

Chapter 10

Rare Earth Element Reduction to Metals



Tommee Larochelle

10.1 Introduction

This chapter presents an overview of the current processes for the reduction of rare earth elements (REE) to metals which is a critical step in the supply chain of many REE used in technological applications. The magnet elements (praseodymium (Pr), neodymium (Nd), samarium (Sm), terbium (Tb), and dysprosium (Dy)) possess unique properties rendering them difficult to replace in permanent magnet applications because of their very high strength to weight ratio. Permanent magnets are used in a multitude of applications, with the main applications including:

- Office equipment: Hard drives, printer drives, and copiers.
- Appliances: Air conditioners, refrigerators, washing machines, and shavers.
- Motors: Elevators, Robots, injection molding, linear and voice coil motors.
- Automobiles: Hybrid/electric drives, generators, air conditioners, power steering, audio system, and sensors.
- Other: MRIs, train motors, wind turbines, and electric bicycles.

The most common REE permanent magnet is neodymium-iron-boron (NdFeB), with samarium cobalt (SmCo) making up a smaller percentage of the market. NdFeB magnets have the highest magnetic strength per weight of all the permanent magnets and no tooling is required in their fabrication. However, they corrode easily, can lose their magnetic strength at relatively low temperatures, and are difficult to initially magnetize [1]. Samarium cobalt magnets are resistant to corrosion, stable in a wide range of temperatures, but they can be expensive as their price is strongly linked to the cobalt (Co) spot price as they require large amounts of Co and are more difficult to make, only coming in simple shapes [1]. Other rare earth

T. Larochelle (✉)

L3 Process Development, Bent Mountain, VA, USA

e-mail: tommee.larochelle@l3processdev.com

metals, such as Dy or Tb, can replace small amounts of the Nd in the NdFeB alloy to alter and upgrade specific properties of the magnets. Dysprosium is added to increase the coercivity and corrosion resistance of the magnet while Tb is added to increase the allowable operating temperature.

A mixed REE alloy is used in the anode of the batteries to improve durability and manipulation characteristics. Typically, La is the alloying REE of choice, but the anodes also contain a variety of other metals. Rare earths make up 3 to 14% of the mass of a battery cell inclusive of its casing [2], which come in various sizes and are used in a multitude of applications. Large batteries are typically used in automobile and energy applications while smaller batteries are used in portable electronic devices such as computers, cell phones, power tools, medical equipment, and other applications.

Metallurgical applications of the REE are mainly comprised of hydrogen (H_2) storage, mischmetal, and specialty alloys. While H_2 fuel is a potential source of alternative fuels being heavily discussed, it presents challenges for storage. High pressures are required because of the gas cryogenic nature (very low-temperature boiling point) and low energy density, requiring a substantial amount of the material. Hydrogen has many beneficial properties as a combustion fuel source since it is not a hydrocarbon (contains no carbon), its combustion only generates heat and water. The favored alternative to high-pressure hydrogen storage is molecular storage [3]. In this process, H_2 is absorbed in or on a compound, forming bonds in a similar fashion as water in hydration bonds. The result is a storage method that does not require high operation pressures, but still maintains a low storage volume per unit of H_2 . Lanthanum-nickel ($LaNi_5$) alloys can store up to 2.2% of their weight through H_2 absorption [4]. This alloy favorably compares to its alternatives and its use is growing.

Light REEs, primarily cerium (Ce) and La, with small amounts of Pr and Nd form an alloy referred to as mischmetal. Mischmetal is added to steel during the steelmaking process in order to bind with contaminant elements such as oxygen (O_2) and sulfur (S) to improve properties of the steel, such as corrosion resistance. When REEs react with O_2 and S, they form rare earth oxysulfides which replace manganese sulfide (MnS) and various oxide inclusions from the steel slag, increasing the overall steel strength and resistance to cracking [5]. High-carbon (C) steels and stainless steels can also be doped with Y and Ce to increase their temperature performance, oxidation resistance, ductility, and other thermal and mechanical properties [5]. Finally, REEs can also be used as alloying elements in a variety of alloys such as magnesium (Mg), aluminum (Al), and zinc (Zn) alloys. The most promising alloy is the aluminum-scandium (AlSc) alloy, which is expected to allow for the welding of aircraft bodies instead of the current riveting processes, reducing weight considerably.

Rare earth metals are produced industrially by metallothermic reduction and by molten salt electrolysis processes. Molten salt electrolysis is a process using electricity as the reducing vector to convert rare earth salts or oxides to metals in a molten salt medium. The molten salt medium is selected to allow for the

solubilization of the rare earth and for operation above the rare earth melting temperature. It is currently the most important commercial process for the reduction of rare earth compounds on a throughput basis. Rare earths heavier than Nd cannot be reduced in the molten salt electrolysis process because their melting temperature is either higher than available molten salt mixture or because they possess multiple stable valences. These rare earth metals are produced using a metallothermic reduction process, in batch or semi-batch mode at relatively low production volumes. The metallothermic reduction processes use a metal with higher stability to reduce the rare earth. The produced rare earth metal is then either distilled or gravity separated from the oxidized slag.

The starting reduction materials are composed of chloride, fluoride, oxide or a mixture thereof. It is important to note that REEs have varying thermodynamic properties and that different reduction processes may be optimal for different elements. The high electropositivity of the REE coupled with their reactivity with water (H_2O) and O_2 prevents the use of aqueous media for their electroreduction. Any attempt to electrodeposit the lanthanides in aqueous media would result in the production of hydrogen at the cathode rather than the reduction of the rare earth.

The current industrial reduction processes for lanthanides have been extensively described by Krishnamurthy and Gupta in their opus on the Extractive Metallurgy of Rare Earths [6] and by Habashi in his Handbook of Extractive Metallurgy [7], both are foundation references in the past and current practices in the industry. Habashi also published a short paper summarizing the current industrial reduction processes in 2013 [8], which in addition of the two previously cited handbooks will serve as a basis for the summary of current industrial rare earth reduction processes contained herein. This summary will be augmented with recent advances in the field when applicable.

Promising innovative reduction processes such as the Electrolysis in Ionic Liquids [9–22], the FFC-Cambridge [23–25], the Infinium Fueled Anode Electrolysis [26–28], and the Carboxylate Reduction Process [29] will also be discussed.

10.2 Industrial REE Reduction Processes

10.2.1 *Metallothermic and Carbothermic Reduction*

Metallothermic reduction processes use a molten metal which reacts with the rare earth compound to form a liquid or solid compound and the rare earth metal. Highly reactive metals usually in the alkali (lithium (Li), sodium (Na), potassium (K)) or alkali-earth (Ca) groups are used for this purpose. The reduction potential of metals toward the lanthanides is a reverse function of their stability. As such, Ca is the only metal more stable than rare earth fluoride and oxides whereas the full suite of common alkali metals (Li, Na, K) and Ca are more stable than rare earth chlorides and can be used to reduce the lanthanide chlorides [30].

The general equation (unbalanced) representing lanthanide metallothermic reduction is:



where Ln is a lanthanide, X is comprised of [F, Cl, O], and M is the reducing metal.

Lanthanide chlorides have the largest suite of suitable reductants possible among the industrial raw materials for the reduction of rare earths. However, the difficulty and cost of producing and handling anhydrous rare earth chloride salts result in a much lower metal product purity rendering chlorides an unattractive medium. Instead, historical metallothermic processes relied on fluoride medium and on the reduction-distillation process of oxides [6]. In the fluoride medium processes, lanthanide oxides were either reacted with hydrofluoric acid (HF) in an aqueous solution and dehydrated using an HF atmosphere (wet process) or directly converted to fluorides using anhydrous HF or ammonium hydrogen fluoride (NH_4HF_2) (dry process). The rare earth fluoride was then reduced using Ca under vacuum in a batch furnace lined with tantalum (Ta) and the system was cooled down. The metal ingot was separated from the calcium fluoride (CaF_2) slag and recovered. Unfortunately, these calciothermic reduction process would leave a significant amount of Ca and Ta in the metal, up to 2% and 0.5% by weight respectively [30]. In order to reduce contamination, the calciothermic process operating temperatures were lowered through the simultaneous introduction of a lower-melting temperature alloying element such as Zn or Mg and/or calcium chloride (CaCl_2). These added compounds would react to form a lower-melting eutectic CaF_2 slag [31]. The alloying metal was then distilled under vacuum and recovered, similarly to the Kroll process [32]. In a study by Carlson et al., the Y produced using this intermediate alloy technique had less than 0.01% by weight total Ca and Mg and only contained minor amounts of Ta [31]. The subsequent introduction of Li metal as a replacement for CaCl_2 in the process leads to further lowering of the reaction temperature through the formation of a lithium fluoride (LiF) slag which has a lower melting point than the CaF_2 - CaCl_2 slag [30].

While the fluoride reduction process proved commercially viable for most rare earths, it was not applicable to the elements possessing a divalent stable state (Sm, europium (Eu), ytterbium (Yb)). During the reduction process, these elements are reduced to their respective divalent salt and never reach the metal state [30]. In order to produce these metals, the reduction process must start from the oxide material. Unfortunately, the use of Ca as a reduction agent for the lanthanide oxides is not a viable commercial production route because of the very high melting temperature of calcium oxide (CaO) resulting in inefficient processing conditions. A specific reduction process referred to as Reduction-Distillation, Lanthanothermic Reduction or as Lanthanothermy [6] was developed using molten La as a reducing agent. In this process, the rare earths oxides are reduced using La metal and subsequently distilled from the molten lanthanum. This process is based on a higher stability of lanthanum oxide (La_2O_3) and on the lower vapor pressure of La metal with regard to other lanthanides.

Aluminothermic reduction is primarily used industrially to reduce scandium oxide (Sc_2O_3) in situ [33] and produce an AlSc alloy for use in the industry. Scandium availability and pricing do not currently support a mass adoption of AlSc alloys, but many prospective producers are advancing their projects as the aerospace industry is evaluating such alloys for the next generation of commercial airliners. Once sufficient low-cost supply capacity exists in the market, it is expected that the AlSc alloys will become ubiquitous in all applications where weight to strength ratio is important.

Calciothermic reduction is still used industrially for the production of high-purity heavy rare earth metals such as gadolinium (Gd), Tb, Dy, holmium (Ho), erbium (Er), Lu, and Y, while lanthanothermic reduction is used industrially for the production of Sm, Eu, Tb, and Yb [34].

Carbon is with Ca, the only other element having the thermodynamic potential to reduce lanthanides. However, no successful industrial processes have been developed for the reduction of lanthanides using carbothermic reduction as a basis because it has many drawbacks such as the formation of carbides and the vaporization of rare earth metal at operating temperatures leading to the reverse reaction occurring in the gas phase with carbon monoxide (CO) [30].

General Motor Corporation has developed and patented a molten salt calciothermic reduction process applicable to oxides [35], oxychlorides [36], and fluorides [37] in which the lanthanides are reduced by Ca metal in a molten CaCl_2 medium. The process is most efficient due to lower operating temperatures when utilized in combination with Fe as an alloying element for the preparation of neodymium-iron (Nd-Fe) alloys, a precursor to the NdFeB magnet alloy. Sharma has also demonstrated that Na metal could be used in lieu of Ca in this process to allow for the in situ reduction of Ca from CaCl_2 [35].

10.2.2 Molten Salt Electrolysis

Molten salt electrolysis (MSE) is an electrochemical reduction process using molten salt as a medium instead of an aqueous solution. The high reactivity of the lanthanide metals with water precludes aqueous electrowinning. MSE is currently the most important industrial process for the reduction of REE by production volume due to its lower comparative energy requirements and its continuous operation mode unlike metallothermic reduction which occurs in batch or semi-batch mode. In the MSE process, a rare earth compound (usually a chloride, fluoride or an oxide) is dissolved in a molten salt medium under an inert atmosphere while an electrical current is circulated through the unit. Historically, the chloride system was favored by the industry; however, intensification imperatives lead to the conversion toward the oxide-fluoride system around the year 2000. Chloride systems offer current efficiencies below 50% while oxide-fluoride systems offer current efficiencies up to 87% [38].

The applicability of molten salt electrolysis as a reduction process for lanthanides is limited to lower-melting lanthanide metals such as La, Ce, Pr, and Nd [34] or to low-temperature melting alloys made with Fe, Mg, Zn, and cadmium (Cd) [30, 39]. Higher-melting lanthanides have melting temperatures resulting in high losses of molten salt medium through vaporization, or above the boiling point of the salt medium.

The molten salt electrolysis of light rare earths (La, Ce, Pr, and Nd) has traditionally been undertaken in small circular 3kA cells using vertical graphite (C) anodes and either tungsten (W) or molybdenum (Mo) cathodes [40]. Recent advances have maintained the design but increased the capacity of the cells to 4–6 kA, and more recently to 10kAV using rectangular cells instead of cylindrical [41, 42]. Typical electrolytes are composed of a mixture of lanthanide fluoride and LiF in proportion 4 to 9:1. Specific operating parameters are usually maintained as trade secrets by Chinese firms, but Milicevic reports a ratio of 7:1 as the proper proportion of lanthanide fluoride to LiF to maximize solubility without detrimentally affecting the physical properties of the electrolyte [43]. The electrolytical reaction system for the electrolysis of Nd, the most important product in value and volume, is described using the following equations: [38, 44]

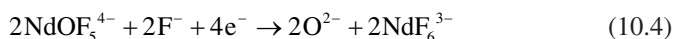
Neodymium dissolution reaction:



Cathode reaction:



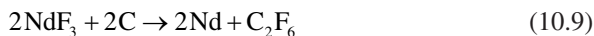
Anode reactions:



Overall reaction (carbon unbalanced):



In addition, perfluorocarbons (C_xF_y) are emitted at the anode due to an anode effect in the system. The anode effect can be described by the following reactions [45]:



Although C_xF_y production from the LiF electrolyte is theoretically possible, its significantly higher voltage requirement makes it unlikely to be a significant contributor to C_xF_y production [44]. Nevertheless modern molten salt electrolysis processes for the reduction rare earths present significant sustainability challenges especially with regard to C_xF_y emissions from anode effect and greenhouse gases emissions as highlighted in numerous life cycle assessments [39, 42]. They are also much more expensive to operate than many other metal reduction processes, prompting researchers to work on optimizing the current processes and on developing a new generation of more sustainable technologies.

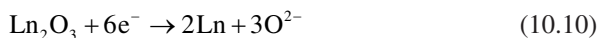
10.3 Novel REE Reduction Processes

10.3.1 FFC Cambridge Process

The FFC-Cambridge Process [22] is a zero liquid discharge process initially discovered by Fray, Farthing, and Chen of Cambridge that is currently being developed by Metalysis for the production of titanium (Ti), Ta, Al, and high-entropy alloys. Metalysis has reported successful production of Ce, Nd, and Y metals using the FFC-Cambridge process and it claims its process is suitable for all rare earth with the exception of La [22]. Lanthanum oxide reacts with molten $CaCl_2$ salt to form an oxychloride which does not electro-reduce to metal. However, it was determined by Zhu et al. [23] that sintering La_2O_3 with nickel oxide (NiO) at sufficiently high temperature prior to the FFC-Cambridge process allowed for the production of $LaNi_5$ H_2 storage alloy powder.

The FFC-Cambridge Process for lanthanides can be described by the following reactions:

Cathode deoxygenation reaction:



Anode reactions:



Overall reaction (carbon unbalanced):



The FFC-Cambridge process is a batch electro-deoxidation process in molten salt medium where the metal oxide is pelletized and reduced in situ at the cathode yielding a metal or metal alloy pellet. The metal pellet is then ground and washed to yield a metal powder product [25]. While it is unlikely that the FFC-Cambridge

process will challenge the oxide-fluoride molten salt electrolysis for light REE, it presents a valuable alternative to metallothermic reduction processes used for the heavier lanthanides and could present an interesting alternative for the production of complex magnetic alloys. The nanometric metal powder nature of the product also increases the attractiveness of the FFC-Cambridge process, enabling the direct production of bonded and sintered magnets.

10.3.2 Fueled Anode Molten Salt Electrolysis

The Fueled Anode Molten Salt Electrolysis process [26] that was being developed by Infinium prior to its closure is a significant evolution of the oxide-fluoride molten salt electrolysis process. It was commercially operated at a small scale to produce ferro-dysprosium alloy (80:20 DyFe) and the company was expected to offer other rare earth elements to the market [26].

In Infinium's molten salt electrolysis process, an oxygen ion (O_2^-) permeable membrane is used to separate the anode from main electrolyte reservoir. Following dissolution, the rare earth ions are reduced at the cathode while the O_2^- is oxidized in the presence of fuel at the anode. Contrary to conventional molten salt electrolysis, the Infinium process used an inert liquid metal anode such as liquid silver (Ag), copper (Cu) or tin (Sn). The injection of fuel in the anodes serves many beneficial purposes such as an increase in energy efficiency and for oxidation protection [27, 28].

Infinium's process was revolutionary in that its configuration and its O_2 permeable membrane precluded the electrolysis of the fluoride ion (F^-) and when operated with a truly inert anode emitted no carbon dioxide (CO_2).

10.3.3 Carboxylate Reduction

The Carboxylate Reduction Process (CRP) is a zero liquid discharge process developed by Hela Novel Metals that is currently being scaled up to demonstration-scale following the successful piloting of the technology. It represents a significant challenge to the legacy molten salt electrolysis and metallothermic reduction processes both from a capital and an operating standpoint. The patent application US20200047256A1 is currently pending on this novel technology [29].

CRP can be operated either as a continuous process in a series of rotary kilns or as a batch process in a static furnace. The configuration versatility of the process is expected to allow its profitable implementation at various scales. CRP uses a proprietary mixture of nitrogen (N_2), ammonia (NH_3), CO, and H_2 to sequentially dehydrate, reduce, and refine rare earth elements into their respective pure metal powders. The process also allows mixtures of metal oxalates to be reduced to an alloy powder mixture of the elements such as NdFeB, SmCo, and AlNiCo alloys. In the first step, a metal oxalate salt is dehydrated into an anhydrous metal oxalate salt at a

temperature between 200 and 440 °C while avoiding any oxalate decomposition. In the second step, the anhydrous metal oxalate powder is decomposed to its metal state and a mixture of oxalic acid ($C_2H_2O_4$) and ammonium oxalate ($(NH_4)_2C_2O_4$) is recovered as a by-product. The reduction step is operated between 320 and 720 °C under pressure. In the final process step, the metal powder is refined to remove any loosely bonded nonmetal impurities such as O_2 , S, and C under a different variation of the proprietary gas mixture at a temperature between 700 and 1300 °C.

As an added benefit, CRP produces a micropowder, allowing the direct utilization of the REE for bonded and sintered magnets. Hela Novel Metal recently submitted a patent application for a process to manufacture rare earth magnetic blocks from carboxylate salts in a single proprietary furnace.

While CRP shows great promise for the reduction of REE to their respective metals or alloys, it is important to note that Hela Novel metals have also demonstrated the applicability of the CRP process to many other critical metals and alloys thereof such as Ti-6Al-4 V, ferroniobium, nuclear grade zirconium (Zr) alloys, and Co alloys. In addition, Hela Novel Metal has identified alternative carboxylates such as ammonium metal carboxylates which provide for reduced energy requirement from the process.

10.3.4 Ionic Liquid Electrodeposition

Details on the ionic liquid (IL) electrodeposition process are provided in detail in Chap. 8. Salient points from that chapter follow.

The use of ILs in electrometallurgical processes promises to significantly reduce the environmental footprint associated with the production of rare earth metal by replacing the energy-intensive molten salt electrolysis and metallothermic reduction processes. A few ventures have already been established to develop a commercial ionic liquid electrodeposition process, but none has yet to succeed.

Key advantages of the utilization of ILs in the electrochemical reduction of the lanthanides include a higher potential window than alternative medium, virtually no vapor pressure at operating temperatures, a high metal salt solubility, a higher conductivity than organic solvents, and more importantly a control over the water content of the electrolyte [9]. In addition, the transition to a low-temperature emission-free process would eliminate the large amount of CO_2 and C_xF_y emissions currently resulting from conventional processes.

It is important to note that the electrical conductivity of ILs at room temperature is approximately an order of magnitude lower than molten salts, resulting in lower electrical efficiency. This disadvantage can be mitigated by operating IL units at high temperature (>100 °C) [10]. Similar to molten salt electrolysis, the existence of a stable +2 valence for Sm, Eu, and Yb creates additional hurdles in ILs.

Various ionic liquids are being investigated for the electrodeposition of rare earth elements.

- *Imidazolium ILs*: Significant issues have been reported using imidazolium ($C_3H_5N_2^+$)-based ILs, notably related to the decomposition of the IL under operating conditions [11, 12]. One potential avenue is the production of transition metal alloys of REE [13].
- *Pyrrolidinium ILs*: Successful deposition of REE metals was observed using pyrrolidinium ($C_4H_{10}N^+$) ILs. Notably, Bourbos et al. successfully prevented the breakdown of the IL anion $[NTf_2]$ by using neodymium chloride in dimethylsulfoxide (DMSO) in a separate anode compartment [10]. This two-compartment design allowed for the utilization of neodymium chloride ($NdCl_3$) as a feed material and the production of gaseous chlorine rather than the decomposition products of the $[NTf_2]$ anions, resulting in much more favorable economic prospects in a more environmentally friendly process.
- *Phosphonium ILs*: All investigations of phosphonium (PH_4^+) ILs as a medium for the electrodeposition of REE have highlighted the critical role played by water in the system. Water is both required for the process to operate and deleterious to the product [14–16]. As such, the potential of phosphonium ILs for the electrodeposition of rare earth elements is rather dubious.
- *Neutral Ligand Complexation ILs*: These represent one of the most promising approaches to the electrodeposition of rare earth metals in ILs. Recent investigations demonstrated that REE could indeed be successfully deposited onto a cathode substrate using a neutral ligand solvent (NLS) to generate a lanthanide IL cation through the dissolution of a lanthanide triflimide salt [17–19]. The potential commercial success of this approach lies in the electrostability of the medium and with its implicit self-regeneration. However, similar to other IL mediums, additional research on the anodic reaction will be required to replace the decomposition of the $[Ntf_2]$ anion with a different anion and allow for its reuse in the production of the lanthanide salt feed material.
- *Aluminum Chloride ILs*: The reduction of Al and Al alloys from aluminum chloride ($AlCl_3$)-based IL medium has been extensively investigated in the past [20–22]. However, these processes have yet been proven to be sufficiently economical to replace legacy industrial processes. The incentives with regard to rare earths such as the utilization of relatively inexpensive chlorides, the absence of fluorides, and a low operating temperature suggest that research into these systems is likely to increase drastically in the foreseeable future. A subsequent distillation step would be required for the purification of the rare earth metal, not unlike current lanthanothermic processes.

10.4 Technology Outlook

Global economics and geopolitical considerations in the last two decades allowed China to consolidate the RE industry vertically. This situation currently raised some alarming flags with respect to RE supply chain and pricing.

No significant REE metal reduction plants exist outside of China with the exception of a small Japanese integrated supply chain. More importantly, the two main obstacles to the establishment of an REE reduction plant outside of China are a stable availability of high-purity separated REE raw materials and the absence of a significant market for the rare earth metals produced. All novel processes discussed in this chapter were also being designed for the production of other technological metals for which conventional processes are onerous and complicated such as for Ti, Zr, and advanced alloys.

The development of a novel more efficient process for rare earth reduction such as the FFC-Cambridge, the Infinium, and the Carboxylate reduction process is not enough in themselves to challenge the domination of the Chinese industry. They can however be part of a larger effort by the Occident to reestablish an industry supply chain starting from deposits to separation to reduction and finally to the production of REE-containing products. The commercialization of new processing technologies across the supply chain would then be the key to a rebalancing of market forces.

In the next decade, additional research on ILs electrodeposition is likely to lead to its implementation in China as a replacement for both the molten salt electrolysis and the metallothermic reduction processes. Its adoption outside of China will likely be precluded by the market forces described above.

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