 – 2,5 et 4,0) et durées (0 – 4 et 24 h, 48h) pour l'injection de  $\text{CO}_2$  ainsi que différentes méthodes de séparation solide/liquide (filtration, évaporation) pour les OTRs co-précipités. Pour

l'étape de lixiviation sélective au HCl, différentes concentrations d'acide, allant de 0,1 à 12 M, ont été testées pour déterminer leur effet sur la lixiviation sélective des ETR carbonatés par rapport aux ETRs non carbonatés.

Les résultats ont montré que la carbonatation de certains OTRs individuels, notamment  $\text{Nd}_2\text{O}_3$  et potentiellement les autres OTRs du groupe A, via l'injection de  $\text{CO}_2$  en solution, était efficace aux conditions atmosphériques, atteignant plus de 90 % de conversion en carbonates de terres rares. La carbonatation du  $\text{Pr}_6\text{O}_{11}$  ou des OTRs du groupe B, pour sa part, se produisait également mais à un degré plus faible, avec moins de 20 % de carbonatation après 24 h. La carbonatation des poudres d'OTRs mélangées mécaniquement a également été efficace avec un gain de masse mesuré d'environ 10 %. La carbonatation sélective des OTRs du groupe A, comparativement à ceux du groupe B, influence peu la lixiviation des OTRs carbonatés (>90 % de solubilisation peu importe la carbonatation), tandis que les OTRs non carbonatés demeuraient principalement sous forme solide (<30 % de solubilisation).

La carbonatation des OTRs co-précipités, qui se rapprochent davantage de mélanges trouvés dans l'industrie, s'est révélée très limitée (<5 %). L'étape de lixiviation sélective a, pour sa part seulement permis une pré-séparation du Ce, avec une efficacité de séparation de 30 %. Carbonater les OTRs co-précipités n'a amélioré que marginalement l'efficacité de séparation par lixiviation. Le remplacement de la filtration par l'évaporation pour récupérer les matériaux carbonatés de la pulpe après 24 h d'injection de  $\text{CO}_2$  améliore légèrement la pré-séparation du Ce par rapport aux autres ETR, particulièrement lorsque la carbonatation était réalisée à pH 1 en utilisant du  $\text{HNO}_3$  pour ajuster le pH. Cette tendance peut s'expliquer par l'augmentation de la concentration de l'acide se produisant durant l'évaporation de la solution acide, menant à l'oxydation du Ce(III), plus soluble, en Ce(IV), moins soluble. Différentes conditions opératoires ont été testées pour déterminer si cette efficacité de pré-séparation du Ce par rapport aux autres REOs pouvait être améliorée. De faibles effets du pH de carbonatation (1,0 – 2,5 – 4,0), du temps d'injection de  $\text{CO}_2$  (0, 4 ou 24 h) ou de la concentration en HCl (de 0,1 à 12 M) ont été observés sur l'efficacité de pré-séparation obtenue. La carbonatation des hydroxydes de terres rares s'est révélée inefficace, en plus de présenter le défaut qu'une masse substantielle des hydroxydes était perdue par solubilisation partielle au pH légèrement acide de l'eau saturée en  $\text{CO}_2$ . La lixiviation sélective de mélanges d'oxydes ou d'hydroxydes co-précipités, avec ou sans carbonatation, n'offre donc pas

d'opportunité de séparation autre que la lixiviation sélective des REOs co-précipités et ne semble donc pas constituer une voie prometteuse pour la pré-séparation.

## ABSTRACT

Rare earth elements (REEs) are crucial elements for the accelerating development of many industries including the storage of energy or military defense and are listed as critical and strategic minerals in several countries. REEs are omnipresent in the modern world, from electric cars, computers, lasers all the way to missiles, planes and many other uses. REEs are notoriously difficult to separate into individual elements and were discovered quite late in the history of science. Despite being strategic for several countries, most of the separation of co-precipitated REOs into high-purity individual REEs is performed in China using solvent extraction, which requires hundreds of mixer/settler units. It is therefore important to discover new separation techniques in order to diversify REE production. A previous study suggested that the injection of CO<sub>2</sub> under supercritical conditions allowed the separation of REOs into two groups, with some REOs tending to form carbonates in the presence of CO<sub>2</sub> under supercritical conditions, while others do not. The hypothesis is that REOs from group A can be carbonated and selectively recovered by HCl leaching, while group B REOs would remain insoluble (or much less so). This would hypothetically separate REEs into two different groups reducing the solvent extraction difficulty significantly.

The main objective of this MSc research project was to investigate this novel pre-separation technique for REEs using atmospheric carbonation (or CO<sub>2</sub> injection) of rare earth oxides (REOs) followed by selective leaching using HCl. To achieve this objective, carbonation experiments were conducted on different REE-bearing materials including individual Nd<sub>2</sub>O<sub>3</sub> or Pr<sub>6</sub>O<sub>11</sub>, Nd-/Pr-oxides mixtures as well as mechanically mixed REOs (using equimolar and REO ore ratios), co-precipitated REOs and co-precipitated REOHs to better understand the effect of REE-bearing materials to selectively carbonate REOs from group A but not those from group B. Different operating conditions were tested to try and improve pre-separation efficiencies of the carbonation step, using various pH (i.e., 1.0 – 2.5 and 4.0) and durations (0 – 4 and 24 h) of CO<sub>2</sub> injection as well as solid/liquid separation (i.e., filtration, evaporation) for co-precipitated REOs. For the selective HCl leaching step, different acid concentrations, ranging from 0.1 to 12 M were tested to determine its effect on the selective leaching of carbonated REEs from non-carbonated REOs.

Results showed that the carbonation of some individual REOs, namely Nd<sub>2</sub>O<sub>3</sub> or group A REOs, via CO<sub>2</sub> injection in solution was successful at ambient conditions, achieving more than 90% REO to carbonate conversion. The carbonation of Pr<sub>6</sub>O<sub>11</sub> or group B REOs also occurred, but to a

lower extent, with less than 20% carbonation after 24 h. The carbonation of mechanically mixed REO powders was also successful with a measured mass gain of about 10%. Whether using a carbonation step or not, the selective leaching of group A REOs in comparison to group B REOs occurred, with carbonation having almost no effect on the leach selectivity of mechanically mixed REOs.

Carbonation of various co-precipitated REO mixtures, better analogs of mixtures found in the industry, proved insignificant (< 5%). The selective leaching step led to coherent dissolution of all REEs, except for Ce for which a pre-separation efficiency of 30% was obtained. Carbonating co-precipitated REOs only marginally improved leaching separation efficiency. The replacement of filtration by evaporation to recover carbonated materials from the pulp after 24 h of CO<sub>2</sub> injection slightly improved the pre-separation of Ce from other REEs, especially when the carbonation was performed at pH 1 using HNO<sub>3</sub> to adjust the pH. This trend can be explained by the increasing concentration of the acid occurring during the evaporation of the oxidizing acidic solution, leading to the oxidation of highly soluble Ce(III) to less soluble Ce(IV). Different operating conditions were tested to determine if this pre-separation efficiency of Ce from other REOs can be improved. Tests were also performed investigating the effects of the pH of carbonation (1.0 - 2.5 - 4.0), CO<sub>2</sub> injection time (0, 4, 24, 48 h) or HCl concentration (from 0.1 to 12 M) on the pre-separation efficiency of Ce from the rest of the REOs. Carbonating rare earth hydroxides (REOHs) also proved ineffective, an additional issue being the substantial portion of the REOHs lost due to the partial solubilization of REEs under the slightly acidic pH of CO<sub>2</sub> saturated water. Therefore, selective leaching of carbonated REOH or REO mixtures does not offer any significant improvement in separation beyond that obtained by leaching co-precipitated REOs.

Carbonation of individual or mechanically mixed REOs via CO<sub>2</sub> injection was achieved up to 90% carbonation efficiencies for some individual REOs, namely neodymium. This was evidenced by IR carbon measurements, as well as mass gain and crystal formation assessed using SEM analysis (for experiments performed with Nd only). Group B REOs such as praseodymium, submitted to the same conditions, tend to carbonate to a lesser extent (<20%) and at a much slower rate. However, the major limitation of this approach as a separation method is that carbonation only happens to a notable extent when REOs are used as individual or mechanically mixed powders. Indeed, the carbonation process seemed to be ineffective (<5%) under the conditions tested for co-precipitated REOs, whether at equimolar or REO ore ratios, thereby limiting the applicability

of this pre-separation process at industrial scale. The selective leaching step also followed a similar pattern, showing that carbonated Nd-/Pr-oxides or mechanically mixed REOs could be separated via selectively HCl leaching ( $> 80\%$  for REOs from group A vs.  $< 20\text{-}30\%$  for REOs from group B), whereas co-precipitated REOs only allowed for around a 30% separation of Ce in comparison to other REOs. Different operating conditions were tested to determine if this pre-separation efficiency of Ce from other REOs can be improved. Low effects of the pH of carbonation (1.0 - 2.5 - 4.0),  $\text{CO}_2$  injection time (0, 4 or 24 h) or HCl concentration (from 0.1 to 12 M) were observed on the pre-separation efficiency of Ce from REOs. The replacement of filtration by evaporation to recover carbonated materials from the pulp after 24 h of  $\text{CO}_2$  injection seemed to improve the pre-separation of Ce from other REEs, especially when the carbonation was performed at pH 1 using  $\text{HNO}_3$  to adjust the pH. This trend can be explained by the concentration of the acid occurring during the evaporation of the acidic solution, leading to the oxidation of highly soluble Ce(III) to less soluble Ce(IV). Despite extensive investigation across a wide range of carbonation and HCl leaching conditions, co-precipitation REOs were not effectively pre-separated between Group A and Group B elements. Instead, all REEs tend to leach coherently, with the exception of Ce which remains insoluble.

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## LISTE OF SYMBOLS AND ABBREVIATIONS

|      |                           |
|------|---------------------------|
| ETR  | Élément de terres rares   |
| HREE | Heavy rare earth elements |
| LREE | Light rare earth elements |
| OTR  | Oxyde de terres rares     |
| REC  | Rare earth Carbonate      |
| REM  | Rare earth mineral        |
| REO  | Rare earth oxide          |
| REOH | Rare earth hydroxide      |
| REOX | Rare earth oxalate        |

## CHAPTER 1 INTRODUCTION

### 1.1 Context

In a world increasingly dependent on high level technological advancements, the requirements for specific elements with targeted physico-chemical properties also increases, leading to an intensification and diversification of the exploitation of mines worldwide. Rare earth elements (REEs) are used in many modern technologies that are strategic for several industrial sectors, including energy storage and military defense. Due to their use in the manufacturing of magnets (Nd, Pr, Tb, Dy), planes, aircraft carriers, missiles, wind turbine, and electronic devices, REEs are now considered critical and strategic elements by several jurisdictions around the world, including the United States, the European Union, Canada and Quebec. Despite growing demand, the worldwide production of REEs, which is mainly located in China, faces several challenges associated with the complexity to individually recover each REE once effectively solubilized. Although issues related to the separation of REEs are not new, there are still limited options available to efficiently replace solvent extraction (SX), a separation method which is the most common technique used at industrial scale. Identifying efficient pre-separation methods allows for a potential decrease in the number of mixer/settler units to separate each pair of neighboring REEs during solvent extraction. This can be very interesting to reduce operating costs and the number of steps. Several pre-separation methods, focusing on the selective oxidation/precipitation of Ce, reduction/precipitation of Yb or Eu, have been developed in the last few decades (Goode, 2016a). Selective REO carbonation followed by acid leaching has been proposed by Yanagihara (1991) as a potential pre-separation step to selectively recover some REEs, which would be transformed in carbonates under CO<sub>2</sub> injection under supercritical conditions, from other REEs which would not carbonate. Despite promising carbonation results obtained on individual rare earth oxides (REOs), proof that REEs can be separated based on their ability to form carbonates and then be leached using HCl is lacking. There is no information about the performances of this approach using mixed rare earth oxides (REOs) originating from the extraction of REEs from primary ores.

## 1.2 Research objectives and hypotheses

The main objective of this thesis is to evaluate the performance of the selective carbonation-HCl leaching process to pre-separate REEs. To achieve this main objective, two specific objectives (SO) and research hypotheses have been defined as follows:

SO 1. Evaluate the effect of carbonation conditions (i.e., mode of CO<sub>2</sub> injection, pH, retention time) on the efficiencies to produce easily HCl-leachable REE-carbonate from individual, mechanically mixed and co-precipitated REOs at room temperature.

Hypothesis 1.1 Atmospheric carbonation using a saturated CO<sub>2</sub> solution, while slower, offers a viable alternative to REO carbonation as compared to supercritical CO<sub>2</sub> carbonation.

SO 2. Investigate the effect of REE-bearing materials preparation (individual REOs, mechanically mixed REOs, co-precipitated REOs, co-precipitated REOHs) on the performance of the selective carbonation-HCl leaching pre-separation process.

Hypothesis 2.1: Only REOs found in some forms of REE-bearing materials can be transformed into REE-carbonates through the injection of CO<sub>2</sub> at ambient temperature and pressure, while others will stay as REOs.

Hypothesis 2.2: Newly formed REE-carbonates can be selectively leached in mildly acidic conditions, while REOs will remain insoluble, allowing efficient pre-separation of REOs from different REE-bearing materials.

## 1.3 Thesis Structure

This MSc thesis is organized into 5 main chapters. Chapter 1 provides an overview of the general context of the research and outlines the research objectives and hypotheses. Chapter 2 presents a literature review of the challenges associated to the separation of REEs to produce high-purity individual REE. First, it briefly introduces the REEs and their main applications as well as the location of the main REEs deposits. Then, the extraction routes used to extract REEs from different primary ores are presented, including the preconcentration of REE-bearing minerals, the solubilization of REEs from concentrates and the removal of the main impurities before to co-precipitate REEs as oxides. Principles, advantages and limitations of current and emerging technologies used to separate REEs in order to produced high-purity individual REEs are also

discussed. Chapter 3 describes the methodology used in this study to achieve the general and specific objectives previously defined, including the experimental setup and conditions, the equipment and reagents used as well as their scientific basis. Chapter 4 presents and discusses the results obtained. This chapter is divided into several subsections, each corresponding to a research focus: i) evaluation of the effect of selective carbonation-HCl leaching process on a simplified Nd/Pr system, ii) evaluation of the performance of the selective carbonation process on mechanically mixed REOs, iii) evaluation of the performance of the selective carbonation process on co-precipitated REOs as well as the factors possibly affecting its performance, iv) determination of the potential to use this selective carbonation-HCl leaching process on co-precipitated REOHs. Finally, Chapter 5 summarizes the main conclusions, reviews the research hypotheses and presents recommendations for potential future work.

## CHAPTER 2 LITERATURE REVIEW

### 2.1 Definition, application and production of REEs

Rare earth elements (REEs) are a group of 17 elements which includes lanthanides, elements with atomic numbers between 57 and 71, along with yttrium and scandium (Goode, 2019). At the beginning of the 21<sup>st</sup> century, despite their exceptional conductive and magnetic properties, these elements had limited industrial applications. Therefore, they were rarely exploited on a wide scale due to the complexities implicated in their separation processes to produce high purity individual REEs. Recently, a notable change has occurred, especially for elements such as neodymium and dysprosium, which have found several uses (Klinger, 2015). They are now omnipresent in modern life, from electric cars to computers and war planes. [Section 2.1](#) aims to describe the unique chemistry of REEs and demonstrate their significance in our modern society. The different forms REEs can take, the common uses of REEs and a brief market analysis will be presented. [Section 2.2](#) will discuss the exploitation of rare earth minerals (REMs) and the performance of hydrometallurgical processes used to extract REEs from primary ores. While the main focus of this thesis is related to the separation processes applied for the selective recovery of individual REEs will be presented in [Section 2.3](#).

#### 2.1.1 Definition and chemistry of REEs

As mentioned previously, REEs are a group of 15 elements belonging to the lanthanide (Ln) series situated at the bottom of the periodic table as well as Sc and Y, elements with similar electronic configuration. Their similar chemical reactivity is governed by identical 5d and 6s outer orbitals, while the number of inner 4f electrons varies from one REE to another one, giving each REE its specific optical and magnetic properties (Zhou & Fiete, 2020). This strong chemical similarity of REEs renders their separation by hydrometallurgical processes particularly challenging. The REEs can be classified in several ways, most commonly into light (LREEs, La-Gd) and heavy (HREEs, Tb-Lu and Y) categories. LREEs have unpaired 4f-electrons, while HREEs have paired ones, which gives HREEs slightly higher reactivity and improved optical and magnetic properties in comparison to LREEs. Although Y and Sc do not fit into these definitions, they are included in the REEs group as they generally co-occur with lanthanides in nature (Goode, 2019).

Depending on the water chemistry, REEs form various compounds such as chlorides [ $\text{LnCl}_3$ ], carbonates [ $\text{Ln}_2(\text{CO}_3)_3$ ] and oxides [ $\text{Ln}_2\text{O}_3$ ]. Elemental REEs readily oxidize in air, converting back to their corresponding oxides. Therefore, handling elemental REEs requires caution due to their tendency to react with atmospheric oxygen (Adachi & Imanaka, 1998). Owing to their trivalent oxidation state, most REEs form sesquioxides ( $\text{Ln}_2\text{O}_3$ ), while Ce, Pr and Tb are usually found in different forms namely:  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$  and  $\text{Tb}_4\text{O}_7$  (Adachi & Imanaka, 1998). This higher-valence oxides exhibit higher chemical resistance; for example,  $\text{CeO}_2$  is resistant to acidic leaching. Rare earth oxides (REOs) can slowly react with moisture and  $\text{CO}_2$ , producing minor amounts of hydroxides and carbonates (Bernal et al., 2006). This enhanced stability of higher-valence REOs may explain the differences observed in the conversion of REOs into rare earth carbonates in contact with  $\text{CO}_2$ , especially under supercritical conditions (Yanagihara et al., 1991)

### 2.1.2 Applications and production

Due to their unique optical and magnetic properties, REEs have many applications, the most popular ones being magnets and catalysts. A summary of the actual industrial uses of REEs is presented by use and element in Figure 2-1.

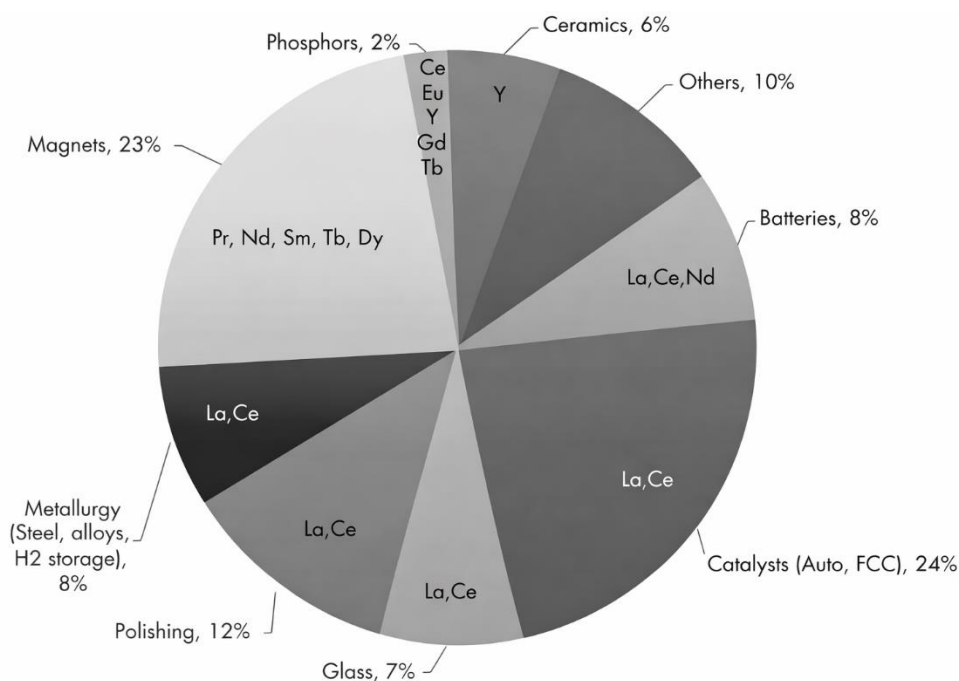


Figure 2-1 Reported industrial uses for different REEs (from Goode, 2019)

Even if not directly shown in [Figure 2-1](#), REEs are also extensively used in military technologies including aircrafts, ships and, missiles (Goodenough et al., 2018). A major issue for military applications is that nearly all rare earth elemental production (or transformation) is concentrated in China (Goode, 2016c), making these elements a strategic concerns for several countries worldwide, including Canada and the United States. At least 70% of the REE compounds imported to the United States originate from China (Mineral Commodity Summaries 2025, 2025). As presented in [Table 2-1](#), the USA has slowly restarted their REE operations in the last 5 years to limit their dependence toward China to produce a mix of REEs themselves, while it remains unclear if the separation of individual REE is carried out in the USA or elsewhere. US production rose to about 45,000 tons of concentrate (from the global 390,000 tons) and about 1300 tons of final products (compounds and metals).

Table 2-1 Evolution of REE Price and United States production from 2020 to 2024 (Mineral Commodity Summaries, 2025)

| Category                                                                                 | 2020   | 2021   | 2022   | 2023   | 2024   |
|------------------------------------------------------------------------------------------|--------|--------|--------|--------|--------|
| Production (tons of mineral concentrates)                                                | 39,000 | 42,400 | 42,500 | 41,600 | 45,000 |
| Production (tons of compounds and metals)                                                | —      | 120    | 95     | 250    | 1,300  |
| Price (\$/kg)                                                                            |        |        |        |        |        |
| CeO <sub>2</sub> - 99.5% minimum purity                                                  | 2      | 2      | 1      | 1      | 1      |
| Dy <sub>2</sub> O <sub>3</sub> - 99.5% minimum purity                                    | 261    | 410    | 382    | 330    | 260    |
| Eu <sub>2</sub> O <sub>3</sub> - 99.99% minimum purity                                   | 31     | 31     | 30     | 27     | 27     |
| La <sub>2</sub> O <sub>3</sub> - 99.5% minimum purity                                    | 2      | 2      | 2      | 1      | 1      |
| Nd <sub>2</sub> O <sub>3</sub> - 99.5% minimum purity                                    | 49     | 98     | 134    | 78     | 56     |
| Tb <sub>2</sub> O <sub>3</sub> or Tb <sub>4</sub> O <sub>7</sub> - 99.99% minimum purity | 670    | 1,346  | 2,051  | 1,298  | 1,800  |

Regardless of their end use, mixed REEs almost always require to be separated into individual elements or groups of elements to function properly. For example, high-performance magnets require an almost pure Nd-Pr mixtures, while Ce-La mixtures are commonly used as polishing

powders (Goode, 2019). Therefore, some individual or mixed REEs are highly valuable (Table 2-1) and in high demand while others are far less valuable and sometimes even considered as impurities, efficient separation is essential. For example, the market price of Nd is at least 40 times higher than that of Ce and La.

Separating a mixture of all REEs into individual elements or groups of specific elements is very challenging and can be quite expensive. Therefore, depending on the value of each REE and its concentration in the mixture to be treated, the separation of some individual REE may not be economically viable. The focus here is on improving REE separation process by developing pre-separation techniques.

### 2.1.3 Mineralogy and location of the main REE deposits

To date, more than 200 REE-bearing minerals have been discovered and listed worldwide (McNulty et al., 2022), but the most commonly found minerals are monazite, bastnaesite and xenotime (Table 2-2) (Whitty-Léveillé et al., 2018). REE-bearing minerals (REMs) are mostly found in carbonatites, pegmatites, and other igneous rocks, while REEs can also be found in ionic clays deposits where the REEs are substituted with other cations. As presented in Table 2-2, the main REMs groups are phosphates (i.e., monazite, xenotime) and carbonates (i.e., bastnaesite). While the exploitation of phosphate REE-bearing minerals offers the opportunity to potentially recover phosphate as a by-product, the extraction of REEs from monazite presents some challenges associated with the presence of fluorine, which forms hydrofluoric acid under the acidic conditions used in the acid baking process.

Table 2-2 Main REMs currently being processed for REE production (Kanazawa & Kamitani, 2006)

| Mineral Class                        | Mineral examples and chemical formulae |
|--------------------------------------|----------------------------------------|
| Carbonates                           | Bastnaesite, $(Ln)(CO_3)F$             |
| Phosphates, Arsenates, and Vanadates | Monazite, $(Ln)PO_4$                   |
|                                      | Xenotime, $Y(Ln)PO_4$                  |

Despite their name, REEs are not particularly rare and can be found in higher proportion than some precious metals commonly exploited worldwide. Indeed, with concentrations ranging from 0.5 to

64 ppm (with LREE found in higher proportion than HREE), these “rare” REEs are present in the earth’s crust in higher proportion than gold (0.0018 ppm), silver (0.05 ppm) or palladium (0.0005 ppm) (Taylor & McLennan, 2003). However, REMs deposits can contain a much higher grade of REOs, such as China’s Bayan Obo deposit (estimated reserve of 48 Mt of REOs with an average grade of 6%), Mountain Pass deposit in the USA (estimated reserve of 25 Mt at 5-10% REO) and Mt. Weld in Australia (estimated reserve of 7.7 Mt at 12% REO) (Kanazawa & Kamitani, 2006).

## 2.2 Extraction of REE from primary ores

After being excavated from the deposit, REE-bearing ores must undergo beneficiation (i.e., REM concentration), metallurgical extraction (i.e., REEs extraction from the REMs-concentrate) and purification (i.e., for impurities removal and individual REEs separation) processes as shown in [Figure 2-2](#). Beneficiation and extraction processes are selected based on : i) the nature of REMs and their physico-chemical properties (i.e., particle size distribution, magnetic susceptibility, surface properties, degree of liberation), ii) the nature of gangue minerals, iii) the environmental and geographical context of the mine site (i.e., remote location, availability and costs of energy and chemicals). It should be noted that ionic clay deposits, where REEs are substituted, will not be discussed further in this manuscript, mainly because these deposits are rare (mainly located in China and Brazil) and marginal in current global REE production (Goode, 2019).

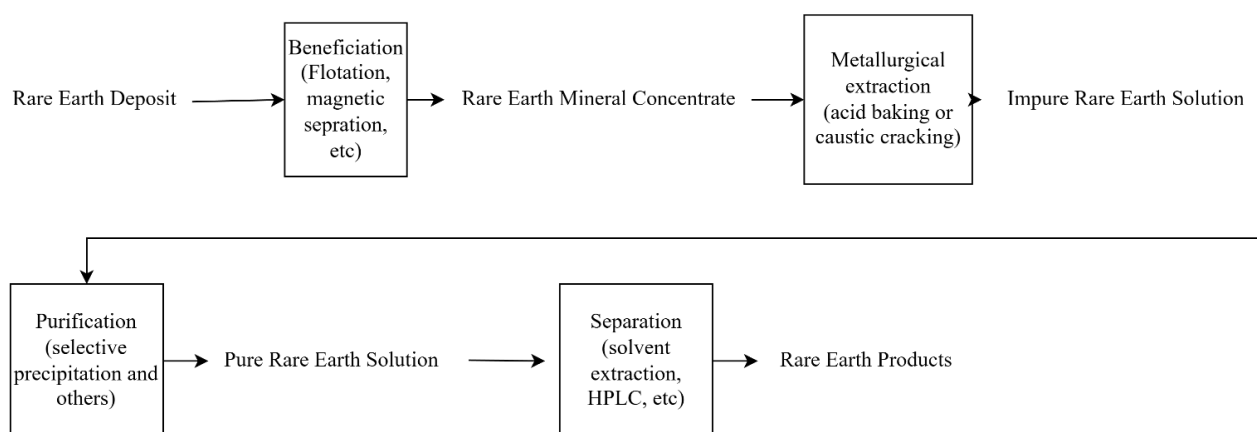


Figure 2-2 General REE processing flowsheet from REM-bearing deposits (inspired by Goode, 2019)

### 2.2.1 Preconcentration of REE-bearing minerals using flotation

Extensive research work has been conducted over the last three decades to improve the performance of the beneficiation processes to selectively concentrate REMs from gangue minerals and produce an enriched REM-concentrate containing 40-60% REOs (equivalent to 34-51% or REE – Goode, 2019). Only a brief overview of the studies carried out will be presented here, with an emphasis on flotation, which is the most widely used beneficiation process for concentrating REMs in almost all REE processing plants worldwide. For example, flotation is used to concentrate REMs from the ores from Bayan Obo, Mountain Pass and Mount Welt, prior to REE metallurgical extraction. For all these example deposits, REMs are mostly associated to carbonatites, indicating that gangue minerals are quite similar and consist of carbonates (i.e., dolomite).

Flotation is a well-known beneficiation process involving the separation of hydrophobic minerals (i.e., REMs) from hydrophilic minerals by adding chemicals (to adjust mineral surface properties) and air bubbles (to create a hydrophobic attachment point) to the pulp. Hydrophobic minerals adhere to the air bubbles and are recovered at the surface in the collected foam, while hydrophilic minerals will remain in the pulp. Although some minerals are naturally hydrophobic, chemical reagents such as collectors are still used to increase the hydrophobicity of the particles of interest and improve their floatability. Other chemicals including activators (to increase the adsorption capacity of the collector at the surface of targeted minerals), depressants (to decrease the hydrophobicity of gangue minerals), pH-regulators and frothers can be added to improve the performance of the flotation process. Usually performed in stirred reactors called flotation cells, the concentrate is introduced in the form of pulp. The main factors influencing the performance of REMs flotation include: i) the degree of REM liberation, ii) the nature and dosage of the reagents (i.e., collector, depressant, frother), iii) residence time, iv) the fraction of solids in the pulp, and v) the temperature (Wang et al., 2012). Commonly reported collectors for the flotation of REMs include hydroxamic acids and fatty acids, while sodium silicate is mainly used as depressant and dispersant (Marion et al., 2020). Previous studies reported that the addition of sodium silicate as depressant is required since monazite tends to float with gangue minerals, while the optimal temperature seemed to be around 64 °C. Considering the zeta potential of monazite ( $\text{pH}_{\text{pzc}}$  around 5.5), the optimal pH for the flotation of REM has been identified to be close to 8.0 (Chelgani et al., 2015). [Table 2-3](#) presents a summary of the performance of various collectors/depressant and operating conditions (i.e., pH) on the selective flotation of REMs.

Table 2-3 Examples of different flotation conditions for the most important REMs (Julapong et al., 2023)

| Type        | Collector                     | Mineralogical composition of ore               | pH   | Depressants             | Recovery (%) | Concentrate REO grade (%) |
|-------------|-------------------------------|------------------------------------------------|------|-------------------------|--------------|---------------------------|
| Carboxylate | Sodium oleate                 | Monazite, hematite, quartz                     | 9    | Sodium silicate, starch | 61           | 6.3                       |
|             |                               | Bastnaesite, calcite, barite                   | 9-10 | Lignin Sulfonate        | 86-90        | 11-33                     |
|             |                               | Xenotime, zircon, schorl, staurolite, ilmenite | 9    | Ammonium lignosulfonate | 33-52        | 52.3-59.6                 |
| Hydroxamate | Octanol hydroxamic acid (OHA) | Bastnaesite, fluorite                          | 9    | EDTA                    | 80-88        | 68                        |
|             |                               | Monazite, calcite                              | 9    | Sodium silicate         | 80           | -                         |

### 2.2.2 Extraction of REEs from concentrates

REMs exhibit strong bonds which require harsh chemical or thermal conditions to efficiently break and subsequently extract REEs and favor their solubilization (Kanazawa & Kamitani, 2006). The main process used at industrial scale to extract REEs from REMs is acid backing, although caustic cracking represents a viable alternative but is less commonly applied. One of the main challenges related to the extraction REEs is the non-negligible presence of radioactive elements (i.e., Th, U) within REMs and in other Th- or U-bearing minerals associated to REE deposits. These radioactive elements have an ionic radius of around 1.00 Å, which is close to those of REEs and other elements such as Na<sup>+</sup> and Ca<sup>2+</sup>. Combined with a similar oxidation state and coordination numbers, this leads to REMs containing up to 5% (w/w) uranium and 20% (w/w) thorium (Whitty-Léveillé et al., 2018). Both acid baking and caustic cracking processes have some advantages and limitations in the separation of radioactive elements from REEs during the extraction processes (Traore, 2025).

### Acid baking

Many REMs are processed by acid baking to efficiently recover REEs, monazite is presented in this section as a representative example due to its industrial importance. Acid baking consists of mixing REM concentrate with highly concentrated sulfuric acid ( $> 98\%$ ) and heating the mixture to temperatures above  $300^{\circ}\text{C}$  for approximately 3 hours to convert insoluble REMs into water-soluble REE sulfates (Demol et al., 2019). After acid baking, a water leaching step is conducted to solubilize REEs and the REE-concentrated leachate is then purified to remove impurities prior via selective precipitation (Figure 2-3).

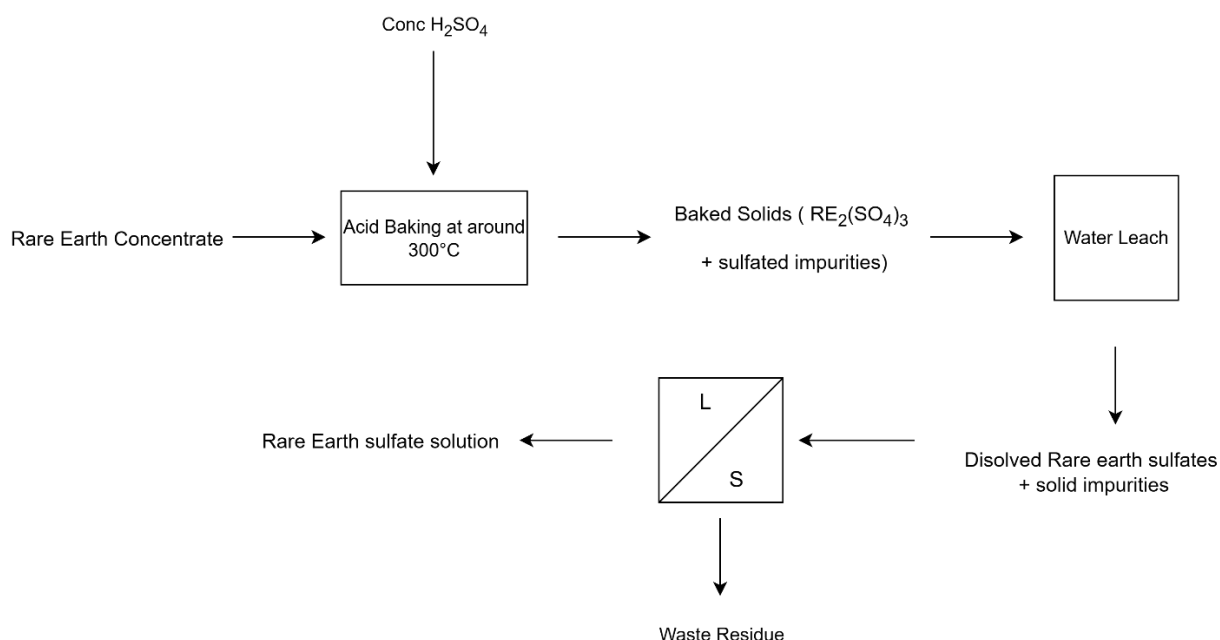
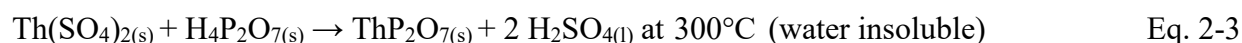
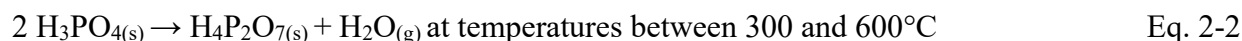


Figure 2-3 Typical acid baking flow sheet adapted from Demol et al. (2019)

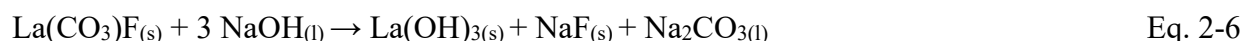
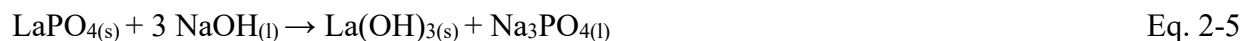
Industrial operation of this process can be challenging because numerous chemical reactions occur between REMs, gangue minerals and H<sub>2</sub>SO<sub>4</sub> over different temperatures and retention times. Therefore, strict control of both temperature and retention time is needed to favor the formation of water soluble REE sulfates and limit the co-extraction of Th, an undesirable radioactive impurity. Indeed, at temperatures close to  $300^{\circ}\text{C}$ , thorium tends to form insoluble phosphate (Equations 2-1 to 2-3), while REMs are converted into water-soluble REE sulfates (Equation 2-4) (Demol et al.,

2019). This simultaneous immobilization of Th and conversion of insoluble REMs into water-soluble rare earth sulfates is advantageous, although operating at temperatures near 300°C may slightly decrease the efficiency of REM conversion to water-soluble rare earth sulfate, therefore reducing their subsequent recovery by water leaching.



### **Caustic cracking**

Caustic cracking is an alternative to acid baking in which a strong base is used instead of sulfuric acid to break down the crystallographic structure of REMs and form rare earth hydroxides (REOHs). Caustic cracking is usually operated at industrial scale using highly concentrated NaOH solutions or molten NaOH, which reacts directly with REMs. Chemical reactions occurring between REMs and NaOH are presented in the Equation 2-5 for monazite and Equation 2-6 for bastnaesite (Goode, 2019). It should be noted that caustic cracking of REMs leads to the formation of  $\text{Th}(\text{OH})_4$  and its removal required strict control of pH during the subsequent leaching step. As shown in Figure 2-4, leaching of REOH(s) occurs at a pH above 4, while  $\text{Th}(\text{OH})_4$  and other impurities precipitated as hydroxides remain in their solid form until a lower pH allowing for separation. Phosphorus can be recovered as trisodium phosphate (Equation 2-5), which has commercial value (Goode, 2019).



Despite its efficiency to selectively leach REEs from other impurities precipitated as hydroxides and the potential for phosphorus recovery, caustic cracking is less widely used than acid backing. Indeed, Verbaan et al. (2015) showed that only three out of eighteen new REEs projects use caustic cracking. This can be explained by the higher costs of NaOH in comparison to  $\text{H}_2\text{SO}_4$ , even when a partial recycling of the caustic solution is implemented (Elmas, 2017). Using NaOH therefore increases cost and brings associated recycling operating challenges but increases co-valorization sources in the form of phosphorus.

### **2.2.3 Impurity removal from REE-rich leachate and REE precipitation**

Following the acid baking or caustic cracking process, REE-enriched leachates are produced containing high concentrations of REE as well as impurities such as Fe, Al, Ca, Mg, Th, and U, which originate from the gangue minerals and the reagents used. In addition to potentially contaminating the final individual REEs products, the presence of these impurities complexifies the operation of REEs separation while increasing costs (Goode, 2019). The main objective of post-baking or cracking treatment is to produce a solution enriched in REEs with minimal impurity content, before proceeding to the REE separation step. The performances of different processes including selective precipitation, solvent extraction and ion exchange are discussed in detail in Talan & Huang (2022). The removal of impurities including Fe(III), Al(III), Th and U separation is mainly conducted by neutralization of the acidic REE-enriched leachate to a pH around 4 to selectively precipitate impurities while limiting the precipitation of REE as hydroxides (Figure 2-4; Goode, 2019). Despite selective precipitation's performances in removing impurities, residual concentrations of thorium and some radioactive elements (i.e., Ra, Pb) can still be measured in the leachate after precipitation, requiring additional purification steps. Radium can be removed by co-precipitation as  $(\text{Ba,Ra})(\text{SO}_4)_2$  with the addition of  $\text{BaCl}_2$  and  $\text{Na}_2\text{SO}_4$  (Pillai, 2007). Solvent extraction is another proposed method to efficiently remove Th and U from REEs, particularly when using organophosphorus (i.e., DEHPA, EHEHPA, Cyanex 272, Cyanex 923, TBP) or amines (i.e., Alamine 336, Primene JMT) solvents (Goode, 2019).

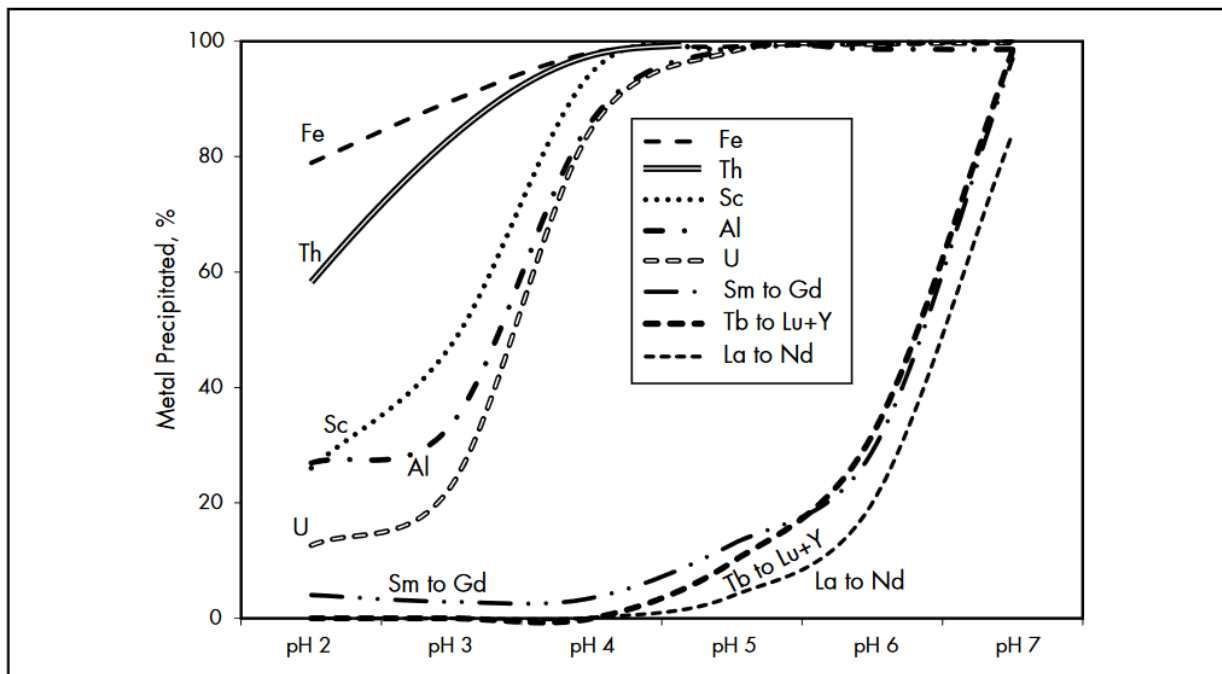
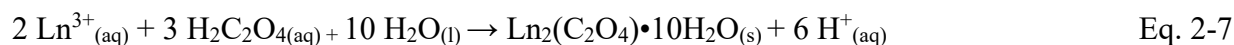


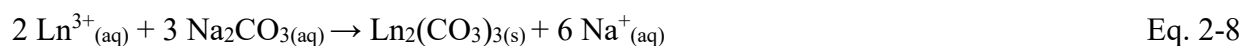
Figure 2-4 Precipitation of impurities as hydroxides from REE-enriched chloride media as a function of pH (Goode, 2019)

Following selective impurities removal, REEs are precipitated as oxalates or carbonates from the purified REE-enriched solution to produce a mixed REOs product used for the subsequent individual REE separation step (Goode, 2019; Lucas et al., 2015). The precipitation of REEs as oxalate involves the addition of a solution of oxalic acid (10%) to the purified REEs-enriched solution to favor the formation of insoluble oxalate REE-complexes as described in Equation 2-7. The purified REE-enriched solution can also be treated for separation directly if the separation plant is present in situ.



REEs precipitation as oxalate is highly selective, most of residual impurities remain soluble, except Th, which is completely precipitated, and Ca, Ba, and Sr which can partially precipitate (Goode, 2019). It should be noted that the precipitation of REE as oxalate requires strict control of the pH and the amount of oxalate ions added. Prior to calcination at temperature between 500 and 1,000°C,

the precipitate is rinsed with water and dried to remove residual soluble impurities (Lucas et al., 2015; Qi, 2018) To perform the precipitation of REEs as carbonates, ammonium or sodium bicarbonate are added to the purified REE-enriched solution to allow the formation of insoluble REEs-carbonates as described in Equation 2-8.



The composition of the mix of REOs obtained is dependent on the composition of the purified REE-enriched solution, the precipitating agent used (oxalic acid allowed the formation of high-purity mixed REOs in comparison to bicarbonates) and the temperature of the calcination (Verbaan et al., 2015). However, only few studies documented the chemical composition of the REOs precipitates obtained (Goode, 2025). In the absence of extensive data, it can be assumed that the original distribution of REEs within the ore (Goode, 2019) is maintained in the mixed REOs precipitates obtained. Table 2-4 presents the composition of mixed REOs precipitates calculated from the initial composition of the ore and making the following assumptions: i) flotation did not affect the distribution of individual REEs; ii) acid baking and water leaching efficiencies follow those reported by Dresinger et al. (2020) and iii) all impurities were efficiently (100%) removed from the REE-enriched solution prior to the precipitation as oxalates. The resulting REEs ratios are consistent with values reported in the literature (Balaram, 2019; Goode, 2025; Goodenough et al., 2018; Turgeon et al., 2019). As expected, the mixed REOs precipitates are mainly composed of Ce (most abundant but least valuable element), La, Nd (significant economic importance) and Y. To be noted that the chemical composition of the mixed REOs precipitates strongly influence the performance of the subsequent separation steps to produce high-purity individual REEs.

Table 2-4      Calculated REO composition (%) of mixed REOs precipitates produced from different REEs deposits around the world

|                                 | Price<br>(US\$/kg<br>oxide) | Bayan<br>Obo<br>China | Mianning<br>China | Mountain<br>Pass<br>USA | Mt. Weld<br>Australia | Longnan<br>China | Xinfeng<br>China | Serra<br>Verde<br>Brazil | Dubbo<br>Australia | Strange<br>Lake<br>Canada | Foxtrot<br>Canada |
|---------------------------------|-----------------------------|-----------------------|-------------------|-------------------------|-----------------------|------------------|------------------|--------------------------|--------------------|---------------------------|-------------------|
| La <sub>2</sub> O <sub>3</sub>  | 1                           | 25.32                 | 29.18             | 32.48                   | 25.30                 | 2.85             | 27.66            | 35.14                    | 20.04              | 11.14                     | 17.48             |
| CeO <sub>2</sub>                | 1                           | 49.08                 | 48.18             | 50.21                   | 47.43                 | 0.58             | 2.05             | 4.48                     | 38.61              | 27.41                     | 40.87             |
| Pr <sub>6</sub> O <sub>11</sub> | 65                          | 5.70                  | 4.40              | 4.49                    | 5.30                  | 1.15             | 6.41             | 6.65                     | 4.14               | 2.93                      | 4.70              |
| Nd <sub>2</sub> O <sub>3</sub>  | 71                          | 16.81                 | 15.21             | 11.99                   | 18.60                 | 5.88             | 22.53            | 21.52                    | 14.58              | 10.51                     | 16.68             |
| Sm <sub>2</sub> O <sub>3</sub>  | 1                           | 1.56                  | 1.17              | 0.59                    | 2.34                  | 4.39             | 4.70             | 3.40                     | 2.22               | 2.65                      | 2.85              |
| Eu <sub>2</sub> O <sub>3</sub>  | 48                          | 0.11                  | 0.22              | 0.10                    | 0.42                  | 0.33             | 0.72             | 0.20                     | 0.08               | 0.14                      | 0.14              |
| Gd <sub>2</sub> O <sub>3</sub>  | 10                          | 0.28                  | 0.58              | 0.03                    | 0.09                  | 6.84             | 4.60             | 3.03                     | 2.01               | 2.63                      | 2.47              |
| Tb <sub>4</sub> O <sub>7</sub>  | 377                         | 0.18                  | 0.11              | 0.02                    | 0.06                  | 1.37             | 0.73             | 0.47                     | 0.28               | 0.60                      | 0.36              |
| Dy <sub>2</sub> O <sub>3</sub>  | 205                         | 0.16                  | 0.18              | 0.02                    | 0.10                  | 8.65             | 3.72             | 2.69                     | 1.78               | 4.22                      | 1.88              |
| Ho <sub>2</sub> O <sub>3</sub>  | 0                           | 0.02                  | 0.04              | 0.02                    | 0.06                  | 1.55             | 0.72             | 0.53                     | 0.34               | 0.95                      | 0.36              |
| Y <sub>2</sub> O <sub>3</sub>   | 4                           | 0.60                  | 0.60              | 0.00                    | 0.09                  | 57.14            | 22.80            | 18.57                    | 13.90              | 30.05                     | 10.34             |
| Er <sub>2</sub> O <sub>3</sub>  | 21                          | 0.02                  | 0.05              | 0.02                    | 0.06                  | 4.86             | 1.77             | 1.66                     | 0.99               | 3.05                      | 0.98              |
| Tm <sub>2</sub> O <sub>3</sub>  | 0                           | 0.08                  | 0.03              | 0.02                    | 0.06                  | 0.63             | 0.18             | 0.26                     | 0.14               | 0.50                      | 0.13              |
| Yb <sub>2</sub> O <sub>3</sub>  | 0                           | 0.01                  | 0.04              | 0.01                    | 0.05                  | 3.39             | 1.28             | 1.26                     | 0.78               | 2.87                      | 0.67              |
| Lu <sub>2</sub> O <sub>3</sub>  | 0                           | 0.09                  | 0.01              | 0.01                    | 0.05                  | 0.39             | 0.14             | 0.14                     | 0.11               | 0.35                      | 0.07              |
| REO<br>feed<br>(%)<br>mixed     | —                           | 5.5                   | 7                 | 8.5                     | 15                    | 0.06             | —                | 0.148                    | 0.9                | 1.1                       | 1                 |
| REO<br>(\$/kg)                  | —                           | 17.51                 | 15.41             | 12.42                   | 18.07                 | 32.04            | 32.98            | 28.80                    | 19.37              | 22.89                     | 21.65             |

### 2.3 Current and historical separation processes for REEs

As mentioned previously, REEs are typically only useful when separated into individual elements or small groups of elements, one example being the use of high purity neodymium to produce magnets. Previous studies showed that the presence as impurities of other REEs such as La or Ce can be problematic to the production of ferromagnets (Goode, 2019). While the presence of Pr seems to not be detrimental for this application. Therefore, depending on the use of REEs, their complete separation from other REEs is not necessarily required, while for some applications, high purity REE are requested. Separation processes, which will be discussed in detail in the following sub-section, aim to selectively recover each individual REEs from the mixed REOs precipitate previously formed. Although their efficiency will vary depending on the process and the composition of mixed REOs, complete individual separation, which is quite challenging, remains the main objective. While pre-separation processes, to be discussed in [Section 2.4](#), aim to separate some REEs from others to produce different groups of REEs to be further separate to obtain individual REEs to decrease the number of separation steps required to produce high purity individual REEs. Conventional separation processes include liquid-liquid extraction (solvent extraction), selective precipitation/crystallization, high performance liquid chromatography (HPLC), ion exchange, while emerging approaches include free flow electrophoresis (FFE), molecular recognition technology (MRT), chlorination, selective sorption on organic metallic frameworks (MOFs) as presented in [Table 2-5](#).

Table 2-5 Summary of the principles, advantages and limitations of actual and emerging REEs separation methods

| Name                                        | Principle                                                                                | Advantages                                                                                   | Disadvantages                                                                                                                           | Reference                               |
|---------------------------------------------|------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------|
| Solvent extraction                          | Different affinities of REEs for the organic and aqueous phases.                         | Typical separation method used in the industry, can treat REE solutions at industrial scale. | Contains many steps, Chinese monopoly, trade secrets, requires many mixer/settlers.                                                     | Turgeon et al. (2019)                   |
| Selective Precipitation and Crystallization | REEs crystals tend to appear in slightly different conditions.                           | Historical significance, efficient at separating REEs from impurities.                       | Low separation performances requiring multiple cycles for separating individual REEs. Overshadowed by all modern separation techniques. | Kaczmarek (1981)                        |
| HPLC                                        | Different affinity of the REEs for the stationary and the mobile phases.                 | Very efficient at separating REEs into their individual elements.                            | Currently, cannot be done at industrial scale, only in small quantities, technique to be developed.                                     | Goode (2016)                            |
| Ion-exchange                                | Resins have a higher affinity for some REEs more than others and are eluted differently. | More efficient at separation REEs than solvent extraction.                                   | Use of expensive resins, regeneration can be challenging.                                                                               | Kaczmarek (1981)                        |
| Free Flow Electrophoresis                   | REEs have different interactions with an electric potential.                             | Good separation into individual elements.                                                    | Very few details, appears abandoned, small-scale, high-energy use.                                                                      | Barrolier et al. (1958); Hanning (1961) |
| Molecular Recognition Technology            | Special ligands bind selectively to certain REEs and not others.                         | Good separation achieved after only 3 steps.                                                 | Heavily proprietary, little available information, appears unsuccessful.                                                                | Izatt et al. (2016)                     |
| Chlorination                                | $\text{LnCl}_2$ has a different vapor pressure from $\text{LnCl}_3$ .                    | Good separation between two elements.                                                        | Prototype, only works for separating Nd and Sm so far, high energy and reactant usage.                                                  | Uda et al. (2000)                       |
| Metal-Organic Frameworks                    | Some organic frameworks ligands have more affinity for one element than another.         | Good separation between some elements.                                                       | Prototype, does not separate all elements, high usage and cost of reactants.                                                            |                                         |

### 2.3.1 Liquid-liquid extraction

Liquid-liquid extraction, also known as solvent extraction (SX), is a highly efficient, versatile and easily scalable process commonly used for the purification of organic and inorganic compounds. Solvent extraction is based on the separation of organic or inorganic compounds according to their solubilities and affinities across two immiscible phases. Typically, the aqueous phase is mixed with an organic phase which contains the extractant diluted in an organic solvent (i.e., diluent) to favor the transfer of targeted inorganic or organic compounds to be recovered in the organic phase, which is known as the *loading stage*. Then, the impurities loaded to the organic phase are selectively removed using a scrubbing solution, which is known as the *scrubbing stage*. The recovery of the targeted compounds loaded to the organic phase is performed using a stripping solution, which is known as the *stripping stage*. Over the last decades, different types of extractants were developed including, cationic, anionic and neutral extractants. For the separation of REEs, cationic extractants (i.e., bis(2-ethylhexyl) phosphate - P-507 [Figure 2-5](#), D2EHPA, Cyanex 272, Cyanex 302), which are efficient for the recovery of cationic species including  $\text{Ln}^{3+}$ , are the most used. The performance of solvent extraction is dependent on the selectivity, solubility and immiscibility of the organic phase.

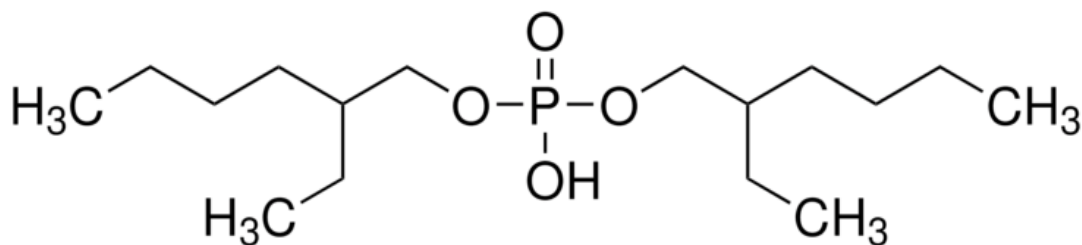


Figure 2-5 Skeletal chemical structure of bis(2-ethylhexyl) phosphate P507

Upon deprotonation of the central phosphate group, three  $\text{R}_2\text{PO}_4^-$  ligands typically coordinate with a single  $\text{Ln}^{3+}$  ion to form the metal–extractant complex. The reversible reaction presented in [Equation 2-9](#) represents the main equilibrium governing liquid–liquid extraction of REEs.



SX process is based on a mass transfer reaction between reagents (i.e.,  $\text{Ln}^{3+}$ ,  $\text{R}_2\text{H}_2$ ) and products (i.e.,  $\text{Ln}(\text{R}_2\text{H})_3$ ,  $\text{H}^+$ ). Therefore, an equilibrium constant ( $K_{\text{eq}}$ ) can be calculated for each REEs as described in Equation 2-10.

$$K_{\text{eq}} = \frac{[\text{Ln}(\text{R}_2\text{H})_3] \times [\text{H}^+]^3}{[\text{Ln}^{3+}] \times [\text{R}_2\text{H}_2]^3} \quad \text{Eq. 2-10}$$

The equilibrium equation allows us to predict the changes in concentration of one specie as the others change, which is used to control the different stages of separation (Goode, 2016b). For example, if protons are added through the addition of a strong acid during the scrubbing or stripping phases, this will push the equilibrium towards the metal being back in the aqueous phase. Two additional parameters, distribution coefficient ( $D_i$ ) and separation factors ( $\beta_{i,j}$ ) should be defined to better evaluate the performance of SX to separate the different REEs. The distribution coefficient,  $D_i$ , is the ratio between the equilibrium concentration of the REE in the organic ( $[\text{Ln}(\text{R}_2\text{H})_3]$ ) and the aqueous ( $[\text{Ln}^{3+}]$ ) phases as described in Equation 2-11.

$$D_i = \frac{[\text{Ln}_i(\text{R}_2\text{H})_3]}{[\text{Ln}_i^{3+}]} \quad \text{Eq. 2-11}$$

Where “i” denotes a certain rare earth element.

The separation factor  $\beta_{i,j}$  is defined by the ratio between distribution coefficients of two REEs elements ( $\text{REE}_i$  vs.  $\text{REE}_j$ ) as described in Equation 2-12, which is a good indicator of the difference of affinities for two REEs for the organic phase and the performance of the separation of two REEs.

$$\beta_{i,j} = \frac{D_i}{D_j} \quad \text{Eq. 2-12}$$

Higher values of  $\beta_{i,j}$  indicate that the separation between two REEs will be effective. Typical separation factors between the different REEs using D2EHPA as extractant are presented in [Figure 2-6](#) (Turgeon et al., 2019). In comparison to Ni and Co,  $\beta_{i,j}$  values measured for each REEs combination are 1200 to 4500 times lower, indicating that REE separation will require multiple extraction stages to produce high purity individual REEs.

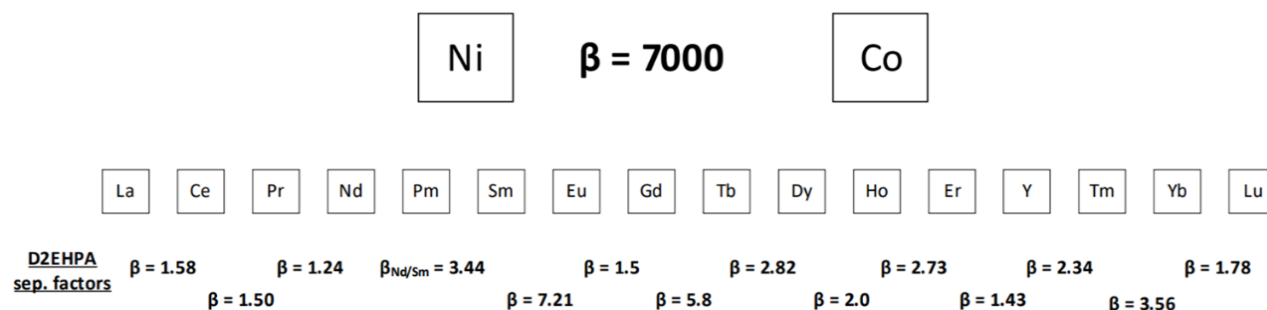


Figure 2-6 Typical separation factors between different REEs using D2EHPA adapted from Turgeon et al. (2019)

As previously mentioned, a typical SX separation circuit is composed of 3 stages of separation (i.e., extraction, scrubbing, stripping) and 1 stage of saponification (Goode, 2016b), which are operated in counter-current or cross-current mode. [Figure 2-7](#) presents the SX separation circuit of Dy and Ho using P-507 as an extractant in counter-current mode, which is the most common way to operate SX separation circuits at industrial scale. In counter-current mode, the **extraction stage** is performed by contacting the REEs-concentrated (Ho-Lu+Y) organic phase obtained from the stages of extraction and from the feed solution with the dilute (Ho-Lu+Y) aqueous phase, while the dilute organic (Sm-Dy)-organic phase is mixed with the (Sm-Lu)-concentrated aqueous phase. In the **scrubbing step**, the (Ho-Lu+Y)-concentrated organic phase is mixed with a mildly acidic scrubbing solution to separate Sm to Dy further as a second separation step. By slightly increasing the concentrations of  $H^+$  in the scrubbing solution, the lighter REE-organic complexes present in the organic phase tend to be solubilized and be transferred to the aqueous phase first, while the heavier REEs will remain in the organic phase. In the present example, light REE (from Sm to Dy) that were partially transferred to the organic phase will be transferred to the aqueous phase, while Ho to Lu and Y will remain in the organic phase. In the stripping stage, the (Ho-Lu+Y)-concentrated organic phase will be eluted using a very acidic solution. As presented in

Equation 2-9, high amounts of  $H^+$  ions in the system will favor the transfer of Ho to Lu and Y in the aqueous phase, while regenerating the organophosphorus acid group of the extractant.

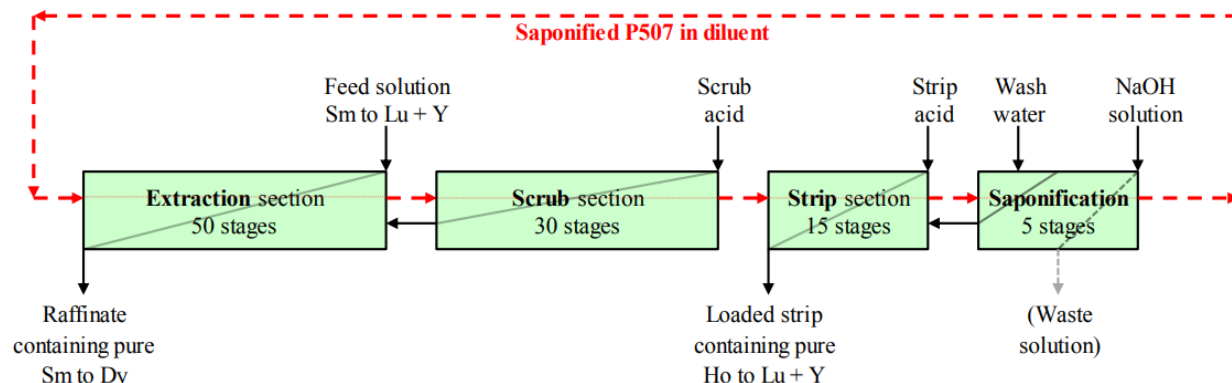


Figure 2-7 Typical solvent extraction diagram, here between Dy and Ho (Goode, 2016b)

Nowadays, solvent extraction is the main separation technique used to produce high purity individual REEs or groups of elements from mixed REOs at an industrial scale (Chen et al., 2022; Goode, 2019). However, only little information on the solvent used and the way that SX is performed at industrial scale, mainly in China, are available in the literature (Qi, 2018). At industrial scale, liquid-liquid extraction of REEs from mixed REOs is performed in mixer-settlers (Figure 2-8). The performance of solvent extraction is dependent on the selectivity, solubility and immiscibility of the organic phase.

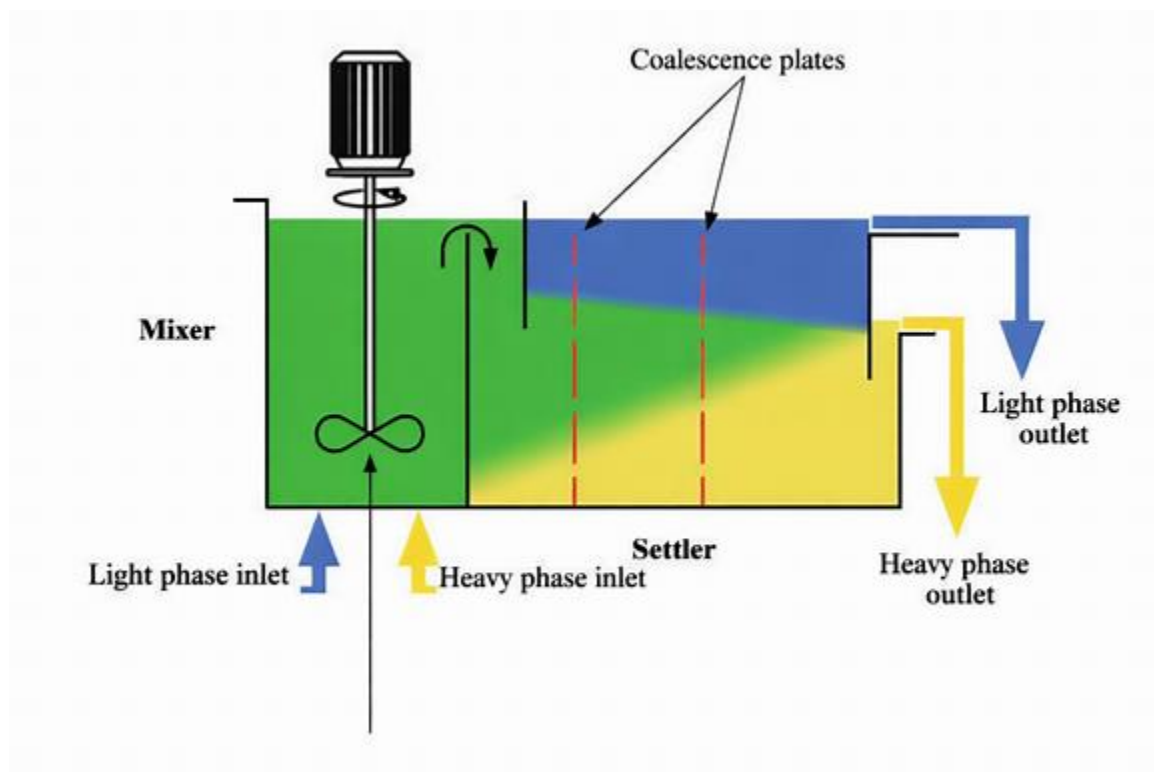


Figure 2-8 Diagram of a typical mixer settler (Turgeon et al., 2019)

As previously mentioned, the separation factor ( $\beta_{i,j}$ ) is a good indicator of the performance of the separation of two REEs and can be used to determine the number of mixing/settling stages to achieve substantial separation between two REEs. Based on Figure 2-9, the number of mixer/settlers is exponentially increasing as the separation factor decreases, meaning that the separation of two REEs using D2EHPA with  $\beta_{i,j}$  values ranging from 1.5 to 7.2 will require between 15 and more than 70 mixer/settler for each pair of neighboring REEs.

Considering the challenges associated with the complex operation of multiple mixing/settling steps to achieve satisfactory REE separation, significant research efforts have focused on improving the performances of existing processes or developing alternatives to REE separation. The following sub-sections will summarize alternative separation methods capable of separating individual REEs, outlining their advantages and limitations. Fractional crystallization, which was the first method used to separate REEs, suffer from limited efficiencies, requiring thousands iterative crystallization cycles to selectively recover each REEs. Chromatography techniques, including high performance liquid chromatography (HPLC), ion exchange (IX) and capillary electrophoresis (CE) involves the

use of traditional solvent extraction chemistry in a chromatographic mode. These techniques are highly efficient for the separation of REEs, achieving high separation resolution within short periods of time. To be noted that some of these alternatives are progressing toward industrial deployment, while other remain at laboratory scale.

## How many mixer settlers?

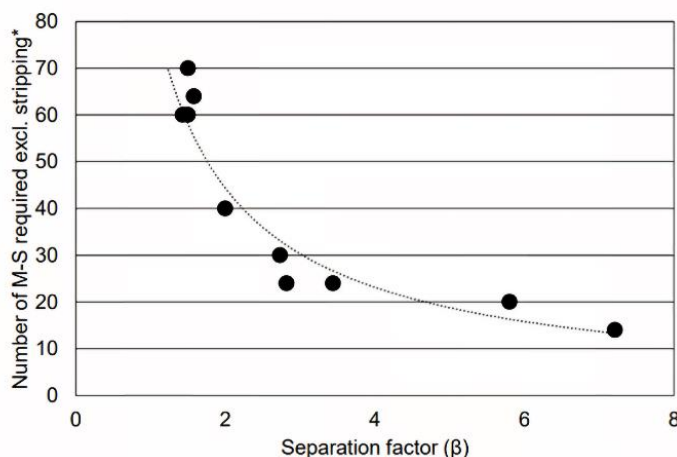


Figure 2-9 Diagram showing the number of mixer settlers as the separation factor diminishes (Turgeon et al., 2019)

### 2.3.2 Precipitation and crystallization

Fractional crystallization is a separation technique which consist in selectively recovering compounds from a solution based on differences in solubilities. By controlling the temperature (evaporation, cooling), dissolved compounds with lower solubilities will crystallize first, allowing them to be selectively recovered from the solution. However, individual REE compound tend to crystallize at the same time, but with slightly different distribution ratio. This means that numerous iterative crystallization steps were required to achieve good purity of one element over another one. Therefore, this separation process is long and labour-intensive, even more so than SX (Goode, 2016b). Typical compounds used to induce fractional crystallization included double ammonium nitrates, double manganese nitrates and bromates, with separation factors lower than 1.1, indicating the low performance of this separation technique (Kaczmarek, 1981). This limitation was particularly evident in the work of Georges Urbain at the end of the 1800s, who isolated Dy after

10,000 successive crystallization cycles and later Lu and Y after nearly 15,000 crystallization cycles. Fractional crystallization is considered to be of historical significance only and is no longer in use in modern REE separation.

### **2.3.3 High performance liquid chromatography (HPLC)**

High performance liquid chromatography (HPLC) is a promising technique to separate each pair of neighbouring REEs, based on the differential affinities of each REE for the functional groups of the stationary phase and the mobile phase (i.e., eluent) to favor their effective separation. This technique has been used for more than 25 years for analytical purposes (Figure 2-10) to improve the separation of REEs prior to their individual quantification (Bruzzoniti et al., 1996). Significant improvements in the selectivity of stationary phase (i.e., synthesis of new and efficient functional groups) have led to better REE separation and enhanced peak sharpness (Goode, 2016b). Indeed, broad and not well separated peaks can be noticed for each REE from a study performed in 1996 (Figure 2-12a) in comparison to sharp and narrow peaks which are well separated, except for some light REEs (i.e., La, Ce, Nd, Dy or Eu, Gd) with very small peak overlap (Figure 2-10b,c).

Despite its high efficiencies in separating individual REEs in a single step, there is no industrial application of this technology worldwide due to some limitation to using HPLC at large scale. Indeed, this process requires very controlled conditions to maintain REE separation efficiencies that restrict its large-scale application: i) use of specific type and shape of stationary phase, ii) injection of a specific concentration of the mobile phase at a targeted flowrate, iii) operation of the system at high pressure, and iv) small-scale equipment allowing the introduction of few milliliters at a time, restricting large-scale application. For now, scaling this technique at an industrial scale presents several unresolved challenges (Goode, 2016b). For example, it is not evident if the scale-up of the stationary phase would require increasing the quantity of small particles, which will need substantially higher pressure to maintain flow uniformity or to substitute then with larger particles, which will potentially affect the contact of the REE with the stationary phase and therefore separation performance. Overall, these engineering constraints illustrate the considerable hurdles associated with applying HPLC to REE separation at industrial scale. To date, the Norwegian company REEtec, which is currently among the leading industry investigating the use of HPLC for REE separation, has not fully succeeded in demonstrating a full-scale operation separation processing plant based on information available in the literature (Goode, 2016b).

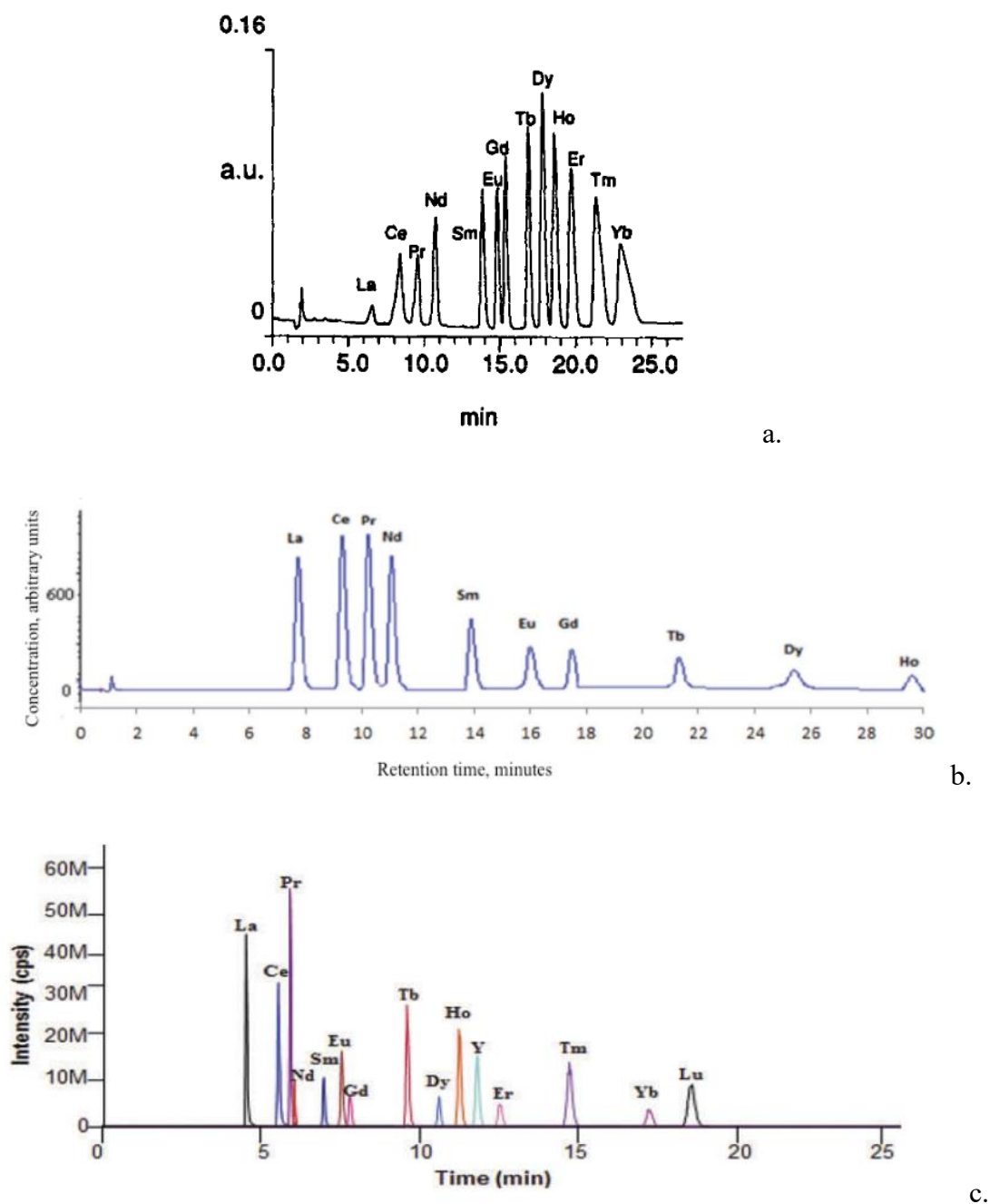
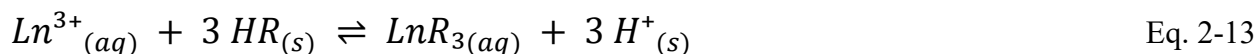


Figure 2-10 Evolution of HPLC efficiencies in separating REEs for analytical purposes with chromatograms obtained from Bruzzoniti et al. (1996) (a.) (IonPac CS5/CG5 stationary phase, pH 5, 15 min from 80 mM oxalic acid to 26 mM oxalic acid), Goode (2016a) (b.) (not specified besides “DEHPA-impregnated HPLC column”) and Ramzan et al. (2016) (c.) (0.0-0.3 M HNO<sub>3</sub>, 30 min, H[TMPeP] stationary phase)

According to REEtec, they have only been operating an industrial scale demonstration plant since 2019, but there is only limited information related to the knowledge advancement since 2016 available (<https://www.reetec.no>).

### 2.3.4 Ion-Exchange

Ion-exchange, which is a separation technique based on the difference of affinities of the targeted compounds for the functional groups of the solid phase (resin or ion exchanger) to favor their selective recovery, can be seen as the precursor to HPLC. Ion exchange resins are composed of cross-linked polystyrene matrix carrying ion-exchanging functional groups and associated counter-ions. Depending on the functional group, there are four categories of resins available including cationic (i.e., sulfonic acid or carboxylic acid groups), anionic (i.e., secondary, ternary or quaternary ammonium groups), chelating or impregnated resins. Typically, the solution containing the elements of interest is put in contact with the selected resin that has the properties of stoichiometrically and reversibly exchange the counter-ion present at its surface with the element of interest (Equation 2-13) (Kaczmarek, 1981).



Common functional groups of commercial resins used for REEs separation include aminomethyl-phosphonic acid (i.e., Purolite S940, Lewatit TP260, Amberlite IRC-747), sulfonic and phosphonic acids (i.e., Purolite S950), iminodiacetic (i.e., Purolite S930Plus), sulfonic acid (i.e., Purolite C150, Dowex 50Wx8), impregnated phosphonic acid (i.e., Lewatit TP 272) (El Ouardi et al., 2023). Selective sorption of individual REEs is quite challenging using chelating or impregnated resins, this technique is mainly used to selectively recover LREE from HREE. Depending on the eluant used to desorb REEs from the resin, selective recovery can be achieved (Figure 2-11). Ion-exchange has been completely replaced by solvent extraction and HPLC (Goode, 2016b) for now, until new resins are discovered that have a particular affinity for individual REEs.

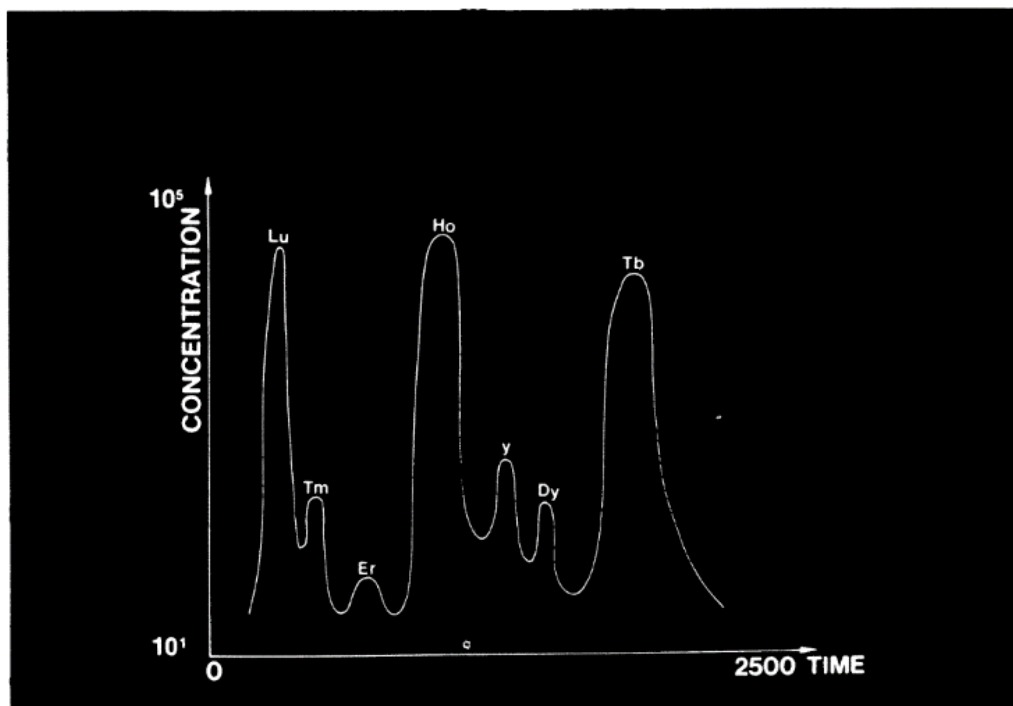


Figure 2-11 Laboratory scale elution of REEs from an ion exchange resin (natural zeolites) using 5% citrate at pH 3.2 (Kaczmarek, 1981)

### 2.3.5 Free Flow Electrophoresis (FFE)

Free flow electrophoresis (FFE), also known as carrier-free electrophoresis, has been introduced to the scientific community by Barrolier et al. in 1958 and Hanning in 1961. This separation method involves passing the REE-enriched solution through a channel while applying perpendicularly to the liquid flow an electric field that separates individual REEs based on their interaction with the field (Goode et al., 2016a). Based on different electrophoretic mobilities, each REE migrate differently, individual REEs exit into separate small channels, forming distinct high purity individual REE fractions (Figure 2-12). In the example presented in Figure 2-12, FFE is used to separate heavy REEs from each other, and it appears to be quite successful putting Yb, Eu and La into separate channels.

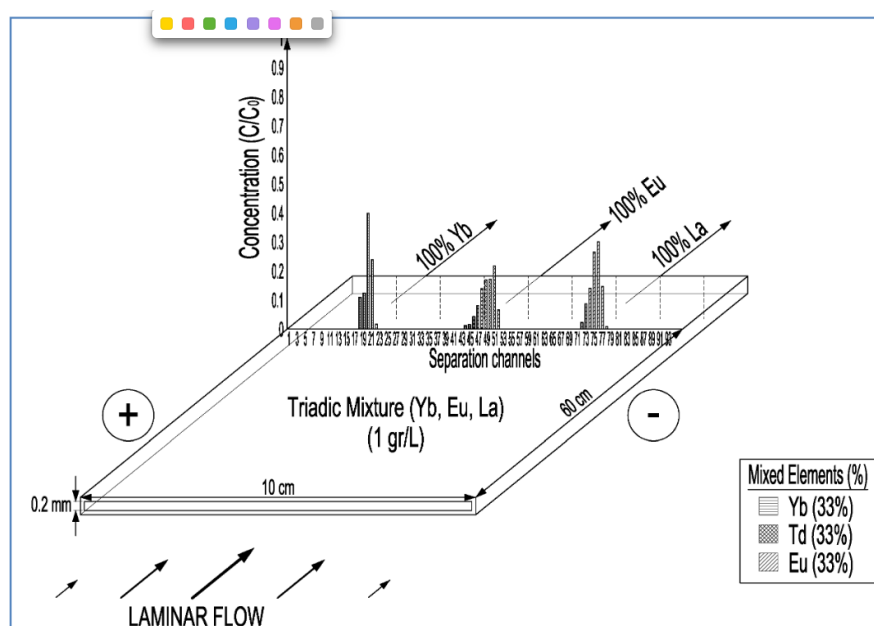


Figure 2-12 Diagram of a FFE device from Géoméga (Goode, 2016b)

First described for the preparation of sample for analytical purposes, this separation method has evolved into one promising approach for the separation of REEs and the company Geomega is now attempting to scale-up this method for industrial REE separation (Patent WO 2014/190434 A1, 2014). This scale-up is quite challenging considering the actual size of the plate available (0.2 mm high, 10 cm wide and 60 cm long), accommodating very small flowrates (only few mL per hour in comparison to several thousand liters per hour requested for industrial purposes). Achieving practical applications would require a very large number of small cells, which can be as difficult as several thousand mixer/settlers to operate. Progress in FFE application at industrial scale remain unclear. Despite 10 years of research and development made by Geomega, little advancement has been shared with the scientific community, suggesting that the scale-up remain challenging. The need to operate with high voltage (>750 V required for small-scale unit) to deal with the resistance of the solution also pose limitations to the industrial application of FFE, increasing energy demand and generating heat to be handle.

### 2.3.6 Molecular Recognition Technology (MRT)

In the 1960s, Charles Pederson discovered that polyethers could selectively form metal complexes (Goode, 2016b). In the 1980s, this concept was further developed by Reed Izatt and James Christensen, and many highly selective ligands were discovered – a contribution recognized in 1987 with the Nobel Prize in chemistry. The molecular recognition technology (MRT) is based on selective recognition of specific metal ions, including REEs, by specific macrocyclic compounds or ligands chemically bounded to solid matrices such as silica gel or polymers, allowing selective individual separation. Over the last years, numerous ligands with significant selectivity have been synthesized, improving the performances of MRT and extending its application to the selective recovery of several inorganic compounds from contaminated wastewaters. In collaboration with the company UCORE, Izatt applied MRT to the separation of each REEs since they are considered very difficult to separate (Izatt et al., 2016). According to their results, individual REEs were recovered as carbonates with final products purity >99% in only three steps. However, despite promising performance in separating REEs, no significant developments have been reported recently. Since MRT is based on the use of trademarked ligands, Superlig®, there is limited information available on the last developments to use this technology for the separation of REEs

### 2.3.7 Emerging separation methods

#### Chlorination

Chlorination and selective vaporization is a REE separation method based on the 10-100 times higher vapor pressure of  $\text{LnCl}_3$  in comparison to  $\text{LnCl}_2$ . Therefore it will vaporize  $\text{LnCl}_3$  first then  $\text{LnCl}_2$ . (Uda et al., 2000). By adding a reducing agent, it is possible to reduce specific  $\text{LnCl}_3$  to  $\text{LnCl}_2$  and then favor their separation using selective vaporization properties. As presented in [Figure 2-13](#), the addition of  $\text{AlCl}_3$  as a reducing agent led to the selective reduction of  $\text{SmCl}_3$  to  $\text{SmCl}_2$ , while neodymium remains in the form of  $\text{NdCl}_3$ .  $\text{NdCl}_3$  then can be easily extracted first by selective vaporization as a chloride gas. Despite its high REE separation efficiency, this process suffers from several limitations including: i) the need to operate at high temperature to favor  $\text{LnCl}_3$  vaporization, ii) the use of chlorine which requires strict safety rules to avoid any incidents, iii) the use of different reducing agent for each pair of neighbouring REEs to selectively reduce the targeted REE and iv) the complexity of operating this system at large scale. This technique could potentially be used to separate one particularly difficult pair of elements such as Nd and Sm, as

was described in the literature. The authors state potentially using Nd metal to selectively reduce  $\text{NdCl}_3$  to  $\text{NdCl}_2$  in the  $\text{NdCl}_2\text{-PrCl}_3$  system but provide no further explanation.

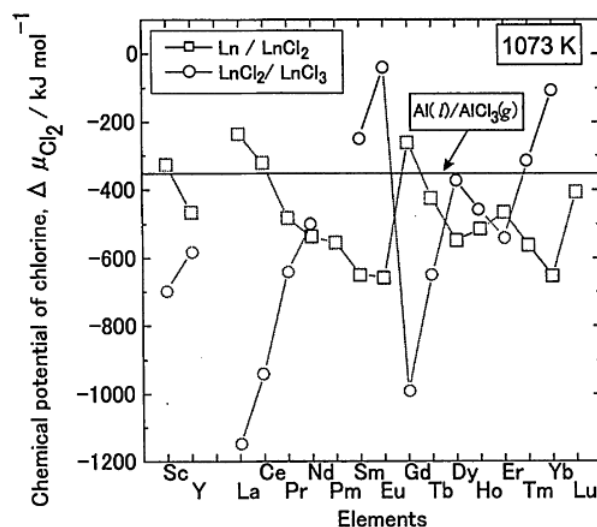


Figure 2-13 Chlorination separation diagram to separate Sm and Nd (Uda et al., 2000)

### Metal-Organic Frameworks (MOFs)

In the last 20 years, metal-organic frameworks (MOFs) have gained increasing attention due to their high surface area, tunable pore structure, high sorption capacity, and selectivity towards a wide range of organic and inorganic compounds including metals. Being composed of metals or metal clusters (nodes) and multifunctional building blocks, MOFs are classified as crystalline and porous organic-inorganic hybrid materials (linkers). Despite the application of MOFs in a wide range of applications, their affinity for REEs is still challenging, especially in acidic media due to potential replacement of MOF's metals nodes by REEs, leading to the degradation of the MOFs' structure and to the contamination of REE by-products. The modification of ligands in MOFs, named pre-synthetic or post-synthetic modifications, is required to improve their performance to selectively and efficiently sorb REEs (Sutherland, 2025). O'Connell-Danes et al. (2022) used a tripodal amido-arene (also called *L*) as ligand to encapsulate selected REEs in nitric acid (Figure 2-14).



Despite significant improvements to improve the performance of MOFs to selectively sorb REEs, their practical application at industrial scale remains constrained by some critical issues including: i) low selectivity of ligands to separated pair of neighbouring REEs, ii) fine particle size of MOFs, restricting their recovery by conventional solid/liquid separation methods, iii) their potential degradation through metal-ligand bounds hydrolysis and subsequent metal node leaching, iv) high costs of MOFs.

## 2.4 Pre-separation methods

Pre-separation methods, including cerium oxidation, reduction of europium, reduction of ytterbium, selective carbonatation-HCl leaching, are designed to be used as preliminary step to the conventional individual separation methods to selectively recover one REE or one group of REEs to be further separate to obtain individual REEs. This pre-separation methods can help to decrease the number of separation steps by increasing the separation factor between pair of neighbouring REEs. Table 2-6 presents a summary of the principles, advantages and limitations of some pre-separation REEs processes that will be discussed in more details in the following sub-sections. Other pre-separation methods might be possible using selective oxidation or reduction of individual REEs, however the methods presented below are the ones discovered and well researched so far. Others would likely require similar techniques to Yb with special solvents and reactants.

### 2.4.1 Oxidation of cerium

REE-bearing minerals from the earth's crust typically contain 30-50% of Ce, while the distribution of critical REEs required for the energy transition of our society is 2 to 30 times lower (Table 2-7). Despite higher concentration of La and Ce in REE-bearing minerals, their value are very low (Gambogi, 2016), due to limited applications such as glass polishing (Janoš et al., 2015) and high market availability. In other words, La and Ce are usually considered as impurities or deleterious REEs to be removed prior to the recovery of valuable REEs such as Nd, Tb or Dy (Mineral Commodity Summaries 2025, 2025; Turgeon et al., 2019). There is therefore a substantial interest in the scientific community in removing Ce before undergoing the typical REEs separation process. In the last decades, researchers have used its tetravalent and insoluble form  $\text{CeO}_2$  (Figure 2-16), which is an unusual oxidation state amongst other REEs, to selectively remove Ce (Adachi & Imanaka, 1998). The strategy is therefore to oxidize  $\text{Ce}^{3+}$  into  $\text{Ce}^{4+}$  and precipitate it as  $\text{Ce}(\text{OH})_4$  or  $\text{CeO}_2$  without precipitating any of the other REEs.

Table 2-6 Summary of the principles, advantages and limitations of the main pre-separation REEs processes

| Name                        | Principle                                                                                                                 | Advantages                                                                                    | Disadvantages                                                                                      | References                           |
|-----------------------------|---------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|--------------------------------------|
| Selective cerium removal    | Cerium has a tetravalent oxidation state which is stable. It can be selectively precipitated.                             | Cerium is abundant and inexpensive. A way to selectively remove Ce is very beneficial.        | Can potentially be more expensive and complicated than just using solvent extraction.              | Papangelakis (2021)                  |
| Selective europium removal  | Europium has the lowest reduction potential and can be easily reduced to Eu(II) and then selectively removed.             | A way to selectively remove an expensive element found in low quantity is desired.            | Europium is in low abundance, and the use of reducing agent can be quite expensive.                | Preston & Du Preez (1996), Qi (2018) |
| Selective ytterbium removal | Yb has a lower reduction potential than its two neighbors and therefore can be selectively reduced.                       | It is more efficient than solvent extraction at separating Yb from Tm and Lu.                 | It must be done in a special solvent, in an inert atmosphere and only separates Yb from Tm and Lu. | Li et al. (2025)                     |
| Carbonation/ Leaching       | Some REOs easily transform into carbonates while subjected to supercritical CO <sub>2</sub> conditions and others do not. | Can selectively pre-separate multiple elements at the same time improving solvent extraction. | A prototype method not extensively tested on co-precipitated REOs".                                | Yanagihara et al. (1991)             |

Table 2-7 Distribution of some REOs and their prices (Mineral Commodity Summaries 2025, 2025; Turgeon et al., 2019)

| Oxide                                        | Weight (%) | Value (\$/kg oxide) |
|----------------------------------------------|------------|---------------------|
| Lanthanum oxide ( $\text{La}_2\text{O}_3$ )  | 17.4       | \$1                 |
| Cerium oxide ( $\text{CeO}_2$ )              | 37.5       | \$1                 |
| Neodymium oxide ( $\text{Nd}_2\text{O}_3$ )  | 17         | \$56                |
| Europium oxide ( $\text{Eu}_2\text{O}_3$ )   | 0.1        | \$27                |
| Terbium oxide ( $\text{Tb}_4\text{O}_7$ )    | 0.3        | \$1,800             |
| Dysprosium oxide ( $\text{Dy}_2\text{O}_3$ ) | 1.9        | \$260               |

As shown in the Eh-pH diagram of Ce, its oxidation occurred under slightly acidic to alkaline conditions at Eh values higher than 0.5-1.0 V (Figure 2-16). To oxidize Ce(+III) into Ce(+IV), several oxidants were tested including hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), Caro's acid ( $\text{H}_2\text{SO}_5$ ), sodium hypochlorite ( $\text{NaOCl}$ ), and potassium permanganate ( $\text{KMnO}_4$ ) (McNeice, 2018). Among the oxidant tested,  $\text{H}_2\text{O}_2$  appeared to be the most performant in terms of Ce(+III) oxidation efficiency, ease of implementation at industrial scale, degradability into  $\text{H}_2\text{O}$  and  $\text{O}_2$  limiting the production of residual salinity and operating costs (Eul et al., 2001).

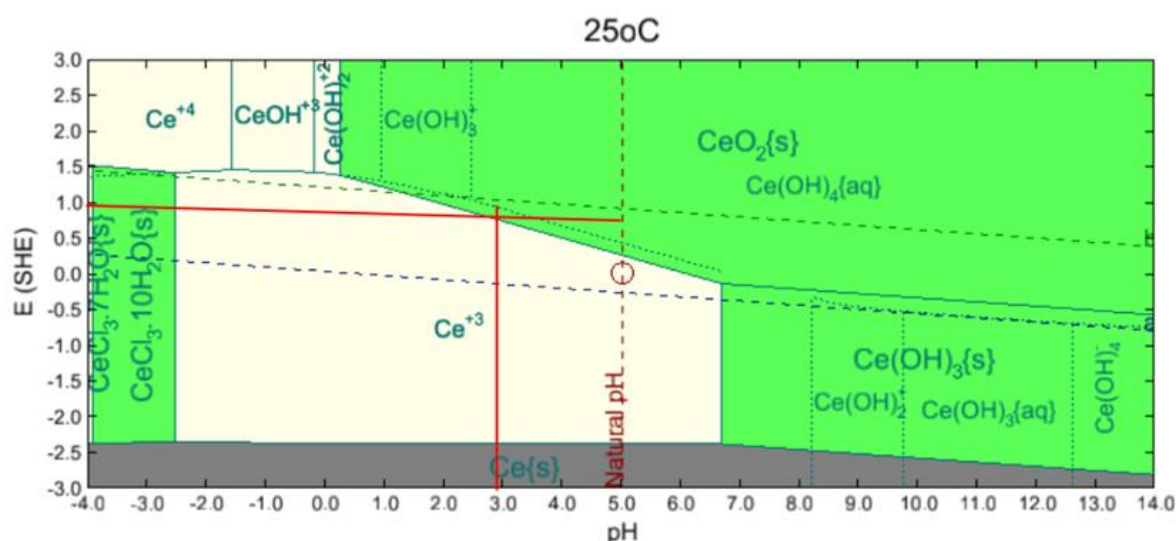
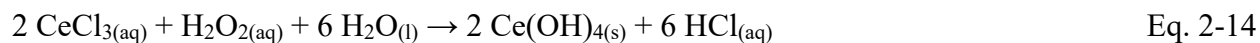


Figure 2-16 Pourbaix Diagram of Ce (25°C, 0.406 M Ce, 101.3 KPa (Papangelakis, 2021))

The overall chemical reaction of Ce(III) in the presence of  $\text{H}_2\text{O}_2$  is presented in Equation 2-14 as described by Nechaev et al. (2016) and McNeice (2018).



This chemical reaction suggests that the  $\text{H}_2\text{O}_2/\text{Ce}$  stoichiometric ratio required is only 0.5/1. However, McNeice (2018) showed that low precipitation efficiencies of Ce were obtained (<15-30%), even when using  $\text{H}_2\text{O}_2$  at a 150% stoichiometric ratio (Figure 2-17).

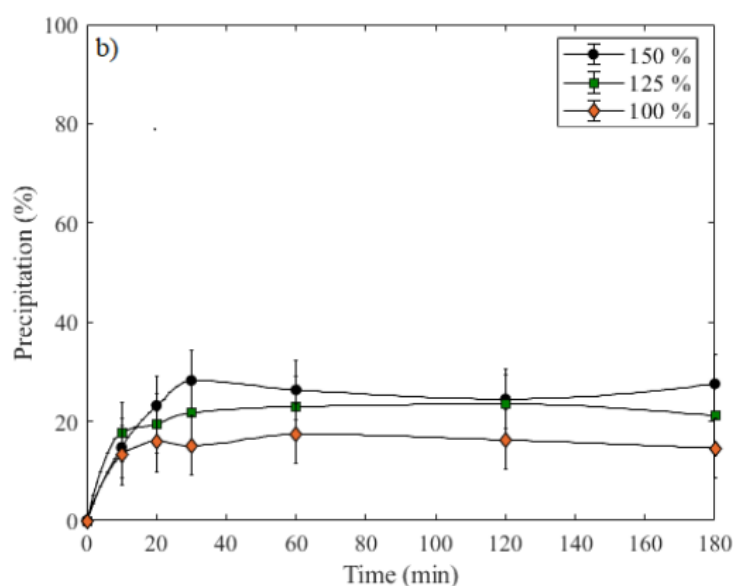
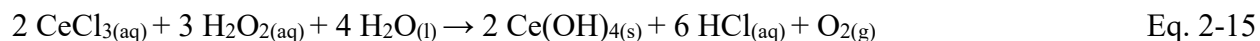


Figure 2-17 Effect of  $\text{H}_2\text{O}_2$  dosage and retention time on the oxidation and precipitation efficiencies of Ce (McNeice, 2018)

Based on these results, another chemical reaction occurring between Ce(III) and  $\text{H}_2\text{O}_2$  has been proposed by Papangelakis (2021) as presented in Equation 2-15, indicating the requirement of a  $\text{H}_2\text{O}_2/\text{Ce}$  stoichiometric ratio of 1.5/1 instead of 0.5/1 to efficiently oxidate Ce as evidence by the results obtained by Papangelakis (2021) with precipitation efficiencies ranging from 72.2 and 75.5% at pH 4 after or before 3 h of ageing.



Ageing the slurry at pH 2.5 under heating at 80°C promotes the release of co-precipitated REE-hydroxides or REEs sorbed onto  $\text{Ce}(\text{OH})_4$  (McNiece, 2018). Indeed, the precipitation of Ce seemed to be more selective at pH 4 after 3 h of ageing (72.2% for Ce vs. 11.2-27.4 for other REEs) than at pH 4 without ageing (75.5% for Ce vs. 39.2-71.1% for other REEs) (Papangelakis, 2021). Based on these results, the most performant conditions to selectively precipitate Ce were: stoichiometric ratio  $\text{H}_2\text{O}_2/\text{Ce}$  of 1.5/1 at pH 4.0 followed by an ageing treatment performed at pH 2.5 and 80°C for 3 h, leading to the precipitation of 72% of Ce, while ~ 85% of other REEs remain in solution. Although this approach seemed to be very promising to selectively recover Ce, important losses of critical REE including Nd (11%) and Pr (18%) may limit the economic viability of this pre-separation method.

Previous studies showed that Ce can also be selectively recovered by using its alternative tetravalent oxidation state through roasting-based approaches. Goode (2019) mentioned that REE-concentrate from Molycorp were roasted at 650°C and then leached under mildly acidic conditions, achieving almost complete solubilization of REEs, except Ce. Another approach consisting of multiple roasting steps on REE-carbonates and REE-oxalates followed by HCl leaching to selectively remove Ce from other REEs has been reported by Silva et al. (2019).

### 2.4.2 Reduction of europium

Europium is considered as a high-value REE, which is essential for niche technologies such as phosphor coatings of computer monitors and TVs and quite comparable in market importance to neodymium. Eu is among the least abundant REEs, representing around 0.1% of the REEs present in the earth's crust, which contributes to its critical or strategic value (Morais & Ciminelli, 2001). As most lanthanides, Eu is typically present as  $\text{Eu}^{3+}$  in aqueous environments. However, the redox potential of  $\text{Eu}(+\text{III})/\text{Eu}(+\text{II})$  is higher than for other REEs (Equation 2-16 - Preston & Du Preez, 1996), allowing its efficient separation from other REE.



This higher redox potential can be used to selectively recover this critical REE as a pre-separation route analogous to that used for cerium. As previously mentioned, the separation factor between Eu and Gd is very small ( $\beta_{\text{Eu/Gd}} = 1.5$ ), indicating that approximately 60-70 mixer/settler units will be required to efficiently separate them using conventional SX. Therefore, identifying another technique to selectively recover Eu is highly advantageous. Indeed, once reduced from  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ , Eu can be selectively recovered by precipitation with suitable counter-ions or by SX using typical organophosphorus solvent such as DEHPA (Horwitz & Mason, 1961). Previous studies showed that the use of Zn as reducing agent and DEHPA for the subsequent SX step, high-purity Eu can be achieved (99.98%) with less than 1 ppm of other REEs. The use of light at 190 nm as well as external voltage are other promising ways to reduce Eu (Qi, 2018). However, there are still some challenges related to the use of reducing agents such as  $\text{Zn}(0)$  or an electrochemical set-up to efficiently reduce  $\text{Eu}^{3+}$  into  $\text{Eu}^{2+}$ . Moreover, despite the possibility to selectively recover Eu by using its higher redox potential, little information is available in the literature about its industrial application. Based on these observations, europium reduction combined with SX appears to be an efficient technique for europium pre-separation, which can be quite easy to integrate in actual SX circuits.

### 2.4.3 Reduction of ytterbium

Another recent selective pre-separation technique for REE is based on the reduction of  $\text{Yb}(+\text{III})$  to  $\text{Yb}(+\text{II})$  using metallic magnesium, as described in Equation 2-17 (Li et al., 2025).



As for Eu, this pre-separation method is based on the fact that Yb has a relatively low redox potential of -1.17 V compared to its neighbours Tm (-2.278 V) and Lu (-2.28 V) (Li et al., 2025). This redox potential is still very high, meaning that in aqueous conditions, Yb will simply donate its electron to water, which is one of the main limitations of this technique. Indeed, this pre-separation technique must be performed in a mixture of ethanol and dioxane (a dual ether), which can be quite expensive in comparison to water. This pre-separation methods suffer from several limitations including the need to carefully manage the ratio of ethanol/dioxane and to operate in an inert atmosphere (Figure 2-18), which can complexify its industrial application.

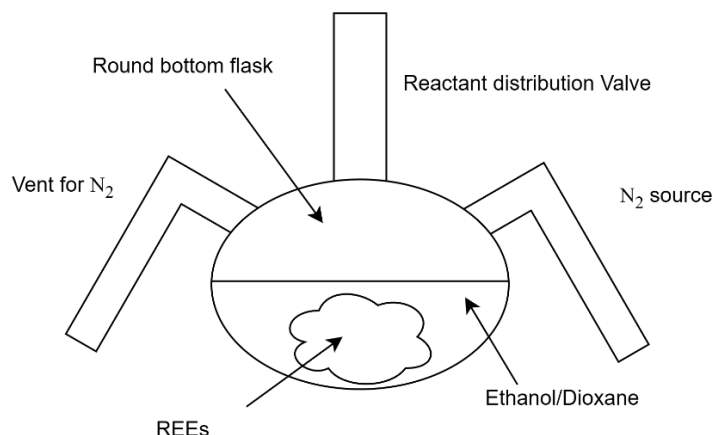


Figure 2-18 Typical setup used for the reduction of Yb (adapted from Li et al. (2025))

Li et al. (2025) also reported that a strict control of operating conditions such as the amount of metallic Mg added and the temperature is required to ensure an efficient and selective reduction of Yb. As presented in Table 2-8, an increase of the temperature from 20 to 60°C led to an important decrease in Yb recovery (from 70.8 to 59.9%), while the co-precipitation of Lu increased (from 6.06 to 37.8%), strongly influencing the selective precipitation of Yb. It must be noted that in this study, the authors did not separate Yb from all REEs, as was previously demonstrated for Eu or Ce. They simply separated Yb from its two neighbors Lu and Tm.

Table 2-8 Effect of temperature on Yb separation (adapted from Li et al. (2025))

| Temperature (°C) | Ytterbium recovery (%) | Lutetium recovery (%) |
|------------------|------------------------|-----------------------|
| 20               | 70.79                  | 6.06                  |
| 30               | 69.09                  | 6.67                  |
| 40               | 70.18                  | 11.07                 |
| 50               | 55.65                  | 24.91                 |
| 60               | 59.85                  | 37.75                 |

In summary, this selective pre-separation of Yb could be useful, even if being challenging. Separating Tm, Yb and Lu from each other requires about 200 steps of solvent extraction (Li et al., 2025). It might therefore still be economically viable to perform this pre-separation step, even

though it requires very strict control of operating conditions, an inert atmosphere and cannot be performed in water. According to the authors, a recovery of 70.89% and a purity of 97.5% of Yb(II) can be reached in one step. Using a simulator designed by Keven Turgeon , it was calculated that in similar conditions one step of solvent extraction would only manage a recovery of 53% of Yb, while achieving a purity of only 78.8% (Section 2.5; Turgeon, 2023).

#### **2.4.4 Selective carbonation and HCl leaching**

The selective carbonation/HCl process is based on the discovery of Yanagihara et al. (1991) who have evidenced that some REOs tend to produce REE-carbonates when subjected to supercritical CO<sub>2</sub> conditions, while others remained as REOs. A summary of the REOs that do (group A) and do not (group B) transform into REE-carbonates when injecting supercritical CO<sub>2</sub> is presented in [Table 2-9](#). Based on this selective carbonation of some REOs, there is potential to categorize them into two distinct families: i) REEs that “do carbonate” or group A and ii) REEs that “do not carbonate” or group B. Indeed, carbonated REEs from group A can potentially be selectively solubilized during HCl leaching, while uncarbonated REEs will remain insoluble ([Figure 2-19](#)).

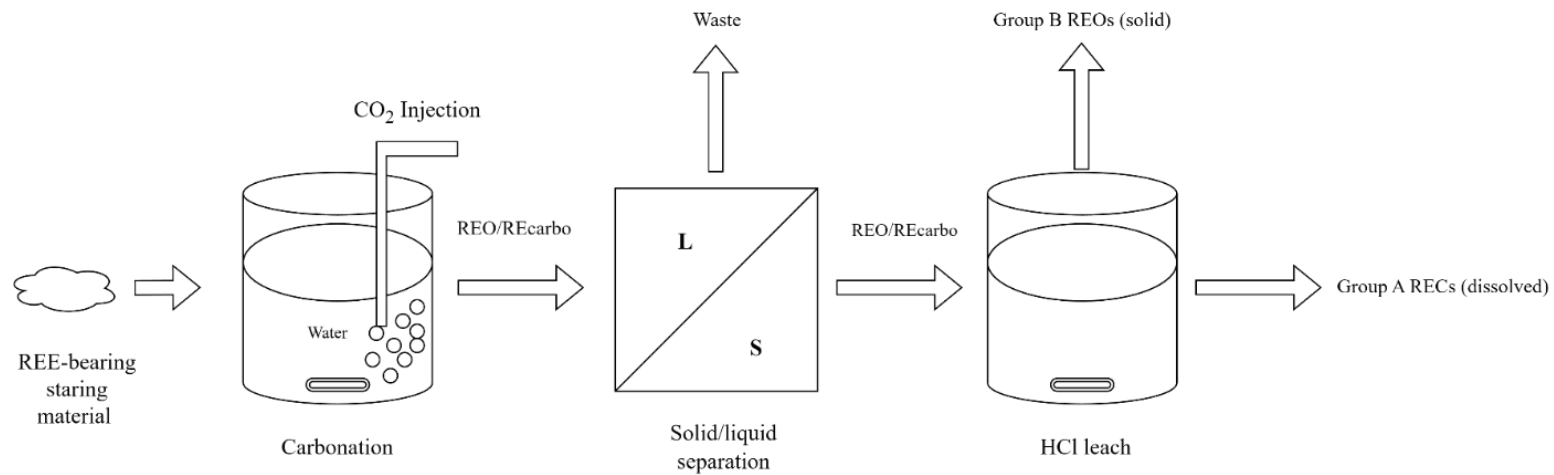


Figure 2-19 Schematic representation of the potential pre-separation of REEs using the carbonation/HCl leaching process

Table 2-9 Performance of supercritical injection of CO<sub>2</sub> to transform REOs into REE-carbonates (Reaction conditions: REOs: H<sub>2</sub>O ratio: 0.04/1; reaction time: 1 h; temperature: 40°C; pressure: 2800 psi - Yanagihara et al. (1991) )

| Element      | Oxide                           | Carbonation efficiency (%) | Group |
|--------------|---------------------------------|----------------------------|-------|
| Lanthanum    | La <sub>2</sub> O <sub>3</sub>  | 97.6                       | A     |
| Neodymium    | Nd <sub>2</sub> O <sub>3</sub>  | 95.4                       |       |
| Samarium     | Sm <sub>2</sub> O <sub>3</sub>  | 97.2                       |       |
| Europium     | Eu <sub>2</sub> O <sub>3</sub>  | 96.9                       |       |
| Gadolinium   | Gd <sub>2</sub> O <sub>3</sub>  | 97.1                       |       |
| Dysprosium   | Dy <sub>2</sub> O <sub>3</sub>  | 96.9                       |       |
| Holmium      | Ho <sub>2</sub> O <sub>3</sub>  | 96.3                       |       |
| Cerium       | CeO <sub>2</sub>                | —                          | B     |
| Praseodymium | Pr <sub>6</sub> O <sub>11</sub> | —                          |       |
| Terbium      | Tb <sub>4</sub> O <sub>7</sub>  | —                          |       |
| Erbium       | Er <sub>2</sub> O <sub>3</sub>  | —                          |       |
| Ytterbium    | Yb <sub>2</sub> O <sub>3</sub>  | —                          |       |

The different behavior of REOs from group A and group B during the carbonation step carried out under supercritical conditions can be explained by the dual nature of REOs (Adachi & Imanaka, 1998). As summarized in [Figure 2-20](#), REE that usually exist as sesquioxides (Ln<sub>2</sub>O<sub>3</sub>) with trivalent oxidation state of the REE (i.e., La(III), Nd(III)) tend to easily carbonate, while for REOs with higher oxidation states (i.e., Ce(IV)), their transformation to REE-carbonates is inefficient.

While this pre-separation process seemed simple as a concept, the authors only investigated very specific conditions for the carbonation step, which seemed to be efficient at low solid/liquid ratio (4%, w/v) under supercritical conditions: at high pressure of CO<sub>2</sub> (> 100 atm, equivalent to > 1470 psi) and a temperature of 40°C (Yanagihara et al., 1991). According to the authors, the selective carbonation of REE from group A seemed to occur, even under non-supercritical conditions, with lower carbonation efficiencies, but there is no scientific data in the paper to support this statement. However, it should be noted that laboratory experiments were performed on individual REOs to evaluate, one at a time, their tendency to produce REE-carbonates. While no experiments were conducted on mixed and co-precipitated REOs to confirm the potential pre-separation performance of REE using selective carbonation/HCl leaching process. The authors

briefly mentioned some experiments conducted on mixed REOs, but no specific results were provided in their paper (Yanagihara et al., 1991). The authors slightly expand this idea, hinting at a separation potential, in their patent without supporting data (Fernando et al., 1991). Additional research work will be needed to determine if REOs' behavior from co-precipitated REOs originating from the acid baking route is similar to individual REOs. Industrial application of pre-separation REO processes is strongly favored by ambient-pressure conditions, which are less expensive and simpler to implement than high-pressure systems. For this reason, the feasibility of selective carbonation of REOs from group A under non-critical CO<sub>2</sub> conditions is desired, even if a longer retention time would likely be needed.

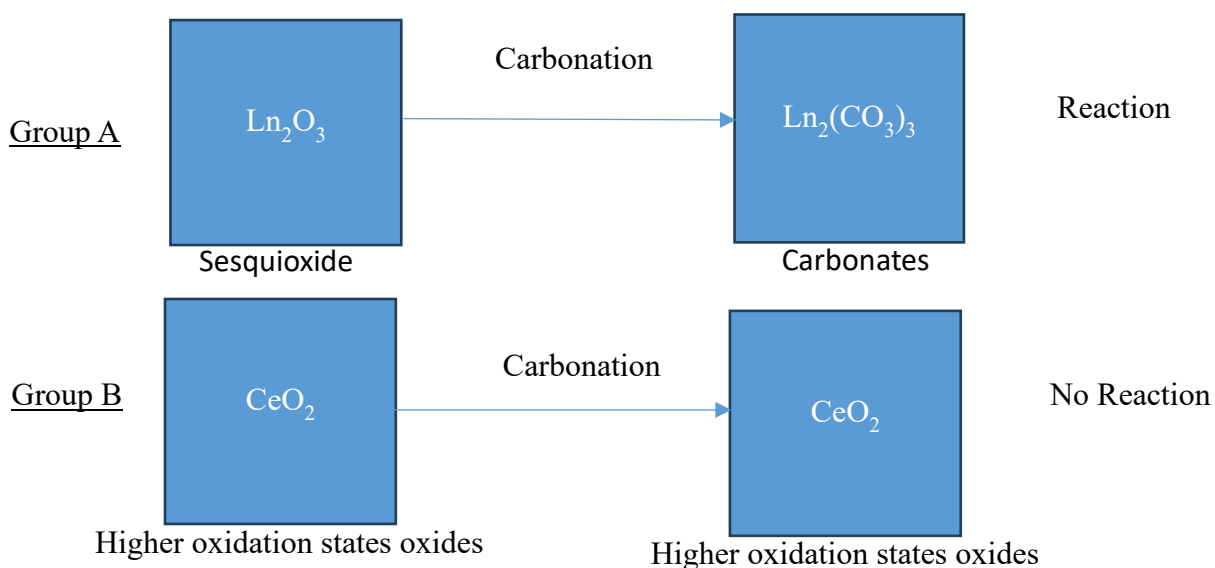


Figure 2-20 Diagram depicting the two families of REOs and their potential reaction to carbonation

## 2.5 Simulation of REEs pre-separation

### 2.5.1 Introduction

As mentioned by Goode (2016a) and Turgeon et al. (2019), the separation of REEs is mostly done by SX and requires several mixing/settling units. The question then becomes: how many steps exactly? Since REE separation via SX requires hundreds mixing/settling steps, there is essentially no way to perform the separation experiments in different conditions empirically every time for all REEs, such approach will be time-consuming and very expensive, requiring the development of simulations to predict the separation performance. Solvent extraction follows relatively simple rules in each individual mixer/settler unit, which simply consist of a ratio between equilibrium constants also known as separation factors. This becomes very much more complex when higher numbers of mixer/settler units are added and, not only that, but SX is performed in a counter-current mode, which is quite complex to simulate. Counter-current operation of SX simply means that most concentrated REEs in aqueous solution come in contact with the concentrated organic phase to maintain an extraction balance (Figure 2-21).

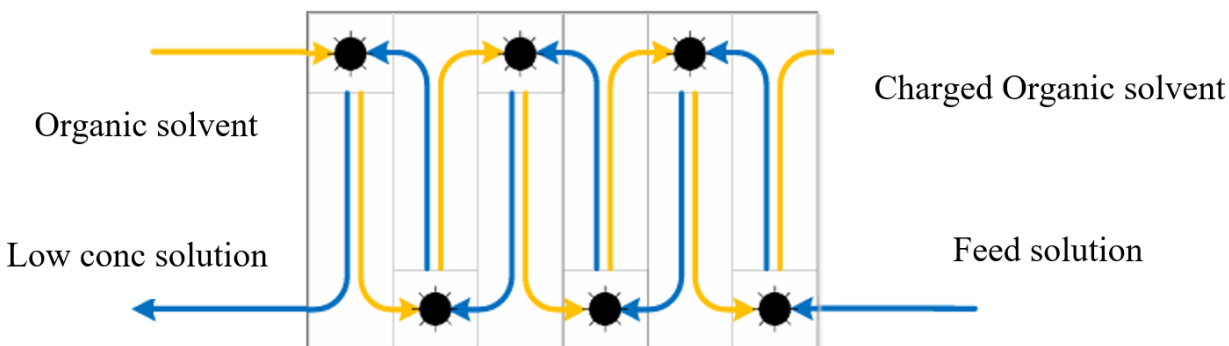


Figure 2-21 Schematic representation of multiple mixer/settler units arranged in a counter-current mode (Turgeon, 2023)

The presence of multiple mixer/settler units implies that the concentrations of most of the streams feeding one mixer/settler unit is not known, except for the circuit feeds, and that an iterative process needs to occur in order to describe the accurate concentrations at the end of each of the extraction, scrubbing and stripping circuits.

### 2.5.2 Historical and previous simulators

Simulating the performance of SX to separate REEs is computationally intensive, and meaningful attempts only emerged recently, once computers become more accessible and powerful. Early SX simulation work, relying on Kremser equation (Eq. 2-18), began with Voit (1988), followed by Reddy et al. (1992). This equation is useful but suffers from major drawbacks as: i) it can be applied only to one REE at a time, ii) it assumes constant distribution coefficients which is not accurate in industrial application, and iii) it neglects solvent consumption and acid releases.

$$N = \frac{\log \left( \left[ \frac{(X_f - Y_i/D)}{(X_n - Y_i/D)} \right] \left[ 1 - \frac{1}{E} \right] + \frac{1}{E} \right)}{\log E} \quad \text{Eq. 2-18}$$

Where  $N$  : number of stages,  $X_n$  : exit aqueous concentration,  $Y_f$ : aqueous feed concentration,  $Y_i$ : inlet solvent concentration,  $D$ : distribution coefficient,  $E$ : extraction factor

More recently, another modeling approach was developed by Pr. G. Xu, which relies on a different mathematical formulation to solve and simulate SX system (Qi, 2018; Zhang et al., 2016). This modeling approach is based on several assumptions, that are only partially accurate in practice: i) REE can be separated only into groups with sufficiently high separation factors – for example, separating La-Ce-Pr from Nd-Sm-Eu – but not individual pairs of neighbouring REEs (i.e. La/Ce); ii) acid releases occurring during SX can not be considered in the simulation, iii) the solvent can be entirely reused (no solvent consumption occurring). Although it imposes several constraints on the SX system, this alternative modeling approach provides significantly higher accuracy than previous simulators developed by Voit (1988) and Reddy et al. (1992). While this modeling approach represents a valuable first step to design REE separation plants, its applicability remains constrained by these limitations.

Turgeon (2023) developed a simulator that implies the use of SX equilibrium constants across a series of mixer/settler units, iterating until equilibrium is reached in each mixer/settler unit. This simulator enables estimation of the required number of mixer-settler units, as well as reagent consumption, and can be used to assess how pre-separation strategies influence the complexity of solvent extraction circuits needed to obtain high-purity individual rare earth elements.

### 2.5.3 Example of Turgeon's simulator application and brief examination of the simulator

To illustrate the basis of Turgeon's simulator, a simple case study with one element in a single mixer/settler unit is presented, followed by a brief overview of Turgeon's approach. Considering only one REE, the chemical reaction and associated equilibrium constant ( $K_{eq}$ ) occurring during a SX process are presented in Eq. 2-19 and 2-20, respectively.



Where  $\text{Ln}$  represents any lanthanide,  $i$  is the oxidation state,  $\text{RH}$  represents the organic acid

$$K_{eq} = \frac{[\text{LnR}_i] \times [\text{H}^+]^i}{[\text{Ln}^i] \times [\text{RH}]^i} \quad \text{Eq. 2-20}$$

Where  $K_{eq}$  is the equilibrium constant for a certain lanthanide  $i$ ,  $\text{Ln}$  represents any lanthanide,  $i$  is the oxidation state of the lanthanide,  $\text{RH}$  represents the organic acid

Because the equilibrium constant expression is defined for a system at equilibrium, it must be rewritten in terms of the initial and equilibrium concentration of  $\text{Ln}$ . The following equation (Eq. 2-21) uses the initial concentration of  $\text{Ln}$  present in the aqueous phase before mixing with the organic phase, a negligible influence of water on  $[\text{H}^+]$  and it also adds the variable “x” for  $\text{LnR}_i$  produced.

$$a = \frac{[x] \times [ix]^i}{[b - x] \times [c - ix]^i} \quad \text{Eq. 2-21}$$

Where  $a$  is the equilibrium constant for a certain  $Ln$  in a certain solvent,  $b$  is the concentration of  $Ln$  at the beginning,  $c$  is the concentration of organic acid at the beginning,  $i$  represents the oxidation state of a certain  $Ln$ ,  $x$  is the concentration of the  $Ln$ -organic acid complex produced “ $LnR_{ni}$ ”

For one mixer/settler unit, Eq. 2-21 can be re-written as follows (Eq. 2-22).

$$a (b - x) (c - ix)^i - ix^{(ix+1)} = 0 \quad \text{Eq. 2-22}$$

This equation can be applied to any SX system containing one lanthanide with known initial concentration and the equilibrium constant defined for the organic solvent under study. For example, this equation can be expressed as follows Eq. 2-23 for the extraction of lanthanum using P507 as extractant, with initial La and R-H concentrations of 1 M and an initial concentration of  $H^+$  of 0 M. The resolution of this equation give us the concentration of La in the organic phase at equilibrium Eq. 2-24. The low concentration of La in the organic phase at equilibrium estimated using Eq. 2-23 is consistent with expectations, as La exhibited one of the lowest affinities for the organic phase.

$$0.00195 (1 - x) (1 - 3x)^3 - 3x^{(3+1)} = 0 \quad \text{Eq. 2-23}$$

$$x = [La^{3+}]_{org} = 0.113 \text{ M} \quad \text{Eq. 2-24}$$

The general equation used in Turgeon’s simulator to determine the equilibrium concentration of one targeted REEs in a specific mixer/settler unit in the SX circuit using an iterative approach is presented in Eq. 2-25.

$$K_{eq;i} = \frac{\left(Y_{i:0} + \frac{\Delta_i}{R_{OA}}\right) (X_{H:0} + \sum_1^N n_i \Delta_i)^{n_i}}{(X_{i:0} - \Delta_i) \left(Y_{RH:0} - \sum_1^N \frac{n_i \Delta_i}{R_{OA}}\right)^{n_i}}$$

Eq. 2-25

Being similar to the simplified Eq. 2-21 previously used to simulate the behavior of a single REE for one mixer/settler unit, the Turgeon's formulation introduces additional variables, namely  $Y_{i:0}$  which represents the concentration of the specific REE at equilibrium found in the organic phase coming in from another mixer/settler unit and  $X_{H:0}$  which is the concentration of outside  $H^+$  coming from the previous system. Most importantly, this new equation Eq. 2-25 accounts for the acidity released by the transfer of other REEs in the organic phase through the term  $\sum_{i=1}^N n_i \Delta_i$ . This release of acidity – and the associated consumption of the organic phase – is the key feature that distinguishes Turgeon's model from previous SX models. Moreover, the use of equilibrium constants instead of distribution coefficients ensures that the acidity effects are explicitly considered in Turgeon's model.

## 2.6 Summary and research Needs

REEs constitute an essential foundation of modern technological society due to their unique physico-chemical properties. They are used to produce advances devices ranging from electric vehicles, wind turbines, phones, computers to high-performance military platforms including fighter jets, aircraft carriers and missiles. Nowadays, China maintains a near-monopoly over the global REE production. Diversifying REEs manufacturing capacity worldwide should therefore be considered a strategic priority to decrease our dependency to China and enhance supply-chain resilience. The main challenges associated to REE exploitation are mainly related to the difficulties in separating REEs to produce high-purity individual REE. Nowadays, solvent extraction (SX) is the most used process at industrial scale to separate each pair of neighbouring REEs, requiring several hundreds of mixer/settler units to achieve individual high-purity REE products. Due to the complexity of operating a large number of mixer/settler units and associated costs, several separation processes have been developed over the last two decades including selective precipitation/crystallization, high performance liquid chromatography (HPLC), ion exchange, while emerging approaches include free flow electrophoresis (FFE), molecular recognition technology (MRT), chlorination, selective sorption on organic metallic frameworks (MOFs).

Industrial applications of these separation methods remain challenging and requires additional research development to ensure their performance to separate each pair of neighbouring REEs at a large scale. To reduce the number of mixer/settler units to be used in SX, pre-separation processes targeting the selective recovery of one REE (i.e., oxidation of Ce, reduction of Eu, reduction of Yb) or one group of REEs (i.e., selective carbonation and HCl leaching of some REEs) have been developed. Selective carbonation/HCl leaching process is based on the ability of some REOs to produce REE-carbonates (group A) when subjected to supercritical CO<sub>2</sub> conditions, while others remained as insoluble REOs (group B) in acidic conditions. Experiments, were performed on individual REOs powders under supercritical CO<sub>2</sub> conditions, showed very promising results with the solubilization of more than 95% of REE belonging to group A, while REOs from group B remain insoluble, in a single extraction step. However, there is no scientific proof that this pre-separation process can be efficiently used to separate group A-REEs from group B-REEs from co-precipitated REOs which are produced during the extraction of REEs from primary deposit. The use of supercritical CO<sub>2</sub> conditions may limit industrial applications of this pre-separation process; it will be interesting to determine if the injection of CO<sub>2</sub> under atmospheric temperature and pressure will be as effective as supercritical conditions to carbonate REE from group A. Additional research work is needed to better understand the mechanisms involved in the selective carbonation of some REOs and how the performance of this pre-separation process can be affected by operating conditions or the composition of the starting REE-bearing materials. Several process variables remain unexplored or insufficiently optimized, and computational simulation to determine the number of mixer/settler units to be used offers a valuable tool to better understand the effect of pre-separation processes on the ease of implementation on a SX circuit. At the same time, the development of new pre-separation may help transform an inherently challenging separation process into a more efficient and economically viable process.

## CHAPTER 3 MATERIALS AND METHODS

### 3.1 Methodological approach

This research project is based on the hypothesis, adapted from the one previously formulated by Yanagihara et al. (1991), that some REOs will become carbonates and others will remain as REOs when submitted to CO<sub>2</sub> injection under atmospheric conditions, allowing their separation by subsequent HCl leaching of REE-carbonates from unreacted REOs and achieving a “pre-separation” of REOs (group A vs. group B). It should be noted that Yanagihara et al. (1991) mentioned the use of supercritical CO<sub>2</sub> as a way to improve the kinetics of carbonation of REOs although injecting the CO<sub>2</sub> under atmospheric conditions still presented the main potential selectivity between “carbonatable” and “non-carbonatable”. The methodological approach used to reach our main objective is presented in [Figure 3-1](#).

The flowsheet of the carbonation process used in the present research project, comprising the preparation of the material (i.e., mixing of REOs powders or co-precipitation of REOs), the carbonation (i.e., CO<sub>2</sub> injection in the REOs pulp) followed by a solid/liquid separation step and HCl leaching, is presented in [Figure 3-2](#). While relatively simple, several preparation methods were tested to prepare the starting materials, to confirm/infirm the performance of this process. Previously reported work was carried out mostly on separate REOs (i.e., individual REOs - Yanagihara et al. (1991)) instead of co-precipitated REOs as encountered in the extraction of REEs from primary deposits at industrial scale. Different starting materials tested include: i) individual Nd<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> powder, ii) mechanically mixed Nd<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> powders, iii) mechanically mixed REOs (using an equimolar ratio and REO ore ratio), iv) co-precipitated REOs (using an equimolar ratio only) and v) co-precipitated REOHs (using an equimolar ratio only) as described in [Figure 3-1](#). The effect of operating conditions of the carbonation (i.e., pH of CO<sub>2</sub> injection, solid/liquid separation by evaporation or filtration) and HCl leaching steps (i.e., concentration of HCl used) on the performance of the processes was evaluated in terms of REE-carbonate formation (i.e., measurement of mass gain and carbon content in the solid) and REE selective leaching ([Figure 3-1](#)). As seen in [Figure 3-1](#), some selected tests were done in triplicates to measure variability.

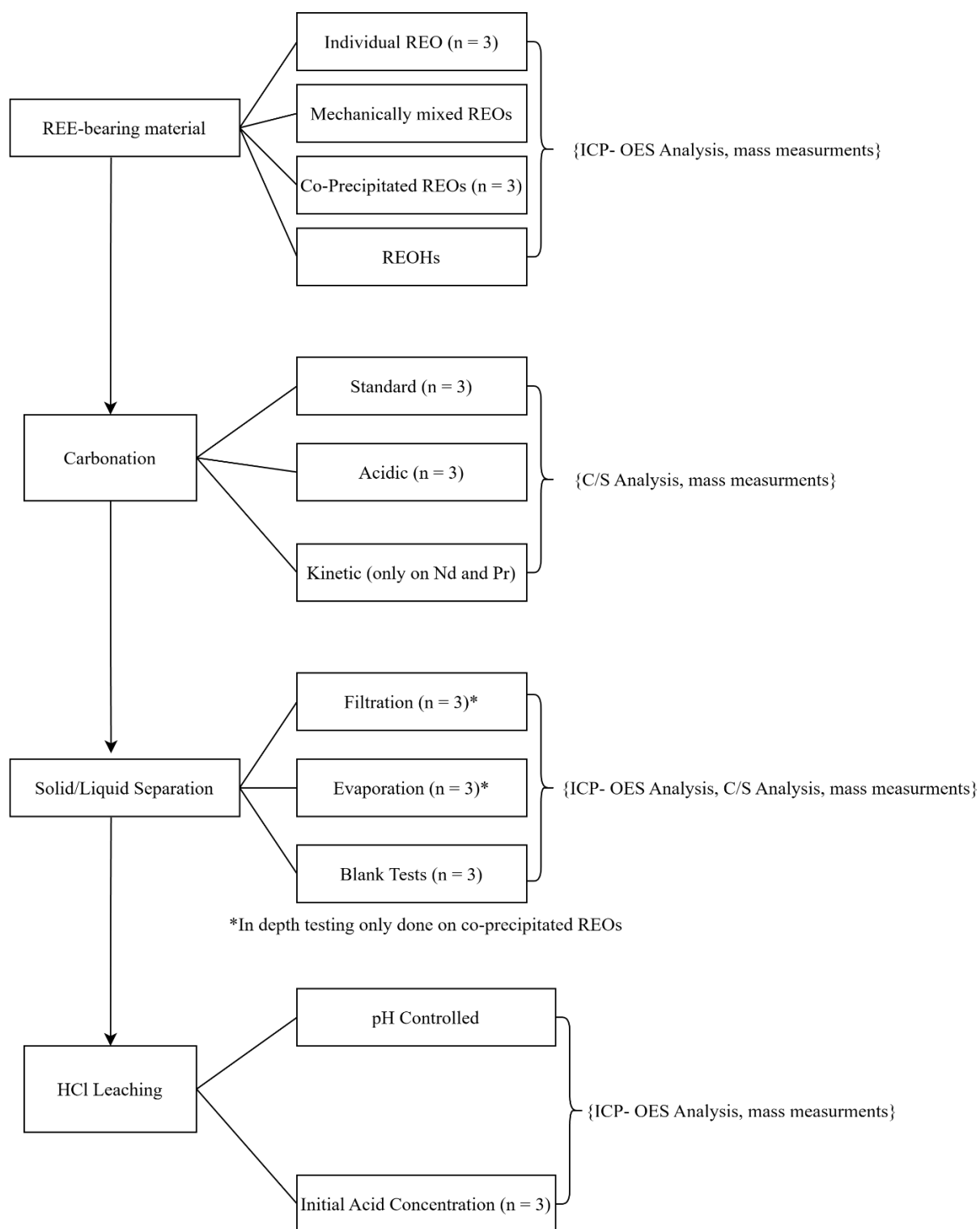


Figure 3-1 Schematic representation of the methodological approach used in this research project

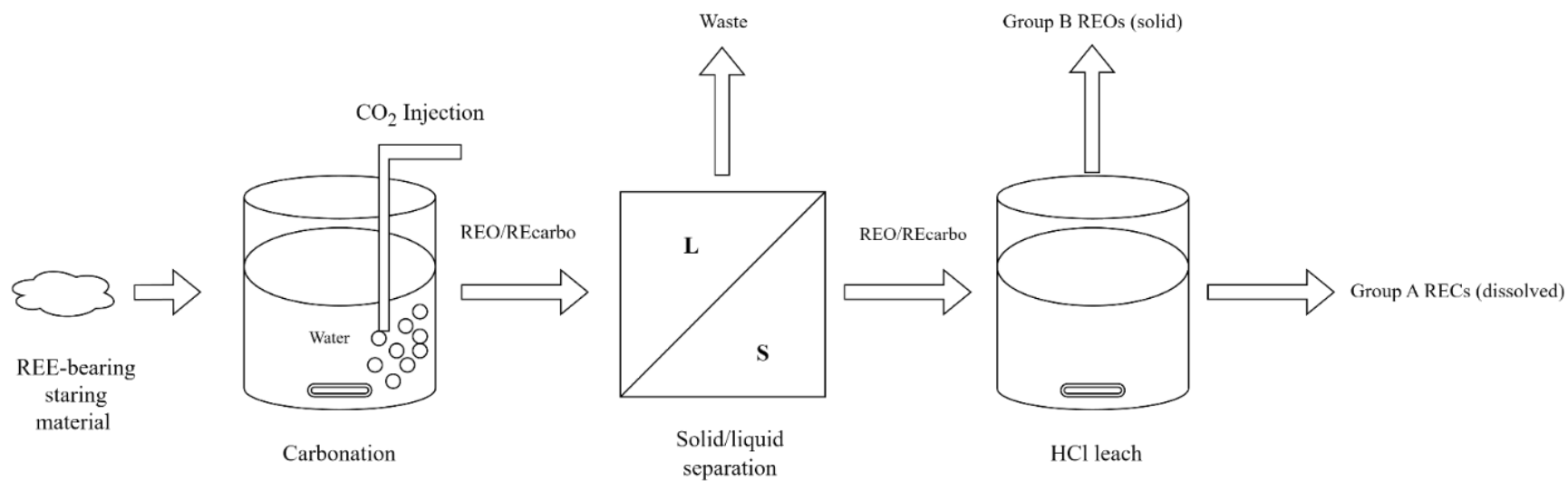


Figure 3-2 Typical flowsheet of the carbonation experiments conducted in this research project

This section described the methodology used for material preparation, the carbonation-leaching process and the analytical methods used to quantify the carbonation efficiencies and REOs pre-separation performances. It should be noted that although the term carbonation is used, the process itself could be more accurately described as “CO<sub>2</sub> injection” since the process only guarantees that CO<sub>2</sub> is inserted into the beaker, with actual formation of carbonates not being guaranteed. The term “carbonation” will still be used in the entire manuscript for concision.

### **3.2 Preparation of rare earth starting materials**

As previously mentioned, carbonation experiments were conducted on different starting materials to better understand the behavior of various forms of REEs when subjected to CO<sub>2</sub> injection followed by HCl leaching. The goal is to identify potential forms of REEs amenable to “carbonation” to pre-separate REEs. This section will present how mechanically mixed REOs, co-precipitated REOs and co-precipitated REE hydroxides were prepared/synthesized.

#### **3.2.1 Preparation of mechanically mixed REOs**

Mechanically mixed REOs were prepared by weighing the requested amount of individual pure REO powders (Figure 3-3a,b) and then mixing them together in a plastic capped jar (Figure 3-3c). It is important to note that mechanically mixed REOs are not exactly representative of mixed REOs produced in REE hydrometallurgical extraction prior to the separation of REEs using solvent extraction, which are co-precipitated out of a mixed leachate. However, mechanically mixed REOs still provide a baseline for carbonation experiments to better understand the behavior of REEs in contact with CO<sub>2</sub>. Two mechanically mixed REOs samples, named “equimolar ratio” and “REO ore ratio” were prepared using different proportion of each REE (Table 3-1) to evaluate the effect of the initial concentration of REEs on the performance of the process.



Figure 3-3 Photo of a pure neodymium oxide powder (a), a pure praseodymium oxide powder (b) and a mechanically mixed REOs composed of 13 individual REOs powders after mixing

The “mechanically mixed ore ratio REOs” were prepared using the average distribution of REOs found in the REO ores following Turgeon et al. (2019), while the “mechanically mixed equimolar REOs” were prepared by mixing the same number of moles of each REO powder (Table 3-1).

Table 3-1 Composition (mass %) of mechanically mixed REOs mixtures used for carbonation experiments (based on compositions from Turgeon et al. (2019))

| Group | Sample | Equimolar REOs | Ore REOs |
|-------|--------|----------------|----------|
| A     | La     | 6.58           | 2.70     |
|       | Nd     | 6.60           | 15.10    |
|       | Eu     | 6.64           | 0.11     |
|       | Gd     | 6.68           | 2.32     |
|       | Dy     | 6.70           | 1.97     |
|       | Ho     | 6.71           | 0.42     |
|       | Y      | 6.05           | 10.16    |
| B     | Sm     | 6.63           | 2.74     |
|       | Ce     | 6.25           | 48.62    |
|       | Pr     | 6.36           | 13.55    |
|       | Tb     | 6.54           | 0.54     |
|       | Er     | 6.73           | 1.06     |
|       | Yb     | 6.76           | 0.73     |

Individual and mechanically mixed REOs represent the simplest form of starting material used for carbonation experiments. These mechanically mixed powders were used to prepare co-precipitated compounds as REOs or as REOHs, following the procedure described in (Sections 3.2.2 and 3.3.3).

### 3.2.2 Synthesis of Co-precipitated REOs

In the industry, after the acid baking and purification stages of REE extraction, what is left is a relatively “pure” solution of mixed REEs (Goode, 2016b). REEs can then be precipitated as rare earth oxalates (REOXs) by the addition of oxalic acid and neutralization using a base such as ammonium hydroxide up to a pH of around 5. These co-precipitated oxalates are then transported to separation facilities to get individual REEs. REOXs, once calcined at 1,000 °C, are transformed

into co-precipitated REOs which are easier to leach (Silva et al., 2019). The approach used for the synthesis of co-precipitated REOs using the “oxalate” route is described in (Figure 3-4). Firstly, mechanically mixed REOs were dissolved into a leaching solution composed of  $\text{HNO}_3$  (Fisher Scientific, 18 M analytical grade) and  $\text{H}_2\text{O}_2$  (Fisher Scientific, 30%) for one hour or until complete dissolution. Nitric acid was added first followed by the REO powder. Hydrogen peroxide was then added slowly until full dissolution, hydrogen peroxide here being used to promote Ce dissolution by reducing it from  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ . As this is an exothermic reaction, the temperature climbs quickly and was managed by controlling addition rate with 1 ml addition of peroxide at a time. After the complete dissolution of the mechanically mixed REOs, the solution became clear with a light salmon pink appearance as seen in Figure 3-4.

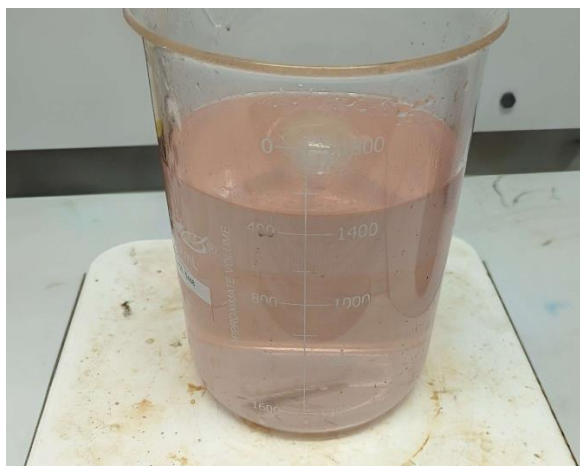


Figure 3-4 Mechanically mixed REOs dissolved in 50%  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$

The composition of the leaching solution was first targeted based on the literature (Janoš et al., 2015), but was also affected by the progressive  $\text{H}_2\text{O}_2$  addition required to fully dissolve REO powders. A functional solid/liquid ratio was found to be 1/10 (w/v), corresponding to 1 g of mechanically mixed REOs dissolved in 10 mL of leaching solution (5 mL of  $\text{HNO}_3$  + 5 mL of  $\text{H}_2\text{O}_2$ ). Once the mechanically mixed REOs were fully dissolved, the required amount of oxalic acid (VWR, 99%) was added at an oxalic acid/REOs mass ratio of 1.5/1 as calculated from their molar ratios. As an example, for 1 g of REOs previously dissolved in the leaching solution, 1.5 g

of oxalic acid was added. This procedure is inspired from Chi & Xu (1999) who suggested the same oxalic acid/REEs ratio of 3/2.

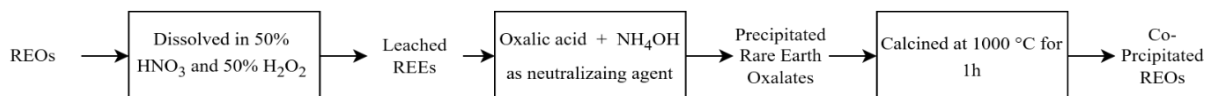


Figure 3-5 Schematic representation of the procedure used for the synthesis of co-precipitated REOs

The pH of the solution was then adjusted to pH 5 using  $\text{NH}_4\text{OH}$  (Fischer scientific, 30% W/W), as suggested by (Chi & Xu, 1999). Ammonium hydroxide was selected as the neutralizing agent to ensure that the amounts of impurities added to the system is of similar nature in terms of elemental composition as the ones previously added to dissolve the REOs (i.e.,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ ). Empirically, it was found that a  $\text{NH}_4\text{OH}/\text{HNO}_3$  ratio of around 1.4/1 (v/v) is needed to neutralize the  $\text{HNO}_3$  solution to a pH above 5. However, a constant monitoring of the pH during the neutralization is strongly recommended to ensure that the targeted value is reached as the end point is always slightly different depending on the reactivity of the REEs powders. Neutralization was also an exothermic reaction and thus, was carried out in a cooling vessel with  $\text{NH}_4\text{OH}$  added ml by ml to avoid substantial bubble formation which would make the solution overflow (Figure 3-6). Once the solution reached a pH of around 2, REOXs started to precipitate, but the neutralization was continued up to a pH of around 5 to ensure most REEs had precipitated. After the pH reaches 5, the solution was left under agitation for 10 minutes to ensure complete neutralization and crystallisation. A vacuum filtration was then conducted using a Buchner funnel and filter (pore size of  $0.45\ \mu\text{m}$ ). The filtrate was then left to dry at  $50\ ^\circ\text{C}$  for 24 hours.



Figure 3-6 Neutralization-precipitation arrangement used to cool down the solution

The final step was to collect the REOHs from the filter and to calcinate them at 1,000 °C in a muffle furnace (Nabertherm p330) for 1 h (Silva et al., 2019) to transform them into orange co-precipitated REOs (Figure 3-7). The resulting powder is called “co-precipitated” REOs and it is expected that their crystallographic structure is more closely representative of the REOs produced during REE hydrometallurgical extraction.



Figure 3-7 Typical orange color of the co-precipitated REO powder used for carbonation experiments

The same procedure as above was used to prepare the Nd/Pr mixture by using equivalent amounts of  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  powders and mixing them prior to the synthesis of co-precipitated REOs. This mixture was made to simplify the number of variables and only examine two elements at once. Neodymium was chosen for its critical usage in permanent magnets production and as a representative REE of Group A, while praseodymium was selected as a representative REE of Group B. Praseodymium is adjacent to Nd on the periodic table and is difficult to separate from neodymium ( $\beta_{\text{Pr/Nd}} = 1.24$ ).

### 3.2.3 Synthesis of Co-Precipitation Rare Earth Hydroxides

Yanagihara et al. (1991) briefly mentioned that the carbonation process can be effective for the pre-separation of REEs from REOHs as well, though little evidence was provided. Therefore, carbonation experiments were also conducted on co-precipitated REOHs. The synthesis of co-precipitated-REOHs began by dissolving mechanically mixed REOs, using the same protocol as for co-precipitated REOs (i.e. dissolution with a leaching solution of 50%  $\text{HNO}_3$  and 50%  $\text{H}_2\text{O}_2$ ). A schematic representation of the procedure used to prepare co-precipitated REOHs is presented in Figure 3-8. After the complete dissolution of mechanically mixed REOs occurred, the pH of the solution was increased using  $\text{NH}_4\text{OH}$  (Fischer scientific, 30% W/W) until it reached a value of 9, conducive to almost complete precipitation of REEs as REOHs (Qi, 2018). After filtration, the partially hydrated co-precipitated REOHs are a yellowish orange precipitate Figure 3-9a, while fully dried co-precipitated REOHs are yellow Figure 3-9b. Manufacturers such as AEM appear to have similar yellow REOH compounds for sale and inorganic textbooks also describe these compounds as “yellow” (Perry, 2011). The information on the color of rare earth hydroxides is rather limited but appears consistent.

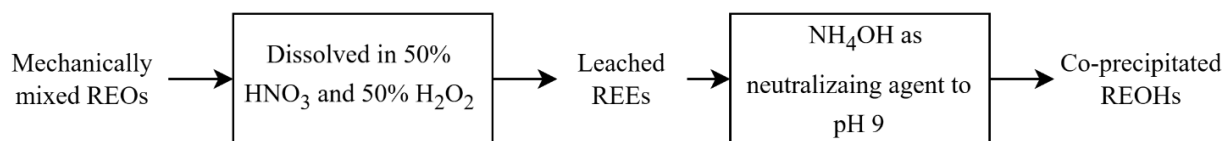


Figure 3-8 Schematic representation of the procedure followed for the synthesis of co-precipitated REOHs



Figure 3-9 Changes observed in the coloration of co-precipitated REOHs before (a.) and after (b.) drying

### 3.3 Carbonation and selective leaching of REOs (or REOHs) for REEs pre-separation

Carbonation and leaching experiments were performed on different starting materials to better understand the effect of operating parameters (i.e., the pH of CO<sub>2</sub> injection and the solid/liquid separation mode) and of starting materials (i.e., composition) on the REE pre-separation performance. This section will first describe carbonation and HCl leach procedure. Then, the different experiments conducted during this research project will be presented.

#### 3.3.1 Set-up of carbonation-HCl leaching test procedure

##### Carbonation

Most carbonation-HCl leaching experiments were conducted as described below, with some adaptations of the apparatus and procedure for specific experiments, which will be clearly defined in [Section 3.3.2](#). Carbonation-HCl leaching experiments were typically conducted on 3 g of the selected starting material inserted into a 400 mL glass beaker containing 75 mL of deionized water. The solid/liquid ratio was fixed at 1 g/25 mL as recommended in the previous work conducted (Yanagihara et al., 1991). The pulp was then mixed using a magnetic stirrer, while CO<sub>2</sub> gas was injected using a porous diffuser at a flowrate of 2 L/min in the system [Figure 3-10a](#). After 10 minutes, the pH of the pulp was measured to ensure CO<sub>2</sub> saturation. As noted by Peng et al. (2013), at atmospheric pressures, the pH of CO<sub>2</sub> saturated water should be around 4.5. As there

is a slight variation in REE powders and pH probes, a slight variation in the pH is expected. In most of the carbonation experiments, the  $\text{CO}_2$  is injected in the system for 24 h, with pH measurements performed after 10 minutes, 4 hours and 24 hours to ensure it remained stable, indicating  $\text{CO}_2$  saturation. After 24 hours of carbonation, the solid was recovered via vacuum-filtration using a  $0.45\ \mu\text{m}$  pore size filter paper on a Buchner funnel in most of the experiments. For indicated tests, the solid was recovered by evaporation of the liquid by drying it at  $50\ ^\circ\text{C}$  for 48 hours. Once collected, the solid was left to dry in an oven at  $50\ ^\circ\text{C}$  for 24 hours and then weighed to determine the potential mass gain due to REE-carbonate formation and compare it to the expected mass gain if all REE belonging to group A were carbonated. This constituted a first indication of carbonation efficiency. A dried solid sample was collected to determine its chemical composition (i.e., S/C and sometimes REE content) and compared with the initial powder. The difference in C content in the solid before and after the carbonation step was also used to determine the carbonation efficiency more accurately (Section 3.4.3). It should be noted that a  $\text{CO}_2$  saturated solution has a pH of around 4.



Figure 3-10 Set-up used for the  $\text{CO}_2$  injection during the carbonation step for the experiments conducted one at a time (a) or in triplicates simultaneously (b)

Triplicate testing was also conducted for some of the carbonation experiments to assess variability. To this end, carbonation was carried out (Figure 3-10b) with the addition of a split system to divide the CO<sub>2</sub> injection tube into three, each inserted in one beaker. In this case, the total flow rate was increased to around 4 L/min and the pH of the pulp was measured to ensure that CO<sub>2</sub> saturation occurred in all the beakers.

### **HCl Leaching**

Dried solid originating from the carbonation step were then submitted to the HCl leaching step. Unless the concentration of the HCl solution used is specified, most HCl leaching steps were performed using 0.25 M HCl, prepared from concentrated HCl (VWR, 12 M technical grade). The concentration chosen here was chosen empirically as will be explained later. Then, 0.2 g of the carbonated REOs were added to the HCl solution and mixed using a magnetic stirrer for 1 h. Then, a solid/liquid separation step was carried out by a filter syringe and liquid samples were collected for further characterization by ICP-OES. Full digestion of a sample of the initial solids (post-carbonation) was also affected using solution of 50% HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> to determine the solids composition using ICP-OES.

### **3.3.2 Evaluation of the influence of operating conditions on pre-separation of REOs**

Different series of experiments were conducted to evaluate the effect of the composition of the starting material (i.e., Nd/Pr vs equimolar ratio REO vs. ore ratio; mechanically mixed vs. co-precipitated REOs or REOHs) and of operating parameters (i.e., carbonation retention time, pH of CO<sub>2</sub> injection, time of CO<sub>2</sub> injection, mode of solid/liquid separation after the carbonation step, HCl concentration during the leaching step) on carbonation efficiencies (i.e., mass gain, carbon gain) and pre-separation efficiencies (i.e., REE leaching efficiencies, group A and group B leaching efficiencies).

### **Nature of REEs starting materials**

Different series of carbonation experiments were conducted to evaluate the effect of the nature of REEs starting materials on the performances of REEs pre-separation. Carbonation experiments were conducted at a solid/liquid ratio of 4% (p/v) for 24 h with and without CO<sub>2</sub> injection on different starting materials : i) individual Nd<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> powders, ii) mechanically mixed Nd/Pr oxides, iii) co-precipitated Nd/Pr oxides, iv) mechanically mixed REOs at equimolar ratio, v) mechanically mixed REOs at ore ratio, vi) co-precipitated REOs at equimolar ratio and

vi) co-precipitated REOHs at equimolar ratio. Post-CO<sub>2</sub> treatment solids were weighted to determine the mass gain and characterized to determine the carbonation efficiencies (Section 3.3.2.2). Then, the “carbonated” materials were leached in agitated HCl (0.25 M) for 1 h at room temperature to evaluate the performances of REE solubilization and pre-separation efficiencies (Section 3.3.3).

### **Carbonation Kinetics Experiments**

Kinetics tests were performed on Nd<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> powders to evaluate the carbonation kinetic of both REOs (one from group A and one from group B) and determine if the carbonation process is chemically- or diffusion-controlled. Carbonation experiments were conducted at a solid/liquid ratio of 4% (i.e., 20 g of Nd<sub>2</sub>O<sub>3</sub> or Pr<sub>6</sub>O<sub>11</sub> powders mixed with 500 mL of water) at pH 4–5 (from CO<sub>2</sub> injection) for 24 h. Pulp samples (20 mL) were collected at different retention times (1, 2, 4, 6, 8, 10, 24 and 48 h) using a 50 mL-syringe. The filter paper and solids were then set to dry in the oven at 50 °C for 24 h. Dried solids were then weighed and sampled for S/C analysis, to determine the mass gain and calculate the carbonation efficiencies (Section 3.4.3). The particle size distribution of the dried solids was also measured using laser granulometry (Section 3.4.3). SEM-EDS observations were also conducted on the dried solids collected at different time intervals to track any changes in particle size, shape or appearance. To ensure that the pulp sampling was accurate, the solid/liquid ratio of the pulp was tracked to ensure that it was close to 4%. These analyses were conducted to try to determine if the REO carbonation process’ limiting step is the REOs reaction with carbonic acid, carbonate nucleation and crystal growth or if it was particle reactions at the surface. If the carbonation kinetics are of the crystallization form, then the Avrami equation (Eq. 3-1) (Erukhimovitch & Baram, 1994) will be the comparison model.

$$Reaction\ completion\ (t) = Rinf(1 - \exp(-\frac{\pi G^3 I t^4}{3})) \quad \text{Eq. 3-1}$$

$$\frac{t}{\tau} = 1 - (1 - Xb)^{1/3} \quad \text{Eq. 3-2}$$

Otherwise, one of the three equations from Levenspiel (1999) would apply. They can either be 1) the “chemically controlled reaction” equation (Eq 3-2) where the rate limiting step is the chemical reaction itself, 2) the “ash-diffusion” equation where the particle remains the same size however reactants must travel through an ash shell to react with the remaining unreacted core or 3) the “gas-film diffusion” where the particle is immediately reacted and no ash remains around it. All three equations were tested to observe which would fit the empirical data best for the kinetics of Pr and Nd.

**Effect of carbonation operating parameters (CO<sub>2</sub> injection, pH of the pulp during carbonation, ultrasonication during carbonation, solid/liquid separation method)**

Different series of carbonation-HCl leaching experiments were conducted to evaluate the effect of operating parameters, including the injection of CO<sub>2</sub>, the pH of the pulp during CO<sub>2</sub> injection, the addition of ultrasounds to limit particles agglomeration during carbonation, the mode of solid/liquid separation, on the performances of REE pre-separation (i.e., mass gain, carbonation efficiencies and selective REEs leaching).

First, carbonation-HCl leaching experiments were conducted on mechanically mixed Nd/Pr oxides or REOs as well as co-precipitated Nd/Pr oxides or REOs at pH 4–5 for 24 h with CO<sub>2</sub> injection at 2 L/min. Blank samples were subjected to the same procedure without CO<sub>2</sub> injection to evaluate the influence of CO<sub>2</sub> injection on the performance of the carbonation-HCl leaching to pre-separate REEs as previous results showed that the injection of CO<sub>2</sub> may not explain the separation as previously suggested by Yanagihara et al. (1991), especially for mechanically mixed REOs systems. Rather, the properties of the individual compounds (resistance to acid attack) would be at play.

The second series of experiments evaluated the effect of pH of the pulp during the carbonation step. To do so, carbonation tests were carried out for 24 h with CO<sub>2</sub> injection at 2 L/min on mechanically mixed REOs and co-precipitated REOs at different pH values of 1, 2.5 and 4–5. For the experiments conducted at pH 1 and 2.5, the pH of the initial liquid solution (before REO addition) had been adjusted to the targeted values using nitric acid prior to CO<sub>2</sub> injection for 24 h. This experiment was carried out to determine if the addition of acid can help break down the crystal structure of co-precipitated REOs, facilitating REE leaching, as inspired by Yu et al. (2019). However, even if the leaching of REEs might be favored under acidic pH, it is expected that the

carbonation of REEs will not be favorable, giving additional information about the role of REE-carbonate formation on the pre-separation efficiencies of REEs.

Some ultrasonication experiments were also conducted on co-precipitated REOs to evaluate the effect of on the carbonation-HCl leaching efficiencies. Particle size distribution analysis of mechanically mixed REOs and co-precipitated REOs showed important differences in the particle size, with larger particles found in co-precipitated REOs ( $d_{80} = 900 \mu\text{m}$ ) and so ultrasound usage appeared relevant. A Qsonica Q700 ultrasound probe was used at 90W applied power for 10 minutes.

A fourth series of experiments were conducted to evaluate the effect of the mode of operation to separate the “carbonated” solid from the liquid after the carbonation step. Some experiments were conducted using vacuum-filtration (pore size:  $0.45 \mu\text{m}$ ), while for other experiments, the liquid was allowed to evaporate at  $50^\circ\text{C}$  for 48 h. These experiments first aimed to address the fact that solid losses were observed during vacuum-filtration as some pulp sticks to the beaker, the  $\text{CO}_2$  injection tube and the watch glass cover during the carbonation process and to the büchner funnel during the filtration process (Figure 3-11). However, as evaporation can be associated with potential cerium oxidation during the evaporation process, its impact on behavior during the subsequent HCl leaching step was studied.

### 3.3.3 Concentration of HCl during the leaching step

Most of the HCl leaching experiments were carried out at a solid/liquid ratio of 0.2 g/12 mL at room temperature for 1 h using a solution of HCl at 0.25 M. This concentration of HCl was selected based on a theoretical calculation of the amount of HCl required to dissolve all the REEs (Eq. 3-3) from (Eq. 3-4), assuming the average atomic mass to be that of lanthanum. This concentration was also validated to be functional at leaching a sufficient portion of REEs through experimentation, namely for the leaching of mechanically mixed REOs. Leaching experiments were also conducted on co-precipitated REOs before and after carbonation (solid/liquid ratio of 4%, 2 L/min  $\text{CO}_2$  injection, 24 h at pH 4–5) using different concentrations of HCl ranging from 0.1 to 12 M to evaluate the effect of the HCl concentration of the leaching behavior of each REE and their pre-separation efficiencies.

$$\text{Moles HCl} = \frac{\text{measured mass La}_2\text{O}_3}{\text{molar mass La}_2\text{O}_3} * 6 \quad \text{Eq. 3-3}$$



### 3.4 Analytical Methods

The various analytical methods used to analyze the solids (i.e., individual REOs, mechanically mixed REOs, co-precipitated REOs, co-precipitated REOHs, post-carbonation materials) and the liquids (i.e., HCl leachate) are described here.

#### 3.4.1 Physico-chemical analysis of solid and liquid samples

The pH was measured with a pH electrode (Orion 915 BNWP double junction Ag/AgCl for pH) connected to a VWR Symphony® multimeter (VWR, Canada), calibrated before each series of measurement using standard solutions (pH 4, 7 and 10).

The sulfur and carbon contents of the solid samples were determined using an induction C/S analyzer (Eltra CS-2000) following MA 301-CS 1.0 method. This destructive analytical method is designed to accurately measure either low concentrations of C and S (between 0.05-0.5%) or high concentrations (1-99%) as mentioned in the analyzer's manual. The principle of this analytical method is based on the oxidation of S and C into SO<sub>2</sub> and CO<sub>2</sub> by heating the sample up to 1360°C in an inductance furnace in the presence of pure oxygen. Dust and water are then removed from the gas using filter and adsorbent before analysis, while remaining SO<sub>2</sub> and CO<sub>2</sub> gas molecules are detected using separate non-dispersive infrared (NDIR) detectors.

The concentrations of rare earth elements (REEs) in HCl leach solutions and digestates were determined using an inductive coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5800-Vertical Dual View (VDV)). With adequate calibration, this analytical equipment can measure REEs concentrations in the range of few ppb to several thousand ppm. The principle is that a small amount of liquid sample is sprayed using a nebulizer chamber from which a smaller amount is then transferred into the argon plasma torch. At around 8000K, all molecules break down into individual neutral atoms and the upper electrons in the atoms are excited to a higher orbital and then drop back down to a neutral state (Olesik, 1991). This dropdown to the neutral state emits

photons with wavelengths that are unique to each atom. The optical detector measures the intensity of these emitted photons to determine elemental concentration of the sample. This equipment allows the measurement of multiple atoms at the same time with modern optical detectors. To ensure the quality of the measurement, the ICP-OES was calibrated using standard solutions before each series of measurements, while certified solutions were analyzed every 20 samples. Solid samples must be fully digested prior to ICP-OES analysis. To do so, 0.2 g of solid samples were digested in 12 mL of the digestion solution composed of 50% of  $\text{HNO}_3$  (16 M) and 50% of  $\text{H}_2\text{O}_2$  (50%) at  $80^\circ\text{C}$  to ensure a total dissolution of REE-bearing materials.

### **Mineralogical analysis of solid samples**

The mineralogical composition of mechanically mixed REOs and co-precipitated REOs was assessed using X-ray diffraction (XRD), using a Bruker D8 Endeavour at 40 mA/40 kV,  $2\theta$  from  $4$  to  $70^\circ$  to identify any changes in diffraction peaks between mechanically mixed and co-precipitated REOs that can explain the different behaviors of mechanically mixed REOs and co-precipitated REOs during carbonation. XRD technique, which is a non-destructive and semi-quantitative analytical method, is based on the diffraction of X-ray beams in contact of the crystal lattice of minerals with a diffraction pattern that serves as fingerprints of the minerals.

A scanning electron microscope (SEM) was used to observe changes in local composition, as well as particle shape and size during the carbonation step of  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  powders. These analyses were performed using a Hitachi TM400 Plus II tabletop electron microscope equipped with energy dispersive spectrometer. The analyzed powders were deposited on to glass slides that were then inserted into the SEM.

### **3.4.2 Carbonation-HCl leaching performance calculations**

The performance of the carbonation-HCl leaching process was determined using mass gain [Eq. 3-5](#), the carbonation efficiency [Eq. 3-6](#), REE solubilization efficiency [Eq. 3-8](#) and REE separation efficiency [Eq. 3-9](#).

$$\text{Mass gain (\%)} = \frac{(m_{\text{carbonated}} - m_{\text{raw material}})}{m_{\text{raw material}}} * 100 \quad \text{Eq. 3-5}$$

Where  $m_{\text{carbonated}}$  is the mass of the dried solid collected after the carbonation step (expressed in g) and  $m_{\text{raw material}}$  is the mass of the dried initial solid sample before the carbonation step (i.e.,  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  powders, mechanically mixed REOs, co-precipitated REOs, co-precipitated REOHs) (expressed in g).

The carbonation efficiency was calculated using the measured and theoretical amount of carbon in the “carbonated” material as defined in Eq. 3-5. The theoretical amount of % C is the carbon that would be present if the product was a pure REC. For example, the theoretical amount of % C in  $\text{Nd}_2(\text{CO}_3)_3$  is 7.69 % C. This calculation is based on some assumptions: i) the only source of carbon is carbonation, ii) measured C is inorganic carbon, iii) all carbonates are of the form  $\text{Ln}_2\text{CO}_3$  ex  $\text{Nd}_2(\text{CO}_3)_3$ . Eq 3-7 shows the calculation for one or several REEs)

$$\text{Carbonation efficiency (\%)} = \frac{C_{\text{measured}}}{C_{\text{theoretical}}} * 100 \quad \text{Eq. 3-6}$$

where  $C_{\text{measured}}$  is the amount of total carbon measured in the dried solid after the carbonation step (expressed in % C) and  $C_{\text{theoretical}}$  is the theoretical mass of carbon that can be found in the dried solid if all REEs were carbonates (expressed in % C) – calculated following Eq 3-7).

$$C_{\text{theoretical}}(\% \text{ C}) = \frac{\text{Molar mass C } (\frac{36.033\text{g}}{\text{mol}})}{\text{Average Molar Mass } \text{REC}_i(\text{Ln}_2(\text{CO}_3)_3)} \quad \text{Eq. 3-7}$$

where  $\text{REC}_i$  is one rare earth carbonate (for example, the molar mass of  $\text{Pr}_2(\text{CO}_3)_3$  is equal to 461.84 g/mol) and mass C is the molar mass of three carbon atoms (36.033 g/mol). In a more complex mixture, it is the average molar mass of all RECs in the mixture.

$$\text{Solubilization efficiency (\%)} = \frac{\text{Mass REE}_{\text{leached}}}{\text{Mass REE}_{\text{initial}}} * 100 \quad \text{Eq. 3-8}$$

where  $\text{Mass REE}_{\text{leached}}$  is the amount of REE leached during the HCl leaching step (expressed in g -  $[\text{REE}]_{\text{leached}} * V_{\text{leachate}}$ ) and  $\text{Mass REE}_{\text{initial}}$  is the amount of REE initially present in the “carbonated” material (expressed in g -  $[\text{REE}]_{\text{dissolved}} * V_{\text{dissolved}}$ ). The initial is calculated from a full dissolution. Solubilization efficiency calculates how much of one element was leached.

Lastly, the separation efficiency was calculated to give an idea of the performance of the carbonation-HCl leaching process to selectively recover one REE (or group of REEs) from another one using [Eq. 3-9](#).

$$\text{Separation efficiency (\%)} = |\mu_i - \mu_j| \quad \text{Eq. 3-9}$$

Where  $\mu_i$  is solubilization efficiency (%) of one element or group of elements and  $\mu_j$  is solubilization efficiency (%) of another element or group of elements.

While using separation factors  $\beta_{i,j}$  may have presented advantages, the formula above allows for easier comparison to previous results from Papangelakis (2021), which is the closest literature comparison point.

## CHAPTER 4 RESULTS AND DISCUSSION

The results section is organized into 4 sub-sections, starting with the performance of the carbonation-HCl leaching process performed on individual or co-precipitated Nd/Pr [Section 4.1](#), followed by its application to mechanically mixed REOs [Section 4.2](#) and co-precipitated REOs [Section 4.3](#). The performance of the selective carbonation-HCl leaching to pre-separate co-precipitated REOHs is presented in [Section 4.4](#). Examining each stage of the procedure individually—carbonation, solid–liquid (S/L) separation and leaching for each REE-bearing material provides a more comprehensive understanding of the performance and limitations of the proposed pre-separation technique.

### 4.1 Performance of selective carbonation-HCl leaching on the pre-separation of Nd- and Pr-oxides

To simplify the system and get a baseline to better understand the mechanisms involved within the carbonation-HCl leaching process, the first series of experiments have been conducted on two individual REOs ( $\text{Pr}_6\text{O}_{11}$  and  $\text{Nd}_2\text{O}_3$ ) separately and then mechanically mixed. These were chosen as praseodymium presents a higher oxidation state and is belonging from group B (unfavorable to carbonation), while neodymium is a trivalent REO from group A of huge interest for the energy transition of our society. Further, Nd and Pr are being next to each other in terms of atomic number, they are difficult to separate via solvent extraction, presenting a separation challenge.

#### 4.1.1 Carbonation efficiency of individual $\text{Nd}_2\text{O}_3$ and $\text{Pr}_6\text{O}_{11}$ powders

Triplicate tests were performed on individual Nd- or Pr-oxides with 24 hours of carbonation to measure variability in  $\text{Nd}_2\text{O}_3$  or  $\text{Pr}_6\text{O}_{11}$  carbonation [Figure 4-1](#). Results showed that almost 80% of  $\text{Nd}_2\text{O}_3$  were carbonated after 24 h while less than 20% of  $\text{Pr}_6\text{O}_{11}$  were carbonated, highlighting a major difference of REE from group A and group B to tend to be transformed as REE-carbonates when  $\text{CO}_2$  is injected under atmospheric pressure and temperature. It should be noted that the injection mode of  $\text{CO}_2$  seemed to play a role in the efficiency and selectivity of REOs carbonation. Indeed, Yanagihara et al. (1991) observed that nearly 99.9% of  $\text{Nd}_2\text{O}_3$  and almost no  $\text{Pr}_6\text{O}_{11}$  were carbonated after 1h when submitted individual REOs to supercritical  $\text{CO}_2$  conditions, while when injecting  $\text{CO}_2$  under atmospheric conditions less  $\text{Nd}_2\text{O}_3$  and more  $\text{Pr}_6\text{O}_{11}$  were carbonated. The

variability, indicated by the error-bars, may be ascribed to some variations in reaction conditions such as mixing speed, sample recovery efficiency (some solid particles remained stuck to the beaker after carbonation which represent a challenge to adequately quantify the carbonation efficiency) and analytical error when measuring the mass of precipitate and total C content in the precipitate. The variability coefficient is quite high with 18.0 % for Nd and 27.7% for Pr.

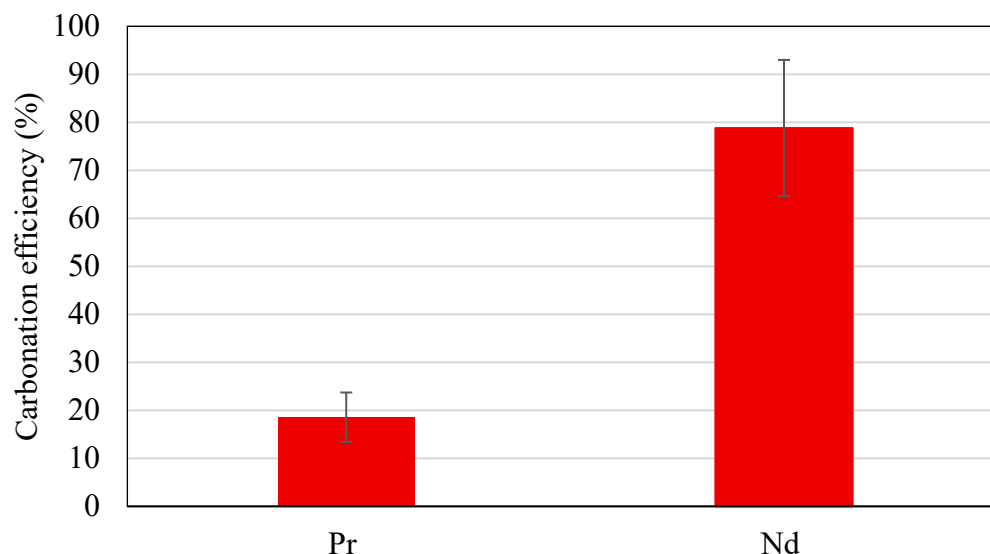


Figure 4-1: Carbonation efficiency observed for individual  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  (S/L ratio of 4% (w/v), 24 h of  $\text{CO}_2$  injection to reach saturation, pH around 4, S/L separation by filtration)

#### 4.1.2 Neodymium carbonation kinetics

Neodymium oxide, classified as a group A-REO, reacts to a greater extent than  $\text{Pr}_6\text{O}_{11}$  with  $\text{CO}_2$  under atmospheric conditions as previously shown in [Figure 4-1](#). A series of individual oxides was used to quantify the kinetics of REE-carbonate formation, beginning with  $\text{Nd}_2\text{O}_3$ , to quantify the rate-limiting step governing the carbonation reaction. The evolution of  $\text{Nd}_2\text{O}_3$  carbonation efficiencies with time showed that carbonation is quite minimal within the first hour, while a sharp increase in Nd carbonation efficiencies is observed after 2 hours, reaching nearly 90%, followed by a plateau after 6 hours ([Figure 4-2](#)).

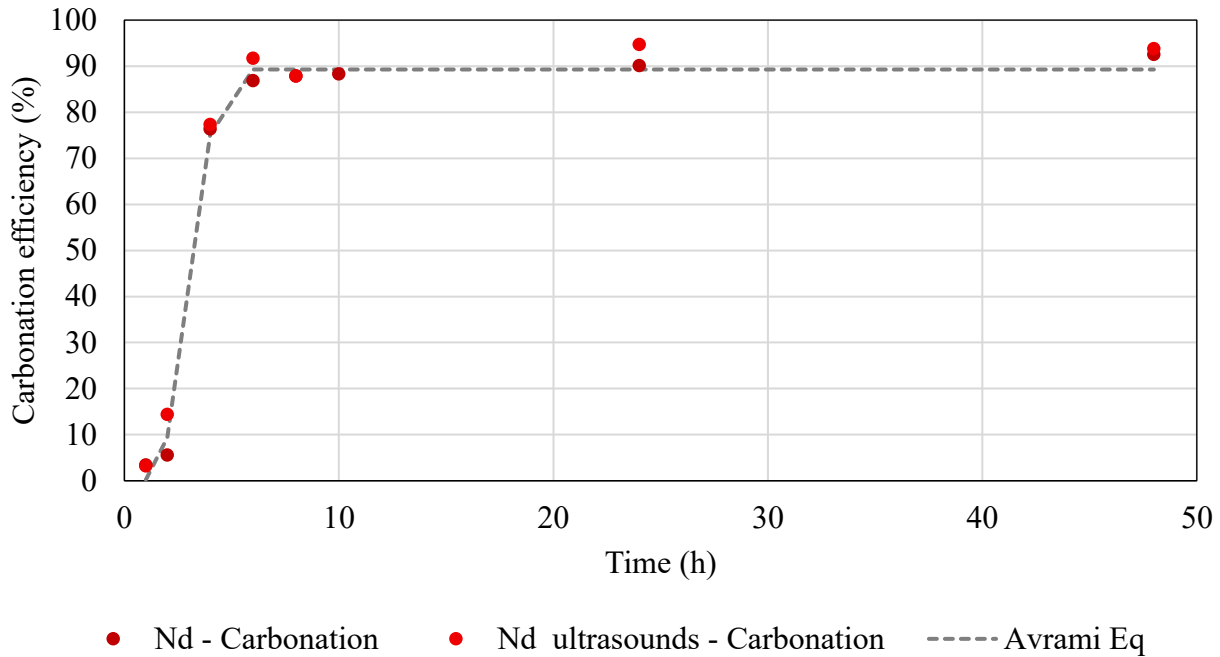


Figure 4-2: Experimental kinetics of  $\text{Nd}_2\text{O}_3$  carbonation efficiencies, with and without ultrasounds, fitted with the Avrami equation with modified parameters ( $\text{CO}_2$  injection : 2 L/min  $\text{CO}_2$ , S/L ratio: 4% (w/v), S/L separation by filtration)

This initial induction period followed by a rapid increase and final stabilization of carbonation efficiency are characteristics of crystallization-controlled kinetics. Such behavior can be described by the Avrami equation (Eq. 4-1), commonly used to model crystallization processes, where  $R_\infty$  represents the maximum of crystallization efficiency,  $t$  represents the reaction time,  $G$  and  $I$  are kinetic constants (Erukhimovitch & Baram, 1994).

$$\text{Reaction completion } (t) = R_{inf} \left( 1 - \exp\left(-\frac{\pi G^3 I t^4}{3}\right) \right) \quad \text{Eq. 4-1}$$

Figure 4-2 illustrates the strong agreement between the experimental Nd carbonation data and the Avrami model, using iteratively estimated parameters ( $R_\infty = 89.29$ ,  $G = 0.30$ ,  $I = 0.26$ ). This behavior reflects an initial induction period associated with limited nucleation to form the first crystal seeds, followed by a rapid crystal growth and a final plateau corresponding to the

equilibrium of the crystallization step. The use of ultrasounds during the Nd carbonation process seemed to improve the kinetics, with carbonation efficiencies reaching 14% after 2 h with ultrasounds in comparison to 5% without ultrasounds. However, the final carbonation efficiency and the reaction time to achieve it remained similar, indicating that ultrasounds didn't influence carbonation efficiencies. This can be explained by the fact that even if ultrasonication promotes particles agglomeration, mechanical agitation alone seemed to be sufficient to achieve effective particle dispersion.

Figure 4-3 provides an initial assessment of the evolution of the particle size distribution (i.e.,  $d_{80}$ ) during  $\text{Nd}_2\text{O}_3$  carbonation in comparison to the carbonation efficiency to better understand the mechanisms involved in the carbonation process (i.e., dissolution of  $\text{Nd}_2\text{O}_3$  and formation of REE-carbonates, direct formation of REE-carbonates on the surface of  $\text{Nd}_2\text{O}_3$ ).

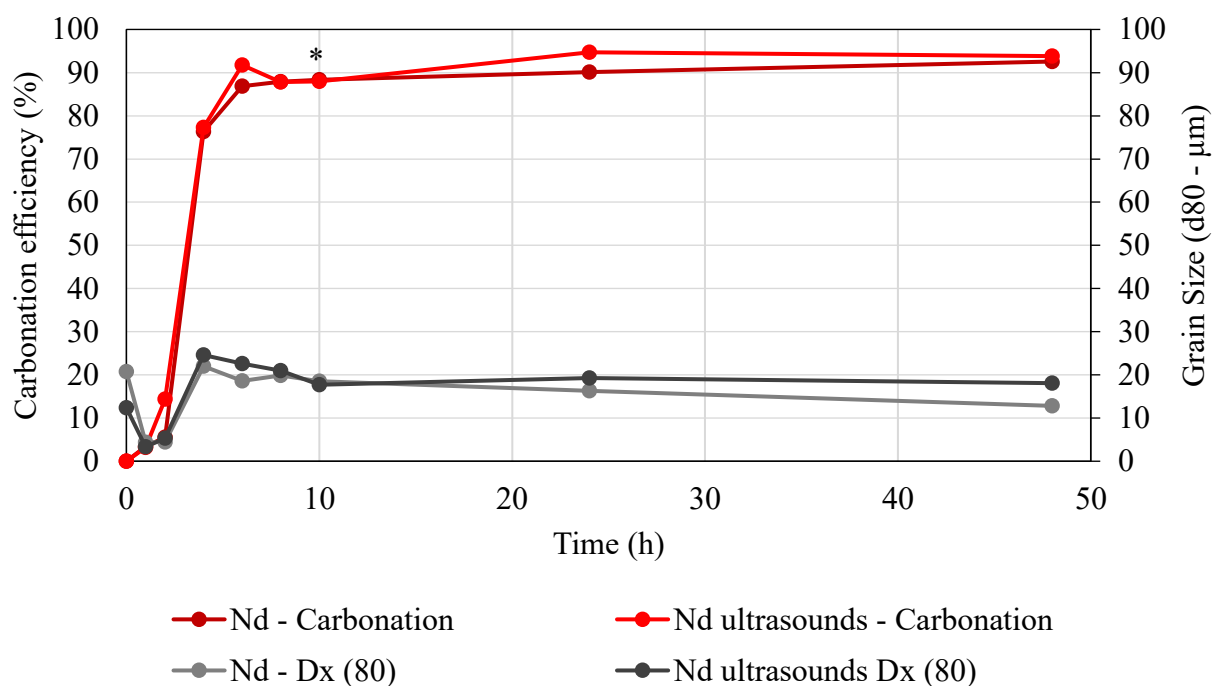


Figure 4-3: Evolution of the particle size ( $d_{80}$ ) and carbonation efficiency of  $\text{Nd}_2\text{O}_3$  with time ( $\text{CO}_2$  injection : 2 L/min, S/L ratio: 4% (w/v), S/L separation by filtration) \* Nd ultrasounds – Carbonation 10 h point was removed as a manipulation error occurred.

Results showed that  $\text{Nd}_2\text{O}_3$  particles were initially highly agglomerated. After 2 hours of mixing, a progressive deagglomeration of the particle is observed through the decrease of particle size distribution. As the crystallization process achieved completion after about 4 hours, the  $d_{80}$  value increases markedly before to slightly decrease. The rapid increase in particle size coinciding with the sharp rise in carbonation efficiency is consistent with crystal formation.

Figure 4-4 and 4-5 present the evolution of particle size distribution over time for  $\text{Nd}_2\text{O}_3$  carbonation without and with ultrasounds' treatment, respectively, to better understand the mechanisms involved in Nd carbonation process. Although initial  $\text{Nd}_2\text{O}_3$  powder is composed of fine particles, with most of the particles below  $8\text{ }\mu\text{m}$ , deagglomeration occurred within the first two hours as the particle size decreases to below  $4\text{ }\mu\text{m}$ . During the crystal growth period, the particle size reached almost  $12\text{ }\mu\text{m}$ , which is consistent with SEM observation.

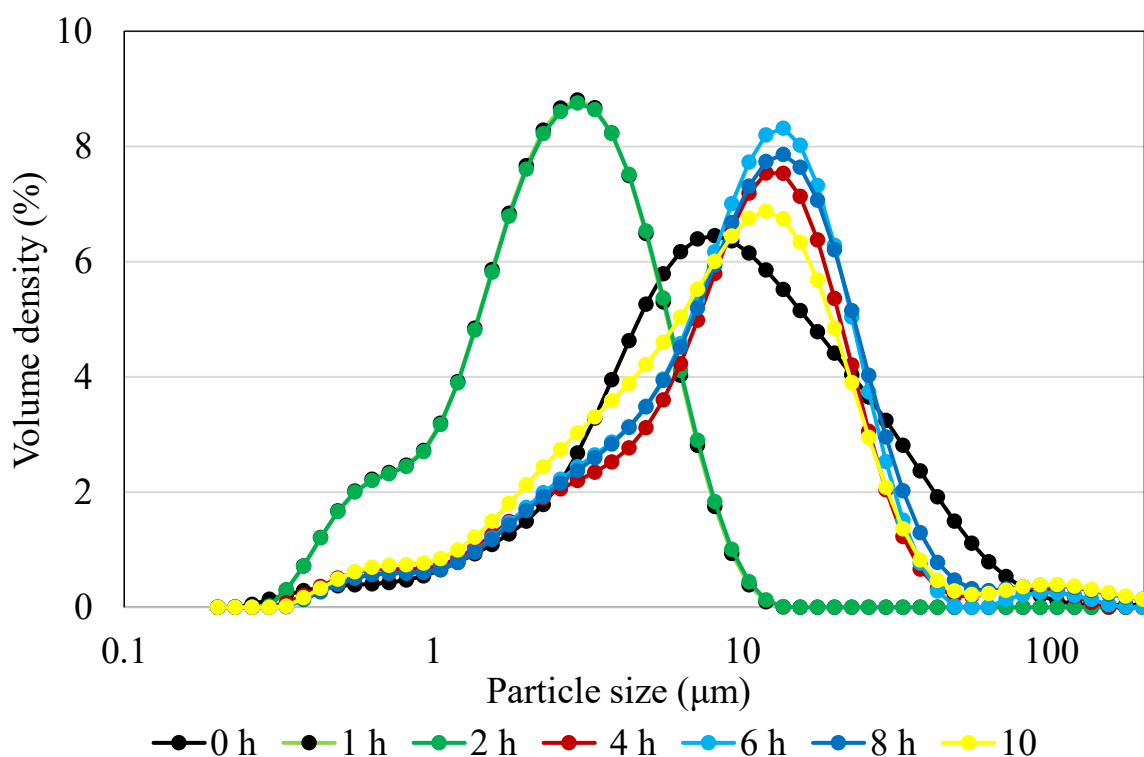


Figure 4-4: Particle size distribution during  $\text{Nd}_2\text{O}_3$  carbonation without ultrasounds ( $\text{CO}_2$  injection : 2 L/min, S/L ratio: 4% (w/v), S/L separation by filtration)

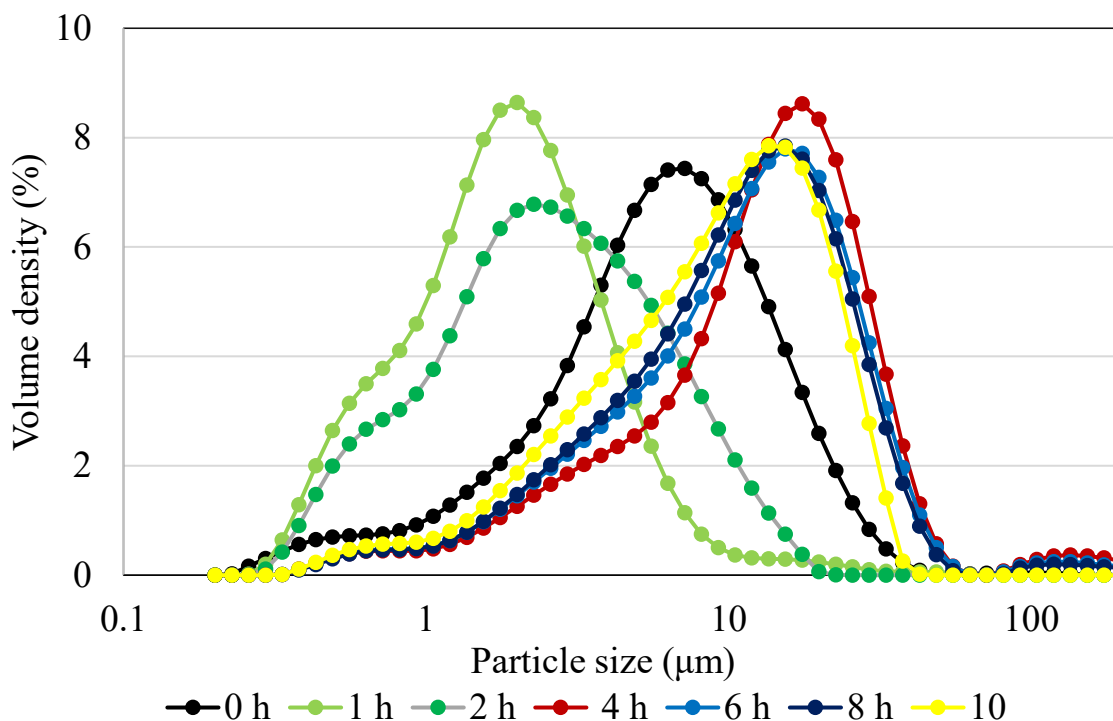


Figure 4-5: Particle size distribution during  $\text{Nd}_2\text{O}_3$  carbonation with ultrasounds ( $\text{CO}_2$  injection: 2 L/min, S/L ratio: 4% (w/v), S/L separation by filtration)

SEM analyses were performed on Nd-bearing materials to confirm the presence of crystalline Nd-carbonates and thereby support the hypothesis that the formation of Nd-carbonate is governed by crystallization-controlled kinetics. Under this hypothesis, it is anticipated that after 1 hour of reaction, the material remained amorphous, while after 4 hours, most of the material is expected to be mainly composed of crystalline  $\text{Nd}_2(\text{CO}_3)_3$ , which is confirmed by SEM observations, highlighting the formation of long prisms of around 10  $\mu\text{m}$  in length, which were also measured via laser granulometry. Cui et al. (2022) provides a comparison point for the formation of  $\text{Nd}_2(\text{CO}_3)_3$  crystals (Figure 4-6). While these crystals are not exactly the same, they appear to follow a similar form of structures documented in this thesis.

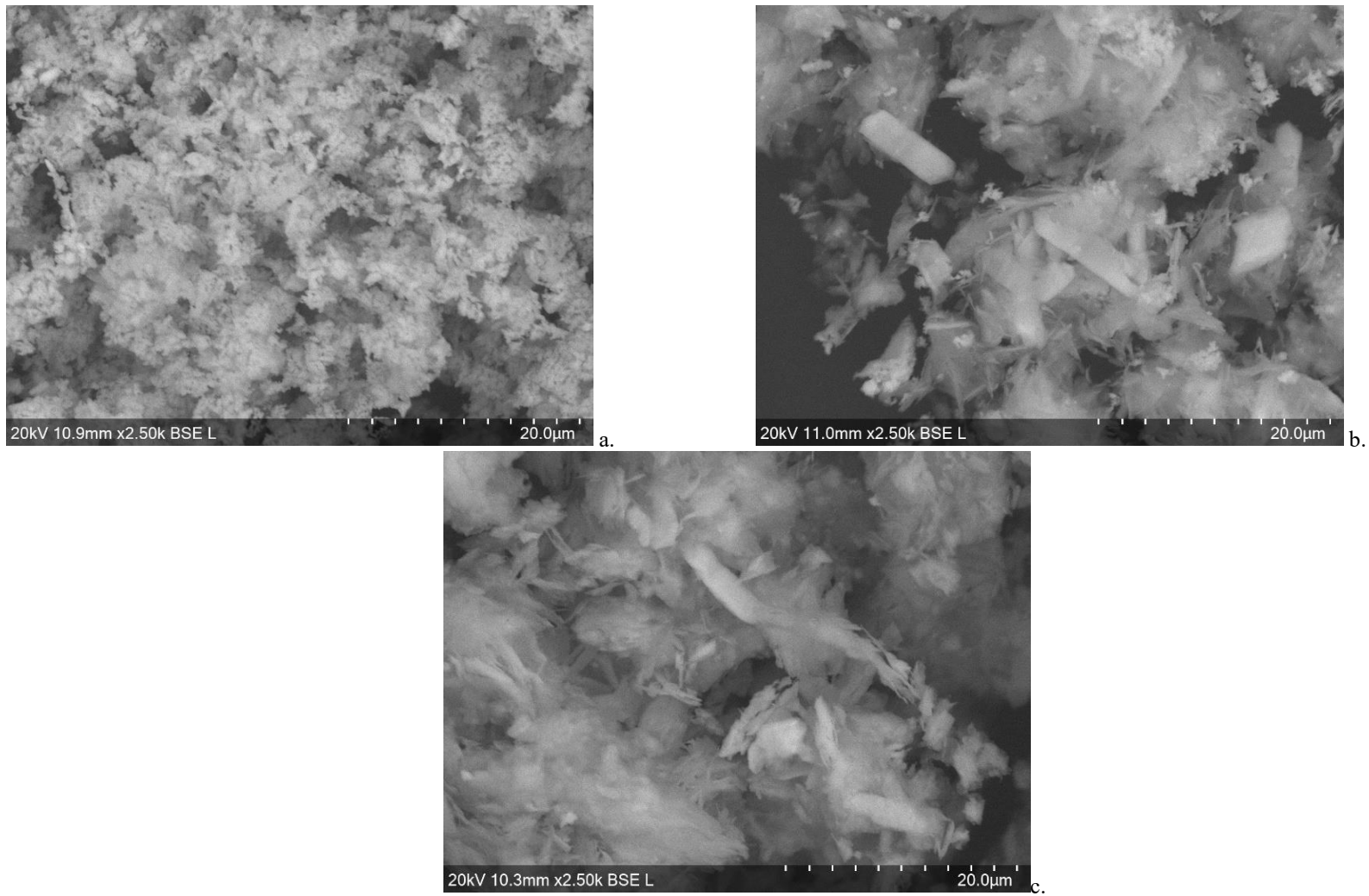


Figure 4-6: SEM observations (2,500x) of Nd-bearing materials at different time of CO<sub>2</sub> injection at room temperature: a) after 1 h, b) after 4 h, c) after 10 h

### 4.1.3 Praseodymium carbonation kinetics

Another series of carbonation kinetic was performed using  $\text{Pr}_6\text{O}_{11}$  powder to quantify the rate-limiting step governing Pr carbonation reaction. For this purpose, the general equation associated with chemically controlled reactions, presented in Eq 4-2, has been used (Levenspiel, 1999). In this formulation,  $t$  represents the reaction time,  $\tau$  represents the total time required to achieve complete conversion to corresponding REE-carbonates and  $X_b$  represents the proportion of REO converted to REE-carbonates.  $R_{inf}$  was determined empirically to be 0.5 or 50%.

$$\frac{t}{\tau} = (1 - (1 - X_b)^{1/3})R_{inf} \quad \text{Eq. 4-2}$$

The evolution of  $\text{Pr}_6\text{O}_{11}$  conversion into Pr-carbonates as a function of time as well as a theoretical approximation using the above reaction-controlled equation with a limit fixed to 50% to consider the apparent asymptote is presented in Figure 4-7. The close agreement between the experimental and theoretical curves suggests that the carbonation of Pr may be represented as a chemically controlled reaction. Deviations from the ideal behavior may be explained by the fact that  $\text{Pr}_6\text{O}_{11}$  particles are not single sized spheres, but rather present a distribution of particle sizes, with smaller particles presenting much shorter reaction times than the larger ones. This explanation is further supported by the limited improvement observed when the Pr oxide pulp was subjected to ultrasounds' treatment, which is typically used to enhance the diffusion processes. Levenspiel equations were used as they are commonly used in chemical engineering.

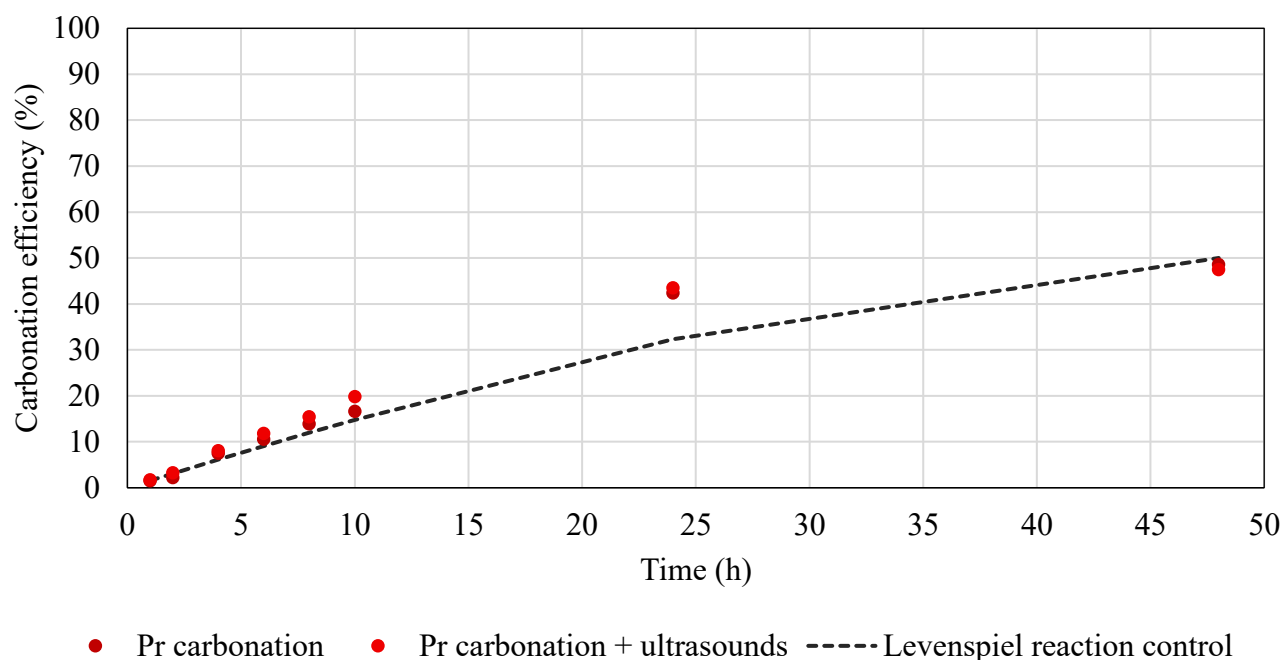


Figure 4-7: Experimental kinetics of  $\text{Pr}_6\text{O}_{11}$ 's carbonation efficiencies, with and without ultrasounds, fitted with Levenspiel chemical reaction control model ( $\text{CO}_2$  injection: 2 L/min, S/L ratio: 4% (w/v), S/L separation by filtration)

Figure 4-8 provides an initial assessment of the evolution of the particle size distribution (i.e.,  $d_{80}$ ) during  $\text{Pr}_6\text{O}_{11}$  carbonation in comparison to the carbonation efficiency to better understand the mechanisms involved in the carbonation process (i.e., dissolution of  $\text{Pr}_6\text{O}_{11}$  and formation of REE-carbonates, direct formation of REE-carbonates on the surface of  $\text{Pr}_6\text{O}_{11}$ ). During mixing, it is expected that Pr oxide agglomerates can be broken apart, and that the application of ultrasounds will strongly accelerates this deagglomeration process. As both the final particle size distribution and carbonation efficiencies achieved were essentially quite identical with and without the application of ultrasounds, it is not possible to conclude that ultrasounds didn't have a significant effect through enhanced deagglomeration. The rate-limiting step therefore appeared to remain the intrinsically slow chemical reaction between  $\text{Pr}_6\text{O}_{11}$  and carbonic acid.

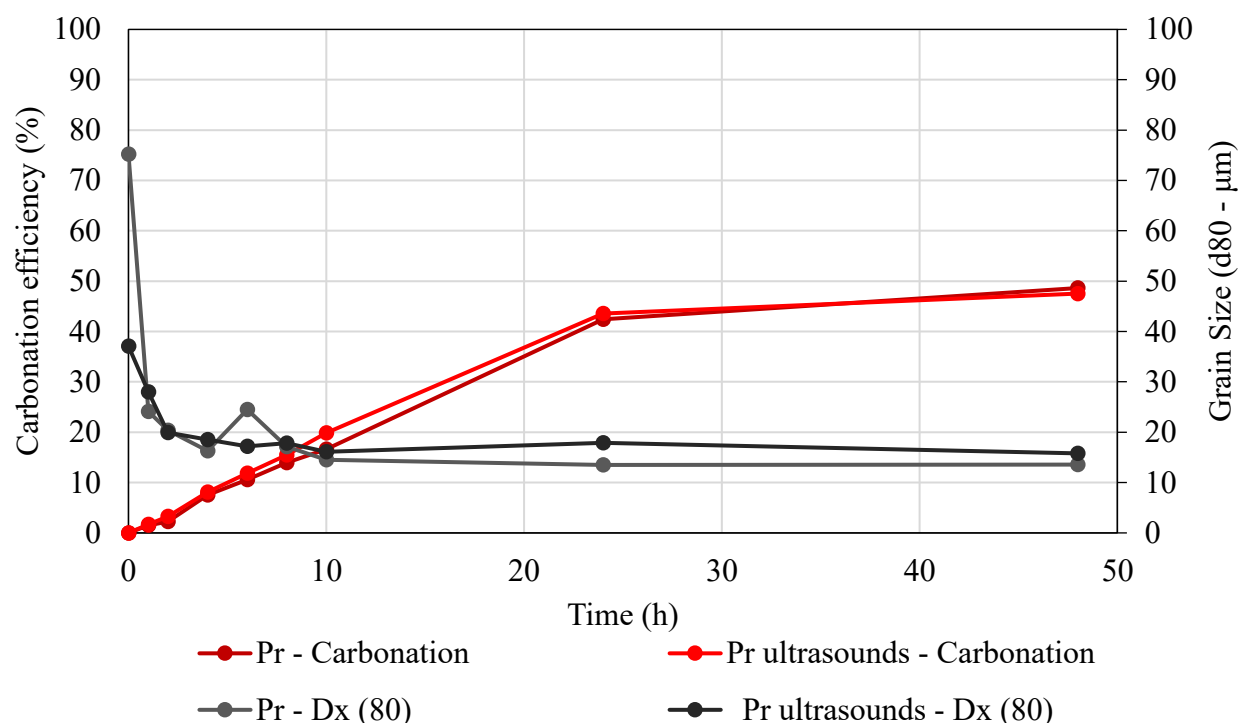


Figure 4-8: Evolution of the particle size (d80) and carbonation efficiency of  $\text{Pr}_6\text{O}_{11}$  with time ( $\text{CO}_2$  injection : 2 L/min, S/L ratio: 4% (w/v), S/L separation by filtration)

The evolution of particle size distribution over time for  $\text{Pr}_6\text{O}_{11}$  carbonation without and with ultrasounds' treatment are presented in Figure 4-9 and 4-10, respectively. The initially large particle size observed for  $\text{Pr}_6\text{O}_{11}$  powder without ultrasound's treatment reflects the presence of agglomerates (Figure 4-9). The diminution of the particles size observed during the first hour of reaction can be attributed to the efficient deagglomeration of  $\text{Pr}_6\text{O}_{11}$  particles with the efficient mixing of the pulp, without any ultrasounds. Aside from the disappearance of some of the larger particles, the overall particle size distribution remains relatively stable over time, indicating that neither significant  $\text{Pr}_6\text{O}_{11}$  dissolution of the primary particles nor growth of secondary of Pr-carbonates seemed to occur. This behavior is consistent with a chemically controlled reaction mechanism, without substantial morphological evolution of the solid phase. The apparent asymptotic limit close to 50% used to fit with experimental data may be explained by the fact that the carbonation reaction seemed to be limited by the slow penetration of carbonic acid, which is a weak inorganic acid, into  $\text{Pr}_6\text{O}_{11}$  oxide and the need to reduce  $\text{Pr}(+\text{III},+\text{IV})$  to  $\text{Pr}(+\text{III})$  prior to its carbonation as  $\text{Pr}_2(\text{CO}_3)_3$ . Similar observations can be made concerning the evolution of particle

size distribution during  $\text{Pr}_6\text{O}_{11}$  carbonation in the presence of ultrasounds, confirming the limited effect of ultrasonication on the carbonation of  $\text{Pr}_6\text{O}_{11}$  (Figure 4-10).

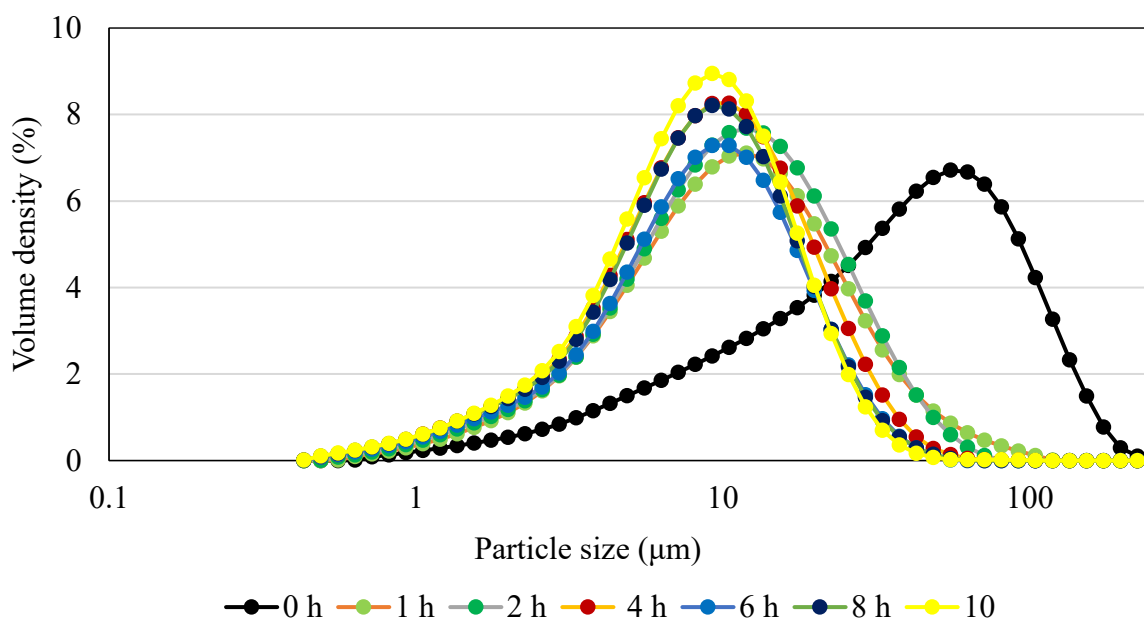


Figure 4-9: Particle size distribution during  $\text{Pr}_6\text{O}_{11}$  carbonation without ultrasounds ( $\text{CO}_2$  injection : 2 L/min, S/L ratio: 4% (w/v), S/L separation by filtration)

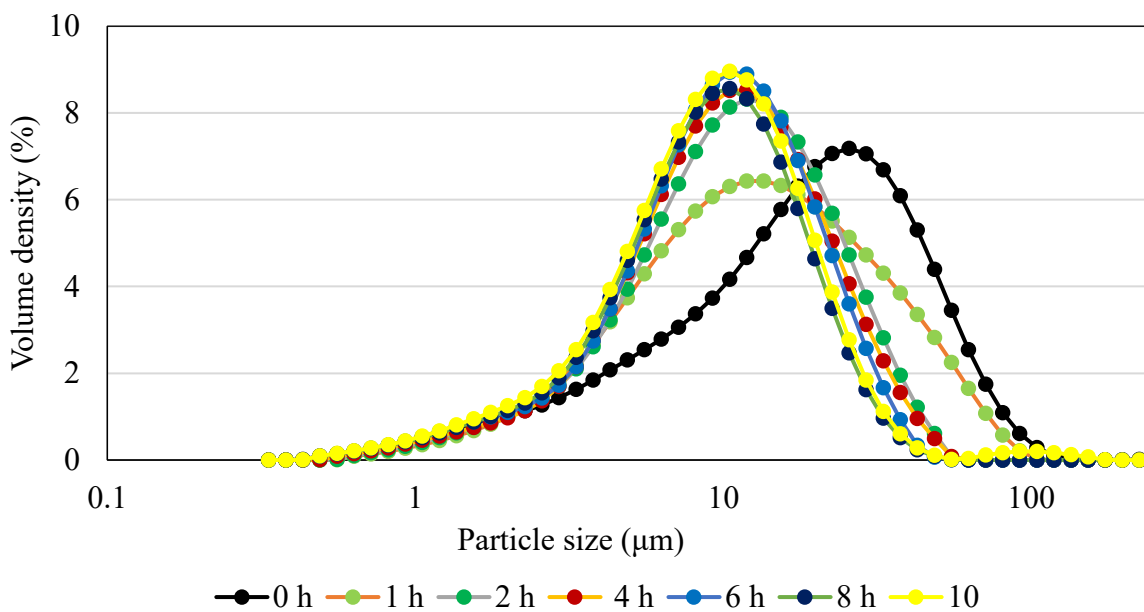


Figure 4-10: Particle size distribution during  $\text{Pr}_6\text{O}_{11}$  carbonation with ultrasounds' treatment ( $\text{CO}_2$  injection : 2 L/min, S/L ratio: 4% (w/v), S/L separation by filtration)

Although the linear kinetic of Pr-carbonate do not indicate a classical crystallization process, SEM observations nevertheless reveal the presence of crystalline phases, forming at a slower rate than previously observed for Nd-carbonates. As shown in [Figure 4-11a](#), the initial  $\text{Pr}_6\text{O}_{11}$  powder appeared to be amorphous, but after 10 hours of carbonation reaction, a major proportion of crystals is observed ([Figure 4-11b](#)), highlighting significant changes in the morphology of Pr-bearing particles, which is consistent with the transformation of  $\text{Pr}_6\text{O}_{11}$  into  $\text{Pr}_2(\text{CO}_3)_3$ . EDS analysis of the newly formed crystals suggests the formation of Pr-carbonates as evidenced by the increased presence of C. EDS analysis on the 1 h-product suggests higher concentrations of oxygen (and so presence of  $\text{Pr}_6\text{O}_{11}$ ), while the 48 h-product has high concentrations of C and less O, suggesting the presence of  $\text{Pr}_2(\text{CO}_3)_3$ . EDS measurements of C and O, however, are not very precise, as the chamber is not in a full vacuum (presence of O) and the background is a carbon compound. After 48 h of  $\text{CO}_2$  injection, the SEM-EDS analysis confirmed the presence of  $\text{Pr}_2(\text{CO}_3)_3$  crystals; however, this observation is based on a localized area exhibiting a higher crystal density. One interesting aspect is that the formation of  $\text{Pr}_2(\text{CO}_3)_3$ , where Pr is trivalent, implies the reduction of at least part of the  $\text{Pr}_6\text{O}_{11}$ , where a majority of Pr is in the 4+ state.

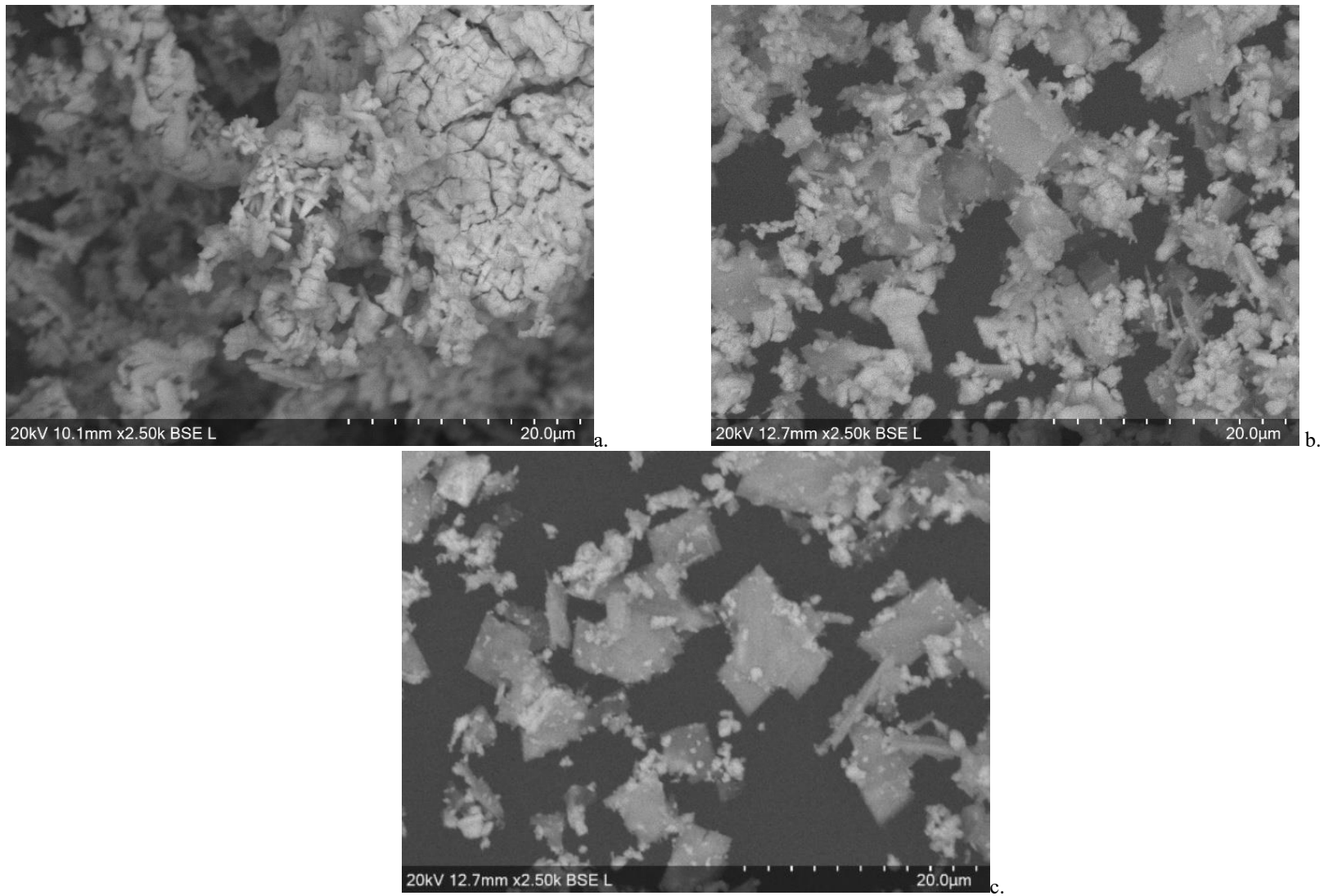


Figure 4-11: SEM-BSE observations (2,500x) of Pr-bearing materials at different time of CO<sub>2</sub> injection at room temperature: a) after 1h, b) after 10 h and c. after 48 h

#### 4.1.4 Carbonation efficiency on mechanically mixed or co-precipitated Nd-/Pr-oxides

Carbonation experiments were performed on a mixture of  $\text{Nd}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  powders, either mechanically mixed or through co-precipitation, with (carbonated) and without  $\text{CO}_2$  injection (pulp). This sub-section will first discuss the effect of the nature of Nd- and Pr-bearing materials on the mass gain and carbonation efficiency followed by the selective leaching of carbonated Nd- or Pr-bearing materials for their pre-separation.

##### **Mass gain and carbonation efficiency**

Figure 4-12 summarizes the mass change observed after 24 h mixing with or without  $\text{CO}_2$  injection, which is a good indicator of the potential formation of REE-carbonates, as REEs-carbonates have a significantly higher molar mass than REOs. As an example, a complete conversion of  $\text{Nd}_2\text{O}_3$  to  $\text{Nd}_2(\text{CO}_3)_3$  will theoretically result in a 39.2% mass increase, neglecting any hydration as well as about a 40.0% increase for complete conversion of  $\text{Pr}_6\text{O}_{11}$  into  $\text{Pr}_2(\text{CO}_3)_3$ . However, using this mass increase to assess carbonation efficiency poses some challenges since mass losses occur during solid/liquid separation such as filtration. Results showed that important mass changes (20-30%) were observed for a  $\text{Nd}_2\text{O}_3$  powder alone or mixed with  $\text{Pr}_6\text{O}_{11}$ , indicating that a large proportion of  $\text{Nd}_2\text{O}_3$  particles may have carbonated (experimental mass gain is equivalent to 50-75% of the theoretical one) while low mass changes (< 10%) were obtained for the  $\text{Pr}_6\text{O}_{11}$  powder, which were equivalent to ~ 25% conversion if all mass gain is equivalent to  $\text{Pr}_6\text{O}_{11}$  carbonation. It should be noted that a low mass gain was obtained for experiments performed on co-precipitated Nd- and Pr-powders, indicating that the carbonation efficiency seemed to be influenced by the nature of the REE-bearing material. This suggests that carbonation does not occur or does so to a very limited extent, even on simple binary co-precipitated mixtures. This is different from what would be expected from Fernando et al. (1991). These results also showed that  $\text{CO}_2$  injection seemed to have a positive effect on the mass gain as quite negligible mass gain (< 2%) were observed for the experiments carried out without  $\text{CO}_2$  injection (“blank”). A strong agreement is observed between the measured mass gains and those calculated from total C content analyses, supporting the formation of carbonate phases and indicating that almost all mass gain observed during carbonation can be ascribed to the carbonation of Nd- and Pr-oxides.

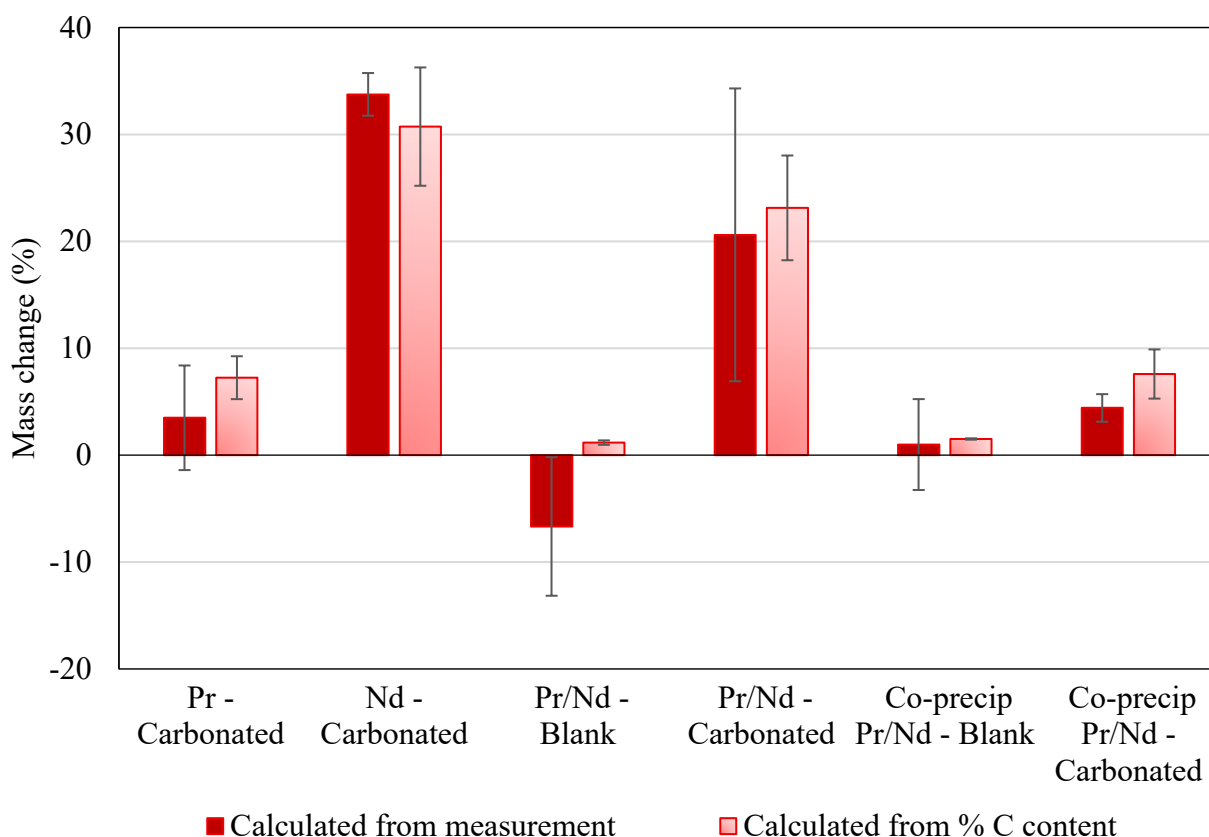


Figure 4-12: Pr/Nd comparison in mass differences from carbonation (direct mass measurement (red) vs mass measurements calculated from C content (light red) (CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration), not carbonated unless stated

### **Carbonation efficiency**

These results are coherent with the carbonation efficiencies observed for the different materials (Figure 4-13). A strong agreement is observed between the measured mass gains and carbonation efficiencies, supporting the formation of carbonate phases. The combination of equimolar amounts of Nd<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> powders through simple mechanical mixing showed a carbonation behavior consistent to the previous carbonation efficiencies observed for individual oxides. Indeed, carbonation efficiency of approximately 60% for the mixture Nd/Pr falls within the uncertainty range of the previous carbonation efficiencies obtained for individual oxides (80% for Nd and 20% Pr is coherent with the 50% carbonation for the Nd/Pr mixture). The comparison of carbonation efficiencies of Nd/Pr mixture with and without (blank) CO<sub>2</sub> injection confirmed that the conversion of Nd- and Pr-oxides into carbonated is driven by CO<sub>2</sub> injection, which is significantly more

pronounced for neodymium than for praseodymium. In contrast, CO<sub>2</sub> injection applied to co-precipitated Pr/Nd oxides leads to substantially lower carbon gain, indicating reduced carbonate formation compared to individual oxides or mechanically mixed Nd- and Pr-oxides. These results provide a first indication that the reactivity of carbonic acid seemed to be affected by the nature of the REE-bearing material and that the performance of selective carbonation cannot be inferred from the behavior of individual powders neither of mechanically mixed REE-oxides. This behavior, termed “coherence” by Horlait et al. (2012), arises questions towards fundamental assumptions of the patent of Yanagihara et al. (1991) (Fernando et al., 1991).

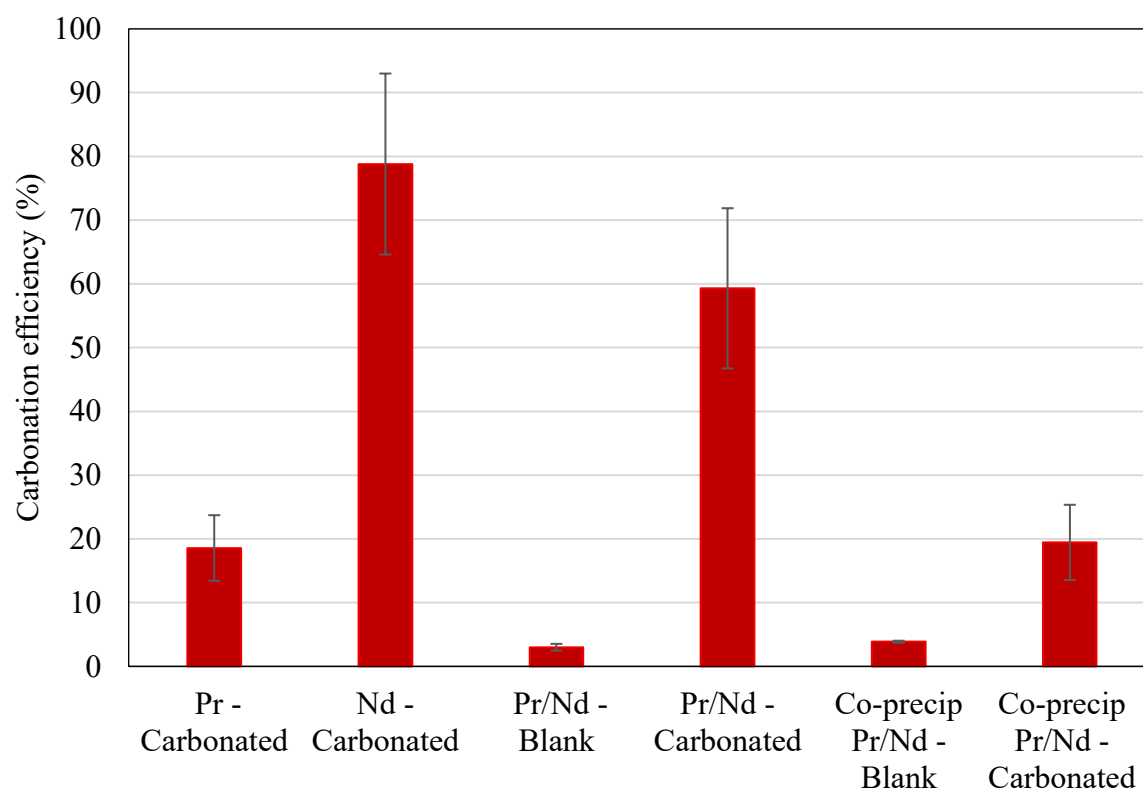


Figure 4-13: Carbonation efficiencies for Pr, Nd and their mixtures (CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration)

#### 4.1.5 Performance of the pre-separation of carbonated Nd and Pr using HCl leaching

As discussed previously, Nd- and Pr-oxides were selectively carbonated through CO<sub>2</sub> injection from individual or mechanically mixed powders, while low carbonation efficiencies were observed for co-precipitated Nd/Pr. From previous studies in the literature, it is expected that the solubilization of carbonated Nd will be greater than those of less carbonated Pr, allowing their pre-separation. Figure 4-14 shows the solubilization efficiencies of Nd and Pr from the different (un-)carbonated materials previously discussed.

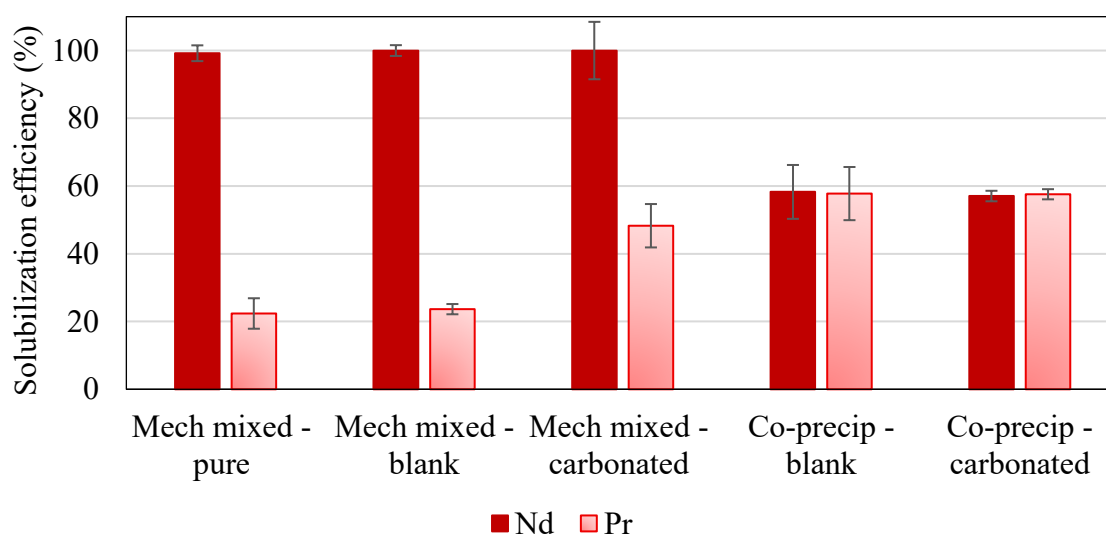


Figure 4-14: Solubilization efficiencies of Nd and Pr using HCl leaching on different Nd-/Pr-bearing materials (carbonation: CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration – HCl leaching: [HCl]: 0.25 M, S/L ratio: 1.7%)

As expected from the literature, the solubilization of highly carbonated Nd (100% leached) from carbonated mechanically mixed Nd/Pr is higher than those of less carbonated Pr (48% leached). This contrast in leaching behavior can be attributed to the higher oxidation state of Pr<sub>6</sub>O<sub>11</sub> oxide. As previously reported by Fahrenholtz (2012), Pr<sub>6</sub>O<sub>11</sub> (Pr(III), Pr(IV)) is thermally stable and hydrates less readily than Pr<sub>2</sub>O<sub>3</sub> (Pr(IV)), while Nd<sub>2</sub>O<sub>3</sub> exhibits chemical reactivity comparable to that of Pr<sub>2</sub>O<sub>3</sub>. Partial dissolution of Pr may be explained by the presence of Pr<sub>2</sub>O<sub>3</sub>, which is soluble in slightly acidic conditions, within the initial Pr<sub>6</sub>O<sub>11</sub> starting material (Adachi & Imanaka, 1998). While the dissolution of Pr<sub>6</sub>O<sub>11</sub> itself is analogous to those of CeO<sub>2</sub> and requires, beyond acidic

conditions, the use of a reducing agent such as  $\text{H}_2\text{O}_2$  (Janoš et al., 2015). Overall, mechanically mixed oxides behaved almost identically as individual oxides, indicating minimal interaction between these oxides. Because  $\text{CO}_2$  injection of mechanically mixed Nd-/Pr-oxides induces partial Pr carbonation, it is not surprising that an increase in Pr solubilization efficiency, from 23 to 48% for blank vs carbonated mixed materials, is observed. This results in a diminution of the pre-separation efficiency of Nd and Pr. The mechanistic pathway by which  $\text{Pr}_6\text{O}_{11}$  is converted to  $\text{Pr}_2(\text{CO}_3)_3$ , potentially involving a reduction step of Pr(+IV) to Pr(+III) which had not been proposed by Yanagihara (1991), is not fully understood at this stage. Most critically, when Pr and Nd are co-precipitated, they both exhibit a similar solubilization efficiency (~57%) during HCl leaching, indicating the ineffective pre-separation of these elements, irrespective of a prior carbonation step or not. Therefore, the carbonation- HCl leaching approach, in the typical industrial sequence, would not result in an effective Nd/Pr separation.

## **4.2 Selective carbonation-HCl leaching for pre-separation of REEs from mechanically mixed REOs**

Mechanically mixed REOs represent another fairly simple system to examine the mechanisms involved in the carbonation-HCl leaching process. As previously mentioned, Yanagihara (1991) conducted experiments on individual REO powders, with some indications that the selective carbonation-HCl leaching process can be applied to mixed REOs. In the current research project, experiments were conducted at laboratory scale on two different mechanically mixed REOs: i) an equimolar REO mixture and ii) ore REO mixture, to assess if the initial composition of the REE-bearing materials can affect the selectivity and efficiency of this pre-separation process.

### **4.2.1 Mechanically mixed REO mixtures carbonation**

Mass variations for mechanically mixed REOs as presented in [Table 4-1](#) for both equimolar and REO ore mixture proportions. REO ore ratio mixture contains a high proportion of Ce, which belong to group B and is not expected to carbonate, indicating that for ore ratio mechanically mixed material, small mass variations are expected in comparison to equimolar mechanically mixed REOs, which contains higher proportions of REOs from group A (can be carbonated). The results showed a slight mass loss after 4 h of carbonation, which can probably result from material losses occurring during filtration. After 24 hours of carbonation, the mass gain observed for the REO ore mixture is quite low (< 1%), while for equimolar mixture, the mass gain is 28 times higher than for

REO ore mixture, which is consistent with the higher proportion of REOs from group A (i.e., La, Nd). However, considering that REOs from group A accounts for 60.3% of the total mass, the measured mass gain indicates an incomplete carbonation, since full carbonation of these elements should have resulted in a 22.5% mass increase. Furthermore, it was determined that even group B elements carbonate to some extent. It should be noted that for this series of experiments, no carbon measurements were taken for mechanical mixtures, carbonation results are limited to mass measurements. Within the previous framework of the performance of the carbonation-HCl leaching process, incomplete carbonation would be detrimental to REOs pre-separation efficiencies but should still enable selective leaching of REOs from group A, a hypothesis examined in the following sub-section.

Table 4-1: Evolution of mass changes observed during carbonation of mechanically mixed REO mixtures with time (CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration)

| REO mixture type               | Carbonation time (h) | Relative mass change (%) |
|--------------------------------|----------------------|--------------------------|
| REO ore representative mixture | 4                    | -3.63                    |
|                                | 24                   | 0.36                     |
| Equimolar mixture              | 4                    | -5.99                    |
|                                | 24                   | 10.72                    |

#### 4.2.2 Leaching of mechanically mixed REO mixtures

Leaching experiments were conducted on mechanically mixed REOs (equimolar and REO ore distribution) to evaluate if carbonation can enhance the selective dissolution of REOs from group A, while retaining REOs from group B in the solid phase (Figure 4-15). Results obtained from equimolar ratio showed that the REOs from group A exhibited efficient leaching (> 80% for most of them), while less than 10% of REOs from group B were solubilized (Figure 4-15a). In the case of Ce, which is present in high proportion in the REO ore ratio material, its solubilization is negligible (~0%). These results are consistent with the initial hypothesis that selective leaching can separate group A elements from group B elements with a difference between efficiencies of almost 60-80%.

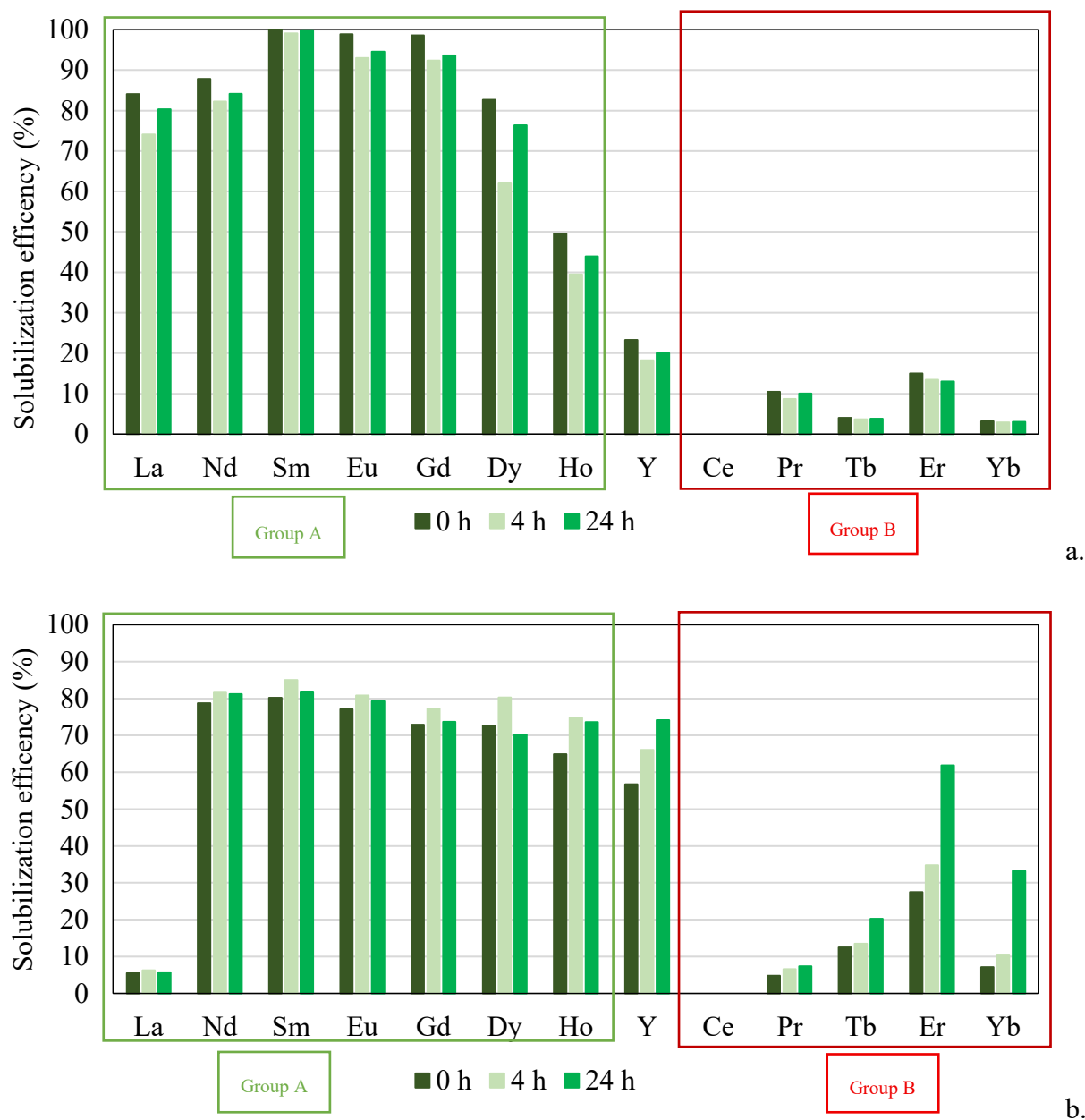


Figure 4-15: REE solubilization efficiency (%) from mechanically mixed REOs at equimolar (a.) and REO ore (b.) ratio (carbonation: CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration – HCl leaching: [HCl]: 0.25 M, S/L ratio: 1.7%, S/L separation: filtration)

However, contrary to expectations, it appeared that carbonation did not influence REOs leaching behavior from both equimolar and REO ore ratio materials. Indeed, comparable solubilization efficiencies were achieved with or without CO<sub>2</sub> injection. While different carbonation times (4 vs 24 h) did not lead to major improvements in the pre-separation of equimolar ratio REOs to

non-carbonated materials, small increases in the leaching efficiencies of group B REOs from REO ore ratio mixture can be seen with increasing carbonation time, especially for Er, Yb and to some extent Tb. For Pr, the results showed that when carbonated within REO mixture (equimolar or REO ore ratio), Pr exhibited lower solubilization efficiency (10%) than when carbonated in the presence of Nd only (20%). One possible approach to elucidate this behavior and its potential relationship with the oxidation state of Pr would be to repeat carbonation experiments while measuring ORP values to correlate redox conditions with Pr carbonation and subsequent leaching using HCl. Overall, carbonation of mechanically mixed REOs, for periods of up to 24 hours, regardless of the REO ratios used, did not appear to have a positive or important effect when attempting to selectively leach mechanically mixed REOs. Instead, the observed behaviour appeared to be quite similar to that of the non-carbonated oxides and remained consistent with the previously identified Group A and Group B patterns.

Concerning yttrium, which was not previously covered in Yanagihara (1991), its leaching behavior place it between REOs from group A and group B, although its average solubilization efficiency is closer to those obtained for REOs from group B than from group A. Lastly, for REOs from group A, it can be noticed that their solubilization efficiency seemed to increase from La up to Eu, and then decrease with atomic number, excluding Sm which behave as an outlier. In contrast, REOs from group B showed uniformly low solubilization efficiencies (<15%), with no clear tendency with their atomic number. The data does not allow confirmation of whether these trends simply reflect leaching kinetics, which could be linked to particle size, or chemical reactivity.

A different trend in the solubilization efficiencies of REOs from group A and group B can be observed for the REO ore's mechanically mixed material (Figure 4-15b) in comparison to equimolar mechanically mixed material (Figure 4-15a). One major difference is the leaching efficiency of La, which was 10 times lower for REO ore's ratio mechanically mixed material in comparison to the equimolar mechanically mixed material. This can be explained by the use of a co-precipitated Ce-La oxide for the selective carbonation-HCl leaching. According to Horlait (2012), REE which are co-precipitated with Ce tend to behave like Ce, especially when the mixture is mainly composed of Ce. Consistent with this observation, limited solubilization efficiency observed for La and Ce from REO ore mechanically mixed material can be explained by the tendency of La to behave similarly to Ce when they are co-precipitated. The results also showed that the pre-separation efficiencies of REOs from group A and B seemed to be less selective for

REO ore mixture in comparison to equimolar ratio, as the solubilization of REOs from group B seemed to be higher for REO ore ratio in comparison to equimolar ratio.

The mechanically mixed leaching tests here were performed by attempting to maintain a pH of 3. This does not work very well as many RECs and REOs are very reactive to acidic attack. As a result, the pH rapidly lowers to around 2 and then quickly jumps back up to around 5 even while adding slowly HCl (3 M). Maintaining a certain pH is therefore not a highly reliable method to leach REOs/RECs. The pH eventually stabilizes when acid is no longer consumed. These tests did, however, provide empirical evidence as to what concentration of initial HCl could be used to leach all acid sensitive REEs, which is around 0.25M and consistent with later findings.

### **4.3 Co-precipitated REO carbonation-HCl pre-separation**

After the acid baking/caustic cracking, leaching and purification stages, primary REE production results in a fairly pure solution of REEs to be either directly transferred to a SX separation plant or precipitated (as a carbonate for instance) for transportation as a solid. In this project, such mixtures were prepared by precipitation as oxalates followed by a calcination (Silva et al., 2019) and the co-precipitated REO powders were subjected to different experimental conditions, aimed at carbonation and selective leaching for pre-separation into Group A and Group B REEs.

#### **4.3.1 Carbonation of co-precipitated REOs**

Figure 4-16 presents the mass variation of the co-precipitated REOs (13 individual REOs leached and re-precipitated as co-precipitated REOs) during carbonation. Substantial relative mass losses were observed, from -0.51 to -20%, except for the pH 1 evaporated experiment where a small mass gain occurred, which can likely be ascribed to the fact that the pH was decreased using  $\text{HNO}_3$ , creating REE-nitrates with higher molar mass than the original REOs. As to the substantial mass losses seen for carbonation at pH 1 and filtered at pH 1, they may stem from dissolution of some REOs at these low pHs. Overall, mass change measurements do not suggest any appreciable degree of REO carbonation, which is in agreement with carbon measurements (Figure 4-17). Indeed, carbonation efficiency for 13 co-precipitated REOs, assessed using IR carbon/sulfur measurements showed that the carbonation extent, at less than 2%, is much smaller than for individual REOs seen previously. While variability appears high in relative terms, it is similar to previous carbonation results in absolute terms.

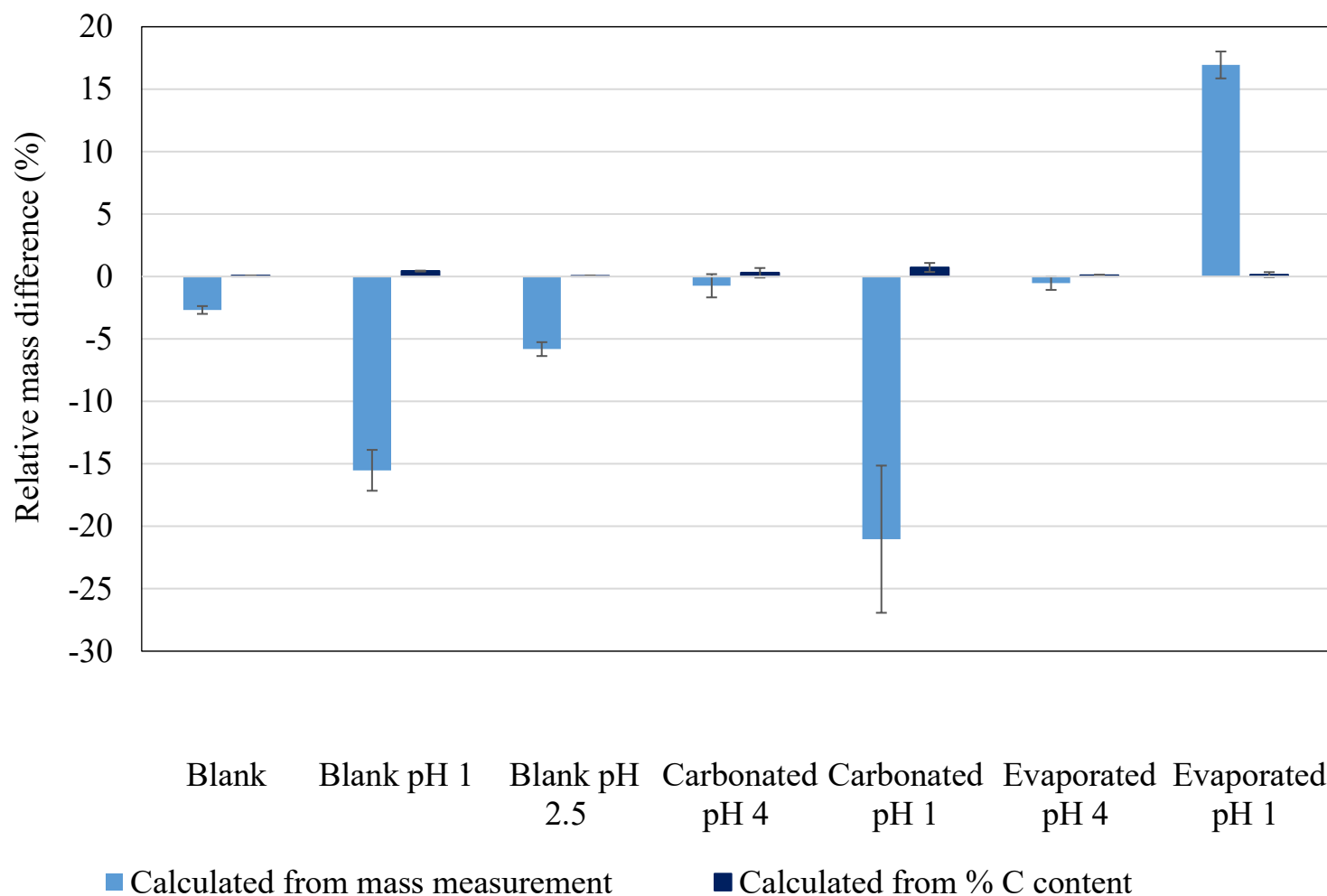


Figure 4-16: Co-precipitated REOs mass changes (%) (direct mass measurement vs calculated from % C content (CO<sub>2</sub> injection: 4 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration or evaporation) not carbonated unless stated)

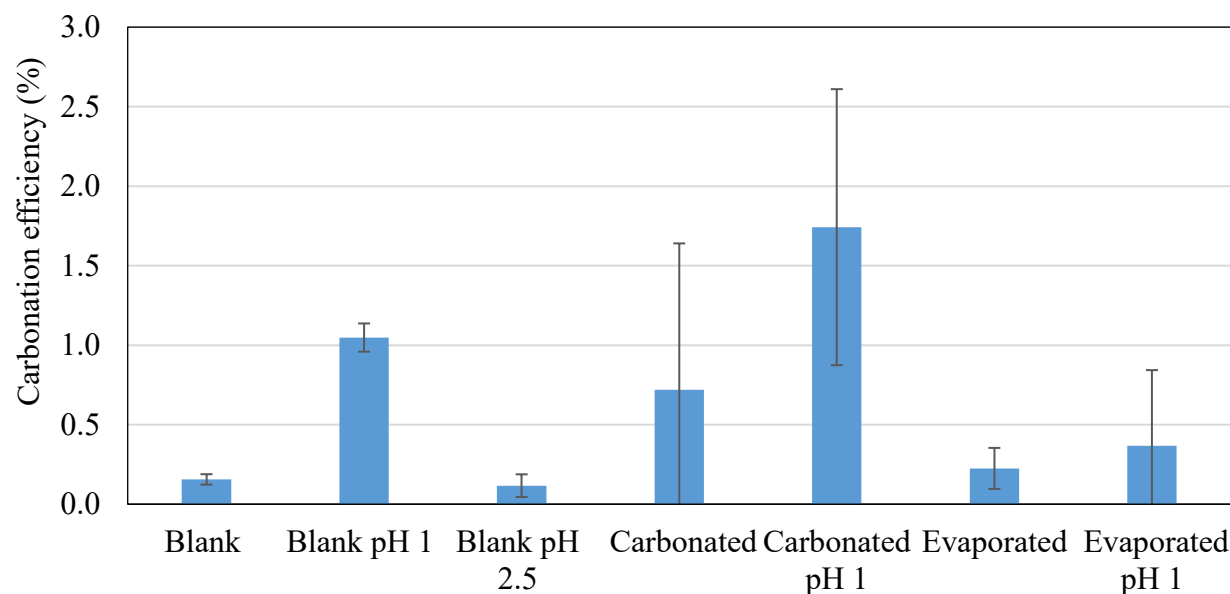


Figure 4-17: Carbonation efficiency for co-precipitated REOs under different conditions (CO<sub>2</sub> injection: 4 L/min for 24 h (when applicable), S/L ratio: 4%, S/L separation: filtration & evaporation)

Overall, it is hard to say whether carbonation occurred at all for any of these carbonation conditions. Carbonation tests conducted at pH 1 and filtered at pH 1 (which has no CO<sub>2</sub> injection) indicate ~1% carbonation efficiency. Preliminary supercritical carbonation experiments were performed on one set of co-precipitated oxides and no mass gain was observed. This again suggests that co-precipitated oxides seemed to not carbonate, regardless of the pressure of CO<sub>2</sub> injection.

#### 4.3.2 Leaching of co-precipitated REOs without any pre-treatment (no carbonation)

This sub-section first reports HCl leaching experiments performed on raw (untreated or blank) co-precipitated REOs, without any intermediary carbonation process. These experiments established a baseline for assessing the leachability of the co-precipitated oxides under mildly acidic conditions. At an HCl concentration of 0.25 M, Figure 4-18 shows that most were simultaneously leached, with solubilization efficiencies ranging from 82 to 94% and Ce exhibiting slightly lower solubilization (76%), leading to a low pre-separation efficiency (< 15%). In comparison to the co-precipitated Nd/Pr mixture (shown in red in Figure 4-18), the leaching

behavior of co-precipitated REOs is quite similar, indicating that co-precipitated materials exhibit similar leaching efficiencies with minimal pre-separation, as in works of others (Horlait et al., 2012). Therefore, the current study tends to suggest that the selective leaching of carbonated REOs is not possible in the absence of a selective pre-treatment, as expected with carbonation pre-treatment.

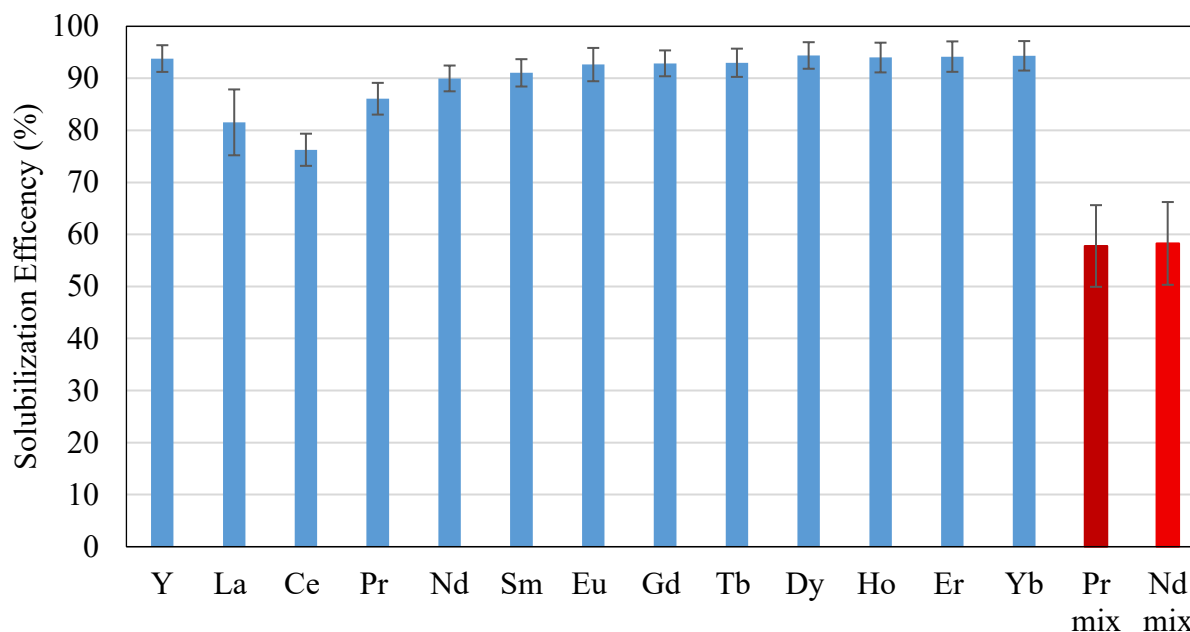


Figure 4-18: Solubilization efficiency (%) of co-precipitated REOs (blue) and Nd-/Pr-oxides (red) (no carbonation – HCl leaching: [HCl]: 0.25 M, S/L ratio: 1.7% (w/v), solid/liquid separation: filtration)

### **Effect of HCl concentration on selective leaching of co-precipitated REOs**

Different HCl concentrations were also tested to determine its effect on the leaching efficiency and selectivity towards individual REEs. Leaching tests were initially carried out with HCl solution with concentrations in the range of 0.01 M to 12 M as seen in [Figure 4-19](#). Results showed that a concentration range of interest emerged between 0.1 and 1 M HCl, where some selectivity against Ce seemed to appear, while no notable pre-separation of other REEs was observed for the conditions tested. At around 0.1 M HCl, there is around 10% separation efficiency between Ce and

all other REEs. Outside this range, all REEs, including Ce, were leached with very similar efficiencies, with an increasing dissolution as acid concentration increases.

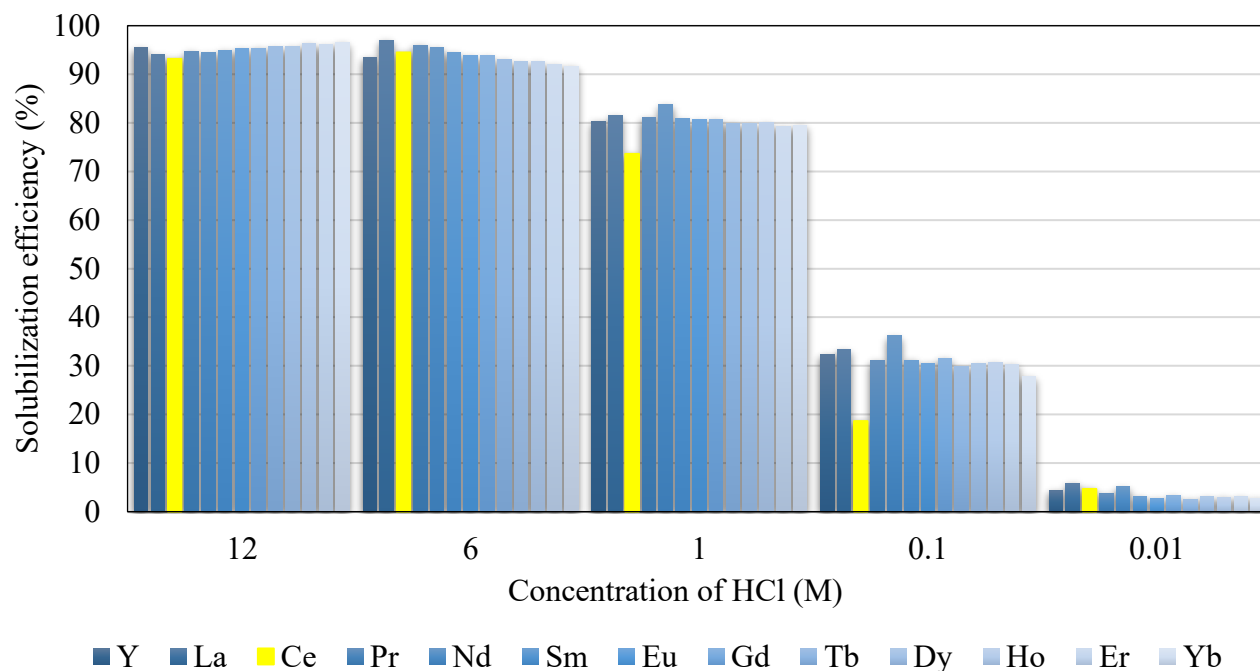


Figure 4-19: Solubilization efficiency (%) of each REEs from co-precipitated REOs at different HCl concentrations (no carbonation – HCl leaching: [HCl]: 0.01-12 M, S/L ratio: 1.7% (w/v), solid/liquid separation: filtration)

As shown in [Figure 4-20](#), additional leaching experiments conducted at HCl concentrations ranging from 0.1 to 1 M did not appear to result in a substantial improvement in REE pre-separation efficiencies when compared to 0.1 M HCl. An HCl concentration of 0.25 M was selected for further leaching experiments for two reasons: i) this concentration is within the range of 0.1 and 1 M for which Ce pre-separation seemed to occur at limited efficiencies ([Figure 4-20](#)) and ii) it enables comparison with previous leaching experiments conducted on mechanically mixed REOs.

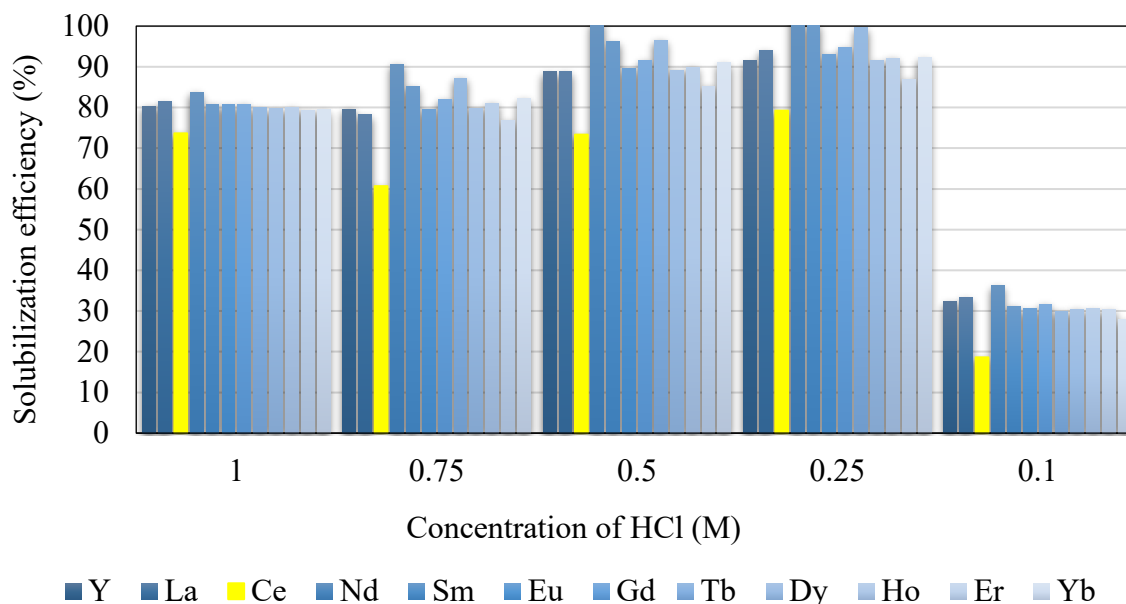


Figure 4-20: Solubilization efficiency (%) of co-precipitated REOs at different HCl concentrations between 0.1 and 1 M HCl (no carbonation – HCl leaching: [HCl]: 0.1-1 M, S/L ratio : 1.7% (w/v), solid/liquid separation: filtration)

### **Effect of the absence of cerium**

Given the partial separation of Ce and its reported ability to influence the behavior of co-precipitated REOs, additional leaching experiments were conducted to assess the effect of Ce removal. As shown in [Figure 4-21](#), in the absence of Ce, all REEs continue to dissolve simultaneously and to the same extent, decreasing the potential for their pre-separation. These results indicated that Ce did not seem to affect the leaching behavior of the other REEs. Nor does the presence of cerium lead to a significant increase in the stability/leachability of REOs, as suggested by some studies (Horlait et al., 2012). XRD analysis would be a valuable tool in assessing whether crystallographic structure, which influences stability, changes between the Ce-free and Ce-bearing REOs (Silva et al., 2019).

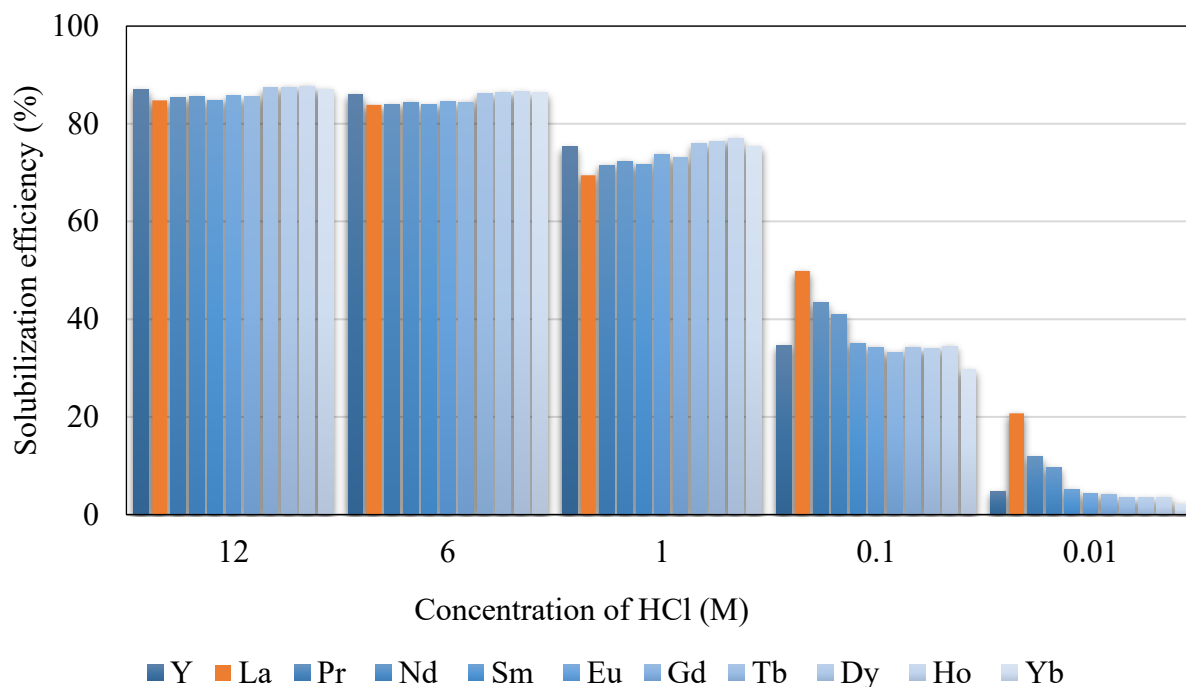


Figure 4-21: Solubilization efficiency (%) of co-precipitated REOs without Ce at different HCl concentrations (no carbonation – HCl leaching: [HCl]: 0.01-12 M, S/L ratio: 1.7% (w/v), solid/liquid separation: filtration)

### 4.3.3 Leaching of carbonated and filtered co-precipitated REOs

#### Acidification-filtration experiments

Filtration experiments were designed to determine whether the filtration step and surrounding operations occurring during the carbonation procedure, rather than carbonation itself, as well as presence of  $\text{HNO}_3$ , can be responsible of changes in Ce oxidation states and therefore influence leaching behavior. To test this, REOs were mixed with water or slightly acidic solutions for 24 h and filtered, prior to HCl leaching using the previously established conditions. As shown in [Figure 4-22](#), the highest Ce/other REEs separation efficiency is achieved for experiment conducted with filtration at pH 1, with a separation efficiency ( $\Delta = \text{Ce leaching} - \text{other REEs leached}$ ) of less than 5%, meaning that filtration, whether or not it is preceded by an acidification to pH 2.5 or 1, offers no significant enhancement for the pre-separation of Ce from other REEs from co-precipitated REOs.

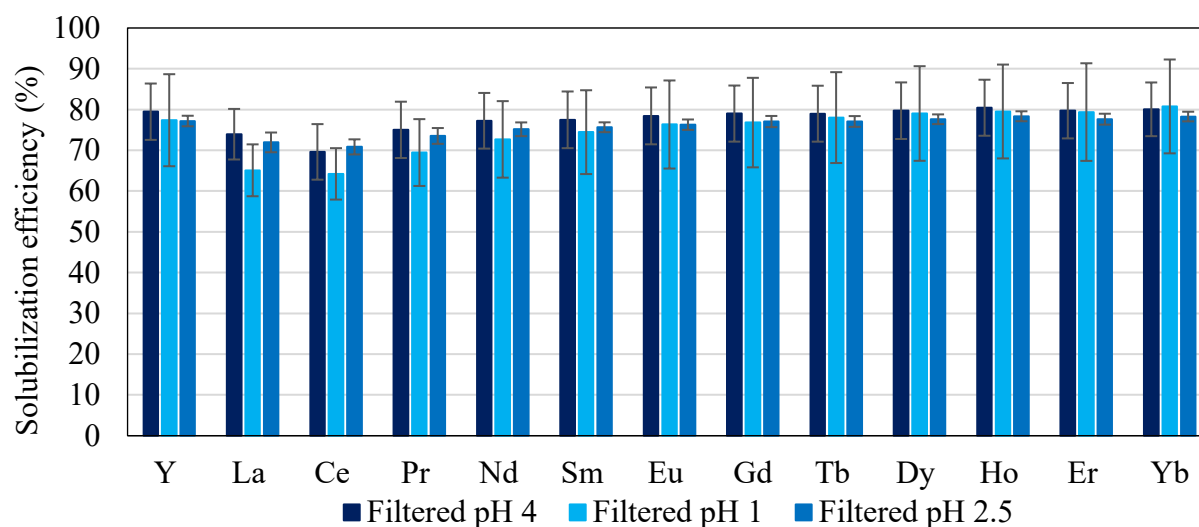


Figure 4-22: Effect of pH of filtration on the solubilization efficiency (%) of REEs from co-precipitated REOs (no carbonation – HCl leaching: [HCl]: 0.25 M, S/L ratio: 1.7% (w/v), solid/liquid separation: filtration)

### **Effect of HCl concentration**

Leaching experiments were also conducted on carbonated REOs using different HCl concentrations within the previously identified range of interest (0.1–1 M). As shown in [Figure 4-23](#), some pre-separation of Ce appeared to occur, with the highest separation efficiency of ~30% at 0.1 M HCl. This pre-separation efficiency is slightly better compared to non-carbonated materials, which might be explained by the limited dissolution of Ce following CO<sub>2</sub> injection as previously reported. The explanation behind this observation is not yet clear but may be related to further oxidation of the Ce present, CeO<sub>2</sub> being notably more difficult to solubilize than most REOs (Horlait et al., 2012).

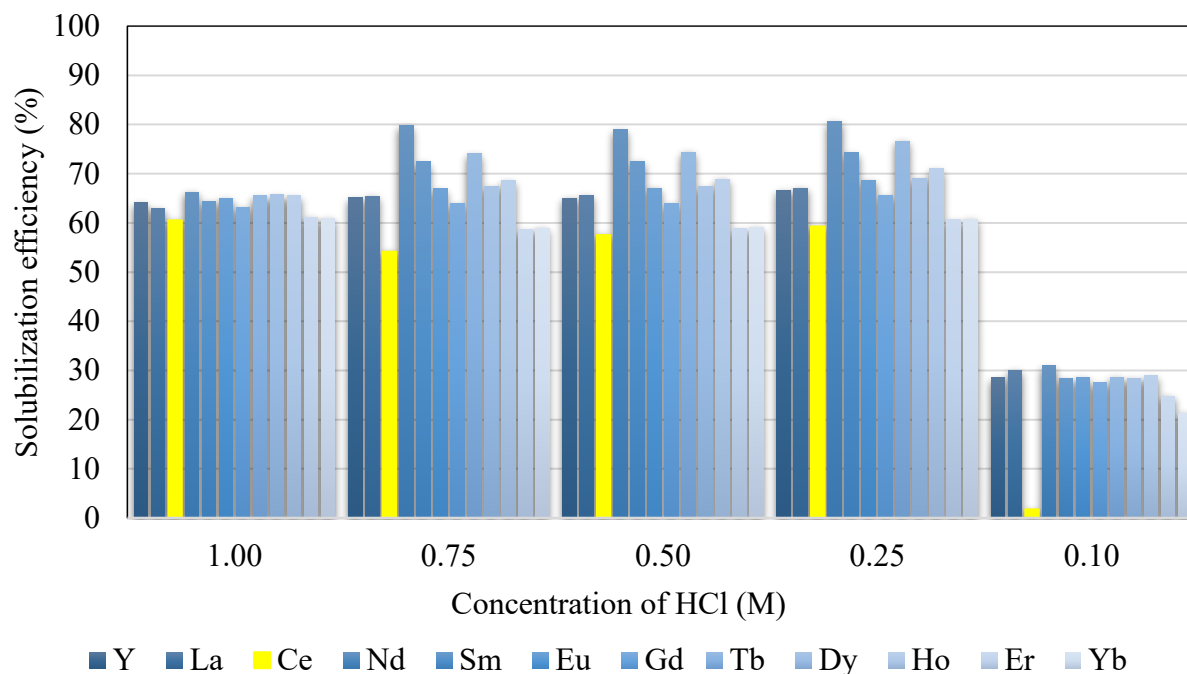


Figure 4-23: Solubilization efficiency (%) of co-precipitated REOs with natural pH carbonation (carbonation: CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation : filtration – HCl leaching: [HCl]: 0.1-1M, S/L ratio: 1.7% (w/v), solid/liquid separation: filtration)

As mentioned previously, at an HCl concentration of 0.1 M, the amount of acid is insufficient to fully dissolve all the REEs present under the conditions tested. This limitation potentially contributes to the preferential retention of Ce in the solid phase, which is more difficult to leach compared to other REOs. While, this selective behavior is of interest, acid-limited leaching constrained overall REE recoveries, resulting in moderate pre-separation efficiencies. Additional research work is required to further investigate lower S/L ratio to ensure that there will be enough acid while maintain HCl concentration between 0.1 and 0.25 M. Overall, carbonation of co-precipitated REOs enabled only limited pre-separation of Ce from the other REEs, with a maximum separation efficiency of approximately 30 % at 0.1 M HCl. As the selective separation of Ce remains a critical challenge in REE processing, as highlighted in previous studies, these results remain of interest.

### Effect of acidification during carbonation

Figure 4-24 presents the results of the HCl leach tests performed on co-precipitated REOs after mixing with CO<sub>2</sub> saturated water at various pH values, the pH being adjusted using HNO<sub>3</sub>. The main objective of acidic carbonation was to attempt to break down the co-precipitated REO molecular structure and allow formation of REE-carbonates. The results showed that even when carbonation is performed before HCl leaching, all the co-precipitated elements tend to be leached simultaneously. Whether carbonating at natural pH (~4), at pH 2.5 or at pH 1, a pre-separation of Ce/REEs efficiency of around 5% is observed, which is quite low compared to other Ce separation processes (Papangelakis, 2021). It was hypothesized that the use of HNO<sub>3</sub>, a known oxidizing agent, promoted Ce oxidation (from +3 to +4) and its stabilization in solid form in subsequent HCl leaching. This did not seem to occur during the acidic carbonation/filtration tests. It should be noted that carbonates are not likely to form at pH 1, as they would likely dissolve back into solution. Carbonation and filtration tests would therefore cause a certain loss of REEs during filtration.

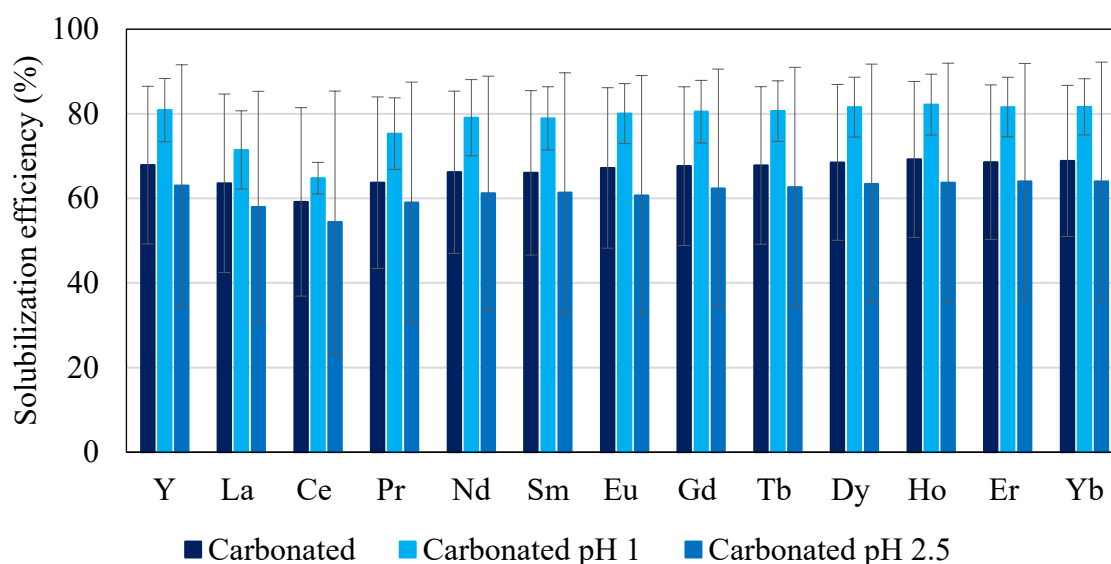


Figure 4-24: Solubilization efficiency (%) of carbonated and acidic carbonated co-precipitated REOs (carbonation: CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration – HCl leaching: [HCl]: 0.25 M, S/L ratio : 1.7% (w/v), solid/liquid separation: filtration)

### Effect of the absence of cerium

The effect of Ce on the leaching efficiencies of REEs from carbonated co-precipitated REOs was also evaluated (Figure 4-25). Results showed that the solubilization of La seemed to be improved for an HCl concentration of 0.1 M in comparison to other REEs, with around +10% difference of leaching efficiencies between these elements. Nevertheless, the resulting La/REE pre-separation efficiency remains quite limited and does not appear to warrant further investigation.

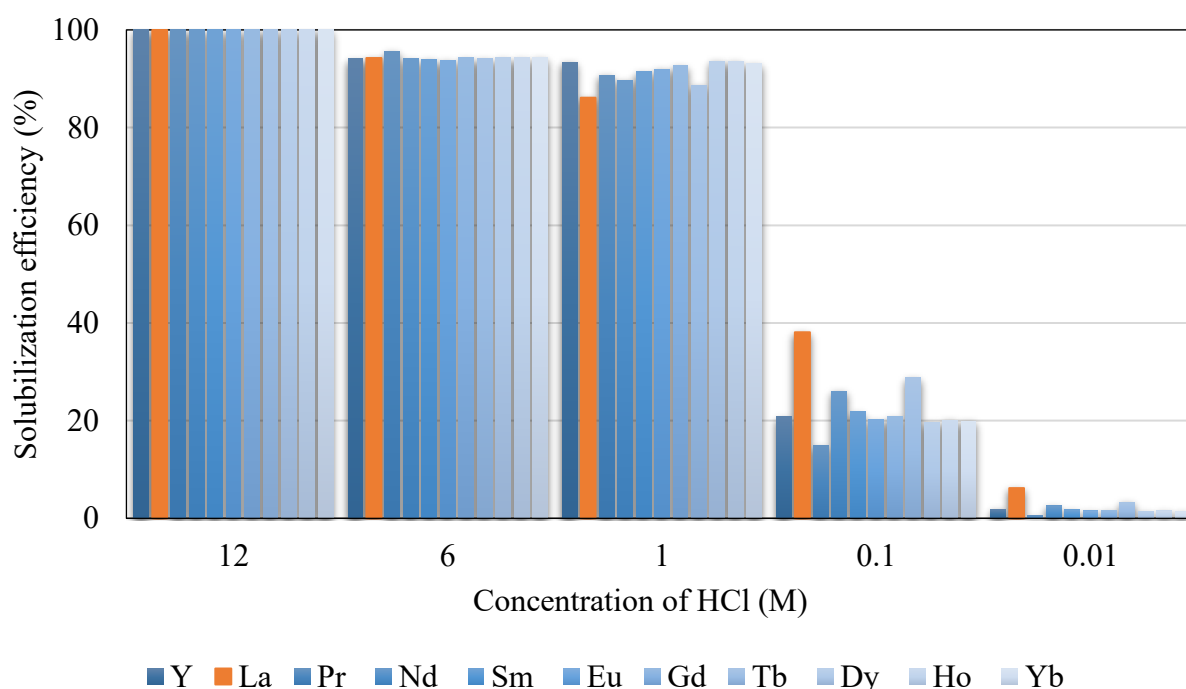


Figure 4-25: Solubilization efficiency (%) of carbonated co-precipitated REOs with no Ce (carbonation: CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation : filtration – HCl leaching: [HCl]: 0.01-12 M, S/L ratio: 1,7% (w/v), solid/liquid separation: filtration)

#### 4.3.4 Leaching of carbonated co-precipitated REOs separated by evaporation

In this section, the solid/liquid separation step conventionally performed by filtration was replaced by evaporation in an oven at 50°C for 24 h. This methodological approach was used for two objectives: i) to enhance mass balance accuracy by minimizing material losses associated with filtration and ii) to assess the effect of Ce oxidation potentially occurring during drying on its different behavior compared to other REEs towards carbonation and selective HCl leaching.

### Effect of pH before evaporation

Three experiments were conducted to evaluate the effect of the evaporation on non-carbonated and carbonated co-precipitated REOs on the leaching behavior of co-precipitated REOs using evaporation for S/L separation instead of filtration. The sample “Evaporated normally” refers to mixing co-precipitated REOs with water for 24 h before evaporating the liquid, while “Evaporated at pH 1” means mixing the co-precipitated REOs in a solution of pH 1, adjusted using  $\text{HNO}_3$ , for 24 h before evaporating. Finally, “Carbonated at pH 1 + evaporated” refers to mixing REO in an initial solution is at pH 1, injecting  $\text{CO}_2$  for 24 h before evaporating the solution. As presented in Figure 4-26, co-precipitated REOs again showed simultaneous leaching behavior to similar extent, indicating limited pre-separation efficiencies between REOs, regardless of pH before evaporation or of  $\text{CO}_2$  injection. Consistently with previous experiments using filtration for S/L separation, a lower solubilization efficiency of Ce in comparison to other REOs was observed. It also appeared that evaporation under normal conditions ( $\text{CO}_2$  injection at pH 4) led to the lowest leaching recoveries, while evaporation at pH 1 seemed to be more efficient. This trend may be attributed to the formation of REE-nitrates under acidic conditions, which are significantly more soluble than the corresponding co-precipitated REOs.

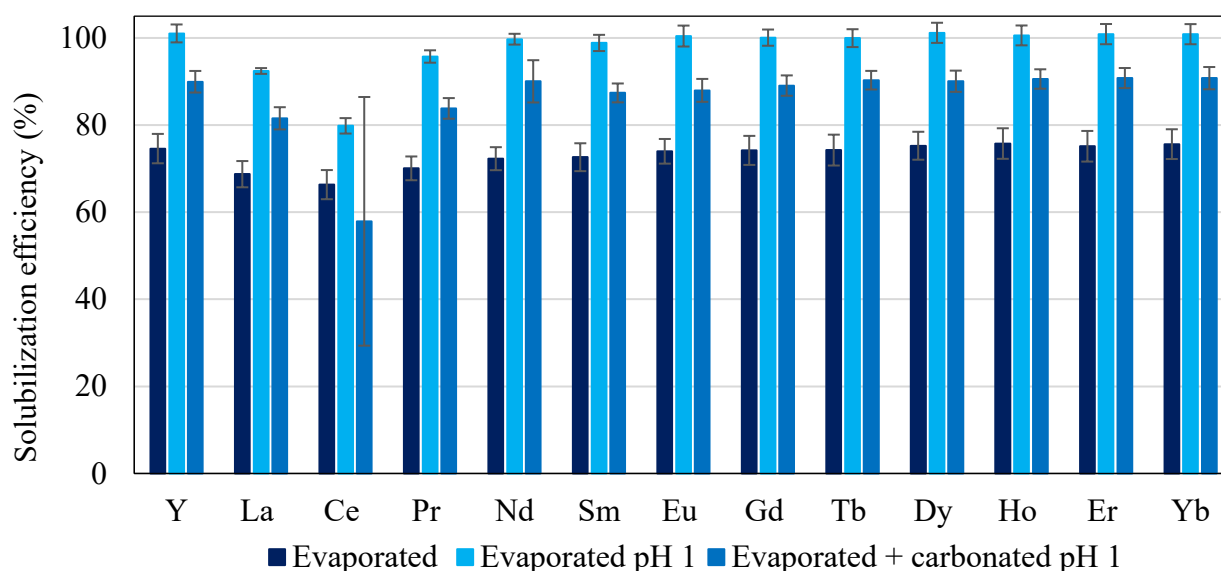


Figure 4-26: Solubilization efficiency (%) of REEs from co-precipitated REOs with or without  $\text{CO}_2$  injection (4 L/min) (mixing: 24 h, at pH 1 or pH 4 (“normal”), S/L separation: evaporation – HCl leaching:  $[\text{HCl}]$ : 0.25 M, S/L ratio: 1.7% (w/v), solid/liquid separation: filtration)

### Effect of HCl concentration after evaporation

Figure 4-27 presents the leaching efficiencies for different HCl concentrations used during the leaching step after carbonation followed by evaporation. At 0.1 M HCl, a distinct leaching behavior of REE is observed: all REEs were solubilized with leaching efficiencies around 40%, while all Ce remained in the solid phase, highlighting interesting pre-separation of Ce from other co-precipitated REOs using CO<sub>2</sub> injection and evaporation prior to HCl leaching. As in previous experiments, the amount of acid at this concentration seemed to be insufficient to fully dissolved all potentially leachable REEs, suggesting that higher separation efficiencies can be achievable by decreasing the S/L ratio. Compared with carbonation at pH 1 with filtration, the carbonation-evaporation sequence improved the pre-separation of Ce from other co-precipitated REOs, indicating that the evaporation-related actions play a role in the pre-separation process. This effect may be attributed to the concentration effect of HNO<sub>3</sub> (used to adjust the pH) occurring during the evaporation of the acidic solution and leading to the oxidation of highly soluble Ce(III) to less soluble Ce(IV).

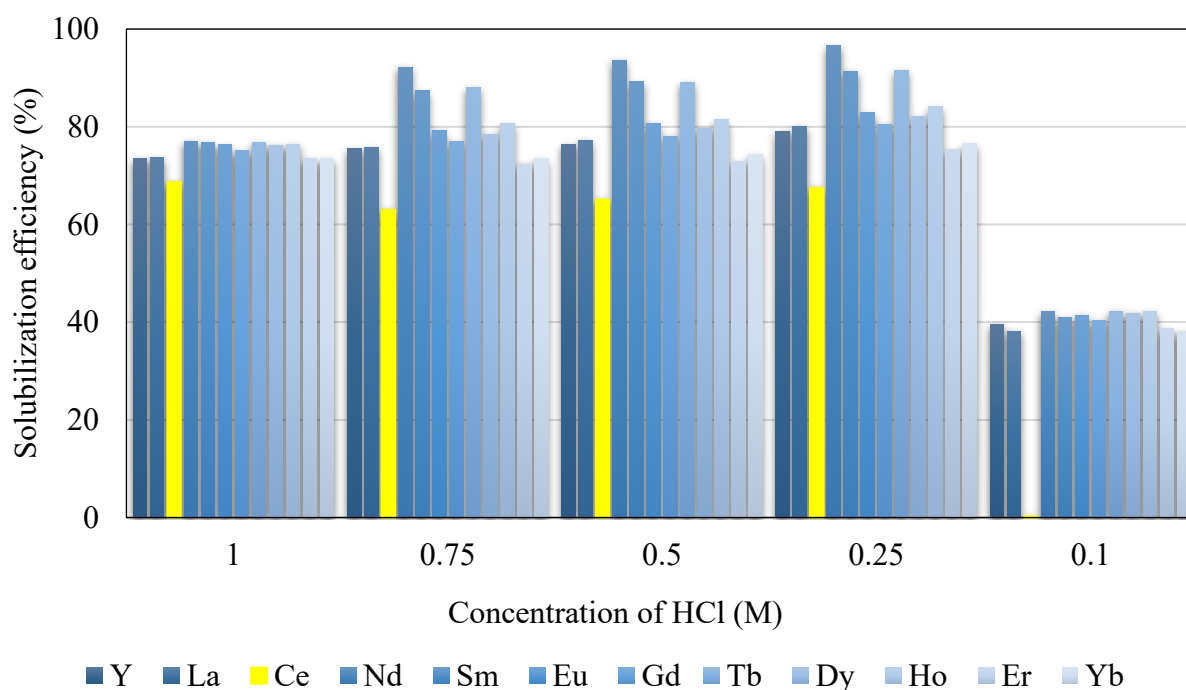


Figure 4-27: Solubilization efficiency (%) of REEs from co-precipitated REOs with carbonation at pH 1 + evaporation (CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: evaporation – HCl leaching: [HCl]: 0.25 M, S/L ratio: 1.7%, S/L separation: filtration)

In summary, despite extensive investigation across a wide range of carbonation and HCl leaching conditions, co-precipitation REOs were not effectively pre-separated between Group A and Group B elements. Instead, all REEs tend to leach coherently, with the exception of Ce which remains insoluble, with explanations for most of the observations.

#### 4.4 Co-Precipitated REOHs Pre-Separation Tests

As previously mentioned, REOHs were described by Yanagihara et al.(1991) as behaving similarly to REOs in carbonation-leaching experiments. This section describes the REEs pre-separation efficiencies for experiments conducted on co-precipitated REOHs to test their behaviour and validate whether the previous observation of Ce pre-separation potential may be different from that using REOs.

##### 4.4.1 Pre-Leach Behavior

Before examining leaching behavior of co-precipitated REOHs during HCl leaching, the behavior that occurs during REOH carbonation, which is represented in [Figure 4-28](#), details how much each REE was solubilized during CO<sub>2</sub> injection.

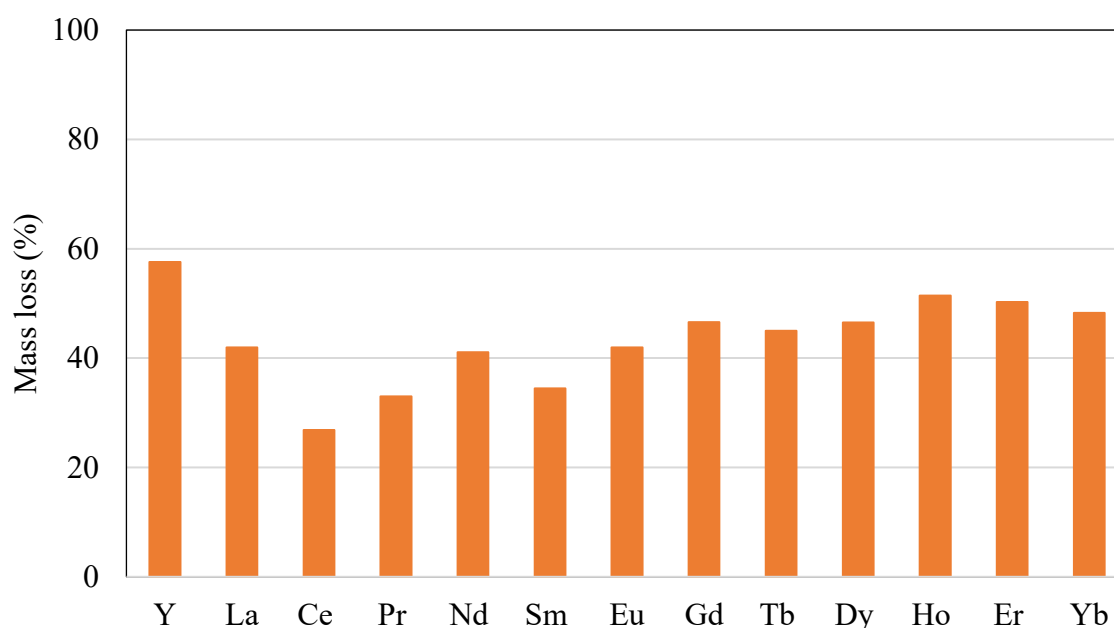


Figure 4-28: Mass loss (%) by element during REOH carbonation CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration)

Results showed that, as the process of carbonation is conducted under saturation of the solution with CO<sub>2</sub>, the solution had a slightly acidic pH approaching 4.0, which appears sufficient to dissolve some of the REOHs present during carbonation, as 27–58% of the various REOHs were solubilized during CO<sub>2</sub> injection. This is consistent with the general assertion that REOHs are easier to leach than REOs (Goode, 2019). The carbon measured after carbonation is significant at 2.5% C, indicating a 33.0% carbonation of the REOHs left in the solid phase. Some small degree of pre-separation occurs between Ce and other REEs. CO<sub>2</sub> injection could also be used to leach REOHs in a more environmentally friendly manner, without introducing counter ions such as sulfates, chlorides or nitrates. The leaching of REOHs during carbonation greatly limits the viability of the carbonation-HCl leaching for the pre-separation of REOHs, as close to 50% REEs losses would be highly impractical for industrial usage.

#### **4.4.2 Effect of HCl concentration**

The post-CO<sub>2</sub> REOH leaching experiments, as seen in [Figure 4-29](#), followed a similar trend to the leaching experiments conducted on co-precipitated REOs, with Ce leaching to a smaller extent than other REEs, achieving a maximum pre-separation efficiency of around 30% at 0.1 M HCl, comparable to that obtained previously. However, considering the substantial mass loss that occurred during the carbonation process, it does not appear to be worth pursuing selective REOH leaching as a pre-separation technique, except maybe for cerium. Future leaching experiments could be performed on REOHs without carbonation to examine their behavior as. Pure REOHs, not subjected to carbonation, avoid the unintended REE mass loss.

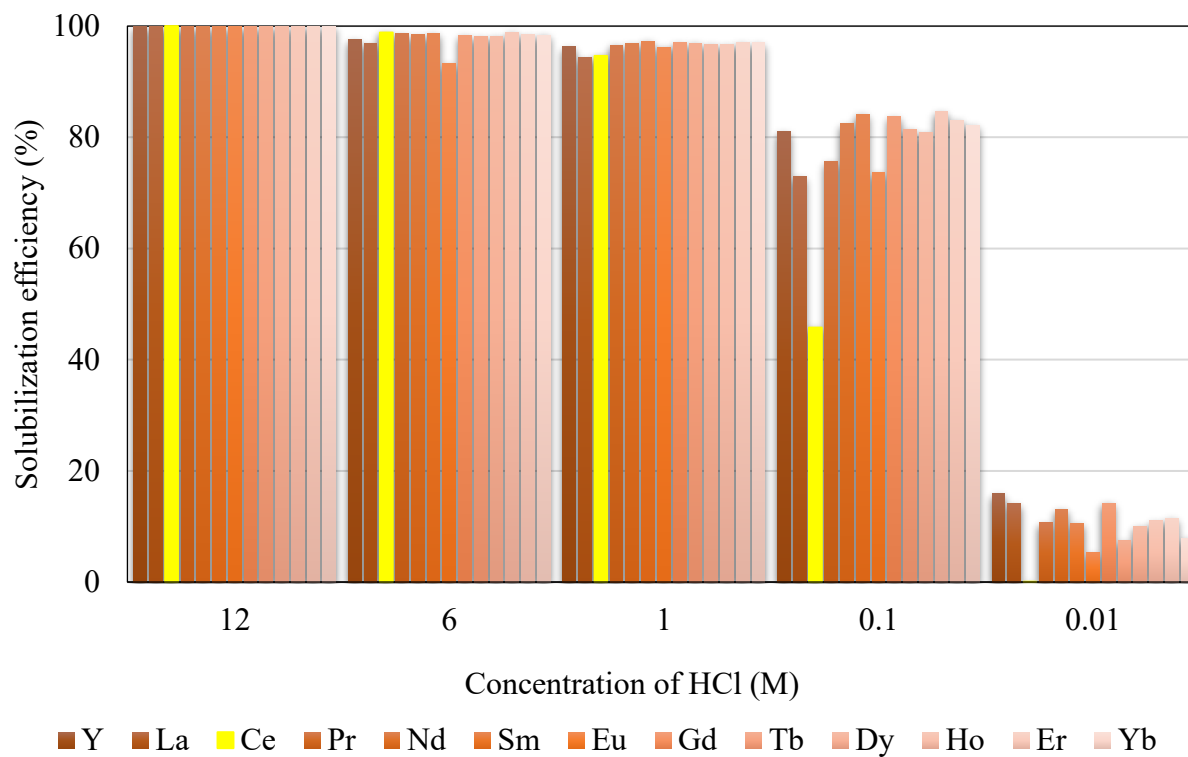


Figure 4-29: Solubilization efficiency (%) of REEs from co-precipitated REOHs with carbonation (CO<sub>2</sub> injection: 2 L/min for 24 h, S/L ratio: 4%, S/L separation: filtration – HCl leaching: [HCl]: 0.25 M, S/L ratio: 1.7%, S/L separation: filtration)

## CHAPTER 5 CONCLUSIONS AND FUTURE WORK

The objective of this thesis was to explore REO carbonation and subsequent selective HCl leaching as a potential pre-separation technique for REEs. First, experiments were conducted on Nd-/Pr-oxides materials, followed by mechanically mixed REOs, co-precipitated REOs and co-precipitated REOHs to better understand how the nature of REE-bearing materials can affect the performance of the carbonation-HCl leaching to pre-separate REEs.

Carbonation of individual or mechanically mixed REOs via CO<sub>2</sub> injection achieved up to 90% carbonation efficiencies for some individual REOs, namely neodymium, and with presumed high carbonation yields for other group A REOs such as lanthanum or europium. This was evidenced by IR carbon measurements, as well as mass gain and crystal formation assessed using SEM analysis (for experiments performed with Nd and Pr only). Group B REOs such as praseodymium, submitted to the same conditions, tend to carbonate to a lesser extent (<20%) and at a much slower rate. However, the major limitation of this approach as a separation method is that carbonation only happens to a notable extent when REOs are in used as individual or mechanically mixed powders. Indeed, the carbonation process seemed to be ineffective (<5%) under the conditions tested for co-precipitated REOs, thereby limiting the applicability of this pre-separation process at industrial scale. The selective leaching step also followed a similar pattern, showing that carbonated (or not carbonated) Nd-/Pr-oxides or mechanically mixed REOs could be separated via selectively HCl leaching (> 80% for REOs from group A vs. < 20-30% for REOs from group B), whereas co-precipitated REOs only allowed for around a 30% separation of Ce in comparison to other REOs. Different operating conditions were tested to determine if this pre-separation efficiency of Ce from other REOs can be improved. The effects of the pH of carbonation (1.0 - 2.5 - 4.0), CO<sub>2</sub> injection time (0, 4 or 24 h) or HCl concentration (from 0.1 to 12 M) had limited impact on the pre-separation efficiency of Ce from REOs. A leaching concentration of 0.1 M yielded the best results for selective Ce removal with a separation efficiency of around 30%. The replacement of filtration by evaporation to recover carbonated materials from the pulp after 24 h of CO<sub>2</sub> injection seemed to improve the pre-separation of Ce from other REEs when the carbonation was performed at pH 1 using HNO<sub>3</sub> to adjust the pH. Carbonation at pH 1 combined with evaporation and a leaching concentration of 0.1 M yielded the best results for Ce separation, around 40% efficiency. This approaches the best industrial method for Ce with a separation efficiency of around 60%

(Papangelakis, 2021). This trend can potentially be explained by the concentration of the acid occurring during the evaporation of the acidic solution, leading to the oxidation of highly soluble Ce(III) to less soluble Ce(IV). Despite extensive investigation across a wide range of carbonation and HCl leaching conditions, co-precipitation REOs were not effectively pre-separated between Group A and Group B elements. Instead, all REEs tend to leach coherently, with the exception of Ce which remains insoluble, with explanations for most of the observations.

Carbonating REOHs proved inefficient for the pre-separation of REOs as an important mass of the material was lost during the injection of CO<sub>2</sub>, which was explained by the solubilization of 27-58% of the various REOHs under the slightly acidic pH of CO<sub>2</sub> saturated water. The carbon measured after carbonation is significant at 2.5% C, indicating a 33.0% carbonation of the REOHs left in the solid phase. Some small degree of pre-separation occurred between Ce and other REEs.

This research project highlighted the challenges associated with the pre-separation of co-precipitated REOs as the tendency of REOs from group A to carbonate is different than for individual REOs or mechanically mixed REOs as previously evidenced by Yanagihara (1991). Further experiments would be required to:

- Understand the role of Ce oxidation state (and other group B REOs) in the structure and stability of various REOs (i.e., Eu, Pr) and their tendency to be carbonated;
- Evaluate the effect of ORP conditions on the pre-separation of REOs or REOHs using CO<sub>2</sub> injection-evaporation-HCl leaching;
- Investigate the potential to improve the pre-separation of Ce using CO<sub>2</sub> injection-evaporation-HCl leaching and the effect of operating conditions (i.e., nature and concentration of the inorganic acid during the leaching step and the concentration of acid during the leaching step).
- Further investigate co-precipitated and mechanically mixed materials using XRD to observe RECs formation and other types of crystals.

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