Investigation into the Separation and Purification of Europium and Yttrium Oxides from Waste Fluorescent Lamps

by

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ABSTRACT

Europium and yttrium are critical materials required for LED, florescent lamp, cell phone screen, and flat panel display production. Nearly the entire worldwide production of europium and yttrium is recovered, as a minor constituent, from mining bastnäsite, monazite ore, or ion absorbing clays from China. The inspiration for this research is ongoing supply risks from Chinese production, environmental legacies from previous operations, and possibilities to minimize waste in the United States while monetizing an untapped resource in the United States. The purpose of this research is to develop an economically and technically viable process to recover purified europium and yttrium from waste fluorescent lamps.

Two different strategies were compared for separating yttrium and europium from waste fluorescent lamps. Scenario 1 examines the optimized conditions ending with saleable 99% mixed REO. Scenario 2 examines the optimized conditions for beginning with a europium and yttrium-rich pregnant leach solution. The optimized conditions for scenario 1 were similar to scenario 2.

Using selective reduction and precipitation, 92.77% europium sulfate was isolated using waste fluorescent lamp powder with more than 80% recovery.

The kinetics of the reaction and the activation energy were determined while conducting time and temperature tests. The order of the reaction was first order and the determined activation energy is 38.95 kJ/mole—indicating that the reaction is diffusion controlled.

A pre-feasibility economic analysis was conducted to determine plant economics for scenario 1 and 2 for building a waste fluorescent lamp recycling facility beginning with presieved, mercury retorted, freight-on-board (FOB) waste lamp phosphor powder and ending with a salable 99% pure mixed yttrium and europium oxide product or ending with 99% pure separate europium and yttrium oxides. The respective NPV’s for scenario 1 and 2 were 24.1 and 2.16 million respectively. The overall economics favor first scenario; however, due to geopolitical factors and supply risks, the 2nd scenario may be more may desired. For example, there are no operating industrial to separate yttrium and europium in the United States.
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CHAPTER 1
INTRODUCTION

Rare earth elements were discovered in 1787 by Carl Axel Arrhenius in Ytterby, Sweden when he revealed a black mineral called ytterbite—which consisted of yttrium. In 1803, near Bastnäs, Sweden, ceria was discovered—which consisted of cerium. By the 1920’s, all 15 lanthanides, yttrium, and scandium were classified as rare earth elements. At this time, the elements were classified into 3 main groups based on their properties evidenced during primary method for separation, crystallization and precipitation. They were, the yttrium (heavy) group elements (Y, Dy, Ho, Er, Th, Yb, Lu, Eu) have most soluble as alkaline double sulfates, and the cerium (light) group of elements (Sc, La, Ce, Pr, Nd, Sm, Tb, Gd) which were minimally soluble. Cerium has a crustal abundance of 68 ppm versus 60 ppm for copper. The “rarity” in these elements describes their unique set of chemical and electronic properties was well as the relative dearth of efficient metallurgical methods to technically, economically, and sustainably separate these elements from each other. Originally, most rare earths came from beach sand monazite deposits in Brazil and South Africa until 1965. Gradually, the bastnäsite rich deposits from Mountain Pass, CA over took them in production. Starting in 1984, China began to produce a significant portion of rare earth production. After the Mountain Pass Mine shut down in 2002, China controlled nearly all of the world production—greater than 90%—until Mountain Pass (which shutdown October 2015) restarted, and Mt. Weld mine started production. The Mountain Pass Mine was sold in bankruptcy to MP Materials in 2017 and restarted production in January 2018. The concentrates shipped to China will be subject to a 10% tariff later this year which is scheduled to rise to 25% in the future.

Furthermore, Rare Earth Salts (RES), a Nebraska-based company, started initial operations of recycling and purifying 99.99+ rare earths from waste fluorescent lamps in 2017 based on the initial feedstock from Russian sources. The main methods for light rare earth separation at the Bayan Obo mine in China include crushing, gravity concentration, magnetic separation, flotation, leaching and molten salt electrolysis. At Molycorp Mountain Pass, the main methods for light are earth separation include, crushing, flotation, roasting, leaching, ion exchange, solvent extraction, and soda ash precipitation. According the patents filed by RES, they are utilizing a form of selective leaching and
Electrowinning to recover and purify rare earths oxides[8][9]. Industrially, most rare earths are produced and sold as oxides and the prices have been steadily falling since July 2011 such that the price of China FOB 99.99% pure europium oxide was 5870 USD/kg during that month and 78.8 USD/kg October 2018[10].

Europium was first isolated from samarium using a series of crystallization by French chemist, Eugène-Anatole Demarçay[11]. Had he known the unique chemistry of europium (II) sulfate (EuSO₄), he could have isolated europium by precipitation. One of the unique chemical properties of europium were discovered in 1906 when Georges Urbain discovered that yttrium oxide doped with europium created a red color. After this discovery, red phosphor was born. Red phosphors are used in LCDs, LED, flat screens, fluorescent lamps, and cell phones. Nearly every modern technology that produces light uses red phosphor. Although researchers at Lawrence Livermore have been working to make lighting with fewer quantities of europium, yttrium, and other luminescent rare earths, as of 2018 there are no technically and economically substitutes for red phosphor [12]. Eduafo et. al[13] demonstrated how europium and yttrium follow each other into solution from the waste.

Waste fluorescent lamp powder consists of powder that is generated by removing the metal caps from fluorescent lamps tubes and blowing out the powder. Some glass enters this process. Also, CFL lamps use a similar process, but more glass enters the product. Unfortunately, tramp metal enters both streams which are placed together. Mercury is retorted (selective vaporization) from this powder as required by federal law. Until recently, most of the powder ended up the landfill or was stored for future beneficiation. However, as of June 2017, Rare Earth Salts, a company based in Nebraska, is producing purified rare earths from waste fluorescent lamps[14]. The upgraded facility should have a initial capacity of 3500 tons per year (tpy) and eventually a capacity of 10,000 tpy[15]. According to Paul Abernathy, the executive director of the Association of Lighting and Mercury Recyclers (ALMR), it is estimated that approximately 6500 tpy of waste lamp powder are being collected and sent to Rare Earth Salts[16] as of October 2018. A similar quantity, 6500 tons, is estimated to be currently discarded into landfill as whole or broken end of life lamps. He mentions that by federal law, government agencies must recovery 100% of these lamps according to federal law. However, it his own experience,
the relative collection of these lamps is minimal. He mentions that, for example, the DOD and EPA have not made a concerted effort to collect these lamps. The Defense Logistics Agency goal for Fiscal Year 2018 was to acquire 430 tons of rare earths[6] which is the exact quantity of rare earth oxides that Rare Earth Salts is scheduled to produce on an annualized basis after production is scaled up[15] in 2019. The same agency solicited proposals for Small Business Innovative Research (SBIR) grant(s) to produce rare earths from waste fluorescent lamps in October 2018[17]. In addition, Rare Earth Salts has signed purchase agreements receive 500 tpy of 95% pure ionic clay concentrates from Minera BioLantanidos in Chile and unknown quantities of monazite concentrates from Medallian Resources from North American Sources beginning in 2019 [18].

The basis of this research was a separate, but now connected, selective leaching and precipitation process conducted at Colorado School of Mines in concert with Dr. Patrick Eduafo under the advisement of Dr. Brajendra Mishra that produced a europium and yttrium concentrate. The research conducted at Worcester Polytechnic Institute begins with a form of that concentrate and separates europium and yttrium using selective reduction, precipitation and solvent extraction.

At Colorado School of Mines, selective reduction and precipitation was used to separate a pure mixture of pure yttrium and europium oxides (13:1 ratio) to produce a 96.00% pure europium (II) sulfate product with 80.13% recovery. At WPI, a study was conducted to optimize the factors relevant for separating a 99% pure yttrium and europium oxides at which were separated from waste fluorescent lamps. The results were studied using Stat-Ease 9. The optimized conditions to maximize purity were pH 3, precipitation time of 1 hour. The variation of the sulfate ratio (10-20x stoichiometric) and pulp density (50-100 g/L) appeared to have minimal effect upon the grade. The model was statistically significant with p-value of .0098. In addition, the same software was used to study the effect of the same factors upon the recovery of europium (II) sulfate. The highest pulp density (100 g/L), the lowest pH (3), the lowest sulfate ratio (10x stoichiometric) maximized the recovery of europium (II) sulfate, and the lowest precipitation time of 1 hour. This model was not considered to be statistically significant with p-value equal to .1250. Therefore, the optimized conditions were precipitation time equal to 2 hour, entrance pH=3, pulp density equal to 100 g/L, and 10x the stoichiometric amount of sulfate. The
determined grade from those optimal conditions are a purity of 93.54% and a recovery of 69.92%. This work was further redefined by removing oxalic acid precipitation after the second stages leaching. The solution was directly pH adjusted and selectively reduced & precipitated. The optimized conditions modified pH conditions were pH=3, 5x sulfate ratio, precipitation time=2 hours, nitrogen gas and reduction time=.5 hours to produce a purity of 92.77% europium (II) sulfate and recovery of 97.37%.

The original flowsheet was created at Colorado School of Mines for recycling waste fluorescent lamps. For that project, the powder was sieved to -74µm. However, composition of the powder received a WPI had a different composition. 96% of the starting powder was already under 44µm as received and it had much lower quantities of silica and higher quantity of rare earths. Therefore, the sieving stage was removed for processing at WPI. Next, it was selectively leached with hydrochloric acid at room temperature to remove the calcium phosphate as well as iron and aluminum bearing constituents into the leachate. Unfortunately, there was a strong exothermic, gas-evolving for a scale-up (2 L solution at WPI). Therefore, an ice water bath was required to keep the bath at room temperature and to control the gas evolution. The resultant solid from the first stage of leaching was recovered by vacuum filtration and leached with hydrochloric acid at 70°C to solubilize the yttrium and europium. Vacuum filtration is used to recover the yttrium and europium leach solution. Originally, this liquid is treated with oxalic acid to purify and to selectively precipitate europium and yttrium oxalate away from the element impurities such as calcium, phosphorus and aluminum. However, the final version of the flow sheet removes the oxalic acid precipitation and places it at the end of the flow sheet. Instead, this solution directly selectively reduced. Typically, the mass-ration of $Y_2O_3$ to Eu$_2O_3$ is approximately 13:1 to 15:1.

The technical requirements of the phosphor powder required for manufacture of fluorescent lamps require less than 100 ppm of impurities as well as or 99.999% pure yttrium and 99.99% pure europium oxide. A typical composition for the three mains types of phosphor powders for red, green and blue phosphors are: $Y_2O_3$:Eu$^{3+}$ (YOX) LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$(LAP), BaMg$_2$Al$_{16}$O$_{27}$:Eu$^{2+}$ (BAM), respectively. The red phosphors, yttria doped with europium ions, are of primary relevance of the research conducted for this thesis. Therefore, a processing strategy capable of producing high purity $Y_2O_3$ and
particularly \( \text{Eu}_2\text{O}_3 \), due to its higher value, is the goal of this research. However, since a 4 or 5 nines pure product was not produced, the strategy is the produce a relatively product and sell it to a rare earth purifying company either as a 99% mixed or pure europium and yttrium oxide product.

Considerable research has been conducted at various institutions to recycle rare earths from phosphor dust collected from waste fluorescent lamps. Meaningful industrial production will begin and is scheduled to scaled up at Rare Earth Salts in Nebraska in 2019. The other international facilities are at Rhodia at La Fons and La Rochelle plants in France. The major roadblocks to success are phosphor powder collection, impurity removal, clean rare earth separation, and economic, environmental disposal of residual apatite and glass, and government action.

This chapter will demonstrate justification for the research, objectives of the research, and scope of the research. In addition, the overall research will be summarized in this document. Finally, the document organization will be delineated.

1.1 Justification for Research Performed

The 2010 Japanese Senkaku boat incident was the Sputnik moment for the alternative energy, recycling and rare earth element (REE) production industry. China reciprocated by temporarily blocking exports of rare earths to Japan. The price of rare earth elements, neodymium in wind turbines, dysprosium in hybrid-electric cars, europium in florescent lamps and LEDs soared to record levels due to supply restrictions from China. In response, the United States Department of Energy crafted the Critical Materials Strategy 2011 report. The report chronicled the applications of various metals including neodymium, dysprosium, terbium, yttrium, and europium by showing how each was important to clean energy and was a supply risk. The basis for this work, which was started at Colorado School of Mines and continued at WPI can be attributed to the event the corresponding report.

Furthermore, a national competition was conducted to award an energy hub to tackle the supply risk of these metals. The Critical Materials Institute (CMI) was created as a consortium of academic institutions and industrial partners, dedicated to creating practical solutions by increasing native supplies of, substitutes for and recycles of critical materials. Armed with 5 years of funding,
the goal was to create industrial methods for greater US critical material generation, substitution, and recycling. The research started at CSM--as part of CMI--was continued at WPI as funded by a startup package.

1.2 Objective(s) of the Research

Final goal of this project is to create a technically and economically viable process to generate a saleable yttrium or europium product from recycled phosphor dust. If mixed yttrium and europium oxide product can be created, it must be 99% pure for a customer to purchase it—at a 25% discount from the China FOB rare prices. If a single species product can be created, in order to “close the loop” for lighting end projects, the purity of these powders must be 99.99%. A 4-nines pure yttrium or europium oxide powder must be produced. However, only 99% europium oxide and 99% pure yttrium oxide was created. There products can be sold at a 12% discount from the freight on board rare earth prices. An economic analysis will be utilized to compare the two different processes for created the two different products.

1.3 Scope of the Research Topic

. The scope of research begins at precipitation of yttrium and europium from solution up until a purified yttrium and europium oxides are produced. There was a slight modification of the flow sheet from waste powder to the europium and yttrium-rich leach solution. In addition, the waste fluorescent powder was characterized as well as a characterization of the final products. Monte Carlo Simulation was used to conduct the research.

1.4 Research Conducted and Presented in the Document

1.4.1 Chapter 1: Introduction
This chapter will introduce the reasons that this research was conducted. In addition, the desired final objectives will be stated. Also, the scope of the research will be discussed, and a statement will be made regarding the specific research conducted by the researcher.

1.4.2 Chapter 2: Literature Review
The literature survey will define and discuss the current state of critical materials. Next, the definition and history rare earths--yttrium and europium in particular--will be examined. Next, primary and secondary REO production strategies will be discussed. Next, the current research regarding separation and purification of phosphor dust—specifically in regard to europium and yttrium oxide—will be reviewed. Finally, the solvent extraction of yttrium will be reviewed.

1.4.3 Chapter 3: Theory
The theory section will consider equilibrium analysis. Specifically, Pourbaix diagrams and thermodynamics related to the europium, yttrium, zinc and hydrogen will be mentioned. In addition, the theory regarding the solvent extraction of yttrium will be discussed. Finally, the kinetics of the reaction will be discussed.

1.4.4 Chapter 4: Experimental Design
This chapter will discuss the experimental information used for waste lamp powder characterization. Additionally, analytical techniques and analytical software will be labelled. Finally, the oxalic acid optimization and selective reduction & europium (II) sulfate precipitation experiments will be examined. The kinetic of the reaction will be discussed. The examination of final yttrium and europium oxide products will be discussed.

1.4.5 Chapter 5: Discussion
The discussion will review the results from the characterization and selective reduction & europium (II) precipitation, solvent extraction results and the kinetic research. Also, the economic analysis will be discussed.

1.4.6 Chapter 6: Conclusion
The final chapter, the conclusion, will briefly summarize the critical results and make recommendations regarding future work.
CHAPTER 2
LITERATURE REVIEW

This literature review is a modification and a continuation of literature review completed for my Master of Science Thesis at Colorado of Mines [19].

2.1 Rare Earths

Rare earth elements are a grouping of 17 chemical elements found in the Earth's crust. These elements are the fifteen lanthanides, plus scandium and yttrium, and are shown in the periodic table (see Figure 2.1.1).

![Periodic Table of Elements](https://example.com/periodic_table.png)

Despite the name, many of these elements are rare or difficult to find in the crust. In fact, some elements are relatively abundant such as cerium which has a higher crustal abundance that as copper at 68 ppm according to Kenneth Barbalance [21] as shown in Figure 2.1.2.
However, they are rarely found concentrated in economically minable ore deposits. The elements are found in small quantities, and the ore deposits tend to have low concentrations—rendering them uneconomical to mine. Rare earth ore reserves tend to be uncommon.

The first rare earth elements were discovered by Carl Axel Arrhenius when he discovered the ore, Gadolinite in 1787. In addition, he is credited for discovering yttrium (Y)[1]. Yttrium and cerium were the only know rare earth elements up until 1833—when more rare earths were discovered[2]. There are two groups of rare earth elements known as the light rare earth elements (LREE) and the heavy rare earth elements (HREE). The elements organized by two respective categories below according to their relative atomic number:
Table 2.1.1: Two categories of rare earth elements are demonstrated below.

<table>
<thead>
<tr>
<th>Heavy Rare Earth Elements (HREE)</th>
<th>Light Rare Earth Elements (LREE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terbium (Tb)</td>
<td>Lanthanum (La)</td>
</tr>
<tr>
<td>Dysprosium (Dy)</td>
<td>Cerium (Ce)</td>
</tr>
<tr>
<td>Scandium (Sc)</td>
<td>Praseodymium (Pr)</td>
</tr>
<tr>
<td>Holmium (Ho)</td>
<td>Neodymium (Nd)</td>
</tr>
<tr>
<td>Erbium (Er)</td>
<td>Promethium (Pm)</td>
</tr>
<tr>
<td>Thulium (Tm)</td>
<td>Samarium (Sm)</td>
</tr>
<tr>
<td>Lutetium (Lu)</td>
<td>Europium (Eu)</td>
</tr>
<tr>
<td>Yttrium (Y)</td>
<td>Gadolinium (Gd)</td>
</tr>
<tr>
<td>Ytterbium (Yb)</td>
<td></td>
</tr>
</tbody>
</table>

The reason for classifying rare earths based on these grouping is that they denote analogous chemical properties and are found together in ore bodies. Before ion exchange technology was developed, rare earth elements were separated and extracted by using crystallization and precipitation. Similarly, rare earths were further classified in sub-groups based on each elements solubility in solution as double sulfates until ion exchange was used during the Manhattan Project in the 1940s [3]. (Copyright protected under Fair use)

There are three main types of minerals that are mined for rare earth elements. The ore types are bastnäsite, monazite, and xenotime. According to Gupta [2], 95% of rare earth elements are found in these three types of ores. In addition, ion-adsorption clays are also a major source of rare earth elements. Among these three ore types and ion-adsorption clays, there are varying ratios of rare earth elements to be found. However, ion-adsorption clays are thought to be a form of highly weathered xenotime. Additionally, research has been conducted on separating and purifying eudialyte, from Norra Karr project, and ancylite, from Bear Lodge project, which according to Professor Corby Anderson from Colorado School of Mines might be economically viable to mine[23][24].

Monazite ore contains primarily light rare earth elements (LREE) and is the second most common ore type source for rare earth extraction (see Figure 2.1.3). Monazite is a very dense mineral, which causes it to congregate in placer sands as a result of sorting, by gravity, of the
products of the weathering of the exposed rock masses in which it originally formed [25]. Also, the ore can be mined in place from several locations. Significant sources of this ore are found in the beach sands of India, Brazil, and Malaysia. According to Hedrick[26], about 6.5% of rare earth production came from monazite in 2007. A major problem with monazite ore, is the existence of thorium, a radioactive element in common forms of the mineral. Mineralogically, thorium can substitute for other rare earth elements due to the similar ionic radius. As a result, monazite mining and extraction from thorium rich ores is challenging due to the health risks of thorium. For example, monazite mined in Malaysia from 2006-2010 had a concentration of 6.87% thorium by mass[27].

![Figure 2.1.3: To the left is a pie chart showing the relative rare earth element percentages in monazite ore (modified from Gupta[2]).](image)

Bastnäsite ore is the most significant source for rare earth elements in the world and it primarily contains LREE, with only low amounts of HREE (see figure 2.3). These ores tend to have high concentrations of cerium, lanthanum, yttrium, and neodymium. Bastnäsite is a
significant source of LREE. There are significant resources of this ore in China, Australia, and the United States. They can also be found in igneous contexts, hydrothermal and bauxite deposits. According to Hedrick[26], about 50% of rare earth production came from bastnäsite in 2007.

Figure 2.1.4: This pie chart shows the relative rare earth element percentages in bastnäsite ore (modified from Haxel 2002[28]).

Xenotime ore is the third most important ore when regarding rare earth elements. The general chemical description for xenotime is yttrium phosphate, however the yttrium can be substituted for several other HREE. In some cases, thorium or uranium may be a byproduct of xenotime ore—which creates hazardous material handling problems. The xenotime mined in Malaysia had thorium content of approximate 1.5% by mass[27]. These ores generally contain HREEs in large abundances (see Figure 2.1.5). Xenotime ores are found in the same place as monazite. Each mineral is formed based on differences temperature and pressure changes. At lower
temperatures and pressures, monazite will form, and at higher temperatures and pressures, xenotime will form [25]. Significant sources of this ore can be found in Norway, Malaysia, and Brazil. According to Hedrick[26], only a small, negligible percentage of world rare earth production originated from xenotime in 2007.

Figure 2.1.5: This pie chart shows the relative rare earth element percentages in xenotime ore (modified from Gupta [2]).

Ion-adsorption clays (see Figure 2.5) are another essential source of rare earth elements and they contain many more HREE (see Figure 2.6). According to Hedrick[26], about 43.5% of rare earth production came from ion-adsorption clays in 2007. The processing ion-adsorption clays is simpler because it can be separated using hydrometallurgy. This clay does not require physical beneficiation processes such as flotation, gravity separation, and magnetic separation. These ion-adsorption clays are not only are easier to produce and extract from, but they are more economical and safer for the environment. However, in practice, because of sheer quantity of illegal mining many of these mines have left significant environmental legacy as it is mentioned in section 2.3.
According to the Center for Energetic Concepts Development (2013), these ion-adsorption clays hold approximately 80% of the world's total HREE resources[29]. However, the problem is that ion-adsorption clays have only been processed in China, allowing them to monopolize the rare earth market. During the 1980s, China became the leader in the rare earth market due to the inexpensive refining costs, making it uneconomical for other operations in other countries. However, as Minera BioLantanidos is set to become the first operating ion-absorption clay mine, outside of China, in Concepcion, Chile.

Figure 2.1.6: The picture is a photograph of ion-absorption clays.[30]
Figure 2.1.7: This pie chart showing the relative rare earth element percentages in ion-adsorption clays (modified from Haxel 2002[28]).

2.1.1 Yttrium

Yttrium is essential to this project. The purification of yttrium oxide important to the project and it is part of the original list of milestones for this project—even though 99.99% yttrium oxide was not achieved. Yttrium is an extremely important rare earth element and it is important to have a supply of it for future generations. With the help of the United States Department of Energy, Critical Materials Strategy Guide[31], Strategic and Critical Materials 2015 Report on Stockpile Requirements and Dr. Doug Stewart's 2013 online information[32], many uses for yttrium can be identified:

- Yttrium is used in the electrolytes for solid oxide fuel cells fuel cells (SOFCs) for distributed power generation.
- Yttrium is used in gas turbines for stationery power generation, as the yttrium is used for thermal barrier coatings of the turbine blades.
- Yttrium is used in the creation of camera lenses and in ceramic glazes to provide shock resistance
- Yttrium is doped with another rare earth element, europium, and is used to produce phosphors, which provide the red color in color television tubes
Yttrium oxide is used to make yttrium iron garnets which are very effective microwave filters; blocking some microwave frequencies, while allowing others to pass through. Yttrium oxide is also used to make the high-temperature superconductor YBCO (yttrium barium copper oxide) to provide a cheaper product. Yttrium-90, a radioactive isotope, is used in treatments of various cancers and in precision medical needles for the spinal cord. Yttrium is used in alloys, which increases the strength of aluminum and magnesium alloys. Yttrium is used as a catalyst in ethylene polymerization. Yttrium and yttrium oxide have substantial but classified uses in classified quantities in the US Defense Logistics Agency supply chain.

As referenced before, yttrium was first discovered in 1787 by Carl Axel Arrhenius at a feldspar-quartz mine and was first confirmed in 1797 by Swedish chemist Anders Ekeberg. Yttrium was the first discovered and confirmed rare earth element. The first yttrium that was extracted, was in Berlin in 1828 when Friedrich Wöhler obtained a gray powder by heating anhydrous yttrium (III) chloride with potassium. To recovery a high purity of yttrium, solvent extraction methods are often employed. Yttrium has unique properties. It is highly reactive. Yttrium will never be found as a free element in nature. It located very low on the Ellingham chart with yttrium oxide having a free energy of formation of 1817 kJ/mole[32]. Yttrium occurs in most bastnäsite ores, monazite ores, xenotime ores, and ion-absorption clays. It can also be found in uranium ores, allanite, samarskite and fergusonite but primarily, yttrium is not extracted from these minerals due to rarity of these minerals. It is also present in almost all other rare earth minerals—sometimes at very low concentrations. Information about these sources can be found above. However, these sources have various amounts of yttrium as shown in Table 2.1.2.

Table 2.1.1.1: This table shows the approximate percentages of yttrium that is in different sources of yttrium (modified from Los Alamos[33]).

<table>
<thead>
<tr>
<th>Source of Yttrium</th>
<th>Approximate Percentage of Ore That is Yttrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bastnäsite Ore</td>
<td>0.2%</td>
</tr>
<tr>
<td>Monazite Ore</td>
<td>3%</td>
</tr>
</tbody>
</table>
The Department of Energy (DOE) Critical Materials Strategy guide was developed to describe information regarding current and future yttrium supply and demand[31]. This guide shows graphs for the short and medium term for yttrium supply and demand, while showing potential trajectories for future yttrium supply and demand based on the percentage of global non-clean energy demand, US

Figure 2.1.1.1: This figure shows the future supply and demand for yttrium oxide [31], clean energy demand, and the rest of the world clean energy demand. The Figure 2.1.8 shows the values of yttrium in kilotonnes per year up through 2025. (Copyright protected under Fair use)

2.1.2 Europium

Europium was unearthed by Eugène-Antole Demarçay in 1896 while assaying samples containing samarium[34]. He discovered than samarium was contaminated by undiscovered europium, and he was able to isolate high grade europium in 1901. Europium is found in nature in monazite and bastnäsite ore where europium substitutes for other rare earth elements in the crystal structure based in similar ionic radii[35].

Table 2.1.2.1: This demonstrate the rare earth abundances in various types of ore (Modified from Gupta).[2] (Copyright protected under Fair use)
As demonstrated in Table 2.1.2.1, europium is rarely found in ore at proportions greater than 0.5%. The current commercial production of europium is solely from China.

![Table 2.1.2.1](image)

Figure 2.1.2.1: This chart shows the short and medium term supply and demand for europium oxide.[31] (Copyright protected under Fair use)
A decision was to focus upon europium extraction at the beginning of this project. The current price of freight on board (FOB) europium oxide is 64.7$/kg[10] as of late November 2018. This price was gathered from Kitco Strategic metals. The price of the europium at the beginning of the project started in Colorado, June 2013, was approximately $1500/kg.

In 2011, China controlled about 97% of the rare earth element supplies. In addition, China intentionally limited exports of these rare earth elements, causing the prices for rare earths to increase rapidly. China took this action to foster and favor the domestic supply chain and to further its strategic foothold on the rare earth supply [36]. Even though the worldwide demand is growing, there are few commercially producing industries that address this increasing demand for rare earth elements. However, there are several technologies and that are scheduled to running at a commercial level by the end of 2019. Rare Earth Salts (Beatrice, Nebraska) is scaling up recycling of fluorescent lamp recycling. In addition, Urban Mining is completing its 100,000 square foot facility in 2019 for recycling Nd-B-Fe magnets San Marcos, TX. Furthermore, as the world turns toward more green technologies, regulations will tighten up making it more difficult to mine these rare earth elements in the manner that they have in the past.

There are supply strategic as well environmental concerns in the manner that China is currently producing rare earth metals as shown below in Figure 2.1.2.2.
Figure 2.1.2.2: This picture shows the environmental problems associated with rare earth element processing in China.[37] (Copyright protected under Fair use)

The photograph above in Figure 2.1.2.2 describes a 10 square kilometer tailings pond, formerly a lake which is now filled with tailing from the mining process. This photograph is from Baotou, China which is the largest source for rare earths in the world. The minerals are mined approximately 120km north as a secondary by product of the Bayan Obo Mine, but are processed in Baotou. About two-thirds of China's global output of rare earths are produced at this location. This tailings pond contains many kinds of toxic chemicals. For example, one dangerous element contained is thorium which, if ingested, may cause cancers of the pancreas, lungs and leukemia[37]. Professor Kingler from Boston University, refers the situation in her book Rare Earth Frontiers as under subheadings “Radioactive Rivers and Cancer Villages” and “Chronic Arsenic Poisoning, Skeletal Fluourosis, and Long Tooth Disease” [38]. Other effects of this tailings pond include the failing of growing crops. Many crops will not grow anymore, or some fruits would grow, but not produce any actual fruit. The citizens would inhale solvent vapor, especially sulfuric acid, and coal dust which is clearly visible in the air. The soil and groundwater are polluted
with toxic substances. Many farmers had to divest themselves of livestock as toxins were killing them all off. Families in the area are affected by illness on a regular basis. In summary, the environment plays a huge role in rare earth element mining as it is important to limit the risks associated with them to allow for successful production and to ensure cooperation from citizens and society. As result of these environmental practices and the effect upon the public health of the citizenry, other countries shown supply rare earth elements with much better environmental protections and safeguards.

2.2 Critical Materials

The Critical Materials Institute was created to address supply risks to various materials that are instrumental to high technology fundamental to clean energy. The original report on critical materials title “Mineral, Critical Materials, and the U.S. Economy” was written by many industry professionals in conjunction with the National Research Council (NRC). This report was promptly ignored by the government after it was written. However, after the Senkaku incident, Congress acted and the US Department of Energy created the US Critical Materials Strategy Report was completed in 2011[31]. As result of this report, the CMI was created. The CMI has defined the factors that affect supply risk as global availability, competing technology demand, political/social/regulatory factors, cross-market codependence, and producer diversity[31]. Similarly, CMI explains “Importance to Clean Energy” as a combination of material necessity for magnets, batteries, photovoltaic films, phosphors and substitutability limitations for each respective.
Figure 2.2.1: This figure shows the short term (0-5 years) criticality of various elements.[31] 
(Copyright protected under Fair use)
As Figures 2.2.1 and 2.2.2 demonstrate, europium, yttrium and terbium, as well as valuable components of phosphor dust highlighted in red, have been designated by CMI as having significant supply risks and being essential to clean energy. The basis for this research project is to ameliorate this supply risk by developing a method to recover the corresponding rare earths from recycling waste fluorescent powder.

2.3 REO Primary Production Processing Strategies

As of 2011, China was the only country processing rare earth elements (REE) commercially. As a result of the escalation of rare earth prices in 2011, Molycorp Mountain Pass and Lynas Mount Weld began to process rare earths[4]. However, Molycorp has declared bankruptcy and Mountain Pass has ceased production as of October 20, 2015, a large part due to decreased rare earth prices. Regarding europium, yttrium, and terbium oxides, there have been China is the only country, in the near term, commercially generating those products from mines [31]. There are two main methods by which heavy rare earths are extracted and processed. The foremost technique is practiced at the Bayan Obo mine located in Sichuan, China.
Figure 2.3.1: This chart demonstrates an extraction technique for rare earths in at Bayan Obo. (Modified from Rare Earth in China [39].)
Figure 2.3.2: This chart demonstrates the technique used to extract rare earths in the 6 Provinces in southern China.[30]
The second process, described in Figure 2.12, is used to extract ion-absorbing clays a dominant HREE source[30]. This process is often conducted illegally on public land in China. This method of in-situ leaching, more commonly used in the uranium industry, is relatively inexpensive as there is no mining, heap or tank leaching, or tailings deposition. Several thousand shallow vertical drill holes are made 1-2 meter in diameter at a mountain top. Similarly, thousands of 3-4 inch drill holes are made on the side of an incline. The leaching process takes about a month for the rare earth carbonate slurry to be collected. The collected solution is filtered and impurities are precipitated with a weak solution ammonium sulfate. Next, a concentrated solution of ammonium sulfate precipitates the rare earths and the slurry is dewatered by filter press. The cost of this in-situ leaching is $4000-5000 per ton saleable rare earth. Unfortunately, the majority of this money received for this concentrate is used to bribe local officials. and the leaching is conducted on public land that is abandoned in a toxic state. Recoveries can be up to 75%.

Molycorp Mountain Pass, which recently shut down production in October 2015, has its own unique process for REO production.

![Flow Sheet for Rare Earth Production at Molycorp Mountain Pass](image)

Figure 2.3.3: This is the flow sheet for rare earth production at Molycorp Mountain Pass.[7]

The Mountain Pass process for rare earth production is not typical for most types of mines. The typical mine, crush, float, leach process is typical[7]. However, the cracking/leaching process used to extract cerium oxide, a likely roasting, oxidation of insoluble cerium (IV) oxide and hydrochloric acid leaching of the ore, used to manufacture Sorbx, is a trade secret[7]. However,
use a Dowex 50 ion exchange resin to remove iron and uranium. Furthermore, they use solvent extraction to separate light and heavy rare earths. With regard to the HREE, they are alkalized, shipped to China, and separated & reduced via oxyflouride molten salt hydrolysis. The light rare earth elements separated via lanthanum or neodymium/praseodymium via PC-88a via solvent extraction. Neodymium and praseodymium are further separated via 39 mixer settlers. The previous owners of Molycorp shipped an unknown in quantity of these oxides to Estonia for further purification reduction at NPM Silmet when it was a subsidiary of Neo Performance Materials. Now that Neo Performance Materials and Molycorp Mountain Pass are separate, it is not certain this shipment still occurs. Recent

2.4 REO Secondary Production

The Rhodia, a subsidiary of the Solvay group, began recycling the rare earths from phosphor dust in 2012. This process treats more than 2000 tons a year of recycled phosphor dust[40]. There were two facilities associated with the recycling, the Saint Fons and La Rochelle facility in France. At Saint Fons facility, the upstream hydrometallurgical processes are conducted[41]. The feed from the waste fluorescent powder recyclers, where the collected lamps’ end caps are removed and mercury retorted, is sent to Saint Fons. The powders are sieved, halophosphates are separated with a hydrocyclone, pressure leached using 18 M sulfuric acid and filtered[42]. The mixed rare earth filter cake is collected, dried, and sent to the La Rochelle plant for separation and purification[41]. The mixed rare earth oxide roasted, re-suspended in solution and leached with nitric acid. The leach solution is separated by solvent extraction to separate lanthanum, cerium, europium, terbium, gadolinium and yttrium. Each of these is individually precipitated by oxalic acid, filtered and calcined to obtain six purified rare earth oxides. These individual purified REO are reprocessed into new lamp phosphors such as Y₂O₃:Eu³⁺ (YOX) and LaPO₄:Ce³⁺,Tb³⁺ (LAP)[43]. The overall recovery is approximately 80%[44].

In addition, a German lighting company in Freiberg, Narva Light Sources GmbH, in conjunction with a phosphor dust recycler, FNE Frieberg, and TU Frieberg are currently commercially recycling rare earths from phosphor dust via the SepSelsa process[45]. They use solid-state chlorination of phosphor powder with ammonium chloride to create water soluble yttrium and europium chlorides. Researchers at TU Frieberg compared the optimal conditions for recovery for end of life (EOL) phosphor dust and production scrap. The varied the time (2-4
hours), ammonium chloride to phosphor dust ratio (2-4 g/g) and temperature (300° to 400° C). The recoveries are generally higher for EOL phosphor dust for europium and yttrium ranging from 81-100% versus 71-92% for production scrap, respectively. The principal investigator (PI) for the laboratory scale work at TU Frieberg, Martin Bertau, indicates that this process has been used recovery all the rare earths from phosphor dust as well as Nd from FeNdB magnets[46]. However, there is no published work regarding the details of the separation and purification of rare earths for this process. Furthermore, there no information listed about this process after 2015.

Rare Earth Salts, a Beatrice, Nebraska based company, is in the process of scaling up production of waste fluorescent powder into 99.99% pure separated REOs. It is scheduled to be at full production product next year producing 430 tpy of REO[15]. The final production of four 9’s pure REO will include 500 tpy that will be purified from an unstated volume of North American monazite from Medallion Resources Ltd and 500 tpy 95% pure concentrates from ion-absorption clay Minera BioLantanidos should reach 3500 tpy of 4 nines pure REO[15]. According to Joseph Brewer of Rare Earth Salts, the initial production is supposed to process 5000 tons per year of waste fluorescent lamp powder. Based on this information, and information reported Paul Apernathy, this means at least 1500 tons per year is being stockpiled for future use at the site or elsewhere. Also, Dr. Brewer indicates that that final goal in 2-5 years is for 10000 tpy to be produced. In addition, Rare Earth Salts is has received a $875,000 grant from the DOE to study the purification of REO from coal[47].

The process described in the patents filed by Dr. Brewer is very unique. He uses the same procedure for both fluorescent lamps and rare earth containing ore. It is assume a form of physical preconcentration is used on the feed, but the patent does not state this information[48]. He uses a nitric acid or hydrochloric acid to leach the rare earths into solution as well as some impurities such as aluminium, zinc, copper nickel, titanium or iron[48]. The details regarding leaching are very vague and are likely mean to be kept secret. The solid is separated as waste. The solution is titrated with MgO to remove iron hydroxide precipitates to pH 4. Next, the solution is solution is precipitated with oxalic acid or some rare earths hydroxides separated with a form of sequential separation using MgO up to pH 7, and the remaining rare earths in solution are precipitated with a carbonate. The precipitates are roasted to produce a rare earth concentrate. The main remaining constituent of the solution is magnesium nitrate is separated by evaporation. It is thermally decomposed to MgO and NO₂—which is bubbled back into to recycle nitric acid. The rare earth
concentrate is roasted with ammonium chloride, similar to the SepSelsa Process, between 250-350°C to produce a more pure concentrate. Next, these rare earth chlorides dissolved into solution and electrowinnned. They are separated based on electronic potential. 16 rare earths are sequentially separated in solution by 16 different cells and different potentials. It is not stated how the minor amount of one of two impurities per cell are removed. There are a lot of advantages of this system including reagent recycling and separating rare earths based on potential. The tradition manner of separation, solvent extraction, uses more expensive reagents and has high operating cost, however this technology may have higher capital costs while minimizing operating costs.

2.5 REO Secondary Production from Phosphor Dust: Separation and Purification

There are many methods from the literature regarding phosphor dust physical separation. Possible physical separation methods include sieving, magnetic separation, flotation, and gravity separation methods. The goal these processes is to separate the older halophosphate type of phosphor dust, which contains no rare earths, from the rare earth containing phosphor dust which has a size of 4-7µm[49]. Many of these have been demonstrated to effective at the laboratory scale, but few have been successful at the industrial scale. Takashi et al. [50] used a centrifugal pneumatic separator to increase the purity but it significant decreased the recovery. He improved the recovery of the process by increasing the air flow; however, the upgrade ratio was not as meaningful. The highest recovery achieved was 70%, and the rare earth percentage increased from 13.3% to 29.7%. Similarly, dense media separation was used to particles based on density using diiodomethane. The specific gravity of halophosphates is approximately 3.07 white the rare earth containing phosphor varies from 4.34-5.23. During the float/sink tests, the purity of rare earth phosphors increased by up to a factor 5, but the recovery of the sink product was less than 3% Hirajima et al. [51] utilized the same media using centrifugal separation. The phosphors were pretreated with sodium oleate. 97% of the rare earth phosphors were recovered in the sink product with a purity of 48.6%. Unfortunately, dense media separation (DMS) has little commercial applicability, and therefore, a hydrocyclone was utilized to scale up this separation. Using a hydrocyclone, the attained purity of the rare earth phosphor was 27%--an upgrade ratio of approximately 2. Using a Mozley multi-gravity separator (MGS) the purity was 21% and the upgrade ration was approximately 1.5. Unfortunately, the recoveries were not particularly high. Rhodia La Fons uses a hydrocyclone to remove particles over 20 µm—which has been used to remove 50% of the remaining halophosphates[42] from solution.
Front flotation is another method to remove halophosphates from the rare earth containing waste fluorescent lamps. Zeta potential varies with pH for each type of phosphor. In addition, the point of zero charge (PZC) is 4 for halophosphates, 7.7 for red, 6.8 for green and 4.8 for blue phosphor[52]. Based on this information, rare earth phosphors have a positive zeta potential at a slightly acidic pH. Utilizing 2 stage froth flotation with collector dodecyl ammonium acetate at pH 2.5 and sodium dodecyl sulfate at pH 9.6, they achieved recoveries of the rare earth phosphors between 60 and 80% and grade of approximately 80%.

In addition, researchers have separated individuals rare earth powders (red, green, blue) based on modifying their surface properties. The phosphors were made hydrophobic by a surfactant that was placed at the interface of a polar and non-polar liquid. Based on these properties, green phosphors were collected in the first stage with purity and yield of 90% and 95%, a separation between red and blue phosphor yielded 92% and 91% with a purity of 95% and 92% respectively[53].

Also, magnetic separation has been employed to separate various types of phosphor powders. The magnetic susceptibilities in order from highest to lowest are green, blue, red, and halophosphate. Green phosphor is 1-2 orders of magnitude more magnetically susceptible than the other phosphors[54]. Using two stages of high-gradient magnetic separator (HGMS) with a maximum 2 Tesla field, the purity of green phosphor (LaPO4:Tb,Ce) was 86%. Repeating the two stage operation on the green phosphor upgraded the purity to 90%. According to the research, a green phosphor purity of 96% has nearly the same properties as primary production green phosphor powder. Unfortunately, it is unlikely that end producers of LED, flat panel and cell phones would accept even slightly inferior product.

In addition, hydrometallurgical,chemical beneficiation methods have been studied for separation and purification. Currently, these methods seem more viable because they have greater selectivity. As a result, the processed products have higher grade and yield than many physical separation methods.

Ionic liquids have been studied as a method of separating individual phosphors. DuPont et al. [40] used pure amounts of the green, red, blue, and halophosphate (HALO) type phosphors to demonstrate the viability at a larger scale. The researchers used ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][T$_2$N], for dissolving red phosphor, Y$_2$O$_3$:Eu$^{3+}$, because it
represents 20% of the fraction and 80% of the rare earths in phosphor dust. This three stage process, generates only CO$_2$ and uses only oxalic acid—the ionic liquid is regenerated. To begin, the three colors and HALO are added to the ionic liquid and stirred. The solution can solvate 10mg of red phosphor per gram ionic liquid. Next, a stoichiometric quantity of oxalic acid was used to precipitate the europium and yttrium oxalate or “stripping”. The mixture was filtered to separate the ionic liquid from the precipitate. The mixture was calcined to recovery red phosphor with a purity of 99.9%+. Unfortunately, the issues that have kept ionic liquids from being industrially relevant include the high cost of ionic liquids, the low thermodynamic stability and the low throughput of ionic liquid separation processes. Ironically, some research has indicated ionic liquids as a great alternative when even are produced from petroleum, and they have high toxicity.

Direct leaching is often the preferred method for rare earth separation and purification. Takahashi et al. [50] used sulfuric acid to leach at 70°C followed adding ammonia to precipitate the rare earths hydroxides from the impurities. After filtration, hydrochloric acid dissolved the rare earths back into solution where they re-precipitated with oxalic acid. Finally, calcination created a mixed rare earth oxide of 98.2% with a recovery of 65% and 67% from yttrium and europium respectively. In addition, the same group used chelating resins iminodiacetic acid for the Eu/Y fraction and nitrolotriacetic acid for the Tb/La/Ce grouping. They attained purities of greater than 90% for all rare earths, but the recoveries varied from 30% to 90%. Using a similar process, they used solvent extraction using PC-88a to separate yttrium and europium via a 6-stage extraction and 4 stages stripping using mixer settlers. The final grade of europium and yttrium were 97% and 99.3%, and the total recovery was 65%. Also, an attempt to made to use solvent extraction with precipitation reaching a purity of 99.7% for yttrium oxide and 90% for europium oxide.

Rabah et al. [55] used an innovate method for hydrometallurgical separation of phosphor dust. The waste fluorescent powder was leached with hot concentrated sulfuric acid and afterwards, potassium thiocyanate was added. This europium and yttrium fraction was separated by solvent extraction with trimethylbenyl-ammonium chloride. The solvent was stripped with 1 M nitric and N-Tributylphosphate (TBP). TBP was evaporated by gentle heating which left a separate solution of europium/yttrium nitrate slurry. Europium nitrate is insoluble in ethanol and yttrium nitrate is soluble. For the final step, each RE nitrate is reduced to metal by hydrogen reduction. The economic analysis conducted of the process suggests that the process is economic; however, the purity of the final product is not stated.
From the literature, a form of precipitation is used to separate rare earths from phosphor dust. Oxalic acid and sodium/ammonium carbonate are the main precipitating agents used to separate rare earth leach solutions from their impurities. This separation is based on extremely low solubility of rare earth oxalates[56]. Similarly, rare earth carbonates have very low solubility which increases slightly as a function of pH[57]. In oxalate systems, the solubility tends to decrease as a function of acidity which makes low pH phosphor leach solutions ideal separating rare earth oxalates from their corresponding impurities[56]. The solubility of cationic impurities such as aluminum, iron and zinc are greater than rare earth carbonates and oxalates which is why precipitation is used as a purification method. However, Vasconcellos et al. [58] demonstrated that ammonium carbonate precipitation with the addition of hydrogen peroxide could be used to separate yttrium, a soluble peroxycarbonate, and europium, an insoluble peroxycarbonate. Chi et al. [59] explores the optimum conditions to precipitate rare earths via oxalic acid. Similar to phosphor leach solution, calcium, magnesium and aluminum impurities consume measureable amounts of oxalic acid. It was determined that a 60% stoichiometric excess of oxalic acid, based on the quantity of rare earths in solution was one of those conditions. However, this paper[59] contradicted another the previous paper [56] by demonstrating increasing the pH increases the recovery or decreases the solubility of rare earth oxalates as show in Figure 2.4.1. An attempt was made to replicate this research. However, it did not work and the research did not respond to emails.
2.5 Europium and Yttrium Separation

There is a significant challenge to separating rare earth elements from each other because most methods are non-selective. Selectivity is a crucial factor in hydrometallurgical processes. The primary methods for solution purification and concentration are ion exchange, solvent extraction, adsorption on activated carbon, crystallization, and precipitation & cementation. The desired end product is 99.99%+ pure europium oxide—which is the minimum requirement to manufacture phosphor powders. The desired total recovery is at least 70%. From a review of literature, Frank Spedding has published groundbreaking work regarding using ion exchange resins to separate rare earths. However, none of the recent literature considers ion exchange as a possibility for selective europium removal and no industrial methods use ion exchange for europium separations. Also, it tends to be slow and expensive. Specifically, there are no ion exchange resins made selectively for europium or yttrium. Regarding carbon absorption, it has poor
selectivity so it must be eliminated as a possibility for europium recovery. Solvent extraction (SX) is a possibility and is currently used at Rhodia.

Generally speaking, the difficulty in separating rare earth via solvent extraction is related to their chemical and physical properties which can be reflective of their similarities in their ionic radii as shown in Figure 2.15,

![Atomic radii and valences of rare earth elements]

Figure 2.5.1: The figure shows the atomic radii and valences of rare earth elements. (Modified from Shannon and Prewitt[60]) (Copyright protected under Fair use)

Specifically, separating europium and gadolinium, both having the +3 cationic state, based in 95 and 94 picometers, theoretically should be very difficult via solvent extraction (SX). The difference between yttrium 3+ and europium 3+ is 95-90=5 picometers which suggests that there is a greater possibility of separation. The difference is sufficient such that SX is technically possible but there will likely be small separation factors. In practice this means, multiple stages of extraction of loading and stripping will be required for small separation factors. More stages means, higher capital cost and higher operating costs. For example, Molycorp requires 39 mixer/settlers to separate neodymium and praseodymium which have a 1 picometer difference in ionic radii.
A new Cytec REE specific SX reagent Cyanex 572, as shown in Figure 2.5.2, demonstrates a theoretical separation factor of 9.1 of yttrium over europium in a Matrix. The separation factor is 9.1:1 and the ratio of yttrium to europium is, for example, 30:1 for this reagent. As a result, this reagent would be effective at recovering europium (but perhaps yttrium in many stages) from a mixed solution. From the literature, there are few examples demonstrating europium was separated directly from yttrium-based solutions with solvent extraction. However, because these two REE are not generally co-extracted in ore, this lack of information is not unexpected. Only in fluorescent lamps are these found together in high concentrations. Typically, europium is res Fu [61] (2006) modeled the separation europium and yttrium from nitric leach solutions with PC-88a in Shellsol D70; however, no mention of grade or recovery was stated. Tunsu developed a hydrometallurgical
process of separating rare earth from fluorescent lamps [62] similar to the process developed by Eduafo et. al[63]. Tunsu’s process begins before mercury was removed. First KI/I₂ is used to remove Hg. Next, 1 M nitric acid is used to leach remove 90% of the calcium. Then, the filter cake is leached to remove europium and yttrium using 2 M nitric acid. The europium and yttrium rich solution undergoes solvent extraction. Using 3 stages of Cyanex 923, O:A=2:1, 99.9% of Eu/Y is recovered. Similarly, it is stripped with 4 M HCl using O:A=1:2 with 99.9% recovered. Finally, the concentrate is precipitated with oxalic acid and roasted to recover 99.96 RE) (94.61% yttrium oxide, 5.09% europium oxide). There is no mention of any further refining. Despite the relative lack of information in this area of research and a lack of experimental data, there is a basis regarding the viability of solvent extraction for separating europium from yttrium. The roots of this basis relate to fact that most commercial rare earth extraction processes, like the Rhodia plants that separates europium and yttrium, use solvent extraction. Next, crystallization was never considered due to due the difficulty in separating rare earth elements and the dearth of industrial methods that use crystallization for to separate rare earth elements.

From the literature, there are several methods for separating europium from mixed REE leaching solutions[64][65][66][65][67][68][69][70]. The papers that discuss europium recovery begin at a middle rare earth concentrate that was leached from monazite, subjected to cerium removal and retrieved from the rare earth cake using SX with reagent D2EPHA[65][66] [68]. These middle rare earth concentrates typically contain Eu³⁺, Gd³⁺, and Sm³⁺. In some cases, samarium is immediately removed by solvent extraction[69][70]. As demonstrated by Figure 15, these ions are difficult to separate because they have similar ionic properties. However, samarium and europium can be reduced to divalent state.

\[
\text{Eu}^{3+} + e^- = \text{Eu}^{2+} \quad E^0 = -0.36 \quad (T=298 \text{ K})[71]
\]

\[
\text{Sm}^{3+} + e^- = \text{Sm}^{2+} \quad E^0 = -1.55
\]

Many methods have been developed to selectively reduce europium in solution including photochemical reduction, radiochemical reduction, electrolytic reduction and chemical reduction using zinc, zinc amalgam, europium amalgam and magnesium. Photochemical reduction uses fewer reagents and is considered to be more environmentally responsible than some other methods[72]. This process uses an excimer laser, high-pressure mercury lamp (HPML), or low-pressure mercury lamp (LPML). The difference between these irradiation sources can be
characterized by power, energy of proton emission and wavelength. HPML is higher power, lower energy photo emission and higher wavelength (310 to 365nm) versus LPML (185-254nm)[73].

The most common lasers used are ArF at 193nm, KrF at 248nm, and KrCl at 222nm.

Photochemical reduction occurs at the molecular level in the charge transfer band—the movement of an electron from a complexed ligand to the metal ion. This reaction requires a radical scavenger, typically an alcohol or ester, to prevent the reaction from reversing itself. However, these systems are optimum at dilute levels of europium[73][72]. The recovery and grade of the final europium oxide vary from 88% and 98.5%[72] to 99% and 90% [73] respectively. However, the reduction times for europium and yttrium leach solutions can approach 75 hours[72].

The other separation techniques have been tried with varying degrees of success. Photochemical separation has demonstrated recent success from the literature [72]. Radiochemical separation of europium from rare earth solutions has been successful, but no attempt has been made to industrialize the process[74]. Similarly, some success was shown with electrolytic reduction of europium, but no recent academic or any commercial scale work has been attempted[75].

A method that has demonstrated the of success in terms of purity, recovery, and potential for commercialization are cementation or selective chemical reduction of europium (III) to europium (II) and precipitation of europium (II) sulfate. A generalized for recovering europium oxide from middle rare earth solutions from monazite shown in Figure 2.5.3.

Molycorp developed the first industrial process flow sheet to purify europium oxide from dilute solutions bastnäsite concentrates. Figure 2.5.3 describes a process of recovering pure europium oxide as described by Gupta[2]. As stated in The Extractive Metallurgy of Rare Earths[2], zinc does not reduce samarium or ytterbium in the presence of small amounts of europium—rather europium is reduced. As described from Figure 2.5.4, Molycorp designed a similar process for extracting and purifying europium oxide from bastnäsite rather than monazite leach solutions as shown in. Similarly, zinc amalgam is used to reduce europium and sulfuric acid is used to precipitate it as Europium (II) sulfate. However, older research such as from the Molycorp Mountain Pass flow sheet [2] from separate and purify 200ppm europium oxide from bastnäsite leach solutions using 10% HDEHP in kerosene, stripped with 4M HCl and precipitated away from the impurities at pH 3.5 with soda ash.
Figure 2.5.3: This diagram demonstrates the flow sheet for recovering europium oxide from monazite.[2] (Copyright protected under Fair use)
Figure 2.5.4: This schematic demonstrates the flow sheet for recovering europium oxide from Molycorp Mountain Pass.[2] (Copyright protected under Fair use)

No detail is given beyond the precipitation stage; it is to be noted that impurity removal is conducted with sodium carbonate at pH 3.5 by preferentially precipitating rare earth carbonates while iron and zinc stay in solution due to their high solubility.

Different chemical reductants have been studied. Preston et al. [66] studied the use of sodium-mercury, zinc-mercury, europium-mercury amalgams as well as magnesium, zinc, sodium borohydride, hydrazine, and hydroxylamine. The experiment began with screening experiments in ethanol/water solution with synthetic middle rare earth solution—similar in composition to what is extracted what is extracted industrial from monazite with D2EPHA. The composition of this middle rare earth solution contained 7.5 g/L europium, 5 g/L neodymium, 35 g/L gadolinium, 25 g/L samarium in a 1.5M chloride medium. He proposed using a single stage apparatus for both reduction and precipitation and added ammonium sulfate, the precipitating agent was added before adding the reductant. The relevant standard reduction potentials are as follows:

\[ \text{Na}^+ + e^- = \text{Na} \quad \quad \quad E^0 = -2.7 \text{ V} \] [66]
The later three reductants, borohydride, hydrazine, and hydroxylamine failed to reduce europium. In addition, magnesium produce a recovery of the precipitation product, europium (II) sulfate, and there was significant hydrogen evolution. Sodium borohydride also caused significant hydrogen evolution. For screening experiments, sodium-amalgam was used at pH 6.4, zinc-amalgam at pH 2.9-3.1, europium-amalgam at pH 4.5, pure zinc 99.8% at pH. A choice as avoid pure zinc because it was difficult to separate unreacted zinc from europium (II) sulfate and the potential for significant hydrogen evolution by using pure zinc.

Figure 2.5.5: This graph shows the europium recovery, as europium (II) sulfate versus time for different reductants for synthetic middle rare earth monazite solutions.[66] (Copyright protected under Fair use)
As Figure 2.5.5 demonstrates, sodium-amalgam reduced europium precipitates, but the recovery was 12%. Based on the technical difficulties europium amalgam and poor results recoveries of europium (II) sulfate with sodium amalgam, the researchers decided to use zinc amalgam for further experiments.

Figure 2.5.6: This diagram shows the recovery of europium as europium (II) sulfate versus time for authentic middle rare earth leach solutions (solid lines) versus synthetic leach solutions using zinc amalgam from Figure 2.5.4 (dotted lines) [66]. (Copyright protected under Fair use)

As Figure 2.5.6 indicates, synthetic solutions containing europium are reduced and precipitated at a shorter precipitation time (dotted line) than authentic solutions. The quantity of solution used with synthetic solutions was 200mL whereas the volume used for actual industrial leach solutions was 1.6L. The hypothesis is that iron (III) in authentic leach solutions interferes with reduction of europium[66]. The recovery of the europium using the zinc amalgam was greater than 90% after two hours of precipitation experiments using synthetic leach solutions. From this junction, several routes were taken to recover europium (II) sulfate. Europium (II) sulfate was reacted with sodium carbonate followed by carbonate dissolution with hydrochloric acid. The .2M europium (II) chloride product was reacted with 1.2 times the stoichiometric amount of ammonium sulfate to form 96.5% pure europium sulfate with small amounts of gadolinium, cerium, praseodymium,
neodymium and 92% total recovery. In addition, the rare earth impurities integrated into the europium (II) sulfate crystal lattice have greater prevalence with lower atomic number and higher ionic radius, similar to Eu$^{2+}$ cation which has a radius of 116pm which is most similar in size to La$^{3+}$, 106pm, and dissimilar to Gd$^{3+}$, 94pm, and Y$^{3+}$, 90pm[60][66].

\[
\text{EuSO}_4 + \text{Na}_2\text{CO}_3 = \text{EuCO}_3 + \text{Na}_2\text{SO}_4
\]

\[
\text{EuCO}_3 + 2\text{HCl} = \text{EuCl}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{EuCl}_2 + (\text{NH}_4)_2\text{SO}_4 = \text{EuSO}_4 + 2\text{NH}_4\text{Cl}
\]

The initial procedure used by Preston et al. [66] involved reducing purity europium (III) chloride solutions with approximately twice the stoichiometric quantity of the reductant in a system flushed with pure nitrogen. The .2M europium (III) chloride was stirred with magnetic stir bar for 45 minutes and the pH was adjusted by acetic acid to maintain it within the 3-6 range. Next, 20mL of 2M ammonium sulfate was added and the stirring was maintained for additional 15 minutes. The europium (II) sulfate settled at the bottom of the flask. The remaining concentration of europium in solution was determined by titration with a .03M EDTA solution. The experiments using synthetic leach solutions introduced 100% excess ammonium sulfate before adding the reductant.

The same author, on the same research paper, used solvent extraction to increase the europium purity, beginning with a europium (II) chloride product. Solvent extraction using europium (II) via organophosphorus reagents has been shown have significantly smaller extractions than europium (III) fraction [76]. Similarly, the extraction of gadolinium and samarium ions happens at nearly the same pH as europium (III)[66].

Similar to the paper described above from Preston et al. [66] to more recent paper produced high grade (Eu$_2$O$_3$ >99.99%+) europium oxide produced from an Brazilian research group [77] after multiple stages of reduction and precipitation from a solution containing europium and gadolinium, a choice was made to investigate the possibility of europium reduction using zinc or zinc amalgam and precipitate to separate europium and yttrium in solution.
Figure 2.5.7: This figure demonstrates the solvent extraction of different metals in 1M ammonium chloride solution by 1M Versatic 10 acid in xylene versus pH.[66] (Copyright protected under Fair use)

Figure 2.5.8: This figure demonstrates the purity of europium attained with various reagents and number of stages[66]. (Copyright protected under Fair use)

From the literature, there are several approaches. Regarding the selection reduction phase, all of the cementation papers use zinc or zinc amalgam to achieve the europium reduction[66][78][68][73][67][65]. Despite the potential environmental and technical obstacles required to use mercury for the amalgam, only has zinc amalgam has been used to [77] create 99.99% pure europium oxide. In addition, that paper indicates that the advantage of mercury amalgam is that it retards the formation of a zinc oxide coating—which inhibits europium (II) formation and lowers europium oxide recovery. Both ammonium sulfate and sulfuric acid have been used for the precipitation stage of the experiment. Although Morais et al. [77] suggests that using sulfuric acid returns a lower recovery of europium oxide that ammonium sulfate--94.5%
versus 94.8% respectively—the corresponding purity of europium oxide hovers around 95% versus 90% when using ammonium sulfate. In addition, this author used the continuous addition of sulfuric acid in order to increase the purity rather than an instantaneous direct addition of the precipitant. From that paper, the optimum conditions of the feed solution was 5.0g/L Eu₂O₃, pH 2.5, and a SO₄²⁻/Eu ratio=5.3.

Rabie et al. [65] suggests different optimal conditions for europium oxide separation from a Gd/Eu leach solution. Zinc is used instead of zinc amalgam. Similar to Morais et al. [73] a sequential batch operation zinc reduction column and precipitation vessels are utilized. Rabie et al. [65] studies the purity and yield of the final europium oxide product at various conditions of the entrance solution of the zinc column. The overall recovery of europium and soluble zinc in the leach solution was studied as a function of entrance solution pH. The relationship was proportional for both factors.

![Figure 2.5.9](image.png)

Figure 2.5.9: This figure demonstrates the effect of the feed pH upon the concentration of soluble zinc in the solution and recovery of europium[65]. (Copyright protected under Fair use)

This paper suggests there is competitive interaction between zinc competing to either to reduce europium (III) to europium (II) or reduce the hydronium ion to hydrogen gas.

\[
2\text{H}^+(\text{aq}) + \text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \quad K=1.81 \times 10^{26} \quad T=20^\circ \text{C} \\
2\text{Eu}^{3+}(\text{aq}) + \text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Eu}^{2+}(\text{aq}) \quad K=7.81 \times 10^{13} \quad T=20^\circ \text{C}
\]
In addition, this study found that in entrance solutions above pH 3, the solubility of europium and other rare earth oxides have a decreased solubility. Reduction time, precipitation time, sulfuric acid concentration and feed solution concentration were also modeled.

Figure 2.5.10: This figure demonstrates the feed solution’s affect upon the recovery of europium[65]. (Copyright protected under Fair use)

Figure 2.5.11: This figure demonstrates of the effect of sulfuric acid concentration of the precipitant upon the recovery of europium[65]. (Copyright protected under Fair use)
In addition, different zinc column specifications were used in this paper. Lengths between 60 and 120 cm, inner diameters between 1.2 and 2.5 cm, and column materials such as glass and PVC were used to fabricate different designs. Ultimately, the researchers used a glass column 60 cm high and a diameter of 1.2 cm based on a slight advantage in separation efficiency. There is no statement regarding the numerical advantage of this specifications; however, it hints that the advantage is relatively minimal over the other designs. In addition, it suggests that the choice column specifications should be based on feed flow rates, europium concentration, type and concentration of impurities. Rabie et al. [65] selected a entrance feed flow rate equal to 1.5
mL/min. The optimal conditions suggested include: feed pH 2.5-3, as high europium concentration as possible, zinc powder sized at 20-30 mesh in the column, 60 minute reduction time, 2 hour precipitation time using 3M H₂SO₄ as the precipitating agent. The overall flow plan is demonstrated below in Figure 2.5.14.

![Flow diagram](image)

Figure 2.5.14: This figure shows the final flow plan suggested by Rabie et al. for europium oxide purification[65]. (Copyright protected under Fair use)

The most recent research conducted at KU Leuven regarding europium oxide purification from phosphor dust leach solutions utilizes photochemical reduction—rather than zinc cementation—and europium (II) sulfate precipitation using ammonium sulfate[72]. The basis for the author’s choices are the desire to minimize mercury pollution, solid Zn waste generation, hydrogen gas evolution, and higher selectivity towards europium (II) formation. For this paper, a
LPML with electromagnetic outputs at 185 and 254 nm is used. Europium has a charged transfer band at 188 nm. The reaction to spectra output at this wave length is a follows[72].

\[
[Eu(H_2O)_n]^{3+} \xrightarrow{188\text{nm}} [Eu(H_2O)_{n-1}]^{2+} + OH^+ + H^+
\]

A reverse reaction is possible if 366 nm light is applied.

\[
2Eu^{2+} + 2H^+ \xrightarrow{366\text{nm}} 2Eu^{3+} + H_2
\]

A significant basis this paradigm for this separation of europium from yttrium lies in the differences in solubility. As Van den Bogaert explains, the solubility of the most desire intermediate, europium (II) sulfate, is .001 g/100 g H₂O versus 2.1 g/100 g H₂O for europium (III) sulfate and 7.47 g/100 g H₂O for yttrium (III) sulfate. The last two species are possible but less likely to form in the precipitate based in the differences in solubility. The chosen ratio of the precipitating agent, Eu:Sulfate was chosen to be 5:1 for this set of experiments based on a similar ratio of 7:1 used by Morais et al. [73]. The author states that the viability of photochemical reduction is limited such that a minimum of 3% of europium oxide from a purified mixed yttrium/europium oxide powder recovered from phosphor dusts and in practice up to 10% of the mixed rare earth oxides could be europium oxide. In theory, the ratio of the rare earths used in red phosphors could be up to 1:1, however, the price of europium oxide has limited this ratio. Therefore, the author explores molar ratios from 1/1 to 1/20 europium/yttrium for the experiments. The conclusions of the paper were that up to 95% recoveries were attained and a 98.5% pure europium (II) sulfate was made. Unfortunately, more than 40 hours of illumination time was needed to attain that purity. The energy conversion efficiency was also very low. A reaction that requires days for moderate value products is not desirable in commercial applications; however, the author suggests a monochromatic (single frequency) and a higher power light source, to prevent the reverse reaction from occurring, in order to make this process industrially relevant.
Chapter 3
THEORETICAL CONSIDERATIONS

Chapter 3 will explore and discuss theory relevant to this research. Much of this theory will discuss thermodynamics. Using Pourbaix diagrams and speciation diagrams, a greater understanding of the various chemical elements of the system will be gained. This section is a modification and expansion of the theory section for the Master of Science thesis submitted to Colorado School of Mines[19].

The theoretical basis for the research performed lies in chemistry. Thermodynamics, equilibrium solubility, electrochemical reaction potential will be discussed in this section. In addition, the nature of reaction chemistry can be described by Pourboix (Eh-pH), speciation diagrams, and Gibb minimization plots will be created using HSC 5.11.

3.1 Equilibrium Thermodynamics

Before undertaking research, thermodynamic relationships must be understood. Specifically, the thermodynamics of possible reactions, desirable and undesirable reaction must be explored. For this research, one way to quantify thermodynamics is to study the Gibbs free energy (ΔG) of a reaction. If the overall Gibbs free energy is negative, the reaction is spontaneous, and the forward reaction can occur.

\[ \Delta G = \Delta H - T \Delta S \]

For this research, the entropy (ΔS) plays less of an effect as the temperature, for most of the aqueous experiments the temperature hovers around 20-25°C. Therefore, the enthalpy (ΔH) plays the determining role for spontaneity. Similarly, the equilibrium constant, \( K_c \), can be used to describe the thermodynamics of a system. In the equation below the activities of species are replaced with their actual concentrations because there is no simple method to measure the activities of concentrated species in high ionic strength solutions.

\[ aA + bB \rightleftharpoons cC + dD \]

\[ K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
The value of $K_c$ gives an indication of the equilibrium reaction state of the system. An equilibrium system states where the concentrations are unity and the molar coefficients are one gives a $K_c$ value of 1. This equilibrium constant is immediate in spontaneity which may that it may be possible under certain conditions. Correspondingly, very small $K_c$ values--below $10^{-3}$ and lower--indicate a reaction that is unlikely to happen and large $K_c$ values, above $10^3$, indicate a reaction that is very likely to occur.

$$2RE^{3+} + 3H_2C_2O_4 \Leftrightarrow (RE)_2(C_2O_4)_3 \times xH_2O(s) + 6H^+ \quad (3.1)$$

As this reaction demonstrates, the formation of rare earth oxalate, a common strategy to purify RE leach solutions, generates hydronium ions.

The solubility product constant, $K_{sp}$, is the equilibrium constant used to describe the dissolution of a solid in solution. The lower the $K_{sp}$ of a solvation reaction, the lesser the thermodynamic favorability of dissolving that solid in solution. Chung[56] uses several methods to model the solubility of rare earth oxalates. The solubility decreased as the oxalic acid concentration increased and nitric acid concentration increased. The reported $K_{sp}$ for yttrium and europium were $5.1 \times 10^{-30}$ and $4.2 \times 10^{-32}$ respectively.

Solvation of yttrium oxalate can modeled by the equation

$$Y_2(C_2O_4)_3 \Leftrightarrow 2Y^{3+} + 3C_2O_4^{2-} \quad (3.1.1)$$

$$K_{sp} = [Y^{3+}]^2[C_2O_4^{2-}]^3 \quad (3.1.2)$$

Based on yttrium oxalates slight larger solubility constant, yttrium oxalate should dissolve more (or precipitate less) than europium oxalate.

In addition, the formation of europium (II) sulfate precipitate, and intermediate in the europium separation experiments.

HSC 5.11 was used to explore the possible reactions for the oxalic precipitation work and selective reduction and precipitation of europium (II) sulfate.

$$Eu^{2+} + SO_4^{2-} = EuSO_4 \quad K_c=5.94 \times 10^8 \quad (T=25^\circ C) \quad (3.1.3)$$

Europium (II) is part of chloride complex in a system with excess chloride ions, so the following 3 equations describes the solvation, precipitation and

$$Eu_2O_3 + 6HCl(aq) = 2EuCl_3(aq) + 3H_2O \quad K_c=7.36 \times 10^{55} \quad (T=25^\circ C) \quad (3.1.4a)$$

60
2EuCl₃(aq) + 4HCl(aq) + Zn = 2EuCl₄²⁻(aq) + ZnCl₂(aq) + 4H⁺ \quad K_c=1.62 \times 10^{16} \text{ (T=25°C)} (3.1.4b)

EuCl₄²⁻(aq) + H₂SO₄ = EuSO₄ + 2HCl(aq) + 2Cl⁻ \quad K_c=1.39 \times 10^{13} \text{ (T=25°C)} ((3.1.4c)

Some of the possible by products of the reaction include europium (III) sulfate and yttrium (III) sulfate.

\[ YCl^{2+} + 1.5SO_4^{2-} + 4H_2O = 0.5Y_2(SO_4)_3 * 8H_2O + Cl^- \quad K_c=4.90 \times 10^{-1} \text{ (T=25°C)} (3.1.5) \]

\[ EuCl^{2+} + 1.5SO_4^{2-} + 4H_2O = 0.5Eu_2(SO_4)_3 * 8H_2O + Cl^- \quad K_c=1.31 \times 10^5 \text{ (T=25°C)} (3.1.6) \]

3.2 Oxalic acid precipitation

The precipitation of REO from leach solutions can be selective by using soda ash or oxalic acid. However, soda ash requires a higher pH for this process to be effective. The original Molycorp process, as shown in Figure 2.5.3, used sodium carbonate. However, oxalic acid is more selective than soda ash at lower pH's and high levels of zinc, aluminum and iron in solution. The theoretical reaction for the precipitation of rare earth oxalate is as follows:

\[ 2RE^{3+} + 3H_2C_2O_4 \leftrightarrow RE_2(C_2O_4)_3 * xH_2O(s) + 6H^+ \] (3.2)

Equation 3.2 demonstrates how an insoluble rare earth oxalate is formed from a leach solution. Based on Le Châtelier's principle a lower pH leach solution should cause more of the oxalate. However, there is a possibility of a different mechanism.

3.3 Pourbaix (Eh-pH) diagrams

An attempt was made to simulate the conditions of some of the experiments using Pourbaix diagrams. Specifically, for the simulation of the europium separation, the precipitation conditions were demonstrated. The molality utilized for elements yttrium, chlorine, europium, sodium, sulfur and zinc in the precipitation vessel was used an input to generate the plots. The pertinent species were shown and a method termed the “Mass Balance Point Method”[79] was used generate these multi-component graphs. The basis of this method is Gibbs free energy minimization.

Figure 3.3.1 shows that the yttrium stays in solution until approximately pH 8. Fortunately, the europium sulfate precipitation vessel functions much below that pH.
Using europium as the dominate species, Figure 3.3.2 indicates which species are present. The most important species in the system, the europium (II) sulfate precipitate, can be formed under reducing conditions—at relatively intermediate pH conditions. However, the potential for europium hydroxide formation, above pH 8, is significant. Therefore, it is important that both the input solutions for the precipitation reaction, dilute sulfuric acid and zinc reduced europium (II) and yttrium (II) solution be below pH 8 and/or be in a highly reduced state, to minimize the formation of europium hydroxides. However, the real issue to be concerned about is the formation of yttrium hydroxides as shown in Figure 3.3.1 above pH 8. Because europium hydroxides will follow the europium sulfate into solid phase the formation of europium hydroxides is less of a concern. The goal is for the solid phase is have as few impurities from yttrium and zinc as possible.
Figure 3.3.1: This figure represents typical Eh-pH conditions present in the precipitation vessel column using yttrium as the predominant element[19].
Figure 3.3.2: This figure represents typical Eh-pH conditions present in the reduction column using europium as the main element[19].
The formation of zinc hydroxides that could co-precipitate with europium (II) sulfate are undesired. However, a relatively high pH, above 7.3 is required to precipitate zinc hydroxide. Fortunately, in practice the pH precipitation vessel gets close to or just above pH = 7.3.

3.4 Species Distribution: Gibbs Minimization experiments

The purpose of this section is model the speciation of the experiments separating europium and yttrium. Three stages are the primary preparation stage for the mixed rare earth oxides. Second, the selective reduction of europium is by zinc. Third, europium (II) sulfate is precipitated by sulfuric acid.
Figure 3.4.1: This figure shows the effect of pressure and temperature in the precipitation stage of our experiment. Principal (one) Eu-Species Distribution as a Function of Temperature for Equilibrated-System configured for Precipitation of EuSO$_4$ after Reduction of Eu$^{III}$ to Eu$^{II}$ by Zn$^0$ and addition of H$_2$SO$_4$ as Sulfate Source. Initial Configuration: \( \tilde{C}_{Eu^{II}} = 0.045 \) m, \( \tilde{C}_y = 0.92 \) m, \( \tilde{C}_{Cl^-} = 4.50 \) m, \( \tilde{C}_{Na^+} = 1.50 \) m, \( \tilde{C}_{H^+} = 3.00 \) m, \( \tilde{C}_{Zn^{II}} = 0.20 \) m and \( \tilde{C}_{H_2SO_4} = 0.10 \) m.

The obvious question from Figure 3.4.1 why does more europium (II) sulfate form at lower pressure of hydrogen? The europium tetrachloride complex either forms europium (II) sulfate as shown in Figure 3.4.1 or a europium (III) ion as shown in Figure 3.4.2. The assumption is that greater hydrogen will shift the reaction Figure 3.4.2 to the right decreasing the formation of europium (III) which will lead to the reaction in Figure 3.4.1 moving to the right. In this scenario, it is uncertain as to the reason that Gibbs minimization shows the a lower pressure is more optimal while using
EuCl₄(-2a) + SO₄(-2a) = EuSO₄ + 4Cl(-a)

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</table>

Figure 3.4.1: This table shows the effect of temperature upon the equilibrium constant of the reaction[19].

2EuCl₄(-2a) + 2H(+a) = 2Eu(+3a) + H₂(g) + 8Cl(-a)

<table>
<thead>
<tr>
<th>T</th>
<th>deltaH</th>
<th>deltaS</th>
<th>deltaG</th>
<th>K</th>
<th>Log(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>kcal</td>
<td>cal/K</td>
<td>kcal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>-30.81</td>
<td>-73.952</td>
<td>-8.391</td>
<td>1.12E+06</td>
<td>6.05</td>
</tr>
<tr>
<td>40</td>
<td>-36.724</td>
<td>-93.148</td>
<td>-7.554</td>
<td>1.87E+05</td>
<td>5.273</td>
</tr>
<tr>
<td>50</td>
<td>-42.315</td>
<td>-110.725</td>
<td>-6.534</td>
<td>2.63E+04</td>
<td>4.419</td>
</tr>
</tbody>
</table>

Figure 3.4.2: This table shows the effect of temperature upon the equilibrium constant of the reaction[19].
Figure 3.4.1: This figure shows the effect temperature for various species at a pressure at .8 bar hydrogen gas [19].

Minor (five) Eu-Species Distribution as a Function of Temperature for Equilibrated-System configured for Precipitation of EuSO₄ after Reduction of Eu³⁺ to Eu²⁺ by Zn⁰ and addition of H₂SO₄ as Sulfate Source. Initial Configuration: \( \tilde{C}_{Eu}^{II} = 0.045 \text{ m} \), \( \tilde{C}_{Y}^{III} = 0.92 \text{ m} \), \( \tilde{C}_{Cl}^- = 4.50 \text{ m} \), \( \tilde{C}_{Na}^+ = 1.50 \text{ m} \), \( \tilde{C}_H^+ = 3.00 \text{ m} \), \( \tilde{C}_{Zn}^{II} = 0.20 \text{ m} \) and \( \tilde{C}_{H_2SO_4} = 0.10 \text{ m} \).

3.5 Electrode Reactions Pertinent to Eu³⁺ Reduction to Eu²⁺ by Zn⁰

The reactions relative to this research involve, europium, zinc and hydrogen. Using IUPAC convention, all reactions are written as a reduction. The equations below represent the relevant electrode reactions:

\[
Eu^{3+} + e^- \Leftrightarrow Eu^{2+} ; E^0 = -432mV \ (3.5.1)
\]

\[
Zn^{2+} + 2e^- \Leftrightarrow Zn^{0} ; E^0 = -760mV \ (3.5.2)
\]

\[
2H^+ + 2e^- \Leftrightarrow H_2 ; E^0 = -0mV \ (3.5.3)
\]
These three reactions represent the essential electrode reactions. In the selective reduction system, the oxidation reduction potential (ORP) is measured in respect to the AgCl/Ag electrode.

Figure 3.5.1: This figure represents the method of measure the ORP in respect to standard hydrogen electrode (SHE) [80]. Copyright protected under Fair Use.

However, in practice and in the system, none of these electrode potentials are in equilibrium or at unit activity. Therefore, the Nernst equation must be used to demonstrate the actual potential experienced by the system by a real system.

$$E = E^o - \frac{RT}{zF} \ln \frac{a_{red}}{a_{ox}} \quad (3.5.4)$$

In a simplified form, the Nernst equation can be written as:

$$E = E^o - \frac{59.2}{n} \log_{10} \frac{a_{red}}{a_{ox}} \quad (3.5.5)$$

For example, a non-equilibrium potential for equation 3.5.1 can be written as:

$$E = -432 \text{mV} - \frac{59.2}{1} \log_{10} \frac{a_{Eu^{2+}}}{a_{Eu^{3+}}} \quad (3.5.6)$$
For example, if there is 10 times the activity $Eu^{2+}$ of $Eu^{3+}$ in solution. The approximate potential will be -490 mV. However, since the system is be measured in respect to AgCl/Ag, the ORP would have to read -712 mV in order for this observation to be correct. The reality is, however, in complex system with multiple or dozens ions with various

![Diagram of Zn-Reductant Electrode-Reaction Mechanism](image)

**Figure 3.5.2**: Schematic of Zn-Reductant Electrode-Reaction Mechanism by which $Eu^{III}$ species present in the Aqueous Electrolyte is Reduced to $Eu^{II}$ simultaneously with $H^+$ to generate hydrogen gas which is: a) evolved as gas-bubbles ($H_2(g)$), and b) simultaneously solubilized in the electrolyte ($H_2(aq)$). The electrons for these two cathodic-reactions are donated *insitu* as a result of the Oxidation/Dissolution of $Zn^0$ at the sites shown. [81]

**Figure 3.5.2** describes the manner in which the zinc behaves as a galvanic surface. The hydronium ion absorbs to the zinc surface. Electrons are transferred from one site to another on the zinc surface. Next, the electrons are transferred to the hydronium ions to form $H_2(g)$ and $H_2(aq)$. This theory suggests that saturating the solution with dissolved hydrogen gas may favor the electronic charge transfer to europium and minimize the electronic charge from zinc to the hydronium ion.
3.6 Determination of Chemical Kinetics

Reaction kinetics are based on the rate of reaction. The rate of reaction is completely independent of thermodynamics. The reason for understanding kinetics is to fundamentally understand how quickly reactions proceed with time. The first step is to determine the rate law.

\[ r = k[X]^a[Y]^b \]  \hspace{1cm} (3.6.1)

Where \( r \) is the rate of reaction, \( k \) is the rate constant, \( a \) and \( b \) are the individual orders of the reaction whose sum equals the overall order, and \( X \) and \( Y \) are the initial concentration of molarity of the reactant. \( k \) is not actually constant, but it is related to factors such as ionic strength, temperature, and surface area. However, in order to determine the rate law, the behavior of the reaction system must be studied versus time. Specifically, the concentration of the reactant(s) must be studied as a function in time.

There are two different methods to determine the order of the reaction. The method of initial rates can be used, but this method is not so robust. It requires that concentration measurements be made in very short time intervals after the beginning. Unfortunately, due to the nature reaction measurements for reaction 3.1.4b. This method is inappropriate. It very challenging to directly measure the concentration of \( \text{Eu}^{2+} \) as a function of time. Spectroscopic methods have successfully measured \( \text{Eu}^{2+} \) concentration but are imperfect because they expose the solution the air and therefore, cause a meaningful portion of the europium (II) ion to reoxidize back to europium (III). Therefore, the concentration after precipitation reaction 3.1.4c is measured. It is assumed that the precipitation reaction goes to completion. Instead, the integral method was used. The integrated rate law for a first order reaction is

\[ \ln[A] = -kt + \ln[A_0] \]

where \( A_0 \) is the initial concentration. If the graph demonstrates a straight line, the slope of the line is \( k \) is equal to the reaction constant. Next, if the reaction is run at two different initial concentrations, the rate constants can be compared to determine the order of a specific reactant. For example, if the initial reaction rate is 1 M/s at concentration \( X \) and 2 M/s at concentration 2\( X \), the reaction order, or \( Y \), from equation 3.6.2, is 1, in respect to reactant \( X \).

\[ \frac{\text{Rate 1}}{\text{Rate 2}} = \frac{[X]^Y}{[2X]^Y} = \frac{1}{2} \]
Another way to explain it is if you plot natural log concentration versus time and result is linear, the order of the reaction is one. Also, the slope of the line is the k value.

3.7 Determination of Activation Energy

After the rate constant, k has been determined, the activation energy can be determined. Using the Arrhenius relationship, one may plot the chemical reaction of constant k calculated different temperatures.

\[ \ln(k) = \ln(A) - \frac{E_a}{RT} \]

Afterwards, the slope of the line is equal to the activation energy, Ea, divided by R. From this value, the activation energy can be determined.
CHAPTER 4
DETAILS OF EXPERIMENTS CONDUCTED
INTRODUCTION

The purpose of this chapter is to describe the various methods for characterizing and extracting rare earth elements. First, the procedures for the characterization experiments and analytical techniques will be listed. Next, the analytical software and design of experiments will be described. Finally, the methods for the bench and laboratory experiments regarding the selective reduction of europium and precipitation of europium sulfate will be investigated. This chapter is a modification and a continuation of experimental methods completed for my Master of Science Thesis at Colorado of Mines[19].

Figure 4.0: This chart demonstrates show the Theoretical flow sheet used for a research basis for REO recovery from phosphor dust.
Figure 4.0 shows how the complete flow sheet that has developed for recovering mixed rare earth oxides. The portion of the flow sheet inside red dotted lines represents the area of research experiments conducted.

4.1 Characterization Experiments: Phosphor Dust

Several different methods were used to characterize phosphor dust including, XRF, XRD SEM, QEMSCAN, and Microtrac particle size analysis.

4.2 Analytical Techniques

4.2.1 ICP-MS

Induction coupled plasma mass spectrometry (ICP-MS) is an analytical device utilized to determine elemental concentrations in solutions. In general, the detection limits are low and the speed of analysis are higher than other liquid analysis methods. The standard range of elemental detection is 1 ppb to 10 ppm. The components of the ICPs are the sample delivery system, the torch, a coil, the vacuum, the interface, the detector, the quadrupole, and the data controller. This machine samples ion created as argon is passed through the torch and electromagnetic energy is applied to coil. A spark is added to the argon atoms and electrons are taken from the argon to form plasma. The limitations of ICP-MS include that it struggles to differentiate between atoms that have the same atomic mass, but different element compositions. Often, argon will combine with element in the system to form polyatomic ions which are difficult to distinguish from single elements having the same atomic mass. In addition, choice of internal standard has an effect upon the elemental analysis. The correct internal standard must have a similar molecular weight as the elements analyzed, it must not be present in any of the sample, and it must not have spectral interferences. In this machine, tellurium is used an internal standard because rare earths are similar in atomic mass as tellurium. Similarly, elements that are significantly lower (or higher) that tellurium (atomic mass 127.6), are less accurately measured. In addition, the choice of matrix affects the accuracy. For example, rare earths should not be used with a fluoride matrix. In this machine, a nitric acid matrix was used.

The samples were prepared by diluting 200µm of sample in 10 mL of analytical grade 2% nitric acid. The samples were in 15 mL centrifuge tubes. The machine parts are turned on sequentially. Using the propriety software, Q-ICAP and QTEGRA a performance report is run. After it passes, the machine is reading the run the sample. The 5 dilution standards 1ppm to 10
ppm are run and the samples run with a rinse cycle in between. After the run is completed, the data is imported to .csv files and analyzed via Microsoft Excel.

4.2.2 ICP-OES

Induction coupled plasma optical emission spectroscopy is analytical tool used to measure dilute element compositions in solutions. The optimal detection limits for this instrument are approximately 50 ppm. The accuracy is generally greater for ICP-OES than ICP-MS. Using diffraction grating, this unit divides the light emitted from the plasma into wavelengths. For each element, there is a discrete wavelength associated with it. A charged coupled device (CDD) is used to measure the intensity of that wavelength. Based on this intensity, numeric values for concentrations are assigned.

4.2.3 XRF

X-ray fluorescence is analytical technique used to measure the composition of a sample either solid or solid. First, a sample is treated with radiation from x-rays with an energy between 20 to 60 kV to excite a broad range of atom numbers of element. Atomically, the x-ray excites an electron from the inner shell of the atom. Next, the atom fills the inner shell with an electron from a higher energy orbital shell. As the electron moves from the higher energy level to the lower energy level, a fluorescent x-ray is emitted. The emitted energy is equivalent to the difference between the two quantum levels. The basis for XRF lies in Plank’s Law

$$\lambda = \frac{hc}{E}$$

Where \( \lambda \) is the wavelength, \( E \) is the energy, \( h \) is Plank’s constant and \( c \) is the speed of light. The emitted X-ray photo ionizes detector ions with change that is proportional to the energy of the photo. Each charge is collected and recorded. Using proprietary OXSAS software, each peak is converted to an element, and the elemental analysis of a sample can be determined. Based on the element analysis, a relative compositional assay be determined. If it is known, for example, all of the metals are in oxide form, a percent composition of sample can be determined in oxide form. XRF can be standardized or can be used semi-quantitatively.
4.2.4 XRD

Similarly, X-ray diffraction crystallography (XRD) is analytical tool used to identify the crystalline structure of chemical species. First of all, a sample of discrete composition must be obtained—without any distortions or imperfections. In addition, it can identify polymorphic forms, amorphous and crystalline forms and the percentage of a compound that is crystalline. The x-rays are emitted from cathode ray tube. Next, the x-rays are filtered to create a monochromic (discrete frequency) rays. Then, the x-rays are focused toward the sample. Bragg’s law

\[ n\lambda = 2d \sin \theta \] (4.2.4)

can be used to measure the wavelength of the constructive interference created when the x-ray reaches the sample. This inference is commonly referred to as diffraction pattern. Using Fourier transforms, two dimensional images of the crystal at different orientations can converted to a three-dimensional image. The computational model can be references by databases in order to match the crystal and its structure with a sample in the database.

4.2.5 ESEM

An environmental scanning electron microscope (ESEM) is a tool used to examine the morphology of any sample, wet or dry. A focused electron beam and electromagnetic lens are used to identify the surface morphology of sample. The electrons hitting the surface produce various electromagnetic signals that are recorded by the detector. From these signals, an image is formed that represents the surface of the sample.

The sample chamber is under a vacuum created by at least two stages of pumping. The electron gun is placed a meaningful distance above the sample chamber—inside the first pumping chamber. The electron beam inter the second chamber by a small hole in the aperture. Again, the second chamber has a pump to create an even stronger vacuum. Thirdly, there is a small aperture separating the 2nd chamber from the sample chamber. The electron beam pass through two apertures to reach the sample. As the electrons interact with the specimen, x-rays, light, and backscattered electrons are generated—which are recorded by the signal detector.

ESEM has several advantages over regular SEM. For example, wet samples can be run. The gas is used as a detection matrix. There is smaller signal to noise ratio. Also, non-conductive samples do not need the surface to be made conductive in order for the sample to run. Finally, the samples be run much more quickly and efficiently than traditional SME.
4.3 Analytical Software

The analytical software used from this research include HSC 5.11 and Stat-Ease 9, as well to a less extend Microsoft Excel 2013, Golden Software Grapher 14, and Origin Pro 9.0. Greater detail will be given for HSC 5.11 and Stat-Ease 9.

4.3.1 HSC 5.11

HSC Chemistry, by Outotec is a thermodynamic software used to model many different types of calculations into usable outputs. From its database, it can calculate reaction Gibbs free energy, enthalpy and entropy with thousands of chemical species modeled over a range of temperatures. In addition, using Gibbs minimization calculations, the equilibrium composition of a set of species can be determined for a range of temperatures and pressures based on the starting components. Also, Pourbaix diagrams or Eh-pH diagrams can be generated using a broad range of elements, chemical species, and variable concentrations or pressures. These diagrams can be combined to demonstrate how speciation changes under a set of chemical concentrations or pressure. This specific software was particularly invaluable in regard to modeling the dissolution, selective reduction and precipititation of europium (II) sulfate.

PROCEDURES for
PERFORMING HSC SIMULATIONS
(Stage 1 Stage 2 Stage 3 Processing-Sequence)

Stage 1

a) Input Data (Closed System with “Infinite-Size” Gas-Phase)

1) Temperatures: 10, 20, 30, 40, 50 °C

2) Gas Phase: Barometric Pressure: 0.80, (1.00) and (1.20) bar – each for temperature-range indicated // N2: 800kmol, O2: 200kmol.

3) Amounts of Constituents in Aqueous Phase (kmol): Eu2O3, Y2O3, Na+ and H2O (55.51kmol of solvent); also chloride # as Cl⁻ and the same amount of H⁺ # the chloride amount has to be reduced relative to the “amount” of HCl (12M) that was employed – this has to be performed in an iterative manner (in accordance with the step which follows next) so as to achieve (approximately) the pH that you measured in the final (as prepared) electrolyte. Ideally, you should appeal to the “species-activities listing” (for H⁺; pH = - log10(aH+)) to assess, and ultimately determine, when the iterations being performed lead to the requisite amount of Cl⁻ to achieve this (measured) pH.
b) Select the species that are expected in the Electrolyte when the System is in Equilibrium at each of the Temperatures Selected in the Range Specified.

I) These “emerging” species (in equilibrium with each other) include, at a minimum, the following: O₂(g), N₂(g), O₂(aq), N₂(aq), H₂O, *Eu³⁺, *Y³⁺, Cl⁻, *Na⁺, the full-range of aquo-complexes of Cl⁻, with the three cations listed*. Also, in order to include the possibility of hydrolysis of these cations (pH 3.0), the full range of aquo-complexes of OH⁻ should be included as well.

II) It should not be necessary to include any condensed species of the cations – primarily because the “as-prepared” electrolyte does not display evidence of precipitation. Nonetheless, bear in mind that the simulation is the product of HSC Software (the remark that follows applies to any software for that matter) – consequently it is prudent to confirm that its predictions confirm this observation, by including the “most likely” condensed-species cation.

4.3.2 Stat-Ease Design Expert 9

Stat-Ease Design Expert is software used for design of experiment and analysis of the output of design of experiments, statistically and graphically. This software is tailored for multiple level factorial screening of experimental parameters. In addition, three-dimensional or two-dimensional contour plots can be generated to demonstrate the effect of design parameters on various response variables. “Desirability” can be used to qualify the optimization of various response variables from a given set of input parameters. Additionally, the analysis of variance can be used to generate an equation that shows the relationship between input parameters and response variables. This software was used to model the selective reduction and precipitation of europium sulfate.

4.3.3 XLSim: Excel plugin for Monte Carlo Simulation

Sam Savage developed a XLSIM as a plugin for Excel as tool for financial modeling. Unfortunately, it is unable to make work in any operating later than Windows XP, but it appears to work in any version of Excel (Office XP to Office 365). The value of this software is that it allows you to varying the inputs either in a gaussian, random, resampling (ex. vary historical prices), or probabilistic method with between certain limits.
4.4 Economic Analysis

The purpose of this project was to evaluate the economics of the flow sheet beginning with the sieving of the phosphor dust and ending with the precipitation of a mixed yttrium and europium oxide product. A customer was found that was willing to purchase 99% mixed REO for a 25% discount from the Chinese Freight on Board (FOB) prices for both yttrium oxide and europium oxide. Next, a second customer was found willing to purchase 99% pure separated europium oxide and yttrium oxide for a 10% discount on FOB rare earth prices. These two different economic scenarios were studied. A Monte Carlo simulation was carried out using 10000 stimulations varying various parameters in a historical, Gaussian, geometric, or random manner within defined parameter ranges. The boundaries for the two different economic analyzes are demonstrated by the red dotted line in Figures 4.4.1(a) ad 4.4.1(b). Three different books were used for the economic analysis. Principles of Finance with Excel 2nd Edition, by Simon Benninga, Decision Making with Insight, 2nd Edition, by Sam L. Savage (Author), and Plant Design and Economics for Chemical Engineers 5th Edition by Max Stone Peters, Ronald E. West Klaus D. Timmerhaus.

4.4.1 Assumptions

The following assumptions were made for the economic analysis for scenario 1 demonstrated in Figure 4.4.1(a)

- Treated 6500 tons of year of phosphor dust
  - 50% of that fraction is sieved and shipped to the recycling facility
- Used a proprietary FOB price quote given by an industrial siever
  - based on sieving the powder to -74µm and shipping the powder to the recycling facility
Figure 4.4.1(a): The figure demonstrates the mass boundaries of the economic analysis.

- Directly treated 3250 tons per year by the recycling facility
- Operated 350 days/ year
- Operated 24 hours per day
- Operated 3 shifts per day
- Used construction materials that are resistant to diluted hydrochloric acid and sulfuric acid such as glass lined reactors, PVC reactors, PP/PVC pumps
- Used a combination of Alibaba.com, industrial price quotes, 911 metallurgist, confidential information and the .6 rule to size equipment.
- Added 20% to the total capital cost contingency
- Total volume increased by 10% when acid is added to the phosphor powder
- Very energy cost such that the model resamples average state energy costs.
- Includes cost of wastewater treatment
- Includes slight value of apatite waste
- Includes a hydrochloric acid recovery unit
- Excludes value and cost of terbium residue
- Includes cost for purchasing and running an acid recovery unit
- Total recovery of REO is 85%
- Designated sieved powder contained 20% yttrium oxide and 1.26% europium oxide
- Assumed the second leach residue is 30% of the weight of the sieved powder
- Used a 50% excess of oxalic acid
- Purified mixed REO 99%
  - One Saleable product 588 tonnes yttrium and europium oxide
  - 553 tonnes Y$_2$O$_3$
  - 35 tonnes Eu$_2$O$_3$

Figure 4.4.1(b)

The following modifications to assumptions were made for the economic analysis for scenario 2 demonstrated in Figure 4.4.1(b).

- Directly treated 3250 tons per year by the recycling facility
- Operated 350 days/ year
- Operated 24 hours per day
- Operated 3 shifts per day
- Used construction materials that are resistant to diluted hydrochloric acid and sulfuric acid such as glass lined reactors, PVC reactors, PP/PVC pumps
• Used a combination of Alibaba.com, industrial price quotes, 911metallurgist, confidential information and the .6 rule to size equipment.
• Added 20% to the total capital cost contingency
• Total volume increased by 10% when acid is added to the phosphor powder
• Very energy cost such that the model resamples average state energy costs.
• Includes cost of wastewater treatment
• Includes slight value of apatite waste
• Includes a hydrochloric acid recovery unit
• Excludes value and cost of terbium residue
• Includes cost for purchasing and running an acid recovery unit
• Total recovery of REO is 75%
• Designated sieved powder contained 20% yttrium oxide and 1.26% europium oxide
• Assumed the second leach residue is 30% of the weight of the sieved powder
• Used a 50% excess of oxalic acid
• Purified separate REO 99%
  o Two saleable products
  o 488 tonnes Y_2O_3
  o 31 tonnes Eu_2O_3
• Includes added cost of chemical zinc, sulfuric acid, Cyanex 923 and kerosene versus scenario 1, and nitrogen
• Includes a stir tank for selective reduction another for precipitation
• A counter current mixer settler system with 2 stages for loading and 1 stage for stripping

4.4.2 Capital Equipment Cost Estimate

The cost of capital equipment was determined from propriety sources as well as from Alibaba. The similar capital equipment was used for first Muller’s (2002), “Factored Capital Cost Estimate Guide”[82] was used to estimate some of the capital costs.

4.4.3 Operating Cost Estimate

The operating costs included the cost to buy land, to build the warehouse, to assemble the facility, to hire labor, to sieve the powder, to power the facility, to purchase phosphor, to purchase hydrochloric acid and to purchase oxalic acid. For the second scenario, oxalic precipitation was removed after the second stage of leaching to the end of the to the end of both unit operations for europium and yttrium purification. For the second scenario, the operating cost included the cost of sulfuric acid, zinc, Shellsol D60 kerosene, and reagent Cyanex 923
4.4.3 Reagent Cost Estimate

Hydrochloric acid and oxalic acid were the reagents used for the economic analysis calculations. The cost per ton of oxalic acid was varied based on historical prices. In addition, the price for concentrated hydrochloric acid is was varied based on historical prices per ton FOB. For the second scenario, the cost of kerosene, zinc varied historically, sulfuric acid (varied historically), Cyanex 923 were varied. Because the solvent extraction experiments failed to produce any meaningful results, the economic analysis of the second scenario is based upon the optimized finding and results of similar system investigated by Tunsu et. al[62].

4.4.4 Net Present Value, IRR, Payback period

The project life for this project was assumed to be 20 years and was depreciated using over those 20 years. The cost of capital was varied from 7.5%-14 % and the operating costs increased by 3% per year. The corporate tax rate was assumed to be 21%. All operating expenses were deducted in the same year in which they were incurred. The mean NPV (p50), p5, and p95 were reported.

4.4.5 Tornado Diagrams, TPC, Sensitivity Analysis

Varying various parameters such as cost of reagents, utilities, maintenance the corresponding effect upon the TPC were demonstrated with tornado diagrams. The goal of tornado diagrams is to demonstrate the sensitivity of various parameters up the TPC of the system.

4.5 Scaling of selective leaching of phosphor powder

Using a 3L apparatus class line Ace Glass reactor, and overhead stirrer, 300g waste fluorescent powder was leached for 15 minutes using 2L of 3M hydrochloric acid. First, an ice water bath was placed surrounding the apparatus after powder was placed into the container. A peristatic pump transferred the acidic solution into apparatus at approximately 200 mL per minute. After 15 minutes of total leaching time (including the transfer time, the solution was filtered using Whatman number 1 filter paper. After the solid was separated and dried in an oven, a 180g/L slurry of 2 M solution with powder was placed in a similar glass reactor. The vessel was heated to 70 C for 1 hour. This solution was filtered to separate the solid and liquid phases. The solution was either 1) saved for a later experiment or 2) precipitated using 1.5 times the stoichiometric ratio of
oxalic required to precipitate yttrium and europium oxalate. A similar reactor at room temperature was used for 1 hour of and and the slurry was filtered. The filter take was roasted via 800°C in a box furnace. The filtrate and filtered cakes were analyzed via ICP-MS to determine the recovery of europium and yttrium in the both portions and to very the mass balance.

Figure 4.5.1 (a)(b). (a) Shows 3L liter vessel used to conducted 2000 mL experiments with a using an ice water bath for temperature moderation. (b) This heated glass reactor with mantle and controller is used to control leaching.
4.6 Selective Reduction Experiments

Based on previous results from Colorado School of mines, an apparatus was constructed investigated ideal conditions for the separation of europium (II) sulfate from yttrium starting with mixed oxides (which are dissolved into solution) or the 2nd stage leach solution. The goal was to create an apparatus that was based on previous work by Morais [77] and Kabie [65] and their relative success using a Jones Reductor [83] a choice was made to using a 200 ml and adding Zn flakes 20-30 mesh to reduce europium. For scenario 1, a volume of mixed yttrium and europium oxides (roasted from oxalate form) was dissolved in concentrated HCl. Boiling water was added to complete the solvation. The alkalinity was adjusted with 3M NaOH to increase the alkalinity within a between pH 2.5 to 3.25. Hydrogen or nitrogen gas was bubbled through the system and zn was added afterwards. The reduction conducted for 15 minutes to 1 hour. Next, 3M sulfuric was pumped into another container. It was degassed to prevent re-oxidation of europium (II)) while the reduced solution was transferred into it. The solution was precipitated for 30 minutes to 2 hours. Next, the solution was filtered. The filter cake was analyzed after lithium borate fusion and filtrate saved for solvent extraction experiments.
Additionally, other significant problems arose in regard to the reduction column. Difficulties such the fluid was channeling and leaving dead zones where no solution was contacting the zinc. In addition, after repeated contact, small amounts of yttrium and zinc hydroxide were forming on the surface of the zinc. However, after continuously recycling the solution overnight through the column, the clear solution precipitated inside of the column and inside of the tubes of the peristaltic pump. This precipitate coated all of the zinc and a choice was made to using a different reduction method. The final reduction apparatus used had a capacity of 200 mL, a course frit at the end, a stir bar, an input for the recycled solution, a slot to funnel zinc, and an input for 96% Ar/ 4% H₂ bubbled through the solution.
Figure 4.6.2: This picture shows the 200 mL glass elbow with frit used for reduction.[19]
4.7 Yttrium solvent extraction experiments

Experiments were conducted on the solution from the previous section. The goal was to isolate the yttrium-rich solution from the impurities and possibility, selectively strip yttrium from there yttrium rich solvent. Using a stock solution isolated from waste, a factorial 135 solvent extraction experiments were conducted investigating the effect of reagent choice (Cyanex 923, 572, and 272, Primene JMT, and D2EHPA), pH (.5, 1.5, 2.5), O:A ratio (1/4, 1:1, 4:1), and concentration (15%, 25% and 35%).
The aqueous phase (the A in O:A) is the filtrate and the organic (O) was the reagent dissolved in Beantown Chemical Kerosene. The solutions were shaken in a 8 centrifuge a time shaker for 15 minutes. The bottom aqueous was separated and analyzed to see the change in concentration and purity of yttrium. All elements removed from the aqueous phase assumed to have transferred into the organic phase.

There these 135 experiments, as decision that made that D2EPHA was the best reagent and a distribution isotherm was constructed. However, a decision was made was that there was some problem with separation. Therefore, Cyanex 572 and 272 were studied. There were similar problems with the distribution isotherm. A re-evaluation of the initial results dissolved that there was some problem with all reagents. Therefore, for the economics a choice was made to use the choices in that article as a base for some aspects of the second scenario.
4.8 Kinetics and Activation energy determination experiments

The speed of reaction (kinetics) and the activation energy were studied. The challenge is the concentration of europium (II) cannot be measured directly—except by spectroscopy methods that leave the system exposed to air. The other issue is that—in the manner reduction vessel was constructed, there is a delay between reaction, retrieving that reacted solution. In kinetic measurements are supposed to be accurate within a few seconds. Also, the reaction occurs at the surface at zinc (mixing near the bottom of the vessel) and temperature control happens the center of the solution. Also, before heating, there was a 2-3 degree centigrade different in temperature measured in thermocouple and the pH probe. Therefore, a and precise system of luer locks and was developed to measure the concentration of europium (III) after precipitation. Unfortunately, no precipitation and the luer lock system after number tries. Therefore, a less precise system of complete experiments—similar the previous selective reduction experiments was undertaken. Concentrations of europium oxide at 5g/L and 2.5 g/L were used for the experiments. Europium oxide was dissolved into solution near 100 C with concentrated acid. The pH was adjust to pH 3. 5X times the stoichometric amount of sulfuric acid was used to precipitate the system. The concentration of the solution filtrate was analyzed by ICP-OES. The rate constant, order of the reaction and activation energy was determined by the reactions.
CHAPTER 5  
RESULTS AND DISCUSSION  
INTRODUCTION

This chapter contains the results of the experiments performed. The first section contains theoretical results and discussion that were found to contribute to hypothesis that led to the design of experiments performed. The second section will discuss the results and how they conform to the hypotheses that were made.

5.1 Theoretical Results and Discussion

5.1.1 Waste Fluorescent Lamp Powder Characterization

Characterization of the phosphor dust was conducted using XRD, SEM-EDS, ICP and XRF, and Microtrac particle analyzer.

Regarding the Microtrac Particle size analyzer, the assumption is that different recycled phosphor dusts will have similar particle size distributions. However, all powder used in this work was homogenized using various mixing techniques such as quartering and roll milling.

5.1.2

5.1.3 Reduction of Europium experiments

There are three stages explored in the selective reduction experiments. The solvation stage, the reduction stage and the precipitation stage. This section will discuss the theory behind these parts.

The preparation stage is used to dissolve the mixed europium and yttrium oxides in solution and the corresponding solution has its alkalinity adjusted to between pH 2.5-3.25—the preparation stage was used in the first scenario. For secondary scenario, the europium and yttrium were already in solution. The choice in starting pH values is related to the optimized conditions from Rabie [65], Morais[77], and Preston [66]. Whereas the previous authors used parameters such as reduction and precipitation time, entrance flow rates, and entrance pH solution values, the goal of this work was to use the ORP during the reduction stage as an indicator for when the prepared solution was reduced to a minimum and use similar precipitation times, up to 2 hours, as indicated by the literature.
The hypothesis was that the measuring the oxidation potential (the different between the platinum and silver-silver chloride electrodes) was a feasible method to judge status of the reduction within the system. The assumption was that primary change measured would be europium (III) ion and europium (II) ion ratio based on the corresponding millivolt measurement. The hypothesis was that the system could be reduced to a 95:5 ration of europium (II) to europium (III) and the corresponding electrode potential would be approximately, 770 mV.

Regarding the precipitation of europium (II) with sulfuric acid, the assumption was that using 100% hydrogen was better than other insert choices such nitrogen. Also, this idea fit into the narrative described by Figure 3.5.2. HSC Gibbs minimization function indicates that higher conversion of europium (III) to EuCl₄²⁻ is be favored in the order 100% H₂>4% H₂, 96%Ar>100%N₂. Using pure hydrogen, predicted equilibrium conversion is closer to 93% rather than 75% rather than as predicted by using 96% Ar/4%H₂ as predicted by HSC at .8 bar and 20°C.

In addition, SEM imagery was conducted on the europium (II) sulfate powder. The hypothesis was that a unique characteristic shape would be found for the compound. There are no SEM images of the compound found in the literature. There is an unique saucer shape found in this morphology.

5.1.4 Economic Analysis

An economic analysis was conducted for waste fluorescent powder recycling process. For scenario 1, this process starts with waste fluorescent powder recycler (Hg removed), and it ends with a saleable mixed europium and yttrium oxide recoved from roasted from the rare earth oxalates. At the current price $68.8 per kg europium oxide and $2.95 per kg yttrium oxides, the process could not be economic. However, if historical prices from the last 8 years are included into this scenario (ex. $6000 europium oxide< for a few weeks) the process could be economic. If the regulatoroitary environment changes, and there is a local supply chain for end manufacturers, the economic of situation, NPV, IRR improve. The same forces that cause ascension of rare earth prices as well as the restart of Molycorp Mountain Pass and significant economic investment to projects such as Rare Earth Resources at Bear Lodge, short-term supply and demand, lead Molycorp to bankruptcy and Bear Lodge to be shelved. However, the ban on the use of Chinese Nb-B-Fe magnets the US military, and the tariffs on importing rare earth as well as exporting rare
earths for processing in China has created new opportunities. Those opportunities may lead to success for Urban Mining and Rare Earth Salts who are trying to create that end manufacturing ecosystem in the United States. In addition, regarding sensitivity analysis, the hypothesis was this project was less sensitive to perturbations in capital costs than operating costs. The s

5.2 Results and Discussion of Experiments Performed

5.2.1 Phosphor Dust Characterization and composition of elements of preparation for later

QEMSCAN and Microtrac Particle Size Analyzer, XRD, and SEM were utilized to analyze the feed waste lamp phosphor powder.

Veolia was fluorescent powder was obtained and characterized in order to identify potential recycling schemes. Various mineralogical and metallurgical properties were analyzed. Cumulative particle size distribution shows the phosphor powder size ranges from 1 to 300 μm (Figure 5.2.1). The difference between the size of this material sieved and unsieved material was not significant. After sieving, the Microtrac demonstrated that the feed material was ~90% under smaller than
microns and the unserved material was 76% under 44 microns. Comparison by weight was even less significant. Approximately, 96% of the material under 44 microns by weight.

Figure 5.2.1.2 shows the TGA for the Veolia powder at WPI.
Figure 5.2.1.2: This shows the XRD for the feed waste fluorescent powder.

Table 5.2.1.1 This table shows the identified patterns on XRD

**Identified Patterns List:** (Bookmark4)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>98-016-0890</td>
<td>84</td>
<td>Ytrium Oxide</td>
<td>0.161</td>
<td>0.862</td>
<td>O3 Y2</td>
</tr>
<tr>
<td>*</td>
<td>98-004-0115</td>
<td>28</td>
<td>Calcite</td>
<td>0.265</td>
<td>0.791</td>
<td>C1 Ca1 O3</td>
</tr>
<tr>
<td>*</td>
<td>98-007-9652</td>
<td>8</td>
<td>Apatite- (CaF)</td>
<td>0.121</td>
<td>0.273</td>
<td>Ca5.061 F0.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O11.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P2.87</td>
</tr>
</tbody>
</table>
The composition of waste fluorescent powder used for at WPI was different than at Colorado School of Mines.

Table 5.2.1.4: This table shows the difference in composition for the powders and WPI versus CSM.

<table>
<thead>
<tr>
<th>Fluorescent Lamp Waste Powder</th>
<th>Oxides</th>
<th>Veolia-WPI (wt%)</th>
<th>Veolia-CSM (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃</td>
<td>31.47</td>
<td>9.77</td>
<td></td>
</tr>
<tr>
<td>La₂O₃</td>
<td>2.97</td>
<td>1.74</td>
<td></td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>2.82</td>
<td>1.76</td>
<td></td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>1.96</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>Tb₂O₃</td>
<td>1.14</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.10</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>22.81</td>
<td>20.53</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.74</td>
<td>8.89</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.58</td>
<td>5.33</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.53</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.25</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>14.38</td>
<td>21.12</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>9.30</td>
<td>24.73</td>
<td></td>
</tr>
</tbody>
</table>

The powder at CSM at high quantities of larger silica pieces, and therefore had to be sieved. However, based on the results of Microtrac and sieving, no effort made to sieve the powder that was leached and/or precipitated to begin the selective reduction experiments. The composition of major elements reporting to various portions of the flow sheet shown in Figure 5.2.1.4.
Figure 5.2.1.4: This figure shows how the major elements reporting to different parts of the flow sheet shown Figure 5.2.1.3.

Figure 5.2.1.5(a)(b). These figures show the Veolia powder used at WPI (left) and CSM (right).

5.2.2 Kinetic and Activation Energy Experiments

The purpose of these experiments was to find the reaction constant, k, determine the order of the reaction, and determine the activation energy to get a better fundamental understanding of the selective reduction equation.
Figure 5.2.1: This graph shows how the concentration varied with time for selective reduction experiments versus time.
The value in figure 5.2.2 is twofold. It determines demonstrates that the relationships between the points are roughly linear. This Linearly indicates a first order reaction in respect to europium. However, the $R^2$ for 20.5°C is not very strong at .786. This could have been due to random error run while running the experiments. It is difficult to harmonize every element of the setup precisely the same every time. For example, sometimes spinner spins after or not at all in the precipitation apparatus. It is assumed that the precipitation is going to completion. However, from experience, with this setup, conversions are lower in the precipitation step when the spinner is not functioning properly. Other issues like gas flow speed, peristatic pump speed, occasion slight leaks, and shifting of the apparatus are all other random errors that have affected the linearity of the graph. Increasing the temperature as show in
Figure 5.2.2.2: This graph shows the natural log of reaction constant k is respect to inverse temperature.

Figure 5.2.2.2 shows how the activation energy is calculated from the slope of the line. Unfortunately, $R^2 = .7275$. This low result is like due to similar issues related to same points from the previous graph. The calculated rate constant is due to a higher than expected at 20.5° C or lower than expected value at 30° C. The lower temperature had no temperature control and was run at ambient room temperature. The higher temperatures were heated with a band heater wrapped around the glass apparatus which was wrapped with a cloth material in order to increase insulation. However, the operation of unit included approximately a 2-3 ° degree overshoot and a 2-3 ° C degree undershoot with the PID controller.

The calculated activation energy 38.95 kJ mole indicates that the reaction is strongly diffusion controlled. There are several possible steps that could be the rate limiting step. The movement the europium (III) to the surface of the zinc, the charge transfer of electrons from zinc to europium (II) or the movement of europium (II). The rate limiting step in diffusion-controlled reaction is the rate at which the reaction. Therefore, the rate limiting step is governed by collision theory. This information means that increasing the stirring or improving the mechanism of mixing. More agitation means more collosions which means more a much faster. In addition, this reaction is exothermic as indicated by HSC. Even though, as Figure 5.2.2.1 shows, increasing the reaction temperature increase the speed of the reaction, the conversion of the reaction is not always improved. However, as HSC indicates the equilibrium constant, $K_e$, increases with temperature and is positively related to the extent of the reaction. Therefore, future work could be run a higher temperatures? It is uncertain because the precipitation reaction has a lower equilibrium constant at
higher temperatures. However, repeats of different more temperatures should be conducted in order to delineate the precision of value with a higher degree of the linearity.

5.2.3 Selective reduction of Europium experiments

The purpose of these experiments was multifaceted. The goal was to isolate and characterize high purity europium (II) sulfate. There is a dearth of information regarding the properties of this compound. Thirdly, the goal was to quantify and optimize the process of europium (II) sulfate. Ideally, these experiments can demonstrate a process in which the reduction potential is measured, and that measurement can be used to maximize ratio in which the Eu$^{2+}$/Eu$^{3+}$ as well as using parameters such as time, flow rates, agitation or pH of the solution for optimization.

To begin the reduction experiments, an yttrium solution (pH=2.5) was compared to an yttrium and europium dissolved system (pH=2.52).
Figure 5.2.3.3: This SEM picture shows the picture of the europium (II) sulfate precipitate.

Europium (II) sulfate has a unique SEM image that has never been demonstrated the literature. These disc like precipitate have a diameters from 10-20µm and a weight of 5-10µm. This characteristic shape was demonstrated using different precipitation times and stirring regimes, but similar types of images appeared each time.

Conducting SEM-EDS, a characteristic spectrum was demonstrated for europium (II) sulfate in Figure 5.2.3.4.
Figure 5.2.3.4: This SEM-EDS spectrum was indicated for europium (II) sulfate.

Table 5.2.3.2: This table indicates the sequence of experiments run for scenario one.

<table>
<thead>
<tr>
<th>Run</th>
<th>Entrance pH</th>
<th>Pulp Density</th>
<th>Eu:SO₄ Ratio</th>
<th>Precipitation Time</th>
<th>Grade of EuSO₄</th>
<th>Recovery of EuSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>100</td>
<td>20</td>
<td>3</td>
<td>89.68</td>
<td>70.79</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>100</td>
<td>20</td>
<td>3</td>
<td>89.66</td>
<td>68.94</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>100</td>
<td>10</td>
<td>3</td>
<td>94.63</td>
<td>73.32</td>
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<tr>
<td>4</td>
<td>2.5</td>
<td>100</td>
<td>20</td>
<td>1</td>
<td>95.93</td>
<td>63.82</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>100</td>
<td>10</td>
<td>1</td>
<td>93.54</td>
<td>69.92</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>50</td>
<td>20</td>
<td>1</td>
<td>93.91</td>
<td>51.82</td>
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<tr>
<td>7</td>
<td>3</td>
<td>50</td>
<td>20</td>
<td>1</td>
<td>94.36</td>
<td>57.32</td>
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<tr>
<td>8</td>
<td>2.5</td>
<td>50</td>
<td>20</td>
<td>3</td>
<td>90.06</td>
<td>59.45</td>
</tr>
<tr>
<td>9</td>
<td>2.5</td>
<td>50</td>
<td>10</td>
<td>1</td>
<td>95.31</td>
<td>54.58</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>50</td>
<td>10</td>
<td>3</td>
<td>93.09</td>
<td>55.19</td>
</tr>
</tbody>
</table>

For scenario one, the goal was to demonstrate the effect pulp density, europium:sulfate, and precipitation time upon the grade and recovery of europium sulfate.
Figure 5.2.3.5: This figure demonstrates the effect pH and precipitation time upon the grade of europium (II) sulfate

Figure 5.2.3.6 (a)(b) These figures demonstrate the effect of precipitation time & sulfate:europium ratio and pulp density & pH upon the grade of europium sulfate.

Table 5.2.3.3: This table indicates ANOVA statistics shown for grade in scenario 1.
The model statistics shown in table indicate the following. The model is significant with $p<.05$. The effect of entrance pH is significant ($pH=3$ is best) upon grade. Also, the effect of precipitation time is significant upon the grade ($T=1$ hour best). Finally, the effect of pulp density and entrance pH are significant interaction. It is uncertain how this interaction may have occurred. This means the effect entrance pH depends on the level of pulp density. Oddly, it does not appear that the sulfate ratio or pulp density effects the grade of europium (II) sulfate.

<table>
<thead>
<tr>
<th>Model Statistics</th>
<th>Grade of Europium (II) Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANOVA for Response Surface</td>
<td>Comment</td>
</tr>
<tr>
<td>Source</td>
<td>Sum of Squares</td>
</tr>
<tr>
<td>Block</td>
<td>3.83</td>
</tr>
<tr>
<td>Model</td>
<td>46.44</td>
</tr>
<tr>
<td>A-Entrance pH</td>
<td>6.46</td>
</tr>
<tr>
<td>B-Pulp Density</td>
<td>0.069</td>
</tr>
<tr>
<td>C-Eu/SO4 ratio</td>
<td>0.29</td>
</tr>
<tr>
<td>D-Precipitation Time</td>
<td>26.13</td>
</tr>
<tr>
<td>AB</td>
<td>1.06</td>
</tr>
<tr>
<td>Pure Error</td>
<td>0.1</td>
</tr>
<tr>
<td>Cor Total</td>
<td>50.37</td>
</tr>
</tbody>
</table>

Figure 5.2.3.7 (a)(b) These figures demonstrate the effect of precipitation time & sulfate:europium ratio and pulp density & pH upon the recovery of europium sulfate.
Although none of the ANOVA statistics indicated any level of statistical significance, it appears that pulp density at lowest pH maximized the recovery. Le Chatelier’s principle indicates that an increase in the concentration in the reactants shifts the reaction toward the products. Generally speaking, there is point of diminishing returns with increasing the pulp density. Next, the oxalic acid precipitation was removed, and selective reduction was conducted on the leach solution in order to simplify the process. Again, trails were conducted a) to reoptimize the process b) to see of the system was robust to the higher impurity levels of the leach solution.

Table 5.2.3.3: This table indicates ANOVA statistics shown for grade in scenario 1.
Figure 5.2.3.8 (a)(b): These figures show the effect of sulfate entrance speed and sulfate ratio for (a) using nitrogen and (b) using hydrogen

Figure 5.2.3.9 (a)(b): These figures show the effect of precipitation time and entrance pH for (a) using nitrogen and (b) using hydrogen

Figure 5.2.3.9 (a)(b): Demonstrate the effect of entrance pH and precipitation time upon the grade for nitrogen (a) and hydrogen (b)

Table 5.2.3.4: This table indicates ANOVA statistics shown for grade in scenario 2.
The results showed from Table 5.2.3.4 that model is significant for the effect of grade. Clearly, lowest sulfate ratios (5X) shown in Figure 5.2.3.8 (a)(b) maximized the grade significant manner. This result is expected. The effect of sulfate entrance speed (the highest speed of 3) maximizes grade. Generally, a slower speed would allow the unreacted acid to better react the unreacted reduced solution. This is unexpected. This may be cause the highest speeds were conducted at higher reduction times, but this interaction is not evident from the table. It can be understood why these is an interaction between entrance pH sulfate ratio. Clearly, the level of sulfuric acid affects the effect of pH upon the grade (interaction AB). What is more uncertain is the explaining the significant interaction (BD). Why does the choice of gas (hydrogen or nitrogen) affect the effect of the sulfate ratio upon grade?

The follow conclusions can made.

- There is a strong, statistically significant relationship between sulfate entrance speed and grade. The highest speed studied (actual rate can be shown later) of 3 is best.
• There is a strong, statistically significant inverse relationship between sulfate ratio and grade. Sulfate ratio=5X has the highest grade.

• There is a strong, statistically non-significant relationship precipitation time and grade. Two hours is showing the highest recovery. There are doubts about this result based on the previous work.

• Entrance pH, gas and reduction time are showing minimal no visual or statistical effect upon upon the grade.

• The optimized conditions are when pH=3 (based on previous work), sulfate ratio=5x, Sulfate entrance speed=3, reduction time=.5 hours, precipitation time=2 hours. Based on the information and plots provided, there is not a clearly more favorable gas in these experiments. Hydrogen “appears” to be move favorable in Figures 9,10, and 11, but result is not significant. For the moment, a 2 hour precipitation time is assumed to be optimal even if the previous result is counter to this information. However, previous research by other authors in other situations have found 1-2 hours to give nearly the same result.

• Run 2 has the closest to the optimized conditions.

The composition of Run 2 is listed in the tables and chart below.

![Percentage Relative Rare Earth Oxides Versus total REO: Sample 2](image)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>% Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuSO₄</td>
<td>92.77</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.27</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>0.17</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>0.03</td>
</tr>
<tr>
<td>Tb₂O₃</td>
<td>0.00</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.21</td>
</tr>
<tr>
<td>CaO</td>
<td>1.09</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.57</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.76</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.78</td>
</tr>
<tr>
<td>MgO</td>
<td>0.40</td>
</tr>
<tr>
<td>MnO</td>
<td>0.00</td>
</tr>
<tr>
<td>Sb₂O₅</td>
<td>0.01</td>
</tr>
<tr>
<td>SrO</td>
<td>0.95</td>
</tr>
<tr>
<td>BaO</td>
<td>0.80</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.15</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Y₂O₃</th>
<th>EuSO₄</th>
<th>La₂O₃</th>
<th>Ce₂O₃</th>
<th>Tb₂O₃</th>
<th>Gd₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>99.30</td>
<td>0.25</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 5.2.3.10: This chart shows the compositions of the most idealized condition.
The major impurities are phosphor and calcium—of which—calcium is must difficult remove. A more optimized first stage of selective reduction would have removed more apatite which would have let to less calcium and phosphate in the europium sulfate.

5.2.4 Solvent Extraction of Yttrium

Solvent extraction was used to attempt purify yttrium oxide from and yttrium rich leach solution gathered from solvent reduction. The native pH if the filtrate was .89. 135 reactions were conducted to study of the effect of reagent (Cyanex 572, 272, 923, Primene JMT and D2EHPA), pH(5, 1.5, and 2.5), O:A (4:1, 1:1, 1:4) and concentration (15%, 25%, 35%). Beantown Chemical Kerosene was used for the tests. The initial results showed that D2EHPA as the best results.

Figure 5.2.4.1: This figure shows the reagents vs. pH and the effect upon recovery.
Figure 5.2.4.2: This figure shows an example of distribution isotherm (brown). Copyright protected under Fair Use. [62]
Figure 5.2.4.3: This figure shows the distribution isotherm for D2EHPA.

After completing more D2EHPA test and plotting as a distribution isotherm, the results did not fit any functional pattern for solvent extraction. The lowest O:A’s had the highest calculated organic concentration, but the corresponding aqueous concentrations did not fit into any pattern of expected results. Reexamining the previous results, they gave similar trends as in Figure 5.2.4.4.
Figure 5.2.4.4: This figure shows the reagents vs. pH and the effect upon recovery for D2EHPA.

An expert was contacted in order to discover the problem[84]. Dr. McNulty suggested that the kerosene might be causing the problems. Unfortunately, no time as given to rerun the experiments with the new kerosene. Therefore, Tunsu, et. al. 2016 was use an an analogous model to create 99% europium oxide.
5.2.5 Economic Analysis

Table 5.2.4.1: The table shows the capital equipment, power consumption and number of units.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Specifications</th>
<th>Number of units</th>
<th>kW</th>
<th>Hours/day</th>
<th>kWh/Day</th>
<th>Total Cost $</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stir Tank</td>
<td>10000 L PVC</td>
<td>1</td>
<td>15</td>
<td>3</td>
<td>45</td>
<td>42000</td>
<td>Alibaba</td>
</tr>
<tr>
<td>Plate &amp; Frame Filter Press</td>
<td>320/1500U (1000L)</td>
<td>3</td>
<td>2.2</td>
<td>3</td>
<td>19.8</td>
<td>360000</td>
<td>Alibaba</td>
</tr>
<tr>
<td>Pan Filter</td>
<td></td>
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<td>11</td>
<td>6</td>
<td>0</td>
<td>0 Confidential</td>
<td>Confidential</td>
</tr>
<tr>
<td>Glass lined reactor</td>
<td>12000L, Jacketed</td>
<td>1</td>
<td>19</td>
<td>6</td>
<td>114</td>
<td>30000</td>
<td>Alibaba</td>
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<tr>
<td>Boiler for reactor</td>
<td></td>
<td>1</td>
<td>102</td>
<td>6</td>
<td>102</td>
<td>18000</td>
<td>Confidential</td>
</tr>
<tr>
<td>Tray Dryer oven</td>
<td>RXH-54-B, CT-4. 400kg, 8</td>
<td>1</td>
<td>2.2</td>
<td>9</td>
<td>19.8</td>
<td>240000</td>
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</tr>
<tr>
<td>Pumps</td>
<td>75 GPM@40', CPVC, PP</td>
<td>10</td>
<td>1.1</td>
<td>10</td>
<td>110</td>
<td>26400</td>
<td>Alibaba</td>
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<td>Air Compressor</td>
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<td>1</td>
<td>7.5</td>
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<td>22.5</td>
<td>6000</td>
<td>Confidential</td>
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<tr>
<td>Pallet jack</td>
<td></td>
<td>3</td>
<td>3</td>
<td>324</td>
<td>3600</td>
<td>Confidential</td>
<td></td>
</tr>
<tr>
<td>Barrel Cart</td>
<td></td>
<td>3</td>
<td>3</td>
<td>324</td>
<td>3600</td>
<td>Confidential</td>
<td></td>
</tr>
<tr>
<td>1 ton Scale</td>
<td></td>
<td>1</td>
<td>1</td>
<td>2400</td>
<td>Confidential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powder Loader</td>
<td></td>
<td>3</td>
<td>3</td>
<td>72000</td>
<td>Confidential</td>
<td></td>
<td></td>
</tr>
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<td>Scrubber</td>
<td></td>
<td>1</td>
<td>1</td>
<td>18000</td>
<td>Confidential</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baghouse</td>
<td></td>
<td>1</td>
<td>1</td>
<td>18000</td>
<td>Alibaba</td>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
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<td><strong>Total</strong></td>
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<td></td>
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<td><strong>433.1</strong></td>
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<td>+20% energy contig</td>
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<td></td>
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<td></td>
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<td></td>
<td><strong>181902</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2.5.2: This table shows total operating costs per year.

Two scenarios were used for the economic analysis. The goal was to compare the technical and economic effects of the two different scenarios. Ultimately, one scenario should emerge as the better scenario.
Table 5.2.5.3: This table shows NPV and IRR for scenario 1.

<table>
<thead>
<tr>
<th>Monte Carlo Simulations</th>
<th>NPV</th>
<th>TPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>p50 (Median)</td>
<td>$24,131,894</td>
<td>$9,787,258</td>
</tr>
<tr>
<td>p5</td>
<td>-$30,076,350</td>
<td>$13,737,954</td>
</tr>
<tr>
<td>p95</td>
<td>$94,367,424</td>
<td>$21,290,164</td>
</tr>
<tr>
<td>IRR (p50)</td>
<td>62.93%</td>
<td></td>
</tr>
<tr>
<td>Prob of Positive NPV</td>
<td>77%</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.2.5.1: This graph shows the cumulative net present value for scenario 1.
Figure 5.2.5.1.1: This graph shows the cumulative total product cost for scenario 1.

Table 5.2.5.4: This table shows NPV and IRR for scenario 2.

<table>
<thead>
<tr>
<th>Monte Carlo</th>
<th>NPV</th>
<th>TPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulations</td>
<td>10000</td>
<td>10000</td>
</tr>
<tr>
<td>p50 (Median)</td>
<td>$2,163,924</td>
<td>$15,974,250</td>
</tr>
<tr>
<td>p5</td>
<td>-$50,713,284</td>
<td>$10,847,896</td>
</tr>
<tr>
<td>p95</td>
<td>$63,575,584</td>
<td>$23,555,944</td>
</tr>
<tr>
<td>IRR (p50)</td>
<td>10.88%</td>
<td></td>
</tr>
<tr>
<td>Prob of Positive NPV</td>
<td>53%</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.2.5.2 This graph shows the cumulative net present value for scenario 2.
Figure 5.2.5.2.1: This graph shows the cumulative total product cost for scenario 2.
5.2.5.3: This table shows the tornado diagram for scenario indicating the sensitivity of Total Product Cost (TPC) for scenario 1.

5.2.5.3.1: This table shows the tornado diagram for scenario indicating the sensitivity of Net Present Value (NPV) for scenario 1.
Figure 5.2.5.4: This table shows the tornado diagram for scenario indicating the sensitivity of Net Present Value (NPV) for scenario 2.
Figure 5.2.5.4.1: This table shows the tornado diagram for scenario indicating the sensitivity of Total Product Cost (TPC) for scenario 2.

The NPV is much higher for scenario 1 versus scenario 2. Scenario 1 requires 25% discount from REO prices with an 85% total recovery, but scenario 2 requires 10% discount from REO prices. In addition, the equipment costs for (1) 9.7 million USD versus (2) 15.9 million USD are much higher. Scenario (2) is much more complicated, requires more reagents and more uncertainties in the model. However, scenario 1 assumes that REO separator and purified can easily be found. If there were limitations on supply or laws against using imported rare earths, clearly scenario 2 appears to be practically viable option. In (2) Europium and yttrium have already been separated. They just need to purified. More stages of solvent extraction can be used to separate and purify yttrium oxide. Similarly, multiple SX can be used to separate and purify europium oxide.
CHAPTER 6
CONCLUSION
INTRODUCTION

This portion of the report has several parts. First, there is a discussion of accomplishments and shortcomings. Next, there is a list of enumerated conclusions. Finally, recommendations will be made regarding future work.

6.1 Summary and Retrospective of the Research Conducted.

A characterization of phosphor dust was completed of the waste fluorescent powder. Different analyzes were used to quantify the powder. ICP-OES showed the difference in composition the starting materials powders used at different school. SEM indicated a new morphology that has never been described in the literature.

The kinetics and activation energy for the selective reduction of europium were determined. The reaction was determined to be first order regarding europium. The activation energy was determined to be 38.95 kJ/mole.

The selective reduction of europium (III) to europium (II) in solution along with precipitation of europium (II) sulfate was indicated as imporante method to separate europium from yttrium. The optimized conditions for the formation of 92.77% europium sulfate are pH=3, nitrogen gas or hydrogen gas precipitation. This process is ready for scale up at a pilot level for pre-commerical production.

An economic analysis of was conducted using Monte Carlo simulation indicates that the NPV, IRR, TPC of first scenario are respectively. Similarly, the second scenario indicates a very different NPV, IRR, TPC. However, at current prices, the project is highly uneconomic. More work research should conducted to see how to add value by recovering terbium, cerium and lanthanum in recovery to the process.

6.2 Enumerated Conclusions
1) There is an unique morphology to europium (II) sulfuate
2) Selective reduction and precipitation appears to be robust.

3) Europium sulfate was separated with a 92.77% purity with more than 80% recovery in the optimized conditions.
4) Pre-feasibility study of the economic analysis and plant design completed using 2 scenarios, both of which is economic, but the first is much more strongly.

5) Gibb minimization modeling completed for 3 stages of selective reduction unit operations. The manipulation of pH was done by addition of NaOH prior to reduction of Eu(III) to Eu(II) by Zn⁰.

6) Characterized europium (II) sulfate with SEM imagery. Signature of compound identified.

7) The activation energy for selective reduction was determined to be 38.95 kJ/mole

6.3 Recommendations.

1) Conduct leaching experiments to place terbium in solution from the residue using magnetic separation and alkali fusion.

3) Scale up the selective reduction apparatus to pilot scale

4) Improve uncertainty of economic analysis. Incorporate zinc scrap recycling in scenario 2.

6) Conduct Gibbs minimization simulations on further scenarios of the selective reduction apparatus. Using Gibb minimization to simulate the second cycle of this apparatus.

7) Complete the solvent extraction research to recover yttrium oxide
### APPENDIX A

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt.%</th>
<th>Est.error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>63.48</td>
<td>0.19</td>
</tr>
<tr>
<td>F</td>
<td>7.77</td>
<td>0.16</td>
</tr>
<tr>
<td>Ca</td>
<td>6.50</td>
<td>0.07</td>
</tr>
<tr>
<td>Sr</td>
<td>6.39</td>
<td>0.05</td>
</tr>
<tr>
<td>Px</td>
<td>4.28</td>
<td>0.041</td>
</tr>
<tr>
<td>Ba</td>
<td>3.41</td>
<td>0.017</td>
</tr>
<tr>
<td>La</td>
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<td>0.0071</td>
</tr>
<tr>
<td>Ce</td>
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</tr>
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<td>Si</td>
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<td>Eu</td>
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<td>0.019</td>
</tr>
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<td>Tb</td>
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<td>0.029</td>
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<td>Pu</td>
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<td>0.020</td>
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<td>Am</td>
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<td>0.028</td>
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<tr>
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</tr>
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<td>Ru</td>
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<td>0.0070</td>
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<td>K</td>
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</tr>
<tr>
<td>Fe</td>
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<td>0.0025</td>
</tr>
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</table>

Figure A.1: This figure shows the XRF results the WPI waste fluorescent powder sample 1.
<table>
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<th>Element</th>
<th>Wt%</th>
<th>Est.Error</th>
</tr>
</thead>
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<td>64.26</td>
<td>0.32</td>
</tr>
<tr>
<td>F</td>
<td>7.63</td>
<td>0.41</td>
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<tr>
<td>Sr</td>
<td>6.42</td>
<td>0.12</td>
</tr>
<tr>
<td>Ca</td>
<td>6.42</td>
<td>0.12</td>
</tr>
<tr>
<td>Px</td>
<td>4.23</td>
<td>0.10</td>
</tr>
<tr>
<td>Ba</td>
<td>3.19</td>
<td>0.44</td>
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<td>La</td>
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<td>0.06</td>
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<td>Ce</td>
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<tr>
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<td>Pu</td>
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<td>0.12</td>
</tr>
<tr>
<td>Tb</td>
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<td>0.026</td>
</tr>
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<td>0.10</td>
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<td>Mo</td>
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</table>

Figure A.2: This figure shows the XRF results the WPI waste fluorescent powder sample 2.
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<th>Element</th>
<th>Wt%</th>
<th>Est.Error</th>
</tr>
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<tbody>
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<tr>
<td>F</td>
<td>7.19</td>
<td>0.42</td>
</tr>
<tr>
<td>Ca</td>
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<td>0.12</td>
</tr>
<tr>
<td>Sr</td>
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<td>0.12</td>
</tr>
<tr>
<td>Px</td>
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<td>0.10</td>
</tr>
<tr>
<td>Ba</td>
<td>3.49</td>
<td>0.45</td>
</tr>
<tr>
<td>La</td>
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<td>0.06</td>
</tr>
<tr>
<td>Ce</td>
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<td>0.06</td>
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<td>Sb</td>
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<td>Cs</td>
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<tr>
<td>Cd</td>
<td>0.123</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Figure A.3: This figure shows the XRF results the WPI waste fluorescent powder sample 3.
References Cited


[30] Administrator, “Analyzing China’s Heavy Rare Earth Element Reserves (Part 1): Ion-


[38] M. Klinger, Rare Earth Frontiers. 2017.


P. Vanysek, “Electrochemical Redox Potential.” [Online]. Available:


\[ Zn^{2+} (aq) + 2e^- = Zn \quad \text{E}^o = 76 \text{ volts} \]