Metal Leaching and G-METS Distillation for Neodymium Magnet Scrap Recycling

By

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Abstract

The importance of rare earth metals for clean energy technology and the threat to their supply has prompted several researchers to consider alternative techniques to mining. One strategy that is gaining traction in this area is recycling. Recycling has been proposed as a promising potential supply source to meet some of the US rare-earth demand for use in permanent magnets. Besides reducing the environmental impact of mining for rare earth metals, recycling offers manufacturers a commercially viable alternative. Studies show that the concentration of rare earth in end-of-life devices and waste streams is higher than in ores. The high growth rates of products that use rare-earth magnets, particularly wind turbines and electric and hybrid vehicles, highlight that their stock in use is on the rise and, in the near term, will become available as scrap feed for recycling. Various studies have shown that the magnet-to-metal recycling method, in which rare earth metals such as neodymium, praseodymium, and some traces of dysprosium and terbium can be leached from the magnet and obtained as recycled mixed rare earth metal which may be used as a precursor for the manufacturing of rare earth magnets.

This thesis provides an introduction to magnet recycling technologies. It evaluates the techno-economic analysis of liquid metal leaching and distillation, including the effect of a new continuous gravity-driven multiple effect thermal system (G-METS) metal distillation technology on energy use and overall cost. The G-METS system can potentially reduce the energy consumption of the overall process to 64 kWh/kg, which is about 30% less than metal production from ore and 61–67% less than the conventional process distillation. A commercialization study is also presented. It suggests that the commercial viability of rare earth magnet scrap recycling depends on a consistent supply of high-quality scrap material, the demand for rare earth magnets, and the cost of virgin rare earth metals from primary production. Incentivizing the collection of rare earth magnet scraps and their recycling can foster the development of viable recycling technologies. This study further assesses the leaching and distillation of rare earth magnets using magnesium. It demonstrates magnesium’s effectiveness as a leaching agent for rare earth metals. It further presents a reduced-order model that predicts a three-effect distiller's distillation temperatures and production rates. The effect of neodymium activity on the distillation of magnesium-neodymium alloy compared to pure magnesium is presented. The results of the reduced-order model were benchmarked using a third-party distillation model for magnesium-aluminum-zinc alloys. Models of distillation for magnesium and bismuth can be used for scale-up reactor engineering.

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God bless you.

Chapter 1

Background and Introduction

1.1: Introduction

Lanthanides, scandium (Sc), and yttrium (Y) comprise the seventeen elements known as rare earth metals. The term "light rare earth elements" (LREEs) refers to the lower atomic weight elements lanthanum (La) to samarium (Sm) with atomic numbers 57 to 62. Elements from europium (Eu) to lutetium (Lu) comprise the "heavy rare earth elements" (HREE) with atomic numbers 63 to 71. The chemistry of Sc 3+, Y 3+, and Lu 3+ have many similar characteristics, perhaps even more than Y 3+ and La 3+. The prevalence of Y III in ores rich in 'heavy' rare earth is a result of this correlation, which is based on the similar ionic radii of Y 3+ and Lu 3+ (and more so for Holmium 3+/Erbium 3+)[1], [2]. Due to scandium's slightly different characteristics from the other REEs, it is typically omitted, and the lanthanides and yttrium are given more attention.

Although they are referred to as rare earth, their abundance in the Earth's crust does not necessarily connote rarity. It is comparable to those of many other significant elements, including uranium (1.7 ppm), germanium (1.3 ppm), copper (27 ppm), tin (27 ppm), and lithium (17 ppm). For example, cerium which is the most abundant of the rare earth has 43 parts per million (ppm) abundance level, followed by lanthanum and neodymium (Nd), both having a 20 ppm level and yttrium with 19 ppm[3].

1.2: Geographical Production Concentration

The global REE deposits held by major nations, including China, Brazil, Vietnam, Russia, and India, are around 130 million tonnes, with China owning one-third of the world's reserves[4]. Figure 1.1 shows rare earth oxide production rates in metric tons between 1950 and 2022. It vividly depicts the United States' emergence into the market in the mid-1960s, when demand for color television surged. As China began exporting rare earths at extremely low costs in the late 1980s and early 1990s, the US mine was forced to close because they could no longer profit.

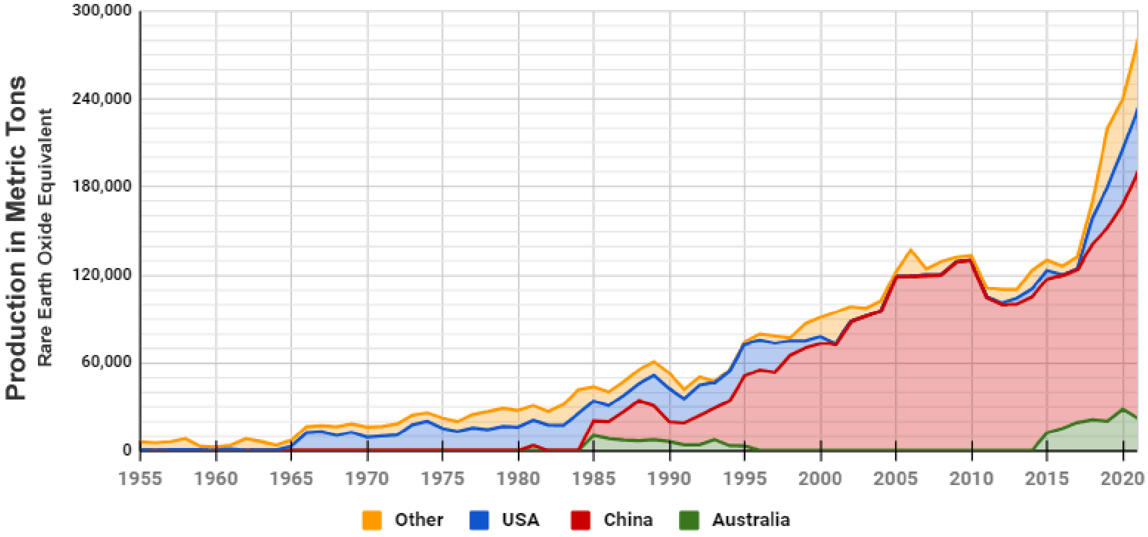


Figure 1.1: Rare Earth Oxide Production Rates in Metric Tons[2]

In the United States, Mountain Pass, in the upper Mojave Desert of California, had the largest rare earth production rate from the 1960s until the 1980s when China began growing to dominate the world production. The rare earth content in Mountain Pass is hosted chiefly by bastnasite, which is majorly the LREEs like Ce, La, and Nd. In 1998, mining activities in Mountain Pass stopped because of their inability to compete with China's prices and environmental concerns in their surrounding areas. Other notable exploration initiatives in the US outside Mountain Pass are the Bear Lodge, Bokan-Dotson Ridge, Round Top, and La Paz projects. The Companies Rare Element Resources and Ucore Rare Metals are working to develop the REE resources in the Bear Lodge Mountains in Wyoming and the Bokan Mountain in Alaska, respectively, including the minerals bastnaesite and monazite. HREE concentration in both deposits is substantial. It will take three to four years for the Ucore Rare Metals project in Alaska to start operating. Also, rare earth concentrates can be obtained commercially from uranium and thorium-bearing rare earth ore in White Mesa Mill, Utah. Energy Fuel Company has reported the potential to recover commercially viable rare earth concentrates while recovering uranium from the ores[5].

In 1999 and 2000, more than 90% of REEs required by the U.S. industry came from deposits in China. There are a variety of underlying causes for the quick shift from relative self-sufficiency before 1990 to practically total dependence on imports from majorly China. These include the sustained growth of electronics and other industries in Asia, the favorable number, size, and HREE composition of Chinese deposits, and the ongoing environmental and regulatory issues at Mountain Pass. Additionally, China has lower labor and regulatory expenses than the US[4],[6],[7]. Figure 1.2. displays how the magnet industry's supply chain is heavily focused in China, mainly as it descends from metal refining and mining to magnet production.

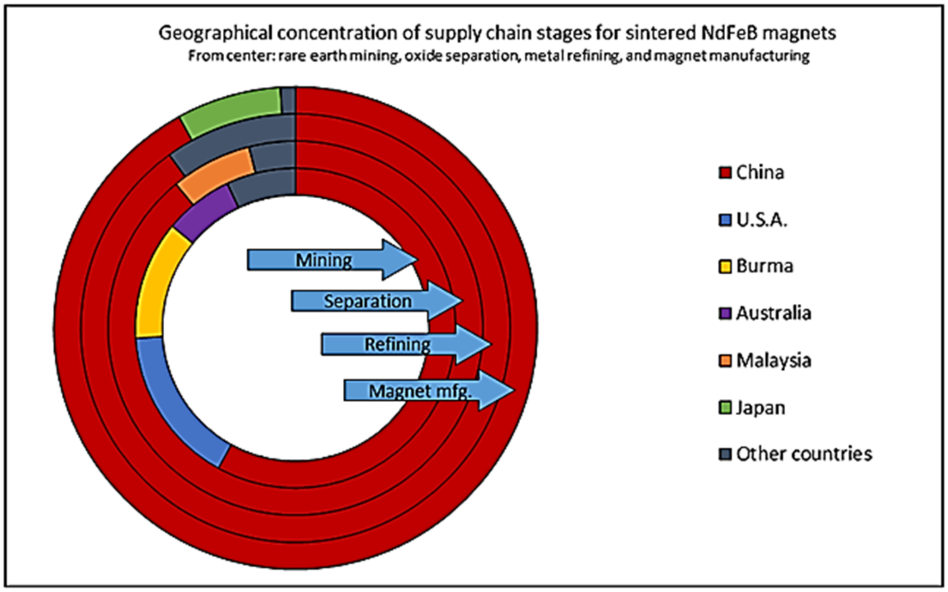


Figure 1.2: Geographical Concentration of Supply Chain Stages for Sintered NdFeB Magnets[8]

The competitiveness of the United States rare earth magnet supply chain depends on factors such as net import reliance, price volatility, geopolitical sensitivity of trade partners, and substitutability across the supply chain. Although efforts have been made in recent years to increase domestic production capacity and diversify foreign supply sources in the United States, the supply chains for rare earth elements and magnets have not become resilient because US manufacturers continue to face difficulties in remaining competitive, particularly in the midstream stages of the supply chain.

Sintered neodymium magnets used in wind turbines and electric vehicles can only be produced economically in small quantities domestically in the United States. At the same time, China currently controls all of the key supply chain stages. Even more strikingly, this concentration of production in China grows at every stage further along the supply chain. From a 58% share of annual global rare earth mining in 2020 to a 92% share of the annual global magnet production—the stage with the highest added value—China now accounts for 92% of all annual global production. Consequently, regaining U.S. competitiveness at many points along the supply chain is necessary to create a robust domestic magnet manufacturing industry[8].

In general, the production of many energy transition minerals is more concentrated than oil or natural gas. The top three producers of lithium, cobalt, and rare earth elements collectively account for over three-quarters of global production. In some cases, a single country can account for over half of the global production of these minerals. In 2019, over 70% and 60% of the world's cobalt and rare earth element output came from the Democratic Republic of the Congo (DRC) and the People's Republic of China (China), respectively. The concentration level is significantly higher for processing operations, which China dominates globally. Around 35% of nickel is refined in China, 50% to 70% of lithium and cobalt, and around 90% of rare earth elements[9].

Mining, separation, refining, alloying, and manufacturing are the processes that make up the rare earth element supply chain. The inadequacy of refining, alloying, and fabrication capacity that might handle any future output of rare earth is a massive impediment to REE growth in the United States. Samarium cobalt (SmCo) permanent magnets are made by one American company, Electron Energy Corporation (EEC), in Landisville, Pennsylvania. Meanwhile, neodymium-iron-boron (NdFeB) magnets are not currently produced in the United States. However, Noveon Magnetics and MP materials have facilities to start producing soon in the coming years[10]–[12].

1.3: The Clean Energy Revolution

The shift from fossil energy fuels to clean energy sources has given rise to emerging clean technologies like wind turbines, electric vehicles, energy-efficient lighting, and rechargeable batteries, which all depend heavily on REEs. These technologies are expected to expand significantly over the coming decades as the global energy system is transformed into more sustainable and renewable systems. There is an urgent need to project the tendency for different sectors and REE demand for these technologies, given the diverse development tendencies in these technologies and the fact that individual REE demand varies in these sectors due to the different distribution of REE in natural resources. Around 3 million electric vehicles were sold globally in 2020, increasing their market share to above 4% (IEA 2021). As a result, more than 10 million electric vehicles are on the road worldwide. However, to meet the global climate objectives, their sales share must significantly increase to about 40% by 2030, along with the swift electrification of buses, freight trucks, and light commercial vehicles[9], [13].

Due to its high efficiency, the current technology for powering an electric vehicle remains a permanent magnet traction motor. Nearly all the magnets used for these motors are based on NdFeB, which was discovered in 1982. These magnets use as much as 32 percent Nd and as much as ten percent dysprosium (Dy).

Permanent magnet generators have gone mainstream, particularly in offshore turbines. This is because they offer high yearly energy output at a low lifetime cost, high power density, compact size, and maximum efficiency at all speeds. Most direct-drive turbines have permanent magnet generators, frequently including neodymium and trace amounts of dysprosium[14].

1.4: Rare Earth Permanent Magnet Application

NdFeB is currently the most powerful and economically important magnet material. Other materials with higher properties for large-scale applications have yet to be developed. The bulk of rare earth permanent magnet sales are made up of NdFeB.

NdFeB is beneficial in applications requiring high performance, high efficiency, and small size because of its remarkable magnetic properties. Figure 1.3. depicts a breakdown of the projected industrial uses of NdFeB. Because permanent magnet generators and motors require fewer copper windings with running current than induction designs, this promotes high energy efficiency. These characteristics are required by the wind energy industry, particularly for giant turbines (> 5 MW), where a light turbine design is critical to reducing otherwise difficult mechanical limitations.

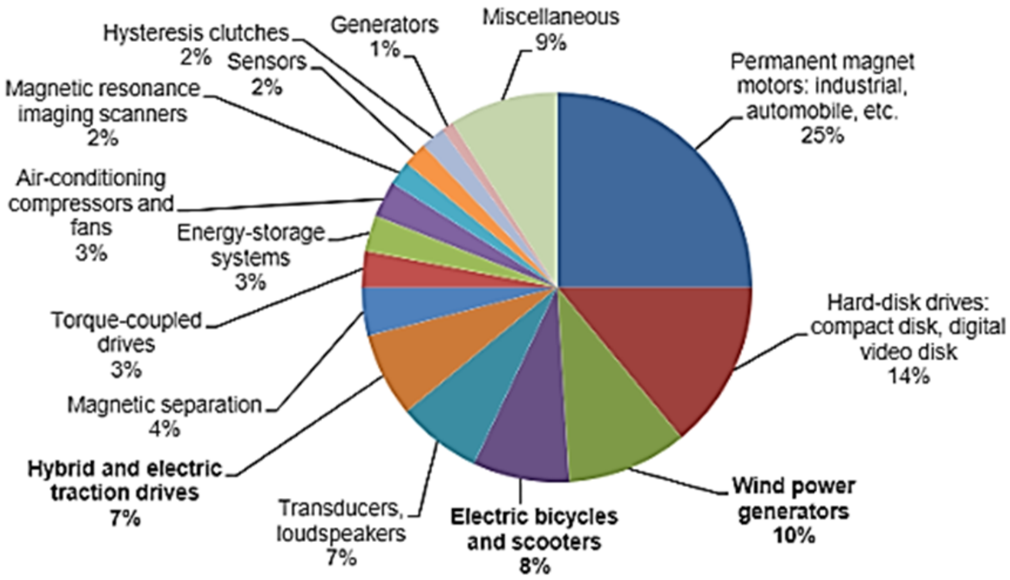


Figure 1.3: Estimated Industrial end-use share of NdFeB magnets[15]

1.5: Rare Earth Applications in Defense Systems

The U.S. Department of Defense (DOD) relies on particular metals and metal alloys, including rare earth magnets, for its operations. Devices using these materials, such as integrated circuits, optical components, and electronic devices, are typically embedded in the structures or components of military platforms and weapon systems that support warfighting capabilities, such as airplane fuselages or ship hulls[16]. Metal alloys such as NdFeB and SmCo magnets are used in various military weapons. SmCo, for instance, finds usage in military technologies like precision-guided missiles, smart bombs, and aircraft because it maintains its strength at high temperatures. NdFeB is considered the world's strongest magnet and can be used in various military applications. Table 1.1 shows the various uses of rare earth metals (REMs) in defense applications.

Table 1.1: Uses of Rare Earth Metals in Defense Applications

REEs used	**Rare Earth Technology**	**Application**	**Selected Examples**
Yttrium (Y), Europium (Eu) and Terbium (Tb)	Energy Resolution Amplification	Targeting and Weapon Systems	Laser-targeting Air-based lasers, FCS Vehicle with Laser Weapon, SaberShot Photonic Disruptor, Laser Avenger (counter-IEDs).
Neodymium (Nd), Praseodymium (Pr), Samarium (Sm), Dysprosium (Dy), Terbium (Tb)	Strong Permanent Magnets	Guidance and Control Systems	Smart bombs, Tomahawk cruise Missile, Joint Direct Attack Munitions, Joint Air to Ground Fin Actuator, Predator Unmanned

			Aircraft.
Neodymium (Nd), Praseodymium (Pr), Samarium (Sm), Dysprosium (Dy), Terbium (Tb)	Strong Permanent Magnets	Electric Drive Motors	CHPS Future Combat, Integrated Starter Generator, Hub Mounted Electric Traction Drive, Zumwalt DDG 1000, Joint Strike Fighter, and More Electric Aircraft.
Neodymium (Nd), Yttrium (Y), Lanthanum (La), Lutetium(Lu), Europium (Eu)	Enhanced Signal Resolution	Radar, Sonar, Radiation, and Chemical Detection	Radar, Sonar Transducers, Multipurpose integrated Chemical Agent Alarm (MICAD).
Numerous REEs	Energy Storage, Density Amplification and Capacitance	Electronic Warfare	Electromagnetic railgun, Ni metal Hydride Battery, Area Denial Systems, jamming devices, Area Denial systems, and Long-range acoustic devices

[10], [17].

1.6: Criticality of Rare Earth Metals

Neodymium and praseodymium (Pr) are the critical LREEs used in producing NdFeB magnets, while terbium (Tb) and dysprosium are the HREEs that are critical materials, often alloyed with the NdFeB Magnets to increase their operating temperatures[10], [18], [19].

The assessment of two characteristics, supply risk and importance, has been mainly attributed to resource criticality. The supply risk is determined by various underlying elements, which vary according to the scope and time frame of the criticality assessment activity. In the short-to-medium term, the supply risk issue is more of a structural dysfunction characterized by the market's inability to adapt to changing conditions. On the other hand, the importance of a constraint parameter depends on the system selected. Taking a product as an example, a resource is chosen primarily because of its critical role in providing essential functions for which no or only a few adequate replacements are available, given the technological and economic feasibility constraints. This indicates how vital a resource is for a product. However, if the resource in issue is not experiencing any supply risk, it will not be considered vital[20]. The scarcity of domestically produced material resources for industrial demands in most Western nations and Chinese embargos on rare earth elements (REEs), which began in 2007 and peaked in 2011, sparked the curiosity of global raw material consumers. This development has a significant global impact, as China controls most of the global REE market- over 90%. Countries with a high level of industrialization and a heavy reliance on raw material imports, such as Japan, Korea, the United States, and European countries, began to routinely analyze the stability of their raw material supply chains. During this period, the United States and the European Union created and published criticality methodologies primarily driven by economic and political factors. For example, using a widely acceptable parameter called Herfindahl Hirschman Index (HHI), Habib et al. estimated the risk of concentrated supply for rare earth elements and other critical metals from 1994 to 2013, considering the geological reserve share of metals by countries. This was used to project the primary supply share of these countries for 2050[21], [22].

A study by the United States Department of Energy assessed the criticality of REEs based on two factors-importance to clean energy and supply risk, as shown in Figure 1.4. They showed that REEs, including Nd, Dy, Tb, Eu, and Y, were the most critical.

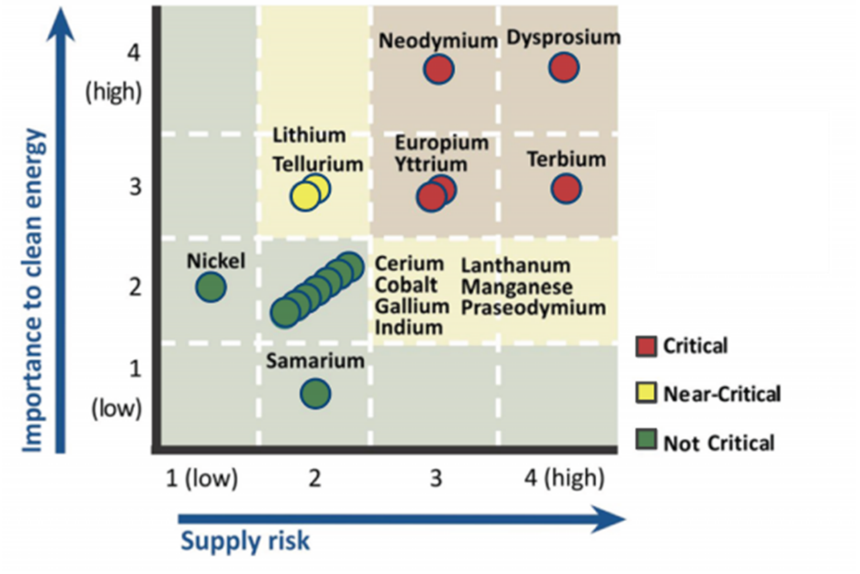


Figure 1.4: Materials Criticality Matrix (2015-2025) [23]

1.7: Research Directions in Addressing Critical Materials

Several studies have been directed towards addressing the criticality of materials, and this can be divided into three key pillars[24]:

1.7.1: Diversify Supply

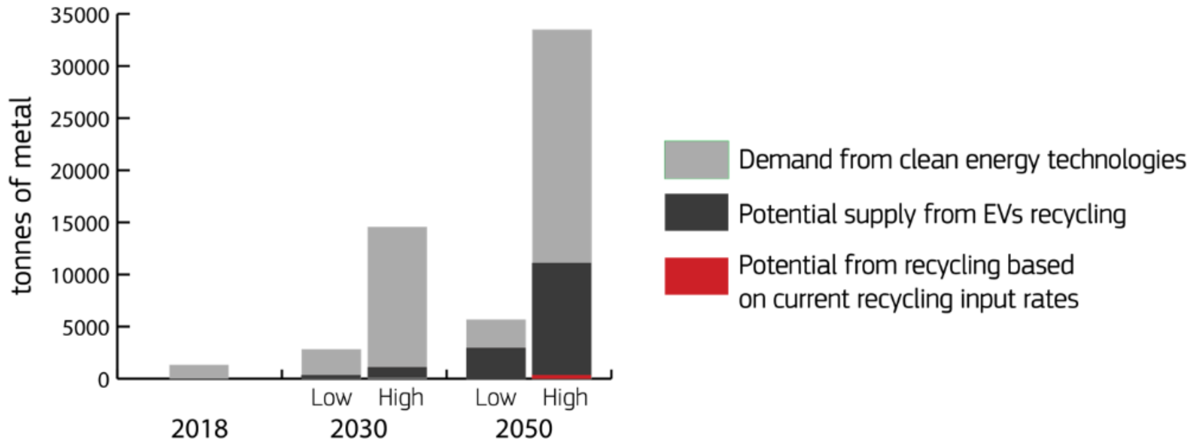
This involves the exploration of non-traditional sources such as mine tailings[25], [26], the use of co-products[27]–[29], wastewater[30],[31], creating advanced separation/extraction techniques and discovering new techniques. This would lead to diverse, secure, and resilient domestic sources and supply chains in the long run. It will result in advanced resource mapping, characterization, and fundamental geoscience understanding.

1.7.2: Develop Substitutes

Substitution of most critical materials with non-critical materials has been ongoing research to develop new alloys, components, and systems[32], [33]. For example, the permanent magnet synchronous traction motor (PSM) containing rare earth is currently the preferred technology for electric cars. For battery electric vehicles (BEV), alternative rare earth-free electric motors (such as asynchronous or electrically stimulated synchronous machines) are available. Because hybrid electric/electric cars dominate the EVs industry today, the absence of a component replacement for PSM in serial manufacturing provides a significant barrier. However, several substitute choices are possible in the R&D or pilot phases[15], [34]

1.7.3: Recycling and Reuse

Recycling could meet up to half the demand for rare earth elements used in electric traction motors, and almost one-third of the demand for clean energy technology in general (wind turbines and electric vehicles). However, as seen in Figure 1.5., this will only occur in the long run if the recycling system is greatly improved. If present recycling input rates of less than 1% for neodymium and dysprosium, and less than 5% for praseodymium, are not increased, this potential will go unmet.



Source: JRC.

Figure 1.5: Projected demand for neodymium, praseodymium, and dysprosium for clean energy technologies compared with the potential supply from the recycling of rare earth from electric vehicles (EVs) (EU-27 and the United Kingdom)

Recycling involves recovering critical materials from end-of-life devices using physical, chemical, and biochemical extraction processes and additive manufacturing[35]–[37].

The short-term potential of rare earth magnet scrap recycling is substantial, offering a readily available source of rare earth elements (REEs) that can help mitigate these critical materials' current shortage and price volatility. Scrap recycling can also reduce the environmental impact of REE production, which is often associated with environmental degradation, toxic waste generation, and human health risks.

The long-term potential of REE scrap recycling can provide a stable and sustainable source of REEs that can help reduce dependence on imports, enhance the security of supply, and promote the development of new technologies that require REEs. Additionally, scrap recycling can reduce the demand for newly mined REEs, thus reducing the environmental impact of REE extraction and production.

However, some challenges are associated with REE scrap recycling, including the technical and economic feasibility of the process, the availability and quality of scrap material, and the need for investment in research and development to improve the efficiency and scalability of the recycling process. Nevertheless, the potential benefits of REE scrap recycling make it an attractive option for addressing the current and future demand for these critical materials.

The long-term goal of recycling would be to develop economic and energy-efficient recovery processes to enable a circular economy for critical materials. To achieve this, an integrated suite of systems, including modeling/simulation, advanced characterization, techno-economic analysis, and lifecycle analysis, would be necessary to mitigate future criticality issues and support domestic supply. Developed prototypes and pilot plant demonstrations will be essential to support commercial-scale production.

1.8: Scope of Thesis

This thesis focuses on molten metal leaching and G-METS distillation for rare earth magnet scrap recycling. This project aims to develop fundamental measurements and modeling for a modified rare earth magnet recycling process, including an assessment of the commercialization potential of the recycling process.

This includes a techno-economic analysis of the proposed technology and its commercial viability, reduced order modeling, and experimental investigation of the leaching and distillation processes. These are covered in the scope of this thesis, which includes:

The Introduction in Chapter 1 and the literature review in Chapter 2. This presents relevant literature on the applications and criticality of rare earth magnets; research directions in addressing criticality; primary and secondary production of rare earth metals; and advances in recycling rare earth magnets. Chapter 3 discusses the techno-economic analysis of rare earth metal recycling using efficient distillation technology. The relationship between energy requirements and the cost of various recycling processes is also discussed in this chapter to provide insights into the advantages of the proposed recycling technology. Chapter 4 discusses the commercialization viability of the liquid metal leaching and low-cost distillation process. This is based on an NSF I-Corps program on customer discovery. Chapter 5 details the experimental investigations of the leaching and distillation processes, demonstrating magnesium as a suitable leaching agent for rare earth magnet scrap. It also presents a reduced-order model developed to estimate the temperature and production rates for magnesium-neodymium alloy distillation.

Finally, Chapter 6 summarizes key findings from this study and provides recommendations for future research.

REFERENCES

[1] T. Behrsing, G. B. Deacon, and P. C. Junk, “The chemistry of rare earth metals, compounds, and corrosion inhibitors | Elsevier Enhanced Reader.” https://reader.elsevier.com/reader/sd/pii/B9780857093479500011?token=DBB0CF0920785E1F48F2361A17FF39B71A6091AB0AFF3F84ED9089E900BB08986952357FCE3E7F74861C251F3153F9B2 (accessed Jul. 09, 2020).

[2] H. King, “REE - Rare Earth Elements - Metals, Minerals, Mining, Uses,” *Geology.com*, Sep. 2021. https://geology.com/articles/rare-earth-elements/?source=content_type%3Areact%7Cfirst_level_url%3Aarticle%7Csection%3Amain_content%7Cbutton%3Abody_link (accessed Jan. 10, 2021).

[3] N. Bilham, “Rare Earth Elements - A briefing note by the Geological Society of London,” The Geological Society, Dec. 2011. [Online]. Available: chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://www.geolsoc.org.uk/~/media/shared/documents/policy/Rare%20Earth%20Elements%20briefing%20note%20final%20%20%20new%20format.pdf

[4] V. Balaram, “Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact,” *Geosci. Front.*, vol. 10, no. 4, pp. 1285–1303, Jul. 2019, doi 10.1016/j.gsf.2018.12.005.

[5] World Nuclear News, “Energy Fuels looks to rare earth to enhance White Mesa operations : Uranium & Fuel - World Nuclear News,” May 2020. https://world-nuclear-news.org/Articles/Energy-Fuels-looks-to-rare-earth-to-enhance-White (accessed Dec. 22, 2020).

[6] G. Haxel, J. Hedrick, and G. Orris, “United States Geological Survey,” United States Geological Survey, 2002.

[7] "Critical Materials Rare earth Supply Chain: A Situational White Paper," U.S. Department of Energy, Apr. 2020. Accessed: Aug. 06, 2020. [Online]. Available: https://www.energy.gov/sites/prod/files/2020/04/f73/Critical%20Materials%20Supply%20Chain%20White%20Paper%20April%202020.pdf

[8] U.S. Department of Energy, "Rare Earth Permanent Magnets - Supply Chain Deep Dive Assessment," Feb. 2022.

[9] "The Role of Critical Minerals in Clean Energy Transitions," International Energy Agency, May 2021. Accessed: Jan. 05, 2022. [Online]. Available: https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions

[10] V. B. Grasso, "Rare Earth Elements in National Defense: Background, Oversight Issues, and Options for Congress," U.S. Congress, Congressional Research Service R41744, Dec. 2013.

[11] "MP Materials Begins Construction on Texas Rare Earth Magnetics Factory to Restore Full U.S. Supply Chain," Apr. 04, 2021. https://mpmaterials.com/articles/mp-materials-begins-construction-on-texas-rare-earth-magenetics-factory-to-restore-full-us-supply-chain/ (accessed Nov. 13, 2022).

[12] "News," *Noveon Magnetics*. https://noveon.co/news (accessed Nov. 13, 2022).

[13] H. Paulick and E. Machacek, "The global rare earth element exploration boom: An analysis of resources outside of China and discussion of development perspectives," *Resour. Policy*, vol. 52, pp. 134–153, Jun. 2017, doi: 10.1016/j.resourpol.2017.02.002.

[14] A. Dias, B. S, C. S, and P. B, "The role of rare earth elements in wind energy and electric mobility: an analysis of future supply/demand balances." Publications Office, LU, 2020. Accessed: May 13, 2021. [Online]. Available: https://data.europa.eu/doi/10.2760/303258

[15] European Commission. Joint Research Centre., "Substitution of critical raw materials in low-carbon technologies : lighting, wind turbines, and electric vehicles.," LU, 2016. doi 10.2790/64863.

[16] R. Parman, “An elemental issue,” *www.army.mil*, Sep. 2019. https://www.army.mil/article/227715/an_elemental_issue (accessed Jan. 13, 2021).

[17] H. Peters, “Defense Primer: Acquiring Specialty Metals and Sensitive Materials,” U.S. Congress, Congressional Research Service Report R43354, Feb. 2021.

[18] M. Humphries, “Rare Earth Elements: The Global Supply Chain,” *Rare Earth Elem.*, p. 31.

[19] K. Binnemans, P. T. Jones, T. Müller, and L. Yurramendi, “Rare earth and the Balance Problem: How to Deal with Changing Markets?,” *J. Sustain. Metall.*, vol. 4, no. 1, pp. 126–146, Mar. 2018, doi: 10.1007/s40831-018-0162-8.

[20] K. Habib, “Critical Resources in Clean Energy Technologies and Waste Flows,” Ph.D., University of Southern Denmark, Odense M, Denmark, 2015. Accessed: Mar. 17, 2021. [Online]. Available: https://findresearcher.sdu.dk:8443/ws/files/173370487/PhD_thesis_Komal_Habib.pdf

[21] D. Schrijvers *et al.*, “A review of methods and data to determine raw material criticality,” *Resour. Conserv. Recycl.*, vol. 155, p. 104617, Apr. 2020, doi: 10.1016/j.resconrec.2019.104617.

[22] K. Habib, L. Hamelin, and H. Wenzel, “A dynamic perspective of the geopolitical supply risk of metals,” *J. Clean. Prod.*, vol. 133, pp. 850–858, Oct. 2016, doi: 10.1016/j.jclepro.2016.05.118.

[23] D. Bauer, D. Diamond, J. Li, M. McKittrick, D. Sandalow, and P. Telleen, “U.S. DOE Critical Materials Strategy,” U.S. Department of Energy Office of Policy and International Affairs, Dec. 2011. Accessed: Jul. 08, 2020. [Online]. Available: https://www.energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf

[24] “DOE Critical Minerals and Materials Strategy,” Department of Energy, 2021.

[25] S. Archambault, “Economic Analysis of Rare Earth Elements Extraction from Clay Waste,” p. 37.

[26] J. Vaughan *et al.*, "Toward Closing a Loophole: Recovering Rare Earth Elements from Uranium Metallurgical Process Tailings," *JOM*, vol. 73, no. 1, pp. 39–53, Jan. 2021, doi: 10.1007/s11837-020-04451-7.

[27] T. Müller and B. Friedrich, "Development of a recycling process for nickel-metal hydride batteries," *J. Power Sources*, vol. 158, no. 2, pp. 1498–1509, Aug. 2006, doi: 10.1016/j.jpowsour.2005.10.046.

[28] L. Zhao, F.-S. Zhang, and J. Zhang, "Chemical properties of rare earth elements in typical medical waste incinerator ashes in China," *J. Hazard. Mater.*, vol. 158, no. 2, pp. 465–470, Oct. 2008, doi: 10.1016/j.jhazmat.2008.01.091.

[29] H. Yang *et al.*, "Recovery of Trace Rare Earth from High-Level Fe3+ and Al3+ Waste of Oil Shale Ash (Fe−Al−OSA)," *Ind. Eng. Chem. Res.*, vol. 49, no. 22, pp. 11645–11651, Nov. 2010, doi: 10.1021/ie101115e.

[30] D. Merten and G. Büchel, "Determination of Rare Earth Elements in Acid Mine Drainage by Inductively Coupled Plasma Mass Spectrometry," *Microchim. Acta*, vol. 148, no. 3, pp. 163–170, Dec. 2004, doi: 10.1007/s00604-004-0260-0.

[31] M. Bau and P. Dulski, "Anthropogenic origin of positive gadolinium anomalies in river waters," *Earth Planet. Sci. Lett.*, vol. 143, no. 1, pp. 245–255, Sep. 1996, doi: 10.1016/0012-821X(96)00127-6.

[32] C. C. Pavel *et al.*, "Substitution strategies for reducing the use of rare earth in wind turbines," *Resour. Policy*, vol. 52, pp. 349–357, Jun. 2017, doi: 10.1016/j.resourpol.2017.04.010.

[33] A. K. Pathak *et al.*, "Cerium: An Unlikely Replacement of Dysprosium in High-Performance Nd–Fe–B Permanent Magnets," *Adv. Mater.*, vol. 27, no. 16, pp. 2663–2667, 2015, doi: 10.1002/adma.201404892.

[34] M. J. Kramer, R. W. McCallum, I. A. Anderson, and S. Constantinides, "Prospects for Non-Rare Earth Permanent Magnets for Traction Motors and Generators," *JOM*, vol. 64,

no. 7, pp. 752–763, Jul. 2012, doi: 10.1007/s11837-012-0351-z.

[35] V. S. Thompson *et al.*, “Techno-economic and Life Cycle Analysis for Bioleaching Rare-Earth Elements from Waste Materials,” *ACS Sustain. Chem. Eng.*, vol. 6, no. 2, pp. 1602–1609, Feb. 2018, doi: 10.1021/acssuschemeng.7b02771.

[36] T. Akahori, Y. Miyamoto, T. Saeki, M. Okamoto, and T. Okabe, “Recovery of Rare Earth Metals in Used Magnets by Molten Magnesium,” in *Magnesium Technology 2014*, TMS (The Minerals, Metals & Materials Society), 2014, pp. 35–38. Accessed: Mar. 03, 2020. [Online]. Available: https://doi.org/10.1007/978-3-319-48231-6_10

[37] M. Kimiabeigi *et al.*, “Production and Application of HPMS Recycled Bonded Permanent Magnets for a Traction Motor Application,” *IEEE Trans. Ind. Electron.*, vol. 65, no. 5, pp. 3795–3804, May 2018, doi: 10.1109/TIE.2017.2762625.

Chapter 2

Literature Review

2.1: Introduction

Rare earth metals are essential to modern technology, including electronics, renewable energy systems, and transportation. Nevertheless, rare earth metal mining and processing pose substantial environmental and social issues, including resource depletion, water pollution, and human rights violations. Recycling rare earth metals from end-of-life devices and manufacturing waste offers a viable solution to these problems by lowering the need for virgin resources and decreasing waste. In recent years, new processes for recycling rare earth metals have evolved, with the potential to recover these critical minerals from end-of-life devices and production waste. These technologies span from conventional procedures like hydrometallurgy and pyrometallurgy to cutting-edge techniques like solvent extraction, bioleaching, and electrochemistry[1]–[12].

This literature review chapter critically assesses the existing information on rare earth metal primary production, secondary sources of rare earth metals, and their innovative recycling methods. This chapter will examine the principles and mechanisms driving these technologies, their benefits, drawbacks, and possible applications in various industrial areas. The literature review will critically evaluate the issue by combining and evaluating a wide range of published studies, highlighting areas that deserve additional exploration.

This literature review aims to lay the groundwork for the dissertation's succeeding chapters and contribute to the larger academic discourse about recycling rare earth magnets. This review can guide policy and industrial decisions that promote resource efficiency and environmental sustainability.

2.2: Primary Production of Rare Earth Metals

The upstream processes in the supply chain of rare earth metals involve mining and beneficiating the rare earth ores. Monazite, bastnaesite, and xenotime are the principal rare earth ore types. Monazite is typically found as a component of mineral sands, which are usually mined primarily for ilmenite, rutile, and zircon. It is predominantly light rare earth (La, Ce, Pr, Nd) phosphate (93–94%). Bastnaesite, a carbonate-fluoride mineral, typically contains light rare earths (Ce, La, Nd, and Pr). About 60% of Xenotime is made up of YPO4, while 30% is made up of other heavy rare earths. While not often present in rare earth ores, scandium can be found in particular uranium and Co/Ni ores[13]–[16]. In the U.S., the Mountain Pass mine operated by MP Materials is the only active mine, with primarily bastnaesite ore[17], producing approximately 26,000 metric tons of ore concentrates in 2019. These concentrates are then exported for separation and processing. Some deposits' mineralogy is so complex and nuanced that extensive studies into developing appropriate processing technology are necessary before they become economically viable operations[18], [19].

2.2.1: Mining

Open pit, underground, or in-situ leaching[20] are all methods of rare earth mining[21]–[24]. The traditional open pit mine technique is similar to other mining activities, such as overburden removal, mining, milling, crushing and grinding, separation, or concentration. After separation, the product of the enhanced concentrate may have about 30% to 70% of rare earth-bearing ore. The method uses more water and energy than other common metals (e.g., 0.2 to 1 GJ energy/t REO, 0.3 to 1.8 ML water/t REO). It generates waste streams such as tailings and wastewater (compared to other metals owing to the very low grade). A conventional open-cut or underground truck shovel mining system is used for hard rock-based deposits. Meanwhile, for mineral sand-based monazite-type deposits, the wet-dredging or dry-mining method is used[25].

2.2.2: Beneficiation and Concentration

Beneficiation is the process of separating valuable minerals from waste rock. In the case of rare earth ores, this process involves using various techniques to separate the rare earth elements from other minerals in the ore. Some standard methods used for beneficiation include gravity separation, flotation, magnetic separation, and leaching. On the other hand, the process of concentration involves raising the percentage of rare earth elements in an ore. This can be accomplished by raising the concentration of the precious mineral in the ore or eliminating contaminants. Separating rare earth elements from other minerals in the ore is normally accomplished by concentration using physical or chemical techniques. For example, researchers have studied the use of a combination of gravity separation and magnetic separation to beneficiate a rare earth ore containing cerium, lanthanum, neodymium, and praseodymium. The results showed that the beneficiation process could separate the rare earth elements from other minerals in the ore with a high degree of efficiency[26], [27]. Sulfuric acid baking is a process used industrially for mineral concentration. Originally, sulfuric acid-based rare earth.

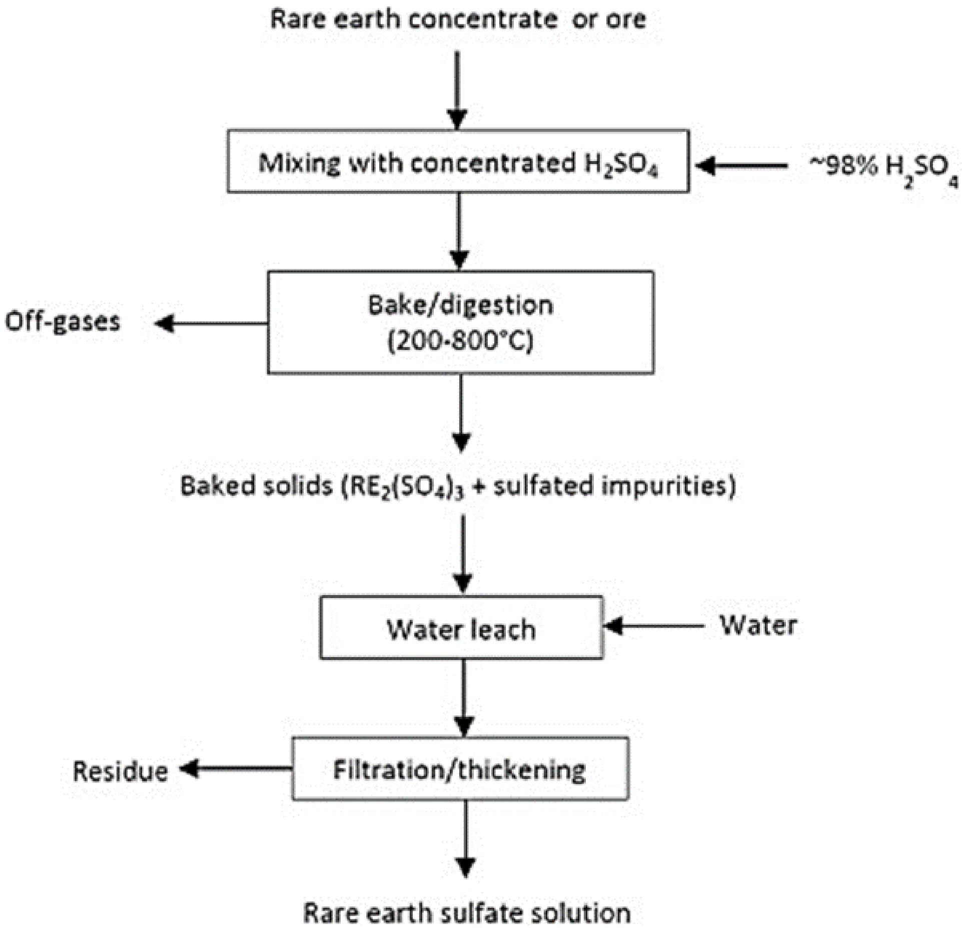


Figure 2.1: Typical process flowsheet for sulfuric acid treatment of a rare earth mineral concentrate[28], [29]

Material breakdown was done in a batch process in a closed but vented reactor[30], but in recent times, this is done industrially using a rotary kiln that enables a continuous operation[31]. A typical flowsheet for the sulphuric acid decomposition process is shown in Figure 2.1.

2.2.3: Separation and Processing

A typical separation and processing flowsheet is shown in Figure 2.2, a Molycorp process used in extracting europium oxide from Mountain Pass bastnaesite leachate. Gupta and Krishnamurthy have investigated a solvent extraction process involving calcining and leaching with HCl solution to produce a chloride solution (100 g/L REO) containing all rare earths except Ce[28]. Two stages of solvent extraction with D2EHPA were used. The chloride solution was first contacted with 10% v/v D2EHPA in kerosene, and the extraction was carried out in five stages of mixers and settlers under conditions that "split" the rare earths, with Sm and all heavier rare earths reporting to the D2EHPA solution, and Nd and all lighter elements reporting to the raffinate solution. The heavy rare earths were removed using a small amount of D2EHPA solution. Gupta and Krishnamurthy found that the resultant rare earth mixture can be processed with considerably smaller mixer settlers, leaving La, Pr, and Nd (most rare earths in the concentrate) in the aqueous raffinate. These were precipitated using ammonium and sodium hydrogen sulfide before being treated on larger-scale equipment. The solution contained more than 98% of europium.

Other studies have reported using solvent extraction to separate industry REMs [32]–[36]. Before the introduction of industrial-scale solvent extraction in the 1960s, the only viable means to separate rare earths in significant amounts were using ion exchange technology[37]–[39]. Ion exchange is currently only utilized to obtain tiny quantities of high-purity rare earth products for electronics or analytical purposes[40].

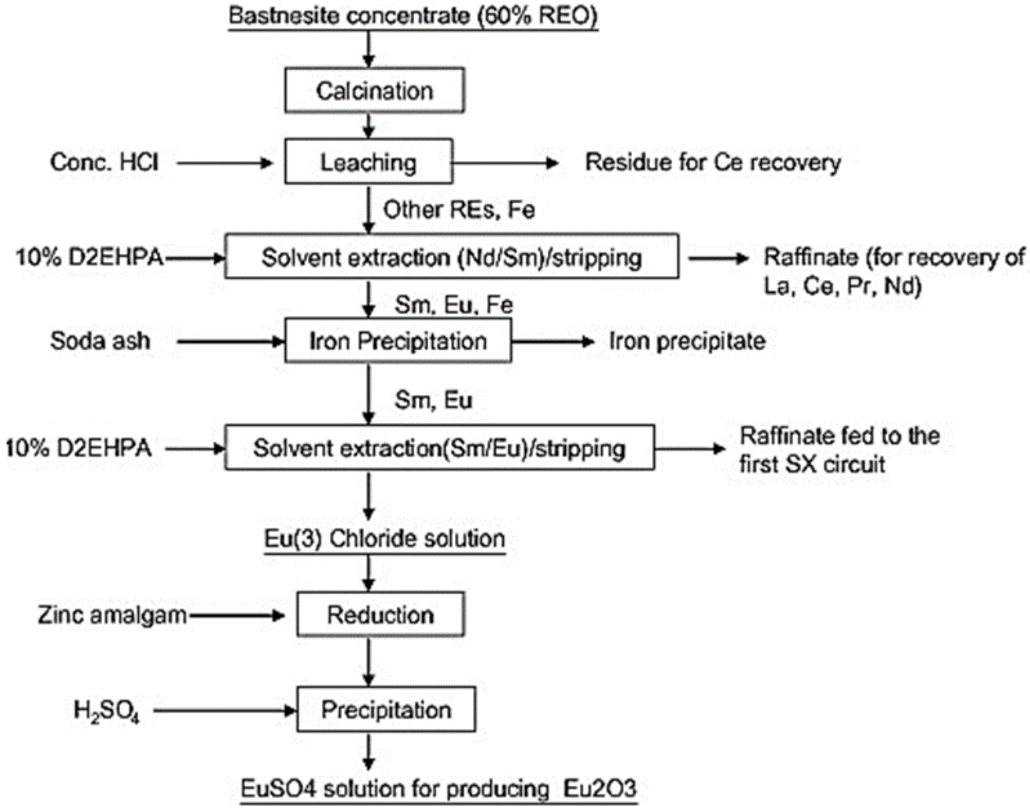
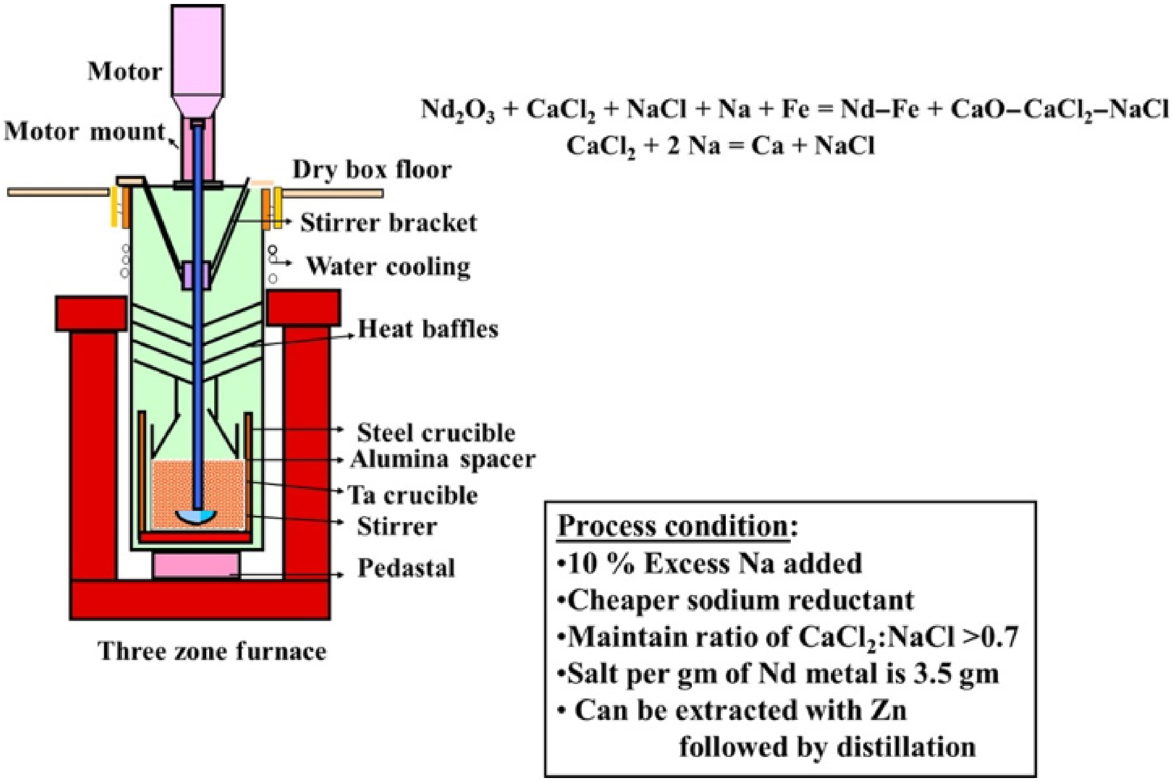


Figure 2.2: Molycorp process for producing europium oxide from the basanite concentrate [28], [29]

Further refining can be carried out to obtain rare earth metal from rare earth oxide. Several approaches investigated include

2.2.3.1: Metallothermic Reduction

Researchers have reported the extraction of rare earth metals using molten metal electrolysis and metallothermic reduction techniques. In the molten metal electrolysis, the feed, a rare earth chloride, is added to a mixture of alkali metal chloride to make up the chloride electrolyte. Graphite anode is used, while the cathode where the rare earth metal gets deposited is inert high-temperature material such as Mo or W metal. For a rare earth oxide feed, the electrolyte has a composition of ReF_3–LiF, sometimes with BaF_2. The anode is carbon, while a Fe cathode can be used for low-melting metals like Mg or Cd. The oxide feed process is like aluminum electrolysis; however, the oxide solubility in the rare earth process is very low. Thus, there is a need for the controlled addition of the feed in the electrolyte. In metallothermic reduction, since the free energy of formation of rare earth halide is lower than the respective metal halide, e.g., calcium halide, the RE oxides have standard free energy of formation higher than CaO. These RE halides or oxides can potentially be reduced by calcium metal. For example, a Neochem process was developed by General Motor Corporation, as shown in Figure 2.3, whereby neodymium oxide was reduced with a molten salt mixture of $CaCl_2$ and NaCl with sodium as the reductant. The Na added forms Ca in situ, which reduces the rare earth oxide, whereas Fe was added to make Nd-Zn master alloy which was vacuum-distilled to obtain pure Nd metal.



$$Nd_2O_3 + CaCl_2 + NaCl + Na + Fe = Nd\text{–}Fe + CaO\text{–}CaCl_2\text{–}NaCl$$
$$CaCl_2 + 2\,Na = Ca + NaCl$$

Process condition:
- •10 % Excess Na added
- •Cheaper sodium reductant
- •Maintain ratio of $CaCl_2$:NaCl >0.7
- •Salt per gm of Nd metal is 3.5 gm
- • Can be extracted with Zn followed by distillation

Figure 2.3: The Neochem process used to extract Nd as Nd-Zn master alloy with sodium reductant. The Nd–Zn master alloy is vacuum-distilled to get pure Nd metal[41]

The reaction is endothermic; hence, a need to supply heat to the reaction. This process has also been used for the extraction of samarium metal from samarium oxide by the addition of Lanthanum (lanthano-thermic reaction), and a similar approach can be used for extracting pure europium and ytterbium[41], [42].

2.2.3.2: Calciothermic Reduction and Electrolysis

Research trends in neodymium production through oxide electrolysis have been carried out by Chinese engineers and scaled up to industrial use as almost 100% of neodymium smelting for the $Nd_2Fe_{14}B$ magnet alloy is controlled by China[43]. The first industrial-scale production of Nd and its alloys was done by Calciothermic reduction of neodymium fluoride and chloride electrolysis[44].

2.2.3.3: Electrowinning

Several studies on electrowinning to produce high-purity rare earth metals from their oxides have been reported[45]–[48]. Dysinger and Murphy prepared neodymium metal of 99.8% purity from neodymium oxide salts dissolved in a molten fluoride electrolyte by electrowinning. This was done at current efficiencies of 50 to 60%. Continuous feeding at a controlled rate was used to ensure an increased sustainable anodic current density and efficiency and improve the cell's overall operation[49].

2.3: Secondary Sources of Rare Earth Metals

The recovery of rare earth metals from waste or scrap materials, contrary to primary sources like mines, is called the secondary production of rare earths. In addition to recovering rare earths from industrial waste streams like coal ash or fly ash can also involve recycling end-of-life items like cell phones and wind turbines.

The ability of secondary production to lessen the adverse environmental effects of rare earth mining and processing and minimize reliance on primary supplies, which may be expensive and environmentally harmful, is one of its key benefits[50], [51]. REM recycling depends on whether the materials are available in enough quantities and at optimum times. Wind turbines that contain several hundred kilograms of REM have a lifetime of 20 – 30 years before recovery; meanwhile, electronic devices that have a short lifespan contain only small concentrations of these rare earth materials. National Defense Stockpile in FY2016 initiated a project goal to develop economical methods of recycling REEs from scrap and investigate technologies to determine whether recycling is feasible in the United States as there is little to no recycling of REEs taking place[52].

A review of the potential of secondary sources was carried out, as shown in Table 1. An analysis of the concentration of REEs in secondary sources observed that some of the most valuable REEs were in higher concentrations in phosphogypsum, coal combustion products, red mud, and polishing powders than the ore grade, as shown in Table 2. Regarding the ability to meet demand, phosphogypsum, and NiMH Batteries had a high annual production of over a billion and a million tons, respectively. Understanding the techno-economic analysis of recovering REEs from these sources is important to ascertain the economic feasibility of methods applied even as their concentrations in specific REEs vary [50], [53].

Table 2.1: Classification of Secondary Rare Earth Element Sources[50]

Secondary Rare Earth Sources		
Coal Combustion Products (CCPs)	**Industrial by-products and wastes**	**Post-consumer electronic wastes**
Ash by-products of energy production from coal (including fly and bottom ash)	Phosphogypsum	Phosphors from LED, LFL
	Dross/Slag	Cell phones
	Tailings	Laptops and desktops
	Red mud	Speakers
		Nickel-Metal Hydrides

Table 2.2: Concentration of magnet REEs in secondary sources compared to ore grade[50]

Secondary Source	**REEs present**	**Amount present compared to ores**
Earbuds	Nd	1.5X
	Dy	6X
	Pr	1.2X
NiMH	Nd	5X
	Pr	4.5X
Polishing powders	Nd	13X
	Pr	15X
Phosphogypsum	Nd	3X
	Pr	3X

2.4: Recycling Processes of Rare Earth Metals

Many recycling methods exist; however, they have several limitations, such as

- *High Energy Consumption*: Rare earth magnet recycling technologies can require significant energy, particularly during the separation and refining processes. This high energy consumption can make recycling less economically feasible and environmentally friendly[51]

- *Limited Scale-up Feasibility*: Some rare earth magnet recycling technologies are still in the developmental stage, and their commercial availability is limited. This lack of availability can hinder the scaling-up of recycling operations[54].
- *High Capital Cost:* Certain rare earth magnet recycling technologies require significant investment in specialized equipment and infrastructure, which can be a barrier to entry for smaller companies or start-ups[55].
- *Environmental Impact:* Some of the current rare earth magnet recycling technologies can still have an environmental impact, such as using strong acids or other chemicals in refining[56].

This project aims to address some of these limitations in contribution to the general body of knowledge in recycling rare earth magnets.

Various studies have investigated the stages of recovering End-of-life (EOL) wastes, including collection, pretreatment, separation/purification, and ultimate recovery. The various elements and compound composition (in wt.%) of REE in EOL products were shown. They proposed that the physical pre-treatment method is preferable to the chemical since the metals' state remains unchanged and can be carried out at the minimum cost. The steps involved in the physical pretreatment- including magnetic and electric conductivity-based separation to separate ferrous metals from plastics and non-ferrous metals were discussed. The pyrometallurgical method of separation/purification was compared to the hydrometallurgical method in terms of ore grade, energy required, pollution, and post-processing. It was shown that the hydrometallurgical process has more advantages since it involves leaching, especially for NdFeB magnets. Leaching can either be total or selective. Lixiviants studied include H_2SO_4 and HCl, where HCL performed better, but H_2SO_4 was more economical. It was shown that temperature, pulp density, acid concentration, and leaching time affect RE's extraction. Other methods of recovery discussed include molten slag extraction ($CaO-SiO_2-Al2O_3$ and $CaO-CaF_2$), glass slag method (B_2O_3), electro cycling, solvent extraction, liquid membrane extraction (flat sheet or hollow fiber liquid membrane), liquid metal extraction (using melted gr IIA metals), bioleaching and supercritical fluid extraction (CO_2)[57], [58]. Several recovery/recycling methods have been discussed. Table 3 shows a summary of various recovery methods with their REE sources.

2.4.1: Solvent Extraction

This is one of the eco-friendliest and commercially viable approaches to extract and separate RE because of ionic liquids and green replacements for the usual molecular solvents[57], [58]. Although several extracting agents have been utilized in industry for the solvent extraction and separation of REEs[59]–[62], they have some disadvantages. These include a low extraction rate, poor selectivity, and poor stripping of the metals from the organic phase. Various organic diluents such as ketones, aliphatic/aromatic hydrocarbons, and high alcohols as media for dissolving the extractants have also been reported. Their equilibrium data, the kinetics of extraction behavior, and thermodynamic models are essential in developing and designing extraction systems. This study prepared the leachate by dissolving 1g of NdFeB powder in 50 mL of 4M HNO_3 and leaching for 24h at 25 ± 1^0C on a magnetic stirrer. Tetraoctyl di glycol amide (TODGA) was used as the extractant. Stripping of the REEs out of the organic phase was carried out using MQ water, and the recovery of REEs was reported to have reached almost 100% Nd, Pr, and Dy[63]. In another study, neodymium and dysprosium were successfully separated using ethylenediaminetetraacetic acid (EDTA) as a selective complexing agent during liquid-liquid extraction. Precipitation with oxalic acid and calcination was done to obtain Nd_2O_3 and Dy_2O_3, with 99.6% and 99.8% purities, respectively[64]. A critical review was also conducted on solvent extraction for recovery and individual separation of REEs from aqueous solutions. Cation exchangers, solvation extractants, and ion exchangers have been extensively studied. Commercially, D2EHPA, HEHEHP, Versatic 10, TBP, and Aliquat 336 are widely used to separate rare earth elements[36]. Acidic, basic, solvating extractants or ionic liquids can be used for solvent extraction.

2.4.2: Membrane Solvent Extraction

Several studies have reported using membrane-based extraction for recovering rare earth metal ions[65]–[69]. A study of the recovery of REEs from scrap magnet feedstocks using membrane solvent extraction (MSX) was successfully carried out using technical grade N, N, N′, N′-Tetraoctyl di glycol amide (TODGA) 30%, isopar 40%, and tri-n-butyl phosphate (TBP) 30% as the extractant – neutral extractant. The feedstock and the REO products were dissolved in nitric acid to determine their elemental composition using ICP-OES. Recovery of more than 95%, purity of about 99.5%, and an extraction rate of 9.3 g/(hm2) was obtained from feed solutions containing REEs of up to 46000 mg/L. The composition of the scrap magnet source and the initial REE concentration determined the extraction rate. MSX is a scalable recovery method for REEs from various electronic wastes[66]. TODGA has been shown to recover Nd, Dy, and Pr selectively with no co-extraction of non-REEs such as Fe and B. This process is an alternative to the traditional equilibrium-based solvent extraction, eliminating the disadvantages of functions like loading, flooding, and third-phase formation. Whereas solvent extraction takes place in two separate steps, as shown in Figure 2.4, MSX combines both steps, continuously circulating the feed and strip solutions without dispersing different phases. A high contact surface area per unit volume, which gives rise to a high REE extraction rate, is achieved using the hollow fiber membrane modules in the MSX system[70].

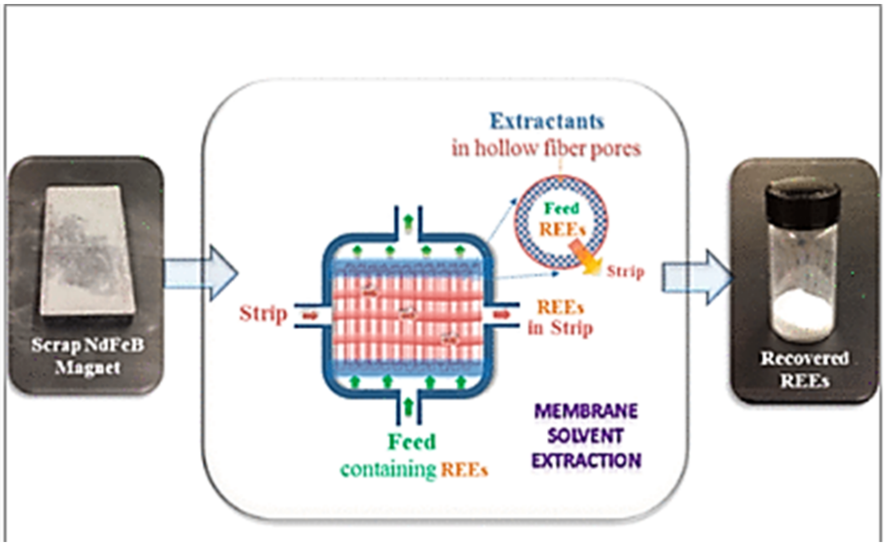


Figure 2.4: Membrane Solvent Extraction Process for REE recovery[70]

2.4.3: Chlorination

Several research investigations involving the use of chlorination in the recovery of rare earth elements from rare earth magnets have been conducted[54], [71]–[74]. Although chlorination is a low-cost process, RE elements recovered as chlorides have limited application after recovery. The process is used alongside molten salt extraction and gas-phase reactions[75].

2.4.4: Ligand-Assisted Displacement (LAD) Chromatography

The use of displacement chromatography in the recovery of rare earth elements has been studied extensively[76]–[80]. Ding et al. studied a two-zone ligand-assisted displacement (LAD)chromatography for producing high-purity Pr, Nd, and Dy from waste magnets. Compared to liquid-liquid extraction, this process required only a few columns, and the productivity was about 100 times higher. The environmentally friendly chemicals could be recycled and reused[81].

2.4.5: Biosorption/Bioleaching

Several biomaterials, including algae, fungi, bacteria, resin, and activated carbon, are potential adsorbents for the recovery of rare earth metals because of their low cost and fast kinetics of adsorption and desorption[4], [82]–[86]. Lanthanum was recovered using algae, bamboo charcoal, bacteria, and activated carbon from rice husk[87]–[89]. In the case of activated carbon, its extended surface area, increase in adsorb, microporous structure, and special surface reactivity is all advantages that make this medium the most popular adsorbent. dysprosium and neodymium have also been reported to be recovered using activated charcoal and carbon, respectively, while europium, erbium, samarium, and praseodymium have been recovered using Sargassum biomass. A continuous mode operation performed industrial applications of biosorption. Meanwhile, batch experiments were carried out to evaluate essential information, such as biosorbent efficiency, optimum experimental conditions, biosorption rate, and the possibility of biomass regeneration. Factors such as pH, temperature, biosorbent dosage, initial metal concentration, agitation rate, and contact period influence the biosorption processes and should be considered[90].

2.4.6: Hydrogen Decrepitation

In hydrogenation or hydrogen decrepitation, the NdFeB magnet is broken down by hydrogen absorption to form a-Fe, Fe_2B, and NdH_2 after de-coating. By degassing the hydrogen under a vacuum, the Nd is recovered. But fresh REEs must be added to improve the magnetic properties of the recycled magnet. As shown in Figure 2.5, in comparison to primary production, fewer fresh REEs are added as low as 0.5-1g for 1kg of the magnet. Thus, the recycling route has a significantly lower environmental impact than the primary production[91]–[103].

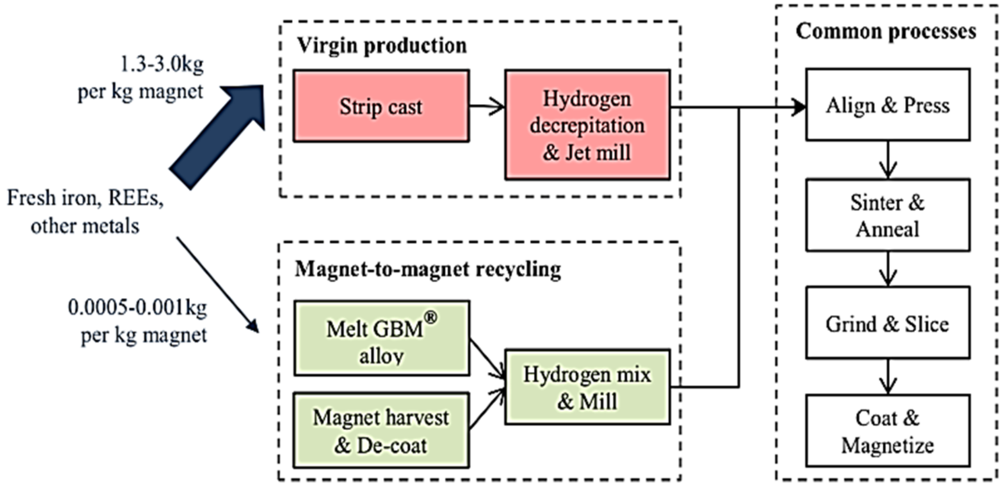


Figure 2.5: Process flows for NdFeB Magnet Virgin Production and magnet-to-magnet recycling[104]

2.4.7: Molten Metal Extraction

This proposes the use of molten magnesium or other group IIA metals[105] that are effective in REM recycling – a technology to extract rare-earth alloys (Nd, Dy) from removed magnets at a temperature of 1273K and Mg/magnet ratio of 10. The Nd and Dy extraction efficiencies were 100% and 60%, respectively.

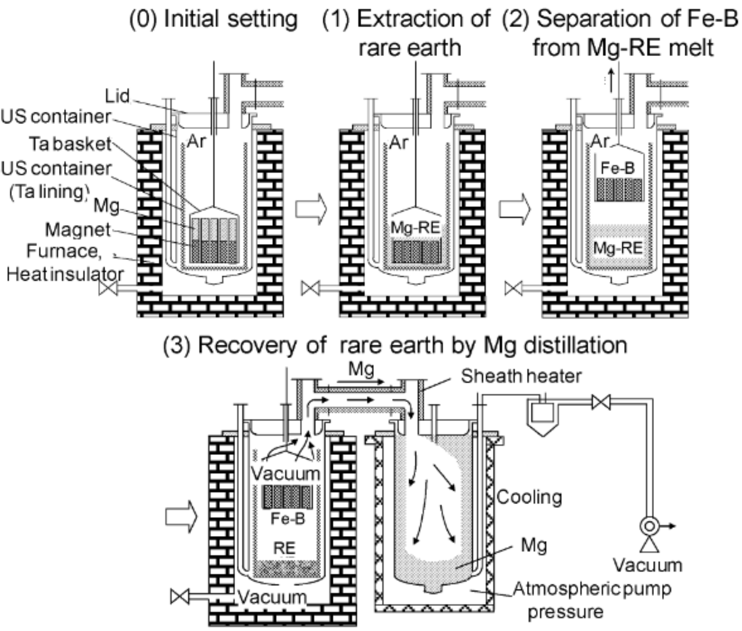


Figure 2.6: Schematic Diagram of the process of recovering rare earth from rare earth magnet by using molten magnesium[106]

The addition of Calcium suppresses the oxidation of Dy. As shown in Figure 2.6, this pyrometallurgical process involved three steps - extraction of the RE metals into molten Mg to form an Mg-RE melt, separating the melt from the Fe-B alloy block formed after RE extraction vacuum sublimation or distillation of the melt to recover both the Mg and RE separately. The heating crucible was made of pure iron and boron nitride (BN) since BN contained little impurity and high heat resistivity[106]–[108].

Table 2.3: Lab-scale Extraction processes of REEs from secondary sources

Method	**REE Source**	**Reference**
Acid leaching	Coal ash, fluorescent lamps	[109]
Hydrometallurgy	Fluorescent lamps, NiMH batteries	[110]
Hydrogen decrepitation	Magnets	[92]
Pyrometallurgy	Magnets	[111]
Alkaline roasting	Fluorescent lamps	[112]
Bioleaching	Coal ash	[113]
Supercritical extraction	coal ash, Fluorescent lamps	[114]
flotation separation	Fluorescent lamps	[115]
liquid metal extraction	Magnets	[106]
ion exchange	Coal ash	[116]
Ionic liquids/solvent extraction	Magnets	[63]
Dense medium centrifugation	Fluorescent lamps	[117]

2.5: Scrap Dismantling Techniques

Although the separation step of RE magnets from their EOL products has been identified as one of the challenges amongst many others for efficient recycling operation[2], [118], a dismantling technology aimed at collecting NdFeB magnets from HDDs and compressors has been developed by Hitachi Group and used to collect about 26 metric tons of magnets from HDD over six years since FY2013. The machine disassembles about 140 HDDs per hour, whereas a person manually takes apart 12 HDDs simultaneously. It works by subjecting the drives to impacts and vibrations as the drum rotates to loosen the screws and automatically disassemble the drive into its parts. The presence of through-holes prevents the sintered REM from being pulverized (Figure 2.7). They created a cycle of resources for recycling and proposed plans to use AI technologies and the Internet of Things. Also, through domestic resource recycling by Tokyo Eco Recycle, CO_2 emissions were reduced to one-tenth the level that would result from the same weight of REM when manufacturing from their ores[49], [119], [120].

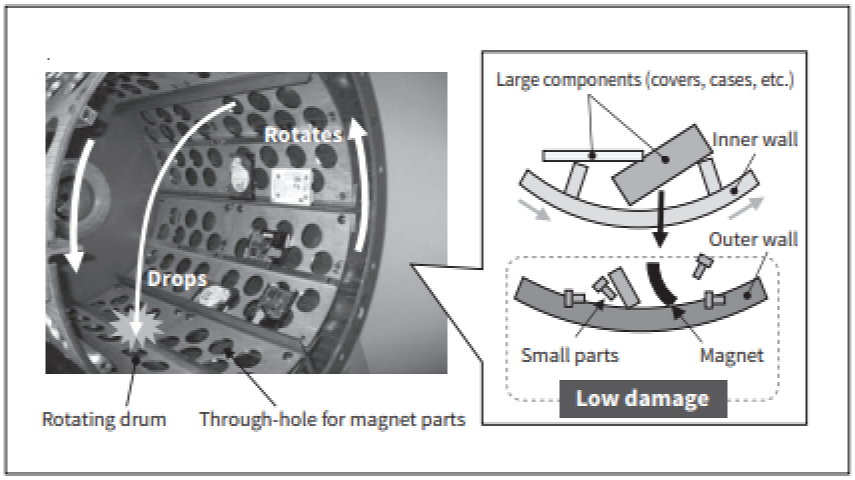


Figure 2.7: Internal Mechanism of Automatic Hard Disk Drive Disassembler[119]

2.6: Conclusion

This literature review has highlighted the current methods of extraction and processing of rare earth metals, including primary and secondary methods.

The reviewed literature demonstrates that several promising technologies for the recycling of rare earth metals have been developed in recent years. These include hydrometallurgical methods, pyrometallurgical methods, and bio-metallurgical methods, each with its own advantages and disadvantages.

One key finding from the literature is that a comprehensive approach to rare earth metal recycling is necessary to address several limitations, such as energy efficiency, scalability, and cost of these recycling technologies, as well as to address the challenges associated with processing complex mixtures of rare earth metals.

Overall, the reviewed literature provides a good platform for further research and development of new technologies for recycling rare earth metals, which can contribute to a more sustainable and environmentally friendly society.

REFERENCES

[1] L. Omodara, S. Pitkäaho, E.-M. Turpeinen, P. Saavalainen, K. Oravisjärvi, and R. L. Keiski, "Recycling and substitution of light rare earth elements, cerium, lanthanum, neodymium, and praseodymium from end-of-life applications - A review," *J. Clean. Prod.*, vol. 236, p. 117573, Nov. 2019, doi: 10.1016/j.jclepro.2019.07.048.

[2] C. Tunsu, M. Petranikova, M. Gergorić, C. Ekberg, and T. Retegan, "Reclaiming rare earth elements from end-of-life products: A review of the perspectives for urban mining using hydrometallurgical unit operations," *Hydrometallurgy*, vol. 156, pp. 239–258, Jul. 2015, doi: 10.1016/j.hydromet.2015.06.007.

[3] Q. Tan, J. Li, and X. Zeng, "Rare Earth Elements Recovery from Waste Fluorescent Lamps: A Review," *Crit. Rev. Environ. Sci. Technol.*, vol. 45, no. 7, pp. 749–776, Apr. 2015, doi: 10.1080/10643389.2014.900240.

[4] C. Ramprasad *et al.*, "Strategies and options for the sustainable recovery of rare earth elements from electrical and electronic waste," *Chem. Eng. J.*, vol. 442, p. 135992, Aug. 2022, doi: 10.1016/j.cej.2022.135992.

[5] R. Ahirwar and A. K. Tripathi, "E-waste management: A review of recycling process, environmental and occupational health hazards, and potential solutions," *Environ. Nanotechnol. Monit. Manag.*, vol. 15, p. 100409, May 2021, doi: 10.1016/j.enmm.2020.100409.

[6] Y. Yang *et al.*, "REE Recovery from End-of-Life NdFeB Permanent Magnet Scrap: A Critical Review," *J. Sustain. Metall.*, vol. 3, no. 1, pp. 122–149, 2017, doi: 10.1007/s40831-016-0090-4.

[7] T. G. Ambaye, M. Vaccari, F. D. Castro, S. Prasad, and S. Rtimi, "Emerging technologies for the recovery of rare earth elements (REEs) from the end-of-life electronic wastes: a review on progress, challenges, and perspectives," *Environ. Sci. Pollut. Res.*, vol. 27, no. 29, pp.

36052–36074, Oct. 2020, doi: 10.1007/s11356-020-09630-2.

[8] E. O. Opare, E. Struhs, and A. Mirkouei, “A comparative state-of-technology review and future directions for rare earth element separation,” *Renew. Sustain. Energy Rev.*, vol. 143, p. 110917, Jun. 2021, doi: 10.1016/j.rser.2021.110917.

[9] S. Stopic and B. Friedrich, “Advances in Understanding of the Application of Unit Operations in Metallurgy of Rare Earth Elements,” *Metals*, vol. 11, no. 6, Art. no. 6, Jun. 2021, doi: 10.3390/met11060978.

[10] U. K. Mudali, M. Patil, R. Saravanabhavan, and V. K. Saraswat, “Review on E-waste Recycling: Part II—Technologies for Recovery of Rare Earth Metals,” *Trans. Indian Natl. Acad. Eng.*, vol. 6, no. 3, pp. 613–631, Sep. 2021, doi: 10.1007/s41403-021-00231-0.

[11] V. Rai, D. Liu, D. Xia, Y. Jayaraman, and J.-C. P. Gabriel, “Electrochemical Approaches for the Recovery of Metals from Electronic Waste: A Critical Review,” *Recycling*, vol. 6, no. 3, Art. no. 3, Sep. 2021, doi: 10.3390/recycling6030053.

[12] A. Marra, A. Cesaro, and V. Belgiorno, “Recovery opportunities of valuable and critical elements from WEEE treatment residues by hydrometallurgical processes,” *Environ. Sci. Pollut. Res.*, vol. 26, no. 19, pp. 19897–19905, Jul. 2019, doi: 10.1007/s11356-019-05406-5.

[13] “Rare Earth Ores - an overview | ScienceDirect Topics.” https://www.sciencedirect.com/topics/chemistry/rare-earth-ores (accessed Nov. 13, 2022).

[14] A. P. Jones, F. Wall, and C. T. Williams, *Rare Earth Minerals: Chemistry, Origin and Ore Deposits*. Springer Science & Business Media, 1995.

[15] W. Wang, Y. Pranolo, and C. Y. Cheng, “Metallurgical processes for scandium recovery from various resources: A review,” *Hydrometallurgy*, vol. 108, no. 1, pp. 100–108, Jun. 2011, doi: 10.1016/j.hydromet.2011.03.001.

[16] A. M. Clark, “Chapter 2 - Mineralogy of the Rare Earth Elements,” in *Developments in Geochemistry*, P. Henderson, Ed., in Rare Earth Element Geochemistry, vol. 2. Elsevier, 1984,

pp. 33–61. doi: 10.1016/B978-0-444-42148-7.50007-1.

[17] J. Lucas, P. Lucas, T. L. Mercier, A. Rollat, and W. G. I. Davenport, *Rare Earths: Science, Technology, Production and Use*. Elsevier, 2014.

[18] B. J. Smith, M. E. Riddle, M. R. Earlam, C. Iloeje, and D. Diamond, "Rare Earth Permanent Magnets - Supply Chain Deep Dive Assessment," USDOE Office of Policy (PO), Feb. 2022. doi: 10.2172/1871577.

[19] T. Uysal, "Economic analysis of rare earth element processing methods for Mountain Pass ore," Jul. 2022. http://www.scielo.org.za/scielo.php?script=sci_arttext&pid=S2225-62532022000700011 (accessed Jan. 30, 2023).

[20] M. Seredkin, A. Zabolotsky, and G. Jeffress, "In situ recovery, an alternative to conventional methods of mining: Exploration, resource estimation, environmental issues, project evaluation and economics," *Ore Geol. Rev.*, vol. 79, pp. 500–514, Dec. 2016, doi: 10.1016/j.oregeorev.2016.06.016.

[21] J. Liu and J. C. Bongaerts, "Mine Planning and Equipment Selection Supply Chain of Rare Earth Elements (REEs)," in *Mine Planning and Equipment Selection*, C. Drebenstedt and R. Singhal, Eds., Cham: Springer International Publishing, 2014, pp. 1419–1426. doi: 10.1007/978-3-319-02678-7_136.

[22] D. J. Packey and D. Kingsnorth, "The impact of unregulated ionic clay rare earth mining in China," *Resour. Policy*, vol. 48, pp. 112–116, Jun. 2016, doi: 10.1016/j.resourpol.2016.03.003.

[23] L. M. Suli, W. H. W. Ibrahim, B. A. Aziz, M. R. Deraman, and N. A. Ismail, "A Review of Rare Earth Mineral Processing Technology," *Chem. Eng. Res. Bull.*, pp. 20–35, Sep. 2017, doi: 10.3329/cerb.v19i0.33773.

[24] G. Barakos, H. Mischo, and J. Gutzmer, "Chapter 8 - Rare Earth Underground Mining Approaches with Respect to Radioactivity Control and Monitoring Strategies," in *Rare Earths*

Industry, I. Borges De Lima and W. Leal Filho, Eds., Boston: Elsevier, 2016, pp. 121–138. doi: 10.1016/B978-0-12-802328-0.00008-5.

[25] N. Haque, A. Hughes, S. Lim, and C. Vernon, “Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact,” *Resources*, vol. 3, no. 4, pp. 614–635, Oct. 2014, doi: 10.3390/resources3040614.

[26] A. Jordens, R. S. Sheridan, N. A. Rowson, and K. E. Waters, “Processing a rare earth mineral deposit using gravity and magnetic separation,” *Miner. Eng.*, vol. 62, pp. 9–18, Jul. 2014, doi: 10.1016/j.mineng.2013.09.011.

[27] F. Wall, “Rare earth elements,” in *Critical Metals Handbook*, John Wiley & Sons, Ltd, 2014, pp. 312–339. doi: 10.1002/9781118755341.ch13.

[28] C. K. Gupta and N. Krishnamurthy, *Extractive metallurgy of rare earths*. Boca Raton, Fla: CRC Press, 2005.

[29] J. Zhang and C. Edwards, “Mineral decomposition and leaching processes for treating rare earth ore concentrates,” *Can. Metall. Q.*, vol. 52, no. 3, pp. 243–248, Jul. 2013, doi: 10.1179/1879139513Y.0000000084.

[30] L. Eyring, *Progress in the Science and Technology of the Rare Earths*. Elsevier, 2013.

[31] Z. Zhang, Q. Jia, and W. Liao, “Chapter 277 - Progress in the Separation Processes for Rare Earth Resources,” in *Handbook on the Physics and Chemistry of Rare Earths*, J.-C. Bünzli and V. K. Pecharsky, Eds., in Including Actinides, vol. 48. Elsevier, 2015, pp. 287–376. doi: 10.1016/B978-0-444-63483-2.00004-1.

[32] U.S. Geological Survey, “Rare Earth Elements: A review of Production, Processing, Recycling, and Associated Environmental Issues",” Dec. 2012. https://nepis.epa.gov/Exe/ZyNET.exe/P100EUBC.txt?ZyActionD=ZyDocument&Client=EPA&Index=2011%20Thru%202015&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%

5C11THRU15%5CTXT%5C00000005%5CP100EUBC.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=19 (accessed Jan. 20, 2023).

[33] "Rare-earth element - Processing ores | Britannica." https://www.britannica.com/science/rare-earth-element/Processing-ores (accessed Jan. 20, 2023).

[34] P. Josso, S. Roberts, D. A. H. Teagle, O. Pourret, R. Herrington, and C. Ponce de Leon Albarran, "Extraction and separation of rare earth elements from hydrothermal metalliferous sediments," *Miner. Eng.*, vol. 118, pp. 106–121, Mar. 2018, doi: 10.1016/j.mineng.2017.12.014.

[35] P. Rozelle, T. Tarka, and N. Mamula, "The Application of Current Mineral Processing and Extractive Metallurgy Technologies to Potential Rare Earth Ores in the U.S. Coal Measures: Near-Term Opportunities to Fill Out the U.S. Value Chain," United States Department of Energy, Office of Fossil Energy- National Energy Technology Laboratory, GS-23F-0231R, Dec. 2019.

[36] F. Xie, T. A. Zhang, D. Dreisinger, and F. Doyle, "A critical review on solvent extraction of rare earths from aqueous solutions," *Miner. Eng.*, vol. 56, pp. 10–28, Feb. 2014, doi: 10.1016/j.mineng.2013.10.021.

[37] W. D. Jamrack, *Rare Metal Extraction by Chemical Engineering Techniques: International Series of Monographs on Chemical Engineering*. Elsevier, 2014.

[38] M. Kumar, "Recent trends in chromatographic procedures for separation and determination of rare earth elements. A review," *Analyst*, vol. 119, no. 9, pp. 2013–2024, 1994, doi: 10.1039/AN9941902013.

[39] B. R. Reddy, B. N. Kumar, and S. Radhika, "Solid-Liquid Extraction of Terbium from

Phosphoric Acid Medium using Bifunctional Phosphinic Acid Resin, Tulsion CH-96," *Solvent Extr. Ion Exch.*, vol. 27, no. 5–6, pp. 695–711, Dec. 2009, doi: 10.1080/07366290903270031.

[40] V. T. Taniguchi, A. W. Doty, and C. H. Byers, *Large scale chromatographic separations using continuous displacement chromatography (CDC)*. United States: The Metallurgical Society Inc, 1988.

[41] G. Balachandran, "Extraction of Rare Earth for Advanced Applications." Elsevier, 2014.

[42] K. Milicevic, D. Feldhaus, and B. Friedrich, "Conditions and Mechanisms of Gas Emissions from Didymium Electrolysis and Its Process Control," in *Light Metals 2018*, O. Martin, Ed., in The Minerals, Metals & Materials Series. Cham: Springer International Publishing, 2018, pp. 1435–1441. doi: 10.1007/978-3-319-72284-9_187.

[43] H. Vogel and B. Friedrich, "Development and Research Trends of the Neodymium Electrolysis – A Literature Review," in *European Metallurgical Conference 2015*, GDMB Verlag, 2015, pp. 689–701. Accessed: Mar. 25, 2019. [Online]. Available: http://www.metallurgie.rwth-aachen.de/new/images/pages/publikationen/emc_2015_vogel_id_2892.pdf

[44] D. K. Dysinger and J. E. Murphy, "Electrowinning of Neodymium From a Molten Oxide-Fluoride Electrolyte," p. 14, 1994.

[45] Y. Yang, C. Lan, L. Guo, Z. An, Z. Zhao, and B. Li, "Recovery of rare-earth element from rare-earth permanent magnet waste by electro-refining in molten fluorides," *Sep. Purif. Technol.*, vol. 233, p. 116030, Feb. 2020, doi: 10.1016/j.seppur.2019.116030.

[46] H. Tamamura, "New industrial process for electrowinning of Nd-Fe alloy. Yoyuen wo mochiita Nd-Fe gokin no denkai saishu," *Denki Kagaku Oyobi Kogyo Butsuri Kagaku Electrochem. Ind. Phys. Chem. Jpn.*, vol. 59:6, May 1991, Accessed: Jan. 30, 2023. [Online]. Available: https://www.osti.gov/etdeweb/biblio/5417157

[47] T. A. Henrie, "Electrowinning rare-earth and uranium metals from their oxides," *JOM*, vol. 16, no. 12, pp. 978–981, Dec. 1964, doi: 10.1007/BF03378313.

[48] E. Morrice and T. A. Henrie, *Electrowinning High-purity Neodymium, Praseodymium, and Didymium Metals from Their Oxides*. U.S. Department of the Interior, Bureau of Mines, 1967.

[49] D. K. Dysinger and J. E. Murphy, “Electrowinning of Neodymium From a Molten Oxide-Fluoride Electrolyte,” p. 14, 1994.

[50] G. Gaustad, E. Williams, and A. Leader, “Rare earth metals from secondary sources: Review of potential supply from waste and byproducts,” *Resour. Conserv. Recycl.*, vol. 167, p. 105213, Apr. 2021, doi: 10.1016/j.resconrec.2020.105213.

[51] K. Binnemans *et al.*, “Recycling of rare earths: a critical review,” *J. Clean. Prod.*, vol. 51, pp. 1–22, Jul. 2013, doi: 10.1016/j.jclepro.2012.12.037.

[52] M. Humphries, “Critical Minerals and U.S. Public Policy,” p. 56, 2019.

[53] M. Peiravi *et al.*, “A Review of Rare-Earth Elements Extraction with Emphasis on Non-conventional Sources: Coal and Coal Byproducts, Iron Ore Tailings, Apatite, and Phosphate Byproducts,” *Min. Metall. Explor.*, vol. 38, no. 1, pp. 1–26, Feb. 2021, doi: 10.1007/s42461-020-00307-5.

[54] T. Lorenz and M. Bertau, “Recycling of rare earth elements from FeNdB-Magnets via solid-state chlorination,” *J. Clean. Prod.*, vol. 215, pp. 131–143, Apr. 2019, doi: 10.1016/j.jclepro.2019.01.051.

[55] I. C. Nlebedim and A. H. King, “Addressing Criticality in Rare Earth Elements via Permanent Magnets Recycling,” *JOM*, vol. 70, no. 2, pp. 115–123, Feb. 2018, doi: 10.1007/s11837-017-2698-7.

[56] S.-H. Shin, H.-O. Kim, and K.-T. Rim, “Worker Safety in the Rare Earth Elements Recycling Process From the Review of Toxicity and Issues,” *Saf. Health Work*, vol. 10, no. 4, pp. 409–419, Dec. 2019, doi: 10.1016/j.shaw.2019.08.005.

[57] N. Swain and S. Mishra, “A review on the recovery and separation of rare earths and

transition metals from secondary resources," *J. Clean. Prod.*, vol. 220, pp. 884–898, May 2019, doi: 10.1016/j.jclepro.2019.02.094.

[58] S. Peelman, Z. H. I. Sun, J. Sietsma, and Y. Yang, "Chapter 21 - Leaching of Rare Earth Elements: Review of Past and Present Technologies," in *Rare Earths Industry*, I. Borges De Lima and W. Leal Filho, Eds., Boston: Elsevier, 2016, pp. 319–334. doi: 10.1016/B978-0-12-802328-0.00021-8.

[59] D. F. Peppard, J. P. Faris, P. R. Gray, and G. W. Mason, "Studies of the Solvent Extraction Behavior of Transition Elements. I. Order and Degree of Fractionation of the Trivalent Rare Earths," *J. Phys. Chem.*, vol. 57, no. 3, pp. 294–301, Mar. 1953, doi: 10.1021/j150504a008.

[60] D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, "Fractional extraction of the lanthanides as their di-alkyl orthophosphates," *J. Inorg. Nucl. Chem.*, vol. 4, no. 5, pp. 334–343, Jan. 1957, doi: 10.1016/0022-1902(57)80016-5.

[61] "Peppard: Liquid-liquid extraction of trivalent rare... - Google Scholar." https://scholar.google.com/scholar_lookup?title=Liquid-liquid%20extraction%20of%20trivalent%20rare%20earths%20using%20acidic%20phosphonates%20as%20extractants&publication_year=1961&author=D.F.%20Peppard&author=G.W.%20Wason (accessed Jan. 30, 2023).

[62] C. G. Brown and L. G. Sherrington, "Solvent extraction used in industrial separation of rare earths," *J. Chem. Technol. Biotechnol.*, vol. 29, no. 4, pp. 193–209, 1979, doi: 10.1002/jctb.503290402.

[63] M. Gergoric, C. Ekberg, M. R. S. J. Foreman, B.-M. Steenari, and T. Retegan, "Characterization and Leaching of Neodymium Magnet Waste and Solvent Extraction of the Rare-Earth Elements Using TODGA," *J. Sustain. Metall.*, vol. 3, no. 3, pp. 638–645, Sep. 2017, doi: 10.1007/s40831-017-0122-8.

[64] S. Riaño and K. Binnemans, "Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets," *Green Chem.*, vol. 17, no. 5, pp. 2931–2942, May 2015, doi:

10.1039/C5GC00230C.

[65] Y. Baba, F. Kubota, N. Kamiya, and M. Goto, “Selective Recovery of Dysprosium and Neodymium Ions by a Supported Liquid Membrane Based on Ionic Liquids,” *Solvent Extr. Res. Dev. Jpn.*, vol. 18, pp. 193–198, 2011, doi: 10.15261/serdj.18.193.

[66] V. G. Deshmane, S. Z. Islam, and R. R. Bhave, “Selective Recovery of Rare Earth Elements from a Wide Range of E-Waste and Process Scalability of Membrane Solvent Extraction,” *Environ. Sci. Technol.*, p. acs.est.9b05695, Dec. 2019, doi: 10.1021/acs.est.9b05695.

[67] A. C. Ni’am, Y.-F. Wang, S.-W. Chen, G.-M. Chang, and S.-J. You, “Simultaneous recovery of rare earth elements from waste permanent magnets (WPMs) leach liquor by solvent extraction and hollow fiber supported liquid membrane,” *Chem. Eng. Process. - Process Intensif.*, vol. 148, p. 107831, Feb. 2020, doi: 10.1016/j.cep.2020.107831.

[68] S. Z. Islam, P. Wagh, J. E. Jenkins, C. Zarzana, M. Foster, and R. Bhave, “Process Scale-Up of an Energy-Efficient Membrane Solvent Extraction Process for Rare Earth Recycling from Electronic Wastes,” *Adv. Eng. Mater.*, vol. 24, no. 12, p. 2200390, 2022, doi: 10.1002/adem.202200390.

[69] K. K. Yadav, M. Anitha, D. K. Singh, and V. Kain, “NdFeB magnet recycling: Dysprosium recovery by non-dispersive solvent extraction employing hollow fibre membrane contactor,” *Sep. Purif. Technol.*, vol. 194, pp. 265–271, Apr. 2018, doi: 10.1016/j.seppur.2017.11.025.

[70] D. Kim, L. Powell, L. Delmau, E. Peterson, J. Herchenroeder, and R. Bhave, “Selective Extraction of Rare Earth Elements from Permanent Magnet Scraps with Membrane Solvent Extraction,” *Environ. Sci. Technol.*, Jun. 2015, doi: https://doi.org/10.1021/acs.est.5b01306.

[71] S. Pavón, T. Lorenz, A. Fortuny, A. M. Sastre, and M. Bertau, “Rare earth elements recovery from secondary wastes by solid-state chlorination and selective organic leaching,” *Waste Manag.*, vol. 122, pp. 55–63, Mar. 2021, doi: 10.1016/j.wasman.2020.12.039.

[72] Y. Mochizuki, N. Tsubouchi, and K. Sugawara, “Selective Recovery of Rare Earth Elements from Dy containing NdFeB Magnets by Chlorination,” *ACS Sustain. Chem. Eng.*, vol. 1, no. 6,

pp. 655–662, Jun. 2013, doi: 10.1021/sc4000187.

[73] K.-H. Lim, C. U. Choi, G. Moon, T.-H. Lee, and J. Kang, "Selective Chlorination of Rare Earth Elements from a Nd-Fe-B Magnet Using Zinc Chloride," *J. Sustain. Metall.*, vol. 7, no. 3, pp. 794–805, Sep. 2021, doi: 10.1007/s40831-021-00380-0.

[74] V. Kaplan, E. Wachtel, K. Gartsman, Y. Feldman, K.-T. Park, and I. Lubomirsky, "Using Chlorine Gas to Recover Rare Earth Metals from End-of-Life Permanent Magnets," *JOM*, vol. 73, no. 6, pp. 1957–1965, Jun. 2021, doi: 10.1007/s11837-021-04592-3.

[75] M. Firdaus, M. A. Rhamdhani, Y. Durandet, W. J. Rankin, and K. McGregor, "Review of High-Temperature Recovery of Rare Earth (Nd/Dy) from Magnet Waste," *J. Sustain. Metall.*, vol. 2, no. 4, pp. 276–295, Dec. 2016, doi: 10.1007/s40831-016-0045-9.

[76] R. M. Ashour *et al.*, "DTPA-Functionalized Silica Nano- and Microparticles for Adsorption and Chromatographic Separation of Rare Earth Elements," *ACS Sustain. Chem. Eng.*, vol. 6, no. 5, pp. 6889–6900, May 2018, doi: 10.1021/acssuschemeng.8b00725.

[77] J. O. Winget and R. E. Lindstrom, "Amino Acids as Retaining Agents in Displacement Chromatography of the Rare-Earth Elements," *Sep. Sci.*, vol. 4, no. 3, pp. 209–216, Jun. 1969, doi: 10.1080/01496396908052252.

[78] O. V. Kharitonov, L. A. Firsova, and E. A. Chuveleva, "The influence of a competing eluting ion content on the efficiency of separation of rare-earth metals in displacement complex forming chromatography," *Russ. J. Phys. Chem. A*, vol. 83, no. 6, pp. 1030–1031, Jan. 2009, doi: 10.1134/S0036024409060284.

[79] D. O. Campbell, "Rapid rare earth separation by pressurized ion exchange chromatography," *J. Inorg. Nucl. Chem.*, vol. 35, no. 11, pp. 3911–3919, Nov. 1973, doi: 10.1016/0022-1902(73)80085-5.

[80] P. P. Nazarov, *Chromatographic separation of transuranium elements, rare earth elements and alkali earth elements*. Japan: Japan Atomic Industrial Forum, Inc, 1981.

[81] Y. Ding, D. Harvey, and N.-H. L. Wang, “Two-zone ligand-assisted displacement chromatography for producing high-purity praseodymium, neodymium, and dysprosium with high yield and high productivity from crude mixtures derived from waste magnets,” *Green Chem.*, p. 10.1039.D0GC00495B, 2020, doi: 10.1039/D0GC00495B.

[82] K. Vijayaraghavan, M. Sathishkumar, and R. Balasubramanian, “Interaction of rare earth elements with a brown marine alga in multi-component solutions,” *Desalination*, vol. 265, no. 1, pp. 54–59, Jan. 2011, doi: 10.1016/j.desal.2010.07.030.

[83] J. P. N. Goldeinstein and J. P. Bassin, “Biosorption as a Strategy for the Recovery of Rare Earth Elements,” in *Biosorption for Wastewater Contaminants*, John Wiley & Sons, Ltd, 2022, pp. 201–212. doi: 10.1002/9781119737629.ch11.

[84] E. C. Giese, “Biosorption as green technology for the recovery and separation of rare earth elements,” *World J. Microbiol. Biotechnol.*, vol. 36, no. 4, p. 52, Apr. 2020, doi: 10.1007/s11274-020-02821-6.

[85] E. C. Giese, “Natural Biosorbents for Lanthanides Recovery,” *Ind. Biotechnol.*, vol. 18, no. 2, pp. 71–76, Apr. 2022, doi: 10.1089/ind.2022.0009.

[86] L. Tofan, C.-N. Bojoaga, and C. Paduraru, “Biosorption for the recovery and analysis of rare earth elements and platinum group metals from real samples. A review,” *Environ. Chem. Lett.*, vol. 20, no. 2, pp. 1225–1248, Apr. 2022, doi: 10.1007/s10311-021-01330-8.

[87] V. Diniz and B. Volesky, “Biosorption of La, Eu and Yb using Sargassum biomass,” *Water Res.*, vol. 39, no. 1, pp. 239–247, Jan. 2005, doi: 10.1016/j.watres.2004.09.009.

[88] Q. Chen, “Study on the adsorption of lanthanum(III) from aqueous solution by bamboo charcoal,” *J. Rare Earths*, vol. 28, pp. 125–131, Dec. 2010, doi: 10.1016/S1002-0721(10)60272-4.

[89] N. S. Awwad, H. M. H. Gad, M. I. Ahmad, and H. F. Aly, “Sorption of lanthanum and erbium from aqueous solution by activated carbon prepared from rice husk,” *Colloids Surf. B Biointerfaces*, vol. 81, no. 2, pp. 593–599, Dec. 2010, doi: 10.1016/j.colsurfb.2010.08.002.

[90] N. Das and D. Das, “Recovery of rare earth metals through biosorption: An overview,” *J. Rare Earths*, vol. 31, no. 10, pp. 933–943, Oct. 2013, doi: 10.1016/S1002-0721(13)60009-5.

[91] M. Zakotnik, I. R. Harris, and A. J. Williams, “Multiple recycling of NdFeB-type sintered magnets,” *J. Alloys Compd.*, Mar. 2008, doi: 10.1016/j.jallcom.2008.01.114.

[92] A. Walton *et al.*, “The use of hydrogen to separate and recycle neodymium–iron–boron-type magnets from electronic waste,” *J. Clean. Prod.*, vol. 104, pp. 236–241, Oct. 2015, doi: 10.1016/j.jclepro.2015.05.033.

[93] A. Walton and A. Williams, “Rare earth recovery,” *Mater. World*, vol. 19, no. 8, pp. 24–26, Aug. 2011.

[94] M. Kimiabeigi *et al.*, “Production and Application of HPMS Recycled Bonded Permanent Magnets for a Traction Motor Application,” *IEEE Trans. Ind. Electron.*, vol. 65, no. 5, pp. 3795–3804, May 2018, doi: 10.1109/TIE.2017.2762625.

[95] C. Jönsson *et al.*, “The extraction of NdFeB magnets from automotive scrap rotors using hydrogen,” *J. Clean. Prod.*, vol. 277, p. 124058, Dec. 2020, doi: 10.1016/j.jclepro.2020.124058.

[96] I. R. Harris and P. J. McGuiness, “Hydrogen: its use in the processing of NdFeB-type magnets,” *J. Common Met.*, vol. 172–174, pp. 1273–1284, Jan. 1991, doi: 10.1016/S0022-5088(06)80037-8.

[97] M. Xia, A. B. Abrahamsen, C. R. H. Bahl, B. Veluri, A. I. Søegaard, and P. Bøjsøe, “Hydrogen Decrepitation Press-Less Process recycling of NdFeB sintered magnets,” *J. Magn. Magn. Mater.*, vol. 441, pp. 55–61, Nov. 2017, doi: 10.1016/j.jmmm.2017.01.049.

[98] C. J. Ferron and P. Henry, “A review of the recycling of rare earth metals,” *Can. Metall. Q.*, vol. 54, no. 4, pp. 388–394, Oct. 2015, doi: 10.1179/1879139515Y.0000000023.

[99] B. Sprecher *et al.*, “Life Cycle Inventory of the Production of Rare Earths and the Subsequent Production of NdFeB Rare Earth Permanent Magnets,” *Environ. Sci. Technol.*,

vol. 48, no. 7, pp. 3951–3958, Apr. 2014, doi: 10.1021/es404596q.

[100] A. Piotrowicz, S. Pietrzyk, P. Noga, and Ł. Myćka, "The use of thermal hydrogen decrepitation to recycle Nd-Fe-B magnets from electronic waste," *J. Min. Metall. Sect. B Metall.*, vol. 56, no. 3, pp. 415–424, 2020.

[101] E. H. Lalana, M. J. J. Degri, A. Bradshaw, and A. Walton, "Recycling of Rare Earth Magnets by Hydrogen Processing and Re-Sintering," in *European Congress and Exhibition on Powder Metallurgy. European PM Conference Proceedings*, Shrewsbury, United Kingdom: The European Powder Metallurgy Association, 2016, pp. 1–6. Accessed: Mar. 04, 2023. [Online]. Available: https://www.proquest.com/docview/2036731035/abstract/B895AFCC9FBB48ACPQ/1

[102] B. Michalski, M. Szymanski, K. Gola, J. Zygmuntowicz, and M. Leonowicz, "Experimental evidence for the suitability of the hydrogen decomposition process for the recycling of Nd-Fe-B sintered magnets," *J. Magn. Magn. Mater.*, vol. 548, p. 168979, Apr. 2022, doi: 10.1016/j.jmmm.2021.168979.

[103] C. Li *et al.*, "Recycling of scrap sintered Nd–Fe–B magnets as anisotropic bonded magnets via hydrogen decrepitation process," *J. Mater. Cycles Waste Manag.*, vol. 17, no. 3, pp. 547–552, Jul. 2015, doi: 10.1007/s10163-014-0279-1.

[104] H. Jin *et al.*, "Life Cycle Assessment of Neodymium-Iron-Boron Magnet-to-Magnet Recycling for Electric Vehicle Motors," *Environ. Sci. Technol.*, vol. 52, no. 6, pp. 3796–3802, Mar. 2018, doi: 10.1021/acs.est.7b05442.

[105] R. O. Suzuki, A. Saguchi, W. Takahashi, T. Yagura, and K. Ono, "Recycling of Rare Earth Magnet Scraps: Part II Oxygen Removal by Calcium," *Mater. Trans.*, vol. 42, no. 12, pp. 2492–2498, 2001, doi: 10.2320/matertrans.42.2492.

[106] T. Akahori, Y. Miyamoto, T. Saeki, M. Okamoto, and T. Okabe, "Recovery of Rare Eath Metals in Used Magnets by Molten Magnesium," in *Magnesium Technology 2014*, TMS (The Minerals, Metals & Materials Society), 2014, pp. 35–38. Accessed: Mar. 03, 2020. [Online].

Available: https://doi.org/10.1007/978-3-319-48231-6_10

[107] T. W. Ellis and F. A. Schmidt, “Recycling of Rare Earth Metals from Rare Earth-Transition Metal Alloy Scrap by Liquid Metal Extraction,” 5,437,709, Aug. 01, 1995 [Online]. Available: https://patents.google.com/patent/US5437709A/en

[108] H. W. Na, Y. H. Kim, H. Taek Son, I. Ho Jung, H. Shin Choi, and T. Bum Kim, “Effect of Scrap Size on Extraction of Neodymium from Nd-Fe-B Magnet Scrap by Liquid Metal Extraction,” *Curr. Nanosci.*, vol. 10, no. 1, pp. 128–130, Feb. 2014, doi: 10.2174/1573413709666131109002236.

[109] L. Talens Peiró and G. Villalba Méndez, “Material and Energy Requirement for Rare Earth Production,” *JOM*, vol. 65, no. 10, pp. 1327–1340, Oct. 2013, doi: 10.1007/s11837-013-0719-8.

[110] M. A. Rabah, “Recyclables recovery of europium and yttrium metals and some salts from spent fluorescent lamps,” *Waste Manag.*, vol. 28, no. 2, pp. 318–325, Jan. 2008, doi: 10.1016/j.wasman.2007.02.006.

[111] T. H. Okabe, O. Takeda, K. Fukuda, and Y. Umetsu, “Direct Extraction and Recovery of Neodymium Metal from Magnet Scrap,” *Mater. Trans.*, vol. 44, no. 4, pp. 798–801, 2003, doi: 10.2320/matertrans.44.798.

[112] Y. Wu, B. Wang, Q. Zhang, R. Li, C. Sun, and W. Wang, “Recovery of rare earth elements from waste fluorescent phosphors: Na2O2 molten salt decomposition,” *J. Mater. Cycles Waste Manag.*, vol. 16, no. 4, pp. 635–641, Oct. 2014, doi: 10.1007/s10163-014-0295-1.

[113] V. S. Thompson *et al.*, “Techno-economic and Life Cycle Analysis for Bioleaching Rare-Earth Elements from Waste Materials,” *ACS Sustain. Chem. Eng.*, vol. 6, no. 2, pp. 1602–1609, Feb. 2018, doi: 10.1021/acssuschemeng.7b02771.

[114] S. Das, G. Gaustad, A. Sekar, and E. Williams, “Techno-economic analysis of supercritical extraction of rare earth elements from coal ash,” *J. Clean. Prod.*, vol. 189, pp. 539–551, Jul. 2018, doi: 10.1016/j.jclepro.2018.03.252.

[115] A. Otsuki, G. Dodbiba, A. Shibayama, J. Sadaki, G. Mei, and T. Fujita, “Separation of Rare Earth Fluorescent Powders by Two-Liquid Flotation using Organic Solvents,” *Jpn. J. Appl. Phys.*, vol. 47, no. 6S, p. 5093, Jun. 2008, doi: 10.1143/JJAP.47.5093.

[116] R. Chi *et al.*, “Recovery of rare earth from bastnasite by ammonium chloride roasting with fluorine deactivation,” *Miner. Eng.*, vol. 17, no. 9, pp. 1037–1043, Sep. 2004, doi: 10.1016/j.mineng.2004.04.010.

[117] T. Hirajima, K. Sasaki, A. Bissombolo, H. Hirai, M. Hamada, and M. Tsunekawa, “Feasibility of an efficient recovery of rare earth-activated phosphors from waste fluorescent lamps through dense-medium centrifugation,” *Sep. Purif. Technol.*, vol. 44, no. 3, pp. 197–204, Aug. 2005, doi: 10.1016/j.seppur.2004.12.014.

[118] B. Tansel, “From electronic consumer products to e-wastes: Global outlook, waste quantities, recycling challenges,” *Environ. Int.*, vol. 98, pp. 35–45, Jan. 2017, doi: 10.1016/j.envint.2016.10.002.

[119] T. Nemoto, N. Matsumoto, N. Kawakami, M. Sakon, and M. Shike, “Collection Service and Recycling Technology for Information and Telecommunications Electronics,” 2019.

[120] K. Baba, Y. Hiroshige, and T. Nemoto, “Rare-earth Magnet Recycling,” *Hitachi Rev.*, vol. 62, no. 8, pp. 452–455, 2013.

Chapter 3

Techno-Economic Analysis of Rare Earth Magnet Recycling Using Efficient Metal Distillation

3.1: Introduction

The development of permanent magnets has evolved from lodestone in the 1920s to modern neodymium-iron-boron (NdFeB, or "neo") magnets because of the need to obtain a good combination of maximum energy product and high curie temperature. The high energy product value from rare earth magnets and other permanent magnets enables smaller magnets and higher magnetic strength applications. Although there are generally two rare earth magnets, neo magnets, and samarium cobalt (SmCo) magnets, neo magnets are the strongest and most affordable. Dysprosium (Dy) and cobalt addition improve the magnet's high-temperature characteristics[1]. Their applications are seen in technologies that require potent magnets, such as wind turbine generators, vehicle traction motors in hybrid and electric vehicles (HEVs/EVs), speakers and headphones, magnetic resonance imaging (MRI) scanners, computer hard disk drives, and high-performance alternating current (AC) servo motors. According to a forecast by Adamas Intelligence[2], an independent research and advisory company on strategic metals and minerals, there will be an increase in the global demand for NdFeB alloys and powders at a compound annual growth rate (CAGR) of 9.7% from 2020 through 2030, and thus an increase in the need for rare earth elements (i.e., neodymium, praseodymium, dysprosium, and terbium). Meanwhile, global production will increase at a slower CAGR of 7.1%, leading to a supply market struggle to keep up with growing demand. NdFeB alloy global shortage is predicted to amount to 48,000 tons annually by 2030, estimated as the amount needed to produce 25 to 30 million electric vehicle traction motors. Didymium oxide (NdPr oxide) will also experience a shortage rise to 16000 tons in 2030, equivalent to roughly three times Lynas Corporation's annual output and MP Materials' annual output[2]. Therefore, there is a need to ensure a sustainable supply of these elements through recycling methods. In achieving this, it is essential to ascertain the availability of the raw materials for recycling and the economic viability of the methods employed.

Several studies have reported various methods for recycling rare earth from End-of-life (EOL) products. Still, there are limited detailed techno-economic analysis (TEA) studies on these methods. This study reviews various processes for recycling rare earths from EoL magnet products and a techno-economic analysis of a proposed low-cost alternative using a new distillation process.

3.2: Availability of Rare Earth Permanent Magnets

An essential aspect of understanding the recycling potential of rare earth elements (REEs) from EoL products is evaluating the quantities of these elements in secondary sources. Studies have shown that a maximum recycling rate of 20% can be reached in at least ten years with perfect recovery and a continuous growth trend[3]. Nd, Fe, and B primarily make up rare earth permanent magnets, although praseodymium can be added partially (~5%) to offset Nd.

Meanwhile, Dy is a common alloying material added to increase the magnet's operational temperature for applications that involve high temperatures, like EVs and wind turbines. In lower-temperature applications, like magnetic refrigeration systems, very minimal (0.5% max) or no Dy is used. For room temperature applications, such as in computer hard disk drives, Dy is typically around 1.5%[4]. About 31-32% of RE permanent magnets are REEs[5], with Nd being as much as 30%[6]. Thus, knowing the mass of REPM used in secondary sources will estimate the REEs available for recovery.

Dynamic variables considered to ascertain the quantity of REPM scrap available include yearly sales of potential sources, product lifespan, and quantity of REPM available. The most promising urban mining resources that contain rare earth permanent magnets are automobiles, home appliances, acoustic equipment, MRI machines, factory automation tools, and electronic devices [7]. For example, a conventional gasoline engine sedan has approximately 0.44kg of REES, 80% in permanent magnets. An entire hybrid electric vehicle (HEV) that uses nickel metal hydride batteries contains 4.5 kilograms of rare earth, and an HEV with a lithium-ion battery contains approximately 1 kg of REEs[8]. In the US, HEV sales began in 1999 with an annual sale of 9,400 vehicles and reached a peak of 495,500 in 2013. U.S. Plug-in HEV and EV sales started in 2010 with yearly sales of 7,700 and 10,100 vehicles, and since then, annual sales have increased at an average rate of 34.8% and 48.8%, respectively, reaching 122,800 vehicles in 2018 and 242,000 vehicles in 2019 respectively[9].

According to a market analysis report on REEs in Europe, EVs typically have a lifespan of 15 years and can provide more than 11 kt of Nd and close to 1 kt of Dy, likely to be harvested over the next two decades. Also, electric power steering motors of conventional vehicles can supply an estimate of 5 kt of Nd content. Residential air conditioners could provide approximately 2 kt of Nd. This represents approximately 20% of the total annual demand [2], [10].

Offshore wind turbines that use direct-drive permanent magnet generators (DDPMGs) contain about 160 - 650 kg NdFeB per MW of wind power capacity, with 51 - 208 kg of REEs/MW. Due to the enormous power capacity and lower part count, DDPMGs are the top design choice for U.S. offshore wind applications. Only seven offshore wind turbines in the United States with 42 MW of wind power capacity have been installed and commissioned.

In 2019, the US offshore wind project pipeline grew to a potential generating capacity of 28,521MW from 25,824 MW in 2016 across 13 states. Also, an estimate of the onshore wind turbines with DDPMGs in the U.S. has the potential of supplying ~37 tons of REEs in less than two decades from now, considering their average lifespan of 20 years [11]–[13].

Other devices such as microphones, loudspeakers, earbuds, and headphones also contain REEs, which can be recovered[14].

A study on RE availability for recycling reported that REEs from U.S. hard disk drives (HDDs) alone could meet ~5.2% of global Nd-Fe-B magnets demand (excluding China)[15]. Swarfs and slags generated from magnet manufacturing also contain a high concentration of REEs, which are recoverable. An estimated 30% of an original PM material can be generated as plant waste [16]. Also, secondary sources such as phosphogypsum, nickel metal hydride batteries, red mud, and coal ash can provide ~11X the total global demand of Nd, with phosphogypsum having the most significant portion [17], [18].

3.3: Recycling Processes for Rare Earth Permanent Magnets

There are multiple processes for producing new REPMs from old ones. Figure 3.1 shows the rough cumulative energy and cost of the value chain for virgin REPMs from mining to magnet production. In this graph, one can group recycling processes regarding how many “steps back” they take in the value chain to recover rare earth. The magnet-to-magnet approach is the most efficient and loses the least energy and value. Recycled magnets bring in all the impurities from scrap inputs and must be blended with other materials to create different magnet grades. Introducing a decrepitation agent, generally, hydrogen can degrade the properties somewhat, requiring small additions of unalloyed rare earth metals to recover properties similar to virgin magnets. On the other end, solvent extraction and sulfuric acid baking recover a mixed rare earth oxide which can be inserted into the separations process, recovering pure oxides which can be made into any magnet alloy with properties indistinguishable from virgin magnets. But it requires the most energy, as it must re-do the separation, reduction to metal, and alloy production steps. Liquid metal leaching is between these two: it recovers a rare earth magnet mischmetal, preserving the energy of metal reduction, but makes it difficult to tailor the REPM alloy.

The magnet-to-magnet approach has recently seen commercial deployment, as Urban Mining Company has set up operations in Texas. But a pure recycling industry will require one of the other two to supply the unalloyed rare earth metals required for suitable properties.

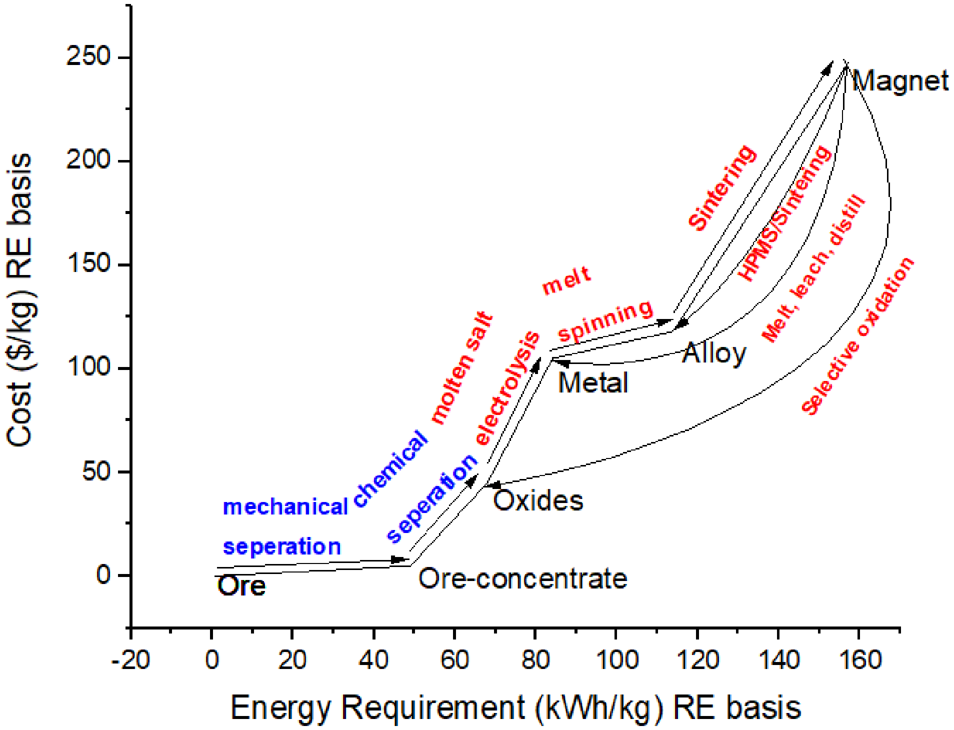


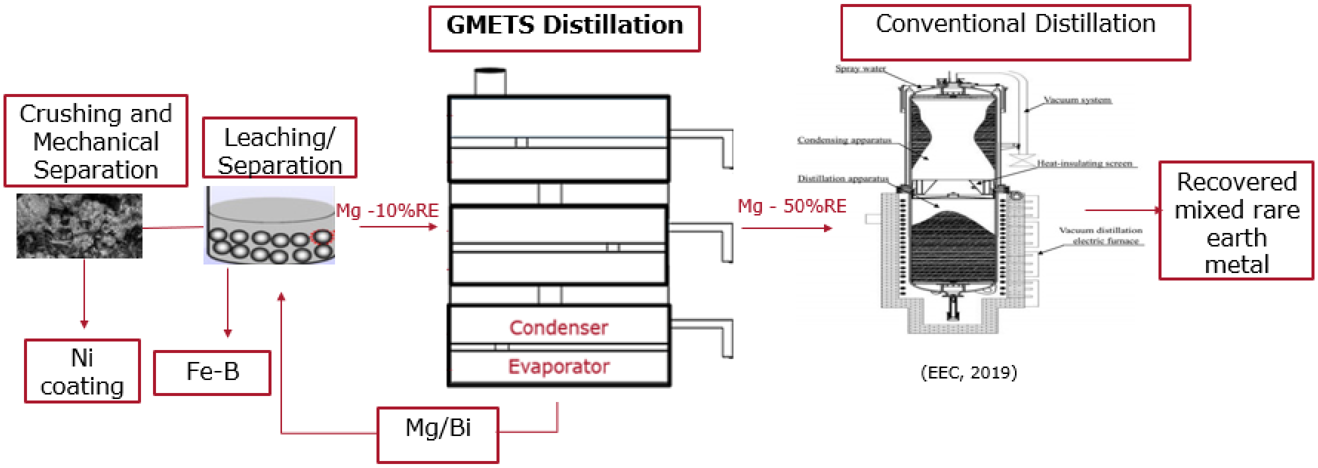
Figure 3.1: Cumulative energy and cost[19]–[22] of various stages of NdFeB magnet production, with alloy production energy use, roughly estimated; “RE basis” indicates per kilogram of contained rare earth metal.

3.3.1: Liquid Metal Leaching and Distillation

This liquid metal extraction process uses molten magnesium or other group IIA metals such as Ca or Ba for rare earth magnet recycling. Previous studies have shown that this technology extracts rare-earth alloys (Nd, Dy) from removed magnets at a temperature of 1273K and an Mg/magnet ratio of 10[23]. The Nd and Dy extraction efficiencies were 100% and 60%, respectively. Furthermore, adding Calcium suppressed the oxidation of Dy, thus increasing the extraction efficiency[24]. Using bismuth (Bi) instead of Mg can increase the Dy recovery above 90%, and using both Mg and Bi enables some separation of light and heavy rare earth[25].

3.4: Proposed Leaching and Distillation Process

The proposed process, as shown in Figure 3.2, is similar to the two-stage leaching using Mg and Bi as described by Ott & McCallum[25] but with a new efficient distillation step called Gravity-driven Multiple Effect Thermal System (G-METS) [26]. It consists of the following steps.



(EEC, 2019)

Figure 3.2: Process Flow Diagram

3.4.1 Crushing and Sorting

The magnet scrap is first processed to remove non-magnetic components, including nickel or other coatings, for example, by preferential degradation[27]. If necessary, further ground to the required particle size for the leaching operation.

3.4.2: Leaching RE Metals into Molten Mg

Crushed magnets and magnesium are fed into a leaching vessel, and heated to the leaching temperature, of 700^0C to 1000^0C. Neodymium is soluble in liquid magnesium, but iron and boron are relatively insoluble, and Mg-B compounds that form remain as solids. Various studies have used Mg: magnet mass ratios from 1:1 to 10:1; this model considers a reference case of 10:1 and a best case of 5:1.

The diffusion coefficient of Nd in liquid Mg was measured at $4.61\times10^{-8} \pm 1.32$ cm^2/s at a leaching temperature of 700^0C. The coefficient was found to increase with leaching temperature to $8.98\times10^{-8} \pm 3.50\times10^{-8}$ cm^2/s at 800°C[28]. Here we assume a leaching temperature of 1000^0C, and a time of 6 hours, following the work of Akahori *et al.*[23]. At that temperature, the Nd recovery rate is close to 100%, and the Dy recovery rate is 60%.

3.4.3: Separating the Melt from Fe-B alloy Particles

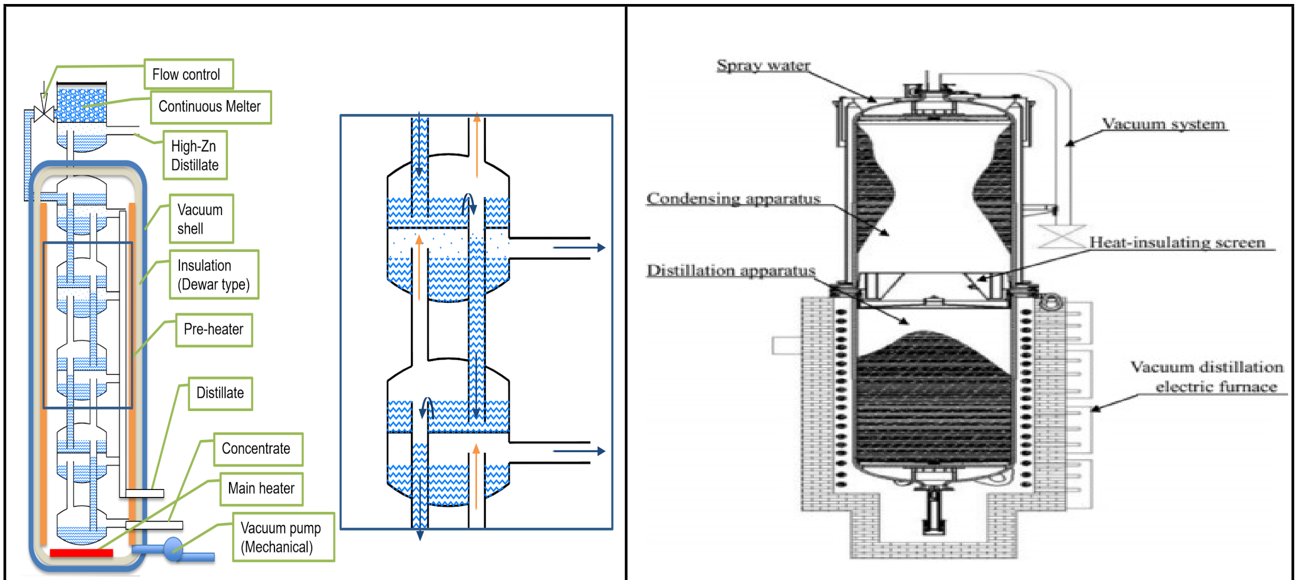
After leaching, liquid Mg-RE and scrap particles are transported to the separation unit. The more dense Fe-B alloy particles settle on the crucible bottom; thus, the Mg-Re solution can be easily separated from the melt. A filtration or centrifugal separation unit completes the separation of liquid Mg-RE from Fe-B alloy particles. We assume a small amount of Mg remains with the Fe-B alloy particles. Due to the limited leaching recovery rate of heavy rare earth elements such as dysprosium, this alloy particle stream contains a large fraction of those elements from the scrap.

3.4.4: G-METS and Vacuum Distillation of the Mg-RE Melt

The G-METS Mg distiller, as shown in Figure 3.3a, uses gravity to create a pressure difference without moving parts. The weight of the column of liquid metal above it raises the pressure of the evaporation chamber. Also, the pressure in the condenser below the evaporation chamber is raised. Heat flows upwards from the main heater, and each condenser feeds heat to the evaporator above it. In recycling, solid or liquid alloys are introduced into the top melter. The melted Mg alloy flows at a controlled rate down into the top evaporator, where a portion of the Mg alloy evaporates. The evaporated portion rises to the top condenser. It condenses while the remaining Mg that does not evaporate here flows down through the liquid standpipe into the next evaporator, where a portion of it evaporates, and so on. Each evaporator-condenser pair is called an "effect." Heat flows upward from effect to effect, from lower condensers to the evaporators above them. Liquid Mg flows downward between evaporators from effect to effect. Mg vapor flows upward within each effect from its evaporator into its condenser above it. Standpipes control the height of liquid Mg alloy in each evaporator.

In contrast, as shown in Figure 3.3b, conventional Mg distillation is a slower batch process producing solid metal in the condenser. Because of the pyrophoric nature of the high surface area condensed Mg crown product, it must be completely cooled before opening the vacuum vessel, resulting in a long cycle time (6-12 hours) and low process throughput.

This flow sheet uses both G-METS and conventional distillation. G-METS efficiently removes most of the Mg from the rare earth metals, producing a liquid product with about 30 wt% RE. Conventional distillation removes nearly all the remaining Mg, producing a product suitable for magnet production. It uses these two processes to separate the heavy rare earth product from the second Bi-metal leaching agent.



(a) (b)

Figure 3.3: Schematic diagram of an (a) four-effect magnesium G-METS distiller, with a detailed view of a single effect; (b)traditional distillation.

The Mg-Re melt is distilled to recover the Mg and RE separately, based on the difference in vapor pressure. This proposed method distills this melt in two steps. The first uses the new G-METS process for distilling most of the Mg. Studies have shown that this process can reduce the energy required to distill magnesium by as much as 90% versus today's batch distillation process [26]. This process flows liquid Mg-RE alloy through a steel distiller, so the maximum rare earth content is limited to 20-30 wt% to prevent steel corrosion. Thus, If the material comes in with 90-97 wt% Mg, G-METS can efficiently remove 65-85% of the magnesium. The second step is less-efficient conventional vacuum distillation using Mg sublimation, leaving behind solid metal almost entirely of rare earth. As a result, the rare earth extraction efficiency mainly depended on the Mg: magnet ratio[23], [24], [28], [29].

3.4.5: Liquid Bismuth Leaching of Fe-B Particles

Leaching in liquid bismuth is used to recover more dysprosium from the Fe-B particle stream after the magnesium leaching process, following[30]. This again selectively removes rare earth, with low iron. But as with 85% target recovery of magnesium using G-METS, the target bismuth recovery will be 80%, with the remainder recovered using traditional vacuum distillation.

3.5: Studies on the Techno-Economic Analysis of Rare Earth Recycling

Several studies have been conducted on various methodologies that may be utilized to analyze and determine the viability of recycling rare earth metals in terms of cost and profit. A study on the bioleaching of rare earth elements from waste materials showed that the primary unit operations and other utilities and costs involved amounted to \$3,030,000 in total annual cost. The estimated payback period was one year, after which net cash flow would become positive. A 44% internal rate of return was realized with a net present value of \$5,780,000 and a discount rate of 8%. The total revenue stream was \$3,880,000, of which \$116,000 was revenue received from the REE sales, and the balance was from collecting spent FCC catalyst at a \$200/ton tipping fee. The annual profit from the plant was estimated at \$855,000. The annual feedstock was 18,838 tons of FCC catalyst, or 10% of the FCC catalyst used in the United States[31].

Cong et al. developed a cost model for recovering Rare earth permanent magnets from hard disk drives. A linear programming method was proposed to determine the optimal disassembly sequence for maximum recovered value. The sensitivity analysis performed on the unit revenue from the dismantled HDD components and materials showed that an increase in unit revenue or a decrease in unit purchase cost led to an increase in profit for the same amount. It also showed that purchasing and dismantling were the major costs and that HDD recovery can be profitable if purchasing cost is zero or negative[32].

An analysis was carried out for coal ash, a relatively abundant source of REE. According to the Annual Coal Ash Production Report in 2016, the United States generates about 78 million tons of fly ash annually with a high concentration of high-value elements like scandium and neodymium. This research was focused on exploring the economic viability of REE extraction from coal ash using supercritical extraction. The recovery method involved supercritical CO2 and TBP (tributyl phosphate)-HNO3. Expenses and revenues were analyzed using combinatorial and sensitivity analysis scenarios. Unlike sensitivity analysis, combinatorics considered multiple process parameters that may change with development, like the reactor size, product yield, and reagent consumption. Four cost and eight revenue scenarios were considered with different combinations of reagent use, the concentration of REEs in coal ash, and scandium yield. It was suggested that this method could be an economically viable method to extract REM based on certain conditions, including a high concentration of high-value REE ash, a 1:20 molar ratio of REE oxides to TBP reagent since TBP is expensive, and high use can diminish profitability and, future prices set by ore based production. The concentration of REE was 934g per ton of coal ash, valued at $557[33].

Also, an analysis was carried out on the economic viability of rare earth elements extraction from clay waste, which was obtained from producing phosphoric acid by processing mined phosphate rock. A pyro-hydrometallurgical method was designed involving leaching, precipitation, and calcination. A staged liquid-liquid extraction and stripping were also performed before precipitation and calcination. The variables used in this analysis were the overall REE phosphate conversion to REE oxides, individual equipment cost variable design, and conversion of sellable byproducts. From this analysis, the recovery of rare earth from phosphoric acid had a favorable economic potential. A net annual profit of $14.4 million was realized. It was noted that a large portion of the profit was from the production of phosphoric acid. Also, about 2% thorium and uranium were produced alongside - a 4,557kg/year production, well above the required 5 kg/year[34].

Nguyen et al. studied the economic assessment for recycling critical metals from hard disk drives using an electro-hydrometallurgical process involving acid dissolution followed by precipitation. They also simulated the end-of-life HDD availability from 2017 to 2027. They realized that a ramp-up in production in 2017 occurred at 61% capacity and reached its peak at 96% capacity from 2018 to 2020, after which it showed a gradual drop in recycling rate until 2027 at 78% capacity. They stated that for a recycling facility of 25,000 mt/year, adding REO recovery to an e-waste base and precious metal recovery process was profitable only when it was done simultaneously with the base and precious metal recovery. Earnings before Interest, Tax, Depreciation, and Amortization (EBITDA) was the economic measure since it reflected operating rather than financial or accounting decisions. Adding REO recovery increased annual EBITDA by 19%, an average of $4.1 million/year. Total revenue increased by 14.6%, given an REO price of $56/kg. varying the REO prices from $16.50/kg to $397.50/kg led to an average EBITDA of $15-$76 million/year. Metal prices and feedstock prices were varied, and It was noted that although the recovery process could use a free HDD feedstock, earnings dropped quickly once the feedstock price approached $2/kg[15].

3.5.1: Techno-Economic Analysis of Proposed Method

This study focused on magnet scrap recycling from EoL NdFeB magnets to obtain RE alloy as a precursor for magnet production.

A process flow diagram was developed to determine the economic feasibility of the magnesium and bismuth leaching process. The techno-economic analysis was carried out using the ARPA-E METALS tool techno-economic analysis spreadsheet v1.0 from the U.S. Department of Energy [34]. A complete material and energy balance was developed and added to the ARPA-E METALS tool. Information was pulled from these to determine the variable cost, including raw materials, utilities, and miscellaneous materials. The mass balance contained 12 elements from the magnet scrap and leaching metal. Various adjustable parameters such as Mg/scrap feed ratio, Bi/Leaching vessel waste ratio, and Mg and Bi losses to waste streams were modeled to determine their effects on the overall target recovery and energy use. Due to the high uncertainty in scrap acquisition cost, which was omitted from this analysis, this cost can be added separately. The streams and composition sheets in the ARPA-E METALS Tool calculated the value flows for each input and output stream based on their compositions and verified the perfect closure of the mass balance for all 12 elements. Various online vendors were used to determine the values for each compound/element, and their best and worst-case scenarios were found.

The energy requirement for the leaching vessel was calculated based on the equation:

$$\sum \dot{m} c_p \Delta T = \dot{m}_{sc} c_{psc} (T_f - T_0) + \dot{m}_{Mg} c_{pMg} (T_f - T_0) + \dot{m}_r c_{pr} (T_f - T_r)$$

In this equation, $\dot{m}_{sc}$ is the mass flow rate of the scrap, $\dot{m}_{Mg}$ is the mass flow rate of the Mg refill, $\dot{m}_r$ is the mass flow rate of the Mg recycled from the distillation operation. Moreover, c_{psc}, c_{pMg}, and c_{pr} are the specific heat capacities of the scrap, magnesium, and Mg recycle, respectively. T_0 is the room temperature at which the scrap will be fed into the leaching vessel, T_r is the weighted average temperature of Mg recycle exiting the G-METS and conventional distillation processes, and T_f is the temperature of extraction of the leaching vessel. This was similarly used to obtain the energy required for the second leaching process with bismuth.

The ARPA-E METALs Tool was used to calculate the costs of utilities and inform best- and worst-case scenarios based on the data for average electricity costs and emissions per kWh for each state from the Energy Information Administration[35]. Estimating labor requirements was based on the textbook by Peters, Timmerhaus, and West[36] using Figure 6-9 on operating labor requirements in the chemical process industry. For a processing plant with an average condition of batch operations and continuous remelting process of Mg, the full-time equivalent (FTE) was obtained. This was based on an output rate of ~1460 kg/hr, which is the sum of the mass flow rates out of the leaching vessels as shown in the material balance, and used correlations for multiple small units or altogether batch operations for 100% traditional distillation and average conditions for the cases with mostly G-METS separation. The principal processing steps were crushing, heat transfer, reaction, and distillation. Without G-METS (assuming only traditional distillation), the operating labor was estimated as having complete batch operations, thus requiring more employee hours per day. This resulted in an estimate of 60 employee hours/day and 12 FTEs, for this case. With G-METS, the estimate is 40 employee hours/day and 8 FTEs. These were used as best-case labor values, 1.5 and 2 times those for reference and worst-case labor values, respectively.

Other labor requirements, such as supervision, laboratory costs, and plant overhead, were estimated as a percentage of the operating labor. Maintenance, insurance, and royalties were estimated as a percentage of fixed capital investment. Indirect costs, such as research and development, distribution, marketing, and other administrative costs, were estimated as a percentage of the sum of the fixed and variable costs. Sensitivity analysis was carried out for the best-case, reference, and worst-case scenarios, and these percentages were varied according to the ranges shown in Table 3.1. The cost implications of integrating the G-METS were studied. This is considered an increase in the full-time equivalent because of an increase in the employee hours because of complete traditional distillation.

Table 3.1: Assumptions used to determine the cost calculations for the best, reference, and worst-case scenarios. FTE is full-time equivalent, FCI fixed capital investment, VC variable, and FC fixed costs.

	Best Case	Reference case	Worst case
Mg/magnet ratio	5:1	10:1	10:1
Mg metal	$3000 per ton	$3000 per ton	$7000 per ton
Bi-metal	$7000 per ton	$7000 per ton	$14000 per ton
Electricity	0.06 per kWh	0.09 per kWh	0.18 per kWh
Operating labor	8FTEs	12FTEs	16 FTEs
Other labor	75% OL	85% OL	90% OL
Maintenance	2% FCI	7.5% FCI	10% FCI
Indirect cost	10% of VC and FC	15% of VC and FC	25% of VC and FC
Insurance	1% FCI	1% FCI	1% FCI
Royalties	1% FCI	1% FCI	1% FCI

3.6: Model Results

Figure 3.4 shows the proportions of each material flow compared to the product flow as calculated in the spreadsheet (supplementary material attached). Thus, for a plant with a target of 205 metric tons of RE alloy per year and an additional 11 tons of Dy metal, about 745 metric tons of scrap feed, ~149 metric tons of Mg, and 104 tons of bismuth will be required. Magnesium and bismuth are recycled after distillation.

The raw material costs can be calculated based on these flows as shown in Table 3.2.

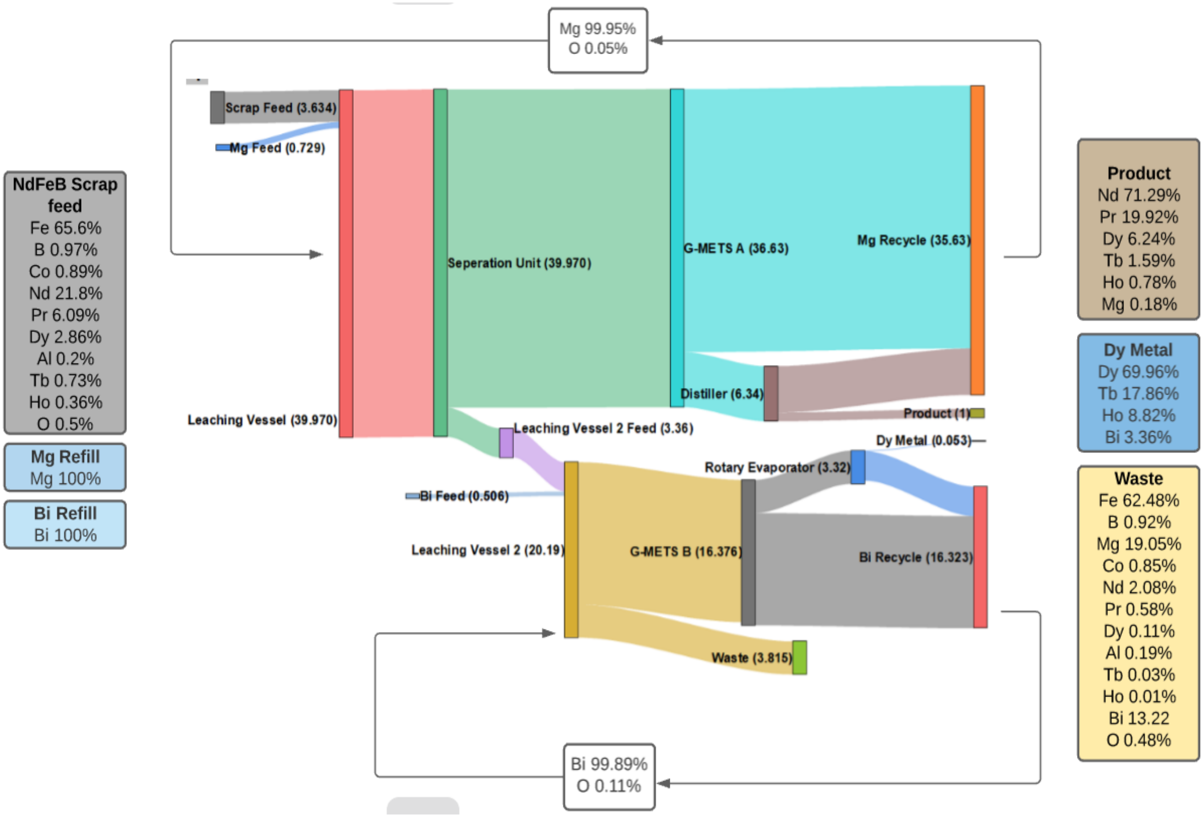


Figure 3.4: Material balance flow ratios for Mg/Bi leaching and distillation process, mass flow rates in parentheses are ratios to the main product output stream.

Table 3.2: Raw materials, flow rates, and values assuming a 205 ton/a RE Alloy recovery and an additional 11 ton/annum of Dy metal(using Bismuth) with an 85% plant capacity factor.

Streams	Flow rate (kg/hr)	Cost (USD/kg)	Annual cost (USD)
Scrap feed	100	-	-
Mg feed	20.05	3	447,866
Bi feed	13.93	7	726,000
Total	133.98	10	1,173,866

The energy requirement for the process can be seen in Figure 3.5, with a total energy usage of 64.28 kWh/kg of RE (mixed rare earth metals obtained). These are given for an Mg/scrap feed mass ratio and Bi/waste mass ratio of 10:1. This increases to 248.1 kWh/kg without G-METs. A decrease in these ratios will lead to an overall decrease in the energy used by the equipment.

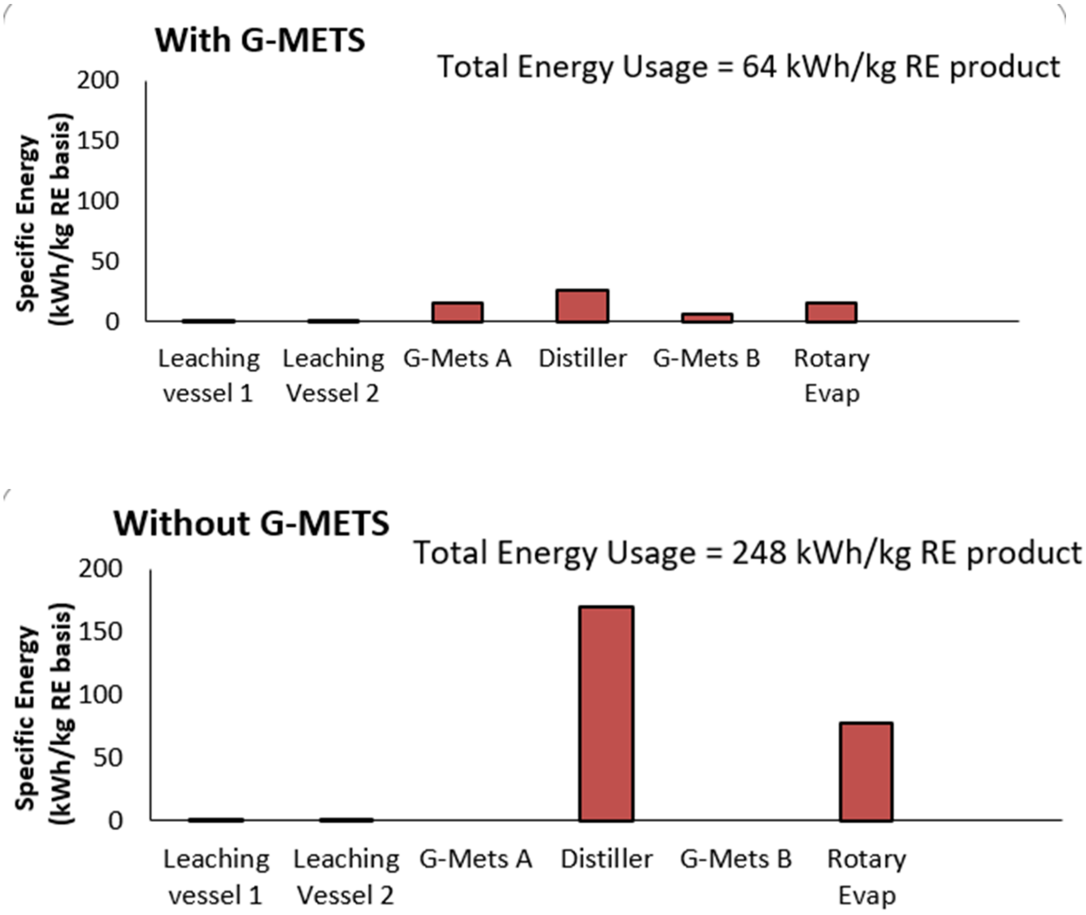


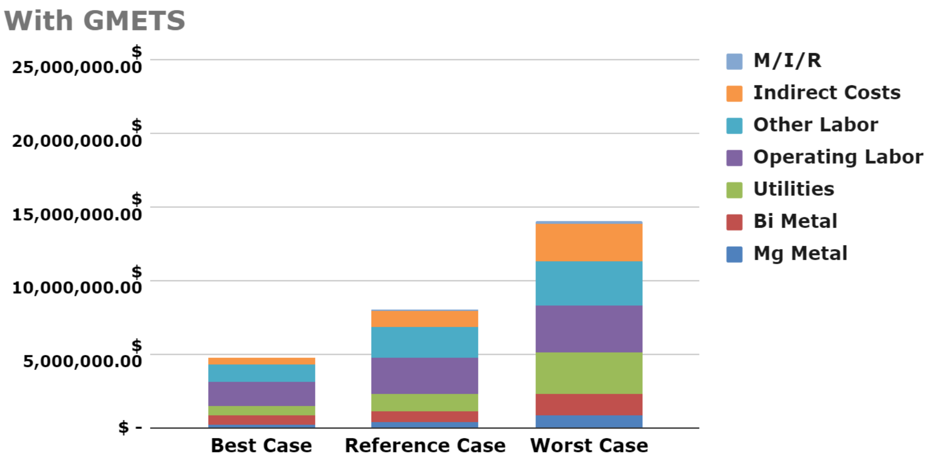
Figure 3.5: Energy requirement of various equipment for the Mg/Bi leaching process with and without G-METS distillation.

The energy consumption for the first G-METS distiller was estimated to be 15.3 kWh/kg of RE product and 6.58 kWh/kg of Dy metal based on the thermal model described in the G-METS distillation patent application[37]. This is estimated for 85% Mg distillation and 80% Bi distillation, respectively. For the conventional distillation and the rotary evaporation, the energy usage was estimated at 25.36 kWh/kg of RE product and 15.75 kWh/kg of Dy, respectively, based on the fraction of Mg and Bi distilled.

Also, assuming a best- and worst-case energy cost of $0.06/kWh and $18/kWh, the annual electricity consumption is expected to be $900,993 and $2,702,980, respectively.

Table 3.3: Cost of utilities, Total annual cost, and cost of RE/Dy per kg with and without G-METs for Best, Reference, and Worst-case scenarios

	With G-METS			Without G-METS		
	Cost of Utilities	Total Annual cost	Cost per kg of RE alloy plus Dy metal	Cost of Utilities	Total Annual cost	Cost per kg of RE alloy plus Dy metal
Best case	$586,996	$ 4,817,432	$ 22.32	$ 1,511814	$ 7,408,612	$ 34.32
Reference case	$ 1,148,766	$ 8,045,319	$37.27	$ 3,505,969	$ 13,365,268	$ 61.91
Worst case	$ 2,747,656	$ 14,062,271	$ 65.14	$ 8,294,015	$ 24,878,820	$ 115.25



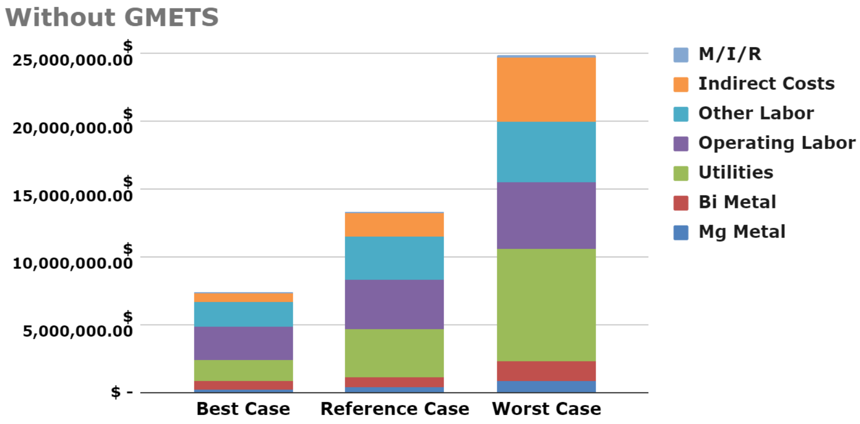


Figure 3.6: Three annual operating cost stack scenarios for a 205ton/a RE alloy recovery and further 11 t/a of Dy(using bismuth) with and without G-METS distillation.

3.7: Discussion

The operating cost estimated here covers the flow sheet from scrap magnet powder input to rare earth magnet mischmetal output and does not include the cost of acquiring magnets or the cost of mechanical separation from the coating and other materials. Prices for NdPr and DyFe alloys for magnets have been around ~$120/kg and $410/kg, respectively[38], implying high operating margins for all but the non-G-METS worst-case above. But these are relatively high; for example, in December 2020, they were around $60-65/kg and $300-350/kg, respectively [38], so reversion to historical average prices could strongly affect operating margins. Rare earth prices are generally given FOB China on the Shanghai exchange. In contrast, these recycling operations could be closer to Western customers and free from supply risk concerns so that the products may command higher prices. It is currently assumed that Fe and B and coatings do not have any value, but future work could look for a way to separate them and sell the resulting metals. Based on how much rare earth metal is consumed in the United States, which is ~500 tons/yr [39], this recycling process operating margin can meet 40% of the US rare earth metal needs. The final conventional distillation step will have to be designed in such a way as to distill the remaining Mg from the Mg-Nd alloy to meet NdFeB magnet specifications.

Capital cost was not discussed here, as there is currently limited information on some processes involved. The G-METS distiller is new/custom, and much remains to be invented, so it is difficult to give a quote on a drawing yet to determine the capital cost. Although, it should differ considerably for the G-METs and non-G-METS cases due to the batch nature and long cycle time of conventional vacuum distillation, as opposed to the high-throughput continuous G-METS.

The introduction of the G-METS system has the potential to reduce the energy required and, thus, the cost of utilities for the process by 67% for the reference case, as shown in Table 3.3. This reduces the total annual and production costs by 40% compared to traditional distillation. This cost can be minimized further by reducing the Mg/scrap ratio, as observed by adjusting the material balance spreadsheet on the ARPA-E METAL Tool. Figure 3.6 shows three annual operating cost stack scenarios for an RE magnesium/bismuth leaching plant. The utility cost is 14% of the total annual cost, while raw materials, including the cost of magnesium and bismuth metal, are ~15%. The bulk of the cost is seen in the operating and other labor, i.e., the laboratory costs, plant overheads, and supervision which amount to 56% of the total annual cost.

Given the high labor fraction in the overall operating costs, a note on process automation is warranted. Much of the labor is required for material handling between unit operations; the operations should not require significant labor inputs. It may be possible to automate some of the material hand-offs from magnet crushing, to liquid metal leaching, to centrifugal separation.

But feeding scrap into the crushing operation, product recovery from the separation and G-METS operations, and feeding and safe product recovery from conventional distillation will be hard to automate. The relatively low production volume of this overall process at this scale would also likely make custom automation solutions require a long time to pay back labor savings.

Meanwhile, Peters, Timmerhaus, and West [36] show a meager labor input scaling exponent of 0.2-0.25, such that a factor of 16-32 increase in scale results in only a doubling of labor. This reflects both automation and larger equipment sizing. The scale of roughly 200 tons/year of rare earth metal production from recycled streams would likely increase considerably. For example, 2020 US sales of 760,000 electric vehicles, and 1 GW/year of wind turbine deployment with rare earth permanent magnet generators, would result in roughly 760 t/and 600 t/a of contained rare earths in magnet scrap, respectively--a total five-fold increase in scrap availability--when they reach end-of-life in 2030-2040.

3.8: Conclusion

Techno-Economic Analysis of recovering REEs from NdFeB scrap using a novel G-METS distillation system was performed for a magnesium and bismuth leaching process. The G-METS system can reduce the energy consumption of the overall process to 64 kWh/kg, which is about 30% less than metal production from ore, and 61-67% less than the process using conventional distillation. The processing cost is also lowered from 34-115/kg for the best-case and worst-case scenarios without G-METS distillation to 22-65$/kg with it. The largest operating cost factor is labor, whose cost per kg of the product would likely decline with increasing scale. These costs compare with today’s NdPr metal prices of $100-120/kg, which would make operating margins much larger with G-METS than without it. Therefore, the G-METS distillation process can be considered a potential enabling technology for liquid metal leaching and distillation.

REFERENCES

[1] R. Ulewicz and E. Wyslocka, *MAGNETS: HISTORY, THE CURRENT STATE AND THE FUTURE*. 2015.

[2] "UBS Rare Earth Forecasts Only Tell Half the Story - Adamas Intelligence," Mar. 24, 2021. https://www.adamasintel.com/ubs-ndpr-forecasts-miss-mark/ (accessed Mar. 27, 2021).

[3] A. C. Powell, "Recycling in Supply Chains for Tomorrow's Low-Carbon Industries," in *REWAS 2019*, G. Gaustad, C. Fleuriault, M. Gökelma, J. A. Howarter, R. Kirchain, K. Ma, C. Meskers, N. R. Neelameggham, E. Olivetti, A. C. Powell, F. Tesfaye, D. Verhulst, and M. Zhang, Eds. Cham: Springer International Publishing, 2019, pp. 9–18. doi: 10.1007/978-3-030-10386-6_2.

[4] C. Booten, M. Mann, and A. Momen, "Critical Material Supply Chain Analysis: Magnetocalorics," National Renewable Energy Laboratory, Clean Energy Manufacturing Analysis Center, DE-AC36-08GO28308, 2020. [Online]. Available: https://www.nrel.gov/docs/fy20osti/75163.pdf

[5] Y. Yang *et al.*, "REE Recovery from End-of-Life NdFeB Permanent Magnet Scrap: A Critical Review," *J. Sustain. Metall.*, vol. 3, no. 1, pp. 122–149, 2017, doi: 10.1007/s40831-016-0090-4.

[6] J. H. Rademaker, R. Kleijn, and Y. Yang, "Recycling as a Strategy against Rare Earth Element Criticality: A Systemic Evaluation of the Potential Yield of NdFeB Magnet Recycling," *Environ. Sci. Technol.*, vol. 47, no. 18, pp. 10129–10136, Sep. 2013, doi: 10.1021/es305007w.

[7] N. Sekine, I. Daigo, and Y. Goto, "Dynamic Substance Flow Analysis of Neodymium and Dysprosium Associated with Neodymium Magnets in Japan," *J. Ind. Ecol.*, vol. 21, no. 2, pp. 356–367, 2017, doi: 10.1111/jiec.12458.

[8] E. Alonso *et al.*, "An Assessment of the Rare Earth Element Content of Conventional and Electric Vehicles," *SAE Int. J. Mater. Manuf.*, vol. 5, no. 2, pp. 473–477, 2012.

[9] S. C. Davis and R. G. Boundy, “Transportation Energy Data Book: Edition 39,” p. 455, 2020.

[10] N. Akil, S. Loutatidou, D. Arslan, E. Festa, P. Circelli, and S. Colella, “WP9 - Market analyses, exploitation and dissemination,” REE4EU, Market Analysis Report, 2019 2015.

[11] R. Wiser *et al.*, “2018 Wind Technologies Market Report,” 2018. [Online]. Available: https://www.energy.gov/eere/wind/downloads/2018-wind-technologies-market-report

[12] IRENA, “Future of Wind,” International Renewable Energy Agency, Abu Dhabi, 2019.

[13] D. D. Imholte *et al.*, “An assessment of U.S. rare earth availability for supporting U.S. wind energy growth targets,” *Energy Policy*, vol. 113, pp. 294–305, Feb. 2018, doi: 10.1016/j.enpol.2017.11.001.

[14] T. Lister, P. Wang, and A. Anderko, “Electrorecycling of Critical and Value Metals from Mobile Electronics,” presented at the Conference of Metallurgists, Canada, Sep. 2014.

[15] R. T. Nguyen, L. A. Diaz, D. D. Imholte, and T. E. Lister, “Economic Assessment for Recycling Critical Metals From Hard Disk Drives Using a Comprehensive Recovery Process,” *JOM*, vol. 69, no. 9, pp. 1546–1552, Sep. 2017, doi: 10.1007/s11837-017-2399-2.

[16] I. C. Nlebedim and A. H. King, “Addressing Criticality in Rare Earth Elements via Permanent Magnets Recycling,” *JOM*, vol. 70, no. 2, pp. 115–123, Feb. 2018, doi: 10.1007/s11837-017-2698-7.

[17] G. Gaustad, E. Williams, and A. Leader, “Rare earth metals from secondary sources: Review of potential supply from waste and byproducts,” *Resour. Conserv. Recycl.*, vol. 167, p. 105213, Apr. 2021, doi: 10.1016/j.resconrec.2020.105213.

[18] K. Binnemans, P. T. Jones, B. Blanpain, T. Van Gerven, and Y. Pontikes, “Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review,” *J. Clean. Prod.*, vol. 99, pp. 17–38, Jul. 2015, doi: 10.1016/j.jclepro.2015.02.089.

[19] I. B. Fernandes, A. Abadías Llamas, and M. A. Reuter, “Simulation-Based Exergetic Analysis of NdFeB Permanent Magnet Production to Understand Large Systems,” *JOM*, vol.

72, no. 7, pp. 2754–2769, Jul. 2020, doi: 10.1007/s11837-020-04185-6.

[20] P. F. Mendez, "Order of Magnitude Scaling of Complex Engineering Problems, and its Application to High Productivity Arc Welding," Ph.D., Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, 1999. Accessed: Oct. 18, 2020. [Online]. Available: http://hdl.handle.net/1721.1/16730

[21] B. Inc, "Rare Earth Elements to Make a Strong Comeback After 2020 Setback, Says Beroe Inc."https://www.prnewswire.com/news-releases/rare-earth-elements-to-make-a-strong-comeback-after-2020-setback-says-beroe-inc-301271188.html (accessed Oct. 01, 2021).

[22] "REO price by type 2020," *Statista*. https://www.statista.com/statistics/617249/price-range-of-selected-rare-earth-oxides/ (accessed Oct. 01, 2021).

[23] T. Akahori, Y. Miyamoto, T. Saeki, M. Okamoto, and T. Okabe, "Recovery of Rare Eath Metals in Used Magnets by Molten Magnesium," in *Magnesium Technology 2014*, TMS (The Minerals, Metals & Materials Society), 2014, pp. 35–38. Accessed: Mar. 03, 2020. [Online]. Available: https://doi.org/10.1007/978-3-319-48231-6_10

[24] T. W. Ellis and F. A. Schmidt, "Recycling of Rare Earth Metals from Rare Earth-Transition Metal Alloy Scrap by Liquid Metal Extraction," 5,437,709, Aug. 01, 1995 [Online]. Available: https://patents.google.com/patent/US5437709A/en

[25] R. T. Ott and R. W. McCallum, "Recovering rare earth metals from magnet scrap," U.S. Patent 10,323,299, Jun. 18, 2019 Accessed: May 17, 2021. [Online]. Available: https://patents.google.com/patent/US10323299B2/en

[26] A. E. Telgerafchi, G. Espinosa, M. Rutherford, A. Powell, and D. Dussault, "Efficient Low-Cost Gravity-Driven Multiple Effect Thermal System (G-METS) Distillation of Magnesium," in *Magnesium 2021*, Orlando, Florida, Mar. 2021, pp. 145–152. doi: 10.1007/978-3-030-65528-0_22.

[27] B. Ott, D. E. Spiller, and P. R. Taylor, "Rare Earth Magnet Recovery from Hard Drives by

Preferential Degradation," in *REWAS 2019*, G. Gaustad, C. Fleuriault, M. Gökelma, J. A. Howarter, R. Kirchain, K. Ma, C. Meskers, N. R. Neelameggham, E. Olivetti, A. C. Powell, F. Tesfaye, D. Verhulst, and M. Zhang, Eds. Cham: Springer International Publishing, 2019, pp. 295–304. doi: 10.1007/978-3-030-10386-6_34.

[28] H. W. Na, Y. H. Kim, H. Taek Son, I. Ho Jung, H. Shin Choi, and T. Bum Kim, "Effect of Scrap Size on Extraction of Neodymium from Nd-Fe-B Magnet Scrap by Liquid Metal Extraction," *Curr. Nanosci.*, vol. 10, no. 1, pp. 128–130, Feb. 2014, doi: 10.2174/1573413709666131109002236.

[29] Y. Xu, L. S. Chumbley, and F. C. Laabs, "Liquid metal extraction of Nd from NdFeB magnet scrap," *J. Mater. Res.*, vol. 15, no. 11, pp. 2296–2304, Nov. 2000, doi: 10.1557/JMR.2000.0330.

[30] "Technology - Recovering rare earth metals using bismuth extractant." http://isurftech.technologypublisher.com/technology/21024 (accessed May 17, 2021).

[31] E. Thompson, "Investigation of Structure and Properties of Certain Iron-Tin-Carbon Alloys," North Carolina State College, Raleigh, North Carolina, 1961. Accessed: Oct. 10, 2019. [Online]. Available: https://mit-worldcat-org.libproxy.mit.edu/oclc/4437662755

[32] L. Cong *et al.*, "Modeling the Value Recovery of Rare Earth Permanent Magnets at End-of-Life," *Procedia CIRP*, vol. 29, pp. 680–685, Jan. 2015, doi: 10.1016/j.procir.2015.02.015.

[33] S. Das, G. Gaustad, A. Sekar, and E. Williams, "Techno-economic analysis of supercritical extraction of rare earth elements from coal ash," *J. Clean. Prod.*, vol. 189, pp. 539–551, Jul. 2018, doi: 10.1016/j.jclepro.2018.03.252.

[34] S. Archambault, "Economic Analysis of Rare Earth Elements Extraction from Clay Waste," University of Tennessee Honors Thesis Projects. Accessed: Sep. 23, 2020. [Online]. Available: https://trace.tennessee.edu/cgi/viewcontent.cgi?article=3086&context=utk_chanhonoproj

[35] "Wholesale Electricity and Natural Gas Market Data," *United States Energy Information*

Administration, Feb. 11, 2021. https://www.eia.gov/electricity/wholesale/

[36] M. Peters, K. Timmerhaus, and R. West, *Plant Design and Economics for Chemical Engineers*, 5th ed. McGraw-Hill Education, 2003.

[37] A. C. Powell, D. M. Dussault, M. R. Earlam, A. Tajima, and C. Raymes, “Method and Apparatus for Efficient Metal Distillation and Related Primary Production Process,” U.S. Patent Application 16/944,147 Accessed: Jan. 05, 2022. [Online]. Available: https://patents.google.com/patent/US20210040633A1/en

[38] “Daily Rare Earth Metals price, Lme Comex Shfe Price of Rare Earth Metals live | SMM - China Metal Market.” https://www.metal.com/Rare-Earth-Metals (accessed Oct. 01, 2021).

[39] D. J. Cordier, “Rare Earth Mineral Commodity Summary 2022,” U.S. Geological Survey, 2022. Accessed: Apr. 14, 2023. [Online]. Available: https://pubs.usgs.gov/periodicals/mcs2022/mcs2022-rare-earths.pdf

Chapter 4

A Commercialization Study of Rare Earth Magnet Scrap Recycling

4.1: Introduction

Rare earth magnets are essential for producing many high-tech devices, including smartphones, EVs, wind turbines, and medical equipment. The global demand for rare earth magnets has rapidly increased in recent years, with a compound annual growth rate of 7.1% expected between 2022 and 2027. The increased use of green technology and the rising demand for electronic gadgets drives this expansion[1]. Primary production of rare earth magnets, which initially involves mining, has substantial environmental and social impacts, such as land degradation, environmental pollution, and supply risk. Recycling rare earth magnets from end-of-life goods can mitigate these consequences while conserving resources and creating economic value[2].

This study was part of the National Science Foundation Innovation Corps (NSF I-Corps) program, designed to encourage and support science and engineering research commercialization. The program provides funding and resources to help teams of scientists, engineers, and business experts validate their ideas and transition them into successful startups. It provides a significant opportunity for companies to investigate potential markets, identify consumer requirements and preferences and facilitate more robust commercialization initiatives. Customer discovery helps evaluate the assumptions about the market and refine the product-market fit. Teams of researchers, entrepreneurs, and business experts work together to validate or invalidate the commercial potential of their idea or concept[3]. This study assessed the feasibility of commercializing a new technology for recycling rare earth magnets. The analysis considered several factors that can impact the commercial success of rare earth magnet recycling, such as competition, potential collaborators, and the availability of recycling materials. The study presents a preliminary business model canvas that outlines the structure of a typical rare earth magnet recycling facility. This knowledge can provide insights into the market conditions for rare earths and help potential start-ups or companies make informed decisions about commercialization, investment, production, and marketing strategies. Policymakers can understand the market dynamics and make sound judgments about regulations and policies that affect the rare earths industry.

4.2: Methodology

This study was funded by the NSF as part of the NSF I-Corps. A team comprising an entrepreneurial lead, co-entrepreneurial lead, technical lead, and industry mentor was set up to conduct stakeholder interviews[4]. Over 130 stakeholder interviews were completed with individuals from rare earth magnet companies, rare earth magnet recycling companies, National laboratories, metal alloy companies, and metal recycling companies, as shown in Table 4.1. Stakeholders from end-user companies, especially rare earth magnet-cutting companies and electronics manufacturers, were also interviewed to assess scrap magnet availability for recycling. Interviewees were identified from contacts on LinkedIn, warm referrals, and several conferences, exhibitions, and trade shows. Interviews were conducted via video conferencing sessions and in person during company site visits and conference attendance. Several questions were asked based on the hypotheses formulated in the sections of the business model canvas, especially the value propositions and customer segment. Examples of questions asked include:

- What is feasible regarding feedstock, scale, timing, composition, marketing, and customers of a rare earth magnet recycling facility?
- Can magnet misch metal of NdPrDy be used in magnet production?
- What are you looking for in prospective partners?
- What is being done with the available swarf and discarded magnets in magnet-cutting companies?
- What are the challenges in setting up a rare earth magnet recycling plant in the United States?
- What scrap feedstock is available for rare earth magnet recycling?
- What factors should a rare earth recycling company consider in scaling up?
- What are the risks in starting up a rare earth magnet recycling company in the United States?

A saturation point was reached during the interviewing stage as most interviews conducted halfway through began reinforcing specific themes like feedstock availability, incentivizing rare earth magnet recycling, the importance of partnerships, awareness of scrap collections, and the stage-gate approach. The information obtained from the interviews and studies about the rare earth industry and market were used to refine the business model canvas to develop a structure for a typical rare earth magnet recycling facility.

Table 4.1: Stakeholders Count

S/No	Stakeholders	Number Interviewed
1.	Customers	20
2.	Suppliers	15
3.	Outside Experts	45
4.	Government	53
	Total	**133**

4.2: Rare Earths Market Study

Mining is still the primary source of rare earth metals today. Because recycling technology is still in its early stages, only a minimal amount of material is collected. Fewer than 5% of post-consumer rare earth magnets are recycled, and less than 1% of new demand is met by recycling, although it has been projected that recycling could account for 25% of the rare earth market in ten years[5]. Understanding various factors influencing the viability of rare earth magnet recycling is essential.

4.2.1: Competition

Although there are little to no recycling of rare earth magnet being carried out in the United States on a commercial scale, several start-up companies continue to spring up from research innovations in tertiary institutions and National Laboratories. This can, in the future, create competition among rare earth magnet recycling companies. MP Materials, the only rare earth mine in the United States, mines rare earth ores and is looking to commence the production of rare earth magnets in the coming years by developing a fully integrated source of separated rare earth oxides, particularly neodymium-praseodymium. This lays the groundwork for MP to become a downstream magnet manufacturer by 2025[6]. MP accounts for nearly 15% of worldwide rare earth mine production, the most significant of any non-Chinese rare earth firm. Despite controlling the mine, MP must ship products to China for processing[7]. As a result, the total lead time from extraction to the finished product could take several weeks. Although MP Materials is looking to start separation processes in the U.S. for mostly light metals, heavy metals are more valuable and essential for many magnet types.

Another company, Noveon Magnetics, formerly Urban Mining, is unique because it does not mine or work with virgin raw materials. Instead, it concentrates on using recycling to create high-quality, long-lasting magnets. They claim to be the only producers of rare earth magnets in the United States [8]. Noveon utilizes a variety of material streams and end-of-life channels to purchase scrap material at a reasonable price for its customers. This company also claims to have reduced CO_2 emissions by 11 tons for every ton of magnet produced, as well as techniques that are more than 90% more energy efficient than traditional production. However, Noveon faces increasing material prices, as many suppliers charge higher fees than in previous years, as growing clean technologies increase demand for rare earth. Noveon also must add a small amount of rare earth metal to achieve the properties specified by customers. Thus while Noveon may be considered a competitor, it may also be viewed as a prospective partner, which could potentially sell them rare earth metals [9],[10].

TdVib is a competitor with a similar strategy to this proposed technology for recycling rare earth magnet scrap. But unlike the proposed technology that requires a cycle of leaching and distillation, TdVib, has the benefit of not requiring coating removal, employing a water-soluble method to dissolve the magnets rather than acid-based, thus enabling an environmentally friendly process compared to other methods. It does not involve heating the scrap materials to high temperatures. Furthermore, their capacity to scale has increased their energy efficiency from 70% to 90%. They are projected to generate 3 - 5 tons of rare earth metals in less than two years[11], [12].

Phoenix Tailings has also developed a method for recovering rare earth metals from mining waste by "separating REOs through selective halogenation and reducing them with mixed halide salts"[1001]. While this proposed technology looks to source magnet scraps from discarded magnets, End-of-life (EOL) devices, and swarfs, the latter recover rare earth metals from mine tailings. They have reported recoveries of neodymium(Nd), dysprosium(Dy), and ferro-dysprosium(Dy-Fe) alloy[13]. Phoenix Tailings is potentially the only direct competitor to such a recycling facility, although they differ in their feedstock source.

4.2.2: Key Partners

Establishing solid relationships with potential suppliers is vital to commercializing this technology. It is critical to engage with firms such as vehicle scrap recyclers, electronics manufacturers, and magnet producers to obtain feedstock for recycling. For example, scrap yards or metal recycling firms might arrange monthly contracts with manufacturers to sell them a specific amount of metal scrap. Depending on the metal recycler, several cost structures exist for feedstock supply, such as scrap purchase, ranging from $0.05 to $2.00 per pound[14]. Also, charging tipping fees, i.e., fees companies pay to have their scrap metal or discarded mechanical components disposed of by an external party. Lastly, the collection of scrap metals can be done for free based on the nature of the agreement established with the recycler.

4.2.3: Context Analysis

The following two decades are poised to be the most suitable time to explore new recycling technologies. Countries across the globe are making concerted efforts to significantly reduce their carbon emissions, with a significant number setting ambitious targets for achieving carbon neutrality within a specific timeframe. Alongside these efforts, various industries have undergone numerous legislative changes. For example, the United States recently enacted the Inflation Reduction Act of 2022, which represents the country's largest-ever climate investment and is expected to reduce emissions by approximately 40% by 2030. Looking further ahead, the European Union has enshrined the European Green Deal in its Climate Law, which mandates that all EU member nations must achieve carbon neutrality by 2050[15]. The drive to reduce emissions has generated significant interest in minimizing the need for mining critical mineral resources. Finding sustainable ways to provide rare earth metals (REM) to the constantly expanding manufacturing industry is a worthwhile endeavor. This interest is not limited to policymakers but is also deeply ingrained in the cultures of these nations, which have taken substantial steps to encourage consumer recycling and reuse of household items. For example, California has introduced a fee for each plastic bag used at grocery stores[16], while New Jersey has banned their use entirely[17]. As evidenced by these measures, both governmental regulations and societal pressure are in line with the mission of the proposed recycling technology.

4.2.4: Addressable Markets

The market the rare earth recycling plant would be approaching is a two-sided market comprising the feedstock as well as target customers. The feedstock supply could be challenging as most devices like EVs and wind turbines are yet to reach their end of life. Thus, it will be important to approach commercialization through stage gates [18], looking out for early adopters, starting with places like data centers for hard disk drives. The target customers can be understood in terms of the total addressable, serviceable addressable, and serviceable obtainable markets.

Total Addressable Market (TAM)

This describes the largest market size for rare earth metal, i.e., the global rare earth element market, valued at $2,607.4 million in 2020, as shown in Figure 4.1. By 2028, this market is expected to grow to $5,520.2 million. The Asia-Pacific region accounts for a sizable portion of this industry, accounting for up to 78% of the total. The global demand for rare earth metals is expected to increase significantly in the coming years due to the rapid growth of technologies such as EVs, wind turbines, and advanced electronics. For example, the demand for neodymium, a rare earth metal used in making magnets for electric vehicles, is expected to grow at a CAGR of over 7% between 2020 and 2025[19].

Serviceable Addressable Market (SAM)

The SAM describes the most significant market that could be reached right now, which considers the rare earth metal market in the United States. Being a significant consumer of various applications that use rare earth magnets and having a strong military base, the United States has an estimated market share of $1.4B. In 2019, the United States produced approximately 26,000 metric tons of rare earth elements, according to the US Geological Survey. While this is a significant increase from previous years, it is still a relatively small amount compared to global production. To meet the growing demand for rare earth metals, the US has invested in developing new production capabilities, including mining projects in California and Wyoming. The US rare earth metal market will continue to see a substantial growth impact if other technologies, such as offshore wind projects, begin to gain approval through legislative processes [20].

Serviceable Obtainable Market (SOM)

SOM refers to the market that can be reached using the recycling technology's current resources, strategies, and capabilities. Given the amount of feedstock available for recycling, this can be estimated at 1% of the total addressable market. Although several competitors are soon entering the rare earth materials recycling market, this is a new field of study; thus, the entire United States and global rare earth metal market is arguably available[21].

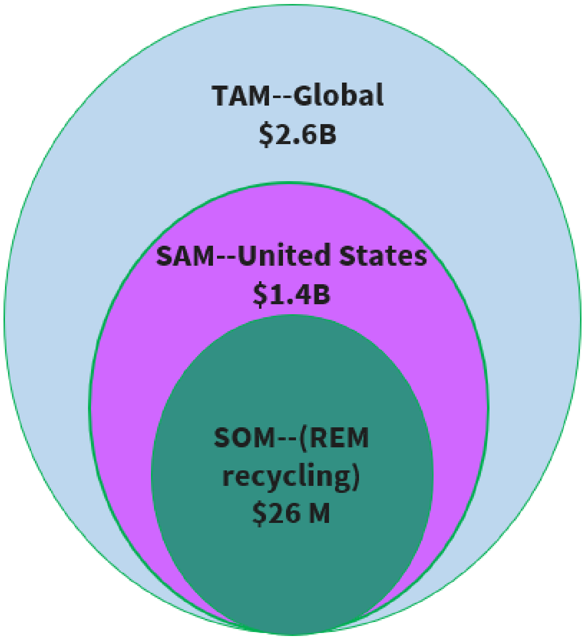


Figure 4.1: TAM/SAM/SOM for Rare Earth Metal Market

4.3: Feedstock Availability

The quantity and stability of rare earth magnets available for recycling are crucial to the economic and commercial viability of a rare earth recycling facility, as reinforced by most of the interviews conducted. EOL devices that include rare earth magnets, such as hard disk drives, speakers, and motors, are one possible source of feedstock for rare earth magnet recycling. First-generation Prius and Chevy volts are beginning to show up now as EOL devices after over a 10-year lifespan. Manufacturing scrap, which includes broken or out-of-spec magnets created during production, is another potential source. Government laws and incentives, market demand for recycled magnets, and alternative materials can all impact feedstock availability for rare earth magnet recycling. Low feedstock for recycling will remain a drawback until most of these applications, like electric vehicles and wind turbines, reach their end of life[22], [23]. Also, 30% of waste magnets or swarfs are generated during magnet production—hard disk drives (HDD), mainly in data centers. A study reported that REEs obtained from U.S. HDD alone could meet up to 5.2% of global NdFeB magnet demand. A forecast of rare earth magnet scrap availability for recycling was based on the lifespan and quantity of rare earth permanent magnets in consumer electronics. This was estimated to be ~36,000 metric tons of NdFeB by 2026. This will continue to increase in the coming years, considering other EOL products that will be retired[24], [25].

4.3.1: Magnet-cutting Companies in the United States

There are minimal or no production capacity for NdFeB magnets in the United States. However, several original equipment manufacturers (OEMs) that use NdFeB magnets can import them directly or indirectly through a supply chain. Also, several companies, including manufacturers, distributors, and wholesalers, import NdFeB magnets into the U.S. However, several companies like Noveon Magnetics and MP Materials are in the developmental stage with full-blown commercialization operations estimated to be in 2 to 3 years from now[6], [7].

A few examples of these companies include:

- BJA Magnetics - BJA Magnetics is a supplier of NdFeB magnets offering custom-designed magnets and magnetic assemblies based in Massachusetts[26]
- Arnold Magnetics Technologies– Arnold Magnetic Technologies is a leading manufacturer of high-performance magnets and magnetic assemblies, including NdFeB magnets. The company has manufacturing facilities in Rochester, New York, and Marietta, Ohio[27]

- CMS Magnetics is a supplier of magnets, including NdFeB magnets, based in Texas[28].
- Adams Magnetic Products is a family-owned business that produces a wide range of magnetic products, including NdFeB magnets, at its facility in Elmhurst, Illinois[29].
- Alliance LLC manufactures magnetic materials and components, including NdFeB magnets, at its facility in Valparaiso, Indiana[30].
- Dura Magnetics manufactures and distributes magnetic products, including NdFeB magnets, based in Ohio[31].
- K&J Magnetics is a supplier of magnets, including NdFeB magnets, based in Pennsylvania[32].
- Viona Magnetics is a distributor of NdFeB magnets based in California[33].
- Bunting Magnetics Co. produces a range of magnetic equipment and components, including NdFeB magnets, at its facilities in Newton, Kansas, and Elk Grove Village, Illinois[34].

4.3.2: Post-Consumer Scrap Magnets

Post-consumer magnets introduce their own collection challenges. With a few exceptions, the collection of post-consumer goods with magnets is not a mature industry, though exceptions include the motor vehicle and white goods markets. It is also possible to collect hard disk drives from data centers, though the quantity and value of magnet material are relatively low: 6-10 g magnets with 2-3grams rare earths are worth just 24-36¢ per hard drive (based on $120/kg for NdPr). It is possible to automate magnet physical separation from hard disks [35],[36].

Most products require physical separation of the magnets from the products, whether from small hard disk motors or larger vehicle traction motors. And some vehicle motors, such as Tesla's, have laminated magnets, including adhesives.

For motor vehicles and white goods (large steel consumer products such as refrigerators, washers/dryers, etc.), there is a mature collection system with the following components and streams:

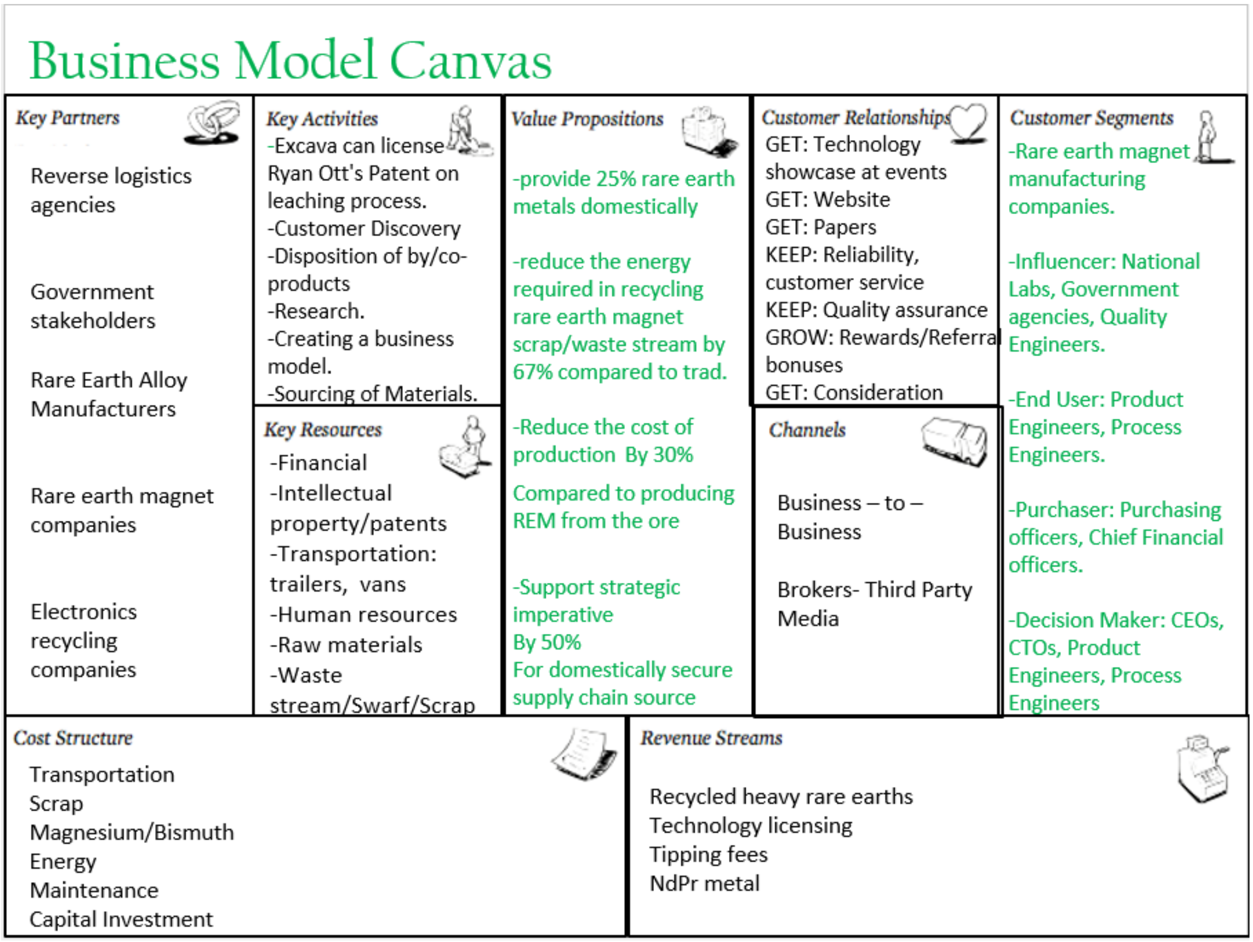
- Dismantlers take end-of-life vehicles and some white goods and remove components which they can sell to body shops, such as headlights, interior trim components, and possibly catalytic converters, as well as those which are dangerous to the downstream processes, such as airbags, tires, gasoline tanks, and batteries. They often flatten the remaining vehicle bodies to facilitate shipping.
- Shredder companies use large hammer mills to tear vehicle bodies into pieces no larger than 10 cm. Magnetic separation creates a high-quality ferrous metals stream, and eddy current separation a non-ferrous metals stream. The remaining Auto Shredder Residue (ASR) is mainly sent to landfills.
- "Meatballs" are in a stream rejected by the hammer mill as too ductile for the physical breakdown; this often includes electric motor components with rare earth magnets.

Rare earth magnets would be dilute and hard to separate from in the ferrous, non-ferrous, or ASR streams but might have concentration worth noting in the "meatballs" stream. The critical question is: Would rare earth's value in traction and other motors provide sufficient incentive to remove them from the vehicle? A typical vehicle traction motor has 0.5-1 kg NdPr, worth about $60-120 at the end of the recycling process, but a much smaller amount before magnet separation. Given the high value of metals such as cobalt, nickel, and lithium in electric vehicle batteries, dismantlers have a solid incentive to remove and sell them; this may also be feasible for rare earth magnets in the traction of other motors in the vehicle. White goods may or may not meet this threshold of sufficient scrap metal value for motor removal.

Since HDDs have security issues associated with them, most are shredded. However, a company in Texas, Reconext, has developed a unique method of wiping the information from the drives and sending it out to magnet suppliers, thus eliminating the shredding step and allowing for just punching out magnets, producing higher content feedstock[37].

4.4: Business Model Canvas (BMC)

As part of the NSF I-Corps program, creating a business model canvas (BMC), as shown in Figure 4.2, was necessary to lay down the content of doing business, especially in describing the value propositions and customer segment [38].



Business Model Canvas

Key Partners

Reverse logistics agencies

Government stakeholders

Rare Earth Alloy Manufacturers

Rare earth magnet companies

Electronics recycling companies

Key Activities

-Excava can license Ryan Ott's Patent on leaching process.
-Customer Discovery
-Disposition of by/co-products
-Research.
-Creating a business model.
-Sourcing of Materials.

Key Resources

-Financial
-Intellectual property/patents
-Transportation: trailers, vans
-Human resources
-Raw materials
-Waste stream/Swarf/Scrap

Value Propositions

-provide 25% rare earth metals domestically

-reduce the energy required in recycling rare earth magnet scrap/waste stream by 67% compared to trad.

-Reduce the cost of production By 30%
Compared to producing REM from the ore

-Support strategic imperative
By 50%
For domestically secure supply chain source

Customer Relationships

GET: Technology showcase at events
GET: Website
GET: Papers
KEEP: Reliability, customer service
KEEP: Quality assurance
GROW: Rewards/Referral bonuses
GET: Consideration

Channels

Business – to – Business

Brokers- Third Party Media

Customer Segments

-Rare earth magnet manufacturing companies.

-Influencer: National Labs, Government agencies, Quality Engineers.

-End User: Product Engineers, Process Engineers.

-Purchaser: Purchasing officers, Chief Financial officers.

-Decision Maker: CEOs, CTOs, Product Engineers, Process Engineers

Cost Structure

Transportation
Scrap
Magnesium/Bismuth
Energy
Maintenance
Capital Investment

Revenue Streams

Recycled heavy rare earths
Technology licensing
Tipping fees
NdPr metal

Figure 4.2: Business Model Canvas

The workflow for the recycling company, as shown in Figure 4.3, will initiate from feedstock supplied by the primary production of rare earth magnets. The company will interface with key partners like reverse logistics agencies, influencers, and the customer segment. The reverse logistics agencies are paramount for the supply of scrap materials for recycling from EOL devices like electronic devices, EVs, and other applications. Some players in this field include electronic recycling companies and automotive scrap recyclers who can supply scrap magnets for recycling. Influencers will comprise several government agencies responsible for regulating electronic waste management and promoting sustainable materials management practices. They may also be interested in partnering with rare earth metal recycling companies to support their sustainability goals and compliance requirements. Such agencies include the Department of Defense, the Department of Energy, and various National Laboratories.

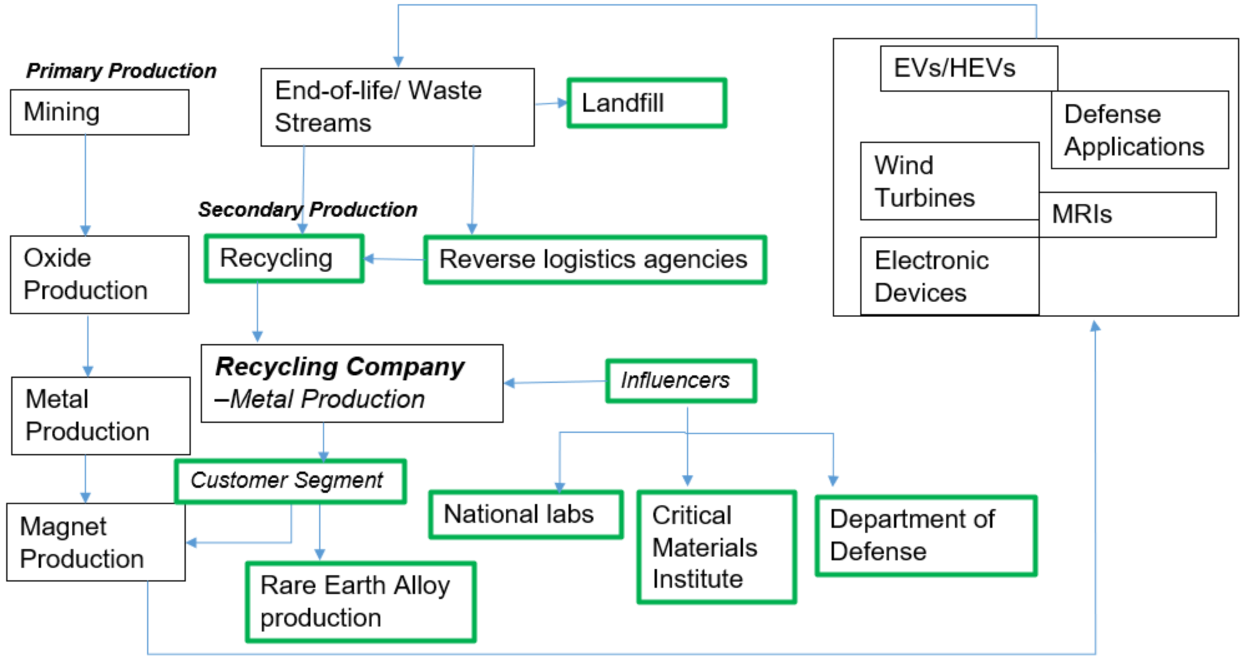


Figure 4.3: Workflow of a Typical REM Recycling Company

4.4.1: Value Propositions

Establishing a REM recycling company, especially in the United States, with the novel low-cost distillation technology can offer a variety of benefits to customers, such as

I. *Reduced cost of materials:* recycling rare earth magnets can be a cost-effective alternative to purchasing new magnets. According to a techno-economic analysis carried out on the low-cost distillation technology, the energy reduction, which is ~70% compared to conventional distillation and ~30% compared to primary production, can lead to a reduction in operating cost and successively lower the cost of recycled rare earth metal[39], [40].

II. *Reduced dependence on foreign sources*: Recycled rare earth magnets can help customers reduce their reliance on these critical materials' foreign sources. This can increase supply chain security, lower the likelihood of supply interruptions and reduce shipping lead time[41]–[44].

III. *Environmental sustainability*: Several companies have launched their campaigns and demonstrated a commitment to sustainability by pledging to use recycled rare earth magnets in their devices. For example, in 2020, Apple established a mandate to become carbon neutral by 2030 and, as part of this goal, pledged to use 100% recycled rare earth metals in its devices[45], [46]. Dell has announced its commitment to manufacturing more than half of its products using recycled or renewable materials by 2030. It will use 100 million pounds of recycled materials in its devices, including recycled rare earth metals[47], [48]. BMW has mentioned its efforts to partner with recyclers to increase the number of recycled materials in its products[49].

Thus, customers prioritizing environmental responsibilities can demonstrate their commitment to using recycled rare earth magnets.

4.4.2: Customer Segments

Rare earth magnet-producing companies like Hitachi Metals, Shin-Etsu, Vacuumschmelze, and Noveon Magnetics will be a significant customer segment for recycled rare earth metals. Although Noveon is the only rare earth magnet-producing company in the United States, this is expected to improve as MP Magnetics begins operation and other companies spring up with new processing technologies coming to the limelight. Also, companies that recycle rare earth magnet scrap using the magnet-magnet process will still require the addition of rare earth metal to avoid downgrading the magnetic properties.

Metal alloy companies are also target markets as they use rare earth metals to manufacture alloys, e.g., magnesium-rare earth (Mg-RE) alloys. Several studies have evaluated substituting traditional Mg-based alloys with Mg-RE. These studies have shown that Mg-RE alloys have considerably enhanced characteristics such as improved hardenability, strength, thermal properties, corrosion resistance, and biocompatibility[50]–[56].

4.4.3 Revenue Streams and Channels

Revenue can be obtained through sales of recycled rare earth metals to customers, as shown in Figure 4.3, representing 80% - 90% of the total revenues. This can be by selling rare earth metals to magnet companies or magnesium-rare earth alloys to metal alloy companies. A techno-economic analysis of the novel low-cost distillation technology[39],[40] has shown that recycled rare earth metal can cost 30% less than the current price for the rare earth metal sold today at $120/kg[57]. Also, tipping fees are an essential revenue source for waste disposal facilities. They can help cover the costs of operating and maintaining the facility and comply with environmental regulations[58]. In this case, the recycling company can directly liaise with the company disposing of such wastes like discarded magnets and RE-containing EOL devices. Technology licensing could be another stream of income whereby the recycling company can profit from allowing other companies to use their patented technology. However, this will require a certain level of financial and operational maturity.

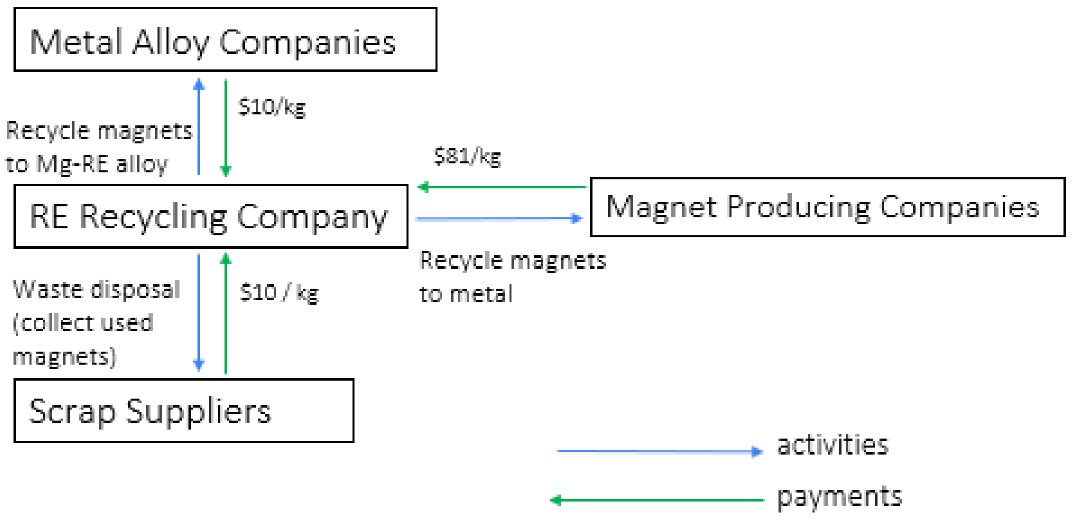


Figure 4.4: Revenue Streams

Recycled products can be sold through various outlets, such as brokers or distributors, and directly to customers through the business-to-business channel. This is illustrated in Figure 4.4, where examples of these channels are listed.

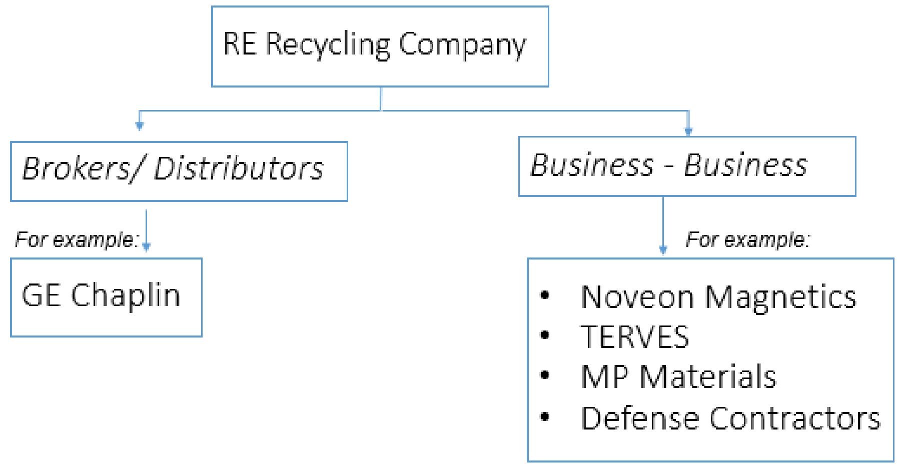


Figure 4.5: Distribution Channels

4.5: Conclusion

This study has shown that the commercial viability of rare earth magnet scrap recycling depends on a consistent supply of high-quality scrap material, the demand for rare earth magnets, and the cost of virgin rare earth metals from primary production. Recycling feedstock can originate from different sources. These sources include swarfs, discarded magnets from companies that cut magnets, and post-consumer magnets such as "meatball" streams from recycling motor vehicles and white goods. Additionally, hard disk drives (HDDs) no longer used in data centers can be recycled. Recycling rare earth magnet scrap may be more cost-effective in some scenarios than mining, mainly if rare earth metals are expensive. Also, several challenges to overcome would include raising awareness on the collection of rare earth magnet scrap just like is being done for plastics, setting recycling-friendly legislations, and incentivizing the recycling of rare earths which could be done by paying a premium to offset the cost. The Department of Defense can particularly do this as they started setting requirements for domestically sourced REEs. Establishing partnerships with certain agencies like national laboratories and reverse logistics for scrap collection will also be important. The availability of a stable feedstock supply is expected to improve in the coming years as the automotive industry transitions to clean energy technologies, increasing the demand for rare earth magnets. Rare earth magnet scrap recycling is becoming increasingly economical and appealing for companies trying to decrease their environmental impact and enhance their sustainability due to increased demand for sustainable materials and the development of more effective recycling processes. Recycling rare earth magnet scrap can mitigate the supply risk issues and criticality of various metals to commercial applications and national security.

REFERENCES

[1] PRNewswire, “Global Rare Earth Magnet Market Report 2022: Anticipated Increase in the Demand for Power Generators to Boost Sector Growth,” *PRNewswire*, Oct. 18, 2022. https://www.yahoo.com/now/global-rare-earth-magnet-market-133000849.html (accessed Apr. 11, 2023).

[2] S. H. Ali, “Social and Environmental Impact of the Rare Earth Industries,” *Resources*, vol. 3, no. 1, Art. no. 1, Mar. 2014, doi: 10.3390/resources3010123.

[3] “NSF’s Innovation Corps (I-Corps^{TM}),” *Beta site for NSF - National Science Foundation*. https://beta.nsf.gov/funding/initiatives/i-corps (accessed Jul. 13, 2022).

[4] S. Blank and B. Dorf, *The Startup Owner’s Manual: The Step-By-Step Guide for Building a Great Company*. John Wiley & Sons, 2020.

[5] D. Kinch, “Recycling could account for 25% of rare earths market in 10 years: Mkango CEO,” Nov. 03, 2021. https://www.spglobal.com/commodityinsights/en/market-insights/latest-news/metals/110321-recycling-could-account-for-25-of-rare-earths-market-in-10-years-mkango-ceo (accessed Feb. 09, 2023).

[6] F. Kozak, “Rare earths player MP Materials returns, riding on the back of a SPAC,” *InvestorIntel*, Nov. 20, 2020. https://investorintel.com/critical-minerals-rare-earths/rare-earths-player-mp-materials-returns-riding-on-the-back-of-a-spac/ (accessed Feb. 09, 2023).

[7] F. Kozak, “The Top 5 Rare Earths Companies for 2021,” *InvestorIntel*, Jan. 09, 2021. https://investorintel.com/critical-minerals-rare-earths/kozaks-top-5-rare-earths-companies-for-2021/ (accessed Feb. 09, 2023).

[8] “Noveon Magnetics,” *Noveon Magnetics*. https://noveon.co (accessed Feb. 09, 2023).

[9] D. Oberhaus, “Rare Earths for America’s Future,” Progressive Policy Institute, Washington, D.C., Jan. 2023.

[10] “Why We Do It,” *Noveon Magnetics*. https://noveon.co/why-we-do-it (accessed Feb. 09,

2023).

[11] “Charged EVs | TdVib works to commercialize acid-free process for recovering rare earths from electronic waste - Charged EVs.” https://chargedevs.com/newswire/tdvib-works-to-commercialize-acid-free-process-for-recovering-rare-earths-from-electronic-waste/ (accessed Feb. 09, 2023).

[12] “ARPA-E Project | Novel Technique for Domestic Rare Earth Oxide Separation and Rare Earth Metal Reduction,” *arpa-e.energy.gov*. http://arpa-e.energy.gov/technologies/projects/novel-technique-domestic-rare-earth-oxide-separation-and-rare-earth-metal (accessed Feb. 09, 2023).

[13] “Home -.” https://phoenixtailings.com/ (accessed Feb. 09, 2023).

[14] “Scrap Metal Prices | Greenblott Metal Co. | Binghamton, NY,” *Greenblott Metal*. https://www.greenblottmetal.com/scrap-metal-prices (accessed Apr. 06, 2023).

[15] “European Climate Law.” https://climate.ec.europa.eu/eu-action/european-green-deal/european-climate-law_en (accessed Mar. 16, 2023).

[16] S. of California, “Ban on Single-Use Carryout Bags (SB 270 / Proposition 67) Frequently Asked Questions (revised April 2017),” *CalRecycle Home Page*. https://calrecycle.ca.gov/plastics/carryoutbags/faq/ (accessed Mar. 16, 2023).

[17] “Ban on Plastic Bags and Polystyrene Foam Food Service Products.” https://business.nj.gov/bags/plastic-ban-law?locale=en (accessed Mar. 16, 2023).

[18] R. G. Cooper, “The Stage-Gate® Product Innovation System: from Idea to Launch,” in Wiley Encyclopedia of Management, John Wiley & Sons, Ltd, 2015, pp. 1–13. doi: 10.1002/9781118785317.weom130024.

[19] R. and M. ltd, “Global Rare Earth Metals Market Outlook to 2027 - Research) and Markets.” https://www.researchandmarkets.com/reports/5553324/global-rare-earth-metals-market-outlook-to-2027 (accessed Feb. 17, 2023).

[20] T. W. House, “FACT SHEET: Securing a Made in America Supply Chain for Critical Minerals,” *The White House*, Feb. 22, 2022. https://www.whitehouse.gov/briefing-room/statements-releases/2022/02/22/fact-sheet-securing-a-made-in-america-supply-chain-for-critical-minerals/ (accessed Feb. 17, 2023).

[21] “Scientific Investigations Report 2011–5094.” https://pubs.usgs.gov/sir/2011/5094/ (accessed Feb. 22, 2023).

[22] R. T. Nguyen, L. A. Diaz, D. D. Imholte, and T. E. Lister, “Economic Assessment for Recycling Critical Metals From Hard Disk Drives Using a Comprehensive Recovery Process,” *JOM*, vol. 69, no. 9, pp. 1546–1552, Sep. 2017, doi: 10.1007/s11837-017-2399-2.

[23] N. Haque, A. Hughes, S. Lim, and C. Vernon, “Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact,” *Resources*, vol. 3, no. 4, pp. 614–635, Oct. 2014, doi: 10.3390/resources3040614.

[24] “Hard disk drive (HDD) unit shipments 2010-2021,” *Statista*. https://www.statista.com/statistics/275336/global-shipment-figures-for-hard-disk-drives-from-4th-quarter-2010/ (accessed Feb. 22, 2023).

[25] I. C. Nlebedim and A. H. King, “Addressing Criticality in Rare Earth Elements via Permanent Magnets Recycling,” *JOM*, vol. 70, no. 2, pp. 115–123, Feb. 2018, doi: 10.1007/s11837-017-2698-7.

[26] “Home,” *BJA Magnetics*. http://www.bjamagnetics.com/ (accessed Feb. 22, 2023).

[27] “Permanent Magnet Division,” *Arnold Magnetic Technologies*. https://www.arnoldmagnetics.com/permanent-magnets/ (accessed Aug. 16, 2020).

[28] “CMS Magnetics, Inc.” https://www.cmsmagnetics.com/ (accessed Feb. 22, 2023).

[29] “Home,” *Adams Magnetic Products Co.* https://www.adamsmagnetic.com/ (accessed Feb. 22, 2023).

[30] “Alliance LLC Permanent Magnets & Magnetic Assemblies.” https://allianceorg.com/ (accessed Feb. 22, 2023).

[31] “About Dura Magnetics, Inc. | Dura Magnetics,” Jun. 13, 2013. https://www.duramag.com/about-us/ (accessed Feb. 22, 2023).

[32] “K&J Magnetics - Strong Neodymium Magnets, Rare Earth Magnets.” https://www.kjmagnetics.com/ (accessed Feb. 22, 2023).

[33] “Neodymium Magnets, Samarium Cobalt, Flexible & Ceramic Magnets,” *Viona Magnetics*. https://www.vionamag.com/ (accessed Feb. 22, 2023).

[34] “Custom Magnet Applications and Magnets,” *Bunting-DuBois*. https://bunting-dubois.com/ (accessed Feb. 22, 2023).

[35] T. McIntyre, J. Harter, and T. Roberts, “Development and Operation of a High Throughput Computer Hard Disk Drive Recycling Enterprise (CRADA NFE-16-05989),” ORNL/TM--2019/1374, 1606869, CRADA/NFE-16-05989, Nov. 2019. doi: 10.2172/1606869.

[36] T. E. Lister *et al.*, “Recovery of Rare Earth Elements from Recycled Hard Disk Drive Mixed Steel and Magnet Scrap,” in *Rare Metal Technology 2021*, G. Azimi, T. Ouchi, K. Forsberg, H. Kim, S. Alam, A. A. Baba, and N. R. Neelameggham, Eds., in The Minerals, Metals & Materials Series. Cham: Springer International Publishing, 2021, pp. 139–154. doi: 10.1007/978-3-030-65489-4_15.

[37] “Circularity Powered by Ingenuity,” *Reconext*. https://www.reconext.com/ (accessed Apr. 13, 2023).

[38] A. Osterwalder and Y. Pigneur, “Business Model Generation: A handbook for visionaries, game changers and challengers,” *Afr. J. Bus. Manag.*, vol. 5, no. 7, Apr. 2011.

[39] C. Chinwego, H. Wagner, E. Giancola, J. Jironvil, and A. Powell, “Technoeconomic Analysis of Rare-Earth Metal Recycling Using Efficient Metal Distillation,” *JOM*, vol. 74, no. 4, pp. 1296–1305, Apr. 2022, doi: 10.1007/s11837-021-05045-7.

[40] C. Chinwego, H. Wagner, E. Giancola, J. Jironvil, and A. Powell, “Low-Cost Distillation Technology for Rare-Earth Recycling,” in *Rare Metal Technology 2022*, T. Ouchi, G. Azimi, K. Forsberg, H. Kim, S. Alam, N. R. Neelameggham, A. A. Baba, and H. Peng, Eds. Cham: Springer International Publishing, 2022, pp. 41–50. doi: 10.1007/978-3-030-92662-5_4.

[41] X. Du and T. E. Graedel, “Uncovering the Global Life Cycles of the Rare Earth Elements,” *Sci. Rep.*, vol. 1, Nov. 2011, doi: 10.1038/srep00145.

[42] M. L. Keilhacker and S. Minner, “Supply chain risk management for critical commodities: A system dynamics model for the case of the rare earth elements,” *Resour. Conserv. Recycl.*, vol. 125, pp. 349–362, Oct. 2017, doi: 10.1016/j.resconrec.2017.05.004.

[43] K. Baba, Y. Hiroshige, and T. Nemoto, “Rare-earth Magnet Recycling,” *Hitachi Rev.*, vol. 62, no. 8, pp. 452–455, 2013.

[44] J. H. Rademaker, R. Kleijn, and Y. Yang, “Recycling as a Strategy against Rare Earth Element Criticality: A Systemic Evaluation of the Potential Yield of NdFeB Magnet Recycling,” *Environ. Sci. Technol.*, vol. 47, no. 18, pp. 10129–10136, Sep. 2013, doi: 10.1021/es305007w.

[45] C. Staub, “Apple rolls out robot for iPhone dismantling,” *E-Scrap News*, Apr. 26, 2018. https://resource-recycling.com/e-scrap/2018/04/26/apple-rolls-out-robot-for-iphone-dismantling/ (accessed Feb. 25, 2023).

[46] “Apple expands global recycling programmes,” *Apple Newsroom (United Kingdom)*. https://www.apple.com/uk/newsroom/2019/04/apple-expands-global-recycling-programs/ (accessed Feb. 25, 2023).

[47] “Accelerating the Circular Economy | Dell USA.” https://www.dell.com/en-us/dt/corporate/social-impact/advancing-sustainability/accelerating-the-circular-economy.htm (accessed Feb. 25, 2023).

[48] “What Goes Around, Comes Full Circle,” *Dell*, May 11, 2021. https://www.dell.com/en-us/blog/what-goes-around-comes-full-circle/ (accessed Feb. 25, 2023).

[49] BMW, “Sustainability Report,” BMW Brilliance Automotive Ltd., 2020.

[50] U. Riaz, I. Shabib, and W. Haider, “The current trends of Mg alloys in biomedical applications—A review,” *J. Biomed. Mater. Res. B Appl. Biomater.*, vol. 107, no. 6, pp. 1970–1996, 2019, doi: 10.1002/jbm.b.34290.

[51] V. Gärtnerová, Z. Trojanová, A. Jäger, and P. Palček, “Deformation behaviour of Mg–0.7

wt.% Nd alloy," *J. Alloys Compd.*, vol. 378, no. 1, pp. 180–183, Sep. 2004, doi: 10.1016/j.jallcom.2003.11.172.

[52] X. Zhang, G. Yuan, L. Mao, J. Niu, and W. Ding, "Biocorrosion properties of as-extruded Mg–Nd–Zn–Zr alloy compared with commercial AZ31 and WE43 alloys," *Mater. Lett.*, vol. 66, no. 1, pp. 209–211, Jan. 2012, doi: 10.1016/j.matlet.2011.08.079.

[53] B. Lv, J. Peng, Y. Peng, and A. Tang, "The effect of addition of Nd and Ce on the microstructure and mechanical properties of ZM21 Mg alloy," *J. Magnes. Alloys*, vol. 1, no. 1, pp. 94–100, Mar. 2013, doi: 10.1016/j.jma.2013.02.011.

[54] E. Aghion, Y. Gueta, N. Moscovitch, and B. Bronfin, "Effect of yttrium additions on the properties of grain-refined Mg–3%Nd alloy," *J. Mater. Sci.*, vol. 43, no. 14, pp. 4870–4875, Jul. 2008, doi: 10.1007/s10853-008-2708-9.

[55] M. Sun, X. Hu, L. Peng, P. Fu, W. Ding, and Y. Peng, "On the production of Mg-Nd master alloy from NdFeB magnet scraps," *J. Mater. Process. Technol.*, vol. 218, pp. 57–61, Apr. 2015, doi: 10.1016/j.jmatprotec.2014.11.036.

[56] P. H. Fu, L. M. Peng, H. Y. Jiang, C. Q. Zhai, X. Gao, and J. F. Nie, "Zr-Containing Precipitates in Mg-3wt%Nd-0.2wt%Zn-0.4wt%Zr Alloy during Solution Treatment at 540°C," *Mater. Sci. Forum*, vol. 546–549, pp. 97–100, 2007, doi: 10.4028/www.scientific.net/MSF.546-549.97.

[57] "Pr-Nd Alloy today | Rare Earth | SMM - China Metal Market." https://www.metal.com/Rare-Earth-Metals/201102250182 (accessed Feb. 27, 2023).

[58] A. Amato *et al.*, "Sustainability analysis of innovative technologies for the rare earth elements recovery," *Renew. Sustain. Energy Rev.*, vol. 106, pp. 41–53, May 2019, doi: 10.1016/j.rser.2019.02.029.

Chapter 5

Liquid Metal Leaching and G-METS Distillation of Rare Earth Magnets: Experimental Investigation and Reduced-Order Model

5.1: Introduction

Rare earth magnet recycling is gaining traction due to the criticality of these metals and the supply risk they pose, as their mining and processing are limited to a few countries. Several research studies have explored recycling methods for rare earth magnet scraps, including solvent extraction[1]–[11], hydrogen decrepitation[12]–[26], and bioleaching[27]–[33]. Solvent extraction involves the selective separation and recovery of rare earth metals from scrap magnets using suitable solvents. The rare earth is recovered in its oxide form and would require further reduction to obtain rare earth metal that can be used for magnet production. Hydrogen decrepitation is a magnet-to-magnet approach that still requires the addition of pure rare earth metals to avoid downgrading the final product. Liquid metal leaching and distillation is a potential method to obtain pure rare earth metal that can serve as a precursor for magnet production[34]–[38]. This liquid metal extraction process uses molten magnesium or other group IIA metals such as Ca or Ba for rare-earth magnet recycling [37],[39]. These extracting agents were identified based on the reaction mechanism, behavior of the RE elements, extraction efficiencies, and formation of intermetallic compounds during the leaching process.

Among several metals, including magnesium (Mg), silver (Ag), copper (Cu), and bismuth (Bi), to be used as extracting agents, Mg stood out for several reasons- its strong affinity for Nd, it hardly reacts with iron, it has a relatively low melting point of 649^0C. It shows high vapor pressure of over 800^0C; thus, it can be easily distilled and transported throughout the gas phase[39].

Previous studies have shown that the liquid metal extraction technology best extracts rare-earth elements (Nd, Dy) from scrap magnets at a temperature of 1000^0C and an Mg/magnet ratio of 10. Nd and Dy extraction yields of 100% and 60%, respectively. Furthermore, adding calcium suppressed the oxidation of Dy, thus increasing the extraction efficiency[37],[38]. Using bismuth (Bi) instead of Mg can increase the Dy recovery above 90%, and using both Mg and Bi enables some separation of light and heavy rare earth [34]. After leaching, the molten Mg-RE alloy is distilled to recover the rare earth metal. Conventional vacuum distillation (CVD) and vapor compression distillation (VCD) are state-of-the-art distillation processes. CVD is a slow batch process that produces solid metal in the condenser. The Mg must be completely cooled before opening the vacuum vessel because of the pyrophoric nature of the high surface-area condensed Mg crown product. This results in a long cycle time (6-12h) and a low process throughput thus, the potential of scaling up this process flow to a commercially viable venture is far-fetched. VCD uses mechanical compressors or pumps to generate the compression that increases the pressure of magnesium vapor between an evaporator/condenser heat exchanger. The higher pressure of the condenser side allows the magnesium vapor to condense, transferring the heat of condensation to the evaporator side, thus providing the energy to evaporate the magnesium vapor.

This study focussed on assessing the potential of integrating a novel low-cost distillation technology into the liquid metal leaching and distillation recycling process. The low-cost distillation technology is called gravity-driven multiple effects thermal system (G-METS) distillation, discussed in detail in section 5.2. One advantage of the G-METS over the VCD process is the absence of added inert gasses. Modeling reveals that non-magnesium vapors significantly degrade condensing efficacy, and improvement in Batch METS performance with effective removal of contaminant gasses seems to agree with these modeling results. Running under a vacuum should significantly improve condenser performance[40].

The suitability of magnesium as a leaching agent was assessed, and the effect of the rare earth magnet scrap particle size and coatings were analyzed. Distillation experiments were carried out. The reduced order model was developed using a three-effect scenario to obtain the temperature and production rates for magnesium-neodymium alloy distillation in the G-METS.

5.2 Gravity-Driven Multiple Effects Thermal System (G-METS) Distillation

Multiple-effect distillations is a highly efficient method that reuses condensation energy for evaporation, i.e., the heat released during condensation provides much of the heat required for evaporation. This is obtained by running the condenser at a higher pressure than the evaporator, resulting in a higher boiling point and heat flowing from the higher-temperature condenser to the lower-temperature evaporator. This pressure difference is created by gravity as the liquid alloy to be distilled flows at a controlled rate down into the distiller effects of evaporators and condensers. This occurs when the distillation system operates at low pressure (i.e., under vacuum). As illustrated in Figures 5.1 and 5.2, the metal alloy, e.g., magnesium-rare earth alloy, flows into the top evaporator, where a portion of the magnesium evaporates. The evaporated portion rises to the top condenser. It condenses, while the remaining Mg-RE that does not evaporate here flows down through the liquid standpipe into the next evaporator, where a portion of it evaporates, and so on. Each evaporator–condenser pair is called an "effect." Heat flows upward from effect to effect, from lower condensers to the evaporators above them. Liquid Mg flows downward between evaporators from effect to effect. Mg vapor flows upward within each effect from its evaporator into its condenser above it. Standpipes control the height of liquid Mg alloy in each evaporator. A vent enables some vapor to exit the condenser and enter a second condensing chamber. Because the outgoing vapor is high in volatile metals like zinc, the magnesium in the condenser is purer than without the vent and counter-flow condition. This resembles an ammonia-water separation system[41], [42].

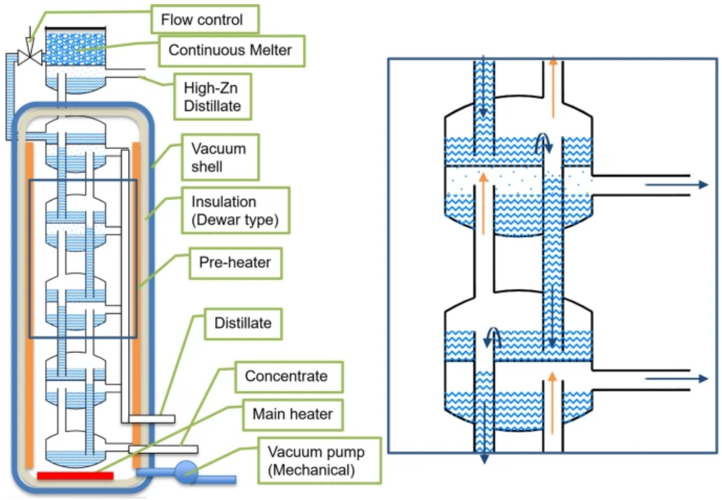


Figure 5.1: Schematic diagram of a four-effect magnesium G-METS distiller, with a detailed view of a single effect.

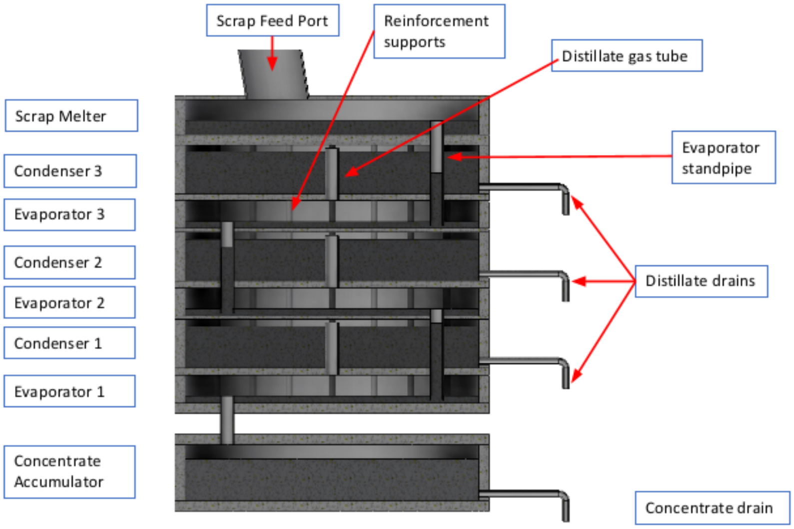


Figure 5.2: Cross-section of a three-effect G-METS Distiller

The distillation process currently in use domestically (MagPro) is a sublimation process [43]. Magnesium scrap is heated at low pressure. The magnesium vapor condenses as a "frozen crown" on a cooled cover plate. Once the system is cooled, the crown is manually scraped off the cover. The crown is then remelted and cast into magnesium bars that may be used for alloying. This study's proposed novel magnesium-rare earth alloy distillation process has two significant advantages over conventional distillation:

Energy and Operating Cost Reduction – the G-METS distiller will use 20% or less of the energy consumed by conventional distillation. Furthermore, the G-METS is a continuous distillation unit, i.e., there is no labor associated with harvesting the frozen crown or the additional energy required to remelt and cast the magnesium into bars. And unlike conventional batch distillers, it does not require hours of cooling between batches, increasing capital utilization and decreasing capital and operating cost.

Liquid product – the liquid magnesium-rare earth alloy produced by the G-METS allows for the direct production of alloys, eliminating the energy and labor of re-melting the magnesium bars.

The major drawback of the G-METS over the VCD is that operating under a vacuum complicates material input and removal from the distiller. A load lock or valving will be required, but eliminating the compressor will compensate for this added complication.

Introducing a novel gravity-driven multiple effect thermal system (G-METS) distillation techniques into a liquid metal leaching and distillation recycling process can potentially reduce the energy use from 5 to 7 kWh/kg today to as little as 0.5–1 kWh/kg, a nearly 90% reduction[40].

5.3: Experimental Investigation of Magnesium as a Leaching Agent

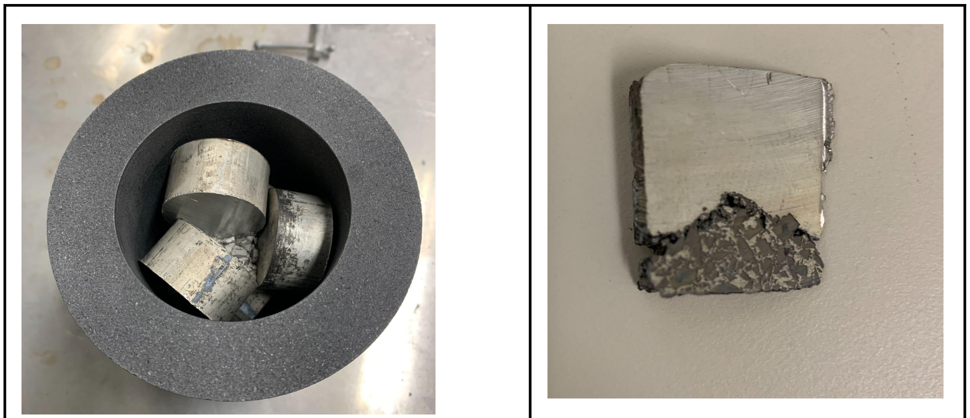
5.3.1: Introduction

Molten metal leaching, also referred to as liquid metal extraction (LME) is a promising technique for recovering Nd from NdFeB magnet scraps. Several studies have investigated and shown a rapid diffusion behavior of Nd from NdFeB into Mg melt[44]–[47]. In this study, experimental analyses were carried out in order to demonstrate the leaching behavior of Mg for NdFeB magnets and understand the effect of particle size and coatings on the leaching efficiency.

5.3.2: Methodology

The leaching was carried out in a Mellen furnace at 900^0C for 2 hours, using a graphite crucible. Magnesium rods purchased from Strem were cut into smaller pieces. The rare earth magnets obtained were demagnetized at 350^0C, and the coatings were removed for the first experiment and left on for the second. The particle size analysis was carried out on the uncoated magnets. The uncoated magnets were crushed to particle sizes ranging from 250 microns to 1 mm; thus, these were differentiated in terms of small, medium, and large particle sizes. The magnesium-to-magnet ratio variation used throughout the experiment was 3:1. The magnesium and magnet particles were placed in the graphite crucible, as shown in Fig 5.3a. The experiment was run under an argon-rich environment, and an oxygen sensor was used to monitor the leaching environment and ensure no oxygen was in the furnace chamber.

After a 2-hour hold time, the furnace was shut down, and the samples were left to cool down. Cross-sections of the samples were cut, as shown in Figure 5.3b, and characterized using SEM/EDX. Particles of the leached samples were also taken at different parts for ICP-OES analysis. The Nd to Mg ratios for the top section, midsection, interface, and bottom section of the leached sample were determined by ICP-OES, as shown in Table 1. The praseodymium and other traces of heavy rare earth metals were also analyzed using ICP-MS, as shown in Table 2. In the bottom section, the large, medium, and small particle sizes were also characterized.



(a) Before leaching

(b) After leaching

Figure 5.3: Magnesium and magnet samples before and after leaching [48]

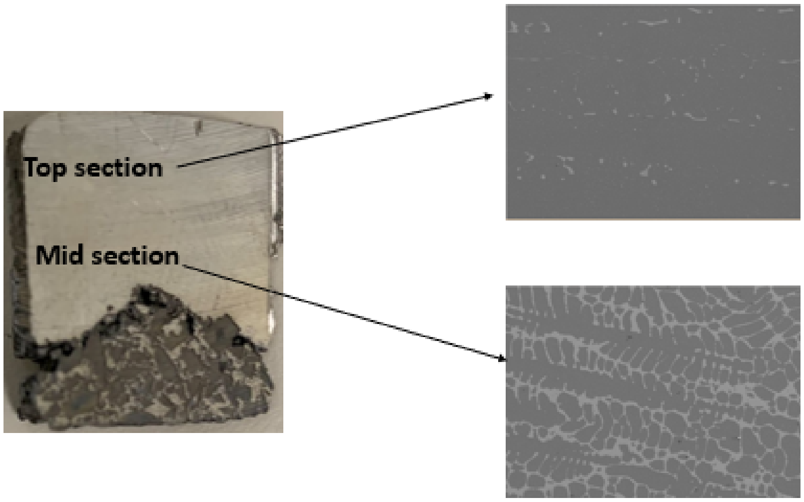
5.3.3: Results and Discussion

Table 5.1 shows the Nd to Mg ratio. It is highest at the bottom of the sample for the small particle size than the medium and large particle sizes. It is lowest at the sample's top, indicating that the Nd's leaching occurred. At the interface, where there is a clear distinction between the magnet particles and the solid magnesium, we can see a relatively higher Nd/Mg ratio than the mid and top sections. This experimental analysis was carried out to understand the effects of particle sizes on the leaching efficiency. It can be deduced that a reduction in the particle size of the magnet by crushing or otherwise can increase the leaching efficiency.

Table 5.1: Neodymium to Magnesium ratio of sample section based on ICP-OES Analysis

	Top	Mid	Interface	Bottom (small particle size)	Bottom (medium particle size)	Bottom (large particle size)
Nd/Mg ratio	0.004	0.014	0.133	0.311	0.267	0.234

The SEM images of the top and mid sections of the leached sample are presented in Figure 5.4, which show very high Nd concentration in regions with strong electron x-ray signals, indicating that Nd concentrates in intermetallic precipitates in the alloy forming Mg-Nd alloy. It was observed that there was a gradient in the Mg-Nd concentration with an increment from the mid to top section because the magnesium liquid closer to the magnets will contain most of the Nd initially. This is expected to extend to the top section with increased time and agitation.



SEM image after leaching – Top section taken at 500micron and 15kV

SEM image after leaching - Midsection taken at 500micron and 15kV

Figure 5.4: SEM images of the leached sample showing the formation of Mg-Nd precipitates in the Mid and Top sections

In an attempt to identify trace rare earth elements, ICP mass spectroscopy was carried out. It was observed that some of the praseodymium was leached into the magnesium, as shown in Table 5.2, but no observable amounts of Dy or Tb entered the Mg alloy. This observation was supported by the EDS analysis of the top section sample, as shown in Figure 5.5.

Table 5.2: Elemental analysis of other rare earth elements present using ICP-MS

	Pr (%)	Dy(%)	Tb(%)
Top	0.14	0	0
Mid	0.47	0	0
Interface	2.91	0.02	0.02
Bottom(small particle size)	1.08	0.01	0
Bottom(medium particle size)	1.69	0.02	0.01
Bottom(large particle size)	1.63	0.02	0.01

The EDS images in Figure 5.5 and Table 5.3 show the percent weight concentration of the precipitates and base metal. The light grey precipitates contain 31.6 wt.% NdPr and 65.8wt% Mg. The dark grey area is the base metal, Mg, with a concentration of 99wt.%. The large area spectrum indicates average Nd content of about 2.3 wt%, which is not far from the 3.5 wt% Nd concentration indicated by ICP-OES characterization.

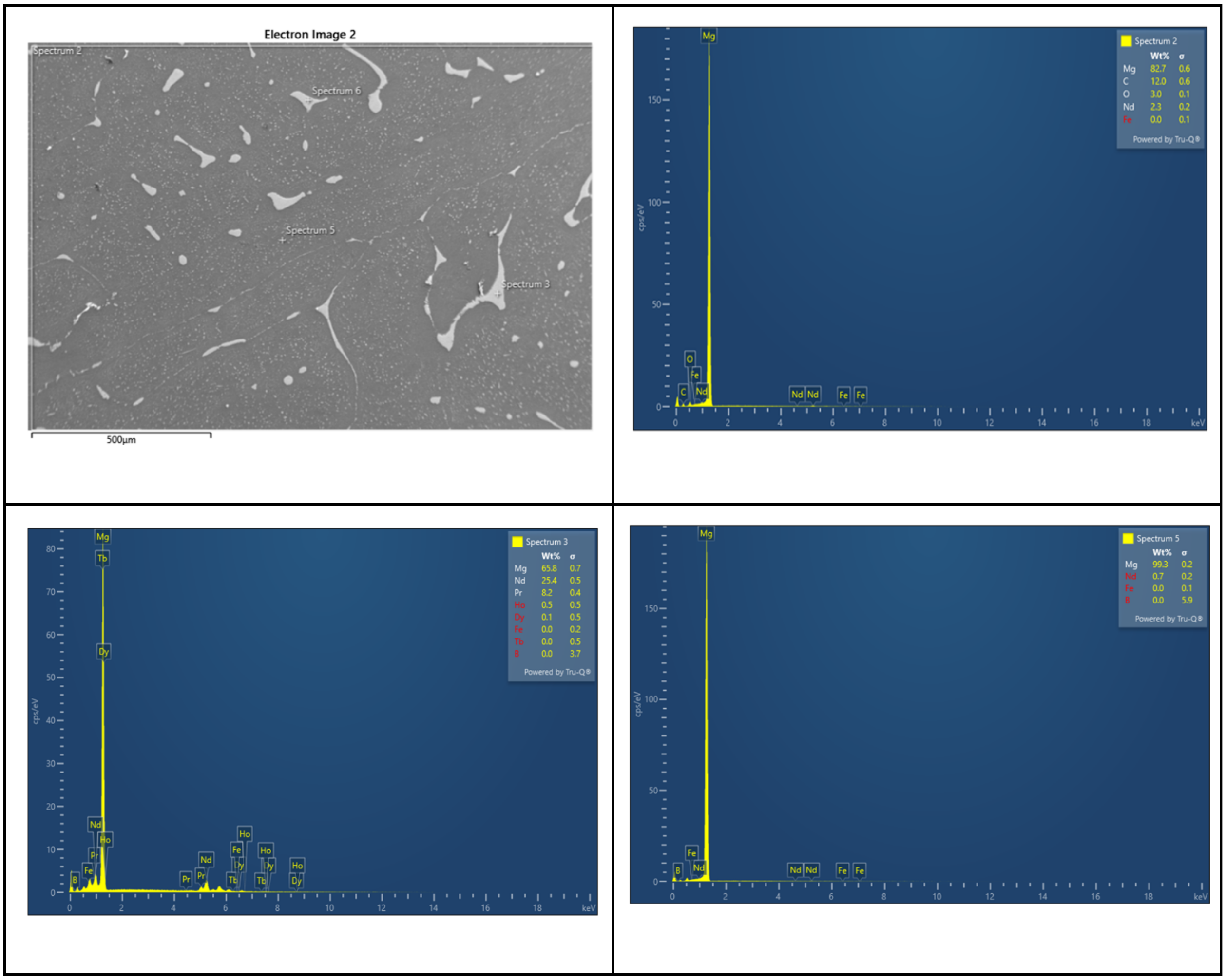
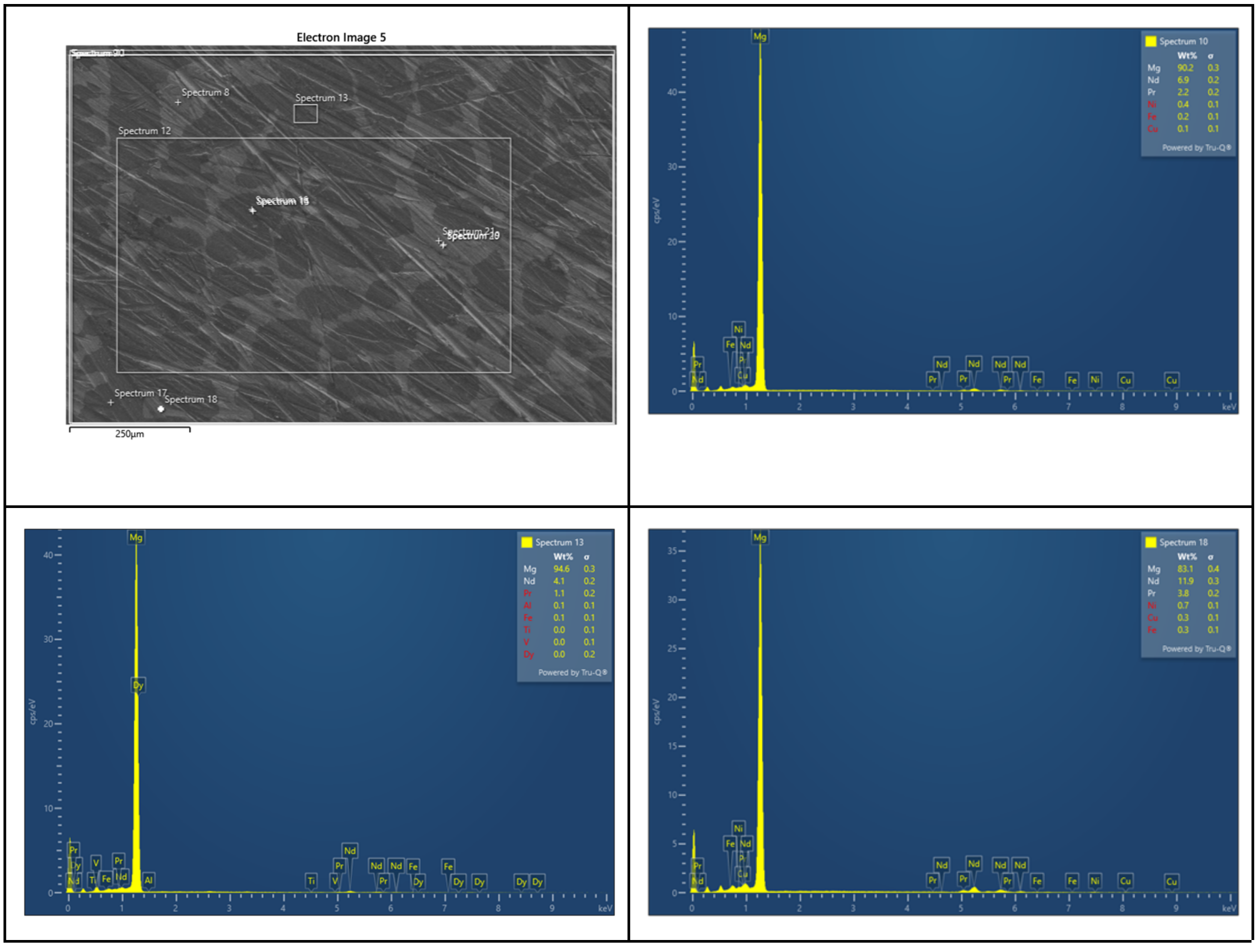


Figure 5.5: EDS analysis of Mg alloy top sample after leaching: (top left) backscatter image showing locations of EDS analysis (Spectrum 2 in the top right covers the whole field of view); (bottom left and right) EDS spectra 3, and 5 showing 25%, and 0.7% Nd respectively [48]

Table 5.3: Concentration of Elements shown in Figure 5.5

Spectrum/Element	Mg (%wt.)	Nd (%wt.)	Pr (%wt.)
Spectrum 2	82.7	2.3	-
Spectrum 3	65.8	25.4	8.9
Spectrum 6	99.3	0.7	-

Figure 5.6 shows the SEM/EDS result of the coated magnet leached sample showing the presence of Mg-Nd precipitates. It is difficult to explain why the experiment with the coatings did not result in high nickel content in the magnesium. It has been speculated that there may have been some passivation of the nickel[49]. If it is possible to leach the rare earth without removing the coatings, that will reduce the cost and complexity of the recycling process. Also, because the Nd concentration in the Mg is not uniform, only an estimate of the amount recovered can be made, but no accurate measurement of the amount of Nd leached out of the magnet.



Spectrum 10	Wt%	σ
Mg	90.2	0.3
Nd	6.9	0.2
Pr	2.2	0.2
Ni	0.4	0.1
Fe	0.2	0.1
Cu	0.1	0.1

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Spectrum 13	Wt%	σ
Mg	94.6	0.3
Nd	4.1	0.2
Pr	1.1	0.2
Al	0.1	0.1
Fe	0.1	0.1
Ti	0.0	0.1
V	0.0	0.1
Dy	0.0	0.2

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Spectrum 18	Wt%	σ
Mg	83.1	0.4
Nd	11.9	0.3
Pr	3.8	0.2
Ni	0.7	0.1
Cu	0.3	0.1
Fe	0.3	0.1

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Figure 5.6: EDS analysis after leaching of coated magnets: (top left) backscatter image showing locations of EDS analysis (Spectrum 10 in the top right covers the whole field of view); (bottom left and right) EDS spectra 13, and 18 showing 11.9%, and 4.1% Nd respectively

5.4: Magnesium-Neodymium alloy Distillation Experiment

5.4.1: Methodology

The distillation experiment was carried out in a 12” inner diameter Mellen furnace in the foundry with an output max of 8.71kW to determine the vertical temperature gradient of a batch distiller and the distillate composition following the separation of magnesium-neodymium alloy. Supplemental furnace insulation with an opening widened to fit a 10” schedule 40 pipe distiller was used. Temperatures were monitored vertically along the outside of the distiller using K thermocouples, as shown in Figure 5.7, with the proper connections to a data logging system, to generate a validation set of temperature distribution within the distiller during the experiment. The distiller was assembled using the design and dimensions in Figure 5.8 and sealed under a vacuum.

Figure 5.7: Side view of assembled distiller showing thermocouple placement along the outside of the chamber [50]

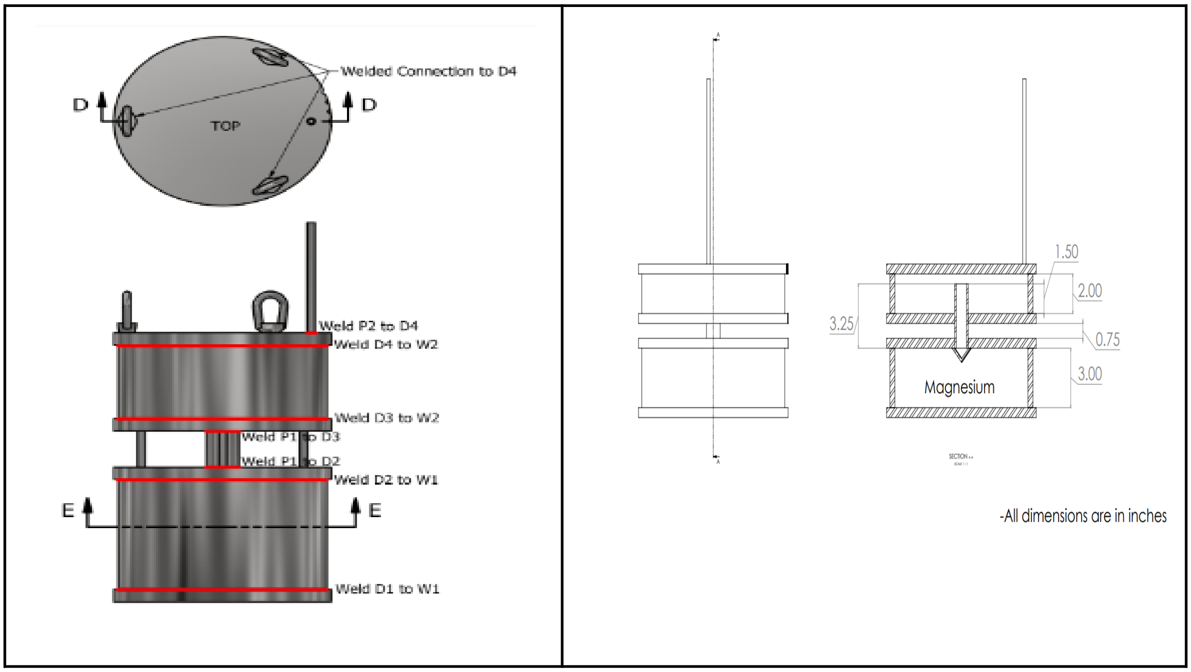


Figure 5.8: Welding and assembly diagram for one-effect batch distiller

The furnace was set to a manual output power of 50% and increased as necessary to reach the desired temperature of 1100^0C. At 1100^0C, the distiller was slowly raised using a gantry crane by 4.5inches until about half of the evaporator was within the furnace. The rest of the distiller was within the secondary insulation, as shown in Figure 5.9. The output power was manually increased or decreased as needed until the thermocouples stabilized with a lower temperature of ~900^0C and an upper temperature of ~700^0C. At this point, the distiller was held for 5 - 6 hours, until a sudden increase in temperature of the lowest thermocouple, indicating a complete distillation of Mg. The alloy makeup before distillation was 95% Mg, 4% Al, and 1% Nd.

Figure 5.9: Secondary insulation elements wrapped in steel foil and tightened with 2 steel straphangers. Secondary insulation resting atop furnace.

5.4.2: Results and Discussion

Figure 5.10: Cut 1-effect distiller after distillation showing the evaporated Mg in the Condenser

Table 5.4: XRF Result of distilled Sample

Element	Mg	Al	Fe	Mn	Zn	Ni	Cu	Sc
%wt.	99	0.58	0.152	0.020	0.085	0.065	0.020	0.075

The distilled sample is shown in the condenser of the 1-effect distiller, as seen in Figure 5.10. X-ray Fluorescence was used to analyze the sample's composition after distillation, shown in Table 5.4. It can be seen that there was an aerosol carryover, i.e., trace elements in the distilled sample, despite the obstruction in the evaporator. This is likely because a lower heating rate led to a lower evaporation rate and slower gas velocity, resulting in less aerosol separation than a prior study [51],[52]. Based on the distillate composition, it appears that ~15% of the distillate is aerosol carryover, with the remainder being evaporated metal. The percent composition of Mg increased from 95% to 99%, indicating an increase in the purity level of Mg. There is no Nd content in the distilled sample. However, the presence of Sc might indicate rare earth content since rare earth elements have similar chemical properties, and their spectral signals can overlap. The distiller comprises nickel-free steels, but some of the tubes are stainless, which could be the reason for the 0.1% Ni the Mg. This is not a problem for the Mg because it is re-circulated to leach the magnet again. However, the evaporator must be lined with a material such as molybdenum to prevent the Nd from absorbing iron and other metals from the distiller.

5.5: Reduced-order Model for Magnesium-Neodymium Alloy Distillation

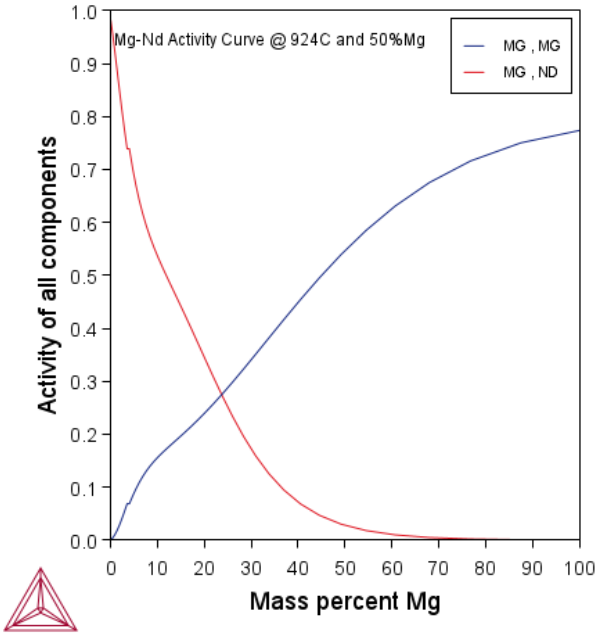
5.5.1: Methodology

A reduced-order model which uses the general solution model, the general form of traditional geometrical models, can be used to calculate and predict several properties in a thermodynamic system[53], [54]. In general, heat transfer up through the distiller limits the distillation rate, which is majorly a result of the heat conduction through the steel evaporator and liquid Mg-Nd alloy in the evaporator. For pure Mg distillation, the vapor flow requires only a small pressure difference, so within an effect, the magnesium vapor pressure at the evaporator surface is very close to the vapor pressure at the condenser surface.

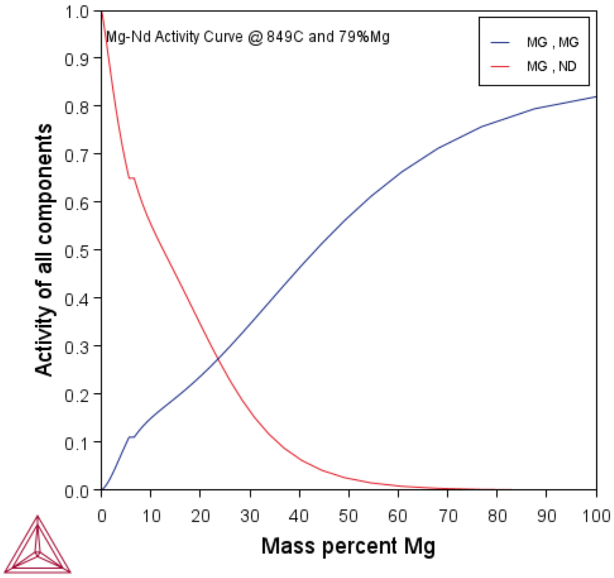
Here the effect of Nd activities was considered in the case of Mg-Nd distillation. Using parameters from Meng et al. for the Mg-Nd binary system[55], a continuous flow thermal model was used to predict the Mg-Nd alloy distillation temperatures and production rates in a three-effect distiller. The activities of Mg-Nd were calculated using the TCMG6 database for Mg alloys in Thermocalc software. The vapor pressures and composition fractions were calculated. The mass flow rates were used to predict the production rate difference compared to pure Mg by carrying out several iterations of the temperatures at the bottom of the condensers, mass flow rates, and activities of the Mg-Nd alloy.

5.5.2: Results and Discussion

From the activity models, as seen in Figure 14, the activities of Mg-Nd alloy were estimated as 0.04, 0.002, and 0.001 at evaporator temperatures 924^{0}C, 849^{0}C, and 763^{0}C in effects 1, 2 and 3 respectively. This was calculated based on a mass flow rate of 125kg/hr of Mg-Nd, assuming the Mg-Nd precipitate contained in the alloy was 25kg/hr, where 50% of this was Nd. Thus Mg fractions of 50% in Effect 1, 79% in Effect 2, and 86% in Effect 3 were estimated.



(a)



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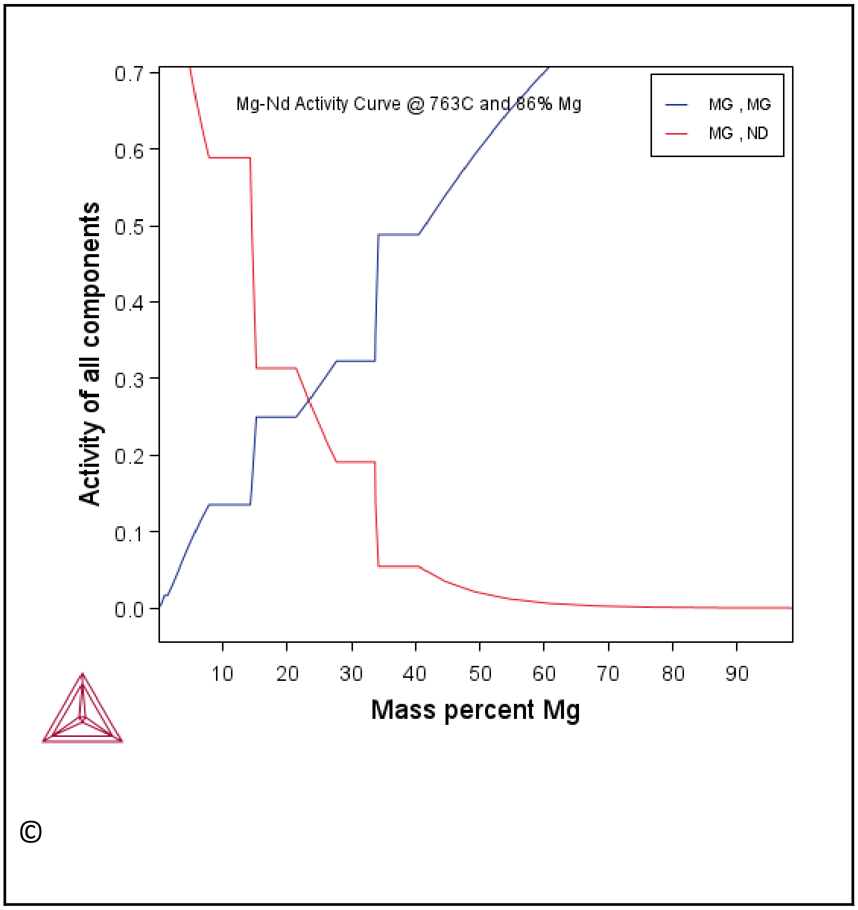

Figure 5.11: (a,b and c) Activity Curves for Mg-Nd for the three-effect distillation model

Using the distiller parameters in Table 5.5 and assuming a bottom heater temperature of 950^{0}C, and estimating a top condenser temperature of ~750^{0}C, the mass flows for each effect were 22.9kg/hr which was ~53% reduction in production rate compared to the distillation of pure Mg.

The power consumption was 33.48kW. The output power can be increased to increase the production rate, and the bottom and top temperatures are maintained at 950^{0}C and 750^{0}C, respectively. But this could affect the energy consumption and economics of G-METS distillation for magnet recycling, as discussed in Chapter 3.

Table 5.5: Distiller parameters used in the reduced order model for the temperatures of the three-effect distiller

Distiller parameters	
Area, m^2	1
Bottom heat T, °C	950
Top liquid Mg T, °C	750
Steel thermal k, W/m·K	20
Mg thermal k, W-m·K	91
Steel layer thickness, m	0.01
Mg layer thickness, m	0.025
Mg ΔHv, W·h/kg	1462

5.6: Conclusion

The experimental investigation and reduced order model of Mg-Nd alloy has been presented in this chapter. It was shown that Mg is a suitable leaching agent for Nd, and a reduction in the particle size of the Nd magnet will increase the leaching efficiency. Analysis of the leached coated magnet did not show the presence of Ni in the Mg-Nd precipitates. This could be a result of the passivation of the Ni coatings. The reduced order model has predicted a 53% reduction in the production rate of Mg-Nd distillation compared to pure Mg, using a three-effect G-METS distiller.

REFERENCES

[1] V. G. Deshmane, S. Z. Islam, and R. R. Bhave, “Selective Recovery of Rare Earth Elements from a Wide Range of E-Waste and Process Scalability of Membrane Solvent Extraction,” *Environ. Sci. Technol.*, p. acs.est.9b05695, Dec. 2019, doi: 10.1021/acs.est.9b05695.

[2] F. Xie, T. A. Zhang, D. Dreisinger, and F. Doyle, “A critical review on solvent extraction of rare earths from aqueous solutions,” *Miner. Eng.*, vol. 56, pp. 10–28, Feb. 2014, doi: 10.1016/j.mineng.2013.10.021.

[3] M. Gergoric, C. Ekberg, M. R. S. J. Foreman, B.-M. Steenari, and T. Retegan, “Characterization and Leaching of Neodymium Magnet Waste and Solvent Extraction of the Rare-Earth Elements Using TODGA,” *J. Sustain. Metall.*, vol. 3, no. 3, pp. 638–645, Sep. 2017, doi: 10.1007/s40831-017-0122-8.

[4] S. Riaño and K. Binnemans, “Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets,” *Green Chem.*, vol. 17, no. 5, pp. 2931–2942, May 2015, doi: 10.1039/C5GC00230C.

[5] K. K. Yadav, M. Anitha, D. K. Singh, and V. Kain, “NdFeB magnet recycling: Dysprosium recovery by non-dispersive solvent extraction employing hollow fibre membrane contactor,” *Sep. Purif. Technol.*, vol. 194, pp. 265–271, Apr. 2018, doi: 10.1016/j.seppur.2017.11.025.

[6] C. G. Brown and L. G. Sherrington, “Solvent extraction used in industrial separation of rare earths,” *J. Chem. Technol. Biotechnol.*, vol. 29, no. 4, pp. 193–209, 1979, doi: 10.1002/jctb.503290402.

[7] Y. Baba, F. Kubota, N. Kamiya, and M. Goto, “Selective Recovery of Dysprosium and Neodymium Ions by a Supported Liquid Membrane Based on Ionic Liquids,” *Solvent Extr. Res. Dev. Jpn.*, vol. 18, pp. 193–198, 2011, doi: 10.15261/serdj.18.193.

[8] D. Kim, L. Powell, L. Delmau, E. Peterson, J. Herchenroeder, and R. Bhave, “Selective

Extraction of Rare Earth Elements from Permanent Magnet Scraps with Membrane Solvent Extraction," *Environ. Sci. Technol.*, Jun. 2015, doi: https://doi.org/10.1021/acs.est.5b01306.

[9] A. C. Ni'am, Y.-F. Wang, S.-W. Chen, G.-M. Chang, and S.-J. You, "Simultaneous recovery of rare earth elements from waste permanent magnets (WPMs) leach liquor by solvent extraction and hollow fiber supported liquid membrane," *Chem. Eng. Process. - Process Intensif.*, vol. 148, p. 107831, Feb. 2020, doi: 10.1016/j.cep.2020.107831.

[10] B. R. Reddy, B. N. Kumar, and S. Radhika, "Solid-Liquid Extraction of Terbium from Phosphoric Acid Medium using Bifunctional Phosphinic Acid Resin, Tulsion CH-96," *Solvent Extr. Ion Exch.*, vol. 27, no. 5–6, pp. 695–711, Dec. 2009, doi: 10.1080/07366290903270031.

[11] S. Z. Islam, P. Wagh, J. E. Jenkins, C. Zarzana, M. Foster, and R. Bhave, "Process Scale-Up of an Energy-Efficient Membrane Solvent Extraction Process for Rare Earth Recycling from Electronic Wastes," *Adv. Eng. Mater.*, vol. 24, no. 12, p. 2200390, 2022, doi: 10.1002/adem.202200390.

[12] M. Zakotnik, P. Afiuny, S. Dunn, and C. O. Tudor, "Magnet Recycling to Create Nd-Fe-B Magnets with Improved or Restored Magnetic Performance," 9,044,834, Jun. 02, 2015 Accessed: Mar. 19, 2020. [Online]. Available: https://patents.google.com/patent/US9044834B2/en

[13] M. Kimiabeigi *et al.*, "Production and Application of HPMS Recycled Bonded Permanent Magnets for a Traction Motor Application," *IEEE Trans. Ind. Electron.*, vol. 65, no. 5, pp. 3795–3804, May 2018, doi: 10.1109/TIE.2017.2762625.

[14] C. Jönsson *et al.*, "The extraction of NdFeB magnets from automotive scrap rotors using hydrogen," *J. Clean. Prod.*, vol. 277, p. 124058, Dec. 2020, doi: 10.1016/j.jclepro.2020.124058.

[15] I. R. Harris and P. J. McGuiness, "Hydrogen: its use in the processing of NdFeB-type magnets," *J. Common Met.*, vol. 172–174, pp. 1273–1284, Jan. 1991, doi: 10.1016/S0022-5088(06)80037-8.

[16] A. Walton *et al.*, “The use of hydrogen to separate and recycle neodymium–iron–boron-type magnets from electronic waste,” *J. Clean. Prod.*, vol. 104, pp. 236–241, Oct. 2015, doi: 10.1016/j.jclepro.2015.05.033.

[17] M. Xia, A. B. Abrahamsen, C. R. H. Bahl, B. Veluri, A. I. Søegaard, and P. Bøjsøe, “Hydrogen Decrepitation Press-Less Process recycling of NdFeB sintered magnets,” *J. Magn. Magn. Mater.*, vol. 441, pp. 55–61, Nov. 2017, doi: 10.1016/j.jmmm.2017.01.049.

[18] A. Lixandru, I. Poenaru, K. Güth, R. Gauß, and O. Gutfleisch, “A systematic study of HDDR processing conditions for the recycling of end-of-life Nd-Fe-B magnets,” *J. Alloys Compd.*, vol. 724, pp. 51–61, Nov. 2017, doi: 10.1016/j.jallcom.2017.06.319.

[19] C. J. Ferron and P. Henry, “A review of the recycling of rare earth metals,” *Can. Metall. Q.*, vol. 54, no. 4, pp. 388–394, Oct. 2015, doi: 10.1179/1879139515Y.0000000023.

[20] M. Zakotnik, I. R. Harris, and A. J. Williams, “Multiple recycling of NdFeB-type sintered magnets,” *J. Alloys Compd.*, vol. 469, no. 1, pp. 314–321, Feb. 2009, doi: 10.1016/j.jallcom.2008.01.114.

[21] B. Sprecher *et al.*, “Life Cycle Inventory of the Production of Rare Earths and the Subsequent Production of NdFeB Rare Earth Permanent Magnets,” *Environ. Sci. Technol.*, vol. 48, no. 7, pp. 3951–3958, Apr. 2014, doi: 10.1021/es404596q.

[22] C. Li *et al.*, “Recycling of scrap sintered Nd–Fe–B magnets as anisotropic bonded magnets via hydrogen decrepitation process,” *J. Mater. Cycles Waste Manag.*, vol. 17, no. 3, pp. 547–552, Jul. 2015, doi: 10.1007/s10163-014-0279-1.

[23] A. Piotrowicz, S. Pietrzyk, P. Noga, and Ł. Myćka, “The use of thermal hydrogen decrepitation to recycle Nd-Fe-B magnets from electronic waste,” *J. Min. Metall. Sect. B Metall.*, vol. 56, no. 3, pp. 415–424, 2020.

[24] E. H. Lalana, M. J. J. Degri, A. Bradshaw, and A. Walton, “Recycling of Rare Earth Magnets by Hydrogen Processing and Re-Sintering,” in *European Congress and Exhibition on Powder Metallurgy. European PM Conference Proceedings*, Shrewsbury, United Kingdom, 2016, pp.

1–6. Accessed: Mar. 04, 2023. [Online]. Available: https://www.proquest.com/docview/2036731035/abstract/B895AFCC9FBB48ACPQ/1

[25] M. Zakotnik, I. R. Harris, and A. J. Williams, "Possible methods of recycling NdFeB-type sintered magnets using the HD/degassing process," *J. Alloys Compd.*, vol. 450, no. 1, pp. 525–531, Feb. 2008, doi: 10.1016/j.jallcom.2007.01.134.

[26] B. Michalski, M. Szymanski, K. Gola, J. Zygmuntowicz, and M. Leonowicz, "Experimental evidence for the suitability of the hydrogen decomposition process for the recycling of Nd-Fe-B sintered magnets," *J. Magn. Magn. Mater.*, vol. 548, p. 168979, Apr. 2022, doi: 10.1016/j.jmmm.2021.168979.

[27] V. S. Thompson *et al.*, "Techno-economic and Life Cycle Analysis for Bioleaching Rare-Earth Elements from Waste Materials," *ACS Sustain. Chem. Eng.*, vol. 6, no. 2, pp. 1602–1609, Feb. 2018, doi: 10.1021/acssuschemeng.7b02771.

[28] P. Rasoulnia, R. Barthen, and A.-M. Lakaniemi, "A critical review of bioleaching of rare earth elements: The mechanisms and effect of process parameters," *Crit. Rev. Environ. Sci. Technol.*, vol. 51, no. 4, pp. 378–427, Feb. 2021, doi: 10.1080/10643389.2020.1727718.

[29] C. Magrini and K. Jagodzińska, "Can bioleaching of NIB magnets be an answer to the criticality of rare earths? An ex-ante Life Cycle Assessment and Material Flow Cost Accounting," *J. Clean. Prod.*, vol. 365, p. 132672, Sep. 2022, doi: 10.1016/j.jclepro.2022.132672.

[30] R. M. Brown, A. Mirkouei, D. Reed, and V. Thompson, "Current nature-based biological practices for rare earth elements extraction and recovery: Bioleaching and biosorption," *Renew. Sustain. Energy Rev.*, vol. 173, p. 113099, Mar. 2023, doi: 10.1016/j.rser.2022.113099.

[31] D. W. Reed, Y. Fujita, D. L. Daubaras, Y. Jiao, and V. S. Thompson, "Bioleaching of rare earth elements from waste phosphors and cracking catalysts," *Hydrometallurgy*, vol. 166, pp. 34–40, Dec. 2016, doi: 10.1016/j.hydromet.2016.08.006.

[32] B. Monneron-Enaud, O. Wiche, and M. Schlömann, “Biodismantling, a Novel Application of Bioleaching in Recycling of Electronic Wastes,” *Recycling*, vol. 5, no. 3, Art. no. 3, Sep. 2020, doi: 10.3390/recycling5030022.

[33] H. Fathollahzadeh, J. J. Eksteen, A. H. Kaksonen, and E. L. J. Watkin, “Role of microorganisms in bioleaching of rare earth elements from primary and secondary resources,” *Appl. Microbiol. Biotechnol.*, vol. 103, no. 3, pp. 1043–1057, Feb. 2019, doi: 10.1007/s00253-018-9526-z.

[34] R. T. Ott and R. W. McCallum, “Recovering rare earth metals from magnet scrap,” U.S. Patent 10,323,299, Jun. 18, 2019 Accessed: May 17, 2021. [Online]. Available: https://patents.google.com/patent/US10323299B2/en

[35] C. Chinwego, H. Wagner, E. Giancola, J. Jironvil, and A. Powell, “Technoeconomic Analysis of Rare-Earth Metal Recycling Using Efficient Metal Distillation,” *JOM*, vol. 74, no. 4, pp. 1296–1305, Apr. 2022, doi: 10.1007/s11837-021-05045-7.

[36] O. Takeda and T. H. Okabe, “Current Status on Resource and Recycling Technology for Rare Earths,” *Metall. Mater. Trans. E*, vol. 1, no. 2, pp. 160–173, Jun. 2014, doi: 10.1007/s40553-014-0016-7.

[37] T. Akahori, Y. Miyamoto, T. Saeki, M. Okamoto, and T. Okabe, “Recovery of Rare Eath Metals in Used Magnets by Molten Magnesium,” in *Magnesium Technology 2014*, TMS (The Minerals, Metals & Materials Society), 2014, pp. 35–38. Accessed: Mar. 03, 2020. [Online]. Available: https://doi.org/10.1007/978-3-319-48231-6_10

[38] T. W. Ellis and F. A. Schmidt, “Recycling of Rare Earth Metals from Rare Earth-Transition Metal Alloy Scrap by Liquid Metal Extraction,” 5,437,709, Aug. 01, 1995 [Online]. Available: https://patents.google.com/patent/US5437709A/en

[39] M. Z. Rasheed, S.-W. Nam, J.-Y. Cho, K.-T. Park, B.-S. Kim, and T.-S. Kim, “Review of the Liquid Metal Extraction Process for the Recovery of Nd and Dy from Permanent Magnets,”

Metall. Mater. Trans. B, vol. 52, no. 3, pp. 1213–1227, Jun. 2021, doi: 10.1007/s11663-021-02102-z.

[40] A. E. Telgerafchi, G. Espinosa, M. Rutherford, A. Powell, and D. Dussault, “Efficient Low-Cost Gravity-Driven Multiple Effect Thermal System (G-METS) Distillation of Magnesium,” in *Magnesium 2021*, Orlando, Florida: TMS, Mar. 2021, pp. 145–152. doi: 10.1007/978-3-030-65528-0_22.

[41] W. H. Zebuhr, “Ammonia Removal Device,” US 10,011,502, Jul. 03, 2018 Accessed: Sep. 13, 2021. [Online]. Available: https://patents.google.com/patent/US10011502B2/en

[42] W. H. Zebuhr, “Ammonia removal device,” WO2015179272A2, Nov. 26, 2015 Accessed: Mar. 08, 2023. [Online]. Available: https://patents.google.com/patent/WO2015179272A2/en

[43] “Services | Magpro LLC.” http://magprollc.com/page-4/ (accessed Apr. 06, 2023).

[44] M. Sun, X. Hu, L. Peng, P. Fu, W. Ding, and Y. Peng, “On the production of Mg-Nd master alloy from NdFeB magnet scraps,” *J. Mater. Process. Technol.*, vol. 218, pp. 57–61, Apr. 2015, doi: 10.1016/j.jmatprotec.2014.11.036.

[45] H. J. Chae, Y. D. Kim, B. S. Kim, J. G. Kim, and T.-S. Kim, “Experimental investigation of diffusion behavior between molten Mg and Nd–Fe–B magnets,” *J. Alloys Compd.*, vol. 586, pp. S143–S149, Feb. 2014, doi: 10.1016/j.jallcom.2013.02.156.

[46] T. H. Okabe, O. Takeda, K. Fukuda, and Y. Umetsu, “Direct Extraction and Recovery of Neodymium Metal from Magnet Scrap,” *Mater. Trans.*, vol. 44, no. 4, pp. 798–801, 2003, doi: 10.2320/matertrans.44.798.

[47] Y. Xu, L. S. Chumbley, and F. C. Laabs, “Liquid metal extraction of Nd from NdFeB magnet scrap,” *J. Mater. Res.*, vol. 15, no. 11, pp. 2296–2304, Nov. 2000, doi: 10.1557/JMR.2000.0330.

[48] C. Chinwego and A. Powell, “Experimental Investigation of Liquid Metal Leaching for

Rare Earth Magnet Recycling," in *Rare Metal Technology 2023*, T. Ouchi, K. Forsberg, G. Azimi, S. Alam, N. R. Neelameggham, H. Kim, A. A. Baba, H. Peng, and A. Karamalidis, Eds., in The Minerals, Metals & Materials Series. Cham: Springer Nature Switzerland, 2023, pp. 33–37. doi: 10.1007/978-3-031-22761-5_4.

[49] I. Nlebedim, "Coated NdFeB Magnet Leaching with Magnesium," Mar. 21, 2023.

[50 D. McArthur Sehar *et al.*, "Design of the Continuous Gravity-Driven Multiple-Effect Thermal System (G-METS) for Efficient Low-Cost Magnesium Recycling," in *Magnesium Technology 2023*, S. Barela, A. Leonard, P. Maier, N. R. Neelameggham, and V. M. Miller, Eds., Cham: Springer Nature Switzerland, 2023, pp. 161–167.

[51] A. C. Powell, D. M. Dussault, M. R. Earlam, A. Tajima, and C. Raymes, "Method and Apparatus for Efficient Metal Distillation and Related Primary Production Process," U.S. Patent Application 16/944,147 Accessed: Jan. 05, 2022. [Online]. Available: https://patents.google.com/patent/US20210040633A1/en

[52] G. Espinosa, A. E. Telgerafchi, D. McArthur, M. Rutherford, A. Powell, and D. Dussault, "Design of Efficient Low-Cost Recycling of Magnesium Using Gravity-Driven Multiple Effect Thermal System (G-METS)," in *Magnesium Technology 2022*, P. Maier, S. Barela, V. M. Miller, and N. R. Neelameggham, Eds., in The Minerals, Metals & Materials Series. Cham: Springer International Publishing, 2022, pp. 135–140. doi: 10.1007/978-3-030-92533-8_22.

[53] K.-C. Chou, "A general solution model for predicting ternary thermodynamic properties," *Calphad*, vol. 19, no. 3, pp. 315–325, Sep. 1995, doi: 10.1016/0364-5916(95)00029-E.

[54] K.-C. Chou, W.-C. Li, F. Li, and M. He, "Formalism of new ternary model expressed in terms of binary regular-solution type parameters - ScienceDirect," *Calphad*, vol. 20, no. 4, pp. 395–406, Dec. 1996, doi: https://doi.org/10.1016/S0364-5916(97)00002-3.

[55] F. Meng, H. Liu, L. Liu, and Z. Jin, "Thermodynamic optimization of Mg-Nd system," *Trans. Nonferrous Met. Soc. China*, vol. 17, no. 1, pp. 77–81, Jan. 2007, doi: 10.1016/S1003-6326(07)60051-X.

Chapter 6

Conclusions and Future Directions

6.1: Key Findings and Conclusions

This thesis has presented a comprehensive study on recycling rare earth magnets from an economic and technical perspective. Important conclusions from the techno-economic analysis, commercialization studies, experimental investigation, and reduced-order model are presented.

The G-METS distillation system is a low-cost innovation that can reduce the energy consumption of the overall recycling process compared to traditional distillation. The techno-economic analysis has shown that energy consumption can be reduced by ~67% compared to traditional distillation. This can reduce the overall operating cost of the recycling plant, thus increasing the economic feasibility of recycling rare earth magnet scrap in coming years when scrap magnets have a stable feedstock supply. Feedstock supply is gradually becoming available in the United States and other countries as the first-generation Prius and Chevrolet Volts have started being retired. Data centers and magnet-cutting companies are also great sources for post-consumer scrap magnets.

The commercialization study presents a business model canvas in which a company can use the new recycling process with G-METS distillation to profitably address some of the needs of US rare earth magnet producers. It displays a workflow of several key stakeholders necessary to ensure the stability of rare earth magnet recycling. Incentivizing the collection of post-consumer rare earth magnets and promoting a domestic supply of rare earth magnets for defense applications by paying a premium to offset the cost of recycling can ensure an economically viable business.

The experimental investigation has demonstrated that Mg is an effective leaching agent for rare earth metals. It is speculated that the leaching of coated magnets can be achieved because of the passivation of the nickel coatings, reducing the cost and complexity of the recycling process. Also, the leaching efficiency tends to increase with a decrease in particle size. The reduced order model has shown in 53% reduction in the production rates of Mg-Nd distillation compared to pure Mg in a three-effect G-METS distiller.

6.2: Recommendations for Future Research

1. Valorization of the By-Products from the Recycling Process - Fe, B, and Nickel Coatings

Before and after leaching, Ni coatings and FeB are recovered, respectively. Studies on how these can be valorized will go a long way in increasing the economic viability of magnet recycling.

The Fe and B in the leached solid residue can be recycled to produce new NdFeB magnets or other metallic products or to produce alloys with other metals such as cobalt, nickel, and titanium, which can have various applications in the automotive, aerospace, and electronics industries. Also, the recovered nickel coatings can be recycled to produce new nickel-based products, such as stainless steel, batteries, or electronics, or in the production of superalloys, which are used in high-temperature environments like gas turbines or jet engines.

2. G-METS Bismuth Distillation Experiments

As discussed in the techno-economic analysis of this recycling process [1], bismuth will be used in the second leaching step to recover the heavy rare earth metals as studies have shown that Bi is a suitable leaching agent [2] - [5]. Thus, it will be paramount to demonstrate the distillation of Bi-Nd in the G-METS.

3. Two-Effects and Three-Effects Mg-Nd Distillation Experiments

Only a single-effect distillation has been demonstrated thus far in this study. Conducting experiments for a two- and three-effect Mg-Nd G-METS distillation is essential.

4. G-METS Mg-Nd Continuous Distillation Design and Experiments

It is important to design and demonstrate a continuous G-METS distillation as a continuous flow system presents unique challenges that require various design considerations, such as temperature differentials and mass flow rate control.

5. Life Cycle Analysis or Other Ecological Analysis

Life cycle analysis of the process design will be important for comparing the conventional process with the new production.

6. Validation of Techno-Economic Analysis through Stakeholder Perspectives

An exercise to validate the parameters used for the techno-economic analysis through stakeholder perspectives will be helpful.

REFERENCES

[1] C. Chinwego, H. Wagner, E. Giancola, J. Jironvil, and A. Powell, “Technoeconomic Analysis of Rare-Earth Metal Recycling Using Efficient Metal Distillation,” *JOM*, vol. 74, no. 4, pp. 1296–1305, Apr. 2022, doi: 10.1007/s11837-021-05045-7.

[2] “Technology - Recovering rare earth metals using bismuth extractant.” http://isurftech.technologypublisher.com/technology/21024 (accessed May 17, 2021).

[3] M. Z. Rasheed, S.-W. Nam, J.-Y. Cho, K.-T. Park, B.-S. Kim, and T.-S. Kim, “Review of the Liquid Metal Extraction Process for the Recovery of Nd and Dy from Permanent Magnets,” *Metall. Mater. Trans. B*, vol. 52, no. 3, pp. 1213–1227, Jun. 2021, doi: 10.1007/s11663-021-02102-z.

[4] Y.-S. Kim, S.-W. Nam, K.-T. Park, and T.-S. Kim, “Extraction Behavior of Rare Earth Element (Nd, Dy) from Rare Earth Magnet by Using Molten Magnesium,” *Sci. Adv. Mater.*, vol. 9, no. 12, pp. 2166–2172, Dec. 2017, doi: 10.1166/sam.2017.3216.

[5] S.-W. Nam, D.-K. Kim, B.-S. Kim, D.-H. Kim, and T.-S. Kim, “Extraction Mechanism of Rare Earth Elements Contain in Permanent Magnets Using Molten Bismuth,” *Sci. Adv. Mater.*, vol. 9, pp. 1987–1992, 2017.