

Process Development and Techno-Economic Analysis for the Recovery of Rare Earth Elements and Critical Materials from Acid Mine Drainage

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(ABSTRACT)

Rare earth elements (REE) exhibit particular and unique properties that render them essential to technological applications. Of particular interest is their involvement in the transition toward global sustainability and their military applications. The magnetic properties of the rare earth elements is of primordial importance to sustainable development. More specifically, terbium and dysprosium are two elements with no known substitutes in critical applications and with no domestic or allied sourcing available. These elements are currently mined by in-situ leaching of ion-absorbed clays, mostly from illegal operations in Myanmar financed by Chinese companies. The demand from both elements, and for the other magnet rare earths is projected to growth at very high rates through 2035 while the world undergoes a transition toward sustainability, and a drastic reduction in greenhouse gases emissions. Our team has been evaluating the potential of acid mine drainage (AMD) as a source of rare earth elements and critical materials (CM). Acid mine drainage is the result of in-situ generation of sulfuric acid due to the weathering of sulfide ores. It is a significant legacy environmental issue and one of the largest pollutants in many mining districts throughout the world. The objective of the present work is to provides a roadmap for the utilization of AMD as a critical material feedstock to preserve the independence of the United States of America with regards to these materials. To that effect, a fundamental economic assessment of REE/CM recovery from AMD using a network sourcing strategy in addition to a robust,

flexible feedstock separations and refining facility was undertaken. A techno-economic analysis of the extraction, refining, separation and reduction to metal is presented along with a sensitivity analysis. The results of this analysis show that, with the exception of the minimum price scenario, all operational configurations have positive economic indicators with rates of return varying from 25% to 32% for the contemporary price scenario. This is primarily due to the very high enrichment in terbium and dysprosium of AMD. The optimal configuration was determined to be production of Co, Mn, and all REEs except for mischmetal, which is not recovered. Sensitivity analysis and Monte Carlo Simulation show that capital cost and HCl consumption are the two major factors influencing rate of return, thus indicating opportunities for future technology development and cost optimization. In order to reduce both the capital and operation cost of the facility, alternative ionic liquids extractants based on conventional acidic extractants were synthesized and investigated. The results show that the ionic liquids varied in performance, with [c101][D2EHP] and [c101][EHEHP] performing poorer than their conventional counterparts and [c101][c572] performing better. The performance of [c101][c572] was 13% superior to Cyanex 572, 20% superior to EHEHPA and 27% superior to D2EHPA the current commercially used extractants. Recommendations for further study on [c101][c572] include stripping tests, continuous pilot testing, and techno-economic analysis. The test work revealed that zinc and to a lesser extent calcium were significant deleterious elements in the solvent extraction circuit, and that selective removal would significantly reduce the acid-base consumption of the separation circuit. A process was developed to selectively remove calcium and zinc from AMD-derived feedstock and from REE products. The ammonium chloride leach process offers many advantages, including the possibility of closing the cycle by using carbon dioxide sequestration as a step to regenerate the ammonium chloride in a zero-discharge process.

Process Development and Techno-Economic Analysis for the Recovery of Rare Earth Elements and Critical Materials from Acid Mine Drainage

Tommee Larochelle

(GENERAL AUDIENCE ABSTRACT)

A younger me: - What are these elements in the bottom of the periodic table?

My high school chemistry teacher: - "Don't waste time there, these are of no concern."

Twenty years later, technological developments and the imperative to transition away from fossil energy to mitigate climate change have brought the rare earth elements, a series of 17 elements with unique properties to the forefront of the conversation. In addition to an organic increase in demand, the recent supply chain consolidation by China is adding a geopolitical risk to the equation. The magnetic properties of the rare earth elements is of primordial importance to sustainable development and to our military technology. More specifically, terbium and dysprosium are two elements with no known substitutes in critical applications and with no domestic or allied sourcing available. These elements are currently mined from illegal operations in Myanmar, with the support of Chinese companies. The demand from both elements, and for the other magnet rare earths is projected to grow at very high rates through 2035 while the world undergoes a transition toward sustainability, and a drastic reduction in greenhouse gas emissions. Given the importance of the rare earth elements, and the absence of significant deposits in the United States, with the exception of the Bear Lodge and Elk Creek deposits, the Department of Energy has mandated academic institutions to evaluate alternative sources of rare earth elements. Our team has been evaluating the potential of acid mine drainage as a source of rare earth elements and critical materials. Our

team has surveyed many acid mine drainage sources and determined that many sites are highly enriched in terbium and dysprosium. Acid mine drainage is a legacy environmental issue related to past problematic mine development techniques. In the problematic mines, these acidic mine waters are permanently generated and if not treated can have severe impacts on water streams in which they flow. The toxicity of the acid mine drainage on the environment is due to its high acidity and significant levels of toxic metals. Acid mine drainage can be recognized by their yellow to red tint. It is treated by reacting it with a neutralization agent, which results in treated water and a sludge. The sludge is dewatered and stored in tailing impoundments. I have designed a process for the economical recovery of rare earth elements and critical materials from acid mine drainage. The cost to build and operate the facility was derived and it was determined that the project could be further enhanced by reducing the plant chemical reagent consumption. One specific category of chemical referred to as extractant, is central to the rare earth separation process. A novel variation on the standard extractants has been evaluated and promises to provide significant savings. While the extractants were investigated, it was noticed that some impurities such as zinc and calcium created issues in the circuit. I then developed a process for their selective removal. The process also provide a net carbon dioxide sequestration potential.

Dedication

To my wife, Christina, for her unconditionnal love, support and for making this possible.

To my children Charles, William, Catherine and Henry, for reminding me what truly matters.

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Chapter 1

Introduction

1.1 The Rare Earth Elements

The Rare Earth Elements (REEs) is a group composed of 17 metals: 15 lanthanides elements, yttrium and scandium. The latter two elements are usually associated with the lanthanides, with scandium rarely being concentrated in a deposit [192]. The term “rare earths” traces its origin from an old term used to designate a mineral (earth) and their apparent scarcity upon discovery. While no longer considered “rare”, the rare earth do not tend to form highly concentrated deposits and as such present recovery challenges. The REEs from a periodic table are shown in Figure 1.1.

The REEs are typically divided into two or three groups. The two group distinction consisting of light rare earths elements (LREEs) and heavy rare earths (HREEs). LREEs include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm) and europium while HREEs include gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), yttrium (Y) and scandium (Sc). It should be noted that yttrium and scandium are lighter atoms than the LREE, but present an atomic radius, and properties closer to the HREEs. [191]

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16	9 F 19	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.9	36 Kr 83.8
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (271)	111 Rg (272)	112 Uub (285)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116 Uuh (292)	117 Uus 0	118 Uuo 0
6	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175				
7	90 Th 232	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)				

Figure 1.1: The rare earth elements [188] .

A third group referred to as mid rare earth elements (MREE) is also used, and refers to represents samarium, europium and gadolinium. Selected properties of the rare earth elements are presented in Table 1.1.

Table 1.1: Molecular Weight and Crustal Abundance of the rare earth elements.

Atomic Number	Symbol	Name	Molecular Weight	Crustal Abundance (ppm) [148]
21	Sc	Scandium	44.96	26
39	Y	Yttrium	88.91	33
57	La	Lanthanum	138.91	34
58	Ce	Cerium	140.12	60
59	Pr	Praseodymium	140.91	8.7
60	Nd	Neodymium	144.27	33
61	Pm	Promethium	145	-
62	Sm	Samarium	150.36	6.0
63	Eu	Europium	151.96	1.8
64	Gd	Gadolinium	157.25	5.2
65	Tb	Terbium	158.93	0.9
66	Dy	Dysprosium	162.5	6.2
67	Ho	Holmium	164.93	1.2
68	Er	Erbium	167.26	1.2
69	Tm	Thulium	168.93	0.5
70	Yb	Ytterbium	173.04	2.8
71	Lu	Lutetium	174.97	0.5

1.2 Rare Earth Elements Usage

Rare earth elements exhibit particular and unique properties that render them essential to technological applications. The main properties used in commercial and military applications include:

- Strong Magnetism
- Unique Optical Properties

- Fluorescence
- Catalytic Activity
- Glass Polishing Capabilities

Two aspects of the REE usage are of specific interest: their involvement in the transition toward global sustainability and their military applications. The primary property involved in the sustainability transition is the strong magnetism of the magnet rare earths (Pr, Nd, Sm, Tb and Dy). The utilization of REE permanent magnets allows for higher energy generation and energy usage efficiency. Defense applications of the REE is varied, with the primary application being related to magnetism and optical properties. Of specific interest are terbium and dysprosium, two elements with no domestic or allied sourcing available. These elements are essential to high temperature magnets and to various optical and surveillance systems such as displays, fiber optics, lasers, sonars, radars and other advanced detectors [35].

1.3 Rare Earth Elements Supply, Demand and Pricing

Magnet rare earth elements demand is projected to growth at very high rates through 2035 while the world undergoes a transition toward sustainability, and a drastic reduction in greenhouse gases emissions [192]. Demand growth is accelerating as demonstrated by a growth in upward demand growth by adamas from 2020 < 2021 < 2022 [160, 187, 245].

Long term pricing forecast is expected to remain very high compared to traditional prices, between half and the maximum of the 2011 spike. The demand and pricing forecast for NdPr oxide material are presented as Figure 1.2a and 1.2b respectively. Data for these figure has been compiled from junior mining companies corporate presentations, based on

Adamas Intelligence private databases and from other publicly available sources. Given the anticipated demand growth described above, prices for terbium and dysprosium are expected to follow the same trajectory [192]. While deposits containing significant amounts of NdPr such as Mountain Pass, Bear Lodge, Ashram and Elk Creek are currently being developed in North America, their terbium and dysprosium content range from nil to low.

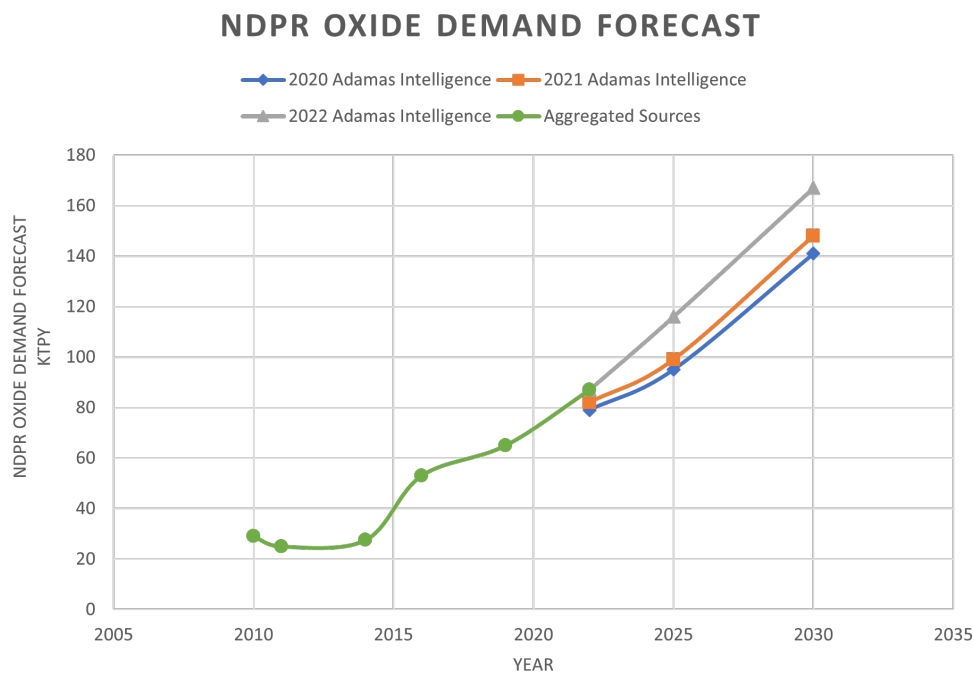
1.4 Rare Earth Elements Resources

Rare earth elements do not tend to accumulate in deposits. As such even the most concentrated deposit only offer grades of 5 to 7% [109]. In addition, deposits usually contain more than one REE-bearing minerals with most of the value being derived from the primary mineral. Three minerals currently represent most of the REE reserves: monazite / xenotime and bastnaesite.

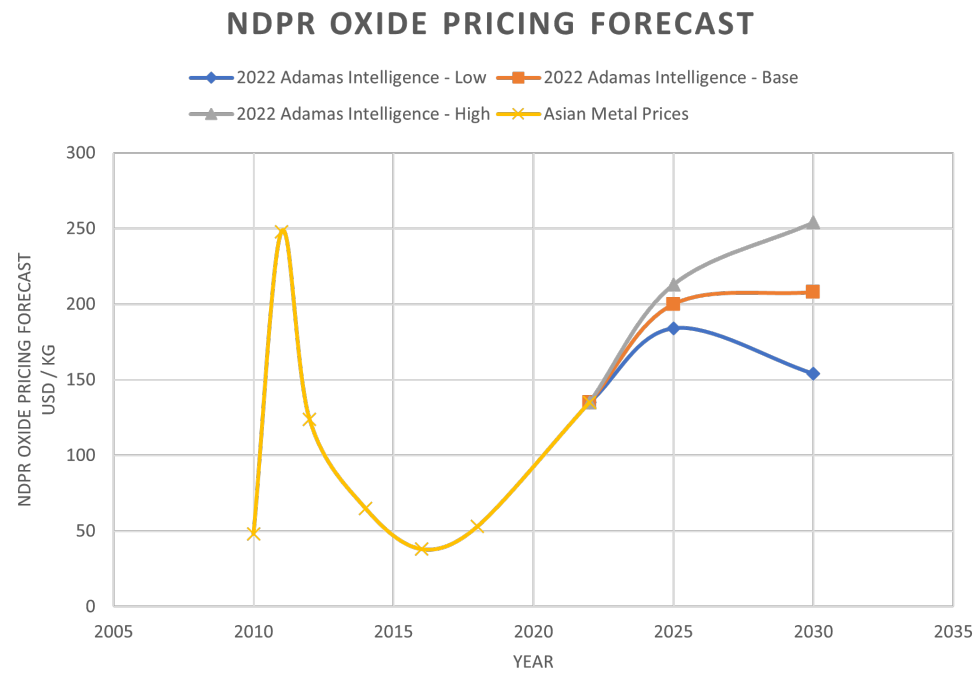
Monazite and xenotime are generally recovered during heavy sand processing and are REE phosphate minerals with calcium and thorium substitution. Monazite minerals are composed of LREE while xenotime is primarily composed of yttrium with high levels of HREE enrichment.

Bastnaesite is a fluorocarbonate REE-mineral found in various rock formations: carbonatites and pegmatites deposits being the most frequent hosts. Bastnaesite minerals are enriched in LREEs, and usually primarily composed of cerium and lanthanum.

In addition to these three minerals, HREEs are also commercially recovered from ion-adsorption clays (IAC) in south Asia. IAC currently supply the vast majority of HREEs



(a) NdPr Oxide Demand



(b) NdPr Oxide Pricing

Figure 1.2: NdPr Oxide Market Forecast

supply [192].

Other REE-bearing materials, such as allanite and eudialyte are currently being evaluated as potential resources for the recovery of REE. Unfortunately, their respective silica matrix leads to processing challenges that haven't been resolved. It is likely that these minerals will supply REEs in the future.

1.5 Building an American Supply Chain from Acid Mine Drainage

Given the foundational function of the rare earth elements in modern technology, and especially in military applications (refer to Section 1.2), supply disruption risks of critical rare earths elements represent an unacceptable risk to America's national security [73]. As such, the US government has directed its agencies to mitigate that risk by fostering the establishment of a national supply chain, from resource extraction through the production of final products. While the Department of Defense initiated contracts with primary mineral producers [247], the Department of Energy initiated a research program aimed at identifying and developing unconventional sources of REEs from coal-based waste streams [10, 249]. This later program has the advantage of a higher social acceptability due to the intrinsic remediation and valorization of waste deposits coupled with supporting communities ravaged by the transition away from coal power production. In addition, the distribution of REE in AMD feedstock is extremely high in terbium and dysprosium, making it a world class resource for these materials.

This work summarize my contribution to one such effort: the recovery of REE from acid mine drainage (AMD).

Acid mine drainage occurs when leftover or stockpiled sulfide minerals are weathered under conditions favorable to the production of sulfuric acid. The acid generated by this process leaches metals in its surroundings and the resulting leach solution laden with heavy metals and containing significant levels of residual acid is discharged to nearby streams, severely degrading the watersheds [214, 216]. AMD leach solutions contains high concentrations of metals, mostly iron, aluminum and manganese. Their typical rust color is due to the presence of ferric hydroxide.

In previous work by our team, Vass et al. surveyed coal-based AMD discharges in the Appalachian region and found significant amounts of REEs.[254, 255]. Their investigations revealed that pH is the single best predictor for REE concentrations, with a cutoff pH between 4 and 5.

AMD with pH superior to 5 have negligible REE concentrations (< 100 ppb), while AMD with pH below 4 can present up to ppm level concentrations. To prevent environmental degradation, regulations force mining companies and public entities such as state and federal agencies to treat the AMD discharges before the waters are discharged in the watersheds. Typical AMD treatment involves the neutralization of the acid and the alkaline precipitation of the contained regulated metals [237]. The treatment processes are designed based on cost effectiveness [215], with quicklime being usually the most cost effective reagent, followed by

caustic soda when lime transportation costs are prohibitive [14, 142, 237].

AMD treatment is one of the major cost centers after mining has concluded and is often viewed as a nuisance waste and an obvious cost center for mining operations.

West Virginia University developed a simple process to recover REEs and other critical minerals from AMD as a pre-concentrate material by cost effective retro-fitting of the current commercial AMD treatment process [290]. In this approach, AMD discharges are initially neutralized to a pH of 4.5, effectively precipitating all iron and most aluminum ions along with a significant amount of silica. The partially neutralized solution is further neutralized to a pH of 8.5, precipitating all other regulated metals to below their discharge limit. In the process, all remaining REEs, most cobalt and manganese are precipitated as a pre-concentrate material. The metal-free water is sent to the permitted discharge point, meeting applicable clean water standards as set by the relevant local, state, and federal agencies.

1.6 Objectives

The present dissertation builds on the work undertaken by our team, with the objective of building a rare earth element supply chain from AMD to reduce the supply risk to our military. In order to do so, conventional and novel approaches for the extraction, refining and separation of REEs from AMD-derived feedstocks were developed and conceptualized. A significant portion of my research was centered around the development of novel extractants, among which ionic liquids and styrene-Phosphorus extractants and the development of cost effective processes for the recovery and purification of REE. One such area of investigation

involves the selective removal of zinc and calcium from REE feedstock and from mixed REE products.

In summary, the itemized objectives of this study are to:

1. Conduct a critical review of recent developments in the utilization of ionic liquids for the extraction, refining, separation and reduction to metals of rare earth elements.
2. Conduct a critical review of state-of-the-art and recent developments in the reduction to metal of rare earth elements.
3. Evaluate the economic potential of AMD as a resource for critical minerals, including rare earth elements.
4. Investigate the utilization phosphonium ionic liquids as a replacement for acidic extractants in AMD-derived sulfate solutions.
5. Investigate the effectiveness of an ammonium chloride cycle in selectively leaching calcium and zinc from mixed rare earth oxide concentrates and from AMD-derived preconcentrate material.

1.7 Organization

This dissertation is organized into six chapters, with the core research consisting of three standalone papers. Two of the papers have been published while the third one is in preparation for publication. An introductory chapter, followed by a literature review chapter containing two book chapters accepted for publication relevant to the dissertation, and a

concluding chapter complete the thesis. References are listed in the last section of the document.

- Chapter 1 provides the reader with an overview of the rare earth element ecosystem including market, pricing and resources. The chapter concludes on a summary of the work presented in this dissertation.
- Chapter 2 provides a comprehensive review of the utilization of ionic liquids in rare earth element processing and on the reduction to metals of rare earth elements. This chapter is composed of two book chapters accepted for publication with the following expected citations:
 - Larochelle, T., Ionic Liquids for the Processing of Rare Earth Elements, "Rare Earth Industry Status and Prospect ", Springer Nature AG, Alvin, M., Murty, Y and Lifton J.
 - Larochelle, T., Rare Earth Elements Reduction to Metals, "Rare Earth Industry Status and Prospect ", Springer Nature AG, Alvin, M., Murty, Y and Lifton J.
- Chapter 3 presents a techno-economic analysis for the recovery of rare earth elements from acid mine drainage using innovative process design techniques. This chapter was published in the peer review journal Minerals with the citation: Larochelle, T., Noble, A., Ziemkiewicz, P., Hoffman, D., and Constant, J., "A fundamental economic assessment of recovering rare earth elements and critical minerals from acid mine drainage using a network sourcing strategy," Minerals, vol. 11, no. 11, pp. 1–18, 2021, doi: 10.3390/min11111298
- Chapter 4 summarizes our investigations into using ionic liquids as a replacement for acidic extractants in AMD-derived sulfate solutions. This chapter was published in the

peer review journal Minerals with the citation: Larochelle, T.; Noble, A.; Strickland, K.; Ahn, A.; Ziemkiewicz, P.; Constant, J.; Hoffman, D.; Glascock, C. Recovery of Rare Earth Element from Acid Mine Drainage Using Organo-Phosphorus Extractants and Ionic Liquids. Minerals 2022, 12, 1337. <https://doi.org/10.3390/min12111337>

- Chapter 5 summarizes our investigations into using an ammonium chloride leach cycle for the selective recovery of calcium and zinc from mixed rare earth oxide concentrates and from AMD-derived concentrate materials. This chapter is being prepared for peer-reviewed publication.
- Chapter 6 summarizes the key findings of this work, describes holistic conclusions, and introduces opportunities for further research and development.

Chapter 2

Review of Literature

2.1 Ionic Liquids for the Processing of Rare Earth Elements

This section was approved for publication as a Chapter in a Book with the expected citation:

Larochelle, T., Ionic Liquids for the Processing of Rare Earth Elements, "Rare Earth Industry Status and Prospect ", Springer Nature AG, Alvin, M., Murty, Y and Lifton J.

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Abstract:

Ionic Liquids are room temperature organic molten salts being investigated for various metallurgical processing applications. Specifically, the application of ionic liquids in the extraction, refining, separation and reduction of the rare earth elements provides many opportunities for reducing the processing economic and environmental costs. The primary fields of research involve the replacement of organic diluents and extractants in solvent extraction, their utilization in flotation and their application in electrometallurgy. Additionally, ionic liquids

are being investigated as a replacement for water, transitioning from hydrometallurgy to solvometallurgy. Advantages of ionic liquids include their low vapor pressure, high thermal stability and significant variability in coordination ability. This later advantage allows researchers to design task specific ionic liquids with targeted characteristics. In electrometallurgy, ionic liquids allow for the electrodeposition of highly water-reactive metals such as the rare earth elements and offer a potential alternative to high temperature molten salt electrolysis and metallothermic reduction processes.

2.1.1 Introduction

This chapter provides an overview of the utilization of ionic liquids (ILs) for processing rare earth elements. Ionic liquids have been extensively researched and many historical perspectives have been published [15, 154, 268, 269]. Ionic liquids are an established field of study with upwards of 3,500 papers published annually [268]. The application of ILs to the rare earth industry is, however, relatively novel.

Ionic liquids are organic salts with melting points usually below ambient temperature. Their melting point is not definitive, and many authors specifically discretize room temperature ionic liquids (RTILs) as a subset of ILs. The definition generally accepted in the rare earths industry is that the melting point of ILs ought to be lower than the boiling point of water. The fundamental criteria distinguishing ILs from other liquid solvents is the absence of molecular species in the liquid phase.

The primary field of research for the utilization of ILs in the extraction and refining of rare earth elements (REE) is as a substitute for the organic phase(s) in the solvent extraction

separation process. Ionic liquids are often described as a green alternative to organic solvent due to their negligible vapor pressure and high thermal stability [154]. Pham [239] reviewed studies on the impact of ILs on the environment and concluded that the ‘green’ designation may not be warranted since the high chemical and thermal stability of ILs combined with their low vapor pressure may be a Faustian bargain. The valuable characteristics of ILs will likely lead to persistence and accumulation in the environment. Most ILs, especially perfluorinated anions and long alkyl chain cations are particularly toxic to aquatic ecosystems. Due to their ionic nature, ILs solvents tend to be more soluble in aqueous phases than their molecular organic counterparts.

Other advantages of ILs as alternatives to the organic components in the solvent extraction systems include their significant variability with regard to viscosity, polarity, solubility and coordination ability [154] allowing for their optimization with regard to specific extraction systems. While deep eutectic solvents such as choline chloride-carboxylic acid present characteristics and behaviors similar to ILs [66], they will be excluded from the present discussion since they do not meet the definition of ILs.

First, the primary ILs being investigated will be discussed followed by an overview of their usage in solvent extraction processes as replacement for conventional extractants and/or solvents. Specific comparisons will be presented for yttrium recovery processes where the value of ILs is most apparent. A new approach to solvent extraction using Aqueous Two-Phase Systems (ATPS) will also be discussed. Following the solvent extraction discussion, the recent investigations into applications of ILs to mineral processing will be reviewed. Finally, electrometallurgical applications of ILs will be discussed. All these applications for ILs in REE processing are integrated into the concept of solvometallurgy.

Solvometallurgy is a recent umbrella term that includes hydrometallurgy and systems with other non-molecular organic solvents such as molten inorganic salts, deep eutectic solvents, polymer solvents and ionic liquid solvents.

Similar to hydrometallurgy, the first step in solvometallurgical processing of REE is to solubilize the lanthanides. Ionic liquids such as betainium bis-(trifluoromethylsulfonyl)imide, [Hbet][NTf₂] have been extensively studied for that purpose using various raw materials such as NdFeB waste magnets [60, 166, 167], bauxite residue [28, 50, 51], lamp phosphor [61, 80] and carbonatite ore [52]. In addition, and to a lesser extent, imidazolium-based ILs have been reported as leaching solutions for lanthanides [28, 67, 201, 206]. The direct utilization of [H][NTf₂] for the leaching of rare earth carbonate prior to the electrodeposition has also been recently reported by Martinez [141]. Subsequent processing steps typically involve solvent extraction, aqueous two-phase systems selective precipitation using bases such as sodium hydroxide and/or acids such as oxalic acid and/or electrometallurgy.

A highly promising approach to solvometallurgy was recently developed by Pr. Binnemans' group at KU Leuven [89, 128, 129]. Rather than use acids to leach metals, they integrated chlorine to chloride ILs, generating [Cation][Cl₃], ILs with oxidative capabilities towards metals [128]. Li then applied this strategy to the separation of REE and transition metals from NdFeB permanent magnets using [P66614][Cl] as the IL underlying the system [129]. This approach only utilizes chlorine and ammonia as reagents, both of which are available as inexpensive commodity materials and which generate little wastewater. Other related processes such as the use of pyridinium chloride [PyrH][Cl] are also investigated for the recovery of metals and alloys in solvometallurgical approaches. Orefice and Binnemans propose a

closed loop process using such an approach where hydrochloric acid, oxalic acid and ammonia are the main reactants [89] In this process, conventional acidic extractants including 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) and Cyanex 923 are used in p-cymene along with C101 IL.

2.1.2 Nomenclature and Molecular Structure of Selected Ionic Liquids Cations and Anions

Ionic liquids are customarily named using both ions of the molecule in brackets, the cation on the left and the anion on the right. No formal naming convention currently exist, yielding various nomenclatures for the same molecules. Table 2.1 and Table 2.2 present the usual nomenclature and alternate names for commonly used cation and anions in ILs. The structure of such ions is also presented in Figure 2.1 and Figure 2.2, respectively. It is customary to use elemental symbols for single elements such as [Cl] for a chloride ion or [Br] for a bromide ion. In addition to their trade names, complex molecules are customarily named using the first letter of the major functional groups in the molecule. 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester is thus commonly referred to as EHEHPA, P507, Ionquest801 or PC-88A. The cation portion of ILs can also be represented by its trade name, by convention using the anion base element and its molecular structure or by a generic molecular descriptor. The Aliquat 336 cation is thus alternatively referred to as [Aq336], [A336], [N1888], [R4N] and/or trioctylmethylammonium.

Acid-base ILs are formed when an acidic extractant is used as an anion for an IL and an ammonium or phosphonium salt is used as a cation. In this combination, it is customary

to refer to the IL using the molecular structure of both ions. An acid-base IL formed using P507 and Aq336 would thus be named trioctylmethylammonium 2-ethylhexyl mono-2-ethylhexyl ester phosphate [N1888][EHEHP]. In most cases the acidic extractant structure is used without the ending ‘A’ since it is no longer an acid. This IL is also referred to as [A336][P507].

2.1.3 Solvent Extraction

Solvent extraction is a natural application for ionic liquids in REE processing as they can be substituted for every phase of the solvent extraction system. While the primary application of ILs in solvent extraction is replacement for the conventional extractants, the replacement of the organic phase with an IL also provides many significant advantages. The replacement of the aqueous phases with ILs has not been as extensively studied since solvometallurgical lixiviation is a nascent field of research.

The fundamental nature of ILs as molten salts composed as an anion and as a cation allows for the creation of highly effective ILs where both ions actively participate in the extraction process. This is referred to as acid-base coupling task specific functional ionic liquids (ABC-TSFILs) and tend to produce the best results in terms of extraction efficiency when both ions have extraction capabilities by themselves. Most of the ABC-TSFIL research is targeted at combining such conventional extractants in an IL form. Since both ions are typically large, the resulting IL tends to be highly viscous, which reduces the phase mass transfer rate and prevents the usage of ABC-TSFILs as solvent. Thus, molecular organic solvents are still relevant.

Table 2.1: Cations of Ionic Liquids Relevant to the Processing of Rare Earth Elements.

Category	Cation	Name	Fig.	Note
Ammonium-Based	[N888],[Am336],[A336]	tri-n-octylammonium	1(a)	
	[N1888],[Aq336], [A336], [TOMA]	trioctylmethylanmonium	1(b)	
	[N4444],[TBA]	tetrabutylammonium	1(c)	
	[N8888], [TOA]	tetraoctylammonium	1(d)	
	[TEHA]	tri-(2-ethylhexyl)ammonium	1(e)	
	[N6222]	n-hexyltriethylammonium	1(f)	
	[OcGBOEt]	trioctyl(2-ethoxy-2-oxoethyl)ammonium	1(g)	
	[DEME]	N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium	1(h)	
Phosphonium-Based	[P66614],[T66614], [THTP]	triethyl(tetradecyl) phosphonium	1(i)	
	[P8884COOH]	(4-carboxyl)butyl-trioctyl-phosphonium	1(j)	
Imidazolium-Based	[C(i)C(i)im]	Alkyl-Alkyl-imidazolium	1(k)	R1=2,4,6,8,10*
	[C(i)COOHC(i)im]	Alkyl-Carboxyl-Alkyl-Imidazolium	1(l)	R2=1,2,4* R1=3,4,5,6,7,8* R2=1,3*
Pyridinium-Based	[C(i)C(i)Pyr]	Alkyl-Alkyl-pyridinium	1(m)	R1=2,4,6,8,10*
	[C(i)C(i)Pip]	n-Alkyl-n-Alkyl-piperidinium	1(n)	R2=1,2,4* R1=2,4,6,
	[N11N11PipGua]	Dis-1,2 Methyl Guanidinium Piperidinium	1(o)	R2=1, 2 R1=1,2*
Other Cations	[EC]	Etylene Carbonate	1(p)	

*: Other alkyl chain lengths are likely possible but haven't been tabulated in the surveyed literature

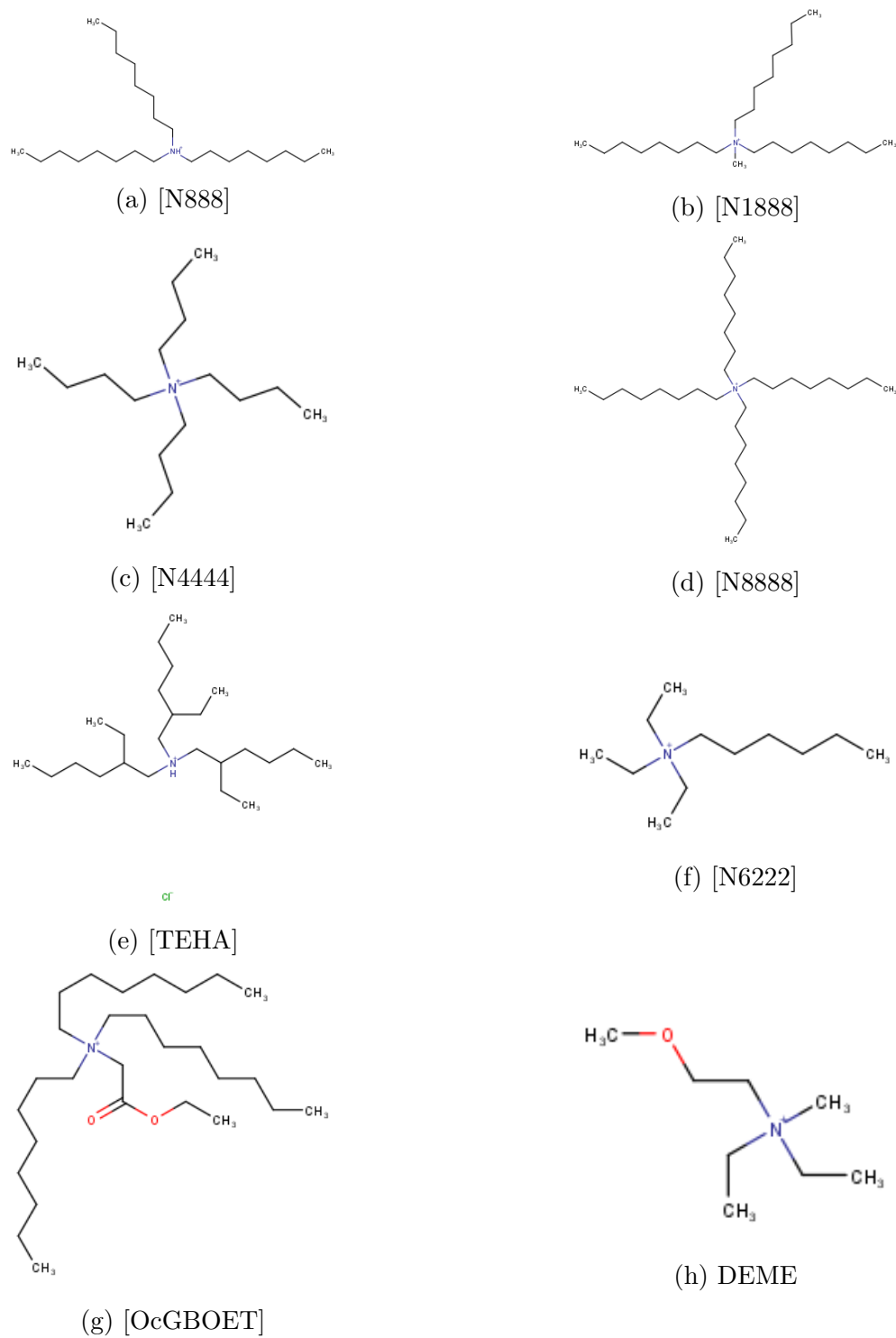
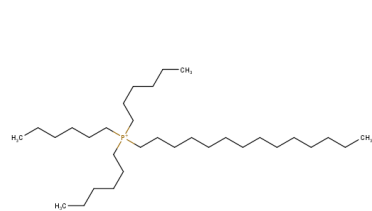
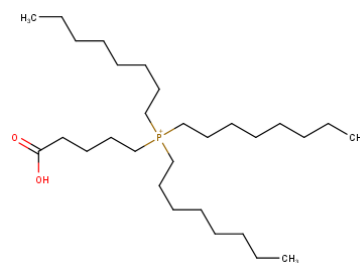


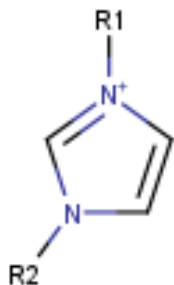
Figure 2.1: Cations of Ionic Liquids Relevant to the Processing of Rare Earth Elements



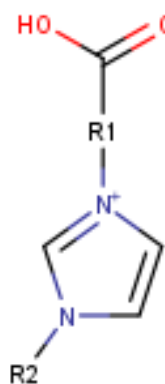
(i) [P66614]



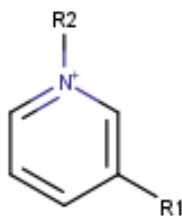
(j) [P8884COOH]



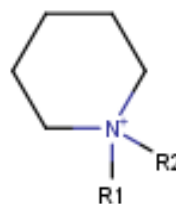
(k) [C(i)C(i)im]



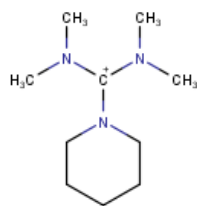
(l) [C(i)COOHC(i)im]



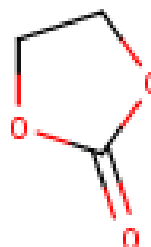
(m) [C(i)C(i)pyr]



(n) [C(i)C(i)pip]



(o) [N11N11PipGua]



(p) [EC]

Figure 2.1: Cations of Ionic Liquids Relevant to the Processing of Rare Earth Elements

Table 2.2: Cations of Ionic Liquids Relevant to the Processing of Rare Earth Elements.

Category	Anion	Name	Figure Number
Fluorine-Nitrogen-Based	[NTf2],[TFSI],[TFSA],[OTF]	bis(trifluoromethylsulfonyl)azanide *	2(a)
	[BETI]	bis(perfluoroethanesulfonyl)azanide	2(b)
	[NfO]	Nonafluorobutanesulfonate	2(c)
Phosphorus-Based	[PF6]	hexafluorophosphate	2(d)
	[C272],[BTMPP]	bis(2,4,4-trimethylpentyl)phosphinate	2(e)
	[D2EHP]	Di(2-ethylhexyl)phosphate	2(f)
	[EHEHP]	Mono-(2-ethylhexyl) 2-ethylhexyl phosphonate	2(g)
OxyAcetate-Based	[SNPAA],[CA100]	sec-nonylphenoxyacetate (R1=7)	2(h)
	[SOPAA],[CA12]	sec-octylphenoxyacetate (R1=6)	2(h)
	[NOPAA],[OCTPOA]	n-octylphenoxyacetate	2(i)
	[DMHPAA],[POAA]	(2,6-dimethylheptyl) phenoxy acetate	2(j)
	[IOPAA]	4,4-isopropylidene bis (phenoxyacetate)	2(k)
Organic Acid-Based	[BA]	Benzoate (R1=Bz)	2(m)
	[DA]	Decanoate (R1=9)	
	[Ol],[OA]	Oleate (R1=17, monosaturated)	
	[LA]	Laurate (R1=11)	
	[PA]	Palmitate (R1=15)	
	[LiA]	Linoleate (R1=17, monosaturated)	
Diglycolamate-Based	[BDGA]	dibutyl diglycolamate (R1=4)	2(n)
	[DHDGA]	dihexyl diglycolamate (R1=6)	
	[DODGA]	dioctyl diglycolamate (R1=8)	

*: Other alkyl chain length are likely possible but havent been tabulated in the surveyed literature

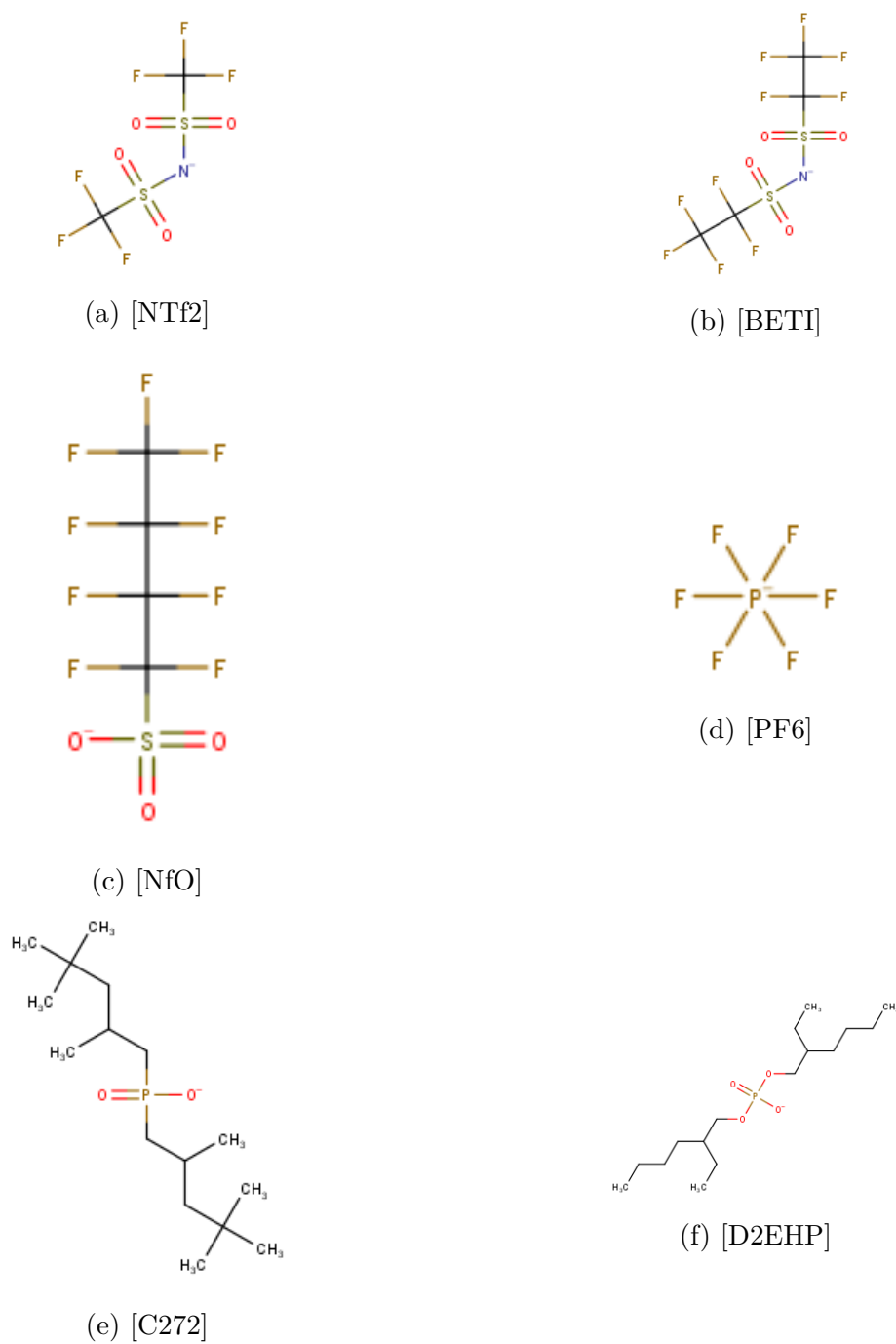


Figure 2.2: Anions of Ionic Liquids Relevant to the Processing of Rare Earth Elements

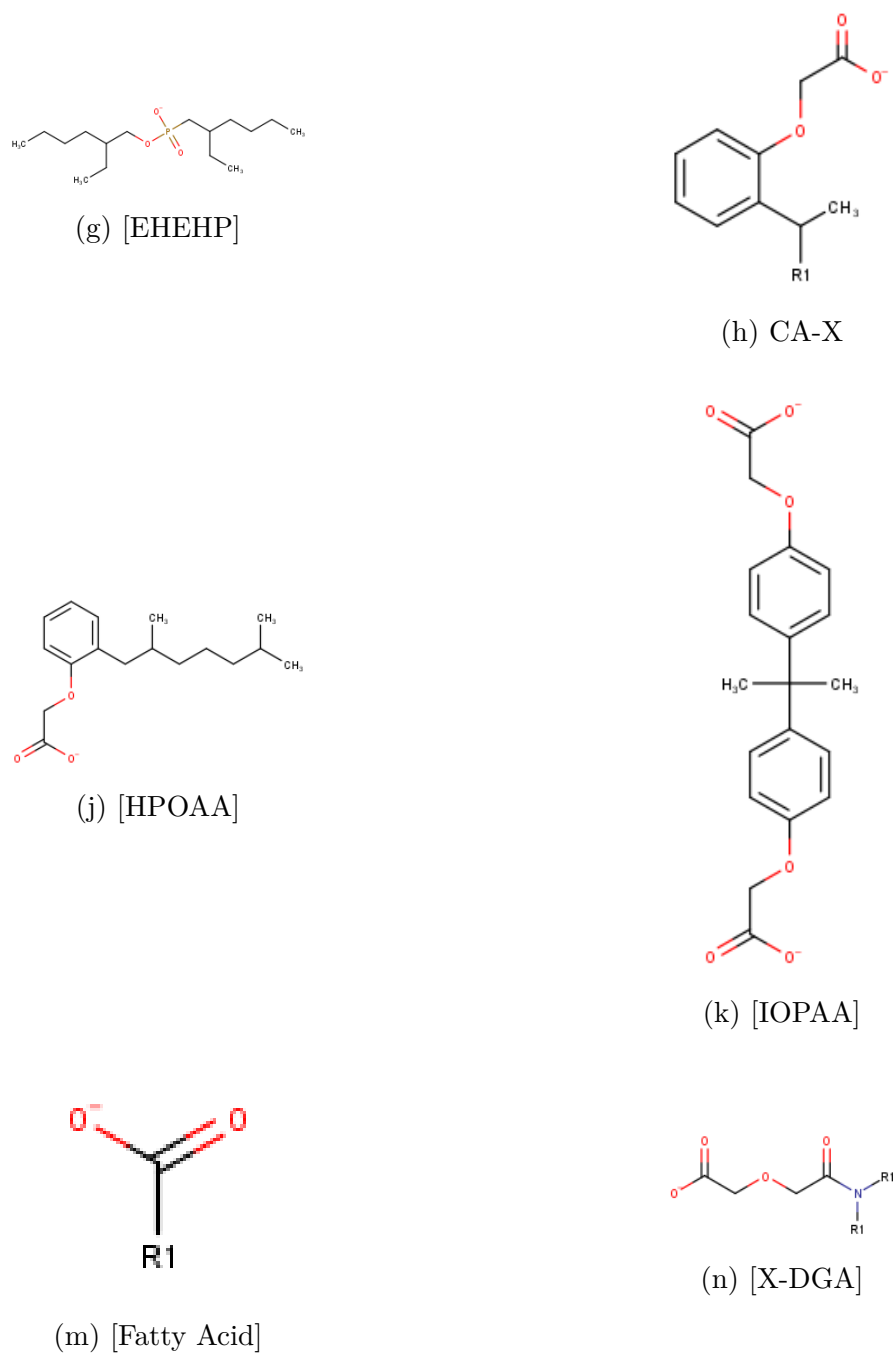


Figure 2.2: Anions of Ionic Liquids Relevant to the Processing of Rare Earth Elements

In parallel, research has been undertaken on the use of ILs as a replacement for molecular organic solvents. In contrast to ABC-TSFILs, ILs targeted for the replacement of molecular organic solvents tend to be composed of a large cation and a smaller halogen anion providing them with a lower viscosity. These include Cyphos 101 IL, [P66614][Cl] which contain functional ions and are referred to as task specific functional (TSFILs), while others such as imidazolium salts [C(i)C(i)im][anion] are non-functional and are referred to simply as IL. It is important to note that many of the IL investigated for the replacement of molecular organic solvents also exhibit a significant extraction potential for REE, allowing the design of very efficient systems through the combination of ABC-TSFIL extractants dissolved in TSFIL or in non-functional ILs.

In addition to the substitution of reagents in the conventional extraction systems, ILs also allow for the design of aqueous two-phase systems (ATPS) which are further discussed in a subsequent section. ATPS consist of an IL phase that is fully soluble in the aqueous phase under specific operating conditions but insoluble under different operating conditions.

Detailed literature reviews on the use of ILs for the solvent extraction of REE have been previously published [20, 261, 262] and technical aspects of the solvent extraction of rare earths have been discussed in Section 2.2. As such, this section will focus on providing the reader with an introduction to the utilization of ILs in the solvent extraction of REE as well as an update on the current state of the literature.

Use of Ionic Liquids as Extractants

The first entry of ILs in the REE industry will most likely be as the replacement of a conventional extractant by its IL equivalent. This process function has been addressed in numerous technical articles, which are summarized in Table 2.3 . While the generally accepted benefits of using ILs (non-flammability, no vapor pressure and high stability) may not be achieved by focusing on the extractant portion of the solvent extraction system, other benefits can be realized without engendering the downside of ILs (high losses in the aqueous phase).

The most significant proposed benefits of a transition to ILs extractants is a potential reduction of the extraction system total volume and number of stages through either higher loading capacities and/or greater separation factors coupled by a potential reduction of wastewater generation through the elimination of saponification and in specific cases a reduction of the stripping acidity required. The losses of ILs extractant is also mitigated when using molecular organic solvent because of a more favorable aqueous partition ratio when compared to the equivalent acidic extractant. Su et al. [221] revealed that the solubility of [Aq336][EHEHP] was around an 0.5-order of magnitude lower than that of EHEHPA in the investigated system. A significant amount of research is still required to fully grasp the challenges and benefits of ILs with respect to their solubility in the aqueous phase.

The most studied acid-base coupling task specific functional ILs are thus unsurprisingly a combination of the leading industrial extractants, D2EHPA and EHEHPA. To a much lesser extent, ABC-TSFILs based on HSOPAA and Cyanex 272 have also been investigated. Given the overlap, many investigations purport to compare ABC-TSFILs with their acidic anion; however, few offer a comparison properly using equivalent equilibrium conditions as a basis

for comparison. A striking example involves most investigations into Cyanex 272-based ILS extractants which have been done using experimental conditions preventing a direct comparison with Cyanex 272 literature and thus are not worthy of discussing in detail. Some of the cases that do provide an appropriate comparison are summarized below. One such IL is Cyphos 104 IL which is a commercial IL of composition [P66614][C272] that is seeing increased activity in the literature.

A study on the extraction of yttrium by Devi and Sukla [56] revealed that [P66614][C272] presented a very similar extraction profile to [Aq336][C272], suggesting that the [C272] anion is the most significant ion in the extraction. Building on the promises of the [C272] anion, Zeng [277] increased the functionality of the cation by adding a phosphoryl unit to the ammonium-based cation, pioneering multifunctional ILS. The application of this novel [N888DOPE][C272] IL to Tm, Yb and Lu revealed increased extraction capabilities and separation factors compared to [N1888][C272]. Hopefully the authors will further investigate this new extractant with regard to other REE.

Deng utilized the steric hindrance property of a phenyl group toward yttrium [265] to theorize and synthesize a functional IL targeted at yttrium purification [53]. However, the separation factors for HREE and Y are lower than with either [P66614][SOPA] or [N1888][ND]. Using similar considerations, Hu designed, synthesized and tested the IL [(CH₂)₇COOHPyr][NTf₂], which yielded separation factors between [P66614][SOPA] and [N1888][ND] [89]. While this later IL contains fluorine, its high separation factor suggests additional work with alternative anions would be warranted.

Of particular industrial interest is the replacement of Sec-octylphenoxy acetic acid (CA-12,

Table 2.3: Utilization of Ionic Liquids as Extractant for Rare Earth Elements Separation.

Anion	Cation	Ionic Liquid	Rare Earth Element(s) [Reference]
[BA]	[P66614]	[P66614][BA]	Nd [174]
[BDOAC]	[P66614]2	[P66614]2[BDOAC]	Nd [222]
[BDGA]	[N1444]	[N1444][BDGA]	LREE [178]
[C272]	[N6222] [Am336]	[N6222][C272] [Am336][C272]	La/Nd [111], Pr/Nd [134] Pr/Nd [134, 135], La/Pr/Nd [136], Tb/Dy [163]
	[Aq336]	[Aq336][C272]	Lu [284], Pr/Nd/Fe/B [169], Tb/Dy [163], La/Y [56], HREE [232, 283]
	[N4444] [P66614]	[N4444][C272] [P66614][C272], Cyphos 104	HREE [232] La/Ni [197], La/Y [56], Sm/Co [153], REE [112, 152], HREE [138]
[Cl]	[P66614] [Aq336] [P8884COOH]	[P66614][Cl], Cyphos 101 [Aq336][Cl] / Aliquat 336 [P8884COOH][Cl]	Nd [252], REE [91, 112] REE [91], Nd [252], Sm/Co [217] REE/Co/Ni [281]
	[P66614]	[P66614][NO3]	La/Sm/Co/Ni [251], Nd/Dy [189], REE [118, 194]
	[P8884COOH] [Am336] [Aq336] [N1444]	[P8884COOH][NO3] [Am336][DGA] [Aq336][NO3] [N1444][NO3]	REE/Co/Ni [281] REE [193] REE [4, 118, 119, 217], Pr/Nd/Dy [113] Nd/Fe [225], Pr/Nd [226]
[D2EHOM]	[C(i)mim]	[C(i)mim][D2EHOM]	REE [120]
[D2EHP]	[C(i)mim]	[C(i)mim][D2EHP]	REE [196]
	[C(i)mpy]	[C(i)mpy][D2EHP]	REE [196]
	[P66614]	[P66614][D2EHP]	REE [230]
	[Aq336]	[Aq336][D2EHP]	Pr/Nd/Fe/B [169], MREE [93, 94], REE [81, 230, 231, 274]
	[N2222]	[N2222][D2EHP]	REE [227]
	[N4444]	[N4444][D2EHP]	REE [196, 227, 230]
	[N8888]	[N8888][D2EHP]	REE [227]
	[Am336] [N88]	[Am336][D2EHP] [N88][D2EHP]	REE [98] REE [98]
[DHDGA]	[OcGBOEt]	[OcGBOEt][DHDGA]	REE [101, 102]
	[Aq336]	[Aq336][DHDGA]	REE [101, 102]

Table 2.3: Utilization of Ionic Liquids as Extractant for Rare Earth Elements Separation.

Anion	Cation	Ionic Liquid	Rare Earth Element(s) [Reference]
[EHEHP]	[Aq336]	[Aq336][EHEHP]	REE [58, 81, 180, 181, 182, 211, 221, 274]
	[N2222]	[N2222][EHEHP]	REE [227]
	[N4444]	[N4444][EHEHP]	REE [227], HREE [232]
	[N8888]	[N8888][EHEHP]	REE [227]
	[P66614]	[P66614][EHEHP]	Lu [284], REE [283]
	[N1888]	[N1888][EHEHP]	HREE [232]
[MA]	[P66614]	[P66614][MA]	REE [194]
[MOx]	[C(i)mim]	[C(i)mim][MOx]	REE [120]

SOPAA) by [P66614][SOPA] evaluated by Dong Yamin [59] for the separation and purification of yttrium. Dong Yamin determined that the IL [P66614][SOPA] had four times the extraction capacity of SOPA and presented greater separation factors at equivalent operating conditions. In addition, [P66614][SOPA] did not require saponification and could be stripped using distilled water as opposed to conventional SOPAA-TBP extraction systems requiring up to 3 molar acidity and 90 percent saponification [264]. A comparison of the separation factors for both systems is presented as Table 2.4.

Table 2.4: Separation Factors for SOPAA and [P66614][SOPA].

Extractant	Ho/Y	Er/Y	Tm/Y	Yb/Y	Lu/Y	Reference
SOPAA	1.74	1.68	1.35	1.27	1.08	[264]
[P66614][SOPAA]	1.94	1.94	2.78	4.17	5.00	[59]

SOPAA: 0.7 M, 15%TBP in kerosene 90%Saponified, 0.3M REE, Initial pH = 4
[P66614][SOPAA]: 0.05M in kerosene no Saponification, 0.003M REE, Initial pH = 3.5

In addition to SOPAA extraction systems, naphthenic acid and neodecanoic acid (NDA) are also used commercially and are the focus of IL research. The investigation of REE extraction by [N1888][ND] by Su revealed that the IL is significantly more efficient in the separation of yttrium from HREE than its NDA precursor [220]. A comparison of the separation factors for both systems is presented as Table 2.5.

Table 2.5: Separation Factors for NDA and [N1888][ND].

Extractant	Ho/Y	Er/Y	Tm/Y	Yb/Y	Lu/Y	Reference
NDA	2.1	2.7	4.1	6.1	6.4	[220]
[N1888][ND]	2.64	4.3	7.7	12.5	16.3	[220]

[N1888][ND] and NDA: 0.3M, NDA is fully saponified. 0.15M REE, pH = 5, O:A = 1

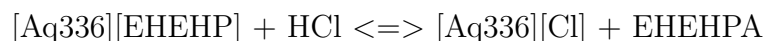
The separation of Eu from Gd using either D2EHPA or [Aq336][D2EHP] in both chloride and nitrate medium was investigated by Ismail [93]. They found that at very low acidity in chloride medium, [Aq336][D2EHP] was superior to D2EHPA but that around 3M HCl, both extractants were equivalent. It was also determined that the nitrate media presented better extraction and separation efficiencies over the complete acidity range studies. Furthermore, [Aq336][D2EHP] was found to be superior to D2EHPA at all evaluated HNO₃ concentrations with optimum nitric acid concentrations of 3.5 M and 3.0 M, respectively. Ismail [94] used their data to simulate a counter-current separation cascade and determined that the number of stages of the cascade could be halved by using [Aq336][D2EHP] instead of D2EHPA in the system. They reported that the extraction cascade could be reduced from 8 stages to 4 stages and that the scrubbing cascade could be reduced from 5 stages to 2 stages. In a follow-up study, Ismail [94] addressed the recovery of Sm from a MREE solution using [Aq336][D2EHP] using bench-scale data to model a cascade which was subsequently piloted. The separation factor Sm/(Eu-Gd) is on the same order of magnitude as the separation factor Sm/Eu = 1.6 and Sm/Gd = 2.53 as reported by Alstad [9].

Investigation into an EHEHPA-based ABC-TSFIL extractant also produced similar results to D2EHPA-based extractants where extraction capabilities of the EHEHPA-based ABC-TSFILs are higher than EHEHPA under similar conditions while maintaining similar separation factors. In their comparative study of [Aq336][EHEHP] and EHEHPA on the extraction of HREE, Dong [58] reported a 50% increased extraction capacity with similar separation

factors for the extraction of HREE in chloride media. Although the [Aq336][EHEHP] system requires a slightly higher stripping solution acidity (0.2M) than the EHEHPA system (0.13M) to recover all REE from the organic phase, the stripping curve slope is less steep suggesting a better scrubbing efficiency at equivalent acidity.

Similar to acidic extractants, synergistic (antagonistic) interactions between ILs extractants have been proven to affect the extraction mechanism of the extraction system more than the sum of the effect of both extractants. Zhao [283, 284] demonstrated that the system [P66614][EHEHP]/[Aq336][C272] produced an antagonistic effect on extraction with regards to using [Aq336][C272] by reducing the stability of the extracted species similar to the EHEHPA/C272 system [179]. This was further demonstrated by a lower required stripping acidity estimated at 1.5M to 2 M for the mixture of ILs compared to 3M to 4 M for the mixture of acidic extractants [133]. In addition, the IL mixture had substantial synergistic impact on the separation factor between the REE. This synergistic impact with regard to C272 was not significant in the acidic extractants study [179].

Notwithstanding the promises of ABC-TSFILs as extractants, similar to conventional solvent extraction research, it is essential to note that most studies are performed under dilute concentrations and may not be directly translatable to commercial applications. Of particular interest is the study of the stability of ILs. Quinn [180, 181, 182] studied the effects of using an HCl medium with the extractant [Aq336][EHEHP]. They determined that under certain conditions, the IL reverted to a combination of its precursors through the extraction of HCl as shown by the following reaction:



Quinn [181] studied this system over a range of pH and chloride ion concentration and concluded that:

“Our results indicate that the combination of Aliquat 336 and EHEHPA behaves as a mixture of R4N EHEHP and R4N Cl⁻ + EHEHPA, with the protonation dependent on the pH, and not as a different chemical form. Hence, regardless of how the IL has been prepared, once it is exposed to acid containing solutions, the acid-base behavior of the IL is indistinguishable from a mixture of the two reagents.”

Undoubtedly, future studies will evaluate other acid-base coupling TSFILs and consider whether they too act as a combination of their precursors or as distinct extractants. Dong [59] found that in the case of Cyphos 101 IL ([P66614][Cl]) and SOPAA, the ABC-TSFIL [P66614][SOPA] was significantly superior to the combination of its precursors indicating sufficient stability to be considered a distinct extractant.

Use of Ionic Liquids as Solvents

The utilization of ILs as a replacement for organic molecular solvents in rare earth solvent extraction processes has been the subject of a significant amount of research in the last decade. Table 2.6 presents a summary of the existing literature on the utilization of ILs as solvents for REE extraction systems.

Initial research focused on imidazolium [C(i)im] and pyridinium [C(i)pyr] cations using hexafluorophosphate [PF6] and bis(trifluoromethanesulfonyl)imide [NTf2] anions for their low

Table 2.6: Utilization of Ionic Liquids as Solvents for Rare Earth Elements Extraction Systems.

Diluent	Extractant - [Reference]
[C(2)mim][Cl]	[P66614][C272] [197]
[P66614][NO ₃]	Self [251]
[P66614][Cl]	D2EHPA [271]
[P66614][NTf ₂]	[N4BMalBbim][NTf ₂] [32]
[Aq336][NO ₃]	Self [118, 119, 189], [Aq336][DGA] [193], TBP [189], Cyanex 923 [189]
[N1444][Tf ₂ N]	Self [196], [N444][D2EHP] [196], [C6mpyr][NTf ₂] [196], [C6mim][NTf ₂] [196]
[C6mpyr][Tf ₂ N]	D2EHPA [196], [C6mpyr][DEHP] [196], [N444][D2EHP] [196]
[Aq336][SCN]	Self [23, 189], TBP [189], Cyanex 923 [189]
[P66614][SCN]	Self [23, 189], TBP [189], Cyanex 923 [189]
[C2mim][PF ₆]	”D2EHPA [276]
[C4mim][PF ₆]	Self [172], D2EHPA [276], TPMDPO [242], CMPO [20, 158], BzAc [171], EHEHPA [170], HQ [172]
[C6mim][PF ₆]	TBP [13], Cyanex 272 [13], D2EHPA [13]
[C8mim][PF ₆]	Self [292], Cyanex 925 [228], N1923 [291], DEHEHP [293]
[C4mpyr][PF ₆]	D2EHPA [276]
[C4mim][NTf ₂]	Self [147], [Aq336][D2EHP] [231], [(C(i)COOHmin)[Tf ₂ N] [39], CMPO [20], DODGAA [273], TPMDPO [242], Diaza-crown [243], TBP [147, 244], TODGA [244]
[C6mim][Tf ₂ N]	[P66614][D2EHP] [230], [Aq336][D2EHP] [230, 231], D2EHPA [11, 196], [C6mim][D2EHP] [196], [N4444][D2EHP] [196, 230], [(C(i)COOHmin)[Tf ₂ N] [39], TOPO [12], TBP [11, 12]
[C8mim][Tf ₂ N]	[Aq336][D2EHP] [231], EHEHPA [110], DODGAA [273], [C(i)COOHpim][PF ₆] [263], [(C(i)COOHmin)[Tf ₂ N] [39]
[C10mim][Tf ₂ N]	[Aq336][D2EHP] [231], [(C(i)COOHmin)[Tf ₂ N] [39]
[C12mim][Tf ₂ N]	DODGAA [273]
[C(i)mim][[BETI]	REE [231]
[C(4,6,8,10)mim][BETI]	[Aq336][D2EHP] [231]
[(C(3,5,7)COOHmin)[Tf ₂ N]	Self [38]

Table 2.6: Utilization of Ionic Liquids as Solvents for Rare Earth Elements Extraction Systems.

Diluent	Extractant - [Reference]
[PEGmim][NTf2]	Self [82]
[C6C2C2C2m3im][I]	Self [183]
[C6C2C2m3im][SCN]	Self [183]
[N888][DA]	Self [146]
[P8884COOH][Cl]	Self [281]
[P8884COOH][NO3]	Self [281]
[N1888][NTf2]	CMPO [195], D2EHPA [195]
[P66614][OPBOA]	Self [223]
[C(4,5,6)mim][NfO]	Self [107]

viscosity and ease of utilization. Extraction of REE in these pure non-functional IL solvents did not prove significant and resulted in heavy losses of fluoride-based ILs in the aqueous phases. In order to increase the extraction capabilities of these systems, complexating agents such as carbamoylmethylene phosphine oxides (CMPO), diglycolamides (DODGA, TODGA) and conventional metal extractants such as Cyanex 923, D2EHPA and EHEHPA have been investigated.

However, environmental considerations reduced the incentive of using such ILs and the focus was reoriented toward non-fluoride ILs, especially TSFILs such as phosphonium and ammonium-based ILs using chloride or nitrate as an anion usually in combination with an extractant. Perfluorinated imidazolium and pyridinium ILs were the first ionic liquids studied as potential replacement for organic solvents in the rare earth separation processes. While they show clear advantages such as their negligible vapor pressure and increased extraction capabilities, the cost of such ILs and the stability of the perfluorinated anion combined with its toxicity [257] in waste water effluents creates significant barriers to their industrial application. To address those issues, biodegradable/incinerable ILs are increasingly the object

of investigations. Such ILs are colloquially referred to as CHON ILs, referencing their elemental composition. Examples of such CHON ILs would include ammonium salts of fatty acids such as [N888][DA] [146, 168] or nitrates of ammonium salts such as [Aq336][NO₃] [118, 119, 189]. Phosphonium-based ILs with CHON or non-fluorine halogen anions also show significantly higher degradation rates than perfluorinated anions ILs [234]. A noticeable additional advantage of the [Aq336][NO₃] CHON IL investigated by Riano [189] and Larsson [118, 119] lies in the simultaneous usage of [Aq336][NO₃] for both the extractant and the solvent. This allows for increased extraction capacity when an additional extractant is added to the IL solvent. Xiong [271] compared using either [P66614][Cl] or [Aq336][NO₃] as the solvent with DEHEHP as an extractant and found that the phosphonium IL has a higher extraction capability than the ammonium IL.

While these non-fluoride-based TSFIL have shown great potential for the replacement of organic solvent, their cost being one to one and a half order of magnitude higher is a major impediment to their widespread adoption in the rare earth industry. It is important to note that solvents are upwards of 35% of the solvent extraction circuit volume, which is a considerable amount for commercial separations plants. Solubility of ILs is also higher in aqueous acidic phases than their organic counterparts, leading to increased operating costs. It is currently unclear if the adoption of ILs solvents in other metals solvent extraction processes will lead to increases in production and reduction in sale prices, leading to a potential adoption by rare earth refiners.

Aqueous Two-Phase System

Aqueous Two-Phase Systems (ATPS), also referred to as Aqueous Biphasic Systems (ABS) consist of a polymer or IL phase that is fully soluble in an aqueous-rich phase under specific operating conditions but is insoluble under different operating conditions. Operating parameters involved in the phase chemistry of ATPS may include temperature, ionic strength, specific component concentration or exposure to a specific wavelength.

First proposed in the mid-1950 by Albertsson [68], ATPS were developed as an alternative to solvent extraction using a combination of a polymer, salt and water. In 2012, Freire [68] proposed a review of the ATPS literature relative to the effect of ILs on ATPS. They concluded that recent advances in IL chemistry are likely to lead to a greater adoption of the technology in the industrial sector based on the significant potential advantages of ATPS over conventional solvent extraction processes. These advantages include the absence of an organic phase, a very high mass transfer rate only limited by the reaction kinetics of the system since the extraction is undertaken in a homogeneous media and rapid phase separation. However, significant barriers remain to the mass adoption of IL-base ATPS industrial processes. The most important of which being the relatively high solubility of the IL phase in the aqueous phase after phase separation, leading to significant losses of ILs in the aqueous phase of the system.

Because of its potential value in the industry, the field of IL-based ATPS research for the separation of metal ions is seeing increased activity. The first reported extraction of a lanthanide using an IL-based ATPS was undertaken in the SolvoMet Group headed by Pr. Binnemans at KU Leuven by Hoogerstraete [88] in 2013. Hoogerstraete used the IL betainium

bis-(trifluoromethylsulfonyl)imide, [Hbet][NTf₂] and the extractant betaine to extract REE and scandium from an aqueous solution using temperature as a phase transition mechanism. They found that lanthanides had a distribution ratio slightly higher than 10 while scandium had a distribution ratio greater than 500. Building on the group's research, Depuydt transitioned away from fluoride-base ILs and demonstrated that a carboxy-phosphonium IL could be used in a ATPS using sodium chloride concentration as a phase separation trigger [54]. The [Hbet][NTf₂] and betaine extraction system was also used by Huang to successfully extract REE from coal fly ash). Unfortunately, none of these authors report losses of IL or fluoride in their experiments, a critical consideration for transition to industrial usage. This recognition lead Mikeli to specifically investigate losses of [Hbet][NTf₂] IL to its strip solution. The losses reported by Mikeli are unsatisfactory for commercial application of the concept even under optimized conditions [150].

Since 2015, additional ATP systems have been successfully investigated. These ATPS include [N1444][NO₃]/NaNO₃ by Sun [225] and [P4444][Br]/NaNO₃ by Chen [40] both aiming at selectively extracting lanthanides from transition metals solutions. More recently, Vargas [253] reported a very high separation efficiency for La/Ce using a [C2mim][Cl]/K₂CO₃ ATPS and Alizarin Red S (ARS) as an extractant. In this study, a separation factor [D_{La}/D_{Ce}] of 2,600 was obtained through the complexation of lanthanum ions with ARS, and its greater affinity for the IL phase following the phase separation trigger.

A novel configuration for ATPS involves its combination with traditional solvent extraction where the ATPS is contacted with an organic phase containing a traditional extractant, followed by tri-phase separation. Both three-phases organic-ATPS-based systems using a polymer and IL-based ATPS have been scarcely investigated, and they present an exciting

research opportunity. Sun [226] successfully used three-phase organic-IL ATPS to separate Nd from Pr and obtain a Nd-rich organic phase, a Pr-rich IL phase and a depleted aqueous phase. In this study, Sun used P507 diluted in dodecane for the organic phase, [N1444][NO₃][NaNO₃] for the IL phase and a HNO₃/NaNO₃ solution for the aqueous phase. Sun concluded that a separation factor as high as 3.5 could be attained by using a three-phase system which is much higher than the separation factor of 1.47 for the conventional solvent extraction process, or the separation factor of 1.22 obtained by ATPS separation. Interestingly, Sun also presented three-phase partitioning data pertaining to the extraction of lanthanides which strongly suggested that this system could be effectively used to separate lanthanides in light/medium and heavy groups with fewer stages than the current processes.

2.1.4 Mineral Processing

The usage of ILs in flotation was first applied in 2012 to the flotation of herbicides from yogurt [126]. In the minerals processing field, it is still a nascent research subject, with its first publication by Sahoo on the flotation of quartz from naturally occurring banded hematite quartzite ore in 2014 [202]. Azizi at University Laval and Montreal Polytechnic had first applied the IL [N4444][D2EHP] to the flotation of rare earth minerals, specifically monazite and bastnaesite [18] in 2016. They demonstrated that [N4444][D2EHP] was superior to the hydroxamic-based collectors for the collection of monazite and bastnaesite from calcite, dolomite and quartz.

Subsequently, Azizi tested liquid-liquid mineral separation (i.e., a combination of heavy liquid separation and flotation) for the same material composed of bastnaesite, monazite, calcite, dolomite and quartz using an aqueous phase containing 0.1M KNO₃ at various pHs and an

organic phase containing either [N4444][D2EHP], [N2222][DiOctP] or [N2222][DEHP] diluted in kerosene [19]. The experiment showed that the [N4444][D2EHP] system was optimum and selective for REE minerals over gangue minerals and would outperform the equivalent flotation system discussed previously. Building on this novel research, Azizi and Larachi studied the liquid-liquid mineral separation of a mixture of bastnaesite, monazite, calcite, dolomite and ankerite using a dual IL system [17]. In this study, the collecting IL was composed of [N4444][D2EHP] while the continuous phase IL was composed of either [EtNH3][NO3], [Emim][SCN] or [Bmmim][BF4]. The study demonstrated recoveries in the order bastnaesite > monazite > ankerite > calcite > dolomite, with both [EtNH3][NO3] and [Emim][SCN] outperforming the aqueous-IL liquid-liquid mineral separation system. [Bmim][BF4] did not allow any separation, which lead the author to conclude that viscosity is a significant factor in the system governing factors.

Research activity in the use of ILs for the flotation of rare earth mineral remains limited with publications on the flotation of bastnaesite using the IL [N2222][EHEHP] by Li in 2020 [127]. The study found that [N2222][EHEHP] was effective for the flotation of hematite and bastnaesite from quartz minerals. However, the affinity was greater with hematite over bastnaesite, leading the author to test and recommend a two-stage approach in which hematite would be floated first by starving the system of the collector, followed by bastnaesite using increased collector dosages.

While the application of ILs for the mineral processing of rare earth ores appears to be promising for low iron-containing ores, the recovery of the IL from the separated minerals has not yet been addressed in the literature and may prove to be cost prohibitive. Further research in the area is expected given the high potential of this new field.

2.1.5 Electrometallurgy

The use of ILs in electrometallurgical processes promises to significantly reduce the environmental footprint associated with the production of rare earth metal by replacing the energy intensive molten salt electrolysis and metallothermic reduction processes. Key advantages of utilizing ILs in the electrochemical reduction of the lanthanides include a higher potential window than alternative mediums, virtually no vapor pressure at operating temperatures, a high metal salt solubility, a higher conductivity than organic solvents and more importantly a control over the water content of the electrolyte [3]. Additionally, the transition to a low temperature emission free process would eliminate the large amount of carbon dioxide and perfluorocarbon emissions currently resulting from conventional processes. It is important to note that the electrical conductivity of ILs at room temperature is approximately an order of magnitude lower than molten salts, resulting in lower electrical efficiency. This disadvantage can be mitigated by operating ILs units at high temperature ($>100^{\circ}\text{C}$) [31]. Similar to molten salt electrolysis, the existence of a stable +2 valence for samarium, europium and ytterbium creates additional hurdles in ILs.

Table 2.7 presents a summary of relevant literature on the electrodeposition of REE in IL medium. Table 2.8 presents the nomenclature associated with the ILs listed in Table 2.7.

Imidazolium-Based ILs

The electrochemical behavior of europium in 1-hexyl-3-methylimidazolium bis (trifluoromethylsulphonyl)imide [C6mim][NTf2] medium was investigated by Rama [184]. Additionally, experiments were conducted where TBP and N, N-dihexyloctanamide (DHOA) were added to the system. A cyclic behavior was observed where Eu(III) would be reduced to Eu(II) at the cathode, but no metal was generated due to break down of the IL at lower voltage than

Table 2.7: Electrodeposition of REE in IL Medium.

Ionic Liquid	Reduction to Metal (V)	Cathodic Limit (V)	Anodic Limit (V)	Basis	[Ref.]
[DEME][NTf2]	-3.3 (Nd)	N/A	N/A	Ag/Ag+	[145]
[N1116][NTf2]	-3.0 (Nd)	N/A	N/A	Fc/Fc+	[205]
[P66614][NTf2]	-2.3 (Nd)	-3.3 (0.4 % H ₂ O) [204], -3.5 (0.1% H ₂ O) [203]	N/A	Fc/Fc+	[203, 204]
[BMPyr][NTf2]	-2.2 (La, Nd), -2.3 (Sm, Dy)	-3.4 to -3.5	N/A	Ag/AgCl	[30, 31]
[BMPyr][NTf2]	-2.45 (Eu)	-3.5	-1.7	Fc/Fc+	[95]
[Me3NBu][NTf2]	-2.2(La), -1.95 (Ce) [86], -2.5 (Nd), -2.3 (Sm), -2.4 (Sm) [141], -2.0 (Eu) [141]	-3.6	N/A	Ag/AgCl	[31]
[Me3NBu][NTf2]	-2.4 (La), -2.85 (Sm), -3.0 (Eu)	-3.0	2.7	Fc/Fc+	[26]
[Bu3MeN][NTf2]	Simultaneous with IL Break Down	-1.9	2.85	Ref. Electrode	[74]
[Ln(TMP)3][NTf2]	-1.25 (Nd, Dy, Gd), -0.85 (Pr)	<-4	> 1.5	Pt	[21]
[Ln(TMP)3][NTf2]	-2.1 (Nd)	< -4	> 1.5	Ag/AgCl	[212]
[Ln(DHOA)3][NTf2]	-3 (Nd, Eu, Dy)	N/A	N/A	Pd	[108]
[P2225][NTf2]	-2.5 (Nd) [104], -3.2 (Dy) [114]	-3.2	3	Fc/Fc+	[104, 114]
[C6mim][NTf2]	Not observed prior to IL Break Down	-1.75	N/A	Fc/Fc+	[104, 114]
[C8MPyr][NTf2]	-1.6 (La)	-2.5	N/A	AgCl/Ag	[123]
[N11N11PipGua][NTf2]	-1 (Dy)	N/A	N/A	Pt	[25]
[BMPyr][DCA]	Simultaneous with IL Break Down	-2	N/A	Fc/Fc+	[186]
[BMPyr][DCA]	-1.35 (NiLa)	-1.6	1.6	Ag/AgCl	[70]
[Emim][DCA]	-1.4 (Fe-Nd)	-1.5	N/A	Pt	[272]
[Bmim][DCA]	-1.05 (La)	-1.7	1.6	Ag/Ag+	[279]
[BMimCl][AlCl3]	-1.0 (AlCe)	N/A	N/A	Al	[131]

Table 2.8: Nomenclature for the Ionic Liquids Used in Electrodeposition of Rare Earth Elements.

Ionic Liquid	Nomenclature
[DEME][NTf2]	N,N-Diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethyl-sulfonyl)amide
[N1116][NTf2]	n-Hexyl-trimethyl-ammonium bis(trifluoromethyl-sulfonyl)amide
[P66614][NTf2]	Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)azanide
[BMPyr][NTf2]	1Butyl1methylpyrrolidinium bis(trifluoromethylsulfonyl)azanide
[Me3NBu][NTf2]	N-trimethyl-N-butylammonium bis(trifluoromethylsulfonyl)azanide
[Bu3MeN][NTf2]	Tri-Butylmethylammonium bis(trifluoromethylsulfonyl)azanide
[Ln(TMP)3][NTf2]	Lanthanide trimethylphosphate tribis(trifluoromethane) sulfonimide
[Ln(DHOA)3][NTf2]	Lanthanide dihexyloctanamide tribis(trifluoromethane) sulfonimide
[Ln(DMI) _x (NO ₃) _y][CF ₃ SO ₃] ₃	Lanthanide dimethylimidazolidinone nitrate trifluoromethanesulfonate
[P2225][NTf2]	Triethyl-pentyl-phosphonium bis(trifluoromethane) sulfonimide
[C6mim][NTf2]	1-Hexyl-3-methylimidazolium bis (trifluoromethyl-sulphonyl)imide
[C8MPyr][NTf2]	1-Octyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide
[N11N11PipGua][NTf2]	Guanidinium bis(trifluoromethylsulfonyl)imide
[BMPyr][DCA]	Butylmethylpyrrolidinium dicyanamide
[Emim][DCA]	1-Ethyl-3-methylimidazolium dicyanamide
[Bmim][DCA]	1Butyl-3-methylimidazolium dicyanamide
[BMimCl][AlCl ₃]	Aluminum chloride 1-butyl-3-methylimidazolium chloride

reduction to metal.

Xu [272] also reported that the reduction of rare earths in 1-ethyl-3-methylimidazolium dicyanamide [Emim][DCA] at a voltage lower than the break down voltage of the IL was not possible. Xu demonstrated that this issue could be circumvented by introducing Fe(II) as a co-deposition element. Similar to the electrodeposition of lanthanides in deep eutectic solvents, the addition of Fe(II) reduces the voltage needed and allows for co-deposition. It is believed that a catalytic reduction reaction occurs following the electrodeposition of a few atomic layers of iron on the cathode. It is important to note however, that the carbon residue from the degradation of the IL was found in the deposited metal. The authors concluded that additional investigation would be beneficial with a longer alkyl chain IL.

This suggestion is in line with work previously undertaken in 2015 by Zhang [279] where 1-butyl-3-methylimidazolium dicyanamide [BMim][DCA] was used with lanthanum chloride to electrodeposit lanthanum while preserving the integrity of the electrolyte medium. The system presented by Zhang offers a promising avenue for the transition to an industrial process since it solves the anode reaction through the use of a chloride ion which is oxidized to chlorine.

Pyrrolidinium-Based ILs

The study of the electrodeposition of lanthanides in pyrrolidinium ILs revealed some discrepancies between the various pyrrolidinium ILs. Legeai reported successful electrodeposition of lanthanum metal using 1-octyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide [C8MPyr][NTf₂]/lanthanum nitrate as an electrolyte [123]. However, the process as de-

scribed was slow and inefficient. In an investigation of the electrodeposition of lanthanides in butyl methylpyrrolidinium dicyanamide medium, Razo reported that a simultaneous reduction of the IL and lanthanides was occurring, preventing the utilization of [BMPyr][DCA] in such processes [186].

Pyrrolidinium ILs behave similarly to imidazolium ILs with regard to their behavior with water [272] and transition metal co-deposition. The simultaneous decomposition of the metal salt and IL can also be avoided in pyrrolidinium ILs by using a dual metal electrodeposition process where the transition metal acts as a catalyst [272]. The preparation of nickel lanthanum alloy with hydrogen evolution catalytic activity was achieved by Gao using [BMPyr][DCA] in combination with lanthanum chloride and nickel chloride as an electrolyte [70]. The performance of the catalyst produced was superior to many comparable nickel rare earth catalyst, proving an interesting research avenue for solvometallurgists. [BMPyr] [NTf₂] was used by Manjum for the co-electrodeposition of samarium cobalt SmCo₇ alloy from samarium and cobalt triflimide salts [140]. However, it was noted that the morphology of the alloy as nano particles and nano wires caused issues with regards to its physical separation and washing from the IL medium.

In contrast, Bourbos reported the successful reduction of lanthanum nitrate in 1-Butyl 1-methylpyrrolidinium bis(trifluoromethane) sulfonimide [BMPyr][NTf₂] [30] and of lanthanum nitrate, neodymium nitrate, samarium trifluoromethanesulfonate and dysprosium bistriflimide in both [BMPyr][NTf₂] and in N-trimethyl-N-butylammonium bis(trifluoromethylsulfonyl)imide [Me₃NBu][NTf₂] [31]. Bourbos noted that fluoride and sulfur were found in the metal product. It was not clear to the authors if the presence of these elements was the result of the sulfonimide ion adsorption or if it represented residual IL that wasn't

washed properly. The authors rejected the possibility of IL breakdown following an analysis of the materials using Fourier transform infrared spectroscopy (FTIR) spectra where no breakdown residue could be observed [30].

Following their initial studies, Bourbos successfully investigated a two-compartment process in which the anode reaction would not result in the breakdown of the IL anion [NTf₂] by using neodymium chloride in dimethylsulfoxide (DMSO) in the anode compartment [31]. While the introduction of a two-compartment unit reduced the efficiency of the process, the use of a chloride salt as a feed material and the subsequent chloride oxidation to gaseous chlorine resulted in much more favorable economics and in a more environmentally friendly process.

A likely early industrial application of electrodeposition of rare earth in IL medium is the electroplating of NdFeB magnets with dysprosium and terbium followed by conventional heat treatment to increase the magnetic properties of the magnets. Suppan used [BMPyr][NTf₂] to electrodeposit dysprosium on NdFeB magnets and increased the magnets coercivity by 20 percent [233].

Phosphonium-Based ILs

The study of the electrodeposition of neodymium in phosphonium ILs revealed that phosphonium-based systems have significant inherent drawbacks to overcome before they can be implemented commercially. In order to reduce neodymium to metal in [P66614][NTf₂] at low temperature with minimum degradation of the IL medium, it appears that a narrow neodymium concentration range (0.1 to 0.5 mol/kg) and water (0.1 to 2%) is required [203]. The pres-

ence of water allows for the electrodeposition process to occur in one step directly from the trivalent lanthanide as opposed to a two-step reduction from the trivalent phase to the divalent phase to the metal phase when the concentration of water is insufficient [100]. However, it is believed that the presence of water, while necessary to ensure proper speciation of neodymium in the IL, also leads to surface oxidation of the deposited metal [204] in addition to reducing the electrolyte electrochemical window [165]. The metal produced also contains significant amounts of phosphorus and sulfur which could either be caused by residual IL being present in the deposit or from break down of the IL itself.

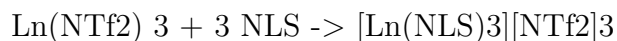
While the effect of water is not explicitly addressed, Matsumiya suggests that increasing the temperature of the system also contributes to the successful reduction of lanthanides in phosphonium bis(trifluoromethane) sulfonimide medium [144]. It is yet to be determined whether operating at higher temperatures would be preferable to the utilization of water with regard to a potential reduction of surface oxidation for the metal produced. In his investigations, Matsumiya successfully solubilized neodymium from a demagnetized NdFeB rod at the anode while simultaneously reducing it to metal at the cathode. His utilization of a Vycor glass filter around the anode prevented any iron from being deposited at the cathode [144].

Early investigations of the electrolysis of neodymium in triethyl-pentyl-phosphonium bis (trifluoromethane) sulfonimide [P2225][NTf2] and [P1116][NTf2] by Kondo had not assessed the impact of water in the system but have reached similar purity results as other investigators of this system [100, 164, 203, 204?] with regard to the metal produced. The poor metal reduction observed in [P1116][NTf2] was suggested to be related to the higher viscosity of [P1116][NTf2] compared to [P2225][NTf2], 153 mPa s vs 88 mPa s, respectively [104]. Ku-

rachi [114] failed to reduce dysprosium without breaking down the IL medium. The produced metal also contained significant amounts of sulfur, fluorine and oxygen. Further studies by Kondo evaluated the impact of lowering the water content of the ionic liquid [P2225][NTf2] and did not identify any significant impact on the electrodeposition of neodymium [103].

Neutral Ligand Complexation-Based ILs

Neutral ligand complexation-based ILs are formed by the dissolution of rare earth salts in neutral ligand solvents (NLS) such as tributyl-phosphate (TBP), trimethyl-phosphate (TMP), 1,3-dimethyl-2-imidazolidinone (DMI) or dihexyloctanamide (DHOA). The overall reaction for the formation of such ILs is represented by:



While [NTf2] is referenced in the equation, both [NTf2] and [CF3SO3] anions are currently being investigated for such systems. During the electrodeposition process, the cation portion of the IL is reduced to create a lanthanide metal and regenerate the NLS following the reaction:



Bagri [21] and Sidhu [212] demonstrated that REE could be successfully deposited onto a cathode substrate using TMP as a NLS to generate a lanthanide IL cation through the dissolution of lanthanide tribis(trifluoromethane) sulfonimide salt. Krishna [108] achieved the same objective using DHOA as a NLS. This approach is likely to be successful commer-

cially since the medium is very stable within the operating conditions (potential, acidity and temperature) required for electrodeposition and the self-regeneration lends itself to a continuous process. However, similar to other IL mediums, additional research on the anodic reaction will be required to replace the decomposition of the [Ntf2] or [CF3SO3] anion with a different anion and to allow for its reuse in the production of the lanthanide salt feed material.

Lanthanide neutral ligands complexes can also be dissolved in ILs such as the phosphonium-based IL [P2225][NTf2] and subsequently electrodeposited. Matsumiya [143] demonstrated such a process following the extraction of the neodymium by TBP/[P2225][NTf2] from aqueous media. Unfortunately, as with other investigations of phosphonium-based electrodeposition, a significant amount of oxidation was present in the deposited metal [103, 104, 165, 203, 204].

Aluminum Chloride-Based ILs

The reduction of aluminum and aluminum alloys from aluminum chloride-based IL medium have been extensively investigated in the past [36, 97, 282]. However, these processes have yet been proven to be sufficiently economic to replace legacy industrial processes. The incentives with regard to REs such as the utilization of relatively inexpensive chlorides, the absence of fluorides and a low operating temperature suggest that research into these systems is likely to increase drastically in the foreseeable future. The first foray in the subject in 1985 by Lipsztajn and Osteryoung [130] using aluminum chloride 1-methyl-3-ethylimidazolium chloride [AlCl3][ImCl]/neodymium chloride as an electrolyte was considered a failure since it resulted in no neodymium deposition.

The first record of successful electrodeposition of a rare earth in aluminum chloride-based IL was achieved in 2001 by Tsuda [240] using aluminum chloride 1-ethyl-3-methylimidazolium chloride $[\text{AlCl}_3][\text{EMiCl}]$ /lanthanum chloride in the presence of lithium chloride and thionyl chloride. It was noted however that the resulting metal layer was quickly passivated, ceasing lanthanum deposition. Building on work by Tsuda, Lisenkov [131] investigated the electrodeposition of an aluminum cerium alloy as a corrosion inhibitor using an aluminum chloride 1-butyl-3-methylimidazolium chloride $[\text{AlCl}_3][\text{BMinCl}]$ /cerium(III) chloride electrolyte. Unfortunately, the corrosion resistance of the deposited alloy was low due to the sequestration of chloride ions in the deposit.

2.1.6 Technology Outlook

The impact of ILs in the REE processing industry will undoubtedly increase tremendously in the coming years. The first point of entry in the commercial production sphere will likely be as a replacement for acidic extractants in the solvent extraction processes for the separation of the REE. The major impediments to this transition from research to industry lies in the inherently conservative nature of industrial separation process operators. The effort, cost and risk associated with the retrofitting of existing processes will certainly delay and may potentially bar the entry of ILs in the legacy industry. It is typical for such changes to be brought about by incumbents challenging the status quo. Such incumbents are currently plentiful in the U.S. as the government has resolved to reduce its dependence on the Chinese supply chain for REE.

A second point of entry lies in the application of ILs and solvometallurgy for the recycling of REE from spent magnets, electronics and batteries. The industry is in its initial devel-

opment and is expected to turn towards new technologies for competitiveness with legacy players. The integration of the full recycling process using ILs to dissolve, purify and reduce the REE from such waste stream is expected to challenge the research community.

Finally, the increased attention towards environmentally friendlier ILs such as the CHON ILs may redeem the initial ‘green’ designation that befelled perfluorinated ILs, further supporting their introduction to the industry as replacements from molecular organic solvents.

2.2 Rare Earth Elements Reduction to Metal

This section was approved for publication as a Chapter in a Book with the expected citation:

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Abstract:

The reduction to metal of rare earth elements is a complex, energy intensive and environmentally damaging process currently undertaken by molten salt electrolysis for the light rare earth elements (La to Nd) and by metallothermic reduction for heavier rare earth elements (Sm to Lu), yttrium and scandium. The primary metals used as reductants in metallothermic reduction processes are calcium and lanthanum. New approaches such as electrolysis

in ionic liquid medium, the FCC Cambridge, Fueled Anode Electrolysis, and Carboxylate Reduction processes are set to disrupt the current industrial practices. Their development is a sustainability imperative as they promise to offer a significant reduction in environmental impact and in energy usage.

2.2.1 Introduction

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

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

The most common REE permanent magnet is neodymium-iron-boron (NdFeB), with samarium cobalt (SmCo) making up a smaller percentage of the market. NdFeB magnets have the highest magnetic strength per weight of all the permanent magnets and no tooling is required in their fabrication. However, they corrode easily, can lose their magnetic strength

at relatively low temperatures, and are difficult to initially magnetize [33]. SmCo magnets are resistant to corrosion, stable in a wide range of temperatures but they can be expensive as their price is strongly linked to the cobalt spot price as they require large amounts of cobalt and are more difficult to make, only coming in simple shapes [33]. Other rare earth metals, such as dysprosium or terbium, can replace small amounts of the neodymium in the NdFeB alloy to alter and upgrade specific proprieties of the magnets. Dysprosium is added to increase the coercivity and corrosion resistance of the magnet while terbium is added to increase the allowable operating temperature.

A mixed REE alloy is used in the anode of the batteries to improve durability and manipulation characteristics. Typically, lanthanum is the alloying REE of choice, but the anodes also contain a variety of other metals. Rare earths typically make up 3 to 14% of the mass of a battery cell inclusive of its casing [190], which come in various sizes and are used in a multitude of applications. Large batteries are typically used in automobile and energy applications while smaller batteries are used in portable electronic devices such as computers, cell phones, power tools, medical equipment, and other applications.

Metallurgical applications of the REE are mainly comprised of hydrogen storage, mischmetal and specialty alloys. While hydrogen fuel is a potential source of alternative fuels being heavily discussed, it presents challenges for storage. High pressures are required because the gas cryogenic nature (very low temperature boiling point) and low energy density, requiring a substantial amount of the material. Hydrogen has many beneficial properties as a combustion fuel source since it is not a hydrocarbon (contains no carbon), its combustion only generates heat and water. The favored alternative to high pressure hydrogen storage is molecular storage [76]. In this process, hydrogen is absorbed in or on a compound, forming

bonds in a similar fashion as water in hydration bonds. The result is a storage method that does not require high operation pressures, but still maintains a low storage volume per unit of hydrogen. Lanthanum-nickel alloys can store up to 2.2% of their weight through hydrogen absorption [173]. This alloy favorably compares to its alternatives and its use is growing.

Light REE, primarily Ce and La, with small amounts of Pr and Nd form an alloy referred to as mischmetal. Mischmetal is added to steel during the steel making process in order to bind with contaminant elements such as oxygen and sulfur to improve properties of the steel, such as corrosion resistance. When rare earth elements react with oxygen and sulfur, they form rare earth oxysulfides which replace manganese sulfide and various oxide inclusions from the steel slag, increasing the overall steel strength and resistance to cracking [44].

High carbon steels and stainless steels can also be doped with yttrium and cerium to increase their temperature performance, oxidation resistance, ductility, and other thermal and mechanical properties [44]. Finally, rare earth elements can also be used as alloying elements in a variety of alloys such as magnesium, aluminum and zinc alloys. The most promising alloy is the AlSc alloy, which is expected to allow for the welding of aircraft bodies instead of the current riveting processes, reducing weight considerably.

Rare earth metals are produced industrially by metallothermic reduction and by molten salt electrolysis processes. Molten salt electrolysis is a process using electricity as the reducing vector to convert rare earth salts or oxides to metals in a molten salt medium. The molten salt medium is selected to allow for the solubilization of the rare earth and for operation above the rare earth melting temperature. It is currently the most important commercial process for the reduction of rare earth compounds on a throughput basis. Rare earths heav-

ier than neodymium cannot be reduced in the molten salt electrolysis process because their melting temperature is either higher than available molten salt mixture or because they possess multiple stable valences. These rare earth metals are produced using a metallothermic reduction process, in batch or semi-batch mode at relatively low production volumes. The metallothermic reduction processes use a metal with higher stability to reduce the rare earth. The produced rare earth metal is then either distilled or gravity separated from the oxidized slag.

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

The current industrial reduction processes for lanthanides have been extensively described by Krishnamurthy and Gupta in their opus on the Extractive Metallurgy of Rare Earths [109] and by Habashi in his Handbook of Extractive Metallurgy [83], both are foundation references in the past and current practices in the industry. Habashi also published a short paper summarizing the current industrial reduction processes in 2013 [84], which in addition of the two previously cited handbooks will serve as a basis for the summary of current industrial rare earth reduction processes contained herein. This summary will be augmented with recent advances in the field when applicable.

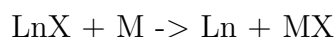
Promising innovative reduction processes such as the Electrolysis in Ionic Liquids [3, 21, 31, 36, 97, 108, 164, 204, 212, 272, 279, 282? ?], the FCC-Cambridge [38, 64, 288], the Infinium Fueled Anode Electrolysis [1, 176, 177] and the Carboxylate Reduction Process [99] will also be discussed.

2.2.2 Industrial REE Reduction Processes

Metallothermic and Carbothermic Reduction

Metallothermic reduction processes use a molten metal which reacts with the rare earth compound to form a liquid or solid compound and the rare earth metal. Highly reactive metals usually in the alkali (Li, Na, K) or alkali-earth (Ca) groups are used for this purpose. The reduction potential of metals towards the lanthanides is a reverse function of their stability. As such, calcium is the only metal more stable than rare earth fluoride and oxides whereas the full suite of common alkali metals (Li, Na, K) and calcium are more stable than rare earth chlorides and can be used to reduce the lanthanide chlorides [109].

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



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

Lanthanide chlorides have the largest suite of suitable reductants possible among the industrial raw materials for the reduction of rare earths. However, the difficulty and cost of

producing and handling anhydrous rare earth chloride salts results in a much lower metal product purity rendering chlorides an unattractive medium. Instead, historical metallothermic processes relied on fluoride medium and on the reduction-distillation process of oxides (6). In the fluoride medium processes, lanthanide oxides were either reacted with hydrofluoric acid in an aqueous solution and dehydrated using an hydrofluoric acid atmosphere (wet process) or directly converted to fluorides using anhydrous hydrofluoric acid or ammonium hydrogen fluoride (dry process). The rare earth fluoride was then reduced using calcium under vacuum in a batch furnace lined with tantalum and the system was cooled down. The metal ingot was separated from the calcium fluoride slag and recovered. Unfortunately, these calciothermic reduction process would leave a significant amount of calcium and tantalum in the metal, up to 2 % and 0.5 % by weight respectively [109]. In order to reduce contamination, the calciothermic process operating temperatures were lowered through the simultaneous introduction of a lower melting temperature alloying element such as zinc or magnesium and / or calcium chloride. These added compounds would react to form a lower melting eutectic calcium fluoride slag [34]. The alloying metal was then distilled under vacuum and recovered, similarly to the Kroll process [235]. In a study by Carlson, the yttrium produced using this intermediate alloy technique had less than 0.01% by weight total calcium and magnesium and only contained minor amounts of tantalum [34]. The subsequent introduction of lithium metal as a replacement for calcium chloride in the process leads to further lowering of the reaction temperature through the formation of a lithium fluoride slag which has a lower melting point than the calcium fluoride-calcium chloride slag [109] .

While the fluoride reduction process proved commercially viable for most rare earths, it was not applicable to the elements possessing a divalent stable state (samarium, europium, ytterbium). During the reduction process, these elements are reduced to their respective divalent

salt and never reach the metal state [109]. In order to produce these metals, the reduction process must start from the oxide material. Unfortunately, the use of calcium as a reduction agent for the lanthanide oxides is not a viable commercial production route because of the very high melting temperature of calcium oxide resulting in inefficient processing conditions. A specific reduction process referred to as Reduction-Distillation, Lanthanothermic Reduction or as Lanthanothermy [109] was developed using molten lanthanum as a reducing agent. In this process, the rare earths oxides are reduced using lanthanum metal and subsequently distilled from the molten lanthanum. This process is based on a higher stability of lanthanum oxide and on the lower vapor pressure of lanthanum metal with regards to other lanthanides.

Aluminothermic reduction is primarily used industrially to reduce scandium oxide in-situ [199] and produce an aluminum-scandium alloy for use in the industry. Scandium availability and pricing do not currently support a mass adoption of AlSc alloys, but many prospective producers are advancing their projects as the aerospace industry is evaluating such alloys for the next generation of commercial airliners. Once sufficient low cost supply capacity exists in the market, it is expected that the AlSc alloys will become ubiquitous in all applications where weight to strength ratio is important. Calciothermic reduction is still used industrially for the production of high purity heavy rare earth metals such as gadolinium, terbium, dysprosium, holmium, erbium, lutetium and yttrium while lanthanothermic reduction is used industrially for the production of samarium, europium, terbium and ytterbium [121].

Carbon is with calcium the only other element having the thermodynamic potential to reduce lanthanides. However, no successful industrial processes have been developed for the reduction of lanthanides using carbothermic reduction as a basis because it has many drawbacks such as the formation of carbides and the vaporization of rare earth metal at operating temperatures

leading to the reverse reaction occurring in the gas phase with carbon monoxide [109].

General Motor Corporation has developed and patented a molten salt calciothermic reduction process applicable to oxides [208], oxychlorides [209] and fluorides [210] in which the lanthanides are reduced by calcium metal in a molten calcium chloride medium. The process is most efficient due to lower operating temperatures when utilized in combination with iron as an alloying element for the preparation of neodymium-iron alloys, a precursor to the Nd-FeB magnet alloy. Sharma has also demonstrated that sodium metal could be used in lieu of calcium in this process to allow for the in-situ reduction of calcium from calcium chloride [208].

Molten Salt Electrolysis

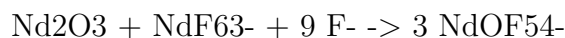
Molten salt electrolysis (MSE) is an electrochemical reduction process using molten salt as a medium instead of an aqueous solution. The high reactivity of the lanthanide metals with water precludes aqueous electrowinning. MSE is currently the most important industrial process for the reduction of REE by production volume due to its lower comparative energy requirements and its continuous operation mode unlike metallothermic reduction which occurs in batch or semi-batch mode. In the MSE process, a rare earth compound (usually a chloride, fluoride or an oxide) is dissolved in a molten salt medium under an inert atmosphere while an electrical current is circulated through the unit. Historically, the chloride system was favored by the industry, however intensification imperatives lead to the conversion toward the oxide-fluoride system around the year 2000. Chloride systems offer current efficiencies below 50% while oxide-fluoride systems offer current efficiencies up to 87% [287].

The applicability of molten salt electrolysis as a reduction process for lanthanides is limited to

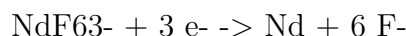
lower melting lanthanide metals such as lanthanum, cerium, praseodymium and neodymium [121] or to low temperature melting alloys made with iron, magnesium, zinc and cadmium [109, 250]. Higher melting lanthanides have melting temperatures resulting in high losses of molten salt medium through vaporization, or above the boiling point of the salt medium.

The molten salt electrolysis of light rare earths (lanthanum, cerium, praseodymium and neodymium) has traditionally been undertaken in small circular 3kA cells using vertical graphite anodes and either tungsten or molybdenum cathodes [207]. Recent advances have maintained the design but increased the capacity of the cells to 4-6 kA, and more recently to 10kAV using rectangular cells instead of cylindrical [259, 275]. Typical electrolytes are composed of a mixture of lanthanide fluoride and lithium fluoride in proportion 4 to 9:1. Specific operating parameters are usually maintained as trade secrets by Chinese firms, but Milicevic reports a ratio of 7:1 as the proper proportion of lanthanide fluoride to lithium fluoride to maximize solubility without detrimentally affecting the physical properties of the electrolyte [151]. The electrolytical reaction system for the electrolysis of neodymium, the most important product in value and volume, is described using the following equations [258, 287]:

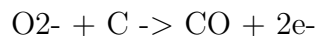
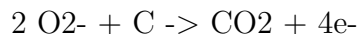
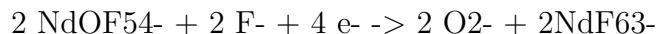
Neodymium dissolution reaction:



Cathode reaction:



Anode reactions:

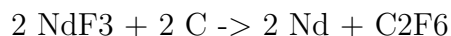
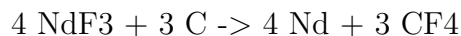


Overall reaction (carbon unbalanced):



In addition, perfluorocarbons are emitted at the anode due to an anode effect in the system.

The anode effect can be described by the following reactions [278]:



Although perfluorocarbons production from the lithium fluoride electrolyte is theoretically possible, it significantly higher voltage requirement makes it unlikely to be a significant contributor to perfluorocarbons production [259]. Nevertheless modern molten salt electrolysis processes for the reduction rare earths present significant sustainability challenges especially with regard to perfluororocarbon emissions from anode effect and greenhouse gases emissions as highlighted in numerous life cycle assessments [250, 259]. They are also much more expensive to operate than many other metal reduction processes, prompting researchers to work on optimizing the current processes and on developing a new generation of more sustainable technologies.

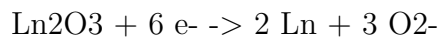
2.2.3 Novel REE Reduction Processes

FFC Cambridge Process

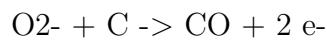
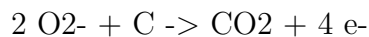
The FCC-Cambridge Process [64] is a zero liquid discharge process initially discovered by Fray, Farthing and Chen of Cambridge that is currently being developed by Metalysis for the production of titanium, tantalum, aluminum and high entropy alloys. Metalysis has reported successful production of cerium, neodymium and yttrium metals using the FCC-Cambridge process and it claims its process is suitable for all rare earth with the exception of lanthanum [64]. Lanthanum oxide reacts with molten calcium chloride salt to form an oxychloride which does not electro-reduce to metal. However, it was determined by Zhu [288] that sintering lanthanum oxide with nickel oxide at sufficiently high temperature prior to the FCC-Cambridge process allowed for the production of LaNi₅ hydrogen storage alloy powder.

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

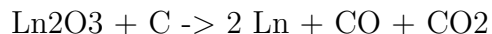
Cathode deoxygenation reaction:



Anode reactions:



Overall reaction (carbon unbalanced):



The FCC-Cambridge process is a batch electro-deoxidation process in molten salt medium where the metal oxide is pelletized and reduced in-situ at the cathode yielding a metal or metal alloy pellet. The metal pellet is then ground and washed to yield a metal powder product [37]. While it is unlikely that the FCC-Cambridge process will challenge the oxide-fluoride molten salt electrolysis for light REE, it presents a valuable alternative to metallothermic reduction processes used for the heavier lanthanides and could present an interesting alternative for the production of complex magnetic alloys. The nanometric metal powder nature of the product also increases the attractiveness of the FCC-Cambridge process, enabling the direct production of bonded and sintered magnets.

Fueled Anode Molten Salt Electrolysis

The Fueled Anode Molten Salt Electrolysis process [1] that was being developed by Infinium prior to its closure is a significant evolution of the oxide-fluoride molten salt electrolysis process. It was commercially operated at a small scale to produce ferro-dysprosium alloy (80:20 DyFe) and the company was expected to offer other rare earth elements to the market [1].

In Infinium's molten salt electrolysis process, an oxygen ion permeable membrane is used to separate the anode from main electrolyte reservoir. Following dissolution, the rare earth ions are reduced at the cathode while the oxygen ions are oxidized in the presence of fuel at the anode. Contrary to conventional molten salt electrolysis, the Infinium process used an inert

liquid metal anode such as liquid silver, copper or tin. The injection of fuel in the anodes serves many beneficial purposes such as an increase in energy efficiency and for oxidation protection [176, 177].

Infinium's process was revolutionary in that its configuration and its oxygen permeable membrane precluded the electrolysis of the fluoride ion and when operated with a truly inert anode emitted no carbon dioxide.

Carboxylate Reduction

The Carboxylate Reduction Process (CRP) is a zero liquid discharge process developed by Hela Novel Metals that is currently being scaled up to demonstration-scale following the successful piloting of the technology. It represents a significant challenge to the legacy molten salt electrolysis and metallothermic reduction processes both from a capital and an operating standpoint. The patent application US20200047256A1 is currently pending on this novel technology [99].

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

hydrous metal oxalate salt at a temperature between 200-440°C while avoiding any oxalate decomposition. In the second step, the anhydrous metal oxalate powder is decomposed to its metal state and a mixture of oxalic acid and ammonium oxalate is recovered as a by-product. The reduction step is operated between 320-720°C under pressure. In the final process step, the metal powder is refined to remove any loosely bonded non-metal impurities such as oxygen, sulfur and carbon under a different variation of the proprietary gas mixture at a temperature between 700-1300°C.

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

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

Ionic Liquid Electrodeposition

Details on the ionic liquid (IL) electrodeposition process are provided in detail in [Section 2.1](#). Salient points from that chapter follow.

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

Key advantages of the utilization of ILs in the electrochemical reduction of the lanthanides include a higher potential window than alternative medium, virtually no vapor pressure at operating temperatures, a high metal salt solubility, a higher conductivity than organic solvents and more importantly a control over the water content of the electrolyte [3]. In addition, the transition to a low temperature emission free process would eliminate the large amount of carbon dioxide and perfluorocarbon emissions currently resulting from conventional processes.

It is important to note that the electrical conductivity of ILs at room temperature is approximately an order of magnitude lower than molten salts, resulting in lower electrical efficiency. This disadvantage can be mitigated by operating IL units at high temperature (> 100 C) [31]. Similar to molten salt electrolysis, the existence of a stable +2 valence for samarium, europium and ytterbium creates additional hurdles in ILs.

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

- Imidazolium ILs: Significant issues have been reported using imidazolium-based ILs,

notably related to the decomposition of the IL under operating conditions [184, 272]. One potential avenue is the production of transition metal alloys of REE [279].

- **Pyrrolidinium ILs:** Successful deposition of REE metals was observed using pyrrolidinium ILs. Notably, Bourbos successfully prevented the breakdown of the IL anion [NTf₂] by using neodymium chloride in dimethylsulfoxide (DMSO) in a separate anode compartment [31]. This two-compartment design allowed for the utilization of neodymium chloride as a feed material and the production of gaseous chlorine rather than the decomposition products of the [NTf₂] anions, resulting in much more favorable economic prospects in a more environmentally friendly process.
- **Phosphonium ILs:** All investigations of phosphonium ILs as a medium for the electrodeposition of REE have highlighted the critical role played by water in the system. Water is both required for the process to operate and deleterious to the product [165, 203, 204]. As such, the potential of phosphonium ILs for the electrodeposition of rare earth elements is rather dubious.
- **Neutral Ligand Complexation ILs:** These represent one of the most promising approaches to the electrodeposition of rare earth metals in ILs. Recent investigations demonstrated that REE could indeed be successfully deposited onto a cathode substrate using a neutral ligand solvent (NLS) to generate a lanthanide IL cation through the dissolution of a lanthanide triflimide salt [21, 108, 212]. The potential commercial success of this approach lies in the electrostability of the medium and with its implicit self-regeneration. However, similar to other IL mediums, additional research on the anodic reaction will be required to replace the decomposition of the [Ntf₂] anion with a different anion and allow for its reuse in the production of the lanthanide salt feed material.

- Aluminum Chloride ILs: The reduction of aluminum and aluminum alloys from aluminum chloride-based IL medium has been extensively investigated in the past [36, 97, 282]. However, these processes have yet been proven to be sufficiently economical to replace legacy industrial processes. The incentives with regards to rare earths such as the utilization of relatively inexpensive chlorides, the absence of fluorides and a low operating temperature suggest that research into these systems is likely to increase drastically in the foreseeable future. A subsequent distillation step would be required for the purification of the rare earth metal, not unlike current lanthanothermic processes.

2.2.4 Technology Outlook

Global economics and geopolitical considerations in the last two decades allowed China to consolidate the RE industry vertically. This situation currently raised some alarming flags with respect to RE supply chain and pricing. No significant REE metal reduction plants exist outside of China with the exception of a small Japanese integrated supply chain. More importantly, the two main obstacles to the establishment of an REE reduction plant outside of China are a stable availability of high purity separated REE raw materials and the absence of a significant market for the rare earth metals produced. All novel processes discussed in this chapter were also being designed for the production of other technological metals for which conventional processes are onerous and complicated such as for titanium, zirconium and advanced alloys.

The development of a novel more efficient process for rare earth reduction such as the FCC-Cambridge, the Infinium and the Carboxylate reduction process are not enough in them-

selves to challenge the domination of the Chinese industry. They can however be part of a larger effort by the Occident to reestablish an industry supply chain starting from deposits to separation to reduction and finally to the production of REE-containing products. The commercialization of new processing technologies across the supply chain would then be the key to a rebalancing of market forces.

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

Chapter 3

Recovery of Rare Earth Elements from Acid Mine Drainage: a Techno-Economic Analysis

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Abstract:

In recent years, acid mine drainage (AMD) has emerged as a promising unconventional

source of rare earth elements (REEs) and other critical minerals (CMs) such as cobalt and manganese. In this regard, AMD provides a natural heap leaching effect that extracts and concentrates REE/CM from the host strata creating a partially enriched feedstock suitable for downstream extraction, separation, and recovery. While several prior studies have described processes and approaches for the valorization of AMD, very few have described the supply chain and infrastructure requirements as well as the associated economic assessment. To that end, this paper provides a fundamental economic assessment of REE/CM recovery from AMD using a network sourcing strategy in addition to a robust, flexible feedstock separations and refining facility. The methodology of this paper follows that of a typical techno-economic analysis with capital and operating costs estimated using AACE Class IV (FEL-2) guidelines. To demonstrate the range of possible outcomes, four pricing scenarios were modeled including contemporary prices (September, 2021) as well as the minimum and maximum prices over the last decade. In addition, five production scenarios were considered reflecting variations in the product suite, ranging from full elemental separation to magnet REE and CM production only (i.e. Pr, Nd, Tb, Dy, Y, Sc, Co, and Mn). The results of this analysis show that, with the exception of the minimum price scenario, all operational configurations have positive economic indicators with rates of return varying from 25% to 32% for the contemporary price scenario. The optimal configuration was determined to be production of Co, Mn, and all REEs except for mischmetal, which is not recovered. Sensitivity analysis and Monte Carlo Simulation show that capital cost and HCl consumption are the two major factors influencing rate of return, thus indicating opportunities for future technology development and cost optimization. Implications of the study and a cooperative profit-sharing model for sourcing are also described.

keywords Techno-economic analysis; Rare Earth Elements; Acid Mine Drainage; Solvent Extraction; Critical Materials; Cobalt; Manganese

3.1 Introduction

Over the last decade, critical minerals have become an increasingly important matter of both technical and societal importance. While several US federal and international agencies (e.g. U.S. Departments of Energy, Commerce, Defense, USGS, the European Commission, the International Energy Agency, Geoscience Australia, etc..) have provided precise definitions for mineral criticality, they all generally capture the combined factors of importance to modern society and risk for supply chain disruptions [27, 92, 157, 162, 238, 246, 248]. Many public and private organizations have developed policies and investment strategies to de-risk critical minerals production, and this trend is expected to continue over the next several decades as the demand for electric vehicles, lightweight batteries, and consumer electronics intensifies. In addition, several US federal agencies have developed early-stage research and development programs to identify alternative and unconventional critical mineral resources. To this end, this study addresses the economic potential of recovering critical minerals from acid mine drainage (AMD), a deleterious byproduct of many mining operations.

One specific subset of critical minerals include several of the rare earth elements (REEs). In general, the REEs, or lanthanides, are a group of 15 elements from La to Lu and often include Y and Sc as they share similar physical and chemical properties. According to the USDOE, the REEs Nd, Dy, Tb, Eu, and Y are considered critical, given their importance in renewable energy technologies. For this paper, the REEs will be further divided into light-REE (LREE), mid-REE (MREE) and heavy-REE (HREE) categories. La, Ce, Pr and Nd are considered LREEs, Sm, Eu and Gd are considered MREEs while other REEs, Y and Sc are considered HREEs. While not rare in terms of crustal abundance [85, 90] REE are rarely found in significant concentrations. This phenomenon is especially true for HREE and scandium. The dispersed nature of REEs therefore limits the economic potential of REE

mining and as expected, most of the world production of LREEs and MREEs is generated as the by-product of iron mining at the Bayan Obo mine in northern China. The majority of the world production of HREE is, in contrast, obtained through in-situ leaching of ion-absorption clays in southern China and Myanmar.[192]

The dependence of the United States on Chinese suppliers is deemed a threat to American sovereignty and a critical vulnerability to its military. The US Senate Bill S.1317 - American Mineral Security Act was introduced to support the recovery of critical minerals. [2]. Global awareness on the supply risks related to REE were first raised during the 2010-2012 restrictions on exports coupled with increasing worldwide demand due to technological applications [46]. Subsequent easing of the export quotas following a period of massive delocalization of the REE supply chain to China and the consolidation of the industry [191] resulted in the bankruptcy of most junior mining companies formed to provide an alternative supply of REE [46].

Given these factors, many countries, including the U.S., initiated intensive research and development campaigns to identify unconventional REE resources and to develop the process technologies needed for extraction and separation. One such program, funded by the U.S Department of Energy, evaluated coal byproducts, including coal mine drainage as a potential feedstock for REE recovery [77, 78, 289].

Acid mine drainage is a well understood phenomena occurring due to the weathering of sulfide minerals resulting in the in-situ production of sulfuric acid. The acid then leaches metals in the surrounding strata and discharges to nearby streams, damaging the environment [214, 216]. AMD often contains high concentrations of "regulated" metals, such as Fe,

Al, and Mn; however, Vass et al. demonstrated that a significant amount of valuable REE are also solubilized in Appalachian coal-based AMD [254, 255]. Surveys in different areas of the world resulted in different, but nevertheless significant REE amounts. Leon et al. estimated the annual REE value of the Iberian Pyrite Belt discharges at 24.1 MM USD [124] while Migaszewski et al. reported REE concentrations up to 24 ppm from the Wiśniówka mining area in Poland [149].

As indicated by Vass et al., AMD pH is the single best predictor of REE load, with a clear distinction at pH of 4 to 5. AMD above this range typically has low or negligible REE concentrations, often less than 100 ppb, while AMD below this range shows higher concentrations up to ppm levels. AMD discharges with low pH water, containing higher levels of metal ions usually are treated using active treatment processes [6, 237]. Alkali neutralization of AMD is one of the most widely used remediation process [237], with lime being usually the most cost effective reagent. In the lime neutralization process, the AMD is neutralized with quicklime or hydrated lime while being aerated, precipitating all metals from the water [14, 142, 237]. A comprehensive review on AMD treatment technologies has been provided by Skousen et al. [215]. Regardless of the treatment approach, AMD is often viewed as a nuisance waste and an obvious cost center for mining operations. Incentivization of AMD treatment through valorization could thus represent a paradigm shift away from the conventional compliance-based approaches.

The notion of the circular economy, as related to sustainable development, has gained traction in various sectors of society such as in governments, businesses, NGOs and academia [72, 105, 219]. While the concept still has some ambiguity in practice [105], it has recently been associated to the recovery of metals from AMD sources. In this conceptualization, AMD

is seen as a resource rather than as a waste stream [142, 161, 236]. The high concentration of iron and aluminum initially attracted investigation into the recovery of those metals. Wei et al. demonstrated that high recovery of both metals was possible in lime neutralization systems, albeit at a purity in the low 90 % range [267]. The production of high purity iron products from AMD was demonstrated by reprocessing the low purity sludge using nitric acid and potassium hydroxide [213] and alternatively through the usage of high cost soda ash neutralization agent [7]. Both options however require expensive reagents to yield low value products. As such, very few if any such commercial projects have been deployed worldwide.

In addition to base metals, high value critical materials can also be recovered from AMD. Specifically related to the rare earth elements, Ayora et al. showed how REE could be recovered to the basaluminite portion of their passive treatment unit [16]. Felipe et al. used cationic resins to recover REE from AMD using ion exchange. However, the resin used favored low value lanthanum and LREE over valuable HREE [63]. Many sorbants have been evaluated to specifically recover REEs from AMD and sorption literature has been recently discussed by both Wei et al. [266] and by Royer-Lavallee et al. [198]. No specific sorption process has been shown to hold economic promise at scale.

In other studies, researchers have shown that REEs can be effectively recovered from acid leachate generated from coarse coal reject [87, 278, 281]. In once case, Zhang and Honaker were able to generate a 94% mixed rare earth oxide product through multi-staged precipitation and re-dissolution of natural leachate from a coarse coal waste pile [278]. In a second study, Zhang and Honaker produced a 98% mixed rare earth oxide product along with Cu, Ni, and Co co-products [281]. A comprehensive review on these and other similar studies on coal-based leachates has been provided by Zhang et al. [87, 278, 280, 281].

The economic potential of recovering REEs from AMD and AMD precipitate using a selective multi-step leaching process was evaluated by Fritz [69]. This study showed that process and operational configuration employed by the researchers were not economically viable at the proposed scale (1000 kg REE/yr) without significant government subsidies. Despite this finding, Fritz et al. provided a valuable framework for subsequent project evaluations. It should also be worth noting that few studies to date have also addressed the simultaneous recovery of REEs and other non-REE CMs, which could significantly increase the value proposition.

Recently, an effective AMD treatment process was developed and patented by West Virginia University to recover REE and other critical minerals from AMD as a pre-concentrate using a two-step precipitation approach [290]. In this process, the AMD stream is first neutralized to a pH of 4 to 4.5 to precipitate all iron and most aluminum. The resulting solution is further neutralized to a pH 8 to 8.5 to precipitate all REE with most cobalt and manganese as a pre-concentrate material. The REE/CM depleted water is sent to the permitted discharge point, meeting applicable clean water standards as set by the relevant local, state, and federal agencies. Processes derived from the work of West Virginia University have been investigated by others such as Moraes et al. investigating the role of A13-polymers in the neutralization process [156]. Moraes et al. concluded that aluminum polymers play a role in the losses of REE to tailings in specific ranges of pH. Their data set is consistent with the West Virginia University Process.

The objective of the present study is to provide a high-level assessment of the economic merits of recovering REE and select CM from AMD sources using an innovative decentralized

network supply chain configuration. This approach relies on two enabling technologies: (1) an on-site pre-concentration process that produces an upgraded, dry REE intermediate suitable for transport; and (2) a centralized separation and refining circuit that allows full REE separation at a capital cost significantly below that of conventional approaches. To meet this objective, the study will provide a detailed analysis of the process cost drivers and the sensitivity with respect to different operational configurations and price scenarios.

3.2 Materials, Process and Methods

3.2.1 Process Description

The rare earth element and critical minerals recovery process used in this analysis was developed by L3Eng in collaboration with West Virginia University and Virginia Tech using pre-concentrate material generated by a patented two-step acid mine drainage (AMD) neutralization process [290]. Since the AMD neutralization process only requires a reconfiguration of the standard AMD treatment process and does not significantly increase its operating cost, it has not been included in this analysis; however, the cost to transport the pre-concentrate to a centralized refining plant is included as a variable operating cost. It should be noted that not all AMD sources are conducive to the recovery of REE and that the study only included those sources with sufficient REE concentration. AMD sources with marginal concentrations of REE may be added to the project at a later stage should their impurity profile allow for the concentration of REE in the pre-concentrate material at levels similar to included sources.

Testing to date on a variety of AMD sources have shown that the pre-concentration process

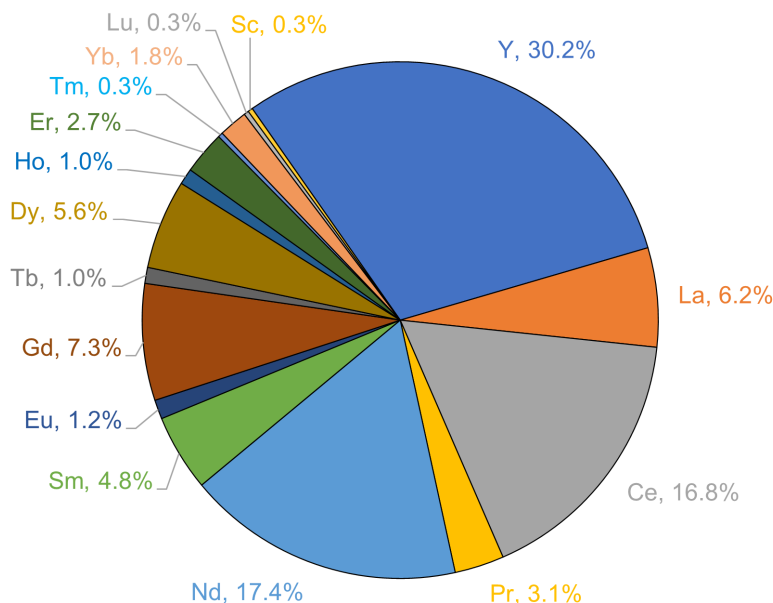


Figure 3.1: Composition of pre-concentrate material generated at Bismarck, WV AMD treatment facility

typically produces an REE precipitate averaging 1% to 5% in grade with moisture as low as 15%. Figure 3.1 shows the REE/CM elemental assay for a pre-concentrate sample produced from an active AMD discharge near Bismarck, WV using the process described in US Patent US20210017625A1 [290]. Assays for this sample were determined by the NRCCE laboratory in Morgantown, WV, using the method described in Vass et al. [255]. As shown, the pre-concentrate contains a significant portion of heavy and critical REEs, with the most abundant element being Y. La and Ce are notably reduced while Dy is increased in this material when compared to conventional REE ore sources. Using current REE pricing, the basket price for this material (including only Sc, Y and the lanthanides) is determined to be: \$ 60.76/kg, which is extremely competitive with and superior to many conventional REE deposits.

After generating pre-concentrate at a number of distributed sites, the material is transported by truck to a central extraction and refining plant. A block flow diagram for the full process

is shown in Figure 3.2. First, the pre-concentrate is leached using hydrochloric acid and the pregnant leach solution is partially neutralized using sodium carbonate. The resulting aqueous solution is processed in a series of solvent extraction units to separate the rare earth elements, cobalt and manganese. Commercially available extractants including Di-(2-ethylhexyl)phosphoric acid (D2EHPA), 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (EHEHPA), sec-octyl phenoxyacetic acid (CA-12), Cyanex 272 (C-272) and Cyanex 572 (C-572) are used in the flowsheet to facilitate the full separation of REEs. The team is exploring reduction processes including one developed by Hela Novel Metals. In this process, rare earth elements and cobalt oxalates are reduced to rare earth and cobalt metals and formed into magnets using their proprietary patent pending Carboxylate Reduction Process (CRP) [99].

The rare earth element recovery units consume hydrochloric acid, ammonium hydroxide, oxalic acid, zinc pellets, sodium hydroxide and sodium carbonate while the cobalt recovery unit consumes ammonium hydroxide, sulfuric acid and oxalic acid. The manganese recovery unit consumes calcium oxide (quicklime) and an internally recycled oxidizing agent. The Hela Novel metals process utilizes a proprietary mixture of nitrogen, ammonia, carbon monoxide and hydrogen.

3.2.2 Techno-Economic Analysis for the Recovery of REEs and CMs from AMD

The techno-economic analysis was performed on a conceptual extraction and refining process designed using a combination of theoretical equilibrium calculations [115] and bench scale

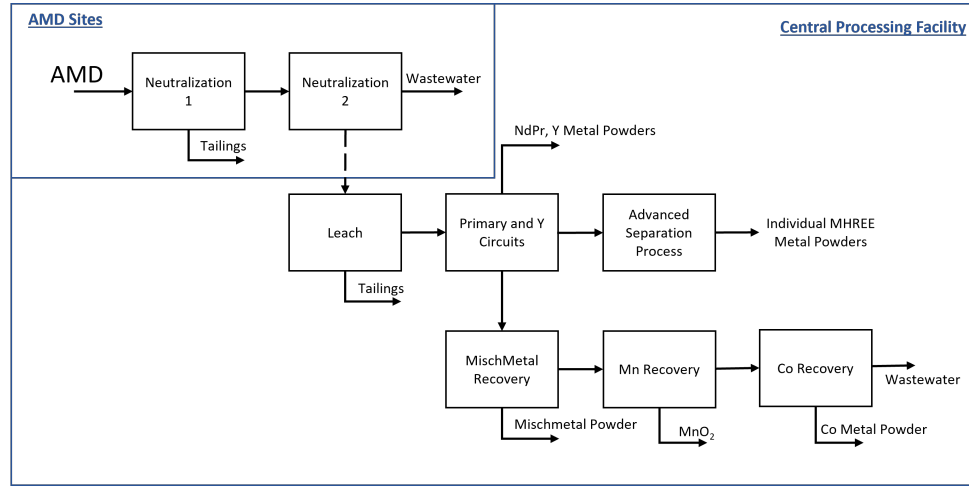


Figure 3.2: Proposed block flow diagram

test work. This method is typical of an innovative process flowsheet development and design project using the Front-End Loading (FEL) process [218]. In this process, the economic viability of the proposed project is evaluated at various project advancement stages, each with increasing investment in time, material and capital. The FEL process was developed to minimize the overall project investment risk. [24]

Economic assumptions, including those regarding the financing structure, escalation rates, tax calculations, and operating period include:

- All amounts are in US dollars.
- The total operational period for the plant is 20 years.
- Inflation was applied to sales revenue and operating costs using a fixed rate of 3% per year.
- Capital costs are spread over a period not to exceed three years, and the allocation between those three years is 10%, 60%, and 30% for years one through three, respectively.

Thus, the total analysis period (capital purchase plus operating) is not to exceed 23 years.

- During the capital expenditure period, capital costs escalate at a constant rate of 3.6% per year.
- The project is debt financed for 50% of the total overnight capital requirement; the remaining 50% is financed by equity.
- The debt repayment terms include: 6% interest rate, 10-year loan period, and no grace period on debt repayment. The re-payment uses a standard amortization schedule with constant payments throughout the payoff period.
- Working capital is not included in this estimate and will instead be borne by the operating entity at no cost to the project.
- The combined federal and local tax rate is fixed at 26%.
- All capital is depreciable, using a 150% declining balance depreciation schedule over 20 years. The depreciation method was not changed to straight line when conditions favored the switch.
- The mineral depletion rate for REEs is 14%. Depletion is charged at the appropriate rate times the net sales revenue after deducting royalties and any severance tax, provided that the total amount calculated by depletion rates does not exceed 50% of the taxable income before depletion.
- The plant is part of a larger commercial entity with sufficient revenue to offset negative taxable income. Thus, losses are not carried forward and are instead calculated as a “negative tax” that indicates the reduction in tax burden required for overall entity.

- No royalties are charged for the productions of REEs, as this cost is assumed to be borne with the feedstock acquisition costs.
- All production is assumed to be sold.

Operating Cost Estimate

The operating cost is calculated based on four generic cost categories.

- Materials, Reagents and Consumables
- Energy
- Labour
- Capital Spares

Reagents, consumables and energy costs were derived from a process heat and material balance, simulated using the commercial simulation program METSIM. When available, bench scale test data was used as a basis for the simulation. When not available, or not practical for the stage of development of the project, literature and thermodynamic simulations were utilized. The solvent extraction circuit, however, was simulated using a simulation method previously developed by the author and described elsewhere [115] using literature data as a basis. The separation factors inputted to the model were derived from literature and are presented as Table 3.1.

Electrical energy costs are primarily consumed by the pumping and agitation. The process plant will also consume natural gas for process heating purposes through hot oil heaters. Labor costs have been estimated for staffing numbers typical for similar plants based on the experience of the design team. At any given time, 17 full time employees are required for the

Table 3.1: Model Separation Factors (factors noted with an "*" were not reported)

	EHEHPA	CA-12	CA-12,C272	C-572
Source	[179]	[264]	[264]	[159]
Reference Element	La	Y	Y	La
La	1	*	*	1
Ce	6.8	*	*	5.9
Pr	13.9	*	*	9.5
Nd	21.5	*	*	14.6
Sm	227.8	*	*	101
Eu	341.7	*	*	189
Gd	1,982	3.73	1.97	252
Tb	>2,000	3.09	1.86	612
Dy	>2,000	2.44	1.75	1,014
Ho	>2,000	1.73	1.41	1,308
Er	>2,000	1.67	1.65	2,013
Tm	>2,000	1.36	2.51	3,961
Yb	>2,000	1.25	5.09	5,611
Lu	>2,000	1.06	6.55	9,583
Y	>2,000	0.15	0.05	1,713
Sc	>2,000	8.00	8.00	38,334

plant operation and maintenance activities. While water treatment costs have been included using typical costs, other waste disposal costs have not been included in the analysis. Capital spares have been estimated at 4.0% of the purchased equipment cost annually.

Bench-marking of the process flowsheet was not possible since no commercial operation is currently extracting and refining REEs and CMs from AMD, and because both the process flowsheet and the process throughput is significantly different than commercial operations. Commercial separation plants typically have capacities in the thousands to tens of thousands of tonnes per year and operate a continuous process with dedicated circuits for each element. These plants also tend to have rigid guidelines for feedstock compositions with little short term flexibility. Our process is at least an order of magnitude smaller than commercial operations, has both continuous and semi-continuous circuits with a built-in flexibility for the processing of different feedstock compositions.

Capital Cost Estimate

The capital cost estimate was developed following the AACE Class IV (FEL-2, or $\pm 40\%$) level engineering study cost estimate guidelines. Process equipment was sized based on the heat and material balance for the process and design criteria either derived from bench scale test work or based on the design engineer's experience for this type of process. The estimate uses major unit operation supply costs factored to installed unit cost, assuming a greenfield generic industrial site. Non-equipment related direct costs are factored using the Peters and Timmerhaus Method [45] based on the design engineer's experience for this type of process. Other direct cost factors are included in Table 3.2.

Most factors were selected at the lower end of the typical range due to the nature of the process. Notably, the large majority of the plant piping will be composed of small diameter plastic or FRP piping because the process involves small flow rates at low temperature and low pressures. Required instrumentation will be mostly located at the feed and discharge of the solvent extraction batteries, resulting in a relatively low instrument factor.

Table 3.2: Other Direct Costs Factors

Direct Cost	Typical Range	Selected Factor
Instrumentation and Controls	10-20%	10%
Piping	20-70%	15%
Electrical	10%	10%
Building and Structure	20-30%	20%
Property Improvements	10%	10%
Utilities	20-50%	20%

Where possible, budget pricing for major cost items have been obtained from vendors based on preliminary specifications developed during engineering. Alternatively, where recent and relevant project data enables an item to be estimated it may be based on that information. Where neither is possible, equipment pricing was obtained from engineering databases. When none of the above was available, allowances were assigned based on experience and judgment of the engineers involved in the study.

Indirect costs were factored on the direct costs and have magnitudes selected to account for the characteristics of the project.

Owner's costs have been assigned according to the design engineer's experience for projects of this type. The scope of Owner's costs included is limited to those defined and other areas

of expenditure may be required.

Financial and Sensitivity Analysis

Life cycle financial analyses were conducted using several REE pricing scenarios as shown in Table 3.3. The baseline case uses 2020 prices, while the additional cases utilize 2021 prices as well as the minimum and maximum prices over the last decade. Given the extreme volatility over this date range, these values are anticipated to represent the limiting thresholds for analysis.

In addition to the pricing scenarios, five distinct plant configurations were also considered. These include: :

- Complete Processing Plant (REEs, Co, Mn, Mischmetal)
- REE plant, with no Mischmetal
- REE, Co plant, with no Mischmetal
- REE, Co, Mn plant, with no Mischmetal
- Only salable products are the magnet REEs (Pr, Nd, Tb, Dy), Y, Sc, Co and Mn

For the purpose of this analysis, an average pre-concentrate composition building on work by Vass et al. and Ziemkiewicz et al. was assumed. Therefore, no alternative scenario based on variations of feed composition was considered. The composite pre-concentrate composition is presented as Table 3.4. It has been estimated that approximately 53,000 mtpy of pre-concentrate material will be required to supply a refinery operating at its design capacity. This value translates into approximately 104,500 cubic meters per hour of treated

Table 3.3: Pricing Scenarios used for Analyses, all values in USD/kg

Product	2020 Price	2021 Price	Min Price	Max Price
MREO	\$26.65	\$39.05	\$16.13	\$47.46
M-HREO	\$73.22	\$117.47	\$46.93	\$143.12
Nd(Pr) micro powder	\$69.65	\$129.11	\$51.60	\$129.11
Y Metal micro powder	\$39.77	\$40.13	\$24.72	\$40.13
Mischmetal micro powder	\$20.45	\$4.89	\$3.27	\$20.45
Cobalt micro powder	\$41.67	\$58.60	\$23.77	\$58.60
Sm micro powder	\$18.40	\$15.01	\$13.25	\$15.01
Crude EuSO ₄	\$7.50	\$7.87	\$7.45	\$7.87
Gd metal micro powder	\$56.81	\$72.31	\$24.21	\$72.31
Tb metal micro powder	\$738.58	\$1,867.41	\$511.19	\$1,867.41
Dy metal micro powder	\$340.88	\$579.23	\$251.59	\$579.23
Ho metal micro powder	\$695.03	\$768.62	\$315.14	\$768.62
Er metal micro powder	\$107.95	\$116.66	\$39.24	\$116.66
Tm metal micro powder	\$857.29	\$925.77	\$379.57	\$925.77
Yb metal micro powder	\$228.28	\$229.18	\$93.96	\$229.18
Lu metal micro powder	\$3,298.76	\$3,451.32	\$1,415.04	\$3,451.32
Sc metal micro powder	\$3,976.99	\$3,314.83	\$1,359.08	\$3,314.83
Manganese oxide	\$1.97	\$1.97	\$1.58	\$3.20

AMD capacity, which is well within the limits of the estimated flows of the survey by Vass et al., especially when supplemented by other coal-based AMD surveys [47, 122] and hard-rock AMD sources [62]. Based on the composition, a maximum contained value assuming full separation and conversion to products was calculated for the four pricing scenarios and is presented as Table 3.5; the contained value indicates the aggregate value of a ton of pre-concentrate material assuming complete recovery of each salable product. While not particularly useful in itself, the contained value metric allows for the comparison of projects with each other and offer an indication of processing efficiency when compared to the [realized] pre-concentrate value discussed in a later section of the article.

A sensitivity analysis was performed by Monte Carlo simulation using Crystal Ball as an add-on to Microsoft Excel. Triangular probability distribution functions were established for the pricing of the various raw materials and consumables. The minimum and maximum of the functions were set respectively to the minimum and maximum market prices for the period 2014 to 2021. Raw material pricing were derived from both publicly available sources such as the USGS commodity survey and private market pricing databases including but not limited to Intratech and Echemi.

Uniform probability distribution functions were established for water treatment and energy costs. With minimum and maximum set in the range 80% - 120%. Energy costs were derived from publicly available utility data.

Capital costs for the various scenarios were assigned normal probability distribution functions with a 95% confidence interval approximating the upper and low bounds of the +/- 40% precision of the capital cost estimation method.

Table 3.4: Pre-Concentrate Composition

Element	Composition
Al	5.03%
Si	19.03%
S	3.93%
Ca	4.92%
Sc	0.002%
Mn	13.32%
Fe	$8.62 \times 10^{-07}\%$
Co	0.390%
Y	0.219%
La	0.077%
Ce	0.220%
Pr	0.030%
Nd	0.148%
Sm	0.038%
Eu	0.010%
Gd	0.053%
Tb	0.008%
Dy	0.046%
Ho	0.009%
Er	0.022%
Tm	0.0028%
Yb	0.016%
Lu	0.002%

Table 3.5: Pre-Concentrate Contained Value in USD/kg

	2020 Price	2021 Price	Min Price	Max Price
Pre-Concentrate Contained Value	\$1,242	\$1,575	\$751	\$1,786

Revenues are calculated from production quantities derived from the heat and material balance and market pricing. The market pricing was evaluated based on publicly available databases as well as private pricing databases such as Roskill, Asian Metal Prices and ISE. When applicable, factors based on proprietary market pricing data from Hela Novel Metals LLC were applied to account for the specific nature of the products.

Four pricing scenarios were evaluated:

- September 2021 Pricing
- December 2020 Pricing
- Minimum Pricing, Period 2014-2021
- Maximum Pricing, Period 2014-2021

The three main elements evaluated as part of the financial analysis are the net present value (NPV), the internal rate of return (IRR) and the realized value of pre-concentrate material.

The net present value is the sum of all cash flows incurred or generated by the project discounted to the present using a discount rate defined by the analyst. In the present analysis, a 10 % discount rate has been applied to all NPV calculations. It is common to indicate the discount rate in parenthesis following the NPV abbreviation. As such a NPV calculation utilizing a 10% discount rate would be noted NPV(10%).

The internal rate of return is the measure of a discount rate that results in a neutral net

present value, $NPV(IRR) = 0$. It offers an indicator to the project management relative to the project profitability and is often compared to a minimum required rate based on risk profiles. [45].

The value of pre-concentrate material is a measure of the level of incentive the project could offer the various AMD neutralization plants to convert their plant to generate pre-concentrate material, assuming the project is operated to meet a IRR of 10%. The basis assumption underlying this metric is a processing plant operating as a cooperative or public service to support the treatment of AMD sources through re-distribution of profits to operators of AMD sites relative to their contribution in feed material quantity and quality. The 10% IRR baseline will provide sufficient capital for improvement projects and to manage market risks.

3.3 Results, Discussion and Recommendations

3.3.1 Engineering Study Summary

A summary of the engineering effort is presented in Tables 3.6, 3.7 and 3.8, representing the capital and operating cost estimate, production and revenues for each scenarios identified in the previous section.

The operating cost for the four plant configurations is broken down in Figure 3.3, revealing that raw materials, notably hydrochloric acid and various alkalis, are the most important operating cost. This is typical of rare earth solvent extraction processes which are significant

Table 3.6: Capital and Operating Cost Summary

Plant Configuration	Capital Cost MM USD	Operating Cost MM USD / year
Complete Facility	\$ 185.81	\$ 25.00
REE, w/ no Mishmetal	\$ 130.79	\$ 21.14
REE, Co, w/ no Mishmetal	\$ 148.60	\$ 22.24
REE, Co, Mn, w/ no Mishmetal	\$ 154.83	\$ 24.41
Magnet REE, Y, Sc, Co, Mn	\$ 142.20	\$ 24.41

Table 3.7: Annual REE/CM Production for Various Operational Configurations

Plant Configuration	REE mtpy	Co mtpy	Mn mtpy
Complete Facility	444	157	5653
REE, w/ no Mishmetal	290	-	-
REE, Co, w/ no Mishmetal	290	157	-
REE, Co, Mn, w/ no Mishmetal	290	157	5653
Magnet REE, Y, Sc, Co, Mn	212	157	5653

Table 3.8: Annual Plant Revenues for Various Operational Configurations and Pricing Scenarios

Plant Configuration (in MM USD)	September 2021	December 2020	Minimum 2014-2021	maximum 2014-2021
Complete Facility	\$ 70.46	\$ 56.07	\$ 33.39	\$ 79.83
REE, w/ no Mishmetal	\$ 49.42	\$ 35.26	\$ 20.25	\$ 49.42
REE, Co, w/ no Mishmetal	\$ 58.59	\$ 41.78	\$ 23.97	\$ 58.59
REE, Co, Mn, w/ no Mishmetal	\$ 69.70	\$ 52.92	\$ 32.89	\$ 76.68
Magnet REE, Y, Sc, Co, Mn	\$ 56.58	\$ 40.77	\$ 27.58	\$ 63.55

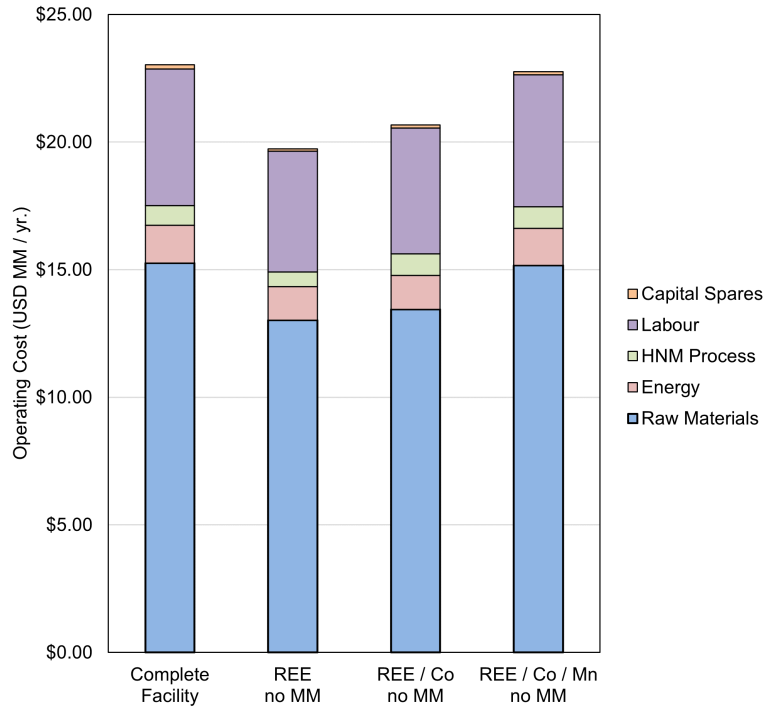


Figure 3.3: Operating cost breakdown for various operational configurations.

consumers of acids and alkalis [121].

3.3.2 Financial Analysis

The three main elements evaluated as part of the financial analysis were the net present value (NPV), the internal rate of return (IRR) and the value of pre-concentrate material (PCV).

The net present value, internal rate of returns and pre-concentrate value of the project for the various plant configurations and pricing scenarios assuming a 10% discount rate are presented in Figure 3.4, 3.5 and 3.6.

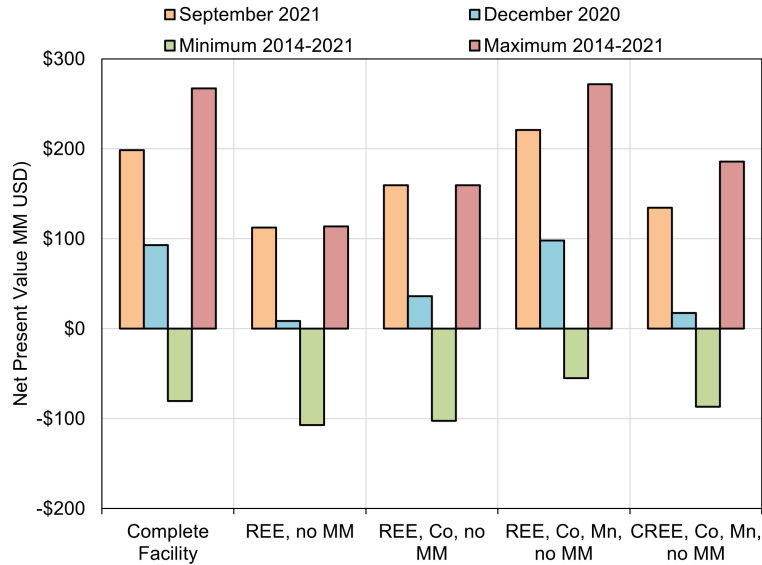


Figure 3.4: Net present value results for various operational configurations and pricing scenarios.

While all three elements of the financial analysis yield the same conclusion since they portray the same patterns, key project insight can be derived from the specific indicators IRR, NPV and PCV. Based on the analysis, the plant configuration where all REEs (except for mischmetal), Co and Mn are produced should be favored and all products should be marketed because it yields the highest IRR and NPV in all comparable pricing scenarios. However, it should be noted that while this plant configuration yields positive returns for all pricing scenarios, it fails to meet the minimum internal rate of return of 10% in the minimum pricing scenario.

Of particular interest is the scenario where only magnet materials, scandium, yttrium cobalt and manganese are sold as products since it represents a more likely scenario since all these products are forecast to be in short supply for the next decade. [192].

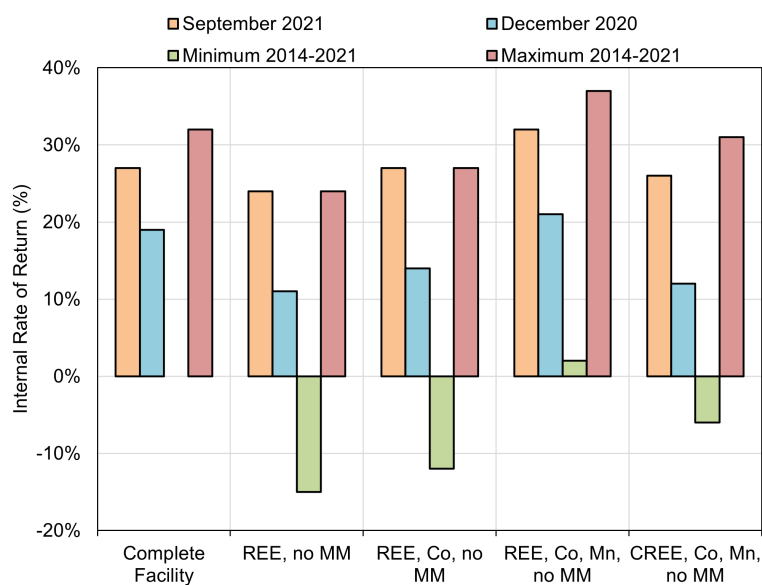


Figure 3.5: Internal rate of return results for various operational configurations and pricing scenarios.

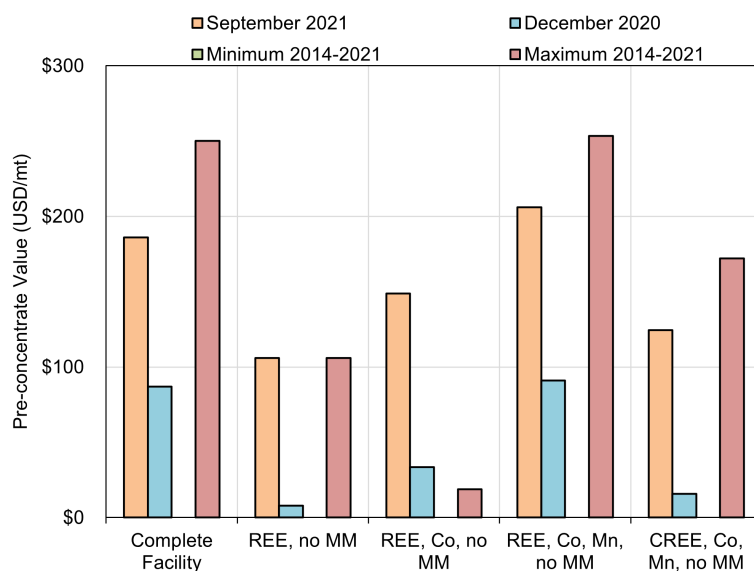


Figure 3.6: Pre-concentrate value results for various operational configurations and pricing scenarios.

3.3.3 Sensitivity Analysis

A sensitivity analysis was performed on the magnet REEs, scandium, yttrium cobalt and manganese scenario using current pricing for revenue determination. The results of the sensitivity analysis are presented as a Tornado Plot in figure 3.7 and in the Monte Carlo Summary in Figure 3.8.

The tornado plot clearly demonstrates that only two project parameters have a significant impact on the profitability of the project, the capital cost of the project and the pricing of hydrochloric acid. The Monte Carlo analysis reveals that the sensitivity of the project tends to be distributed as a normal distribution centered toward 22% with a minimum return around 13% and a maximum return of 38%. The normal distribution of the result is primarily due to the disproportionate effect of the capital cost on the financial indicators studied.

The major takeaway from the sensitivity analysis suggest that any optimization work should be directed at reducing the capital cost of the project and the hydrochloric acid consumption. Both aspects could be simultaneously optimized with a transition to ionic liquids [137] and an optimization of the processing circuit, leaving most heavy elements as a mixture to be stockpiled or processed as needed. Furthermore, the possibility of recycling chlorides from the wastewater streams should be evaluated with respect to hydrochloric acid pricing and a recycling process economic parameters.

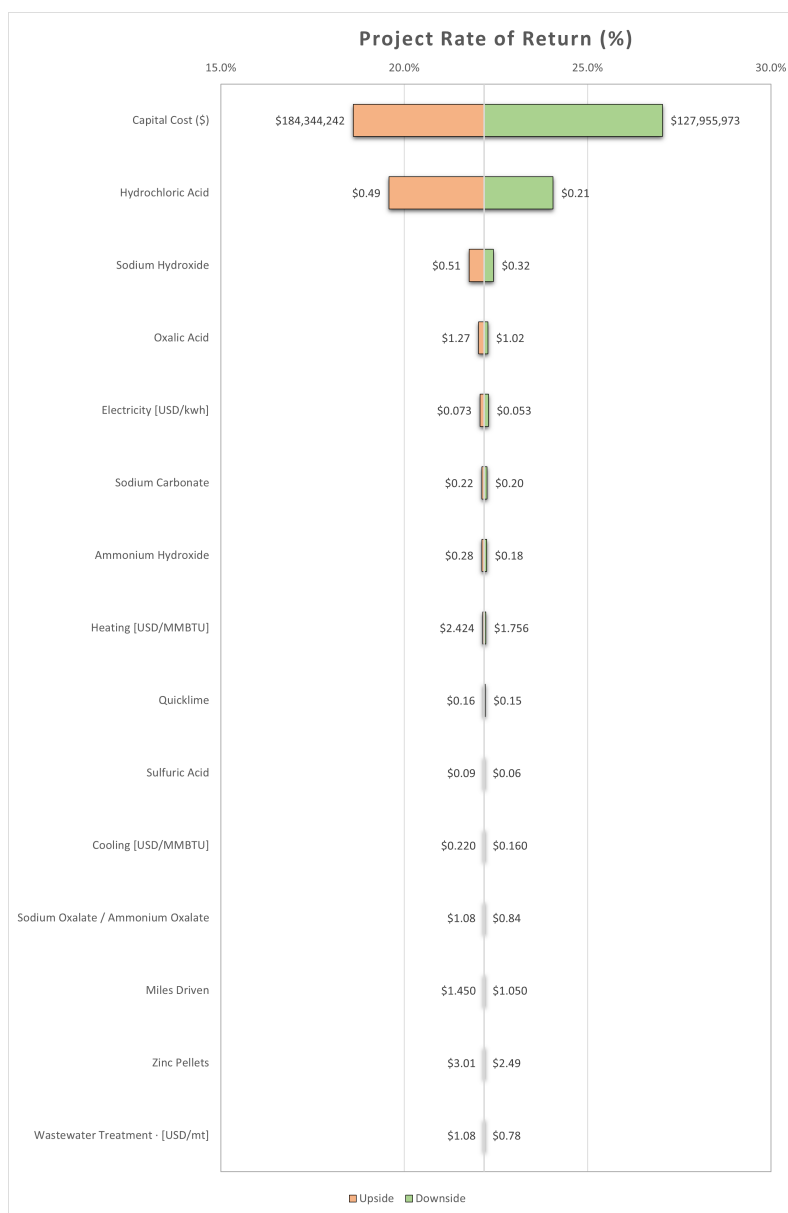


Figure 3.7: Tornado plot showing the sensitivity of several key input factors on the project rate of return. Current pricing, magnet element-only configuration.

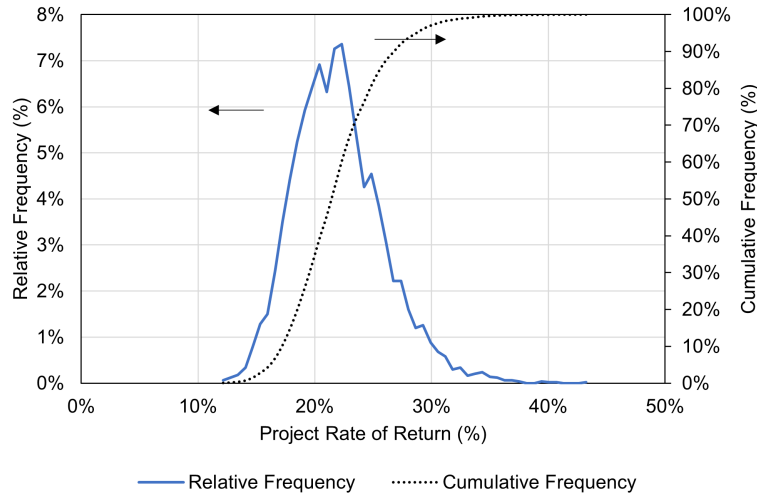


Figure 3.8: Results from Monte Carlo Simulation showing rate of return. Current pricing, magnet element-only configuration.

3.3.4 Implication of the Results

Our study proposes an economically viable and sustainable low volume supply chain for critical minerals and rare earth elements aimed at securing these critical minerals for national security purposes. While the economic indicators are favorable in several scenarios, the analysis suggests a level of risk unacceptable for private enterprise, especially considering the base assumption of free sourcing for pre-concentrate and the potential for price volatility including long periods of low market price. We contend that by re-framing the sourcing strategy of pre-concentrate from a supplier-buyer relationship to a distributed cooperative supply chain, private corporations as well as government agencies will be incentivized in treating acid mine drainage sources to the benefit of communities downstream of the AMD sites. Moreover, this approach provides a mechanism that both incentivize AMD treatment and promotes economic development in regions that have been most impacted by declining coal production, while mitigating a national security need.

The low concentration of REE in AMD limits the scope and size of the central processing plant, as well as the number of such plants per geographical area. Nevertheless, it is likely that the concept could be duplicated in other mining districts, particularly those with pervasive and perpetual acid mine drainage issues. Ongoing study by the authors indicates substantial AMD based REE/CM in other U.S. mining districts. Future analysis will indicate the extent to which they could add to a national supply chain with respect to recovery, compatibility and economic return.

3.4 Conclusions

This study has described a detailed techno-economic analysis of a REE/CM supply chain based solely on acid mine drainage feedstocks. Key enabling technologies of this approach include (1) an on-site pre-concentration process that produces an upgraded, dry REE intermediate suitable for transport; and (2) a centralized separation and refining circuit that allows full REE separation at a capital cost significantly below that of conventional approaches. The current study has assessed the capital and operating costs of the centralized separations and metal production plant and used sensitivity analysis and stochastic simulation to identify the major cost drivers. In addition, scenario modeling was used to evaluate the influence of REE/CM pricing and to identify the optimal product suite under various market conditions. Key conclusions from this work include:

- The contained value of pre-concentrated AMD produced from passive two-stage precipitation [US 2021/0017625 A1] ranged from \$751 to \$1,786 per metric ton when using the minimum and maximum prices over the last decade. The contained value was determined to be \$1,575 per metric ton using contemporary (September 2021) prices. These values are commensurate with or even superior to conventional REE ore

deposits currently under consideration.

- The REE basket price of AMD pre-concentrate was determined to be \$60.76 / kg REE when using contemporary oxide prices. This value is nearly two times that of conventional REE sources, including ion adsorption clays found in South China [75]. This value is largely due to the high content of critical and magnet REEs, including Y, Nd, Pr, and Tb, which collectively constitute over 54% of the total REE content.
- Depending on the plant configuration, the production capacity ranges from 212 to 444 mtpy REE, 157 mtpy Co and 5,653 mtpy Mn. This value is significantly below that of conventional REE separation plants; however, this level of production may be crucial in establishing a baseline for national security purposes. An assessment of the pre-concentrate feed requirements needed for this level of production show that the volume is well within the estimated flows of AMD within the Appalachian region.
- The results of this analysis show that, with the exception of the minimum price scenario, all operational configurations have positive economic indicators with rates of return varying from 10% to 38% for the contemporary price scenario. The optimal configuration was determined to include production Co, Mn, and all REEs except for mischmetal, which is not recovered. The magnet REE, Sc, Y, and CM-only configuration, which is deemed to be the most likely given future demand scenarios, yielded a positive rate of return in all scenarios but the minimum pricing scenario.
- Sensitivity analysis and Monte Carlo simulation demonstrate that the project capital cost and HCl consumption were the only two project parameters that produced a significant impact on overall profitability. This result suggests that further optimization of process design may impart significant financial gains to the enterprise (i.e. the low capital cost estimate produce a 5 percentage point increase to rate of return). No-

tably, additional research and development on the use of ionic liquids [137], rather than solvent-based extractants may produce simultaneous and synergistic improvement of these two parameters.

- While the economic results are moderately favorable under most scenarios, the level of project risk is significant, particularly considering the possibility of prolonged price disruptions. To mitigate this risk, one option could re-frame the sourcing strategy to one of supplier-buyer cooperative whereby the profits are shared between the investor, the operator, and the feedstock suppliers. Given the nature of AMD treatment in the US, which can often include a mix of government and private liability holders, this approach would inevitably require strong public-private partnerships. Nevertheless, this approach will both incentivize AMD treatment and promote economic development in regions that have been most impacted by declining coal production, while mitigating a national security need.
- To better identify and quantify the environmental, social, and governance, benefit of the proposed approach, additional study should address stakeholder assessments, regional economic impact, environmental justice considerations, product life cycle analysis, and legal implications and barriers. Given the promising economic indicators identified at this stage, the research team will evaluate these and other factors as the project progresses.

Chapter 4

Recovery of Rare Earth Elements from Acid Mine Drainage using Ionic Liquids

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Abstract:

Acid mine drainage is a legacy environmental issue and one of the largest pollutants in many mining districts throughout the world. In prior work, the authors have developed a process for the recovery of critical materials, including the rare earth elements, from acid mine drainage using a preconcentration step followed by solvent extraction as a concentration and purification technology. As part of the downstream technology development efforts, we have synthesized a suite of ionic liquid extractants that facilitate greater separation factors leading to lower capital costs and reduced environmental impacts. This article provides a comparison of the conventional extractants D2EHPA, EHEHPA and C572 with their respective ionic liquids [c101][D2EHP], [c101][EHEHP] and [c101][C572] for the recovery of rare earth elements from acid mine drainage. In the study, laboratory-scale, multi-contact solvent extraction tests were conducted at high and low extractant/dosages. The results show that the ionic liquids varied in performance, with [c101][D2EHP] and [c101][EHEHP] performing poorer than their conventional counterparts and [c101][c572] performing better. Recommendations for further study on [c101][c572] include stripping tests, continuous pilot testing, and techno-economic analysis.

Keywords: Rare Earth Elements; Solvent Extraction; Ionic Liquids

4.1 Introduction

The transition of society toward more efficient and advanced technologies have revealed significant risk of disruption in the minerals supply chains. Some minerals, having specific technological applications with no or little replacement options and at risk of supply chain

disruption have been termed “critical minerals” by various government and private entities [27, 92, 157, 162, 248]. While the methodologies for establishing criticality vary from country to country and agency to agency, all definitions encompass the notions of technological importance and supply chain disruption risk. One subset of elements containing many critical minerals is the lanthanide group, also referred to as rare earth elements.

The Rare Earth Elements (REEs) consist of 17 metals, specifically the 15 lanthanide elements, yttrium and scandium, which are typically found in the same mineral deposits as the lanthanides. The term “rare earths” originates from an old term used to designate minerals (earths) and their believed scarcity upon their initial discovery [260]. The rare earths designation is now considered a misnomer because it was demonstrated that the crustal abundance of some rare earth elements, such as cerium, is known to be higher than many common and widely used metals, such as copper [90]. Rare earth elements have chemical, physical, electrical, magnetic, optical, metallurgical, phosphorescent, nuclear, and catalytic properties that are often unique to them. The main properties linked to commercial applications of the REE are [191, 192]:

- Strong magnetism,
- Fluorescent properties,
- Optical properties,
- Catalytic properties, and
- Glass polishing properties.

In an effort to diversify the supply of RE-containing materials, research efforts have recently focused on recovery of REEs from unconventional sources such as mine tailings [57, 175, 241],

bauxite residues [29, 49, 280], electronic waste [55, 125], and acid mine drainage [79, 266, 280]. Acid mine drainage has been shown to be an extremely promising feedstock given it's high content of magnet critical REEs as well as the net environmental benefits associated with its remediation [254, 255].

The weathering of sulfide-bearing rock units in legacy mines often results in oxidation of the sulfides and generation of sulfuric acid [57]. The resulting acid reacts with a plethora of minerals, solubilizing them in the process [214]. Metal-laden discharge waters from these mines, referred to as acid mine drainage (AMD) have been demonstrated to contain a significant amount of rare earth elements [254, 255]. Treatment of AMD is necessary prior to discharge and generally involves acid neutralization, oxidation and metal precipitation. Iron, aluminum, and manganese are the most common regulated metals in AMD. In prior work, the authors of this paper have developed and patented a method for the recovery of critical materials, including the rare earth elements, from AMD by modifying the treatment process to include a preconcentration step followed by solvent extraction leading to a high-grade product [290].

This process sequentially neutralizes AMD in a two-step sequence. First, the AMD is neutralized to a pH of 4.5 to precipitate nearly all iron and most of the aluminum. The resulting solution is further neutralized to a pH 8 to 8.5 to precipitate all REE with most cobalt and manganese as a pre-concentrate material. The REE/CM depleted water is sent to the permitted discharge point, meeting applicable clean water standards as set by the relevant local, state, and federal agencies. The authors have recently shown how the pre-concentrated material can be further refined to produce individually separated oxides and metals of high purity [116].

One approach being investigated for the recovery of REE from AMD involves concentrating the REE by staged precipitation [290] followed by sulfuric acid leaching and solvent extraction utilizing di(2-ethylhexyl) phosphoric acid (D2EHPA) in conjunction with tributyl phosphate (TBP) diluted in kerosene in a mixer-settler battery. The project team successfully operated this extraction circuit for over a year during the construction of a demonstration unit. However, the team noticed that D2EHPA while selective for REEs would also extract significant amounts of calcium and zinc [289].

A novel class of extractants: acid-base coupling task specific functional ionic liquids (ABC-TSFILs) derived from the neutralization of conventional acidic extractants using a basic cation extractant is being heavily investigated as an alternative to conventional acidic extractants. Ionic liquid extractants are attractive because their extraction mechanism does not rely on hydronium ion exchange. Because the extraction equilibrium of acidic REE extractants is a function of the hydronium ion concentration in the aqueous phase, it is often necessary to neutralize the pregnant leach solution between extraction stages to increase extraction efficiency [109]. In addition, the stripping of the organic to recover the rare earths requires high acidity, which requires neutralization during the precipitation process [109].

Another important benefit to the usage of ionic liquid extractants is a reduction of extractant losses in the raffinate. In his investigation, Su et al. [229] discovered that the solubility of [N1888][EHEHP] was approximately five times lower than that of EHEHPA in the same experiment. Most published research on the extraction of rare earth elements using the Trihexyl(tetradecyl)phosphonium cation focuses on the ionic liquid extractant Trihexyl(tetradecyl)phosphonium Bis(2,4,4-trimethylpentyl)phosphinate [P66614][

BTMPP], also marketed as Cyphos 104 IL. Similar to Cyanex 272 from which it is derived, Cyphos 104IL does not appear to be an effective extractant for REEs [56, 112, 138, 152].

Much fewer publications are available with regards to the other combinations of acidic extractants and Trihexyl(tetradecyl)phosphonium. Sun et al., [230] investigated many di(2-ethylhexyl)phosphate [D2EHP] ionic liquids for the extraction of REEs in nitric acid media, in studies on the trivalent actinides / lanthanides separations by phosphorous-reagent extraction from aqueous complexes (TALSPEAK) process. Unfortunately the TALSPEAK process is not applicable to most industrial processes owing to its usage of nitric acid, glycolic acid and diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid. In other studies, Trihexyl(tetradecyl) phosphonium mono-(2-ethylhexyl) 2-ethylhexyl phosphonate was investigated alone and in conjunction with trioctylmethylammonium bis(2,4,4-trimethylpentyl) phosphonate [N1888][BTMPP] by Zhao et al. [285]. An unexpected synergistic effect was observed for the extraction of lutetium from chloride solutions.

Given the significant potential of ionic liquids and the lack of literature on the matter, we have investigated the extraction behavior of the conventional extractants Cyanex 801 and Cyanex 572 and compared them to our conventional D2EHPA-TBP extraction system for the recovery of REE from sulfuric acid AMD-derived pregnant leach solutions. We then prepared Trihexyl(tetradecyl) phosphonium ionic liquids with each of the three extractants and benchmarked the ionic liquids against the conventional extractant and among each other.

4.2 Materials and Methods

4.2.1 Material and Reagents

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) and kerosene were purchased from Fisher Scientific. Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) was obtained from Strem Chemicals, Inc. Tributyl phosphate (TBP) was purchased from MilliporeSigma. EHEHPA was supplied by Future Chemical Industry Co., Ltd. Cyanex 572 was obtained from Cytec Industries Inc. All chemicals were used as received without further purification.

D2EHPA, Cyanex 572, Cyphos 101, and EHEHPA were purchased to synthesize the ILs selected for this study. Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) is a high-purity phosphonium-based ionic liquid. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) are acidic organophosphorus cation exchange extractants. D2EHPA was mixed with tributyl phosphate (TBP), which acts to improve extraction performance. Cyanex 572 is a highly stable mixture of phosphonic and phosphinic acids and acts as a chelating extractant. Kerosene was utilized as a diluent.

4.2.2 Ionic Liquids Synthesis

Three phosphonium ionic liquids were prepared: (1) [c101][c572], (2) [c101][EHEHP], and (3) [c101][D2EHP]. Each IL was synthesized at a concentration of 0.1 mol/L and 1 mol/L respectively. Kerosene was used as a diluent to reduce viscosity of the extractants. The phosphonium ionic liquids were prepared following a bicarbonate neutralization process described elsewhere [65] and used without further purification or separation.

4.2.3 Preparation of AMD-derived Pregnant Leach Solution

The REE pregnant leach solution (PLS) was prepared by acid leaching of well mixed pre-concentrate material with a solids concentration of 1.5% solids. For this study, the pre-concentrate samples was produced from a typical Central Appalachian AMD source using the staged precipitation process described by Ziemkiewicz et al. [290]. Ten gallons of pre-concentrate were mixed with a Cole Parmer mixer at 80 RPM. While mixing, acid was added to the solution until the desired amount of dissolved TREE was achieved. The solution was then flocculated with a diluted polymer solution in the reaction vessel and mixed at 80 RPM for three minutes. The solution was then mixed at 30 RPM for an additional 2 minutes before settled for 30 minutes. The supernatant was pumped out of the reaction vessel and through a 1-micron bag filter. The underflow slurry was filtered with the same bag filter to remove the leaching residuals from the solution.

The PLS filtrate was placed back in the reaction vessel. While mixing at 80 RPM, sodium hydroxide was added to the solution until 90% of the aluminum in the PLS solution precipitated out, which represents a target pH of 4.4. Once the solution was sufficiently neutralized to remove the aluminum, the flocculation method above was repeated. The supernatant was filtered through a new bag filter with a 1 micron pore size. This bag filter was also used to filter the slurry underflow. The neutralized PLS was then used for subsequent solvent extraction testing.

4.2.4 Extraction Procedure

Prior to solvent extraction, the initial pH of the PLS was measured and confirmed to be 4.4. This pH operating point is the natural pH of PLS derived from our AMD-derived pre-

concentrate leach and purification process. During the actual extraction tests, the aqueous phase solution was first poured into the organic phase and agitated using an impeller blade for 10 minutes or until the solution appeared homogenous and equilibrium was reached. After agitation, the solution was poured into a separatory funnel where the disengagement time and color of the phases were recorded. After separating the phases, the volume, pH, temperature, and oxidation-reduction potential were recorded for the raffinate solution. An aliquot of the raffinate was also retained for inductively coupled plasma mass spectrometry (ICP-MS) analysis to determine element concentrations (Agilent 7900). This process was repeated for four successive contacts, each using fresh leachate and the loaded organic resulting from the prior step. All stages were conducted at an organic to aqueous (O:A) ratio of 1:10. Raffinate samples from each contact were analyzed for elemental content, and the resulting data was then used to conduct a mass balance to determine the element concentrations of the organic phase solution. All experimental parameters were held constant throughout the four contacts.

4.2.5 Extraction Extent

The single stage extraction extent (%E) of an element or group of elements (El) is defined as the percentage of that element extracted to the organic phase on a mass basis. It is calculated using Equation (1).

$$\%E = (V_{\text{PLS}} \cdot [\text{El}]_{\text{PLS}} - V_{\text{Raf}} \cdot [\text{El}]_{\text{Raf}}) / (V_{\text{PLS}} \cdot [\text{El}]_{\text{PLS}}) \quad \text{Equation (1)}$$

The cumulative extraction extent (%Ec) of an element or group of elements (El) is defined as the percentage of that element extracted to the organic phase on a mass basis considering all

the extractions performed with the organic phase (n stages). It is calculated using Equation (2).

$$\%Ec = (n \cdot V_{PLS} \cdot [El]_{PLS} - \sum_{i=0}^n (V_{Raf(i)} \cdot [El]_{Raf(i)})) / (n \cdot V_{PLS} \cdot [El]_{PLS}) \text{ Equation (2)}$$

Given these equations and the experimental parameters provided above, negative extraction efficiencies are plausible and represent back extraction of elements from the loaded organic to the new PLS.

4.3 Results

4.3.1 Extraction Extent

The single stage and cumulative extraction extent for the investigated extraction system are presented at Fig 1 to Fig 6. In these figures SEG represents samarium, europium and gadolinium and HREE represents elements heavier than dysprosium such as holmium, erbium, ytterbium, thulium and lutetium. The PLS composition is presented as [4.1](#).

Table 4.1: PLS Composition.

Element	Concentration mg / L
Fe	< 1.0
Ca	76.2
Mg	458.4
Al	41.2
Zn	260.0
Th	< 0.1
U	0.2
Sc	0.02
Y	39.9
La	8.7
Ce	22.3
Pr	4.5
Nd	22.2
Sm	6.4
Eu	1.6
Gd	9.7
Tb	1.4
Dy	7.7
Ho	1.4
Er	3.5
Tm	0.4
Yb	2.0
Lu	0.3

D2EHPA-TBP Extraction Data

The single stage and cumulative extraction extent for low concentration (0.1 mol/L) and high concentration (1.0 mol/L) D2EHPA-TBP extraction system are presented in Figure 4.1.

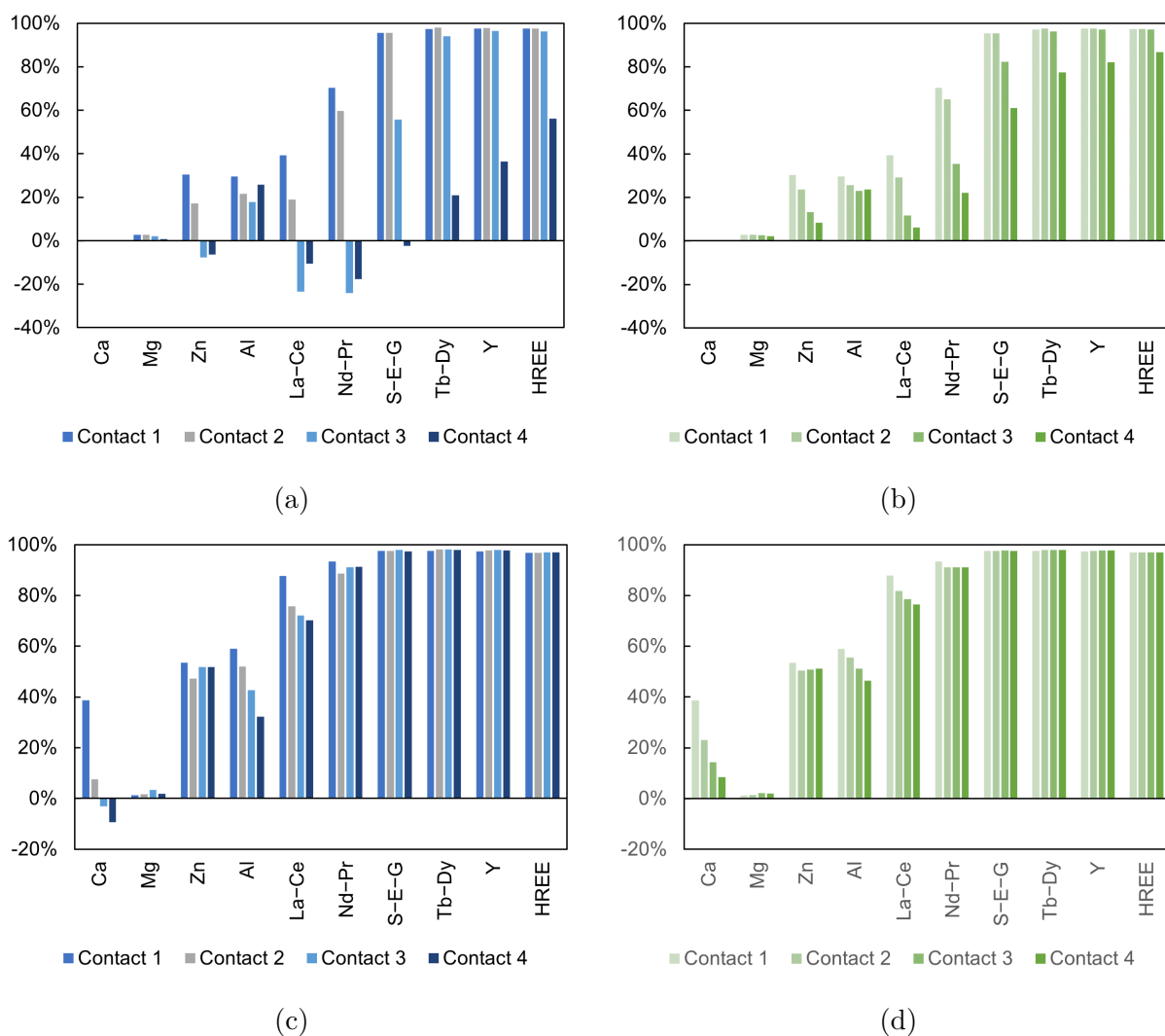


Figure 4.1: (a) 0.1 mol/L D2EHPA Single Stage Extraction Extent; (b) 0.1 mol/L D2EHPA Cumulative Extraction Extent; (c) 1 mol/L D2EHPA Single Stage Extraction Extent; (d) 1 mol/L D2EHPA Cumulative Extraction Extent.

EHEHPA Extraction Data

The single stage and cumulative extraction extent for low concentration (0.1 mol/L) and high concentration (0.9 mol/L) EHEHPA extraction system are presented as Figure 4.2.

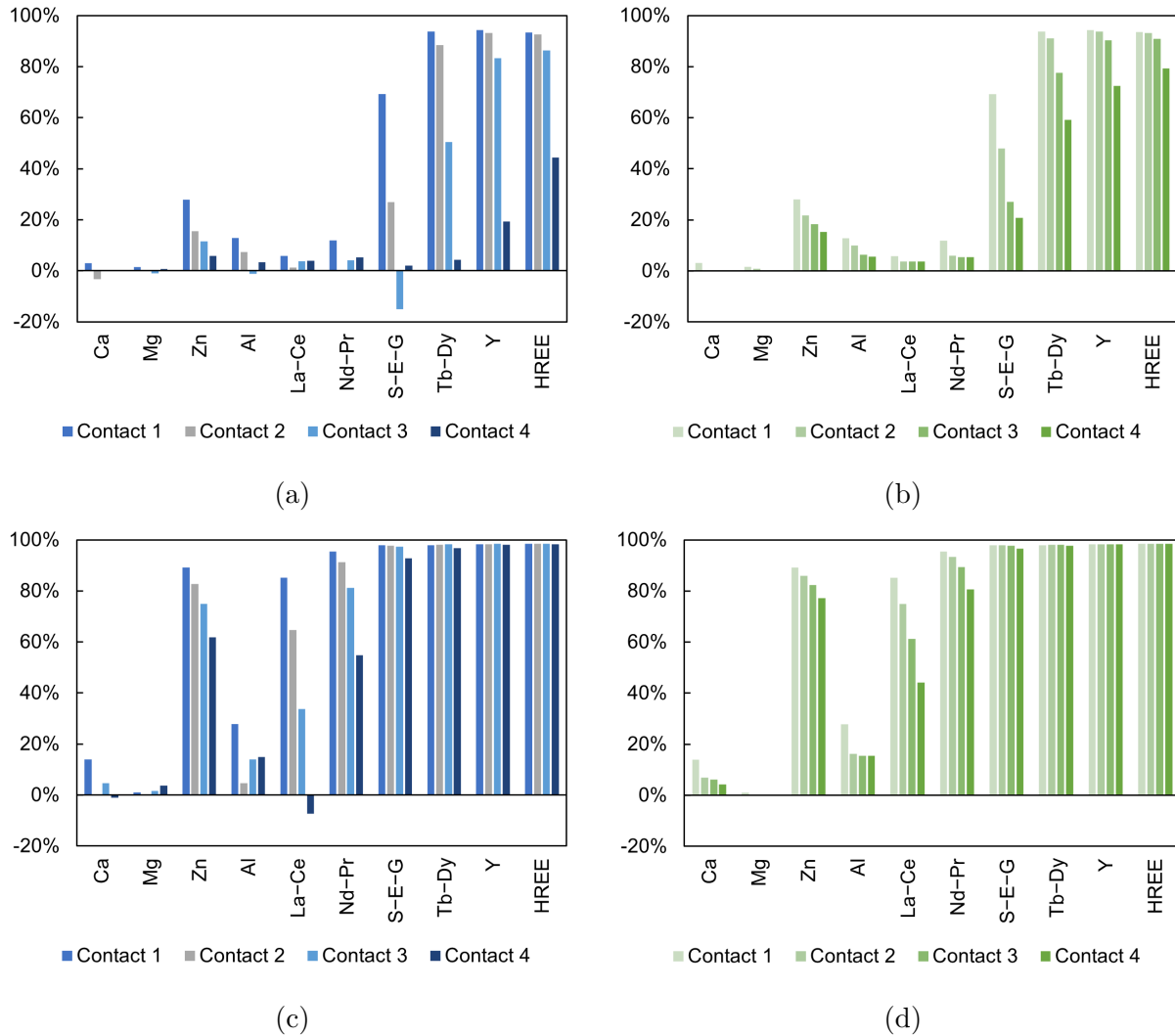


Figure 4.2: (a) 0.1 mol/L EHEHPA Single Stage Extraction Extent; (b) 0.1 mol/L EHEHPA Cumulative Extraction Extent; (c) 0.9 mol/L EHEHPA Single Stage Extraction Extent; (d) 0.9 mol/L EHEHPA Cumulative Extraction Extent.

C572 Extraction Data

The single stage and cumulative extraction extent for high concentration (1.05 mol/L) Cyanex 572 extraction system are presented as Figure 4.3.

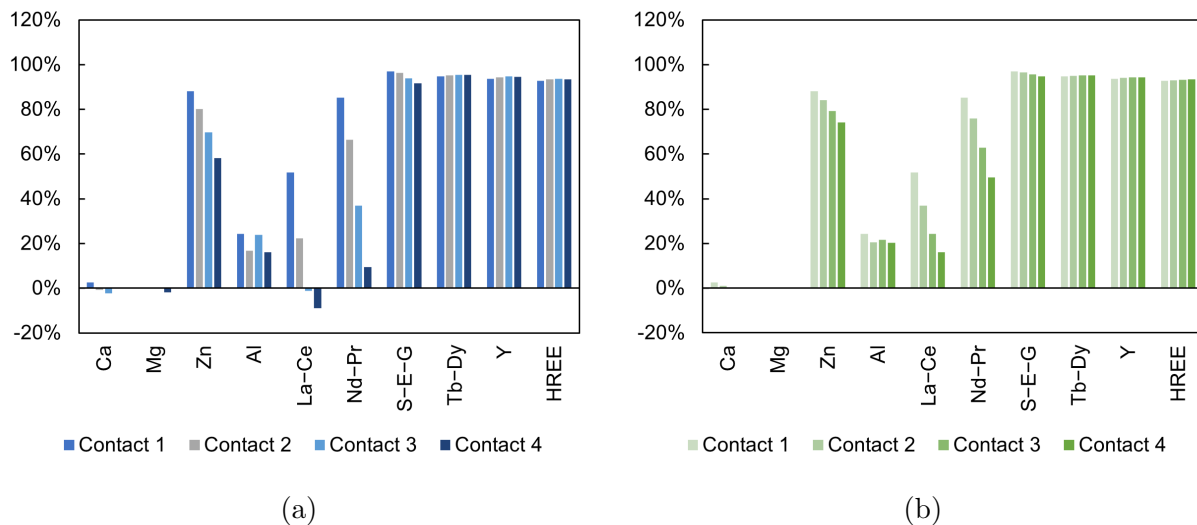


Figure 4.3: (a) 1.05 mol/L Cyanex 572 Single Stage Extraction Extent; (b) 1.05 mol/L Cyanex 572 Cumulative Extraction Extent.

[c101][EHEHP] Extraction Data

The single stage and cumulative extraction extent for low concentration (0.1 mol/L) and high concentration (1.0 mol/L) [c101][EHEHP] extraction system are presented as Figure 4.4.

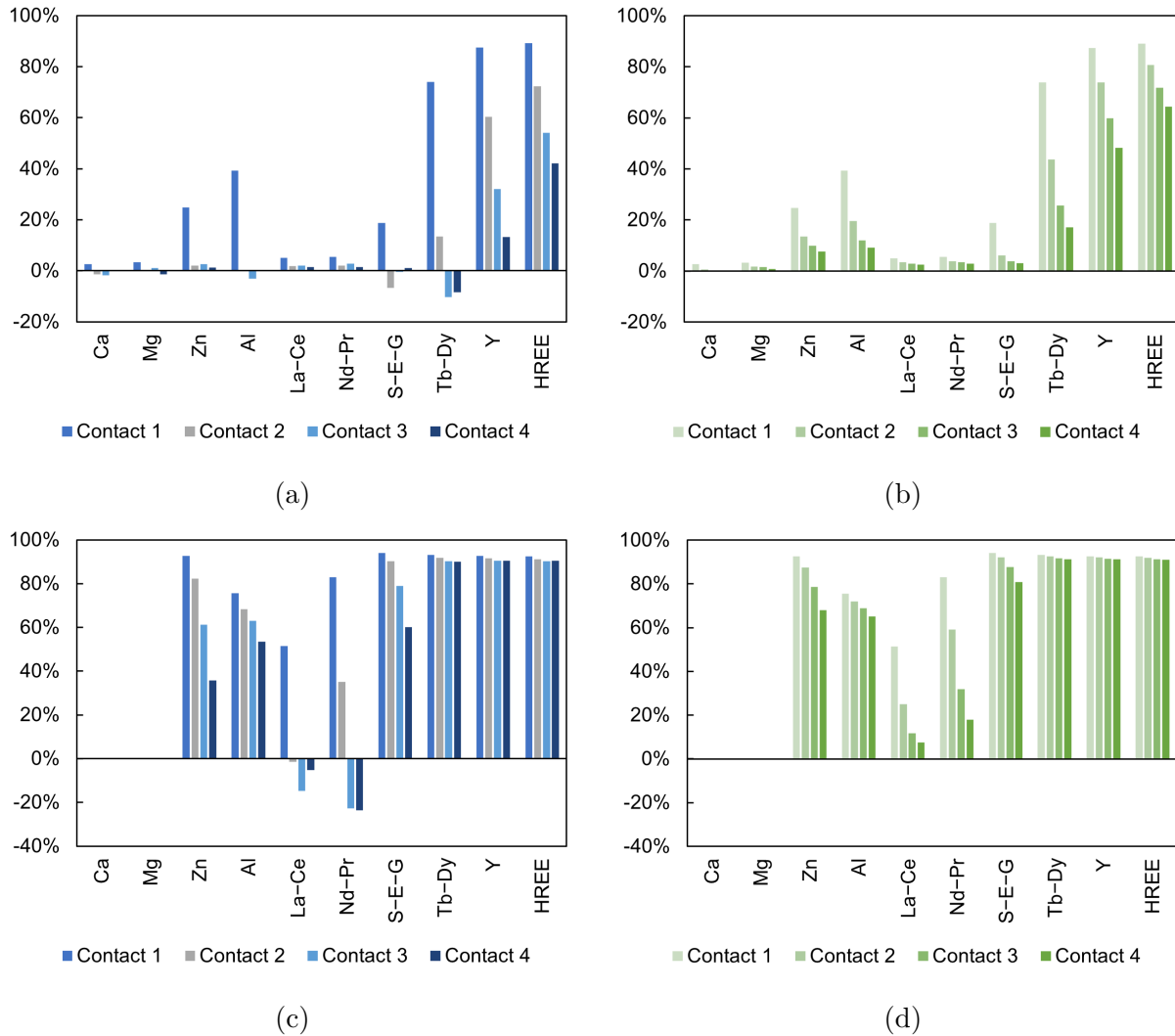


Figure 4.4: (a) 0.1 mol/L [c101][EHEHP] Single Stage Extraction Extent; (b) 0.1 mol/L [c101][EHEHP] Cumulative Extraction Extent; (c) 1 mol/L [c101][EHEHP] Single Stage Extraction Extent; (d) 1 mol/L [c101][EHEHP] Cumulative Extraction Extent.

[c101][D2EHP] Extraction Data

The single stage and cumulative extraction extent for low concentration (0.1 mol/L) and high concentration (1.0 mol/L) [c101][D2EHP] extraction system are presented as Figure 4.5.

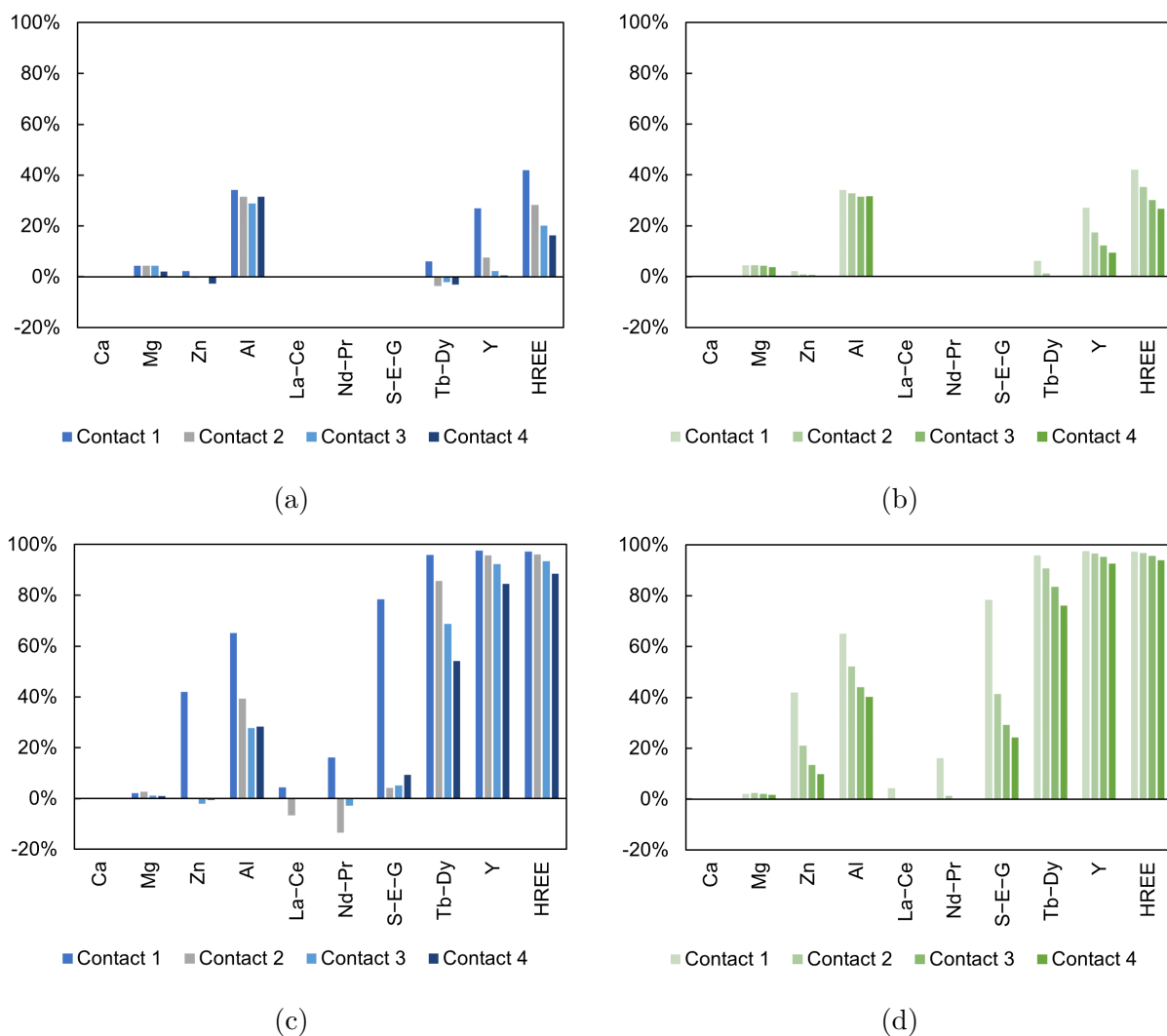


Figure 4.5: (a) 0.1 mol/L [c101][D2EHP] Single Stage Extraction Extent; (b) 0.1 mol/L [c101][D2EHP] Cumulative Extraction Extent; (c) 1 mol/L [c101][D2EHP] Single Stage Extraction Extent; (d) 1 mol/L [c101][D2EHP] Cumulative Extraction Extent.

[c101][c572] Extraction Data

The single stage and cumulative extraction extent for low concentration (0.1 mol/L) and high concentration (1.0 mol/L) [c101][c572] extraction system are presented as Figure 4.6.

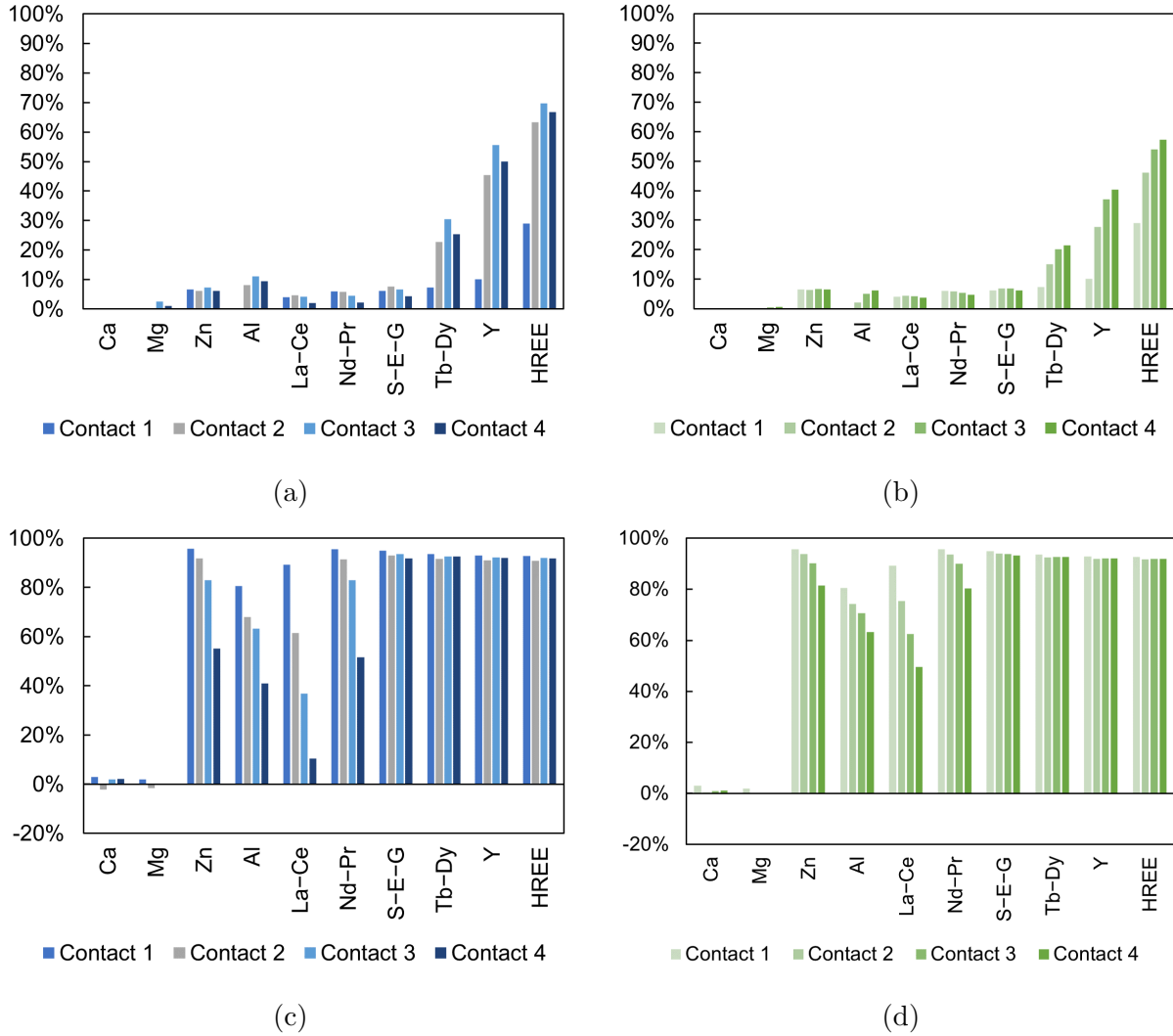


Figure 4.6: (a) 0.1 mol/L [c101][c572] Single Stage Extraction Extent; (b) 0.1 mol/L [c101][c572] Cumulative Extraction Extent; (c) 1 mol/L [c101][c572] Single Stage Extraction Extent; (d) 1 mol/L [c101][c572] Cumulative Extraction Extent.

Distribution Ratio

The distribution ratio of an element is a measure of its affinity for one phase over another. It is defined as the concentration of the element in the organic phase divided by the concentration of that element in the aqueous phase as presented in Equation (3).

$$D_{El} = [El]_{Org} / [El]_{Aq} \text{ Equation (3)}$$

The distribution ratio for a specific element (El) is a function of the elemental concentration of the system as well as of the composition of the organic phase. Distribution ratios of systems with excess extractant with regards to the concentration of elements to be extracted provide a more useful parameter for comparison between extraction systems. Distribution ratios for key elements of the investigated systems fourth contact in order to allow the distribution profile to develop are presented as Figure 4.7.

The data suggests that distribution ratio profiles were not fully established after the fourth contact for elements heavier than samarium in most extraction systems and thus cannot be reliably measured within our investigation. Additionally, the presence of a large concentration of zinc and aluminum likely also contributes to this effect. As such, separation factors usually derived from these distribution ratios were calculated from dilute extractant systems. In order to understand the behavior of a system, it is crucial to understand the interdependencies between the various elements of that system. One such measure, the ratio of distribution ratios between two elements in a system, is termed “Separation Factor” and provides an indication of the relative affinity for the organic phase over the aqueous phase. It is defined as a ratio of distribution ratios, and is calculated using Equation (4). Separation

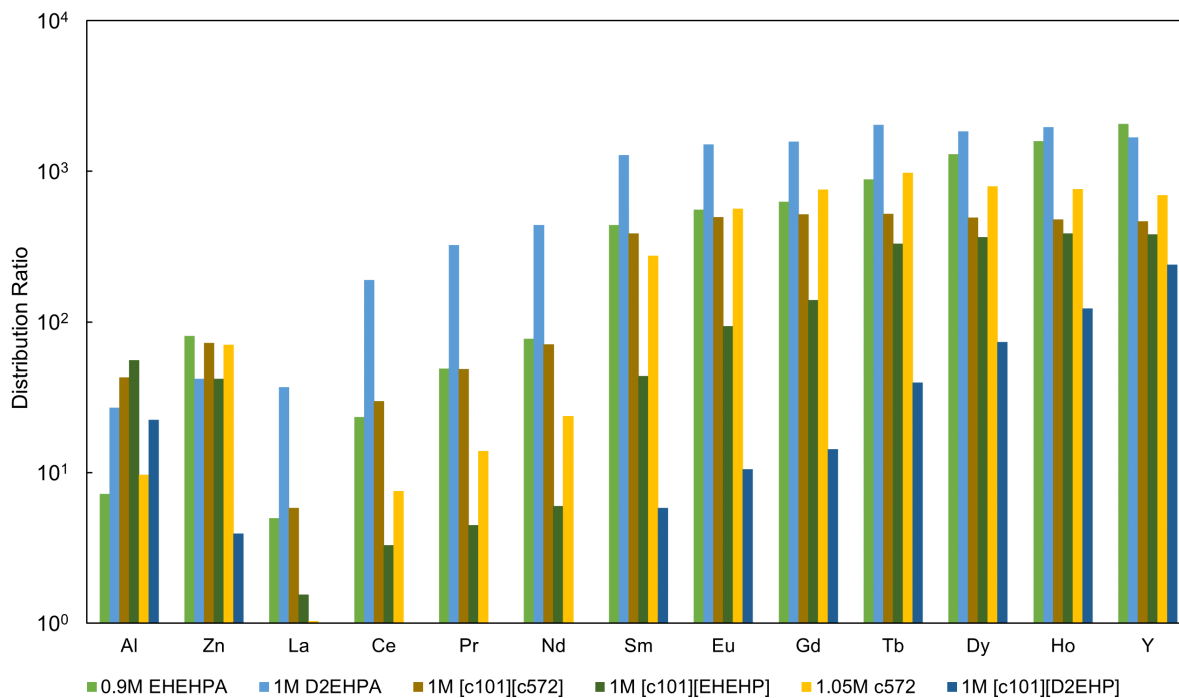


Figure 4.7: Concentrated Extraction System Distribution Ratios

factors are presented as Table 4.2.

$$SF_{(E11/E12)} = D_{E11} / D_{E12} \text{ Equation (4)}$$

The low extraction extents of 0.1 mol/L [c101][D2EHP] prevented the data from being used. Note that no tests were performed using a low concentration of Cyanex 572.

Organic Loading

Total metal loading in the organic represents a measure of the extraction capacity for an organic phase as a function of the aqueous phase composition. In traditional investigations, this data would be utilized to generate McCabe Thiele diagrams [185] and select a number of

Table 4.2: Separation Factors

Element Pair	EHEHPA 0.1 mol/L	[c101][EHEHP] 0.1 mol/L	D2EHPA 0.1 mol/L	[c101][c572] 0.1 mol/L
Al / Pr	1.38	4.26	2.24	1.81
Zn / Pr	3.89	3.67	0.55	1.81
Ce / La	2.04	1.10		1.28
Pr / Ce	0.91	0.81	1.90	0.93
Nd / Pr	1.43	1.47	1.38	1.31
Sm / Nd	2.25	0.80	2.63	1.14
Eu / Sm	1.49	1.03	1.18	1.00
Gd / Eu	1.32	1.44	1.07	1.27
Tb / Gd	1.89	2.29	1.31	2.27
Dy / Tb	1.29	2.01	1.17	1.94
Ho / Dy	1.19	1.92	1.11	1.70
Y / Ho	1.17	1.15	1.50	

operating stages and a O:A ratio for the operation of the continuous circuit. In our investigation, we have compared the total organic loading of the various extractants to narrow down the scope of further investigations. The loading for key elements and the REEs after four PLS extractions is presented as Table 4.3. The total elemental loading for the extractants as a function of the contact number is presented as Figure 4.8.

Table 4.3: Elemental Loading (mg / L)

Element	TREE	Ca	Al	Zn	Total
D2EHPA	4,641	211	1,056	5,308	9,989
EHEHPA	3,226	173	628	6,514	10,542
C572	3,537	0	334	7,701	11,237
[c101][D2EHP]	2,112	0	912	1,030	3,142
[c101][EHEHP]	2,927	0	1,074	7,068	9,995
[c101][c572]	4,223	37	1,045	8,471	12,694

The slope of all extractants in figure 4.8 reveal that they are not fully loaded after 4 contacts and could extract more metal ions. However, [c101][c572] has more extraction capability than

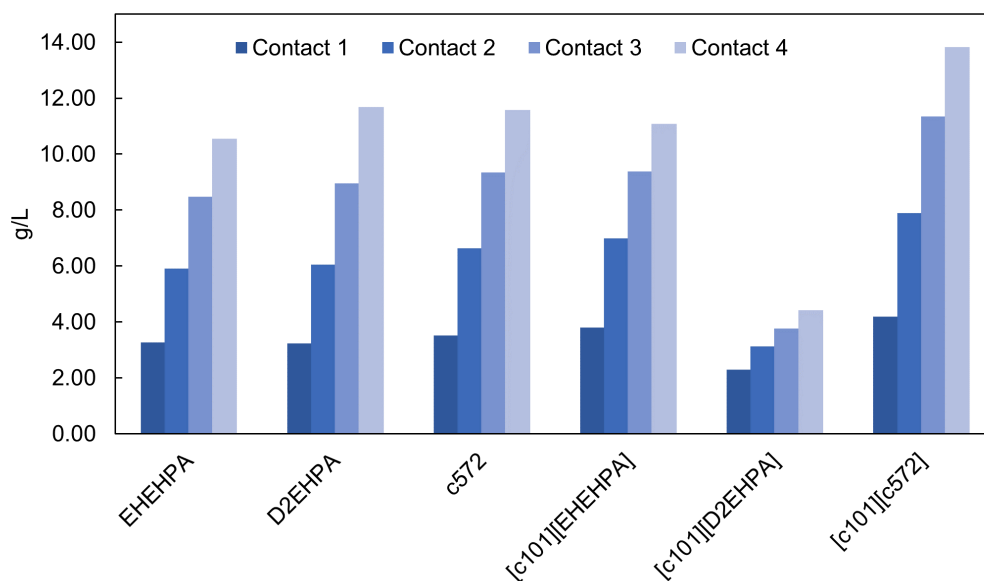


Figure 4.8: Total Organic Elemental Loading (in mg / L)

all other extractants, owing to its ability to extract more zinc than D2EHPA.

4.3.2 Discussion

The contrast between the low and high concentration of extractants provides insights on the applicability of the various extractants for the recovery of REE from AMD-derived PLS. The low concentration test allows comparison off the extraction efficiency between elements or groups of elements and reveals which are favored and if displacement can occur in the system. The degree of displacement is a measure of how well a battery of counter-current extraction stages will allow for the separation of various elements. It represents a crude approximation of the separation factors discussed in section [4.3.1](#).

As expected, all conventional acidic extractants performed well with very high extraction efficiencies, even with multiple contacts, and with a preference for HREEs. The data sup-

ports the pattern predicted by the acidic extractants acid dissociation constant (pK_a) in the extraction efficiency order of D2EHPA > EHEHPA > Cyanex 572 [22, 179].

The key aspect of the experimental results is the large variation of affinity for calcium, aluminum and zinc observed between the acidic extractants. These three metals represent up to 80% of the metal loading in the organic and directly compete with the REEs. D2EHPA and EHEHPA are the only extractants which extract a significant amount of calcium from the PLS with approximately 40% and 15% extraction extent in the first contact respectively. The initial extraction and subsequent replacement of calcium by other metals is likely to result in the oversaturation of calcium sulfate followed by the precipitation of gypsum in the solvent extraction circuit. The presence of gypsum will likely reduce the phase separation efficiency in the settlers and could result in clogged piping, unbalancing the circuit hydraulics. Unfortunately, the operation of D2EHPA in a counter-current circuit will only exacerbate the gypsum precipitation problem. Our findings suggest that D2EHPA should not be used for this application and that Cyanex 572 should be favored since its affinity for calcium is markedly lower than EHEHPA without presenting a very different extraction efficiency for the other elements.

A review of the ionic liquid extraction efficiency reveals that both [c101][D2EHP] and [c101][EHEHP] performed poorly in this system with [c101][D2EHP] performing particularly poorly with regards to both its selectivity for REEs and its overall extraction efficiency. While [c101][EHEHP] offered better extraction efficiencies for REEs, it didn't perform as well as [c101][c572]. From all the ionic liquids investigated in this study, [c101][c572] is the only one that revealed a potential for replacing conventional acidic extractants in the bulk sulfate extraction circuit. [c101][c572] offered extraction efficiencies similar to that of Cyanex 572,

with lower affinity for aluminum, and lanthanum than neodymium and praseodymium while having no extraction capability for calcium.

All extractants offered low separation factors, with D2EHPA having the highest separation factors for LREE and [c101][EHEHP] the highest separation factors for HREEs, followed closely by [c101][c572]. D2EHPA is primarily used in the industry to separate LREE [230], but would be an uneconomic choice in a system such as the one studied, owing to its high HREE concentration. The stripping of HREE from D2EHPA requires high acidity [42] and isn't practiced commercially [109]. Interestingly, [c101][c572] offered separation factor significantly higher than reported in the c572 literature for chloride media. Cytec, the supplier of Cyanex 572 [48] reports separation factors of 1.7 for the pair Dy / Tb and of 1.3 for the pair Ho / Dy, much lower than determined experimentally in our investigation.

4.3.3 Conclusions

The high extraction efficiency, very high loading and high separation factors of [c101][c572], comparable to the strongest commercial extractant: D2EHPA suggest that [c101][c572] may be a very good candidate for the replacement of conventional acidic extractant in the bulk extraction of REEs from AMD-derived PLS in sulfate media. The present work revealed that both zinc and calcium are significant detrimental elements in the current process and should be the subject of specific investigations in order to minimize their presence in the REE extraction circuit. The performance of all extractants is likely to be improved in the absence of these impurities. The performance of [c101][c572] was 13% superior to Cyanex 572, 20% superior to EHEHPA and 27% superior to D2EHPA the current commercially used extractants.

In addition, the separation factors of [c101][c572] were significantly higher than D2EHPA and EHEHPA with respect to HREE separation, a large fraction of the AMD-derived feed-stock distribution. As such, further investigations should evaluate the effect of operating parameters such as pH, temperature, extractant concentration and O:A ratio to design a continuous extraction circuit using the McCabe Thiele method. Stripping should also be evaluated using different acids and acidity levels. Finally, a techno-economic analysis should be performed to evaluate the economic incentive of using ionic liquids in this system.

Chapter 5

Selective leaching of calcium and zinc using ammonium chloride

Abstract: Prior test work has shown that calcium and zinc are deleterious components of AMD-based REE feedstocks, and they tend to partition with the REEs through solvent extraction. Similarly, calcium and magnesium are ubiquitous in REE carbonatite ores and promote higher acid consumption, leading to unacceptable processing costs. These issues highlight the need for a cost-effective removal process, particularly one that could broadly applied to both conventional and AMD-based REE production. An ammonium chloride circuit whereas ammonium chloride is used as a leaching agent and regenerated through carbon dioxide sequestration loop is one such avenue. This work focuses on optimizing at the bench scale the ammonium chloride leach process. First, synthetic material was used, followed by real ore samples provided by Niocorp Development from the Elk Creek Deposit and by Commerce Resources from the Ashram Deposit. High leach efficiencies were obtained under optimum conditions, up to 100% of the available calcium and magnesium and up to 98% of the zinc. Future studies should focus on the regeneration aspect of the process.

5.1 Introduction

Processes for the production of REEs vary greatly as a function of the mineralogy of the deposit being evaluated from acid leach to caustic crack, and even salted water for ionic clays [109, 256]. However, most, if not all these flowsheets consider the production of a mixed rare earth product to be further processed in a separation facility. The two processes generally considered for the production of this REO concentrate are an oxalic acid precipitation followed by a roasting or a sodium carbonate precipitation [109, 112, 256]

In both precipitation processes, two impurities also precipitate along with the rare earth elements: calcium and zinc. These impurities have deleterious effects on the separation processes ranging from increased acid consumption to final product contamination depending on the extractant selected as these elements can compete with REEs in the solvent extraction process.

A review of the extraction isotherm literature for calcium and zinc from various studies reveals the difficulty in managing zinc once it reaches the extraction system since it behaves as neodymium with most extractants. D2EHPA is a notably problematic extractant when calcium and zinc are present since its scrubbing result in heavy losses of neodymium [41, 96, 132]. This competitive extraction can be predicted by comparing the extraction pH-isotherm for various elements. Elements with similar pH-isotherms typically behave similarly in extraction systems. A comparison of the zinc and calcium pH-isotherms in D2EHPA [41] with light rare earths [96] reveals a potential process problem. This issue can be inferred from literature on the recovery of REEs from low concentration sources with significant zinc and calcium when compared to REEs. Specifically, Liu mentions that to effectively scrub

all zinc from a D2EHPA loaded organic, up to 75% of neodymium and higher amounts of praseodymium needed to be scrubbed along with 9% of yttrium [132].

Organo-phosphorus extractant are typically used for REE extraction and separation owing to their high affinity for REEs [270]. An investigation into the recovery of rare earth elements using EHEHPA in nitric media by Yahorava et al. [106] revealed that contrary to D2EHPA, calcium can be scrubbed from EHEHPA organic phases using low acidity scrub solutions with little rare earth losses. However, zinc behaves similarly to neodymium and thus cannot be readily separated using solvent extraction. Similarly to EHEHPA, C-572 presents advantages over D2EHPA for calcium rejection, but also recovers zinc [43]. This overlapping is presented as Figure 5.1, compiled from data published by Ahmadipour et al. [5], for zinc and by Mohammadi et al. [155] for neodymium.

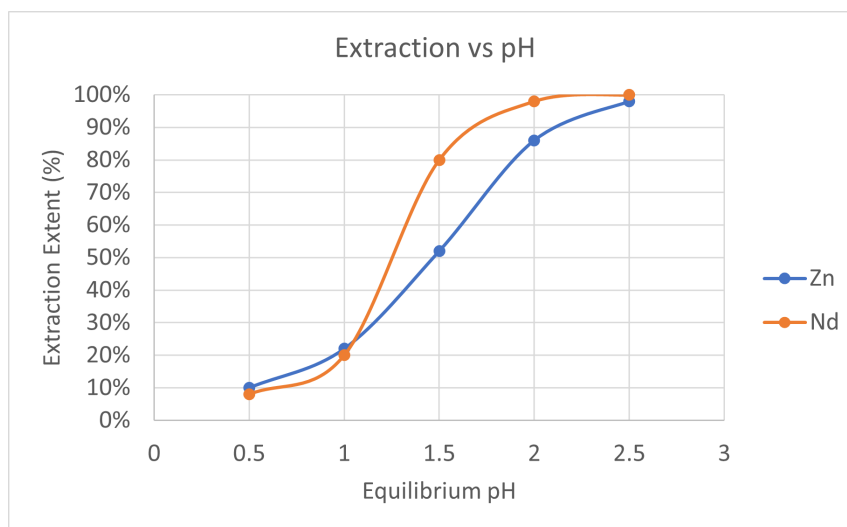


Figure 5.1: Zn and Nd Isotherms

EHEHPA and the analogous Cyanex 572 also present issues with zinc as demonstrated by Cho et al. [43]. In a previous study, our research group identified the affinity for zinc of

Cyphos 101 IL based ionic liquids as a major technical issue requiring additional investigation [117]. The published paper is presented as Chapter 4. We compared the extraction performance of the extractants [c101][D2EHP], [c101][EHEHP] and [c101][c572] with their organo-phosphorus counter parts. All studied ionic liquid: revealed a similar behavior for zinc and neodymium, inferring a solvent extraction process would not allow for the cost effective production of pure neodymium.

Ammonium chloride has been reported as an effective leaching agent for both zinc, calcium and magnesium in various applications unrelated to the recovery of REEs. Wang et al. demonstrated leaching efficiencies of up to 92% for low grade zinc ores [8] while Gargul and Boryczko reported zinc leach efficiencies of over 50% [71]. Sun et al. evaluated the calcium and magnesium leach efficiencies of ammonium chloride and reported very high leaching efficiencies, but differentiated kinetics based on the molecular structure of the feed material. Their study suggest that up to three hours residence time may be required for high calcium oxide materials [224]. The utilization of ammonium chloride as a leaching agent for calcium in conjunction with rare earth element recovery is referenced by Habashi [83] from a presentation by Rusin et al. [200]. Additionally, calcium and magnesium in carbonatite ores bodies is a significant consumer of acid, imposing additional costs on the processing of those materials.

Given the significant impact of zinc, calcium in REE extraction and separation circuits and the high acid consumption associated with calcium and magnesium, the utilization of ammonium chloride to leach zinc and calcium from synthetic materials and from REE-bearing ores provided by Commerce Resources from the Ashram and by Niocorp Development from the Elk Creek Deposit was investigated prior to their initial acid leaching step. The utilization of Ashram and Elk Creek Ore allowed for experimentation on real REE material while

AMD-derived material is being produced.

The investigation was initiated with synthetic materials, generated by mixing pure metal oxide reagents in order to observe the fundamentals and understand effects of various parameters such as temperature, metal and ammonium chloride concentration. These parameters were then validated with real samples provided by Commerce Resources and Niocorp.

5.2 Materials and Methods

5.2.1 Material

Synthetic Material

Synthetic samples were generated by mixing defined amounts of calcium oxide, 99% (Acros Organics, Belgium) with zinc oxide, 99.5%+ (Acros Organics, Belgium) and lanthanum oxide, 99.9% min purity (GE Chaplin, Flemington, NJ). Ammonium Hydroxide 99.9% was sourced from Ecoxall (Brighton, MI).

Ashram Samples

Ashram samples were ground as received from Commerce Resources to 100% passing 150 μm using a disc mill and manually sieved. The sample was then subjected to calcination at 850 C for 1 hour in a muffle furnace to decompose the carbonate materials into carbon dioxide and oxides. Different samples were provided by Commerce, with mineralogy and elemental assays for each sample. A summary of relevant minerals in the raw sample and of elemental composition of the calcine material is provided as Table 5.2 and 5.1 respectively.

Table 5.2: Ashram Sample Mineral Composition (wt%)

Mineral- Sample	COMP-002	COMP-003	COMP-004	COMP-007	COMP-009
Monazite	0.97	0.64	1.78	1.44	2.52
Bastnaesite	1.11	3.79	1.29	1.52	0.39
Apatite	2.79	0.11	0.12	0.00	1.01
Quartz	0.41	4.12	1.14	1.34	1.46
Calcite	0.27	0.16	0.13	0.12	0.21
Dolomite	2.22	3.00	1.46	2.33	2.41
Ankerite	69.73	60.18	69.04	73.39	78.27
Siderite	8.86	20.04	17.78	7.53	4.80
Fluorite	6.66	6.86	5.74	10.97	7.67

Mineral- Sample	COMP-014	COMP-019	COMP-022	COMP-023	COMP-029
Monazite	0.78	0.49	1.81	1.37	1.70
Bastnaesite	2.21	0.94	0.62	1.10	0.42
Apatite	0.84	0.30	0.97	0.97	0.56
Quartz	2.22	8.36	1.12	4.42	0.61
Calcite	0.18	0.05	0.22	0.31	0.19
Dolomite	1.27	0.15	0.32	0.17	1.75
Ankerite	79.21	26.67	69.87	45.69	87.54
Siderite	6.25	59.49	16.68	37.85	2.21
Fluorite	5.95	2.17	6.04	5.45	2.81

Table 5.1: Ashram Calcined Samples Composition

Sample	Fe	Mn	Ti	Ca	Mg	Zn
COMP-002	14.503	1.7925	0.6155	25.581	1.6275	0.1765
COMP-003	17.299	2.736	0.528	21.75	2.413	0.252
COMP-007	11.074	1.913	0.592	25.89	1.568	0.192
COMP-009	11.621	1.992	0.718	28.747	9.695	0.183
COMP-014	11.908	1.783	0.587	23.953	2.098	0.214
COMP-019	36.777	3.517	0.288	9.185	5.645	0.222
COMP-022	18.886	2.357	0.54	21.25	1.231	0.197
COMP-023	26.313	2.644	0.58	16.968	1.473	0.237
COMP-029	11.241	1.799	0.548	26.086	2.945	0.099

Elk Creek Sample

Elk Creek Ore was ground as received from Niocorp Development to 100% passing 150 μm using a disc mill and manually sieved. It was then subjected to calcination at 850 C for 1 hour to decompose the carbonate materials into carbon dioxide and oxides. A bulk sample was provided by Niocorp and its elemental composition assayed using handheld XRF. A summary of relevant minerals and elemental composition is provided as Table 5.3.

Table 5.3: Elk Creek Calcined Sample Composition (wt%)

Element	Fe	Mn	Nb	Ca	Mg	Zn
Composition	15.51	0.59	0.61	15.60	2.24	0.71

5.2.2 Analytical Procedure

In all tests, the elemental contents of the solids were measured by XRF (Niton XL2). The metal concentrations of the aqueous solutions liquors were measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900).

5.2.3 Ammonium Chloride Leach of Synthetic Material

The synthetic material was weighted and mixed in a 500 mL beaker and water was added to obtain a predetermined solids concentration as a slurry. The beaker was placed on a heating plate with magnetic stirrer and the temperature was set. Once the temperature set point was reached or the solution started to boil, a chronometer was started for a predetermined time. After the time had elapsed, the slurry was filtered using a Buchner filtration setup and a sample of the filtrate was taken for assay. The solids were washed with DI water and weighted. The wet solids were then dried overnight and the dry solids were weighted and assayed. The initial parameter tested on synthetic materials are summarized in Table [5.4](#).

Five parameters were evaluated as part of this study using synthetic feedstocks: the leaching temperature, the calcium and zinc molar concentration, the calcium and zinc relative concentration, the excess ammonium chloride in the leach solution and the effect of the leach residence time. The temperature is measured in degrees Celsius, the calcium and zinc to liquid ratio in grams per liters, the ammonium chloride excess as a stoichiometric ratio of the calcium and zinc content in the leach reactor and the residence time in hours.

Table 5.4: Initial Ammonium Chloride Leach Parameters

Test No.	Temperature C	Volume mL	CaO g	ZnO g	La ₂ O ₃ g	NH ₄ Cl g
1	AMB	250	0.7	1.0	5.0	4.0
2	AMB	250	3.5	5.1	5.0	20.1
3	AMB	250	7.0	10.2	5.0	40.1
4	50	250	0.7	1.0	5.0	4.0
5	50	250	3.5	5.1	5.0	20.1
6	50	250	7.0	10.2	5.0	40.1
7	Boiling	250	0.7	1.0	5.0	4.0
8	Boiling	250	3.5	5.1	5.0	20.1
9	Boiling	250	7.0	10.2	5.0	40.1
10	Boiling	250	0.7	1.0	5.0	2.7
11	Boiling	250	3.5	5.1	5.0	13.4
12	Boiling	250	7.0	10.2	5.0	26.8
13	Boiling	250	0.7	1.0	5.0	5.4
14	Boiling	250	3.5	5.1	5.0	26.8
15	Boiling	250	7.0	10.2	5.0	53.5
16	Boiling	250	1.4	0.0	5.0	5.4
17	Boiling	250	7.0	0.0	5.0	26.8
18	Boiling	250	14.0	0.0	5.0	53.5
19	Boiling	250	0.0	2.0	5.0	5.4
20	Boiling	250	0.0	10.2	5.0	26.8
21	Boiling	250	0.0	20.4	5.0	53.7

5.2.4 Ammonium Chloride Leach of Ashram Material

Upon receipt, the various samples were first individually milled using a disk mill and screened manually at minus 150 μm . Two 200 grams sub-samples of each composite materials were then calcined at 850 C for an hour and the mass loss from each calcined sub-sample was recorded. 120g of each resulting material was separated and labeled as (a) and (b) for each calcined composite material.

These sub-samples were then successively subjected to ammonium chloride leaches under

varied parameters. Each (a) sample was leached successively three times with 200 g/l ammonium chloride at 35 C for 2 hour each leach experiment while (b) samples were leached at 90 C, (gentle boiling conditions).

Between each stage of leaching, solids were filtered and washed using a buchner funnel and a small sub-sample of the solid residue was removed and dried in an oven at 100 C to determine its water content. The remainder of the residue was subjected to the subsequent leaching stage. Throughout the test, the masses of leacheates (PLS) and wash samples were recorded. After each leaching stage, a subsample of each dry solid residue sample was pressed into a pellet and analyzed for major contaminant metal (Al, Fe, Ca, Mg, Mn) content using a handheld XRF . Based on the XRF results, a subset of PLS and wash samples were sent for direct ICP-MS analysis.

5.2.5 Ammonium Chloride Leach of Elk Creek Material

Upon receipt, the bulk sample was milled using a disk mill and screened manually at minus 150 μm and calcined at 850 C for an hour. The material was then subjected to ammonium chloride leaches under varied parameters as presented in Table 5.5. Each sub-sample was leached successively two times with ammonium chloride solutions under gentle boiling conditions for 90 minutes. The level of the leach vessel was maintain by adding dionized water. During the first leach step, kinetic samples were taken each 10 minutes for 90 minutes.

Between each stage of leaching, solids were filtered and washed using a buchner funnel and a small sub-sample of the solid residue was removed and dried in an oven at 100 C to determine its water content. The remainder of the residue was subjected to the subsequent leaching

Table 5.5: Test matrix for Elk Creek timed leaching tests

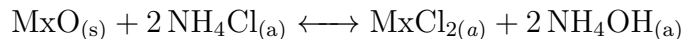
Test No.	[NH ₄ Cl] (g/L)	Solids % (%)	Feed (g)
1	25.0	5	26.4
2	81.3	5	26.4
3	137.5	5	26.4
4	193.8	5	26.4
5	250.0	5	26.4
6	25.0	20	97.2
7	81.3	20	97.2
8	137.5	20	97.1
9	193.8	20	97.1
10	250.0	20	97.2
11	25.0	35	269.3
12	81.3	35	269.4
13	137.5	35	269.4
14	193.8	35	269.4
15	250.0	35	269.4

stage. Throughout the test, the masses of leachates (PLS) and wash samples were recorded. After each leaching stage, a subsample of each dry solid residue sample was pressed into a pellet and analyzed for major contaminant metal (Al, Fe, Ca, Mg, Mn) content using a handheld XRF. Based on the XRF results, a subset of PLS and wash samples were sent for direct ICP-MS analysis.

The primary objectives of the Elk Creek test work are to evaluate the leach kinetics in order to determine the optimum leach residence time, to evaluate the optimum solids density in the leach reaction, to determine the maximum leaching efficiency and to determine the maximum elemental concentration achievable under reasonable conditions for each element.

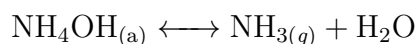
5.2.6 Theoretical Analysis

A review of the relevant literature reveals that the following primary simplified reaction is taking place in the reaction system:

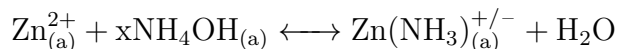


Where Mx is Ca, Mg or Zn. It is understood that the full reaction system also includes hydroxides and aqueous dissolved species of the metals.

In addition, the following temperature dependent reaction is also taking place:



And finally, the system also includes zinc ammonical complexation reactions of the general formula:



These complexes can be identified through simulation using Hydra/Medusa version 18 Aug. 2009 as represented by Figure 5.2, but an exhaustive analysis is outside the scope of this applied investigation. While calcium and magnesium do appear to complex with ammonia, their +2 valence ions are favored over their ammonia complexes.

Two competing factors are believed to control the equilibrium of the system: the initial concentration of ammonium chloride and the equilibrium temperature of the reaction. The concentration of ammonium chloride is expected to force the reaction forward following LeChatelier's Principle. At low temperatures the concentration of aqueous ammonia build up as ammonium hydroxide until the system reaches equilibrium. Increasing the temperature will vaporize ammonia, promoting the forward reaction with the same principle. Therefore, the leach efficiency should increase with an increase in ammonium chloride and of tempera-

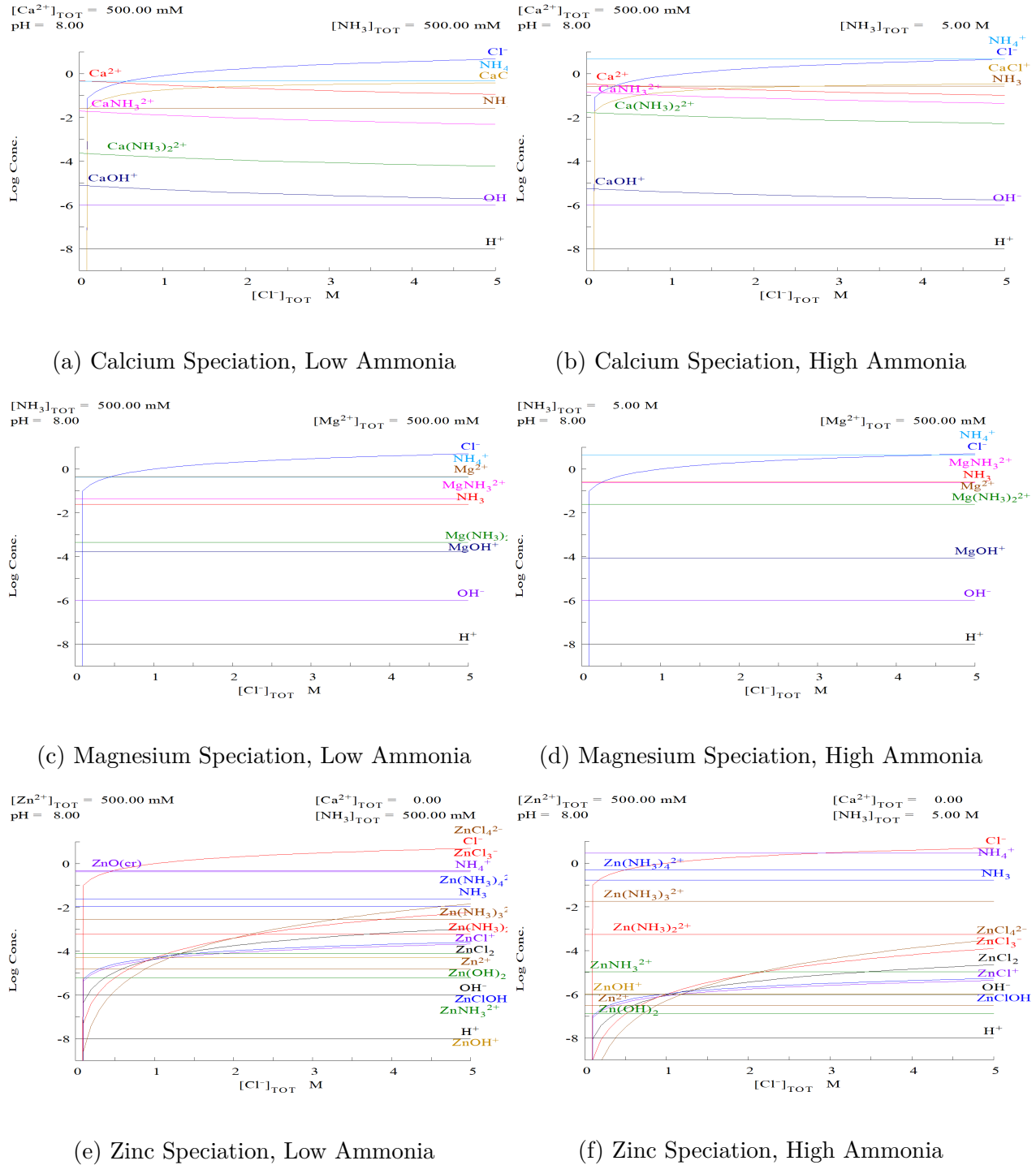


Figure 5.2: Speciation diagrams for calcium, magnesium and zinc in the presence of varying levels of ammonia

ture.

A thermodynamic reaction analysis was performed using HSC 7.1 for the reactions identified as favored by the speciation diagrams in Figure 5.2. The results are presented as Table 5.6 (Ca), 5.7 (Mg) and 5.8 (Zn).

Table 5.6: Thermodynamic Reaction Analysis: $\text{CaO} + 2\text{NH}_4(^+\text{a}) + 2\text{Cl}(-\text{a}) + \text{H}_2\text{O} = \text{CaCl}_2(\text{a}) + 2\text{NH}_4\text{OH}(\text{ia})$

Temperature C	delta H kJ	delta S J/K	delta G kJ	Log(K)
10	-90.486	-226.673	-26.304	4.853
30	-85.673	-210.215	-21.946	3.782
50	-81.769	-197.740	-17.870	2.889
70	-78.001	-186.427	-14.029	2.136
90	-74.013	-175.136	-10.413	1.498
100	-71.861	-169.289	-8.691	1.217

Table 5.7: Thermodynamic Reaction Analysis: $\text{MgO} + 2\text{NH}_4\text{Cl}(\text{ia}) = \text{MgCl}_2(\text{a}) + 2\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$

Temperature C	delta H kJ	delta S J/K	delta G kJ	Log(K)
10	24.362	71.569	4.097	-0.756
30	21.238	60.914	2.771	-0.478
50	17.746	49.768	1.664	-0.269
70	13.893	38.203	0.783	-0.119
90	9.682	26.281	0.138	-0.020
100	7.445	20.204	-0.094	0.013

The thermodynamic analysis reveals that both calcium and zinc are exothermic spontaneous reactions that are likely to be hindered by higher temperatures. The magnesium reaction in contrast is endothermic and appears unfavorable. It is likely to necessitate higher ammonium chloride concentrations and higher temperatures to proceed.

Table 5.8: Thermodynamic Reaction Analysis: $\text{ZnO} + 2\text{NH}_4(^+a) + 2\text{Cl}(-a) + 2\text{NH}_4\text{OH}$
 $(ia) = \text{Zn}(\text{NH}_3)_4(^+2a) + 2\text{Cl}(-a) + 3\text{H}_2\text{O}$

Temperature C	delta H kJ	delta S J/K	delta G kJ	Log(K)
10	-51.028	40.791	-62.578	11.545
30	-51.200	40.205	-63.389	10.923
50	-51.448	39.415	-64.185	10.376
70	-51.757	38.487	-64.964	9.890
90	-52.114	37.479	-65.724	9.454
100	-52.303	36.966	-66.096	9.253

5.3 Results and Discussion

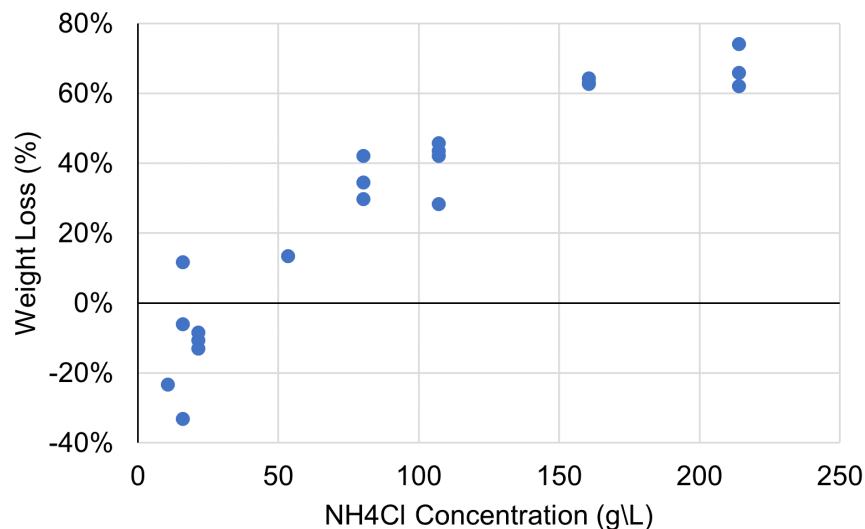
5.3.1 Synthetic Material

Effect of Ammonium Chloride Concentration

The impact of ammonium chloride concentration on leach efficiency for specific elements and as an aggregate loss of sample weight (refer to Figure 5.3) was evaluated for various solids densities and the results indicate that higher concentrations of ammonium chloride resulted in higher leaching extent. More experiments would be required to fully establish the relationship between ammonium chloride concentration and leach extent.

Counter intuitively, the low ammonium chloride leach experiments resulted in weight gain as opposed to weight loss. Analysis of the experiment suggest that this is due to hydration of calcium oxide into calcium hydroxide and possibly the hydrolysis of zinc chloride into zinc hydroxide.

It should be noted that zinc leaching under low ammonium chloride concentration at el-



evated temperature was reduced to nil while having less impact on calcium. A review of the theoretical analysis suggest that high temperatures coupled with low ammonium chloride concentration results in ammonia vapor losses, leading the zinc-ammonium chloride complex to hydrolyse into zinc hydroxide.

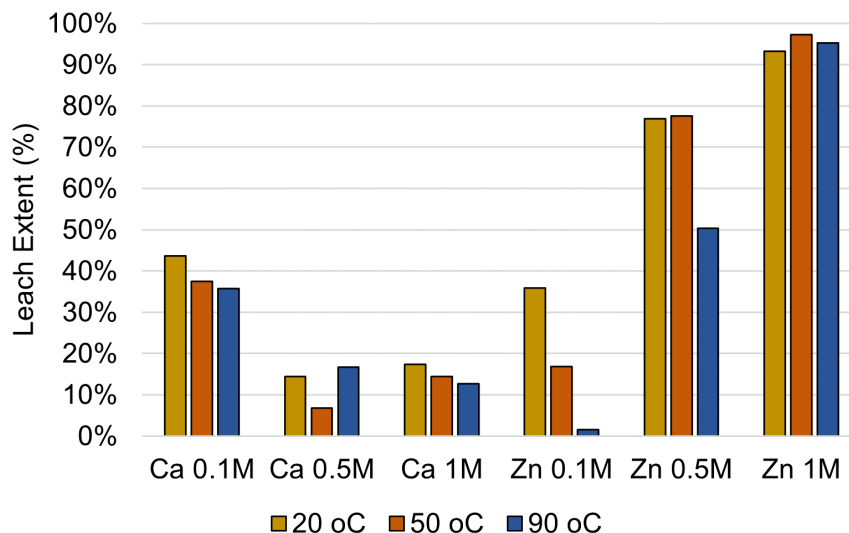


Figure 5.4: Leach Efficiency Versus Reaction Temperature

phase diagrams reveals that some ionic species of zinc are ammoniacal complexes. Under low absolute ammonium chloride concentration and high temperature, when ammonia is off-gassed from the reactor, the solution may lack the required ammonia to complex the zinc. Under high absolute ammonium chloride concentration, the residual ammonium ion may be sufficient to complex zinc.

5.3.2 Ashram Results

While the synthetic data strongly suggest that the optimum leach condition is one of high ammonium chloride concentration, it does not provide an optimum operating temperature. As such, the leach efficiency at low (30C) and high (90C) was evaluated for all provided samples. In aggregate, it is clear that more than one stage is required to fully recover the recoverable calcium, magnesium and zinc from the Ashram sample. Our testwork suggest that two to three stages are required. The average leach efficiencies per element and for each stage are presented as Figure 5.5. The detailed leach efficiencies per element and for both

temperature scenarios are presented as Figures 5.6, Figure 5.7 and Figure 5.8

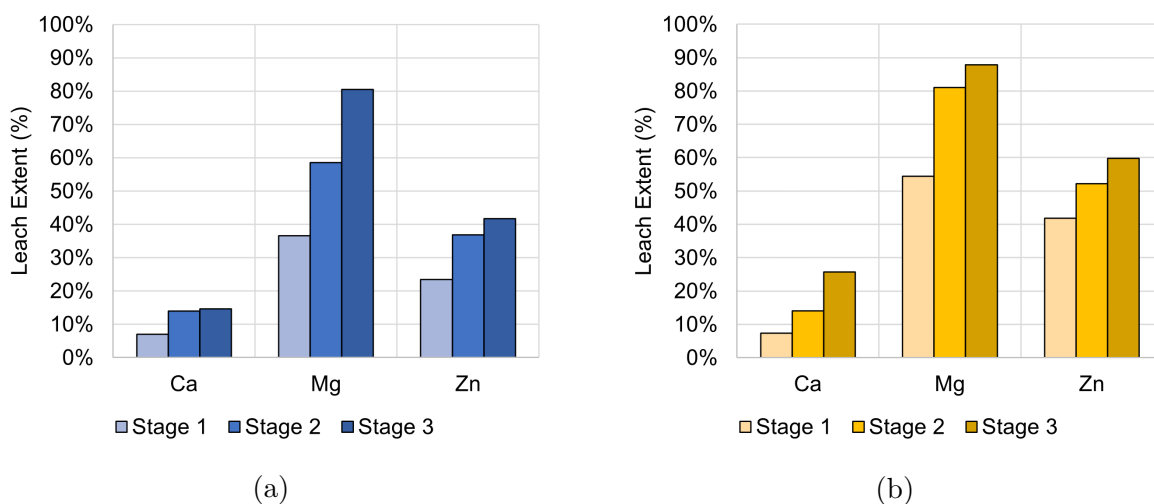


Figure 5.5: Average Leach Efficiency per stage: (a) Temperature = 30 C, (b) Temperature = 90 C

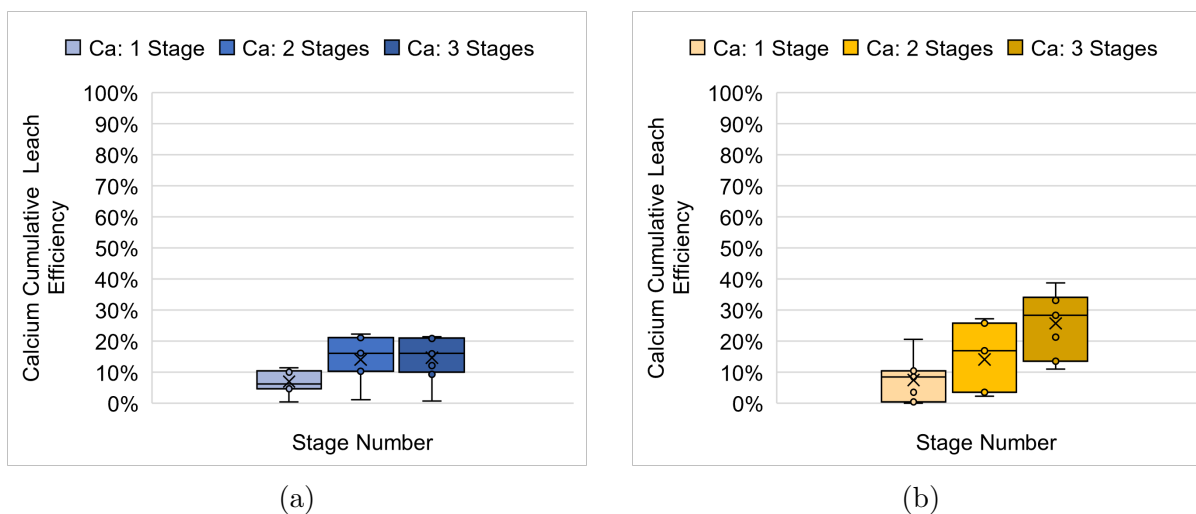


Figure 5.6: Calcium Leach Efficiency per stage: (a) Temperature = 30 C, (b) Temperature = 90 C

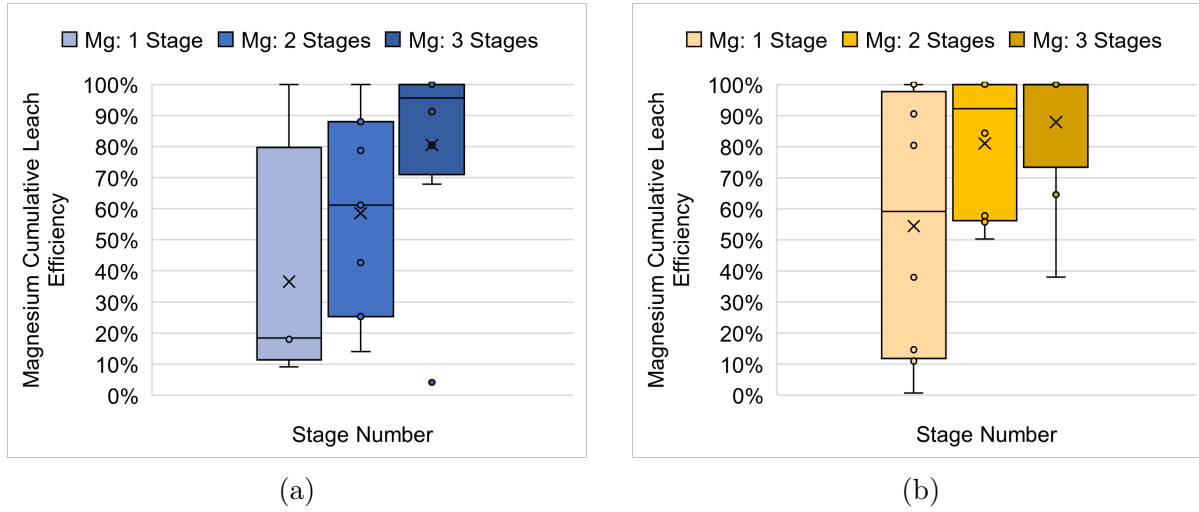


Figure 5.7: Magnesium Leach Efficiency per stage: (a) Temperature = 30 C, (b) Temperature = 90 C

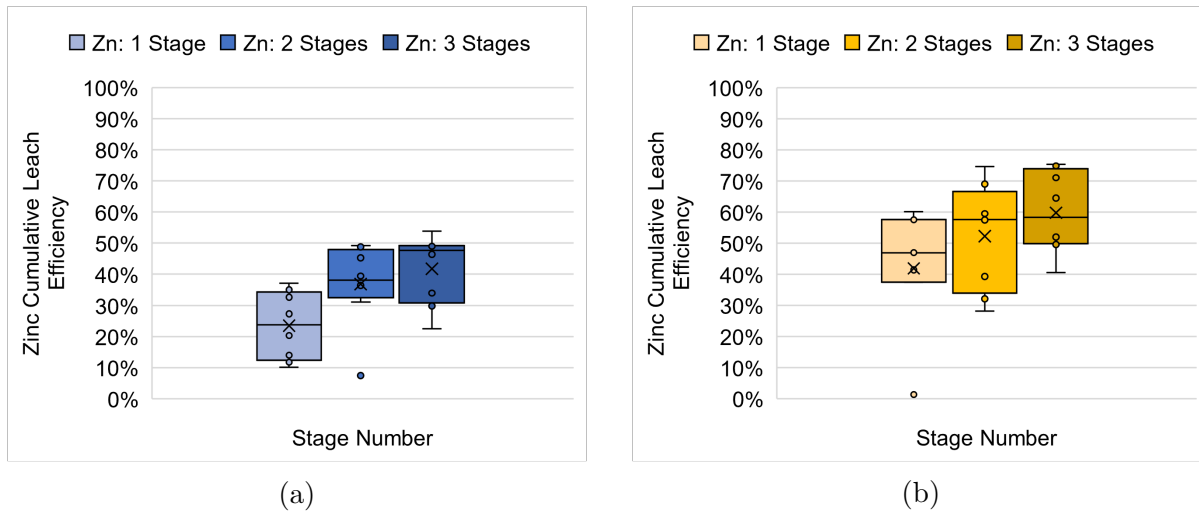


Figure 5.8: Zinc Leach Efficiency per stage: (a) Temperature = 30 C, (b) Temperature = 90 C

It should be noted that not all calcium, magnesium and zinc are present in recoverable matrices. For example, the Ashram material contains a significant portion of fluorite, which is not dissolved by ammonium chloride leach. A review of the mineralogy resulted in the assumption that only carbonatite-related calcium (Calcite, Dolomite, Ankerite) was poten-

tially amenable to ammonium chloride leach. Once the mineralogy is factored in, it appears clear that high temperature leaching is optimum for this material with over 90 % of available calcium leached in three stages. Some data point points exceed 100% leach efficiency, likely due to the imprecise nature of mineralogical analysis.

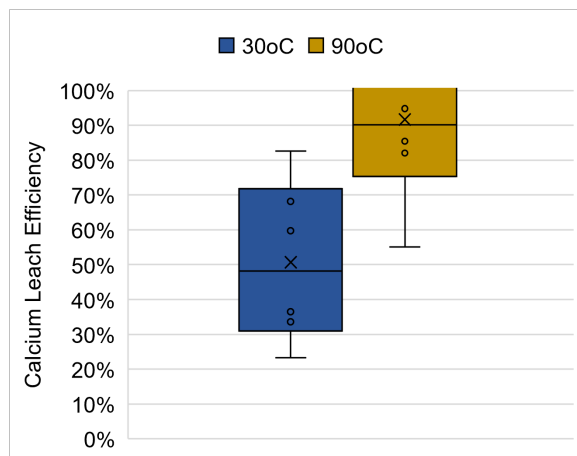


Figure 5.9: Available Calcium Leach Efficiency: (a) Temperature = 30 C, (b) Temperature = 90 C

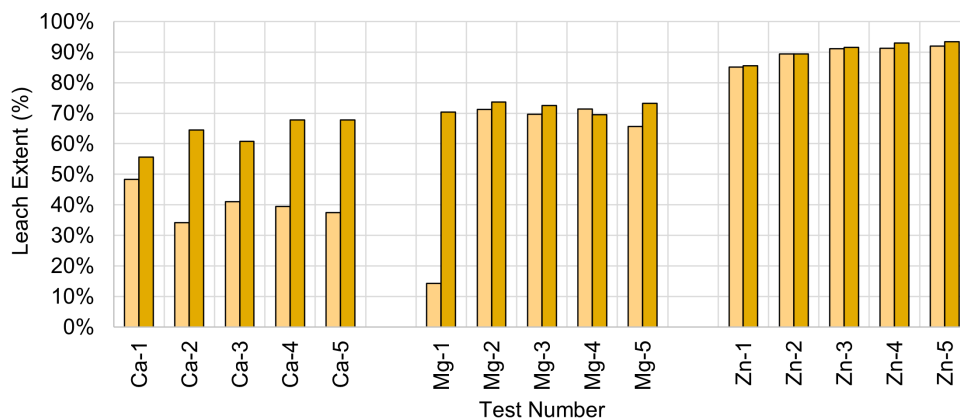
Analysis of pregnant leach solutions revealed elemental solution assays for REEs to be less 1.0 mg/L. Alternatively, calcium concentrations were found to be from 0.01 to 0.65 g/L, zinc was < 0.001 to 0.11 g/L and Mg was 0.01 to 5.39 g/L. Two elemental impurities were also found in the solutions: Si ranging 0.01 to 0.06 g/L and Mn ranging 0.001 to 0.08 g/L. I therefore concluded that the ammonium chloride leach process is selective for these +II ions and does not leach REEs.

5.3.3 Elk Creek Results

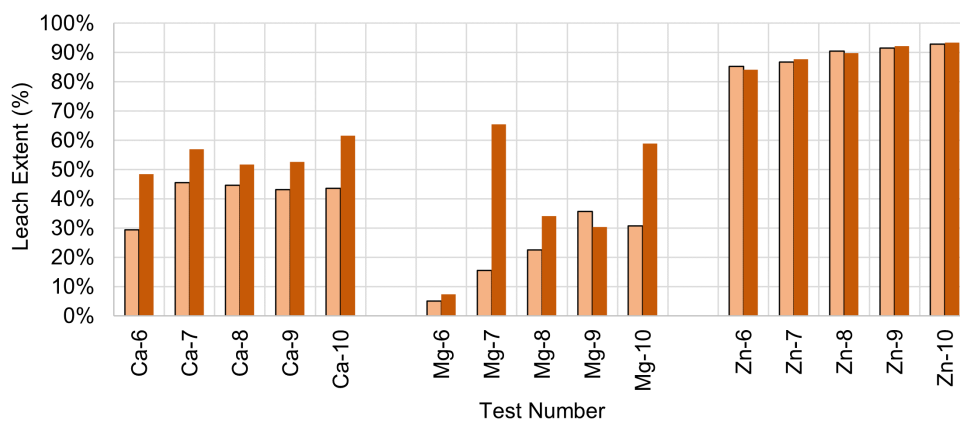
The Ashram test work demonstrated that high temperature reaction was optimum for the ammonium chloride leach circuit. Therefore, all Elk Creek tests were undertaken at 90 C under gentle boiling conditions. A summary of the results is presented as Figure 5.10.

The maximum leach extent and optimum number of stages was determined by using concentrated ammonium chloride solutions and low solids contents. This is best represented by Test 5, as presented in Figure 5.10a. Leach efficiencies of up to 70 % for calcium and magnesium and up to 93% were achieved in 2 stages. Three stages would likely be required in a commercial application.

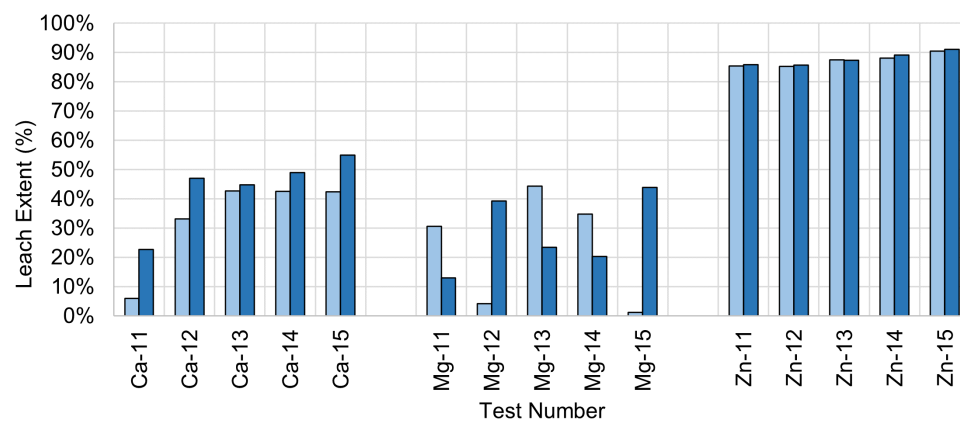
An empirical leach kinetic evaluation was performed and the results are presented as Figures 5.11, 5.12 and 5.13. One of the main observation from the data is a significant difference in reaction kinetics between the various elements. The calcium leaching kinetics appear to be much slower than that of magnesium or zinc. This is especially true at higher solids densities. In both the 20% and 35% solids density scenarios, calcium leaching has not reached equilibrium after 90 minutes while zinc reaches equilibrium after 30 minutes. It is interesting to note that in those scenarios, both zinc and magnesium hydrolyse after reaching their maximum solubilities. More in depth speciation studies would be required to understand this behavior, especially for magnesium. The behavior of zinc can be explained by a reduction of free ammonium ions in solution.



(a) 5 wt% Solids



(b) 20 wt% Solids



(c) 35 wt% Solids

Figure 5.10: Leach Efficiency for Ca, Mg and Zn at various solids and NH_4Cl concentrations

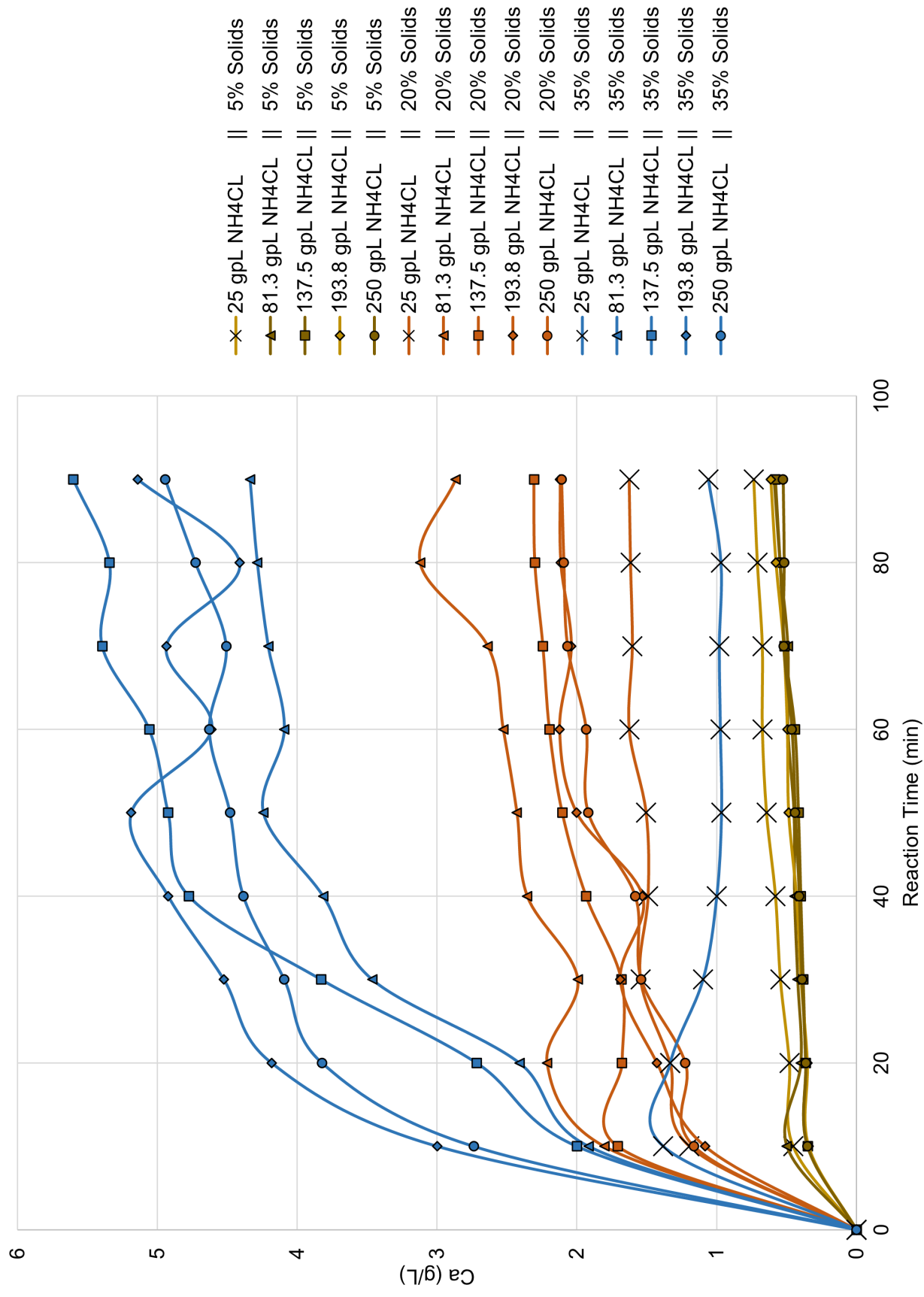


Figure 5.11: Calcium PLS Concentration as a Function of Leach Time

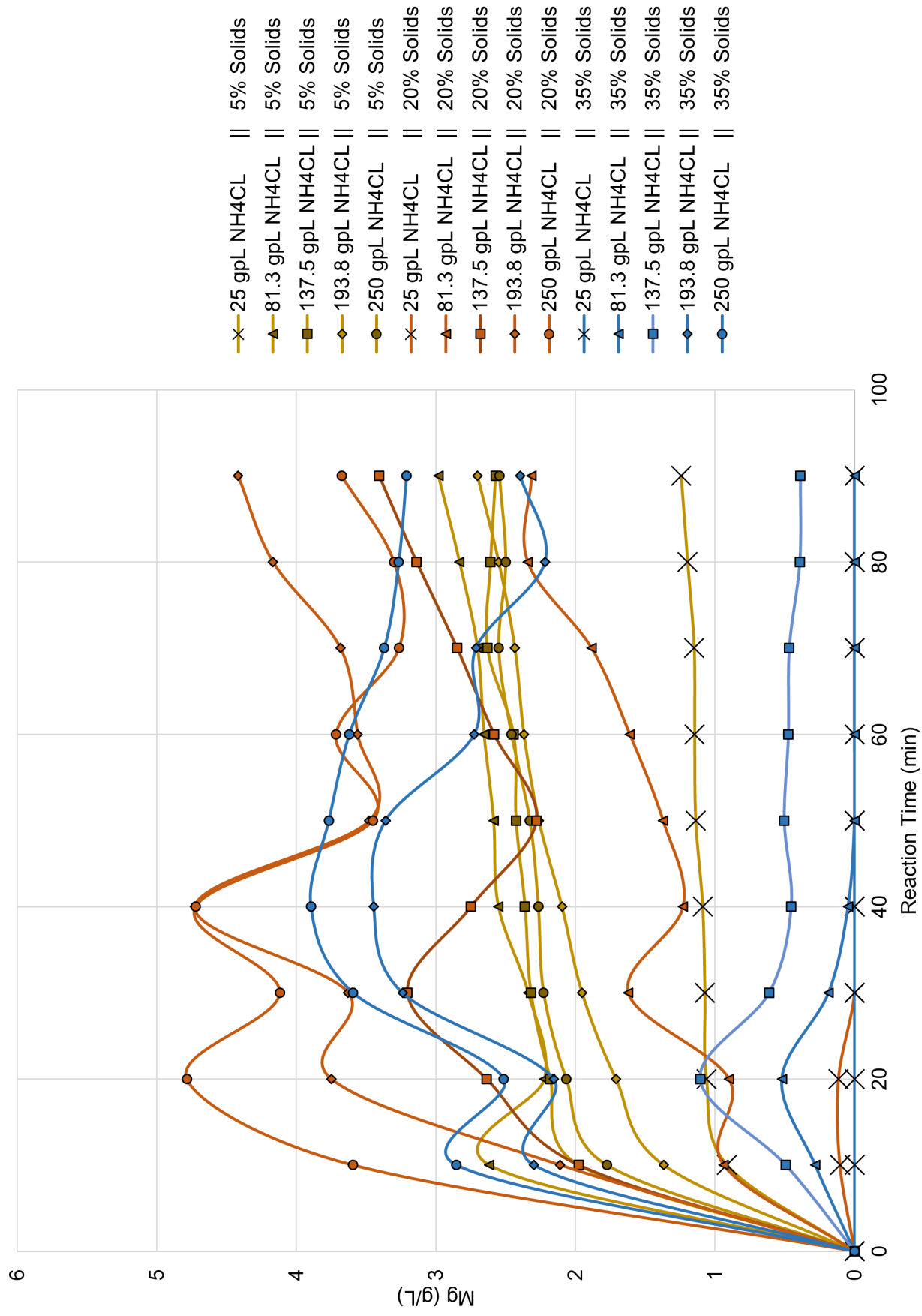


Figure 5.12: Magnesium PLS Concentration as a Function of Leach Time

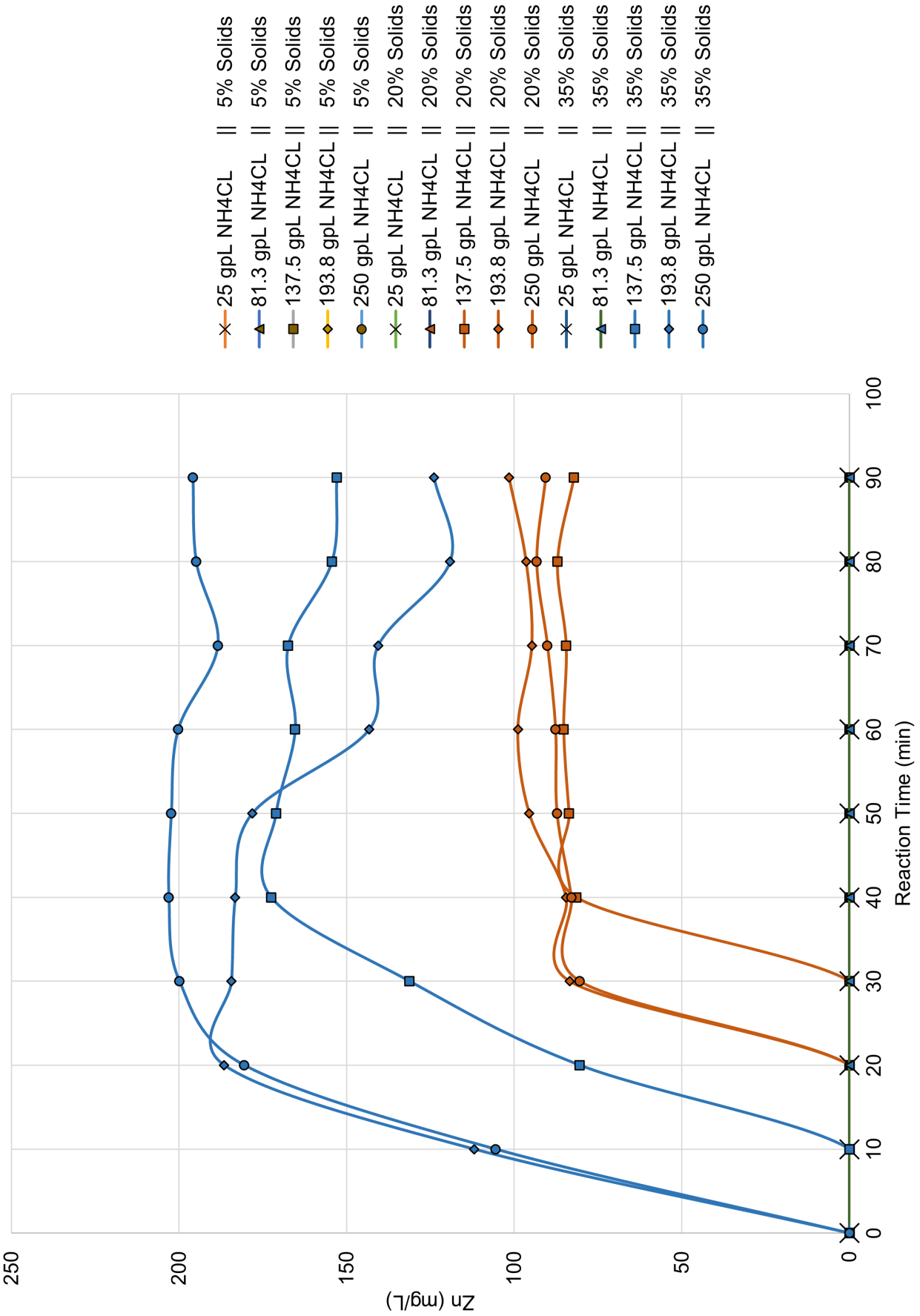


Figure 5.13: Calcium PLS Concentration as a Function of Leach Time

Analysis of the pregnant leach solutions revealed elemental solution assays for REEs to be lower 1.0 mg/L. Alternatively, Ca concentrations were found to be from 0.34 to 5.6 g/L;; Zn was < 0.001 to 0.20 g/L; and Mg was 0.05 to 4.78 g/L. Other elemental impurities were also found in the solutions: Al ranging 0.13 to 0.28 g/L and Ti ranging 0.001 to 0.024 g/L. I therefore conclude that the ammonium chloride leach process is selective for these +II ions and does not leach REEs. The behavior of aluminum and titanium should be investigated during the piloting phase to determine if their presence reflect a true leaching behavior or manipulation and / or analysis errors.

Projections on maximum elemental concentration reveal that calcium concentration up to 6 grams per liter, magnesium concentrations up to 5 grams per liter and zinc concentrations up to 200 milligrams per liter can be achieved. It should be noted that low solids (5% wt solids) zinc assays were below the detection limit after the required dilutions for high concentration elements. Concentration approximately 4 times lower than the 20% solids experiment would be expected for high ammonium chloride experiments and potentially much lower concentrations for low ammonium chloride experiments.

5.3.4 Process Implementation

This ammonium chloride selective leaching process can be applied in two distinct functions within the processing of rare earth elements. First, upstream of an acid leaching process, on raw or calcined feedstock or, alternatively, on a product stream of the solvent extraction process as a selective refining process.

The conceptual process block flow diagram developped during the investigations is presented

in Figure 5.14. In this process, the feed material is reacted with a concentrated ammonium chloride solution (140-180 g/L) at high temperature (80 C to gentle boiling) in a series agitated reactors installed in counter current (or co-current) fashion. The discharge of the last leach reactor is dewatered to generate a product with reduced calcium, magnesium and zinc and the filtrate is cooled to room temperature. The cool filtrate is then used to absorb and condense vaporized ammonia from the leach circuit and carbon dioxide is subsequently injected in the carbon sequestration reactor where calcium, magnesium and zinc are mineralized and precipitated as carbonates while regenerating the ammonium chloride solution.

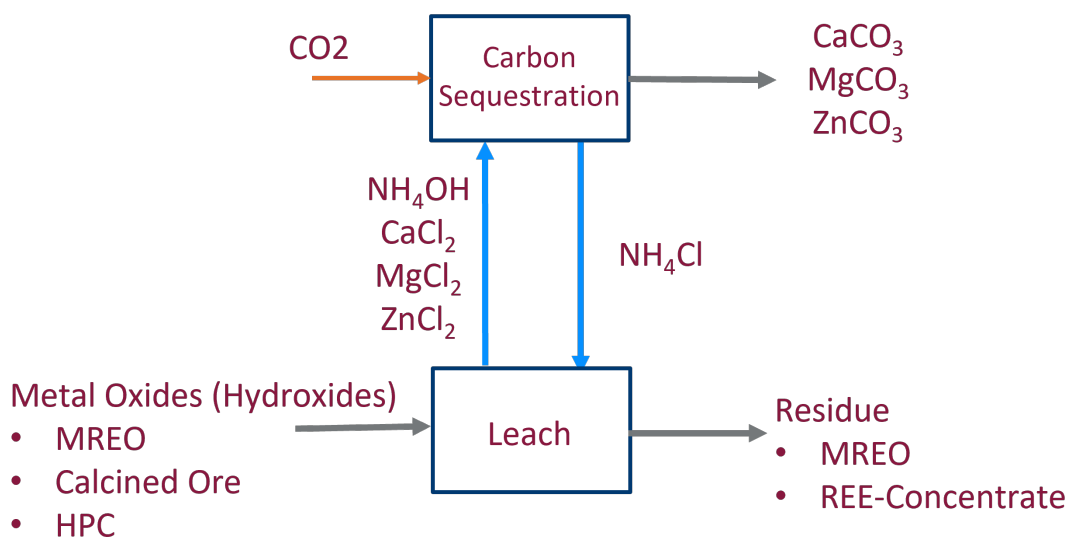


Figure 5.14: Ammonium Chloride Leach Conceptual Block Flow Diagram

5.4 Conclusion

The leaching behavior of calcium, magnesium and zinc in synthetic and real materials with ammonium chloride was evaluated using the following parameters:

- Reaction Temperature
- Ammonium Chloride Concentration
- Solids Content
- Reaction Time

Our investigations demonstrated the potential for this process to be applied for the removal of calcium, magnesium and zinc from calcined carbonatite ore materials provided by Nio-corp Development for the Elk Creek Deposit and by Commerce Resources for the Ashram Deposit. The complex mineralogy of these ores lends them to be effective surrogates for AMD-Derived material. Furthermore, using these materials also highlighted the commercial potential of this process.

Future work should extend the application of this process to AMD-Derived pre-concentrate and to mixed rare earth oxide products contaminated by zinc and calcium.

Economic considerations should dictate the optimum location, configuration and will reveal the economic viability of the ammonium chloride leaching process for specific applications within the critical material industry. Calcium and magnesium removal objectives would indicate that the ammonium chloride leach unit should be installed upfront of an acid leach step. Zinc removal imperatives in contrast require additional economic analysis but it is expected that zinc content lower than that of REEs could be managed by the ammonium chloride leach of the REE products while zinc concentrations larger than REEs would suggest to install the unit prior to the acid leach step. It should also be noted that solvent extraction separation can also be used to separate zinc from REEs, and that any project

needing to manage zinc concentration should rely on project-specific economic analyses.

More broadly, and with regards to environmental, social, and governance (ESG) imperatives and with the need to mitigate climate change, the regeneration of ammonium chloride using carbon dioxide should be parametrized and optimized to reduce the environmental impacts of the process. Other authors have reported such a possibility [139, 286]. The alternative of reusing of the ammonia generated as a neutralization agent in a chloride rare earth solvent extraction process should also be considered.

One important aspect of the ammonium chloride leach cycle with respect to ESG considerations lies in its reduction of acid-base consumption through the removal of calcium and magnesium prior to the acid digestion step. Additionally, the early removal and precipitation of calcium and magnesium as carbonate will lead to a reduction of waste water generation. Trade-off studies considering both the economic and ESG benefits of the process should be undertaken for high calcium and magnesium ores.

Finally, this integrated process should be piloted as a counter current unit to maximize both the leach extent and the elemental concentrations in the solution.

Chapter 6

Conclusion

6.1 Summary

Prior work by members of our research team has shown that AMD is a promising resource for REEs, particularly the heavy and magnet critical REEs. As such, the objective of this dissertation was to demonstrate the economic value of a commercial project aimed at recovering and processing the rare earth elements and select critical materials such as cobalt and manganese from AMD to produce marketable products. Additional objectives included the advancement of processing technologies through the evaluation of ionic liquids as novel extractants and through the development of a new selective leaching process.

My analysis demonstrated that AMD-derived pre-concentrate material has a contained value on par with world class deposit and as such should be developed in priority over other conventional deposits as part of a multi-prong strategy by the American government.

The primary factor supporting the value of AMD-derived REE pre-concentrate is its high enrichment in magnet rare earth elements, especially terbium and dysprosium. The proposed demonstration unit for the recovery of REE from AMD could supply up to 5-10 percent of the current world supply of terbium. The high feedstock value allow for economic operation

at capacities far below that of conventional REE separation plants. It should also be noted that the proposed 1-3 ton per day REO demonstration plant could easily be upgraded to allow for more processing capacity. The two parameters with the most influence on the economic return of the project have been determined to be the project capital cost and the consumption of hydrochloric acid. Ionic liquids [137], rather than conventional acidic extractants may produce simultaneous and synergistic improvement of these two parameters and have been highlighted as the highest priority with regards to further research and development.

Following this techno-economic analysis, I investigated the potential of ionic liquids for the extraction of rare earth elements, initially for the primary extraction of REE from sulfate media, as a replacement for conventional acidic extractants. I determined that [c101][c572] presented extraction performances comparable to the strongest commercial extractant: D2EHPA. This suggest that [c101][c572] may be a very good candidate for the replacement of conventional acidic extractant in the bulk extraction of REEs from AMD-derived PLS in sulfate media. In addition to the superior extraction performance, I observed that [c101][c572] offered significantly higher separation factors over D2EHPA and EHEHPA with respect to HREE separation. The three primary techno-economic benefits of using ionic liquids are the reduction of acid-base consumption in the process, no hydrogen ion being exchanged in the extraction and stripping process coupled with less equipment required per battery due to higher separation factors and smaller extraction cells due to higher elemental loadings.

This study supported empirical findings during the pilot operation and further highlighted the detrimental effect that both zinc and calcium pose in the sulfate media solvent extraction

process. It was determined that calcium extracts in the later cells and back-extracts in the initial cells, leading to precipitation of gypsum in the solvent extraction circuit. Zinc meanwhile behaves similarly to neodymium and its removals required many extraction stages and a significant amount of reagents. This is compounded by the fact that zinc's concentration in AMD-derived PLS is an order of magnitude superior to that of neodymium.

Finally, a novel process for the selective removal of zinc and calcium was designed and tested at the bench scale. This process utilizes ammonium chloride as a leaching media and proved selective for both calcium and zinc. It is anticipated that both the ionic liquid and the calcium and zinc removal unit will provide significant economic benefits to the baseline flowsheet. The selective removal of calcium and zinc coupled with the ammonium chloride regeneration will allow for reagent free recovery of calcium and zinc while sequestering calcium. In turn, the absence of these elements will reduce the hydrochloric acid consumption and the size of the solvent extraction cells due to lower elemental loadings.

6.2 Conclusions

The current generally accepted consensus predicts a major shortage of rare earth elements, especially in the United States of America. This shortage will reduce the deployment of sustainable technologies, hampering the efforts toward mitigating anthropogenic environmental impacts and leave our nation's military vulnerable to adversaries.

This work proposes a conceptual supply chain based on innovative technologies to recover rare earth elements and critical materials from acid mine drainage while incentivizing the treatment of acid mine drainage, providing a net benefit to the watershed and surrounding

communities. Building on this work, my investigations demonstrate the potential of ionic liquids in replacement of acidic extractants. These ionic liquids present an opportunity to reduce the acid consumption of rare earth extraction and separation processes. This dissertation also provided a novel processing route to selectively leach and recover calcium and zinc from rare earth concentrates. These two elements create issues in the rare earth separation processes leading to increased processing costs. Following this work, the refinery block flow diagram was updated to serve as a basis for future techno-economic analyses. The updated block flow diagram is presented as Figure 6.1.

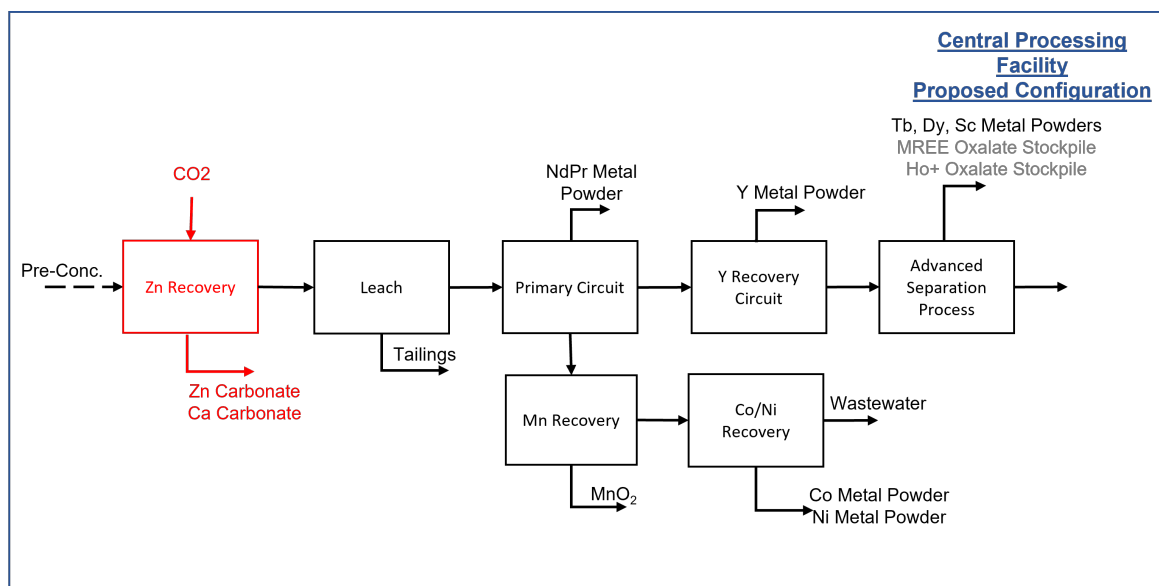


Figure 6.1: Updated refinery Block Flow Diagram

To the author's knowledge, three original contributions to science are disclosed in this dissertation.

- (1) Demonstration of the economic feasibility of recovery REEs and CMs from AMD.
- (2) Development of a process to selectively remove Ca and Zn from REO products.
- (3) Tabulation of novel ionic liquid extractants extraction and separation efficiencies for

REEs in sulfate media.

6.3 Recommendations

In addition to the aforementioned contributions, the research work presented herein opened many research avenues for future investigations.

- (1) Ionic liquid extraction circuits should be piloted to support comparative techno-economic analyses. A specific attention should be given to ionic liquid losses to the aqueous circuit to properly evaluate the operating cost of such a process.
- (2) Novel extractants such as styrene-phosphorus extractant and their ionic liquid equivalent should be evaluated against the ionic liquids discussed herein.
- (3) The opportunity of using the ammonium chloride circuit to sequester carbon while regenerating the ammonium chloride media should be evaluated.
- (4) The applicability of the ammonium chloride circuit to other feedstocks such as fly ash and phospho-gypsum residues as both a carbon sequestration and a rare earth concentration process should be evaluated.

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