

Aqueous Electrochemical Processing of Rare Earth Elements—A Review

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1. Introduction

Rare earth elements (REEs) are employed in metal alloys, rechargeable batteries, automotive catalysts, ceramics, cracking catalysts, polishing powders, permanent magnets, lighting displays, laser and wavelength amplifiers, military defense applications and agricultural applications (Schüler *et al.*, 2011; Bünzli, 2013; Song, Chang and Pecht, 2013; Riba *et al.*, 2016; Zhang, Kleit and Nieto, 2017).

As the world moves towards more environmentally benign chemical processing, factors such as waste prevention, reduction in the use of hazardous chemicals, energy efficiency, and the use of safer solvents are goals (Suresh and Sundaramoorthy, 2015). Electrochemical methods, which can leverage renewable power sourced from carbon free energy sources, are gaining interest as paths to reducing environmental impacts of chemical processes. Metallurgical processes are one of those industrial sectors where electrochemical technologies can have significant impact (Su, 2020). For REEs, aqueous electrochemistry is challenged by the stability of the trivalent oxidation state. For example, the reduction potential of REEs to the metallic state are reported to be over -2.4 V vs the standard hydrogen electrode (SHE) potential which is more negative than that of water (Pourbaix, 1974). In early work, Denis and Lemon investigated the direct electrolysis of REEs in low concentration nitric acid solutions at a Pt electrode where the formation of REE hydroxides at the cathode surface was observed, a consequence of the hydrogen evolution reaction (HER) (Dennis and Lemon, 1915). This limitation has led most work in REE electrochemistry to be performed using either molten salt or ionic liquid-based electrolytes due to a much wider window of electrochemical stability at negative (reducing) potentials (Arenas, De León and Walsh, 2016).

Despite the limitations of water, there is a long and rich history in electrochemically processing REEs from aqueous solutions. Work has taken advantage of metal alloying via liquid metal cathodes (LMC) to shift REE reduction potentials into the stability window for water. Other methods have been developed to dissolve alloys from NdFeB magnets. Finally, some REEs such as Ce and Eu, have redox potentials in the stability window of water, a phenomenon associated with the Ce-Eu anomaly which allows for facile separation (Cicconi *et al.*, 2021).

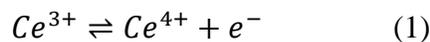
This chapter is a comprehensive review of various technologies and methods related to the separation and extraction of REEs at low temperatures (<100 °C). Addressed are various topics such as Redox-based processing, Liquid Metal Cathode studies, and Electrochemistry-driven REE Magnet Dissolution and Recovery. The chapter begins with an introduction to REEs, their importance in technology and the need for a more sustainable process for REE separation and capture. The second section addresses the Redox-based processing techniques for Ce and Eu separation and details the Eu and Ce anomaly which allow them to be extracted from aqueous REEs unlike the other REEs. The third section focuses on LMC studies using mercury (Hg) where REEs were extracted through electrolytic reduction or galvanic displacement. This section includes early work done prior to 1950, work done at Los Alamos National Laboratory and in the Former Soviet Union. The section also summarizes possible replacements for Hg. The thermodynamics for amalgam formation are also discussed. The fourth section covers electrochemistry driven REE magnet dissolution and recovery. This section discusses dissolution of REE magnets to separate elements such as iron followed by REE precipitation. The final section provides perspective discussing the challenges and future directions in this field.

2. Redox Based Processing

The negative reduction potentials of REEs from the trivalent to the metallic state favors HER over metal reduction in aqueous solution (Abbott and McKenzie, 2006). However, REEs such as Ce and Eu have redox couples, Ce^{IV+}/Ce^{III+} and Eu^{II+}/Eu^{III+} , that permit their separation from other aqueous REEs (Vickery, 1948, 1950; Kronholm, Anderson and Taylor, 2013; Cicconi *et al.*, 2021). This is useful as the separation of aqueous REEs in their trivalent oxidation state are challenging due to their similar chemical properties (Castor and Hedrick, 2006). As an example, Ce(III) is soluble while Ce(IV) precipitates to insoluble CeO_2 in aqueous solution at oxidative potentials (Arenas, De León and Walsh, 2016). Cicconi *et al.* provides an in-depth review on the redox behavior of Eu and Ce and the characteristics that lead to their atypical behavior (Cicconi *et al.*, 2021).

2.1. Cerium (Ce) Processing from REEs

With a standard potential of 1.72 V vs reversible hydrogen electrode (RHE), Ce^{IV+}/Ce^{III+} falls within the potential window of common aqueous electrolytes (Zhao *et al.*, 2019). Furthermore, the strong relationship between the redox couple of Ce and ligand coordination, as well as composition of the electrolyte, permits the adjustment of anionic species or electrolyte composition to enhance electrochemical efficiency (Zhao *et al.*, 2019). The popularity of Ce arises from its diverse applications, abundance, and low cost (Patnaik, 2003; Vasudevan *et al.*, 2005). Equation 1 shows the electrochemical oxidation reaction of Ce(III).



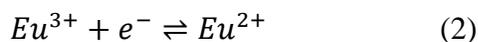
Practical applications involving the separation of Ce from other REEs have been studied. As early as 1915, Dennis and Lemon described the electrolytic oxidation of Ce at Pt electrodes employing electrolyte solutions of cerium salts but provided no further details (Dennis and

Lemon, 1915). Thereafter, Dennis and Meulen examined the decomposition potentials (potential difference between the cathode and anode needed for electrolysis to occur) of Ce among other REEs employing both neutral solutions of Ce chloride and Ce nitrate as electrolytes at a Pt cathode (Dennis and Meulen, 1915). The motivation of this study was to determine if differing applied potentials can be used to separate Ce from other REEs. Decomposition potentials of 2.18 V and 2.36 V for the nitrate and chloride solutions, respectively, were observed.

The study of direct electrolytic oxidation of Ce appears to have gone dormant from the early 1900s to the early 2000s where Vasudevan et al. demonstrated Ce separation from other REEs in aqueous chloride solutions (Vasudevan *et al.*, 2005). Electrolysis was performed at 500 A/m² for 6 hours with up to 60% current efficiency, a REE purity of 95%, and an energy consumption of 3.5 kWh/kg of CeO₂. Arenas et al. published a comprehensive review and study on redox processes pertaining to soluble cerium species (Arenas, De León and Walsh, 2016). In their study, they discussed the effects of oxygen evolution, electrode kinetics, mass transport, and diffusion on the reduction and oxidation of Ce (Arenas, De León and Walsh, 2016).

2.2. Europium (Eu) Separation from REEs

With a standard potential of -0.429 V vs SHE, Eu²⁺/Eu³⁺ is within the aqueous potential window for common electrolytes (Pourbaix, 1974). The electrochemical reduction of Eu(III) can be expressed as:



The separation of Eu from other REEs have been reported using Zn amalgams, alkaline metal amalgams, and Zn powder (Atanasyants and Seryogin, 1995). However, low separation factors,

low yields, difficulties in purification, and high costs are drawbacks to these reported processes. Furthermore, electrochemical studies of Eu reduction in aqueous media are limited.

Atanasyants and Seryogin investigated the reduction of Eu in hydrochloric acid using cyclic voltammetry. Both rotating disk electrode and temperature kinetics methods were employed (Atanasyants and Seryogin, 1995). During their study, they observed the following:

- The cathodic peak density is linearly related to the concentration of Eu.
- Linear dependence of cathodic peak density and scan rate shows a purely electrochemical mechanism.
- Increase in scan rate shows a transition from a reversible to a quasi-reversible (kinetically limited) reaction.
- Current density of Eu reduction is dependent on the disk rotation speed, suggesting first order reaction for Eu(III) to Eu(II).

3. Liquid Metal Cathode Studies

The use of LMCs as a means of processing lanthanides goes back many decades. Processing involves the formation of a metallic alloy, which effectively decreases the reduction potential of the metal to those accessible in aqueous solutions. LMCs are generally composed of elements with a high overpotential (additional potential needed due to slow kinetics) for HER. This offers a wider cathodic potential range to facilitate amalgam formation (Mikkelsen and Schröder, 2003). For the purposes of this chapter, amalgams formed using mercury (Hg) was almost exclusively studied. However, electrochemical studies for Hg have largely ceased due to environmental and health concerns. LMCs offer ease of surface renewability and the ability to

flow the electrode, which gives rise to various process options (Mikkelsen and Schröder, 2003; Surmann and Zeyat, 2005).

From the early to mid-1900s, separation of REEs employing LMCs was achieved by either direct reduction or by galvanic displacement of less noble metals such as K, Li or Na (Dennis and Lemon, 1915; Dennis and Meulen, 1915; Lavrukhina, Kolesov and Tang, 1960; Ryabchikov and Terent'eva, 1960). These studies reported promising results for REE separation before going dormant over half a century ago (Onstott, 1959, 1961; Shvedov and Antonov, 1964). The chlor-alkali process is the closest analog where reactive metals (such as sodium, (Na)) are reduced into an amalgam, as shown in Figure 1 (Venkatesh and Tilak, 1983; Bommaraju, Orosz and Sokol, 2007; Crook and Mousavi, 2016). This long-serving electrochemical process has been phased out, but produced caustic soda, chlorine gas, and bleach products.

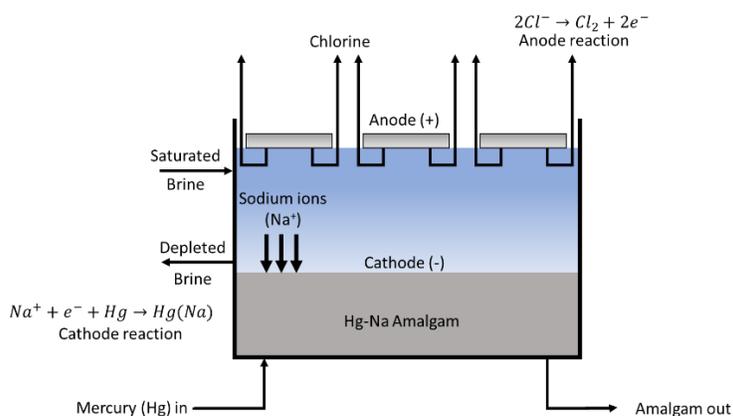


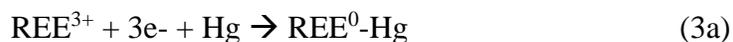
Figure 1. Chlor-alkali process for production of Na metal.

3.1. Application of a Liquid Metal Cathode for REEs Separations

The discovery of amalgam formation in a liquid Hg cathode that permitted metal reduction created methods for reducing REEs in aqueous media. This gave rise to the reduction of REEs

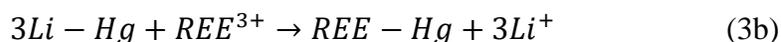
either by direct electrolysis (Equation 3a) or by galvanic displacement (Equation 3b), or by both approaches (McCoy, 1941a).

Direct electrolysis involves the application of a potential across an electrochemical cell to promote reduction (Zoski, 2006). This reaction is can be expressed as



This reduction can be done with or without the presence of a complexing agent, such a citrate or tartrate ion in the electrolyte. One of the most vivid descriptions of the amalgamation process was given as part of a three-part investigation by McCoy where the formation of REE amalgams are described as solid crystals and not merely REE hydroxides (McCoy, 1941a). McCoy elaborated that the use of REE acidic aqueous solutions favors HER, while neutral solutions favor the deposition of hydroxides on the cathode. In both cases, little to no amalgam formation was observed. McCoy also stated that important contributors to achieving amalgam formation are the presence of metals, such as K, citrate ion, and REE acetates. This combination gave the most amalgam at low voltage with encouraging current efficiencies.

Galvanic displacement involves the reduction of REEs by a redox reaction of a metal with a more negative reduction potential (Gough *et al.*, 2016). For example, a reaction involving the use of lithium (Li) as an example can be expressed as



The sections below outline several studies that examined the amalgamation process as a means of separating REEs and were all reported prior to 1970. In 1968, Kolesov and Pankratova presented an in-depth review of Hg LMCs (G M Kolesov and Pankratova, 1968). This also includes work examining adjacent REE separation, such as praseodymium (Pr^{3+}) and

neodymium (Nd^{3+}), which are difficult to separate due to their similar chemical and electrochemical properties (Onstott, 1961).

3.1.1. Early Work

For this review, we refer to early work as studies reported before 1950, which generally provided fewer details in their approach and methods used. Further, work is segregated into the two general approaches: electrolytic and galvanic displacement.

3.1.1.1. Electrolytic Reduction

As early as 1906, electrolytic reduction of REEs from Samarium (Sm) sulfates was reported by Marion (G M Kolesov and Pankratova, 1968). In 1911, Urbain and Burion reported isolation of a Eu compound from a Hg LMC (G M Kolesov and Pankratova, 1968). In 1915, Dennis and Lemon performed metal separation from various REEs amalgams at an Hg cathode (Dennis and Lemon, 1915). Their work involved the separation of lanthanum (La) from La-Pr-Nd- Sm and La-Nd nitrate solutions, as well as the fractional separation of erbium (Er) from ytterbium (Yb). They observed that the precipitation of REEs depended on electrolysis time and the fractionation stage. Shortly thereafter, Dennis and Meulen investigated the fractional separation of various REEs at a Hg cathode (Dennis and Meulen, 1915). Some of the parameters studied were the decomposition potential and the effect of the number of fractionations on REE separation from neutral nitrate solutions.

In the late 1920s, Neckers and Kremers demonstrated the separation of La from La-Pr and La-Nd-Pr-yttrium (Y)-Sm chloride mixtures while employing a Hg cathode and a Pt anode (Neckers and Kremers, 1928). For the La-Pr solutions, electrolysis of >4 hours and a potential > 6V yielded between 80% to 99% La. Similarly, with the La-Nd-Pr-Y-Sm solutions, greater La yields of up to 100% were seen at longer run times and potentials of >7 V. It was also observed that a

5% addition of Na to the La-Nd-Pr-Y-Sm solutions increased conductivity, which sped up the electrolysis without loss of separation efficiency. Attempts to separate Pr from Nd in Pr-Nd chloride solutions yielded no appreciable result.

In 1930, Yntema achieved the separation of Eu from a mixture of Eu, Sm and gadolinium (Gd) chlorides after 6 hours of electrolysis from a sulfate-based electrolyte (Yntema, 1930). Using a similar approach, Ball and Yntema successfully separated Yb to 98% purity from mixed REE chlorides containing Yb, Er, Th, and Y, in dilute sulfuric acid (H₂SO₄) (Ball and Yntema, 1930). Likewise, Audrieth et al. experimented with the electrolytic preparation of Nd and La amalgams at a Hg cathode. They observed that from aqueous solution, formation of an insoluble REE salt precipitate was favored over REE amalgams (Audrieth *et al.*, 1931) (Jukkola, Audrieth and Hopkins, 1934). However, when electrolyzed in ethanol solution, precipitate formation was avoided (Audrieth *et al.*, 1931). This was successfully replicated by Hopkins and Audrieth to create amalgams of La, Cd, Nd, Sm and Yb from ethanol solutions (Hopkins and Audrieth, 1934).

In the early 1940s, a three-part study conducted by McCoy investigated the separation of REEs at amalgam cathodes. The first study was reported in June 1941 where McCoy investigated the formation of Eu and Yb amalgams employing the use of REE acetates and potassium citrate as an electrolyte where simultaneous formation of K amalgams with Eu amalgams were observed (McCoy, 1941a). The presence of the K amalgam occurred either at very high current or during the continued application of a current after deposition of the REE was complete. Following electrolysis of 6.25 hours at a current density of 0.06 A-cm⁻², 100% of the Eu was amalgamated as Hg₁₀Eu and Hg₂Eu₃ crystals. Similarly, amalgams for Yb were also created at 8 volts and 2 A.

A second paper reported the feasibility of separating Eu from Sm when present in equal concentrations in an electrolyte, which was a first of a kind study (McCoy, 1941b). Amalgams yielding 90% Eu were formed using REE acetates and potassium citrate complexing agents. The separation of Eu from other REEs was also investigated with reported yields between 60% and 94%. Furthermore, Sm acetate in potassium citrate also was investigated at an amalgam cathode and yields between 1 and 13 % were observed. It should be noted that irrespective of the REE amalgam, K amalgam was always formed. It was also noted that complexing agents, such as citrates, likely prevented the REE from forming hydroxide precipitates. The recovered REEs were found to be REE oxides (McCoy, 1941b).

Following the success of the first experiments with Eu and Yb, McCoy and Hammond reported a third study which also employed amalgam formation for the separation of Yb from other REEs. This experiment employed a greater amount of REE oxides (4 g) than the first experiment (McCoy and Hammond, 1942). This experiment's purpose was to demonstrate that Yb could be separated into amalgams in larger quantities. The electrolyte was an REE acetate with potassium citrate. Following electrolysis, the REEs in the amalgam were compared to the REE in the electrolyte. REEs remaining in the electrolyte amounted to 0.1 g from the 4 g originally added. Without providing numeric quantification, it was reported that most of the REE yield in the amalgam was Yb with very little Eu (McCoy and Hammond, 1942).

In the late 1940s, Estee and Glockler reported the reduction of Nd at a dropping Hg electrode and observed only a single polarographic wave during reduction of aqueous Nd sulfates that they attributed to Nd⁰ formation (Estee and Glockler, 1948). Other papers have reported polarography of REEs where reduction of Gd (Rabideau and Glockler, 1948), Pr (Swensen and Glockler, 1949) and Sm (Timnick and Glockler, 1948) was observed.

3.1.1.2. Galvanic Displacement (Reduction)

Employing galvanic displacement, West and Hopkins, reacted Na amalgams with alcoholic REEs chlorides to produce new amalgams with 1-3 % REE content (West and Hopkins, 1935). Marsh also employed galvanic displacement using Na amalgams for the separation of Yb, Sm and Eu in REE acetate and chloride solutions (Marsh, 1942a). In subsequent experiments, Marsh observed that >99.99% of Yb from solution was captured in the amalgam (Marsh, 1943b). This method provided a pathway to separate Eu, Sm and Yb into amalgams by shaking in either chloride salts or acetic acid. One of the limitations to Marsh's experiments was the lack of thorough comparison between acetate and chloride salts, although they reported qualitatively that acetate performed better than chloride.

Other work reported by Marsh involved the separation of Nd from Sm and Gd (Marsh, 1942b), and the isolation of Eu (Marsh, 1943a) employing a Na amalgam. It was observed that for acetate, mixtures of Nd-Sm or Sm-Gd, Sm preferentially formed an amalgam. For Eu-Gd-Sm acetate mixtures, Eu and Sm can preferentially form amalgams when in contact with Na amalgam allowing the separation of Gd.

Following Marsh's work, Moeller and Kremers, studied the formation of Yb amalgams in solutions containing different anions (Moeller and Kremers, 1945). They studied Yb with acetate, dichloroacetate, formate, chloride, and perchlorate anions. Dichloroacetate solutions was found to yield no Yb amalgam; however, a >70% yield was observed for perchlorate, chloride, and formate anions following a single extraction time of approximately 15 minutes. Further, there was an increase in Yb amalgam stability from formate solution in comparison with the perchlorate solution. Following five extractions with acetate and formate solutions, each

employing the use of fresh Na amalgams for each extraction, 97% of the original amount of Yb was extracted.

3.1.2. Electrolytic studies at the Los Alamos National Laboratory

Onstott published a four-part study on REE separation at Hg and alkali metal amalgam cathodes. One reported the separation of Sm from Eu by electrolysis using REE acetates and lithium citrate ($\text{Li}_3\text{Citrate}$) solutions as the complexing agent at a Li amalgam cathode (Onstott, 1955). He observed that <10% of Sm from the electrolyte went towards amalgam formation, which is favored at low pH, high cathodic potentials, and low citrate concentrations. As an example, a 95% yield of Eu was obtained.

In a following study, Onstott studied the separation of Sm from Gd and Nd, and the purification of Eu from Sm at a Li amalgam cathode (Onstott, 1956). The electrolytes were REE acetates with lithium citrate. For Sm-Gd electrolytes, separation factors as high as 6200 and 2300 was reported in the presence and absence of citrate, respectively. In this case, the separation factor was defined as the ratio of concentrations of one element to another in the amalgam phase with respect to the bulk electrolyte phase (Onstott, 1961). In the Sm-Nd system, Sm migrated to the amalgam while Nd remained in the electrolyte. 99.98% purity of Sm was recovered from the amalgam. In a follow up study to enrich and purify Eu from $\text{Sm}_2\text{O}_3\text{-Eu}_2\text{O}_3$, >99.9 % purity of Eu_2O_3 was achieved after several cycles of electrolysis (Onstott, 1956).

Due to the success obtained from the separation of Eu from Sm, and Sm from Gd, Onstott extended the approach to the separation of the lanthanide series elements using a lithium amalgam (Onstott, 1959). A monazite mixture containing La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Th oxides was studied as well as Y-earth (heavy REE) and Tb-Dy mixtures. The

electrolyte was either REE perchlorate/Li citrate or REE acetates/Li citrate. From the monazite mixture, 99.7% Eu was electrolyzed after the first fractionation independent of pH. Similarly, Yb was electrolyzed but at a much slower rate. At high pH, electrolysis of Sm and trivalent lanthanides is suppressed. For REEs in the Y-earth mixture, the rate of electrolysis for REEs heavier than Tb was slow and impractical. For the Tb-Dy mixture, Tb was electrolyzed over Dy for all scenarios tested. Some of the important conditions Onstott described that influence electrolysis of trivalent REEs are (Onstott, 1959):

- **Need for an amalgam cathode:** For the electrolysis of most trivalent REEs to take place, there needs to be a cation that can supply a free electron in the presence of Hg. Alkali metals such as K, Li and Na are most suitable.
- **Need for a complexing agent:** Even in the presence of the alkali metals such as Li, appreciable electrolysis of inorganic salts of trivalent REEs was not achieved. However, when coupled with a carboxylic acid anion ligand, the rate of electrolysis was improved.
- **Dependence of electrolysis rates on pH:** The rate of electrolysis of trivalent REEs occurs best between pH 4 and 6 with exception of Eu, which is not impacted by pH.
- **Electrolysis being oxidation dependent:** REE ions such as Eu, Sm, and Yb, with an oxidation number < 3 are readily electrolyzed. For trivalent REEs, electrolysis is slower and is governed by the change in ionic radius, a characteristic known as lanthanide contraction. The smaller the ionic radius the slower the rate of electrolysis.
- **Effect of solvent:** The use of solvents such as methanol, as compared to water, increases the rate of electrolysis while simultaneously increasing the current density. This also improves efficiency because a majority of the REE species form an amalgam.

Finally, Onstott explored the separation of high purity Yb from a mixture of heavy REEs and observed >99.9% removal of Yb from the REE mixture at a Hg cathode. The yield of Yb could be manipulated by changing either the electrolyte pH or the duration of the experiment (Onstott, 1960).

Later work examined the separation of Nd and Pr chlorides in lithium citrate electrolyte with respect to temperature, electrolyte composition, and current density (Onstott, 1961). This work was conducted due to the difficulty in separating trivalent REEs. As the concentration of Pr and Nd in the electrolyte increased, Pr preferentially formed an amalgam. When Pr concentration was lower, separation was improved. The highest separation factor achieved was 3, at current density of $50 \text{ mA}\cdot\text{cm}^{-2}$, with a $\text{Li}_3\text{Citrate}/(\text{Pr}+\text{Nd})$ ratio of 2.5 and a Pr+Nd molarity of 0.4 (Onstott, 1961).

3.1.3. Electrolytic studies in the Former Soviet Union

Antonov and Shvedov investigated the formation of Gd, Tb, Dy, and Ho amalgams (Shvedov and Antonov, 1964). They observed that the factors that drive the migration of REEs into the Hg phase depends on the ratio of the complexing agent to the concentration of REEs in the electrolyte; $\frac{C_{\text{Li}_3\text{Citrate}}}{C_{\text{REE}}}$. Using REE acetates and varying amounts of Li citrate as the complexing agent, they observed that at low (<0.15 M) $\text{Li}_3\text{Citrate}$ concentration, the precipitation of REE hydroxides limited amalgam formation. They further observed that optimal $[\text{Li}]/[\text{REE}]$ for amalgam formation were 12-15, 13,17, and 26 for Gd, Tb, Dy and Ho respectively. Furthermore, for every 100 mg of Hg employed for amalgam formation, 150 mg, 75 mg, 55 mg and 18 mg of Gd, Tb, Dy, and Ho respectively was consumed in amalgam formation. Shvedov and Antonov also investigated the separation of Pr and Nd at a Hg cathode using Li tartrate as the complexing agent (Shvedov and Antonov, 1962). They observed yields of Pr and Nd reaching 100 % in some

cases and separation factors between 30 and 60. They conducted other studies to investigate the influence of factors such as the concentration of REEs, the current density, the time for electrolysis and the $\frac{C_{Li_3Citrate}}{C_{REE}}$ ratio on amalgam formation (Shvedov and Antonov, 1967). They observed that a Li₃Citrate to REE ratio of 9:1 was optimal for separation of Tb and Dy, and 4:1 for Tb and Ho. Separation factors as high as 7.8, 10, 66, 44.5, 75, and 60 were observed for Gd-Tb, Tb-Dy, Gd-Ho, Tb-Ho, Tb-Er, and Tb-Tm respectively. Furthermore, when the concentration of Li₃Citrate was increased, H₂ evolution was favored.

3.1.4. Summary of LMC studies in separating REEs

Distribution of REEs in the Hg phase is affected by the solvent properties of Hg towards metals such as K, Na, and Li to influence the formation of REE amalgams (through galvanic reaction) (Kolthoff, 1952; Onstott, 1956). Li has proven to be the most effective in REE amalgam formation due to its high negative potential (Kolthoff, 1952; Onstott, 1955). Researchers have employed various extractants and complexing agents such as acetates, citrates, and tartrates for preferential amalgamation (McCoy, 1941a; Gennadii Mikhailovich Kolesov and Pankratova, 1968), (Mccoy, Morris and Selwood, 1946). Table 1 is an example of various extraction percentages using Li, Na and K as amalgams.

Table 1. Percentage extraction of rare-earth elements by Li, Na and K amalgams ($C_{Ln} = 0.5$ M) (G M Kolesov and Pankratova, 1968)

| Rare earth | Amalgam* | | |
|------------|----------|----|---|
| | Li | Na | K |
| | | | |

| | | | |
|----|----|----|----|
| La | 38 | 21 | 17 |
| Ce | - | 13 | 8 |
| Pr | 31 | 13 | 14 |
| Nd | 23 | 7 | 5 |
| Sm | 45 | 66 | 50 |
| Eu | 41 | 50 | 50 |
| Yb | 25 | 47 | 37 |

**0.04 M amalgam was used*

In evaluating the various studies, the work at Los Alamos and the former Soviet Union provides the most experimental details for evaluation. For adjacent REEs such as Nd and Pr, Onstott achieved a maximum separation factor of 3 with Li₃Citrate and REE chlorides (Onstott, 1961). However, Shvedov and Antonov reported separation factors from 30 to 60 for Pr and Nd employing REE acetates and Li tartrate (Shvedov and Antonov, 1962). These values seem unusually high given the similarity in reduction potential and lack of binding energy difference for the tartrate anion. Generally, separation factors and migration percentage of REE into the amalgam for studies conducted by Shvedov and Antonov tended to be higher than those reported by Onstott. Onstott reported high separation factors for Eu from an Eu-Sm mixture at very high polarizations (Onstott, 1959), and for Sm from Gd-Sm-Dy mixtures (Onstott, 1956). It is noteworthy to mention that the work reported by Shvedov and Antonov was performed with pure Hg to form Hg-REE amalgams while Onstott employed alkali amalgams (Li, K) (Onstott, 1960). The studies, however, showed high separation factors can be achieved by methods such as amalgam formation at a Hg cathode.

3.2. Potential Substitutes to Hg LMC—Ga and its alloys

Recently, work was undertaken to investigate paths to replace the Hg LMC in REE separation chemistries. This led to a search for other liquid metals with similar characteristics to Hg but are nontoxic (Surmann and Zeyat, 2005). Liquid metals such as Ga, and alloys such as GaInSn, GaIn and GaInSnZn have been investigated as potential substitutes for Hg (Surmann and Zeyat, 2005; Morley *et al.*, 2008; Khan *et al.*, 2014). Table 2 shows the physical properties for these alloys and Hg, as well as the reduction potential for Ga and Hg. Pure Ga has a melting point slightly above room temperature (29.8 °C) coupled with a very low vapor pressure of 1.3×10^{-6} atm at 965 °C. Hg possesses a relatively high vapor pressure which factors into the challenge of working safely with it (Loftness, 1951; Powell, 1968).

Table 2. Property comparison between Ga and Ga-alloys and Hg

| Property ^a | Ga ⁶⁷ In ^{20.5} Sn ^{12.5} | Ga | Ga ^{75.5} In ^{24.5} | Ga ⁶¹ In ²⁵ Sn ¹³ Zn ¹ | Hg |
|---|--|-----------------------|---------------------------------------|--|-----------------------|
| Melting Point (°C) | 10.5 | 29.8 | 15.5 | 7.6 | -38.8 |
| Boiling Point (°C) | >1300 | 2204 | 2000 | >900 | 357 |
| Density (kg/m ³) | 6360 | 6080 | 6280 | 6500 | 1353 |
| Conductivity (Ω^{-1} m ⁻¹) | 3.1×10^6 | 3.7×10^6 | 3.4×10^6 | 2.8×10^6 | 1.0×10^6 |
| Viscosity (m ² /s) | 2.98×10^{-7b} | 3.24×10^{-7} | 2.7×10^{-7} | 7.11×10^{-8} | 13.5×10^{-7} |
| Surface tension (N/m) | 0.533 ^c | 0.7 | 0.624 | 0.5 | 0.5 |
| Water compatibility | Insoluble | Insoluble | Insoluble | Insoluble | Soluble |

| | | | | | |
|--|---|--------|---|---|-------|
| Reduction Potential (V vs SHE) ^d | - | -0.529 | - | - | 0.788 |
|--|---|--------|---|---|-------|

^aValues taken from Morley et al. (Morley *et al.*, 2008)

^bUCLA measurements using a glass viscometer tube are typically closer to 4.0×10^{-7} m²/s.

^cPPPL measurements indicate that oxides can significantly reduce surface tension.

^dReduction potential data from Pourbaix (Pourbaix, 1974)

The ability of Ga to dissolve a host of other metals creates a pathway to produce amalgams of metal and metal oxides (Powell, 1968; Lertanantawong, Lertsathitphong and O’Mullane, 2018; Wang *et al.*, 2018, 2020; Ghasemian *et al.*, 2019; Park *et al.*, 2019; Mayyas *et al.*, 2020; Han *et al.*, 2021). Furthermore, Ga is notorious for the spontaneous formation of a passivating oxide layer when exposed to oxygen containing environments such as air or water, making it extremely difficult to use in aqueous electrolyte (Regan *et al.*, 1997; Scharmann *et al.*, 2004; Cademartiri *et al.*, 2012; Doudrick *et al.*, 2014; Khan, Trlica and Dickey, 2015). A recent study published by Engmann et al. harnessed the oxide capabilities of Ga, as a Hg LMC replacement, for the immobilization of Pr from aqueous solutions (Engmann *et al.*, 2022). They observed that the mechanism involving REE immobilization was complex with a strong reduction feature in the presence of REEs that involved reaction of Ga oxides. The disproportionation reaction of Ga₂O with Pr formed a dark grey precipitate composed of Ga oxides and Pr as seen in Figure 2. The Pr entrained or immobilized was in the form of Pr₂O₃. Ga-REE alloys do not appear to have formed as observed by the Hg systems discussed earlier or were too reactive to observe. This work showed limitations for using pure Ga system as a replacement for Hg in separating REE mixtures as amalgams.

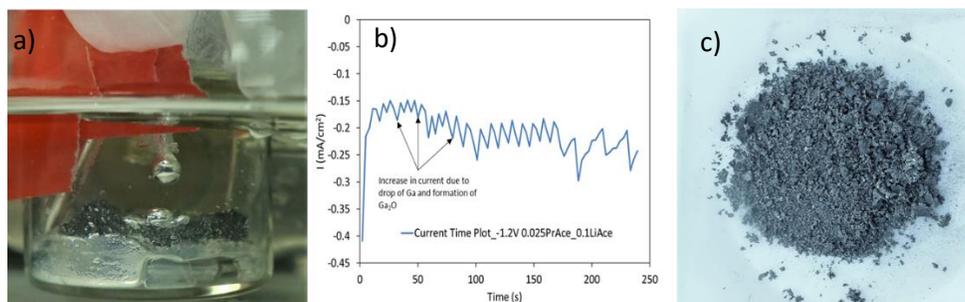
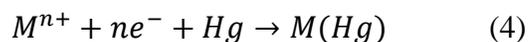


Figure 2. Recovery of REEs from dilute solutions. a) Formation of dark gray precipitate while Ga was dropped into a Ga pool electrode in the presence of 0.05 M Pr Acetate (OAc) and 0.1 LiOAc electrolyte at 30 °C, b) Increase in current vs time as Ga drop hits the surface of liquid Ga pool and c) dark gray precipitate from electrolyte composed of Ga oxides and Pr after separation and drying (Engmann *et al.*, 2022).

3.3. Mechanisms Involving Amalgam Formation

Electron and ion transfer have been speculated to govern the formation of amalgams and act as the rate determining steps during the process (Fawcett, 1989). This process is governed by the equation, in the case of Hg as:



Fawcett (Fawcett, 1989) reported in detail that amalgam formation and kinetics can be described by selecting the adequate rate determining steps among the following elementary steps:

- i. **ion transfer without adsorption:** This occurs when an ion is moved from its current position in the double layer to another location close to the electrode.

Thus, the ion loses some of its solvation sheath and experiences a change in potential but does not come in direct contact with the electrode.

- ii. adsorption of the ion:** This is the movement of the ion from the inner part of the double layer to an adsorption site on the electrode. At this site, the ion is solvated partially by solvent molecules and Hg molecules (in the case of Hg).
- iii. metal incorporation:** This involves the movement of the ion from the adsorption site to the Hg phase.
- iv. electron transfer:** This involves the transport of an electron from the metal phase to the metal ion close to the electrode. The metal ion is not directly in contact with the electrode due to solvation by solvent molecules and complexing of REEs by the organic solvent.

3.4. Thermodynamics and Theoretical Potential of Amalgam Formation

Earlier work involving the thermodynamics of amalgam formation suggests that it can be improved by varying the volume ratio of the electrolyte to electrode (Kolthoff, 1952; Rogers, 1952). Rogers suggests that maximizing the purity of an element is much more important than complete recovery of the element from the electrolyte. This is particularly true when the halfwave potential ($E_{1/2}$) of the two elements have similar values (< 0.2 V) (Rogers, 1952). The formation of an amalgam with Hg is mathematically expressed as

$$E = E_{1/2} - \frac{0.060}{n} \log \frac{(1-x)/V_{ox}}{x/V_{red}} \quad (5)$$

where E is the electrode potential, n is the number of electrons transferred by the atom, $E_{1/2}$ is the polarographic half-wave potential using Latimer (Latimer, 1938) sign convention, V_{ox} is the

volume of the aqueous phase, V_{red} is the volume of the Hg phase, and x is the fraction of the element in the Hg phase. Assuming the volumes of the Hg and electrolyte are the same; $V_{ox} = V_{red}$, for $x=50\%$ or 0.5 , one would observe that:

$$E = E_{\frac{1}{2}} \quad (6)$$

Furthermore, when $x = 0.5$ or 50% , the ratio of the volumes becomes the determining factor of $E_{50\%}$, expressed as:

$$E_{50\%} = E_{1/2} - \frac{0.060}{n} \log \frac{V_{ox}}{V_{red}} \quad (7)$$

where $E_{50\%}$ is the potential at which half of the element of interest is deposited.

A closer look at equation 7 suggests that for elements with different values of n , $E_{50\%}$ changes with the volume ratio, creating a condition for enhanced separation. This could be why certain elements such as Nd and Pr should be difficult to separate. Table 3 lists the halfwave potentials for the various REEs and alkali metal amalgams. The spread of the half wave potentials for the REEs is not very large. For the specific separation of Pr and Nd, there is only a 0.01 V difference suggesting difficulty in separation (based solely on thermodynamics). However, for Pr and Eu, the half-wave potential difference is 0.32 V, indicating that effective separation between both elements is possible. In other words, the greater the difference between half-wave potentials, the greater the chances of separability.

Table 3. Half-wave potential of various rare earth elements, including Li, K, and Na

(Kozlovskii, 1956; Kryukova, Sinyakova and Aref'eva, 1959)

| Reaction / Metal | $E_{1/2}, V$ | Composition of Electrolyte |
|---------------------|--------------|----------------------------|
| | | |

| | | |
|-------------------------------|-------|---|
| $La^{3+} \rightarrow La^0$ | -1.92 | In the presence of .01 M LiCl |
| $Ce^{3+} \rightarrow Ce^0$ | -1.97 | In the presence of .01 M LiCl |
| $Pr^{3+} \rightarrow Pr^0$ | -1.75 | In the presence of 0.1 M LiCl, 0.1% gelatine, and 2.5×10^{-3} M Pr^{3+} |
| $Pr^{3+} \rightarrow Pr^0$ | -1.82 | In the presence of 0.1 M LiCl, 0.1% gelatine, and 8.9×10^{-3} M Pr^{3+} |
| $Nd^{3+} \rightarrow Nd^0$ | -1.81 | In the presence of 0.1 M LiCl, 0.1% gelatine, and 4.1×10^{-3} M Nd^{3+} |
| $Nd^{3+} \rightarrow Nd^0$ | -1.77 | In the presence of 0.1 M LiCl, 0.1% gelatine, and 1.6×10^{-3} M Nd^{3+} |
| $Sm^{3+} \rightarrow Sm^{2+}$ | -1.77 | In the presence of 0.1 M LiCl, 0.01% gelatine, and 5.0×10^{-3} M Sm^{3+} |
| $Sm^{3+} \rightarrow Sm^0$ | -1.96 | In the presence of 0.1 M LiCl, 0.01% gelatine, and 5.0×10^{-3} M Sm^{3+} |
| $Eu^{3+} \rightarrow Eu^{2+}$ | -0.78 | In the presence of .01 M LiCl |
| $Eu^{3+} \rightarrow Eu^0$ | -2.14 | In the presence of .01 M LiCl |
| $Gd^{3+} \rightarrow Gd^0$ | -1.74 | In the presence of 0.1 M LiCl and 8.0×10^{-4} M Gd^{3+} |
| $Tb^{3+} \rightarrow Tb^0$ | -1.85 | In the presence of 0.1 M LiCl and 0.005% gelatine |
| $Dy^{3+} \rightarrow Dy^0$ | -1.85 | - |
| $Ho^{3+} \rightarrow Ho^0$ | -1.85 | - |
| $Er^{3+} \rightarrow Er^0$ | -1.85 | - |
| $Tu^{3+} \rightarrow Tu^0$ | -1.85 | - |

| | | |
|-------------------------------|-------|--|
| $Yb^{3+} \rightarrow Yb^{2+}$ | -1.17 | In the presence of 0.1 M LiCl, 0.005% gelatine, and 5.0×10^{-4} M Yb^{3+} |
| $Yb^{3+} \rightarrow Yb^0$ | -2.05 | In the presence of 0.1 M LiCl, 0.005% gelatine, and 5.0×10^{-4} M Yb^{3+} |
| $Lu^{3+} \rightarrow Lu^0$ | -1.8 | - |
| Li | -2.26 | - |
| K | -2.12 | - |
| Na | -2.04 | - |

Furthermore, tools such as the semi-log plot or the linear plot can be used to assess separability. The semi-log plot is a graph that provides information about the concentration of an element in the Hg and aqueous phase at a given potential. It is constructed by passing a solid line with a slope of $0.060/n$ through the polarographic half potential of the element. An example of this plot has been reported (Rogers, 1952). Also, maximum enrichment can be calculated by taking the difference of the half-wave potentials for a more noble element (M_1) and less noble element (M_2) and dividing by $0.060/n$. For elements with the same half-wave potentials but different electron reactions, separability is obtained at potentials other than the half-wave potential. While semi-log plots allow for the calculation of potentials more than one unit away from $E_{50\%}$, their limitations lie in the fact that at values close to $E_{50\%}$, where the rate of change for x is linear, calculations using a semi-log plot can be awkward. In such instances, a linear plot is helpful (Rogers, 1952). The limitations of the method are that important parameters such as the activity coefficients and effect of overpotential (electrochemical kinetics) are not considered. Also, it is assumed that all reactive species are completely soluble in Hg.

Work reported by Bush and Densen suggests that for a given volume ratio, maximum separation is achieved when the fraction of M_1 in the Hg phase is equal to the fraction of M_2 in the aqueous phase (Bush and Densen, 1948). The Nernst equation, while neglecting activity coefficients for a trivalent specie, then gives:

$$E = E^a - 0.02 \log \frac{C^a}{C^e} \quad (8)$$

where E is the cathode potential, E^a is the standard amalgam potential, C^a is the concentration of lanthanides in the amalgam and C^e is the concentration of the lanthanides in the electrolyte. For two lanthanides with a common electrolytic potential,

$$E_1^a - E_2^a = 0.02 \log \frac{C_1^a C_2^e}{C_1^e C_2^a} \quad (9)$$

One would observe that the arrangement of the concentration is similar to that used to describe the separation factor for ion exchange and solvent extraction (Onstott, 1956).

4. Electrochemistry-driven REE Magnet Dissolution and Recovery

Another application of electrochemical processing of REEs involves the anodic dissolution of REE-based magnets. This section will examine work performed using chemical and electrochemical dissolution as a pathway for REE magnet recycling. Advantages to these methods are potential reductions in chemical use as either of those can be generated *in-situ* or replaced by electrons. Studies involving electrochemical dissolution have taken place either in a single compartment or membrane separated cells.

REE Recovery from Magnet Leachate

Venkatesan et al. explored the separation of Nd from neodymium-iron-boron (Nd-Fe-B) magnet leachate using three approaches with the aim of creating lower impact recovery processes for REEs. The first approach explored the use of a single anode cell for the oxidation of Nd-Fe-B magnet leachate as seen in Figure 3. A nickel wire, titanium/platinum (Ti/Pt) mesh, and silver/silver chloride (Ag/AgCl) were the anode, cathode, and reference electrode, respectively. The process involved the application of current to oxidize Fe^{2+} to insoluble Fe^{3+} in the leachate followed by the precipitation the REEs using oxalic acid (Venkatesan, Sun, *et al.*, 2018). A current of 1.2 A was found to oxidize 98.9% of the Fe^{2+} within four hours. The resulting leachate was filtered and the REEs were precipitated using oxalic acid yielding >97 % recovery with a purity of >99%.

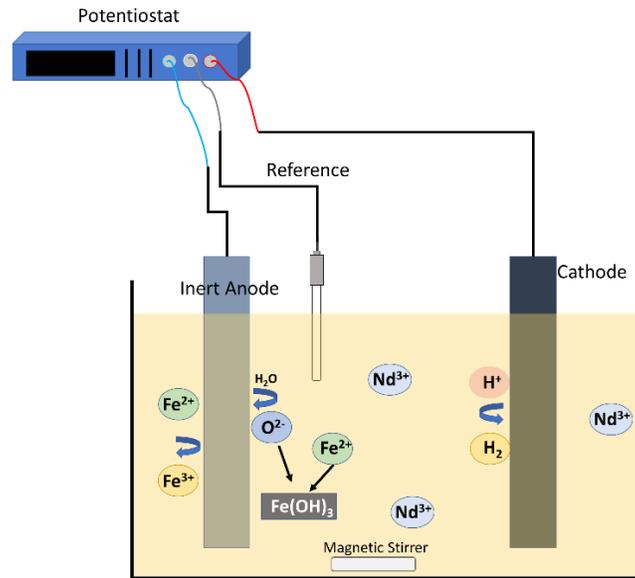


Figure 3. Single anode electrolysis reactor for selective extraction of REEs from Nd-Fe-B magnets.

Nd-Fe-B Magnet as Anode

In 1994, Greenberg described an electrolytic method for Nd extraction from Nd-Fe-B metallic slag that involved using a modified plating tank filled with sulfamic acid (Greenberg, 1994). During electrolysis, Nd was accumulated in the electrolyte and Fe was plated on the cathode. Hydrofluoric acid (HF) was then added to the electrolyte followed by filtration to produce NdF_3 which was then dried. This approach achieved > 95% recovery for Nd with < 3% moisture. More recently, the use of an Nd-Fe-B magnet as an anode was investigated.

The second approach employed by Venkatesan used a dual anode system similar to Figure 4 to separate Nd from Nd-Fe-B magnets using NH_4Cl as electrolyte (Venkatesan, Vander Hoogerstraete, Binnemans, *et al.*, 2018). The Nd-Fe-B magnet and a Ti/Pt DSA electrode were employed as the active and inert anodes, respectively. During electrolysis, the Fe in the magnet was oxidized into the electrolyte as Fe^{2+} then further oxidized at the Ti/Pt anode to Fe^{3+} (See Figure 4), where it was selectively precipitated at pH 3-3.5 (Lakshmanan, Clifford and Samanta, 2009; Önal *et al.*, 2015, 2017; Yang *et al.*, 2015). Following filtration of Fe^{3+} , REEs were selectively precipitated using oxalic acid. The purity of the recovered REE oxalates was between 98.5 and 99% and energy consumption was 3 kWh/kg. It was observed that increasing the electrolyte concentration (NH_4Cl) increased magnet dissolution and decreased energy consumption.

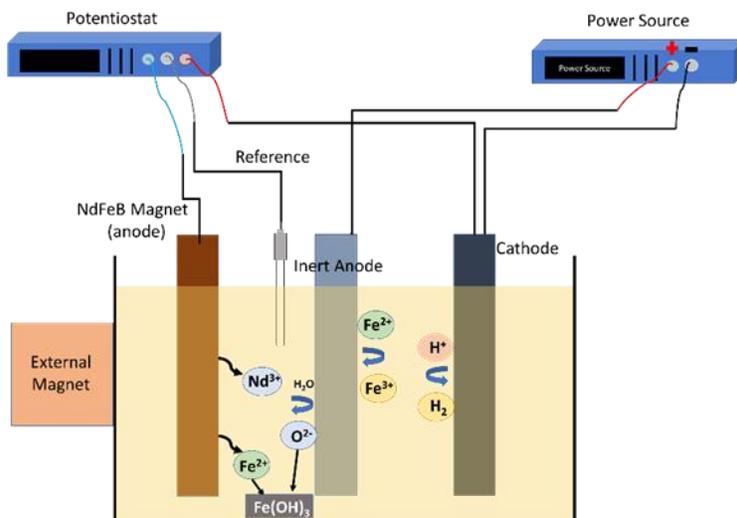
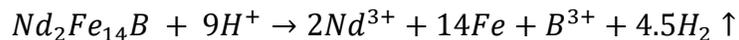


Figure 4. Dual anode electrolysis reactor for selective extraction of REEs from NdFeB magnets.

Xu et al. demonstrated a two-step method for the simultaneous recovery of REEs and deposition of Fe from Nd-Fe-B magnets (Xu *et al.*, 2020). The magnet was attached as the anode, Ag/AgCl electrode was the reference electrode, and the electrolyte was $0.6 \text{ mol L}^{-1} \text{ FeSO}_4$, $0.4 \text{ mol L}^{-1} (\text{NH}_4)_2\text{SO}_4$, 0.175 mol L^{-1} trisodium citrate (Na_3Cit) and 0.4 mol L^{-1} boric acid (H_3BO_3). The role of the $(\text{NH}_4)_2\text{SO}_4$ was to complex REEs and maintain Fe^{2+} and Fe^{3+} as soluble species at negative potentials due to the effects of HER. The addition of Na_3Cit was to further prevent the formation of insoluble REE hydroxides. H_3BO_3 was added to prevent the formation of any metal hydroxides which interfere with the deposition of Fe at the cathode. For a 100 % leaching efficiency, Xu observed that a current density $<50 \text{ mA.cm}^{-2}$ was most favorable. At current densities $>50 \text{ mA.cm}^{-2}$, the oxidation of water is favored with decreased leaching efficiency. A current density of 12.5 mA/cm^2 was chosen for an in-depth analysis and after 8 hours electrolysis time with a current of 200 mA, 99.9% magnet dissolution occurred with an overall reaction of:



The pH was then adjusted to 3.5 and the REEs were precipitated as sulphates using sodium sulfate (Na_2SO_4) with Fe^{2+} and Fe^{3+} remaining in solution. Overall, >93% REEs were recovered with a purity of 99.4 %.

Generation of Leachate Chemistry

The third approach explored by Venkatesan et al. used electrochemistry to generate the conditions needed to dissolve metallic materials containing REEs, such as Nd-Fe-B magnets (Venkatesan, Vander Hoogerstraete, Hennebel, *et al.*, 2018). Figure 5a is a representative system while Figure 5b shows a cross section of the system with anodic reactions and ion flow depicted. The cell used an anion exchange membrane (AEM) that effectively allowed chloride and hydroxide to cross from the cathode side while preventing metal cations from reaching the cathode compartment. Prior to electrolysis, the magnet waste was partially leached by hydrochloric acid (HCl). The leachate and sodium chloride (NaCl) were the electrolytes in the anode and cathode compartments, respectively. Circulation of both the catholyte and anolyte was performed within the cathode and anode compartment, respectively (See Figure 5a and b). Depending on the duration of electrolysis, chloride and hydroxide migrate from the catholyte to the anolyte. The chloride ions that migrate to the anolyte combine with protons produced in the anode compartment form HCl. This created unselective metal leaching and increased the amount of Fe co-extracted into the leachate (See Figure 5b). The role of the AEM during electrolysis was to prevent the migration of Fe^{3+} to the catholyte. Following leaching into the anolyte, the Fe^{3+} precipitates were removed through centrifugation. REEs were precipitated from the filtrate using oxalic acid. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis

showed that no metals presence in the catholyte suggesting the membrane was effective. At a current density of 50 Am^{-2} , REEs and cobalt extraction into solution was greater than 97%.

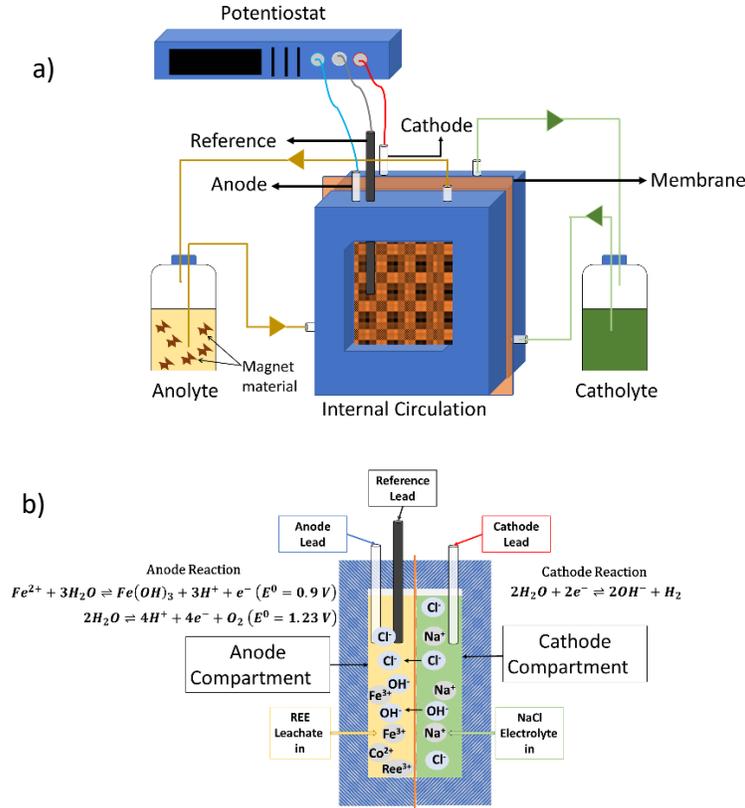


Figure 5. a) Membrane cell for REEs separation and b) cross section of membrane cell and reactions taking place in membrane cell

5. Perspective and Conclusion

5.1. Discussion and Challenges

REEs play a crucial role in technology and will continue to be in huge demand as the green economy develops. Molten salt electrolysis (MSE), metallothermic reduction, and comproportionation (MRC) are established technologies for REE separation and extraction with purities as high as 99.8% (Gray, 1952). Uda et al. calculated a separation factor for a Nd-Sm

mixture to be approximately 570, which is in contrast to the conventional solvent extraction method that gave 9.6 using comproportionation (Uda, Jacob and Hirasawa, 2000).

Scalability, high energy consumption, the use of very harsh chemicals, and the need for an oxidizing environment are concerns with MSE and MRC processes (Sharma, 1987; Meyer, 2007; Kingsnorth, 2015). For example, low melting temperature REEs such as La, Ce, Pr and Nd are liquified via electrolysis with chloride salts between 650°C and 1100 °C (Kobisk and Grisham, 1969). High melting temperature REEs such as Gd, Dy, and Y can be recovered using fluoride salts at temperatures ranging from 1300 to 1700°C. However, due to environmental concerns, the use of REE chloride salts was halted due to hazardous off-gases, low yields, and excessive moisture adsorption (Liu *et al.*, 2020).

From the research discussed above, preferential amalgamation using Hg showed that effective separation of REEs was possible with high separation factors reported for some cases. However, due to its high toxicity, Hg has been banned in most places. There are other low temperature alloys to be studied. Initial work using Ga was not successful. The biggest issue with Ga is the spontaneous formation of a oxide passivation layer which appears to be stable at very negative potentials (Engmann *et al.*, 2022). If this can be controlled or overcome, this approach may have promise. There are few options available for liquid metals or alloys below the boiling point of aqueous solutions.

Furthermore, direct separation of REEs in aqueous media remains a challenge given the favorability of hydrogen evolution rather than REE reduction. However, the dissolution of REE magnets in acid followed by the electrochemical separation of Fe from the REEs is a path to reducing chemical waste as most of the chemicals used in the process can be recycled back into the system. Attaching magnets as anodes to an electrochemical cell is viewed as challenging. It

requires magnets to be isolated from e-waste streams. Hard disk drives, which are typically shredded into fragments, make isolation of the magnets a challenge (Diaz *et al.*, 2016). Methods that generate chemicals through electrochemistry, such as through the membrane approach described earlier [90], are increasingly more attractive.

5.2. Future Directions

While REEs have limited redox activity in the electrochemical window of aqueous solutions, there has been some promising work. The options can be broken down into processes that directly act on REEs and those that act on other constituents to promote REE processing.

Direct processing: There could be opportunities to improve on existing methods that should be investigated, particularly for Ce which is the highest abundance REE. Another area that could be revisited is the use of alloying reactions to access zero-valent states within aqueous electrochemical windows. While briefly investigated (Engmann *et al.*, 2022), there could be promise in pursuing Hg substitutes based on Ga or other alloys with melting points below the boiling point of aqueous electrolytes.

Indirect processing: Indirect methods that act on other constituents in an REE containing solution can be almost unlimited. Indirect processing can involve manipulating bulk or localized chemical environments to remove unwanted species, generate reactive agents, or change the localized pH. A specific area that could be promising is the use of redox mediators that shuttle electrons from the anode or cathode to constituents in solution. This permits the electrodes to be located separately from the material being processed. An example of this would be the generation of oxidizing agents that can dissolve REE based magnets. A redox dissolution scheme

reported by Prodius et al. demonstrated galvanically-driven dissolution of REE magnets using copper (Cu^{2+}) salts (Prodius *et al.*, 2019). In the reaction, the magnet alloy was oxidized with Cu^{2+} to produce dissolved metals ions (including REEs) and Cu^0 . It would be desirable to select a mediator that is ionic in both oxidation states, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$, which can greatly reduce chemical consumption and limit introducing solid material to the waste.

Other options would be to manipulate local pH through HER to selectively precipitate dissolved species. This was recently demonstrated by O'Connor et al. where Eu and Nd were electrochemically precipitated at a conductive carbon nanotube filter cathode over a range of applied voltages and pHs (O'Connor, Coulthard and Plata, 2018). The electrolyte comprised 1 mM REE and 100 mM Na_2SO_4 . Recoveries of Nd and Eu were 72 and 65 %, respectively, at 3.0V in the form of trivalent oxides. The reaction responsible for the trivalent oxides was the reduction of oxygen and water to hydroxides, followed by the formation of REE hydroxide species then the subsequent dehydration to form metal oxides. Interestingly, REE oxides were also recovered as part of a process using a simpler three electrode h-cell setup where REEs were immobilized by a simultaneous chemical and electrochemical processes (Engmann *et al.*, 2022). In scenarios where REE are electrochemically precipitated to eventual oxides, the challenge arises with trivalent REEs where similarities in chemistry promotes recovery as a mixed oxide product.

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