INVESTIGATION OF RECOVERY AND RECYCLING OF RARE EARTH ELEMENTS FROM WASTE FLUORESCENT LAMP PHOSPHORS

by

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ABSTRACT

Characterization techniques and experimental measurements were used to evaluate a process for recycling rare earth elements (REEs) from spent fluorescent lamp phosphors. QEMSCAN analysis revealed that over 60% of the rare earth bearing minerals was less than 10 µm. A representative sample of the as-received feed contained 14.59 wt% total rare earth elements (TREE) and upon sieving to below 75 µm, the grade increased to 19.60 wt% REE with 98.75% recovery.

Based on experimental work, a new process for extracting the chief REEs from end of life fluorescent lamps has been developed. The proposed flowsheet employs a three-stage leaching and precipitation process for selective extraction and recovery of the REEs. Hydrochloric acid was used as lixiviant in batch leach experiments on the phosphor powder. The maximum extraction obtained was 100% for both yttrium and europium under the following leaching conditions: 2.5 M HCl, 70°C, 1 hour, 180 g/L and 600 rpm. However, the solubility of cerium, lanthanum and terbium remained low at these conditions.

Kinetic data of the leaching of yttrium and europium showed best fit to the logarithmic rate expression of the empirical model of leaching. Activation energy was calculated to be 77.49 kJ/mol for Y and 72.75 kJ/mol for Eu in the temperature range of 298 to 343 K.

Precipitation tests demonstrate that at least 50% excess the stoichiometric amount of oxalic acid is needed to recover yttrium and europium efficiently to produce a pure (Y, Eu) mixed oxide. Total recovery of the REEs was achieved even at very low pH or without any base added. Over 99% pure mixed rare earth oxide at 99% recovery has been attained.
An economic assessment of the developed process using operating and capital cost have been undertaken and based on the analysis of the three economic scenarios, two are economic and one is non-economic.

**Keywords**: Rare earth elements, rare earth oxides, phosphor, fluorescent lamp, recycling, leaching, precipitation, kinetics, economic analysis
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Finally, I want to dedicate this dissertation to my mum. There’s no way I can pay you back. But the plan is to show you I understand. You are appreciated. I love you.
PROJECT OVERVIEW

Increasing demand for rare earth elements (REEs) due to rapid technological growth in several high-technology applications such as green energy, defense related applications, efficient fuel vehicles, emissive displays and fluorescent lamps, etc. coupled with shortage of supply has forced a paradigm shift towards finding alternative routes for rare earth production and supply. REEs are never found as free metals in the earth’s crust and their naturally occurring minerals consist of mixtures of various REEs and non-metals. Despite their name, they are relatively abundant in the earth’s crust but in concentrations too small to make mining economical, so global supply relies on a small number of sources. Currently over 90% of the world’s rare earth metal mining and oxide production comes from China. In 2010, the Chinese government implemented new tariffs and mining regulations, which restricted the trade of the precious commodity.

In order to overcome China’s dominance it became important to recycle rare earths from a myriad of sources such as permanent magnets, lamp phosphors, rechargeable Ni-MH batteries and catalysts. Lamp phosphors utilizing rare earth oxides are second in demand only to magnets. Therefore it is imperative to research recycling and reuse of phosphor powder from end-of-life lamps. There has to be improvements to develop the extractive metallurgy aspect and create efficient disposal and collection systems so as to operate at volumes that may make the process commercially viable.

The goal of this project is to characterize phosphor powder, study the chemistry and solubility of REEs in the powder so as to develop an efficient and economic flow sheet to selectively recover the REEs as pure mixed oxides.
CHAPTER 1
BACKGROUND

The rare earth elements (REEs) are a group of seventeen elements, which appear in the periodic table. The group consists of the fifteen lanthanides chemical elements (atomic number 57 to 71) along with scandium and yttrium (Figure 1.1). Scandium and yttrium are considered rare earth elements since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. Scandium is scarcely found in nature and promethium is a radioactive element, therefore, the rare earth elements considered for industrial applications are the remaining fifteen elements in the group. REEs share many similar chemical and physical properties, which is why they occur together in geological deposits but their distribution and concentrations vary. Additionally these similarities are the reason it took over 160 years for all of them to be discovered and separated.

The term “rare earth element” is a leftover from the 15th century where “rare” meant “strange” or “unusual” materials and “earth” referred to any metal or mineral combined with oxygen. Despite their name, rare earth elements are not rare but relatively plentiful in the earth's crust (with the exception of the radioactive promethium). The most abundant REEs are similar in crustal concentration to commonplace industrial metals such as chromium, nickel, copper, or lead. Even the least abundant REE, thulium, is nearly 200 times more common than gold. However, in contrast to ordinary base and precious metals, REEs have very little tendency to become concentrated in exploitable
ore deposits. Therefore they are referred to as “rare” because it is not common to find them in commercially viable concentrations.

Figure 1.1: The rare earth elements on the periodic table [1].

1.1. Short History of Rare Earth Elements

The history of rare earth minerals begins in the year 1751, when the Swedish mineralogist and chemist Axel Fredrik Cronstedt (1722-1765) described an unusually heavy, reddish mineral (later named cerite), which he had found in the quarry of Bastnäs, in Sweden. The famous Swedish chemist Carl Wilhelm Scheele (1742-1786) analyzed it and came to the conclusion that it was only an iron aluminum silicate and the mineral was more or less forgotten for next five decades [2]. The identification of each of the rare earth elements took about 150 years, between 1788 and 1941. K.A. Gschniedner divided
the history of rare earth metallurgy into three stages – The Dark Ages (before 1950), The Enlightenment Age (1950-69) and The Golden Age (from 1970).

1.1.1. The Dark Ages

The Dark Ages began with the discovery of rare earths in the town Yttterby, Sweden in 1788. During this period, identification of most of the rare earth bearing elements was completed and independent scientific research in different countries had come up with novel methods to extract rare earth mixtures from the available sources. Mosander prepared a highly impure form of cerium metal by reduction of cerium chloride by sodium or potassium. More studies were conducted to understand the chemical and physical properties of the rare earths [3].

1.1.2. The Age of Enlightenment

Prior to this period, the rare earths obtained were 90-95% pure. During the Age of Enlightenment, major steps were made into producing high purity rare earth elements. Much work was conducted during this period to establish procedures, which would produce 99% pure rare earths and by the end of this period, rare earth metals with purity as high as 99.99% were produced. The production of such high purity rare earth elements led to a better understanding of their properties. It was during this period that Strnat and his research team discovered the superior permanent magnetic properties of rare earths and cobalt intermetallic. This development lead to the commercialization of rare earth magnets and created an increased demand for high purity rare earths [3].

Furthermore, during this period the scientific community devised a more concentrated and united effort towards rare earth research. The foundation of the Journal
of Less Common Metals in 1959 and the initiation of Rare Earth Research conference in 1960 brought the scientific communities across the globe involved in rare earth research together. Another major achievement and progress during the Age of Enlightenment was the establishment of the Rare Earth Information Center in 1966 by the Ames National Laboratory at Iowa State University [3].

1.1.3. The Golden Age

The fundamental and applied research of the previous two era had laid the foundation that ushered in a new age of rapid progress in the area of rare earth extractive metallurgy and application of rare earths and their alloys in a myriad range of applications. By the Golden Age, most of the chemical, electrical and magnetic properties of the rare earths were fully understood.

1.2. Properties of REEs

REEs are classified into two categories - light rare earth elements (LREEs) and heavy rare earth elements (HREEs) based on their electron configuration (Figure 1.2). The LREEs are defined as lanthanum through gadolinium, atomic number 57 to 64. The HREEs are defined as terbium through lutetium, atomic number 65 to 71, and also yttrium (atomic number 39). Yttrium is generally considered a heavy rare earth since its ionic radius is close to that of the HREE’s, while scandium is not considered either a light or a heavy. All the HREEs have 'paired' electrons whereas the LREEs have unpaired electrons, from 0 to 7. Yttrium is lighter than the light rare earths, but included in the HREEs group because of its similar ionic radius, chemical properties and physical associations with heavy rare earths in natural deposits. Scandium is also trivalent;
however, its other properties are not similar enough to classify it as either a LREE or HREE. The HREEs are relatively less common in nature but more valuable because they frequently occur in ores that are scarcer and harder to process than LREE ores.

Figure 1.2: The Rare earth elements are subdivided into LREE and HREE [4].

Generally, as an element’s atomic number increase, its’ ionic radius also increase as there is addition of more valence electrons; however, this is not the case with REEs, due to a phenomenon known as the “Lanthanide Contraction”. The increase in effective nuclear charge as atomic number increases is offset by the addition of electrons to outer sub-shells and also by the shielding effect of the inner-shell electrons on the outer-shell electrons. As rare earths’ atomic number increases, the additional electrons occupy the inner 4f sub-shell. However, the 5s and 5p orbitals penetrate the 4f sub-shell (which has a diffused shape) so the 4f orbital is not shielded from the increasing nuclear charge. This effect results in a decrease in ionic radius from La$^{3+}$ to Lu$^{3+}$. Thus lanthanum ion, La$^{3+}$, has a radius of 1.06 Å, whereas the heavier lutetium ion, Lu$^{3+}$, has a radius of 0.85 Å. REEs have very similar chemical properties because they generally exhibit the +3 oxidation state and also lanthanide contraction keeps the rare earth ions about the same size. As a result, at least small amounts of each one are usually present in every rare earth
mineral. Lanthanide contraction plays an important role in explaining the chemistry of lanthanides:

1. Basicity - Basicity is a measure of the affinity a species has for an electron or anion. Due to lanthanide contraction the decrease in the size of the cation increases the polarizing power of the ions and the stability of the complex ions thereby reducing the basic character of the lanthanide hydroxides. Consequently, the basic nature of lanthanum hydroxide decreases from La(OH)₃ to Lu(OH)₃.

2. Color - Lanthanide metals are slightly white but their trivalent ions are colored both in the solid state and in aqueous solution.

3. Magnetic properties - La³⁺ and Lu³⁺ have no unpaired electron and do not show paramagnetism while all other trivalent ions of lanthanides are paramagnetic.

4. Physical properties - There is a general increase in rare earth metal hardness, density and melting point from cerium to lutetium.

The individual REEs can vary widely in their relative natural abundance, ranging from cerium, the most abundant, to promethium, which is virtually unknown in ore deposits because it undergoes radioactive decay. Another interesting feature of the lanthanides is that the Oddo-Harkins rule applies to their occurrence in nature, in that the odd-numbered elements occur less extensively than the even-numbered ones. Rare earth metals oxidize at relatively low temperatures, with ignition in air in the temperature range 150˚C–180˚C. Table 1.1 illustrates the various properties of the rare earths elements.
Table 1.1: Properties of rare earth elements [5].

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Lanthanum</th>
<th>Cerium</th>
<th>Praseodymium</th>
<th>Neodymium</th>
<th>Promethium</th>
<th>Samarium</th>
<th>Europium</th>
<th>Gadolinium</th>
<th>Terbium</th>
<th>Dysprosium</th>
<th>Holmium</th>
<th>Erbium</th>
<th>Thulium</th>
<th>Ytterbium</th>
<th>Lutetium</th>
<th>Scandium</th>
<th>Yttrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Weight</td>
<td></td>
<td>138.90</td>
<td>140.12</td>
<td>140.91</td>
<td>144.24</td>
<td>145.07</td>
<td>150.36</td>
<td>151.97</td>
<td>157.25</td>
<td>158.93</td>
<td>162.50</td>
<td>164.93</td>
<td>168.93</td>
<td>173.04</td>
<td>174.97</td>
<td>174.97</td>
<td>44.96</td>
<td>88.91</td>
</tr>
<tr>
<td>Crystal Structure (As a Function of Temperature °C)</td>
<td>dcp &lt; 148 dcp (fcc) &gt; 148 and dcp &lt; 865 fcc &gt; 865</td>
<td>dcp &lt; 865 fcc &gt; 865</td>
<td>dcp &lt; 865 fcc &gt; 890</td>
<td>rhomb &gt; 734 cph &lt; 922 cph &lt; 922</td>
<td>bcc</td>
<td>cph &lt; 1235 bcc &gt; 1235</td>
<td>cph &lt; 1289 bcc &lt; 1289</td>
<td>cph &lt; 1318 bcc &lt; 1318</td>
<td>cph</td>
<td>cph</td>
<td>cph</td>
<td>cph</td>
<td>cph</td>
<td>cph</td>
<td>cph</td>
<td>cph</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atomic Volume (cm³/mol at 24°C)</td>
<td>22.60</td>
<td>17.20</td>
<td>20.80</td>
<td>20.58</td>
<td>20.24</td>
<td>20.00</td>
<td>28.98</td>
<td>19.90</td>
<td>19.31</td>
<td>19.00</td>
<td>18.75</td>
<td>18.45</td>
<td>18.12</td>
<td>24.84</td>
<td>17.78</td>
<td>15.06</td>
<td>19.89</td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³ at 24°C)</td>
<td>6.15</td>
<td>8.16</td>
<td>6.77</td>
<td>7.01</td>
<td>7.26</td>
<td>7.52</td>
<td>5.24</td>
<td>7.90</td>
<td>8.23</td>
<td>8.55</td>
<td>8.80</td>
<td>9.07</td>
<td>9.32</td>
<td>6.97</td>
<td>9.84</td>
<td>2.99</td>
<td>4.47</td>
<td></td>
</tr>
<tr>
<td>Conduction Electrons</td>
<td>3.0</td>
<td>3.1</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
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<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Valence in Water</td>
<td>3.0</td>
<td>3.4</td>
<td>3.3</td>
<td>3.3</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Color in Water (Me³⁺)</td>
<td>colorless</td>
<td>colorless</td>
<td>yellow green</td>
<td>rose</td>
<td>pink</td>
<td>Yellow Sm²⁺ is dark red</td>
<td>Eu²⁺ is pale yellow</td>
<td>colorless</td>
<td>pale pink</td>
<td>pale yellow green</td>
<td>yellow</td>
<td>pink</td>
<td>colorless, Vb²⁺ is yellow</td>
<td>colorless</td>
<td>colorless</td>
<td>colorless</td>
<td>colorless</td>
<td></td>
</tr>
<tr>
<td>Main Absorption band of Me³⁺ in aqueous solution 200 to 1000 nm</td>
<td>210.5, 222.0, 238.0, 252.0</td>
<td>448.5, 469.0, 482.0, 508.5</td>
<td>354.0, 521.8, 574.3, 735.9, 742.0, 797.5, 802.5, 802.3</td>
<td>548.5, 568.0, 702.5, 735.5, 802.0, 808.0</td>
<td>362.5, 374.5, 402.0</td>
<td>375.5, 394.1</td>
<td>272.9, 273.9, 275.4, 275.6, 284.4</td>
<td>350.3, 367.7, 487.2</td>
<td>350.4, 365.0, 910.0</td>
<td>287.0, 361.1, 416.4, 450.8, 537.0, 641.0</td>
<td>364.2, 375.7, 487.0, 522.8, 652.5</td>
<td>360.0, 682.5, 780.0</td>
<td>975</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color of Oxide (Re₂O₃)</td>
<td>white</td>
<td>egg shell</td>
<td>yellow green, black (Pr₆O₁₁), pale blue (Pr₂O₃)</td>
<td>pale blue</td>
<td>pink</td>
<td>cream</td>
<td>white</td>
<td>white</td>
<td>brown (Tb₄O₇)</td>
<td>yellow white</td>
<td>yellow white</td>
<td>pink</td>
<td>greenish white</td>
<td>white</td>
<td>white</td>
<td>white</td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>Number of isotopes: Natural (artificial)</td>
<td>2 (19)</td>
<td>4 (15)</td>
<td>7 (14)</td>
<td>7 (11)</td>
<td>7 (11)</td>
<td>7 (11)</td>
<td>7 (11)</td>
<td>7 (11)</td>
<td>6 (12)</td>
<td>6 (12)</td>
<td>6 (12)</td>
<td>6 (12)</td>
<td>1 (17)</td>
<td>1 (17)</td>
<td>2 (14)</td>
<td>1 (14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionization Potential (eV/g-atom)</td>
<td>5.61</td>
<td>5.65</td>
<td>5.76</td>
<td>6.31</td>
<td>-</td>
<td>5.60</td>
<td>5.67</td>
<td>6.16</td>
<td>6.74</td>
<td>6.82</td>
<td>6.25</td>
<td>5.00</td>
<td>-</td>
<td>6.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.2</td>
<td>(3.12)</td>
<td>1.13</td>
<td>1.13</td>
<td>1.139</td>
<td>1.145</td>
<td>(+2) 0.98</td>
<td>(+2) 1.15</td>
<td>1.16</td>
<td>1.168</td>
<td>1.176</td>
<td>1.184</td>
<td>1.192</td>
<td>1.2</td>
<td>(+2) 1.02</td>
<td>(+2) 1.21</td>
<td>-</td>
<td>1.177</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>918.0</td>
<td>798</td>
<td>931</td>
<td>1021</td>
<td>1042</td>
<td>1074</td>
<td>822</td>
<td>1313</td>
<td>1356</td>
<td>1412</td>
<td>1474</td>
<td>1529</td>
<td>1545</td>
<td>819</td>
<td>1663</td>
<td>1541</td>
<td>1522</td>
<td></td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>3457.0</td>
<td>3426</td>
<td>3512</td>
<td>3068</td>
<td>-</td>
<td>1791</td>
<td>1597</td>
<td>3266</td>
<td>3223</td>
<td>2562</td>
<td>2695</td>
<td>2863</td>
<td>1947</td>
<td>1194</td>
<td>3395</td>
<td>2831</td>
<td>3338</td>
<td></td>
</tr>
<tr>
<td>Heat of Fusion (kJ/Mol)</td>
<td>6.20</td>
<td>5.46</td>
<td>6.89</td>
<td>7.14</td>
<td>-7.70</td>
<td>8.62</td>
<td>9.21</td>
<td>10.00</td>
<td>10.79</td>
<td>11.06</td>
<td>(17.0)</td>
<td>19.90</td>
<td>16.80</td>
<td>7.66</td>
<td>(22)</td>
<td>14.10</td>
<td>11.40</td>
<td></td>
</tr>
<tr>
<td>Heat Capacity at 298K (J/Mol·K)</td>
<td>27.10</td>
<td>26.90</td>
<td>27.40</td>
<td>27.40</td>
<td>(27.3)</td>
<td>29.50</td>
<td>27.70</td>
<td>37.10</td>
<td>28.90</td>
<td>27.70</td>
<td>27.20</td>
<td>28.10</td>
<td>27.00</td>
<td>26.70</td>
<td>26.80</td>
<td>25.50</td>
<td>26.50</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity (W/cm·K)</td>
<td>0.13</td>
<td>0.11</td>
<td>0.13</td>
<td>0.17</td>
<td>(0.15)</td>
<td>0.13</td>
<td>(0.139)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.16</td>
<td>0.15</td>
<td>0.17</td>
<td>0.39</td>
<td>0.16</td>
<td>0.16</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Magnetic Susceptibility (emu/g-atom)</td>
<td>1.01E-04</td>
<td>2.43E-03</td>
<td>5.32E-03</td>
<td>6.56E-03</td>
<td>-</td>
<td>1.28E-03</td>
<td>3.13E-02</td>
<td>3.56E-01</td>
<td>1.93E-01</td>
<td>9.98E-02</td>
<td>7.02E-02</td>
<td>4.41E-02</td>
<td>2.61E-02</td>
<td>7.10E-02</td>
<td>1.79E-02</td>
<td>1.91E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Curie Temperature (°C)</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>17.00</td>
<td>-53.00</td>
<td>-185.00</td>
<td>-254.00</td>
<td>-253.00</td>
<td>-241.00</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>
1.3. Applications of REEs

The unsaturated 4f electronic structure of rare earth elements makes them have special luminescence, magnetism and electronics properties, which could be used to develop many new materials. These properties have now made rare earth elements critical for a diverse and expanding array of high-technology applications, which constitute an important part of the industrial economy of the 21st century. As a matter of fact, rare earths have been listed in the category of strategic elements in many countries, such as the USA and Japan. Presently they are used in almost all guided missile systems, unmanned drones, advanced sonar, secure communication systems, advanced jet aircraft engines, advanced armor, advanced radar, stealth technologies and targeting and triggering systems. Additionally, rare earth metals are important alloying addition to steels. They also play a key role in the green energy sector. Electric and hybrid cars can contain 20-25 pounds of rare earths, which is double that found in a standard gasoline vehicle [6]. The battery itself is made from several pounds of rare earth compounds. REEs are also used in regenerative braking systems and electric traction motors. The motors consist of powerful magnets made from neodymium and dysprosium. REEs are also used to make high capacity wind turbines, advanced solar panels, high efficiency lighting, petroleum and pollution control catalysts for automobiles and high speed rails [6].

Rare earths also hold promising potential in refrigeration and cooling applications, which can help reduce fossil fuel consumption by 15%. They are also being used extensively in fiber optics, advanced electric motors, lasers, X-ray equipment and common modern gadgets like cellphones, computer hard drives, and color televisions. Europium and yttrium, for example, provides red phosphor for televisions and computer monitors and it has no known substitute. Cerium similarly rules the glass-polishing industry. According
to IMCOA (2008), the chief users of rare earth metal by weight are catalysts (68%), ceramics (7%), metal alloys (7%), polishing (5%), glass (5%), magnets (4%) and phosphors (3%) and it is projected by 2014, the major users would be metal alloys (25%), magnets (23%), catalysts (16%), polishing (11%), phosphors (7%) and glass (7%) as shown in Figure 1.3 [16].

These applications of rare earth metals provide opportunities for recycling through strategic end of life management. Many of the applications could provide efficient sources for heavy rare earth elements, which are scarce but critical for development of new technologies. As examples, recycling of compact and linear fluorescent lamps can prove to be a useful source of yttrium, europium and terbium whereas recycling of permanent rare earth magnets used in wind and hydro power generation can become an important secondary source of neodymium, praseodymium, dysprosium and terbium. The elemental content of rare earths in appropriately sized phosphor dust exceeds 5% by total weight.

Figure 1.3: Major users of RE metals.
1.4. Rare Earth Minerals

Rare earths do not naturally occur in their elemental state or as individual rare earth compounds, but rather, as mixtures in rock formations including shales, silicates, basalts, granites, and gneisses. There are about 200 rare earth minerals distributed in a wide variety of mineral classes - oxides, phosphates, carbonates, silicates, etc. [5]. The principal rare earth ores, monazite and bastnaesite, have formed the basis for historical production, with minor contributions from deposits containing xenotime, REE bearing clays (ionic clays), apatite, allanite, euxenite, etc. [6] as shown in (Table 1.2). Rare earth minerals typically contain each of the REEs, but the concentration of each varies greatly by mineral type. Some of the most significant rare earth minerals are found in deposits in China, United States, India, Brazil, South Africa and Australia.

Table 1.2: Significant rare earth minerals found in deposits [5].

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical Formula</th>
<th>REO %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bastnasite</td>
<td>(Ce,La,Pr)(CO(_3)F)</td>
<td>Ce(_2)O(_3) = 36.9 – 40.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(La,Pr,..)(_2)O(_3) = 36.3 – 36.6%</td>
</tr>
<tr>
<td>Euxenite</td>
<td>(Y,Ce,Ca,U,Th)(Ti,Nb,Ta)(_2)O(_6)</td>
<td>(Y,Er)(_2)O(_3) = 18.2 – 27.7%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ce,La,..)(_2)O(_3) = 16 – 30%</td>
</tr>
<tr>
<td>Fergusonite</td>
<td>(Y,Sr,Ce,U)(Nb,Ta,Ti)(_4)</td>
<td>Y(_2)O(_3) = 31 – 42%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ce,La,..)(_2)O(_3) = 0.9 – 6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Er(_2)O(_3) = 0 – 14%</td>
</tr>
<tr>
<td>Gadolinite</td>
<td>(Y,Ce)(_2)FeBe(_2)Si(<em>2)O(</em>{10})</td>
<td>Y(_2)O(_3) = 30.7 – 46.5%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Ce,La,..)(_2)O(_3) = 5.23%</td>
</tr>
<tr>
<td>Loparite</td>
<td>(Na,Ca,Ce,Sr)(_2)(Ti,Ta,Nb)(_2)O(_6)</td>
<td>(Ce,La,..)(_2)O(_3) = 32 – 34%</td>
</tr>
<tr>
<td>Monazite</td>
<td>(Ce,La,..)PO(_4)</td>
<td>(Ce,La,..)(_2)O(_3) = 50 – 68%</td>
</tr>
<tr>
<td>Orthite</td>
<td>(Ca,Ce)(_2)(Al,Fe)(_3)Si(<em>3)O(</em>{12})[O,OH]</td>
<td>Ce(_2)O(_3) = 0 – 6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>La(_2)O(_3) = 0 – 7%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y(_2)O(_3) = 0 – 8%</td>
</tr>
<tr>
<td>Parisite</td>
<td>Ca(Ce,La,..)(_2)(CO(_3))F(_2)</td>
<td>Ce(_2)O(_3) = 26 – 31%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(La,Nd,..)(_2)O(_3) = 27.3 – 30.4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y(_2)O(_3) = 0 – 8%</td>
</tr>
<tr>
<td>Priorite</td>
<td>(Y,Er,Ca,Th)(Ti,Nb)(_2)O(_6)</td>
<td>(Y,Er)(_2)O(_3) = 21.1 – 28.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ce(_2)O(_3) = 3.7 – 4.3%</td>
</tr>
<tr>
<td>Xenotime</td>
<td>YPO(_4)</td>
<td>Y(_2)O(_3) = 52 – 62%</td>
</tr>
</tbody>
</table>
1.4.1. Monazite

Until the discovery of carbonatite-hosted rare-earth deposits, such as Mountain Pass in California, all rare-earth production came from monazite, with beach-sand operations in India and Brazil the leading producers. Monazite is a phosphate mineral and is the second most prevalent source of REEs. It is known to exist in at least four forms, depending on whether Ce, La, Nd or Pr is the principal rare earth component \(((\text{Ce,La,Nd,Pr,Th})\text{PO}_4)\). The rare earth content of pure monazite is approximately 60-62% rare earth oxide (REO), of which 20-30% are cerium oxide and 10-30% are lanthanum oxide [7]. Additionally, yttrium may be found in monazite in amounts upwards of 5% yttrium oxide [5]. Monazite is chemically stable and typically found in placer deposits and beach sands. Its main drawback is its thorium content, with concerns over the potential radioactivity of tailings having effectively rendered it unacceptable as a commercial ore in most parts of the world. There was minor monazite production in Brazil in 2004, according to British Geological Survey data, while Indian production has tailed off completely. Malaysian monazite production comes as a by-product of alluvial tin mining [8].

1.4.2. Bastnasite

Bastnasite, a REE bearing carbonate-fluoride mineral, also has more than one composition, with Ce, La or Y forming the main rare earth constituent \(((\text{Ce,La,Y})\text{CO}_3\text{F})\). Bastnasite is the most prevalent in REE mineral occurrence. It is typically richer in the light rare-earth metals than monazite and thus the primary source of light rare earths. It is usually hosted in carbonatite deposits and is now the main source of world production. It is also present with monazite at Bayan Obo in China, although this is not a carbonatite type deposit. Bastnasite won from Mountain Pass supplied the U.S. market with rare earths for
most of the last 60 years, with small-scale production having resumed in 2008 after a six-year hiatus. Since 1985, production of REE in China has increased dramatically and now China controls more than 90% of the global supply of rare-earth minerals [8].

1.4.3. Xenotime

Xenotime is the third most prevalent source of REEs. It is also a rare-earth phosphate in which yttrium is the major component (YPO$_4$); a number of heavy rare earth elements such as thorium and uranium can replace some of the yttrium in the atomic structure. The REO content of xenotime is mostly HREEs, and thus makes it a major source for HREEs. It is typically found in placer deposits and beach sands since it is usually associated with monazite (0.5-5.0% of the amount of monazite present). The only source of xenotime now is as a by-product from tin mining in Malaysia. However, a significant proportion of the Chinese rare-earth production is sourced from ion absorption clays, which themselves appear to have been derived from the deep weathering of source rocks containing xenotime [8].

1.4.4. REO Primary Production

Commercial production of rare earths began in the 1880's with the mining of the rare earth thorium phosphate mineral monazite in Sweden and Norway. This was to provide material for the production of the incandescent lamp mantle invented by Carl Auer von Welsbach of Austria in 1884. Initially the oxides of zirconium, lanthanum and ytterbium were used [9]. India and Brazil were the principal sources of world rare earth supply, with the United States occasionally contributing, until the late 1940s, when Australia and Malaysia also started regular production. Much of the world rare earth supply between 1950 and 1985 came from the US, the leading producer, and Australia, second
largest producer. However, by 1985, China rose to second place, it overtook the United States in 1988 to become the leading producer. China, the US, the former Soviet Union, Australia, India, Brazil, and Malaysia have all been major rare earth producing countries with South Africa, Canada, Thailand, Sri Lanka, and Zaire occasionally contributing small amounts to the world rare earth production (Figure 1.4).

![Figure 1.4: World REO production (1900 – 2012) and prognosis until 2016 [10].](image)

Monazite was the major rare earth resource from the beginning of the industry until 1965. Thereafter bastnasite production equaled or exceeded monazite production. At present, bastnasite is the world’s major source of rare earths. There is a lot of potential in the production of REO but it is being stockpiled or discarded and that has led to 50% fall in production, and consequently poor investment in mines. The greatest potential for REO
production is in South Africa, which could produce about 41,300 metric tons per year out of the annual production of about 400,000 metric tons. The U.S. could also produce about 32,800 metric tons REO per year, which is over 50% its average annual production in the previous years. China could undoubtedly produce more REO than is reported, for example, by successfully treating Bayan Obo steel slag. There are many new rare earth production projects worldwide that could start within a few years. The highest number of such projects is in Australia.

1.4.5. **Molycorp Mining Operation**

Presently, the only rare earth deposit being mined in the United States is the “Sulphide Queen” carbonatite deposit in Mountain Pass, California, which was discovered in 1949 and is the largest rare earth resource in the United States. This deposit has an overall length of 730 m and width of 120 m and the ore grade is 5-15% bastnasite, 65% calcite, dolomite, or both, and other minor mineral associations including barite, silica, etc [7]. Mining operation at the Mountain Pass deposit began in 1952 and ran almost continuously until 2002, when its permit expired. Mining resumed in 2012 with a target throughput of 972 tonnes/day, which is approximately 20,000 tonnes of REO/year. The Sulphide Queen ore body has been estimated to have approximately 20-47 million tonnes of ore remaining in the deposit [11]. The Mountain Pass process for rare earth production involves ore mining, crushing, floatation and cracking (which involves leaching with HCl) to produce Sorbx, a cerium oxide product. Dowex 50 ion exchange resin is used to remove iron and uranium and solvent extraction is used to separate light and heavy rare earths. With regard to the heavies, they are alkalized, shipped to China, separated and reduced by oxyfluoride molten salt hydrolysis. The light rare earth elements are processed by firstly,
separating lanthanum from neodymium/prasodymium via solvent extraction with 2-ethylheptyl phosphonic acid mono-2-ethylheptyl ester (PC-88a). Neodymium and prasodymium are then separated using solvent extraction with PC-88a and further separated by sedimentation with 39 mixer settlers. A certain quantity of these oxides is shipped to Estonia for further reduction. Hydrochloric acid is recovered using a new chloralkali facility. A high purity rare oxide for lanthanum, cerium, neodymium and prasodymium is produced at Mountain pass.

1.4.6. Lynas Commercial Rare Earth Mine Operation

Lynas Advanced Material Plant (LAMP) has a state-of-the-art-technology and the largest rare earth processing plant in the world covering an area of 100 hectares in Pahang, Malaysia. The rare earths concentrate is delivered to the LAMP in a 2.5 tonnes bulker bag inside shipping containers. The concentrate is safe, non-toxic, and non-hazardous and does not dissolve in water. It is a 40% REO concentrate produced from ore concentrated at Lynas Concentration Plant in Western Australia. The mine site, Mount Weld, is the richest known grade rare earths resource in the world, located 2 km from the Concentration Plant.

Rare earth concentrate processing at LAMP involves three operations - cracking and leaching, solvent extraction and product finishing. During cracking and leaching unit operation, the rare earths concentrate, which is essentially rare earths phosphate mineral, is mixed with concentrated sulfuric acid and cracked at a high temperature in a rotary kiln to convert the rare earth phosphate minerals to rare earths sulfate. Water is then added to rare earths sulfate in the leaching stage and impurities in the form of iron-phospho-gypsum are removed. The solution advances to the neutralization stage to produce the rare earth rich solution as feed to the solvent extraction unit. Solvent extraction employs two liquid phases
and is carried out in liquid-liquid counter current solvent extraction trains. Solvent extraction is divided into two areas, each with three sections: upstream solvent extraction to separate the LREEs (lanthanum, cerium, praseodymium and neodymium) and HREEs (samarium, europium and gadolinium), and downstream solvent extraction to separate the rare earths into groups and individual elements. In the final stage of the process, the REEs are precipitated as carbonates, hydroxides or oxalates. Some are calcined to the respective oxides. The finished products from the LAMP process include lanthanum-cerium carbonate, lanthanum carbonate, cerium carbonate, samarium europium gadolinium and neodymium, praseodymium oxide.

1.4.7. REO Separation and Purification

After the ore is beneficiated, it is chemically treated by means of leaching, ion exchange, and solvent extraction to produce rare earth oxides (REOs), which become the natural starting materials to obtain pure metals by means of reduction. REOs are stable oxides and their direct reduction to metal is difficult. In addition to solvent extraction and ion exchange, REOs can be separated into individual oxides by fractional crystallization, selective oxidation and selective reduction. The separation of a rare earth mixture into individual elements is not an easy task due to the similarity in their chemical and physical properties.

Fractional crystallization is the process of separating the components of a solution on the basis of their differences in solubility. This method is usually most suitable for lanthanides at the lower end of the series [7]. Rare earth solutions are mixed with a salt and then heated. The solutions are then allowed to gradually cool to cause rare earth oxides to crystallize out of solution. In the case of praseodymium and neodymium, ammonium
nitrate salts are commonly used for the separation whereas double magnesium nitrates are
commonly used for the separation of europium, samarium, gadolinium and the ceric group.
Bromates and ethyl sulfates are used in the separation of the yttric group [5].

Selective oxidation can be used to separate cerium, praseodymium and terbium
because they can be oxidized from trivalent state to a tetravalent state, which allows for
separation. The most common oxidizing agents used for these reactions are hypochlorite,
permanganate and persulfates. Air or oxygen is also used as an oxidizing agent [12]. In the
selective oxidation of praseodymium and terbium, Pr$^{4+}$ and Tb$^{4+}$ precipitate as rare earth
oxides because the tetravalent states for praseodymium and terbium are not stable in an
aqueous solution. In aqueous solution rare earths are present in trivalent state. Cerium is
most likely to oxidize to Ce$^{4+}$ and given this property it is the easiest to separate from its
rare earth mixture. In an alkaline solution, Ce$^{3+}$ is readily oxidized to the Ce$^{4+}$ by either
bubbling oxygen or drying the rare earth hydroxide in the presence of air. Ce$^{4+}$ can then be
precipitated from the acidic solution through pH control [5].

Europium, samarium, and ytterbium can be separated by selective reduction
because these rare earth metals can be reduced to a divalent state. McCoy developed the
method commercially used for selective reduction of Eu where Eu$^{4+}$ is reduced to Eu$^{2+}$ by
zinc in a chlorine solution. Eu$^{2+}$ is precipitated from the chlorine solution as a sulfate and is
then dissolved in HCl, to form europium oxide [13]. Samarium and europium can then be
separated by reductive extraction into dilute sodium amalgam [5]. Marsh et al. developed
the commercially used method for the selective reduction of ytterbium and samarium
where rare earth mixtures are placed in an acetate solution.

Rare earth chlorides have lower standard free energy than rare earth oxides.
Therefore, in order to economically reduce rare earth oxides, they are first converted to rare
earth halides, which are then reduced to rare earth metals under less severe conditions. The most common methods used for purification of rare earth metals are shown in Figure 1.5 [14]. Fluoride reduction is widely used for most of the rare earths. It is then followed by vacuum melting and vacuum remelting or vacuum sublimation.

The common method used for rare earth oxide reduction is direct reduction of rare earth oxides, conversion of rare earth oxides to chlorides and reduction of rare earth chlorides, conversion of rare earth oxides to fluorides and reduction of rare earth fluorides and electrolytic preparation of rare earth metals from chlorides and oxide fluorides. Electrolytic process for recovery of rare earth metals accounts for the largest quantity of rare earth production because they are relatively cheaper and less complex as compared to
other reduction mechanisms. Fused salts of rare earth chlorides or a mixture of rare earth oxide and fluorides have been typically used. The obtained rare earth metal is then purified to various degrees.

1.5. **Price of Rare Earth Oxides**

There is a huge demand for rare earth metals in various fast growing sectors: clean energy technologies, colored phosphors, lasers, high intensity magnets, high-tech defense applications and clean energy technologies. Therefore to ensure unhindered technological innovation, it is essential to possess secure supply chains for rare earth elements. Currently, China accounts for 36% of proven world’s reserves and dominates as the producer of over 90% of world output of rare earth minerals [15]. The United States continues to be one of the largest consumers and importer of rare earths and the trend is expected to continue as the demand increases. Since global demand of REEs exceeded supply due to China’s set export quotas, the prices of common metals like Ce, Nd, Sm, La and Y, went up by 150% to 700% within a short period in 2010. North American fluorescent lamp manufacturers reacted to rare earth price escalation by reducing the amount of phosphor used in the lamp, which was enabled by the development of small particle size (3-4 μm) tri-band phosphors. Thus phosphor consumption declined by half in the period 2008-2012 from 720 ktons to 360 ktons.

The average price of rare earths fell in 2012 by about 40% as compared to prices in 2011 (Table 1.3). In order to stop the price fall, firms across China adopted strategies such as production suspensions. However, falling demand in downstream sectors and illegal mining curbed the effects of such strategies. Prices have continued to fall in 2015 partly because of illegal mining in China and producers, notably Lynas Corp. of Australia, took
measures to increase extraction and processing, diminishing China's influence on pricing. However, analysts expect prices to rise gradually in the coming months in tandem with demand, and as labor and environmental costs increase.

Table 1.3: Prices of individual rare earth oxides.

<table>
<thead>
<tr>
<th>Rare Earth Oxide</th>
<th>Freight On Board (FOB) China Average Price*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium Oxide</td>
<td>4.15</td>
</tr>
<tr>
<td>Lanthanum Oxide</td>
<td>5.55</td>
</tr>
<tr>
<td>Praseodymium Oxide</td>
<td>22.25</td>
</tr>
<tr>
<td>Samarium Oxide</td>
<td>22.75</td>
</tr>
<tr>
<td>Europium Oxide</td>
<td>480.00</td>
</tr>
<tr>
<td>Terbium Oxide</td>
<td>350.00</td>
</tr>
<tr>
<td>Dysprosium Oxide</td>
<td>116.50</td>
</tr>
<tr>
<td>Yttrium Oxide</td>
<td>10.25</td>
</tr>
</tbody>
</table>

*Source: metal-pages.com

1.6. REEs as Critical Materials

Despite growing efforts to recycle metals, we fail to recover half of the domestic post-consumer metal scrap reclaimable from end of life products, and we continue to rely on primary metals production to fulfill two thirds of our manufacturing needs. The use of primary metals in lieu of scrap increases global energy consumption and the production of greenhouse gases which can potentially cause global warming. Thus, in order to augment recycling rates the materials community needs to upgrade recovery and recycling processing technologies to maximize the capture of post-consumer scrap and minimize the quantity of manufacturing scrap [14].

In recent years REEs have become strategically critical for both developed and developing economies around the world primarily due to the shortage of discovered minable resources. These developments led to the enactment of the Rare Earths and
Critical Material Revitalization Act of 2010, which aims to establish an R&D program within the U.S. Department of Energy (DOE) to ensure long-term supply of rare earth materials. In order to ensure secure rare earth supply and attenuate supply-demand imbalance post 2014, it is imperative to encourage and support exploration of newer REE reserves, build a rare earth stockpile, challenge China on its export policy and also research recycling and reuse of REEs from secondary sources [17].

According to the U.S. Department of Energy, some of REEs are on the critical material list (Figure 1.6). The criticality of each element depends on the end application demand pattern. The most critical elements were identified to be neodymium, dysprosium, europium, yttrium and terbium - which are known as the heavy rare earth elements in exception of europium [18]. These minerals, with the exception of yttrium are expected to be in short supply over the next 10-20 years. The magnitude and duration of these shortages will mainly depend on the success of REE exploration projects. Therefore various governments and industrial users worldwide have begun to develop strategies to safeguard their REE supplies in order to overcome future supply problems. The criticality of many rare earth metals as assessed by DOE has now made recycling feasible and attractive.

The NSF Center for Resource Recovery and Recycling (CR³) also initiated a research program for developing technologies to recycle rare earth from phosphor dust, which is being carried out at the Colorado School of Mines in partnership with the Worcester Polytechnic Institute. It is anticipated that new projects will be added to look at other waste forms containing rare-earth metals and compounds.
In past years, Global Tungsten and Powders Corporation had a commercial recycling operation of rare earth from end of life fluorescent lamps. Ellis et. al. have reported that recycling of rare earth based materials would have a stabilizing effect on price, supply, and quality [19]. Currently, potential recyclers do not have a large bank of technologies to use when considering recycling waste containing rare earth materials. In addition, there is limited infrastructure for the recycling of rare earth based materials. As a result, there is growing interest in recycling REEs from permanent magnets, lamp phosphors, rechargeable Ni-MH batteries and catalysts.

Extensive research on recycling of rare earths from magnets has been done. Zhong et. al. suggested that 20-30% REE magnets are scrapped during manufacturing stage [20]. Several other researchers have suggested various pyrometallurgical and hydrometallurgical routes to recover REE from these scrapped magnets [21]. Efforts have also been made to recover REE from used Ni-MH batteries. During pyrometallurgical treatment of these
batteries the REEs report to the slag. There have been many hydrometallurgical routes that have been investigated to recover these elements by Zhang et. al. [22], Linyan et. al. [23], and Bertuol et. al. [24]. There hasn’t been much work done in recycling rare earths from catalysts. This may be because catalysts primarily contain low value light rare earths like lanthanum and cerium. However, when the economics of recycling of REE from spent catalysts becomes favorable due to changes in demand, it is expected there will be feasible recovery of these light rare earth elements.

Recycling of rare earths from phosphors provides an efficient way to recover high value heavy rare earth elements. Mei et. al. has provided an overview of various possible recycling methods for recovery of rare earths from fluorescent powder [25]. A comprehensive literature survey shows the extraction of REEs from their mineral deposits (monazite and bastnaesite) in terms of physical beneficiation of the ore, chemical treatment with acidic or basic solutions, solvent extraction or ion exchange and reduction and refining are well studied and documented. Several flowsheets for processing of REEs from their mineral deposits have been developed and used in commercial operations across the world. Some of the flowsheets have been modified and applied to the recycling of REEs from spent florescent lamps. The treatment of the phosphors is similar to the ones used for the processing of REE ores.

1.7. REO Secondary Production

According to the USGS, the world's reserves comprising of rare earths are about 110 million metric tons with China holding around half of it, which gives China the power to control the price of the rare earths since they have their own methods for REE
separation, refining, alloying, fabrication, etc. However, China's cost of production is rising due to low-grade ores, rising labor costs and the growing social and environmental costs.

1.7.1. SepSalsa Process

Narva Light Sources GmbH, a German lighting company in Freiberg, in conjunction with a phosphor dust recycler, FNE Frieberg, and TU Frieberg are currently commercially recycling rare earths from phosphor dust using the SepSelsa process. They use solid-state chlorination of phosphor powder with ammonium chloride to create water-soluble yttrium and europium chlorides [26].

1.7.2. Saint-Fons Process

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 [27]. The Saint-Fons is a commune in the Rhône department in eastern France. The Saint-Fons process begins with the collection of processed and recycled lamp materials. This mixture consists of phosphor dust as well as various sizes of residual glass. The mixture is already void of bigger glass particles, metals and plastic since it is already isolated and recovered by the recyclers. The final mixture goes through a final separation in which glass particles are separated. The recovered phosphor powder is suspended in an aqueous solution in a cylindrical chamber where it undergoes chemical attack. The effluents in this process are treated in another dedicated treatment plant. The treatment plants use one of the best technologies available to treat the effluents. The next step is the liquid-solid extraction in which the powders are retained after separation and then dried. The off gas is treated at a washing and absorption plant. The powder that is produced is sent to the Solvay Plant in La-Rochelle for further thermal and chemical processing [27].
1.7.3. **La-Rochelle Process**

The rare earth concentrate from the Saint-Fons Process is put into ceramic crucibles and placed in a tunnel furnace where it undergoes thermal treatment in order to bring about physical and chemical transformation in the materials to enable recovery of valuable metals. The gas vents are treated in washing columns to remove effluents, which are sent to a treatment plant. The powder that is precipitated is washed and filtered and then attacked with nitric acid. The next step is rare earth separation where the powder passes through batteries that separate the rare earths including lanthanum, cerium, europium, terbium, gadolinium and yttrium. Finally the rare earths goes to the finishing workshops where they undergo precipitation, filtration and calcination.

1.7.4. **Patents for REEs Recovery from Waste Fluorescent Lamps**

Table 1.4 shows some of the US and European patents on the recovery of REEs from waste fluorescent display systems such as fluorescent lamps, cathode ray tubes, screens of color television and monitor.

1.7.5. **Production of Lamp Phosphors**

REEs are used to make phosphors, which are widely used for general illumination (fluorescent lamps) and displays (cathode ray tube, backlights for liquid crystal displays, and plasma display panels). In order to develop efficient recycling routes for waste phosphor, it is imperative to understand how the phosphors are made.

The rare-earth raw materials for the synthesis of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ are highly pure oxides of yttrium and europium. $\text{Y}_2\text{O}_3$ and $\text{Eu}_2\text{O}_3$ are dissolved in hydrochloric acid and coprecipitated as oxalates. The precipitate is oxidized by heating in air and then fired for 1 hour at 1100°C in a hydrogen sulfide atmosphere or a mixture of sulfur and sodium
carbonate. Arsenates, germanates, phosphates, and sulfates of alkaline metals are used as flux. The phosphors obtained is rinsed well, given surface treatment, and pigmented when necessary. The available pigments include cadmium red (Cd(S,Se)) and iron oxide red (Fe₂O₃), but the latter is most widely used for its thermal stability and to avoid environmental pollution [28].

Table 1.4: List of some patents on recovery of REEs from fluorescent lamps.

<table>
<thead>
<tr>
<th>Patents</th>
<th>Name of Patent</th>
<th>Raw Materials</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 4858833</td>
<td>Process for recycling fluorescent and television tubes</td>
<td>Television and fluorescent tubes</td>
<td>Glass and Yttrium compounds</td>
</tr>
<tr>
<td>(1989)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US 005160663A</td>
<td>Fluorescent lamps</td>
<td></td>
<td>Reconstituted phosphors to reuse for lamps</td>
</tr>
<tr>
<td>(1992)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US 5403403</td>
<td>Method for processing fluorescent material</td>
<td>Fluorescent material of coating screen</td>
<td>Fluorescent material for reuse</td>
</tr>
<tr>
<td>(1995)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP 1138741 A2</td>
<td>Method of recycling fluorescent substance for fluorescent lamp, recycled fluorescent lamp and lighting apparatus using thereof</td>
<td>Fluorescent lamps</td>
<td>Glass material and recover fluorescent material for reuse</td>
</tr>
<tr>
<td>(2001)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WO 2007/003722 A1</td>
<td>Cathode ray tubes</td>
<td></td>
<td>Glass and fluorescent powder</td>
</tr>
<tr>
<td>(2007)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP 1817437</td>
<td>Method of extracting europium (iii) and yttrium (iii) from concentrate of lumino-phore dust or sludge</td>
<td>Screens of color TV or monitors</td>
<td>Yttrium and Europium oxides</td>
</tr>
<tr>
<td>(2007)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US 2010/0062673</td>
<td>Method For Integral Recycling For Cathode Ray Tubes</td>
<td>Cathode ray tubes</td>
<td>Glass and fluorescent powder</td>
</tr>
<tr>
<td>(2010)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US 7976798 B2</td>
<td>Method for recovery of rare earths from fluorescent lamps</td>
<td>Fluorescent lamps</td>
<td>RE compounds</td>
</tr>
<tr>
<td>(2011)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE19961017942</td>
<td>Reprocessing rare earth phosphor mixtures from used fluorescent lamps</td>
<td></td>
<td></td>
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<tr>
<td>19960429</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE199991018793</td>
<td>Three-band phosphor, from scrap discharge lamps, is recycled by oxidative mineral acid leaching for impurity removal and carbonate leaching for selective yttrium-europium oxide dissolution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19990426</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RSP20100479</td>
<td>Recovery of basic and precious metals from the fluorescent powders and plant for recovery thereof</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20101108</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The compounds BaCO₃, Mg₄(CO₃)₃OH.3H₂O, and Eu₂O₃ with an appropriate amount of flux material (AlF₂ and BaCl₂) are commonly used as the starting materials to
prepare the blue phosphor, BaMg$_2$Al$_{16}$O$_{27}$:Eu$^{2+}$. The appropriate Eu$^{2+}$ concentration is around 0.1 to 0.2 mole per 2 moles MgO. The mixture is fired at ~1200°C in a slightly reducing atmosphere (for example, 2% H$_2$/N$_2$) for several hours. After cooling in that atmosphere, the sintered cake is reduced to a powder by milling. The sieved powder is fired again under the same conditions as the first firing. In the second firing, a wet gas flow is maintained to yield the most favorable results. The amount of flux to be added influences the hardness of the sintered cake and the particle size of the finished phosphor. The blue phosphor produced has a crystal structure similar to hexagonal β-alumina [28].

The commonly used raw materials for the preparation of the green phosphor, LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$, are La$_2$O$_3$, CeO$_2$, Tb$_4$O$_7$, and (NH$_4$)$_2$HPO$_4$. The optimal Tb concentration is ~ 0.2 to 0.3 mol:PO$_4$. Depending on the application, Ce concentration ranges from 0.15 to 0.4 mol:PO$_4$. Firing is made at 1150 to 1200°C in a slightly reducing atmosphere for several hours. The sintered cake is then milled to produce the powder. The crystal structure of this green phosphor produced belongs to the monazite crystal group [28].

1.8. Recycling Fluorescent Lamp Phosphors

Research on the recycling of rare earths from lamp phosphors is restricted to large fluorescent lamps and compact fluorescent lamps with only few studies currently been carried out yet on the recovery of rare earths from small fluorescent lamps used in LCD backlights or from phosphors used in white LEDs [29]. End of life fluorescent lamps are a rich source of cerium, europium, and terbium, which are optically active because of the presence of 4f electrons. Yttrium and lanthanum are optically inactive due to the absence of 4f electrons.
There are five main rare-earth phosphors found in fluorescent lamps (Table 1.5): the red phosphor \( \text{Y}_2\text{O}_3:\text{Eu}^{3+} \) (YOX), the green phosphors \( \text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+} \) (LAP), \( \text{Gd,MgB}_5\text{O}_{10}:\text{Ce}^{3+},\text{Tb}^{3+} \) (CBT), \( \text{CeMgAl}_{11}\text{O}_{19}:\text{Ce}^{3+},\text{Tb}^{3+} \) (CAT) and the blue phosphor \( \text{BaMg}_2\text{Al}_{16}\text{O}_{27}:\text{Eu}^{2+} \) (BAM). Red, blue and green phosphors are added in different ratio to produce white light.

<table>
<thead>
<tr>
<th>Color</th>
<th>Chemical Formula</th>
<th>Emission Band (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>( \text{BaMg}<em>2\text{Al}</em>{16}\text{O}_{27}:\text{Eu}^{2+} ) (BAM)</td>
<td>452</td>
</tr>
<tr>
<td>Green</td>
<td>( \text{Gd,MgB}<em>5\text{O}</em>{10}:\text{Ce}^{3+},\text{Tb}^{3+} ) (CBT)</td>
<td>542</td>
</tr>
<tr>
<td></td>
<td>( \text{CeMgAl}<em>{11}\text{O}</em>{19}:\text{Ce}^{3+},\text{Tb}^{3+} ) (CAT)</td>
<td>543</td>
</tr>
<tr>
<td></td>
<td>( \text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+} ) (LAP)</td>
<td>544</td>
</tr>
<tr>
<td>Red</td>
<td>( \text{Y}_2\text{O}_3:\text{Eu}^{3+} ) (YOX)</td>
<td>611</td>
</tr>
</tbody>
</table>

Lamps produced by non-Chinese manufacturers can contain about 45% wt% (Figure 1.7) halophosphate phosphor \( (\text{Sr,Ca})_{10}(\text{PO}_4)(\text{Cl,F})_2:\text{Sb}^{3+},\text{Mn}^{2+} \), which is a broadband white emitter. This halophosphate phosphor doesn’t contain any rare earth elements. It is usually mixed with the red phosphor, YOX to obtain good color rendering. Among the individual phosphors used in the lamp, YOX has the highest intrinsic value, because it contains large concentrations of yttrium and europium (about 20 wt%). In lamps with trichromatic phosphors, the concentration of rare-earth oxides can be as high as 27.9 wt% [30]. The recycled lamp phosphors also contain significant amounts of alumina and silica that is used in the barrier layer between the phosphor layer and the glass tube to protect the glass envelope against attack by mercury vapor, and thus prevent mercury depletion and reduction of the lamp lumen output. The barrier layer also improves the efficiency of the lamp by reflecting back the UV light that passes through the phosphor layer to the glass layer [31]. Phosphor dust is generated from fluorescent light bulb wastes after the glass and mercury have been removed.
Figure 1.7: Composition of fluorescent lamp and constituent of phosphor powder [32].

There are two main types of waste fluorescent lamps recycling: dismantling process and shredding technology. Dismantling technology is used for linear tube lamps by cutting of the ends of the tube, and blowing the phosphor powder out (‘‘end cut’’ method). This is predominately used in Europe. The shredding technology is used for other shapes of lamps and especially the compact fluorescent lamps (CFLs). The lamps are crushed and shredded to recover glass cullet, metal (filaments, supply electrodes, caps), plastics (caps, insulators), phosphor powder and mercury (Figure 1.8). Clean glass can be used for the production of new lamps or new glass products while the metal parts are sent to metal recycling facilities and the plastic parts are burnt for energy recovery [31]. Broken glass pieces are separated from the phosphor powder by sieving and gravity separation. This is followed by hot air treatment and Hg vapor is cleaned by active carbon and recycled. At present, this technique has been applied to recycle CFLs in Germany and Japan and most of lamp recycling and treating companies in North America. The crushing method is non-selective, more energy efficient and economical while the end cap method requires more labor and higher operational time to achieve high throughput.
The process of phosphor powder retorting to recover Hg is similar in all operation across North America. The retort volatilizes mercury present in the powder to a gaseous phase under vacuum. The off gases from the retort are captured and routed through a condenser and carbon scrubber system to produce technical grade mercury. The mercury is collected from the condenser, placed in mercury flasks and shipped for purification or packaged for resale. This process isn’t severely energy intensive and gas fired ovens are preferred and much energy efficient compared to the old system of using electric ovens. The mercury specification for the processed phosphor powder is variable but it must pass the TCLP (Toxicity Characteristic Leaching Procedure) test and REE and glass content must be greater than 10 wt% and about 60 wt% respectively for to make commercial

processing of REE from waste lamps economical. The price of the processed powder scrap ranges from $0.50 to $5 per kg based on the glass composition (wt %).

There are 2.4 billion linear fluorescents in use in the US. 1 billion are T-12 lamps (Non REE) and approximately 665 million are discarded per year. Veolia Environmental Services recycles about 27 million lamps per year that produce 1.2 million pounds of phosphor powder per year. The total market for phosphor dust in US is currently 8000 tons per year and is likely to grow significantly as fluorescent lamp fixtures will replace the incandescent light bulbs. Only 30% of the lamps sold per year are recycled (2400 tons per year of phosphor powder). Phosphor dust is generated from fluorescent light bulb wastes after glass and mercury have been removed. Phosphor powders are mainly produced in China but the major manufacturers in U.S. and Europe hold the intellectual property rights.

The dust contains economically recoverable amounts of rare earth metal oxides (REO), estimated at 9.0 to 20.0% of phosphor powder. 7% of the REO demand will be in this application of fluorescent light bulbs and tubes. REE recovery technologies can be divided into three general categories: concentration of metal by physical beneficiation, hydrometallurgical leaching and precipitation as well as potential electrometallurgical or pyrometallurgical processing.

1.8.1. Multistep Method for Recycling REEs from Lamps

The process for recovering REEs from spent florescent lamps include dismantling the lamps mechanically to separate coarse parts, using physical and chemical separation methods to remove the phosphor, hydrometallurgical and pyrometallurgical methods to extract the REEs and recovering them as mixed oxides. The final step is treatment of the
mixed REOs to produce high pure individual REOs. An example of a flowsheet for REE recycling from waste lamps is shown in Figure 1.9.

![Flowchart of the REE separation process](image)

Figure 1.9: Flowchart of the REE separation process [34].

### 1.8.2. Physical Beneficiation

Various methods are being used for the recycling of the different materials fractions of the spent fluorescent lamps. Straight-tube lamps are relatively easy to remove their phosphor air blowing after cutting off both ends (“end cut” method). However, most of such phosphors are of the halophosphate type, and there have limited amounts of the rare earth trichromatic phosphors (red, green, and blue). Recycling of other shapes of lamps and especially the compact fluorescent lamps (CFLs) which contain significant amount of the rare earth trichromatic phosphor is more problematic.
Most of these used lamps are crushed and shredded to recover glass cullet, aluminum/metal materials, phosphor powder, and mercury. The broken glass pieces are separated from the phosphor powder by a wet or dry sieving operation although it is impossible to remove the very fine glass particles. The lamp phosphor fraction can contain up to 50 wt% of glass and constitutes about 3% of the mass of a fluorescent lamp. This glass fraction lowers the intrinsic value of the lamp phosphors, because it dilutes the REEs content and contaminates the feed solutions of separation plant with silicon during REEs extraction at high temperatures [31]. The lamp phosphor fractions can also be contaminated by zinc sulfide phosphors from cathode ray tubes (CRTs) of old color television sets and computer monitors. The zinc sulfide contamination causes problems when the phosphor fractions are dissolved in acids, because highly toxic hydrogen sulfide gas is formed [31].

Depending on the sources of the lamp phosphors, the recycled lamp phosphor fraction contains mainly five rare earth elements: Y, Eu, La, Ce and Tb. The other REEs are largely absent or present in trace amounts. In addition many non-REE elements are present: Ca, P, Si, P in relatively large concentrations, and Ba, Sr, Mg, Mn, Sb, Cl, F, Hg, Pb, Cd in small to trace concentrations. Fe is largely absent in the lamp phosphor fraction but some amount is introduced into the feed during crushing and milling of the lamps. Electrostatic separation for physical beneficiation of lamp phosphor has been tested. The results were poor primarily due to dusting of powders during the test [14].

1.8.3. Physical Separation of Phosphor Powder Mixtures

The separation of lamp phosphors particles by flotation (froth flotation) is possible although not as easy as separation of mineral ore particles, because all phosphor
components are phosphates, oxides, aluminates or borates and thus they are similar in hydrophobicity, and also because the phosphor particle size (5-10 μm) are much smaller than typical mineral particle sizes (~50 μm).

Hirajima et al. have investigated the feasibility of separating lamp phosphor mixtures by flotation using dodecyl ammonium acetate, sodium dodecyl sulfate and sodium oleate as collectors at different pH values. The influence of the dispersant sodium metasilicate was also investigated. At pH values less than 4.5, the blue phosphor was completely dissolved and the halophosphate phosphor could be totally removed from the mixture by flotation, leaving behind the rare-earth phosphor. By using dodecylsulfate as the collector, the halophosphate phosphor could be removed from the froth at pH 9 to 10. They achieved 60 to 80% recoveries of the rare earth phosphors and grade of approximately 80%. They found no conditions to separate the different rare earth phosphors [35].

Jiang et al. have separated individuals red, blue and green rare earth phosphors based on modifying the surface properties. A surfactant was added to make the phosphors hydrophobic and 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 [36].

Flotation experiments have also been conducted on a phosphor dust of particle size less than 75 μm and a total rare earth element (TREE) content of 10.2% using the Denver flotation cell and Cytec’s reagent, AERO 6493 to float apatite from silica in the powder. The rougher float grade increased slightly to 11.3% TREE content and the grade further
increased to 14.5% after the cleaner flotation. The insignificant grade improvement indicates poor selectivity of the collector for REE bearing minerals [14].

Two-liquid flotation is more suitable than froth flotation for the separation of fine particles (< 10 µm) and thus effective for the separation of lamp phosphor particles. The flotation medium consists of a polar solvent (e.g. water or DMF) and a non-polar solvent (e.g. hexane, heptane, octane, nonane) that form two separate phases. The wettability of the particles can be manipulated by means of a surfactant. Separation is achieved by shaking the powder mixture with a mixture of the two immiscible solvents, with a surfactant dissolved in the non-polar solvent. After agitation, the mixture is allowed to settle. One component of the mixture migrates toward the non-polar phase and remains at the interface of two phases, whereas the other component (or a mixture of components) remains in the polar phase [31]. Thus a mixture of red phosphor $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, green phosphor $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ and $(\text{Sr,Ca,Ba,Mg})_5(\text{PO}_4)_3\text{Cl}:\text{Eu}^{2+}$, a less common blue phosphor, could be separated by a two-step two-liquid flotation process, using N,N-dimethylformamide (DMF) as the polar phase and heptane as non-polar phase. The green phosphor was collected at the interface in the first step using dodecyl ammonium acetate as surfactant, and the blue phosphor collected at the interface with sodium 1-octanesulfonate as surfactant, while the red phosphor remained in the DMF phase thereby achieving over 90% recovery and purity for each phosphor [37], [38].

Pneumatic separation of a mixture of lamp phosphor particles in an air stream gave only moderate results, because the differences in particle size have a more pronounced effect on the separation than differences in density between the particles: small heavy particles settle at the same speed as large light particles [39]. A mixture of phosphor particles has been separated in a dense medium (diiodomethane, $\rho = 3.3$ g/cm3) [40]. The
separation of the fine phosphor particles was accelerated by centrifugation and pretreatment of the particles with sodium oleate improved the separation efficiency. However, the process has high cost and the toxicity of diiodomethane is a problem.

It has been proposed to separate the individual phosphors in a mixture by a method based on differences in magnetic susceptibility. Phosphors with a high terbium content such as $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$, $(\text{Gd,Mg})\text{B}_5\text{O}_{12}:\text{Ce}^{3+},\text{Tb}^{3+}$ and $(\text{Ce,Tb})\text{MgAl}_{11}\text{O}_{19}$ are substantially more paramagnetic with respect to the europium-based phosphors or the halophosphate phosphors, and thus they are more strongly attracted towards magnetic fields [31].

1.8.4. Extraction of REEs from reclaimed lamp phosphors

The reclaimed lamp phosphor mixtures are a rich source of REEs, especially the heavy REEs such as yttrium, europium and terbium. However, there is quite a significant loss during phosphor recycling. The concentration of rare-earth oxides in lamps with trichromatic phosphors can be as high as 27.9 wt%, but the actual recycled phosphor fractions contain about 10 wt% of rare earths oxides [30]. In order to recover the rare-earth values, the phosphor mixture has to be chemically attacked to bring the REEs into solution and recovered by precipitation or solvent extraction. Yttrium and europium exist as oxides in the phosphor whereas cerium, lanthanum and terbium occur as phosphates. Therefore the resistance of the different phosphor components towards chemical attack by acids and other chemicals varies widely. For example the halophosphate phosphors and $\text{Y}_2\text{O}_3: \text{Eu}^{3+}$ readily dissolves in diluted acids but the rare earth phosphate phosphor $\text{LaPO}_4: \text{Ce}^{3+}$, $\text{Tb}^{3+}$ (LAP) and the aluminate phosphors $(\text{Ce,Tb})\text{MgAl}_{11}\text{O}_{19}$ (CAT) and $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM) are much more resistant toward attack by acids and difficult to dissolve.
Dissolution of LAP can be achieved by using the same methods for processing of monazite ore, (Ce,La)PO₄ [31].  

Takahashi’s group carried out a series of studies on the hydrometallurgical separation and recovery of rare earths from phosphors in fluorescent lamp wastes [41][42][43]. Sulfuric acid leaching from the rare-earth components was studied under different conditions [44]. After optimization of the leaching conditions, 92% of yttrium and 98% of europium were dissolved at sulfuric acid concentration of 1.5 kmol/m³, temperature of 70°C, leaching time of 1 hour, and pulp concentration of 30 kg/m³. However there was poor dissolution of cerium, lanthanum and terbium.  

Wang et al. have conducted leaching experiments on trichromatic phosphor mixtures and have shown that hydrochloric acid (4 mol L⁻¹) in combination with hydrogen peroxide (4.4 g L⁻¹) is a strong leachant [30].  

Rabah proposed a process for the recovery of europium, yttrium and some valuable salts from spent fluorescent lamps by pressure leaching with a H₂SO₄/HNO₃ mixture at 125°C and 5 MPa for 4 hours and dissolved 92.8% of the europium and 96.4% of the yttrium present in the mixture [45].  

Radeke et al. studied the separation of mercury, calcium, yttrium, and heavy rare earths in disposed fluorescent tubes containing both halophosphate and trichromatic phosphors [46].  

De Michelis et al. carried out leaching tests on phosphor powders with different acids (HCl, HNO₃, H₂SO₄) and ammonia to find the conditions for the most efficient recovery of yttrium [47]. Leaching with ammonia gave very low yttrium recovery, whereas leaching with nitric acid brought the largest quantities of yttrium into solution, although toxic vapors were formed, and leaching with hydrochloric and sulfuric acid gave similar
results. They concluded that leaching with sulfuric acid is to be preferred, since it leads to less co-dissolution of calcium, lead and barium.

OSRAM has developed a process to recover all REEs from spent phosphors [48]. The individual process steps are: mechanical separation of coarse parts, separation of the halophosphates, extraction of RE fluorescent materials readily soluble (Y, Eu oxide), extraction of RE fluorescent materials insoluble in acids (RE phosphates), digestion of the remaining components containing RE (RE aluminates), RE precipitation and final treatment to produce new fluorescent material. Rhodia (Solvay Group) has developed a flow sheet for the recovery of REEs from a mixture of halophosphate and rare-earth phosphors [49]. The phosphors are attacked by hot nitric acid (or hydrochloric acid), and finally by a hot concentrated sodium hydroxide solution or by molten sodium carbonate. The rare earths are recovered from the leach solutions for further separation into the individual elements by a solvent extraction process. Global Tungsten and Powders Corporation also had a commercial operation for recycling rare earth from end of life fluorescent lamps in the USA.

LAP, BAM and CAT phosphors can be chemically attacked by heating them in molten sodium carbonate at 1000°C [50]. YOX dissolves more readily in acids after a mechanochemical treatment using ball milling [51]. The mechanochemical treatment causes disordering of the crystal structures of the phosphor and this allows dissolution under mild conditions. Yttrium, europium, terbium, lanthanum, and cerium were dissolved in 1 kmol/m³ HCl at room temperature after the mechanochemical treatment for 2 hours with more than 80% efficiency [52].

Shimizu et al. have worked on recovering of REEs from lamp phosphors by extraction with supercritical carbon dioxide containing tri-n-butyl phosphate (TBP)
complexes of nitric acid and water [53]. Over 99.5% of the yttrium and europium present in the phosphor mixture was extracted after leaching for 2 hours at 60˚C and 15 MPa. However, control experiments with TBP/HNO$_3$/H$_2$O at atmospheric pressure could only extract less than 40% of yttrium and europium.

Yang and co-workers showed that salting-out agents increase the efficiency of solvent extraction process. They found out that the large amount of Al$_2$O$_3$ present in the phosphor mixture (from the barrier layer) is an advantage if the phosphors are dissolved in nitric acid, because the Al(NO$_3$)$_3$ that is formed can act as a salting-out agent for the extraction of rare earths from the aqueous phase to an organic phase by solvent extraction [54].

Dupont have a method of separating individual phosphors with ionic liquids [55]. They used pure amounts of red, blue, green, and halophosphate phosphors to demonstrate the viability of the process on a large scale. The three-stage process involves firstly, adding all the phosphors to the ionic liquid to dissolve the red phosphor, Y$_2$O$_3$:Eu$^{3+}$. The ionic liquid used is betainium bis(trifluoromethylsulfonyl) imide, [Hbet][T$_2$N]. Secondly, a stoichiometric amount of oxalic acid is used to precipitate the europium and yttrium oxalate. The mixture is filtered to separate the ionic liquid from the precipitate and the ionic liquid is regenerated. The mixture is calcined to recover the red phosphor with a purity of over 99.9%. The process generates only CO$_2$ as by product. The process has yielded good results but there are some inherent problems with this process, which makes it not industrially relevant. Some of the problems include high cost of ionic liquids, low thermodynamic stability of ionic liquid and low throughput of ionic liquid separation processes.
1.8.5. Separation by Solvent Extraction and Ion Exchange

Separation of REEs is very difficult due to the small difference in ionic radius, the preference for interaction with hard-sphere base donor atoms and the dominance of the trivalent oxidation state across the lanthanide series [56]. Methods such as fractional crystallization or precipitation, ion-exchange, selective oxidation/reduction and solvent extraction were developed for individual separation of REEs. Fractional crystallization and fractional precipitation are slow and tedious methods that were used in the past and have been replaced by solvent extraction and ion exchange. Solvent extraction and ion exchange separations are based on the lanthanide contraction – the decrease in ionic radius across the lanthanide series of elements, from lanthanum to lutetium [57]. Therefore, heavy members of the series will create stronger bounds with solute and solvent molecules compared to light members [58], and this allow preferential binding to ion exchange resins, or extraction of the complex into the organic phase [57]. In order to obtain pure rare earth metals (REM), solvent extraction can be used followed by the precipitation of the metals and calcination of the precipitate. Di-(2-ethylhexyl) phosphoric acid (DEHPA) can be used as an extractant for yttrium leaving europium in the raffinate, which can be further removed by selective precipitation or by solvent extraction.

Takahashi et al. have studied the separation of rare earths in phosphor wastes by chelating resins after a two-step leaching process. Iminodiacetic acid and nitrilotriacetic acid-type resins were used for the mutual separation of the (Y, Eu) and (La, Ce, Tb) fractions, respectively. After oxalate precipitation and calcination, each rare-earth oxides were obtained with yields as follows: 50% Y (99.8% purity), 50% Eu (98.3% purity), 30% La and (96.0% purity), 30% Ce and (87.3% purity), and 90% Tb (91.8% purity) [41]. They applied solvent extraction with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-
88A) in kerosene to achieve separation between yttrium and europium from the (Y, Eu) fraction. Mutual separation was achieved by the combination of countercurrent 6-stage extraction and 4-stage stripping using small-scale mixer settlers. The purities of yttrium and europium in the obtained oxides were, respectively, 99.3% and 97% with a total rare-earths yield of 65% [42]. They also studied solvent extraction separation of yttrium and europium from the same leach liquor without precipitation step; that is, yttrium was initially extracted at pH 1.5 and then europium was extracted at pH 2.0 which allowed the extraction of impurities. They obtained the purities of 99.7% for \( \text{Y}_2\text{O}_3 \) and 90% for \( \text{Eu}_2\text{O}_3 \) [43].

Nakamura et al. (2007) studied solvent extraction separation of rare earths and alkali earths using 2-ethylhehyl phosphonic acid mono-2-ethylhehyl ester (PC-88A) in kerosene using the leaching solution of phosphor wastes according to Figure 2.0 [59]. Extraction equilibrium constant for each element was initially obtained assuming the stoichiometry for trivalent rare-earth ions (and \( \text{Al}^{3+} \)) and for alkali-earth ions (\( \text{M}^{2+} \)) as shown in the equation:

\[
\text{M}^{2+} + 3H_2L_{2\text{org}} = M(HL_2)_2(H_2L_2)_{\text{org}} + 2H^+
\]

They then simulated the extraction and scrubbing behavior from the leaching solution of phosphor waste by the equilibrium model for the multicomponent and multistage system. They focused on the selective recovery of europium, terbium and yttrium and established that the effective separation and recovery of these rare earth metals (REMs) is possible in two steps, in a counter-current mixer-settler cascade. Recovery percentages from the leaching solution and the corresponding metal purities were: 97.8% for yttrium (98.1% purity), 52.8% europium (100% purity) and 58.1% terbium (85.7% purity).
Trimethylbenzylammonium chloride has been used to extract the metals from the thiocyanate solution generated after sulfuric acid leach on fluorescent phosphor powder. Maximum extraction was attained at 80°C and extraction percentages of 98.8% (yttrium)
and 96.5% (europium) were achieved using a 2:1 solvent:water molar ratio. The metals in the organic phase were recovered as nitrate salts using N-tributylphosphate in nitric acid. Using 1 M nitric acid at 125°C, a stripping extent of 99% was achieved. The two nitrates were separated by dissolving in ethyl alcohol, in which only yttrium nitrate is soluble. The metals were obtained by thermal reduction using hydrogen at 850°C (for europium) and 1575°C (for yttrium). A metal separation factor of 9.4 was achieved and economic estimations showed that the method could be applied industrially [31].

Mei et al. has proposed a process to efficiently separate artificial mixtures of red, blue and green phosphors by solvent extraction. 2 thenoyltrifluoroacetone (TTA) dissolved in heptane was used to extract the blue powder at alkaline pH. Potassium sodium tartrate (PST) and Na₂CO₃ were used as regulators [60]. In a second step, chloroform was used to extract the green phosphor into the organic phase, leaving the red phosphor in the aqueous phase. Results of the experiment show that the blue phosphor can be extracted selectively into TTA at pH values from 7 to 11. The blue and green phosphors can be extracted into chloroform, with more than 90% recovery at pH values from 7 to 11, leaving the red phosphor in the aqueous phase. TTA was used to extract the blue phosphor. Extraction of red phosphor from the three phosphor mixtures was carried at room temperature and the optimal conditions were found to be: neutral pH, PST concentration from 0.5% to 1.0%, 1-pentanol/chloroform (by volume) in the range of 0.2-0.5%, solid/liquid 5-30 g/L. The grade and recovery of the separated products were as follows: red was 96.9% and 95.2% respectively, blue was 82.7% and 98.8% respectively, and green was 94.6% and 82.6% respectively.
CHAPTER 2

ANALYTICAL TECHNIQUES AND EXPERIMENTAL METHODS

This chapter summarizes the main analytical techniques and experimental methods utilized in this project. The principle of operation of these techniques and methods will be discussed in this section.

2.1. Analytical Techniques

The main analytical techniques used in the experiments were:

1. Microtrac Particle Size Analyzer
2. QEMSCAN
3. X-ray Diffraction (XRD)
4. X-ray Fluorescence (XRF)
5. Field Emission Scanning Electron Microscopy (FE-SEM)
6. Induced Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

2.1.1. Microtrac Particle Size Analyzer

The Microtrac particle size analyzer gives an accurate understanding of the particle size distribution in samples using the patented tri-laser technology. The system consists of three lasers and two detector arrays that are used to take a measurement of scattered light over a 180-degree spectrum. The resultant scattered light information from all three lasers is combined to generate the particle size distribution. Samples were analyzed for particle size distribution using a beam with a wavelength of 0.6328 \( \mu \text{m} \). Large particles produce a scattered light pattern with low angles and high intensity whereas smaller particles produce wide angles and low intensities.
2.1.2. QEMSCAN

QEMSCAN is an acronym for Quantitative Evaluation of Minerals by Scanning Electron Microscopy. It is a registered trademark owned by the FEI Company. It is configured to measure mineralogical variability based on chemistry at the micrometer-scale. QEMSCAN consists of a base scanning electron microscope, equipped with four light element energy dispersive X-ray detectors, a microanalyser and proprietary software controlling automated data acquisition. QEMSCAN utilizes both the back-scattered electron (BSE) signal intensity as well as an Energy Dispersive X-ray Signal (EDS) at each measurement point to create a mineral composition map. QEMSCAN data includes information on mineral and chemical assay, grain size and shape, mineral association, liberation, porosity, matrix density and elemental deportment. Each sample was split into representative aliquots using a rotary micro-riffler. Approximately 1 g split per sample was mixed with epoxy resin in 30 mm molds and left to cure. Sample blocks were ground and polished using water-based lubricants and suspensions finishing with a 1.0 µm diamond polish to obtain a flat surface for X-ray analysis. Samples were then carbon-coated to establish an electrically conductive surface. QEMSCAN analysis was carried out in Particle Analysis (PMA) mode at 2.5 µm resolution using standard operating conditions, i.e. accelerating voltage of 25 kV, specimen current of 5 nA, stage height of 20 mm and a working distance of 22 mm.

2.1.3. X-ray Diffraction (XRD)

X-rays with a relatively low wavelength of up to 0.1 Å (comparable to the size of an atom), are used to probe the crystal structure of materials or minerals. The X-rays are produced using X-ray tubes or synchrotron radiations and the interaction of the X-rays with
the electrons in the sample generates an analysis of crystal structure as well as the phases present. When an X-ray beam is made incident on an atom, the constituting X-ray photons may either be deflected elastically without a change in wavelength (Thompson Scattering) or in-elastically with a change in wavelength due to loss of energy (Compton Scattering). These diffracted beams interact with each other, which produces a resultant intensity modulation. By measuring the diffraction pattern, the user can evaluate the distribution of atoms in the crystal, as the diffracted beam will contain sharp interference peaks with same symmetry as the atomic distribution. This relationship is governed by Bragg’s Law, which establishes a relationship between scattering of an X-ray beam with respect to inter-atomic spacing and the angle of incidence:

\[ \lambda = 2 \ d \ Sin \ \theta \]

Where “\(d\)” is the inter-atomic distance in the crystal lattice, “\(\lambda\)” is the X-ray wavelength, and \(2\theta\) is the angle between incident and scattered beam. The incident angle and scattered angle are varied throughout the analysis as the X-ray source and detector are rotated about a fixed axis as shown in the Figure 2.1. X-ray diffraction was used to characterize the incoming feed material, the leach residue and the precipitation product.

Figure 2.1: A schematic diagram showing the operation of XRD.
2.1.4. **X-ray Fluorescence Spectroscopy (XRF)**

XRF is a phenomenon widely used for chemical and elemental analysis of materials. The principle of operation is a consequence of changes that take place within an atom resulting in the emission of characteristic secondary X-rays from a material that has been excited by bombarding with high-energy X-rays. When a high-energy incident X-ray collides with an atom an electron is ejected from a low energy level and a space is created and an electron from a higher energy level falls into this space. The energy difference as the electron moves between these levels is released as secondary (or fluorescent) X-rays which are characteristic of the element.

2.1.5. **Field Emission Scanning Electron Microscope (FE-SEM)**

The morphology and composition of the particles in the phosphor powder and precipitation products were examined using JEOL JSM-7000F Field Emission Scanning Electron Microscope (FE-SEM) with EDAX Genesis EDS, EBSD capabilities. The basic operating steps for all electron microscopes is that a stream of high-energy electrons is generated in high vacuum, which is then focused into a thin and monochromatic beam using metal apertures and magnetic lenses. The focused beam is accelerated towards the specimen being analyzed. The electron beam interacts with the material and these interactions are detected and transformed into an image. The different types of interactions possible are illustrated in the Figure 2.2. The incident electron beam interacts with electrons in the specimen, which are then excited and undergo various elastic and inelastic collisions. Excited electron with sufficient energy may escape the surface and these are what constitute the Secondary Electrons. The strongest region of interaction between the
incident beam and material is due to secondary electrons and the mount of secondary electrons generated depends largely on the topography of the material.

![Scheme of electron-matter interaction from impact of onto material.](image)

Figure 2.2: Scheme of electron-matter interaction from impact of onto material.

Backscattered electrons (BSE) are the original incident electrons, which are scattered by large angles as they pass through the atoms of the material or sample. The yield of backscattered electrons is material dependent. BSE was utilized to detect the contrast between areas with different chemical compositions, since heavy elements (with high atomic number) backscatter electrons more strongly than light elements (with low atomic number), which make them brighter in the image. Thus using the BSE approach, there is a direct correlation between the atomic number of the element and the color of the particles. Elements with high atomic weight appear brighter since they have high electron density (cross section for scattering effect), which leads to high interaction with the electron beam. Thus there are more backscatter electrons that result in a brighter contrast.
2.1.6. **Induced Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)**

ICP-OES is one of the most common techniques for elemental analysis due to its high specificity, multi-element capability and low detection limits. ICP-OES consists of a plasma source, spectrometer and a multi-element detector as shown in Figure 2.3.

![Figure 2.3: Schematic of ICP-OES.](image)

Different kinds of dissolved samples can be analyzed, varying from solutions containing high salt concentrations to diluted acids. The plasma source produces free electrons and highly charged ions (plasma) temperatures in the range of 7000 to 10,000 K. The plasma is used to produce strong atomic emission from all elements in the sample by dissociating the sample into its constituent atoms or ions, exciting them to a higher energy level. They return to their ground state by emitting photons of a characteristic wavelength depending on the element present. Each excited element emits specific wavelengths $\lambda$, which has a typical emission spectrum. The intensity of the radiation is proportional to the element concentration. The emitted light is recorded by an optical spectrometer, a multi-component part containing mirrors, prism etc. The spectrometer separates the specific wavelengths of interest.

REE have considerably widespread emission spectra within the detection range of ICP-OES. Cerium has more emission lines than any other element, and many of the REE emission lines are closely spaced in the spectral window of ICP-OES leading to...
considerable interference from the REE on other elements, especially other REE’s. Therefore since the atomic emission lines are very narrow lines, a high-resolution detector is essential. Most often a Charge Couple Device (CCD) is used, which provides both high resolution and simultaneous detection which makes it possible to measure all elements of interest at the same time. Simultaneous detection is advantageous because it limits signal variations introduced by sample preparation. When calibrated against standards, ICP-OES provides a quantitative analysis of the original sample.

2.2. Experimental Methods

A brief description of the various experimental methods used in this project is presented in this section. The methods used were dry and wet sieving, leaching, precipitation and lithium borate fusion for sample preparation for ICP-OES.

2.2.1. Dry and Wet Sieving

The set up for sieving is shown in Figure 2.4. Dry sieving method consists of placing the desired sieves in order of decreasing Tyler mesh opening and a vibrating motor to aid the particles to pass through the mesh. The fraction of feed passing the desired mesh is collected in the pan and used for leaching experiments. In the case of wet sieving, a slurry of the feed material was made and poured onto a 10” nylon cloth squares with opening sizes of 10 and 20 µm.

<table>
<thead>
<tr>
<th>32</th>
<th>42</th>
<th>60</th>
<th>80</th>
<th>115</th>
<th>270</th>
<th>325</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.4: Sieve configuration used for sieve analysis.
2.2.2. Batch Leaching

Batch leaching experiments were conducted to establish operating conditions for the leaching experiments. Based on literature review, HCl, H$_2$SO$_4$, HNO$_3$ were used as leaching reagent. The leaching parameters or variables tested were:

1. Acid Concentration
2. Temperature
3. Time
4. Solid to Liquid Ratio (S/L)
5. Agitation speed

The solution was heated to the desired temperature on a hot plate and a magnetic stirrer was added to aid agitation. A weighed sample of the feed material was added to the heated solution and the mixture agitated for the desired time. The amount of sample added was governed by the needed solid-liquid ratio (S/L) or pulp density. The leached residue was filtered, washed and dried for elemental analysis by ICP-OES.

2.2.3. Precipitation

Precipitation experiments were conducted and pH adjustments were done using sodium hydroxide with oxalic acid as precipitant. A pH meter was used to observe the pH changes. The solution was then stirred for 2 hours to allow time for the rare earth elements to precipitate. The solution was then filtered and the residue (mixed rare earth oxalates) was dried and calcined at 900°C to produce the mixed rare earth oxide powder, which was then digested with the lithium borate fusion method before analyzed for the rare earth content with ICP-OES.
2.2.4. Lithium Borate Fusion

Fusion is a method used to solubilize an oxidized sample in a molten flux at temperatures of around 1000°C - 1100°C. It does not consist of heating the sample to its melting temperature, but rather having the oxidized samples dissolved into a solvent, generally a lithium borate flux above their melting temperature but not exceed 1100°C. Thus for optimal dissolution, the right flux composition must be used. Two basic formulations, lithium tetraborate (LiT or Li₂B₄O₇, m.p. 920°C) and lithium metaborate (LiM or LiBO₂, m.p. 845°C) are commonly used in various proportions.

Samples are mixed with 1 g of flux (LiM and LiT, 60:40 wt%) and 2-3 drops of lithium borate (20 mg/L) are added as a non-wetting agent before fused in a Muffle furnace at 1000°C for 45 minutes. The molten melt is immediately poured into a solution of 5% nitric acid and stirred continuously until completely dissolved (~20 minutes) for ICP-OES analysis.
CHAPTER 3
PHOSPHOR POWDER CHARACTERIZATION

Waste phosphor powder samples were obtained and characterized for specific mineralogical and metallurgical parameters. The powder characterization was the starting point to identify potential recycling schemes for waste lamp phosphors.

3.1. Microtrac Particle Size Analysis

The feed samples were all analysed for particle size distribution using the microtrak particle size analyser. Cumulative particle size distribution shows the phosphor powder size ranges from 1 to 700 μm (Figure 3.1).

Figure 3.1: Cumulative particle size distribution of the three feed materials.
A comparison of the size distribution of the three feed materials shows the Veolia feed is much coarser than AERC and Graham Lab feed. The Veolia feed has a \( P_{80} \) of 228.2 \( \mu m \) where as the \( P_{80} \) for AERC and Graham Lab feed are at 148 \( \mu m \) and 176 \( \mu m \) respectively. The Veolia feed was chosen for further experimental work since they are a sponsor of this research work.

3.2. QEMSCAN Analysis

The feed material was analyzed at the QEMSCAN facility at Colorado School of Mine to obtain valuable mineralization information. The aim of the analyses are:

1. Quantify the modal mineralogy;
2. Calculate the particle size distribution;
3. Calculate the grain size distribution;
4. Quantify the locking and liberation characteristics;
5. Quantify mineral associations in the samples.

3.2.1. Modal Mineral Abundance

The feed phosphor powder consists mainly of broken coarse and fine glass, which is obtained from crushing the waste fluorescent lamp tubes (Figure 3.2). Table 3.1 also shows the mass distribution of the constituents of the powder. It consists predominantly of quartz (54.30%) in addition to significant amounts of apatite (16.64%) and Y-bearing minerals (14.98%), small quantities of calcite (4.75%) and monazite (3.45%). The remainder of the material consists of minor concentrations of xenotime, iron oxide, barite, celestine (Sr), phosphate group, europium and terbium bearing minerals and corundum. The rare earth element-bearing phases are monazite ((Ce, La, Nd) PO₄), xenotime (YPO₄) and (Y, Eu, Tb) bearing minerals.
Figure 3.2: Modal mineral abundance in the Veolia feed phosphor dust.

Table 3.1: Mineral distribution (volume %) in Veolia feed phosphor dust.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Abundance (volume %)</th>
<th>Mineral Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monazite</td>
<td>3.45</td>
<td>(Ce, La, Nd)PO₄</td>
</tr>
<tr>
<td>Xenotime</td>
<td>0.56</td>
<td>YPO₄</td>
</tr>
<tr>
<td>Calcite</td>
<td>4.75</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Apatite</td>
<td>16.64</td>
<td>Ca₅(PO₄)₃(OH, F, Cl)</td>
</tr>
<tr>
<td>Quartz</td>
<td>54.3</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Mn Oxides</td>
<td>0.01</td>
<td>MnO</td>
</tr>
<tr>
<td>Fe Oxides</td>
<td>0.12</td>
<td>Magnetite/Hematite/Goethite</td>
</tr>
<tr>
<td>Barite</td>
<td>0.34</td>
<td>BaSO₄</td>
</tr>
<tr>
<td>Celestine (Sr)</td>
<td>0.93</td>
<td>SrSO₄</td>
</tr>
<tr>
<td>Y-bearing minerals</td>
<td>14.98</td>
<td>Minerals containing Y</td>
</tr>
<tr>
<td>Phosphate Group</td>
<td>0.99</td>
<td>Phosphate-bearing minerals</td>
</tr>
<tr>
<td>Tb-bearing minerals</td>
<td>1.01</td>
<td>Minerals containing Tb</td>
</tr>
<tr>
<td>La-bearing minerals</td>
<td>0.13</td>
<td>Minerals containing La</td>
</tr>
<tr>
<td>Ce-bearing minerals</td>
<td>0.24</td>
<td>Minerals containing Ce</td>
</tr>
<tr>
<td>Eu-bearing minerals</td>
<td>0.21</td>
<td>Minerals containing Eu</td>
</tr>
<tr>
<td>Corundum</td>
<td>0.35</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Cuprite</td>
<td>0.26</td>
<td>Cu₂O</td>
</tr>
<tr>
<td>Other Minerals</td>
<td>0.71</td>
<td>Unidentified pixels</td>
</tr>
</tbody>
</table>
3.2.2. Particle Size Distribution

Particle size distribution shows mineral size ranging from <10 μm to >75 μm (Figure 3.3) and 60% of the number of particles in the phosphor dust are less than 10 μm (Figure 3.4). The analysis also shows that 80% by volume of the material is characterized by a particle size greater than 75 μm ($P_{80}$) which is due to the presence of glass in the powder that concentrates in the highest size-classes. As expected, the particles larger than 75 μm occupy more volume in the powder. These large particles is mainly compose of the coarse glass.

Figure 3.3: Cumulative particle size of Veolia feed.
3.2.3. Grain Size Distribution and Mineral Associations

Grain size distribution shows mineral size ranging from >10 μm to >75 μm (Table 3.2). Assessment of the grain size distribution and grain size pictures (Figure 3.5) of the rare earth element-bearing minerals show that they are all less than 30 μm in size with the majority being less than 10 μm (over 60%). Europium, lanthanum and cerium bearing minerals are less than 15 μm. Among the main gangue mineral, apatite is larger than 50 μm and the bulk of calcite, celestine (Sr) and quartz are larger than 75 μm.

Therefore, there is a huge disparity in the particle size of the valuables (REE bearing minerals) and the gangue minerals and this size differences can be exploited in developing efficient recycling REE technology from waste end of life lamps.
Table 3.2: Grain size distribution of minerals in the Veolia feed.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Size Range (µm)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;10</td>
<td>15 - 20</td>
</tr>
<tr>
<td>Apatite</td>
<td>32.43</td>
<td>47.04</td>
</tr>
<tr>
<td>Barite</td>
<td>62.25</td>
<td>33.94</td>
</tr>
<tr>
<td>Calcite</td>
<td>7.70</td>
<td>8.22</td>
</tr>
<tr>
<td>Ce bearing</td>
<td>84.53</td>
<td>15.47</td>
</tr>
<tr>
<td>Celestine</td>
<td>7.62</td>
<td>4.39</td>
</tr>
<tr>
<td>Corundum</td>
<td>67.94</td>
<td>27.73</td>
</tr>
<tr>
<td>Cuprite</td>
<td>27.24</td>
<td>22.70</td>
</tr>
<tr>
<td>Eu bearing</td>
<td>95.96</td>
<td>4.04</td>
</tr>
<tr>
<td>Fe oxides</td>
<td>29.45</td>
<td>25.42</td>
</tr>
<tr>
<td>La bearing</td>
<td>98.69</td>
<td>1.31</td>
</tr>
<tr>
<td>Mn oxides</td>
<td>40.00</td>
<td>15.00</td>
</tr>
<tr>
<td>Monazite</td>
<td>76.12</td>
<td>23.06</td>
</tr>
<tr>
<td>Other minerals</td>
<td>42.64</td>
<td>8.95</td>
</tr>
<tr>
<td>Phosphate Grp.</td>
<td>88.55</td>
<td>10.96</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.61</td>
<td>3.90</td>
</tr>
<tr>
<td>Tb-bearing</td>
<td>84.52</td>
<td>14.53</td>
</tr>
<tr>
<td>Xenotime</td>
<td>51.41</td>
<td>37.02</td>
</tr>
<tr>
<td>Y-bearing</td>
<td>51.97</td>
<td>41.11</td>
</tr>
</tbody>
</table>

Figure 3.5: Grain size image of minerals in the Veolia feed.
3.2.4. Locking and Liberation Characteristics

Liberation and locking data (Table 3.3) shows high level of liberation for the main REE-bearing and gangue minerals: Y-bearing mineral (64.47%), monazite (53.08%), apatite (61.47%), calcite (59.14%) and quartz (87.39%). However, these results seem inaccurate because a look at the liberation of quartz as a function of its particle size (Figure 3.6) shows there are significant middling and locked particles, which is greater than (12.61%). A mineral is completely liberated if over 90% of the particle consists only of the respective mineral and a mineral is ‘locked’ if its area is less than 30% in the entire particle, everything else is called ‘middling’. These numbers do not reflect how easy it is to liberate a mineral by grinding the material or other mineral processing methods.

High levels of liberation were obtained because since liberation is based on the %volume of all particles of the mineral, the large liberated particles exhibit a controlling effect on the total liberation of that mineral. Furthermore there are fine rare earth particles attached to quartz that are considered “locked” even though they can easily be separated from the glass.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Volume %</th>
<th>Liberated</th>
<th>Middling</th>
<th>Locked</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-bearing</td>
<td>64.47</td>
<td>24.41</td>
<td>11.12</td>
<td></td>
</tr>
<tr>
<td>Apatite</td>
<td>61.47</td>
<td>30.84</td>
<td>7.69</td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>59.14</td>
<td>38.10</td>
<td>2.76</td>
<td></td>
</tr>
<tr>
<td>Ce bearing</td>
<td>31.16</td>
<td>37.21</td>
<td>31.63</td>
<td></td>
</tr>
<tr>
<td>Celestine</td>
<td>0.18</td>
<td>90.97</td>
<td>8.84</td>
<td></td>
</tr>
<tr>
<td>Monazite</td>
<td>53.08</td>
<td>32.65</td>
<td>14.26</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>87.39</td>
<td>11.78</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>Eu-Bearing Minerals</td>
<td>21.56</td>
<td>37.06</td>
<td>41.37</td>
<td></td>
</tr>
<tr>
<td>La-bearing mineral</td>
<td>31.81</td>
<td>30.94</td>
<td>37.25</td>
<td></td>
</tr>
<tr>
<td>Tb bearing minerals</td>
<td>27.07</td>
<td>45.13</td>
<td>27.80</td>
<td></td>
</tr>
</tbody>
</table>
The mineral association data (Figure 3.7) shows that the gangue minerals display a moderate association with each other. The majority of HREEs are carried by xenotime and \((Y, \text{Eu}, \text{Tb})\) bearing minerals, and the LREEs by monazite and phosphate group minerals. Calcite shows a weak association with the REE carriers but quartz and apatite have strong association with the HREE carries. Therefore the HREE carriers must be separately concentrated and processed together to maximize the HREE recovery. The distinction of the REE carriers is critical in the metallurgical recovery of the HREE and LREE.
3.3. X-ray Diffraction Analysis

X-ray diffraction was carried out to determine the phases of the minerals present in the Veolia feed powder (Figure 3.8). The major phases identified were fluoroapatite, yttrium oxide, wakefieldite ((La, Ce, Nd, Y)VO$_4$), calcite (CaCO$_4$), monazite ((La, Ce)PO$_4$), and quartz (crystalline SiO$_2$), which could be due to an incomplete fusion of the silica sand (> 98% quartz) used for production of the lamp glass.

Quartz concentrates is barely present in the feed material despite the presence of SiO$_2$ in the feed as revealed by visual inspection and by chemical analysis because the bulk of SiO$_2$ is present as glass which being amorphous is undetectable by X-ray analysis. Yttrium oxide, monazite, and wakefieldite that contain most of REE concentrate are also present in the finest particles present in the powder. There are other REE bearing phases which were undetected by XRD.
Figure 3.8: XRD pattern for phase identification in Veolia feed material. F: fluoroapatite; Y: yttrium oxide; V: wakefieldite; C: calcite; M: monazite; Q: quartz.

3.4. XRF Analysis

The chemical composition of the Veolia feed was analysed with XRF to determine the content of the powder. Table 3.4 shows CaO and P$_2$O$_5$ are present in higher concentration, which is due to the predominant presence of calcium and phosphorus bearing phases.

SiO$_2$, Na$_2$O and K$_2$O are present due to the glass splinters coming from the fluorescent lamps, which are dragged into the powder during dismantlement. Yttrium was the predominant REE (9.77 wt %), while terbium (0.59 wt %) was the REE with the lowest concentration.
Table 3.4: Chemical composition of Veolia feed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Dry solid (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>20.53 ± 3.11</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>21.12 ± 3.40</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.89 ± 0.92</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.40 ± 0.12</td>
</tr>
<tr>
<td>SiO₂</td>
<td>24.73 ± 0.85</td>
</tr>
<tr>
<td>CuO</td>
<td>0.32 ± 0.12</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.43 ± 0.04</td>
</tr>
<tr>
<td>Na₂O</td>
<td>5.33 ± 0.86</td>
</tr>
<tr>
<td>NiO</td>
<td>0.07 ± 0.12</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>MgO</td>
<td>1.11 ± 0.01</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>1.76 ± 0.39</td>
</tr>
<tr>
<td>Eu₂O₃</td>
<td>0.73 ± 0.29</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>1.74 ± 1.18</td>
</tr>
<tr>
<td>Tb₂O₃</td>
<td>0.59 ± 0.22</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>9.77 ± 1.95</td>
</tr>
</tbody>
</table>

3.5. FE-SEM EDS Analysis

The surface morphology of particles in the phosphor powder was detected with FE-SEM BSE. The micrograph was obtained with a zoom of 500x (Figure 3.9) and the elemental composition of the powder at the listed pointed as shown in Table 3.5 was obtained with EDS.

The EDS analysis gives information about the elemental composition and distribution of the elements in the powder. The micrograph shows the particles have different shape and size. The lighter fraction is heavier by atomic weight and thus enriched with the REEs. The darker fraction is comprised of lower atomic weight elements such as silicon, calcium, aluminum, and phosphorus. FE-SEM EDS shows the presence of calcium halophosphate phosphor at point 6, whereas point 1, 5 and 8 represents red, blue and green
rare earth phosphors (Table 3.5). Point 2 and 7 show a combination of calcite and alumina and point 4 shows silica.

![Figure 3.9: FE-SEM micrograph showing the morphology of particles in the Veolia feed.](image)

Table 3.5: EDS elemental analysis of Veolia feed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>28.12</td>
</tr>
<tr>
<td>Al</td>
<td>7.08</td>
</tr>
<tr>
<td>Si</td>
<td>9.13</td>
</tr>
<tr>
<td>Y and P</td>
<td>20.93</td>
</tr>
<tr>
<td>Cl</td>
<td>4.06</td>
</tr>
<tr>
<td>Ca</td>
<td>7.25</td>
</tr>
<tr>
<td>La</td>
<td>2.02</td>
</tr>
<tr>
<td>Ce</td>
<td>5.98</td>
</tr>
<tr>
<td>Eu</td>
<td>3.32</td>
</tr>
<tr>
<td>Tb</td>
<td>1.75</td>
</tr>
<tr>
<td>Fe</td>
<td>1.28</td>
</tr>
</tbody>
</table>
CHAPTER 4

PHYSICAL BENEFICIATION OF PHOSPHOR POWDER

Size based separation was used to determine the size fraction which will eliminate the most gangue materials and retain the bulk of the REE in the phosphor powder. The objective was to remove majority of the coarse glass and concentrate the REEs.

4.1. Dry Sieving

Based on the QEMSCAN analysis it was understood the rare earth bearing minerals in the feed material were locked and also 60% of these particles were less than 10 µm. The fine particle sizes of rare earth bearing minerals make size based separation the most promising beneficiation technique in terms of grade and recovery improvements as well as process economics. Therefore, size based physical beneficiation of the phosphor powder was found to be the logical starting point in an effort to concentrate the powder in rare earth content. Dry sieving were employed in the size separation study.

Particle size distribution was determined (Table 4.1) by using a stack of sieves (Tyler Mesh), to divide the phosphor powder up into various size fractions and eliminate the coarse glass particles. The fine glass or glass dust went to the undersize.

<table>
<thead>
<tr>
<th>Tyler Mesh</th>
<th>Size (µm)</th>
<th>Cumulative % Retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1680</td>
<td>2.24</td>
</tr>
<tr>
<td>60</td>
<td>250</td>
<td>26.78</td>
</tr>
<tr>
<td>100</td>
<td>149</td>
<td>37.98</td>
</tr>
<tr>
<td>150</td>
<td>105</td>
<td>42.67</td>
</tr>
<tr>
<td>200</td>
<td>75</td>
<td>48.78</td>
</tr>
<tr>
<td>270</td>
<td>63</td>
<td>55.40</td>
</tr>
<tr>
<td>325</td>
<td>44</td>
<td>56.72</td>
</tr>
<tr>
<td>Pan</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>
Further size analysis was conducted by sieving the as-received powder with 150, 200 and 325 Tyler mesh to obtain undersized materials at 105 µm, 75 µm and 44 µm. The different size fractions was analyzed for REE and gangue content and the results is shown in Table 4.2).

Table 4.2: Grade and recovery of REE from sieving analysis.

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>Powder wt%</th>
<th>REE Grade</th>
<th>% Recovery</th>
<th>REE</th>
<th>Gangue</th>
</tr>
</thead>
<tbody>
<tr>
<td>+106</td>
<td>42.4</td>
<td>0.75</td>
<td>45.87</td>
<td>0.75</td>
<td>45.87</td>
</tr>
<tr>
<td>-106</td>
<td>57.6</td>
<td>31.43</td>
<td>99.25</td>
<td>54.13</td>
<td>99.25</td>
</tr>
<tr>
<td>+75</td>
<td>48.0</td>
<td>1.25</td>
<td>52.87</td>
<td>52.87</td>
<td>52.87</td>
</tr>
<tr>
<td>-75</td>
<td>52.0</td>
<td>34.38</td>
<td>98.75</td>
<td>47.13</td>
<td>98.75</td>
</tr>
<tr>
<td>+44</td>
<td>55.7</td>
<td>4.44</td>
<td>61.92</td>
<td>61.92</td>
<td>61.92</td>
</tr>
<tr>
<td>-44</td>
<td>44.3</td>
<td>38.55</td>
<td>95.56</td>
<td>38.08</td>
<td>38.08</td>
</tr>
</tbody>
</table>

As expected, the bulk of the REE reported to the undersize. However, there is a greater loss (4.44%) of REE by sieving down to 44 µm. While sieving to 105 µm results in 99.25% REE recovery, there was still some coarse glass particles which will make material handling dangerous.

Therefore, the as-received powder was sieved to 75 µm and this resulted in a REE upgrade of 34.38% with 98.75% recovery. Table 4.3 shows the composition of the powder after sieving into different size fractions.

Table 4.3: Recoveries of individual elements of powder from sieve analysis.

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>REE wt%</th>
<th>Gangue wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y</td>
<td>Eu</td>
</tr>
<tr>
<td>+106</td>
<td>0.58</td>
<td>0.64</td>
</tr>
<tr>
<td>-106</td>
<td>98.37</td>
<td>99.36</td>
</tr>
<tr>
<td>+75</td>
<td>1.07</td>
<td>1.10</td>
</tr>
<tr>
<td>-75</td>
<td>98.93</td>
<td>98.90</td>
</tr>
<tr>
<td>+44</td>
<td>4.05</td>
<td>4.59</td>
</tr>
<tr>
<td>-44</td>
<td>95.95</td>
<td>95.41</td>
</tr>
</tbody>
</table>
A flowsheet (Figure 4.1) is hereby proposed which could lead to higher concentration and recovery of REE and should be investigated in future research. The flowsheet incorporate wet sieving instead of dry sieving.

Figure 4.1: Flowsheet for wet screening to concentrate REE in phosphor powder.

The grade of the REE in the powder would be improved by wet sieving but there is large sample loss and also due to the fineness of the powder, large amount of water would have to be used which will then have to dried by vacuum filtration. Furthermore, the
residue will have to be milled after drying. Thus although there is a slight upgrade in REE content with wet sieving in comparison to dry sieving, this is countered by inherent operation problems and high cost which will be a major setback for industrial application. Therefore the powder was dry sieved to 75 µm, characterized and used for further experimental evaluation of recycling routes to extract the rare earth elements.

4.2. Sieved Powder Characterization

The sieved powder was analysed for particle size distribution using the microtrac particle size analyser and the $P_{80}$ is 57.05 µm. The particles over 75 µm may be some coarse glass particles which managed to go through the screen as some of the mesh openings (pores) become larger over time.

![Figure 4.2: Cumulative particle size distribution of the sieved phosphor powder.](image)
4.2.1. **QEMSCAN Analysis**

The grain size image (Figure 4.3) of the sieved powder shows a uniform size distribution as most of the coarse particles are removed after sieving. The sieved powder is composed of mostly small particles less than 75 µm.

![Grain size image of minerals in the sieved powder.](image)

Figure 4.3: Grain size image of minerals in the sieved powder.

The as-received and sieved powder have the same mineral composition but in different concentrations (Figure 4.4 and Table 4.4). As expected the REEs is more concentrated in the sieved powder and also sieving removes coarse glass (quartz) and calcite. However, the concentration of apatite almost doubles in the sieved powder and therefore has to be removed so it doesn’t cause problems during REE processing and purification. Supplemental QEMSCAN data (cumulative particle size distribution and number of particles as a function of size) is included in Appendix A.
Figure 4.4: Modal mineral abundance in the sieved phosphor powder.

Table 4.4: Mineral distribution (volume %) in the sieved phosphor powder.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Veolia Feed</th>
<th>Sieved Powder (75 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monazite</td>
<td>3.45</td>
<td>4.55</td>
</tr>
<tr>
<td>Xenotime</td>
<td>0.56</td>
<td>0.86</td>
</tr>
<tr>
<td>Calcite</td>
<td>4.75</td>
<td>2.87</td>
</tr>
<tr>
<td>Apatite</td>
<td>16.64</td>
<td>30.13</td>
</tr>
<tr>
<td>Quartz</td>
<td>54.30</td>
<td>24.42</td>
</tr>
<tr>
<td>Mn Oxides</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe Oxides</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>Barite</td>
<td>0.34</td>
<td>0.18</td>
</tr>
<tr>
<td>Celestine</td>
<td>0.93</td>
<td>0.37</td>
</tr>
<tr>
<td>Phosphate Group</td>
<td>1.34</td>
<td>2.40</td>
</tr>
<tr>
<td>Tb-bearing minerals</td>
<td>1.01</td>
<td>1.50</td>
</tr>
<tr>
<td>La-bearing minerals</td>
<td>0.13</td>
<td>0.21</td>
</tr>
<tr>
<td>Ce-bearing minerals</td>
<td>0.24</td>
<td>0.37</td>
</tr>
<tr>
<td>Eu-bearing minerals</td>
<td>0.21</td>
<td>0.51</td>
</tr>
<tr>
<td>Y-bearing minerals</td>
<td>14.98</td>
<td>30.58</td>
</tr>
<tr>
<td>Other Minerals</td>
<td>0.97</td>
<td>0.88</td>
</tr>
</tbody>
</table>
4.2.2. XRD Analysis

XRD also confirms that REEs is concentrated in the sieved powder as the intensity of the yttrium oxide and monazite peaks appear more intense in the XRD pattern of the sieved powder (Figure 4.5). There is significant increase in the ytrrium oxide peak which is the major REE bearing mineral in the phosphor powder.

Figure 4.5: XRD pattern for phase identification in the sieved powder. F: fluoroapatite; Y: yttrium oxide; V: wakefieldite; C: calcite; M: monazite.

4.2.3. XRF Analysis

Table 4.5 shows the chemical composition of the Veolia feed as compared with the sieved powder. XRF also confirms there is concentration of the REEs in the sieved powder. There is also removal of significant amount of silica or glass, from 24.73% in the feed to 16.64% in the sieved powder.
Table 4.5: Chemical composition of Veolia feed and sieved powder.

<table>
<thead>
<tr>
<th>Dry Solid (wt %)</th>
<th>Veolia Feed</th>
<th>Sieved Powder (75 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>20.53 ± 3.11</td>
<td>23.15 ± 2.52</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>21.12 ± 3.40</td>
<td>22.54 ± 2.99</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>8.89 ± 0.92</td>
<td>9.19 ± 0.62</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.40 ± 0.12</td>
<td>0.39 ± 0.09</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>24.73 ± 0.85</td>
<td>16.64 ± 2.62</td>
</tr>
<tr>
<td>CuO</td>
<td>0.32 ± 0.12</td>
<td>0.38 ± 0.13</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.43 ± 0.04</td>
<td>0.29 ± 0.04</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>5.33 ± 0.86</td>
<td>4.18 ± 0.45</td>
</tr>
<tr>
<td>NiO</td>
<td>0.07 ± 0.12</td>
<td>0.15 ± 0.24</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.04 ± 0.01</td>
<td>0.09 ± 0.06</td>
</tr>
<tr>
<td>MgO</td>
<td>1.11 ± 0.01</td>
<td>0.83 ± 0.06</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>1.76 ± 0.39</td>
<td>2.41 ± 0.55</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>0.73 ± 0.29</td>
<td>1.10 ± 0.68</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>1.74 ± 1.18</td>
<td>1.98 ± 0.83</td>
</tr>
<tr>
<td>Tb$_2$O$_3$</td>
<td>0.59 ± 0.22</td>
<td>0.78 ± 0.19</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>9.77 ± 1.95</td>
<td>13.33 ± 1.38</td>
</tr>
</tbody>
</table>

4.3. Physical Methods for REE Separation

Most of the patents on physical methods for REE separation that have been filed obtain good results on artificially made mixtures of phosphors rather than on commercially available end of life feed stock. Research work has been done in Japan for physical beneficiation of phosphors by flotation and dense media separation to separate apatite or halo-phosphate phosphor from the rare earth bearing phosphors. Another approach for REE separation is direct recovery of the REE phosphors using dry classification by density. This method was explored at depth in Japan. However, it was difficult to achieve high purity and there was contamination between phosphors and lamp contaminants like glass, mercury, iron and aluminum. Furthermore, separation of the individual phosphors is difficult because they all have similar density and particle size. Therefore, this method was not commercialized.
Flotation experiments were conducted on -200 Tyler mesh fraction of the as-received powder with 10.2% REE content. The experiments were done using Denver flotation cell and Cytec’s reagent AERO 6493 as collector to float apatite from silica and REEs. REE grade of the rougher float increased slightly to 11.3%, and upon performing cleaner flotation, the grade increased to 14.5%. Insignificant grade improvements indicated poor selectivity of the collector for REE bearing minerals [14]. Electrostatic separation for physical beneficiation also gave poor results primarily due to dusting of powders during the test [14].

The fine particle sizes of the rare earth bearing minerals make size based separation the most promising beneficiation technique in terms of grade and recovery improvements. However, the fine particle size of the phosphor powder is also a bottleneck for processing by physical methods to separate the particle containing REE from each other. Acid leaching methods are thus more suitable with materials of such size.

4.4. Flowsheet Development for REE Recycling

Preliminary experiments and feasibility studies have been done in conjunction as shown in Figure 4.6. Direct acid leaching of REMs from waste lamp phosphors is non-selective, leading to co-dissolution of impurities such as calcium, iron, phosphorus, silicon, and zinc. Calcining the phosphor powder at different temperatures followed by leaching with HCl is not efficient for the extraction of all the chief rare earths especially cerium, lanthanum and terbium. Furthermore, multistage leaching and calcination followed by leaching processes under strong oxidizing conditions using high concentration of acid also resulted in poor extraction of cerium, lanthanum and terbium [61].
Based on experimental results a new process for extracting the chief REEs from end of life fluorescent lamps has been developed. The proposed process employs a three-stage leaching and separation process for selective extraction of the REEs (Figure 4.7). Each process has to be optimized for better recoveries.

This recycling flowsheet involves three steps. First, there is mechanical separation of coarse glass particles from the retorted phosphor powder followed by pretreatment to separate halophosphate, aluminates, and silicates from the REEs. Next, the residue undergoes two stages of chemical digestion to solubilize the REEs to produce two pregnant leach liquors – Eu and Y fraction and Ce, La and Tb fraction. The REEs in the leach liquor undergoes oxalic precipitation to produce RE oxalate, which is calcined to produce a mixed REO concentrate. The mixed REO concentrate can then be separated into their individual REOs using solvent extraction to produce pure REO which is used to make co-precipitates.
LaCeT, (La,Ce,Tb)PO$_4$) and YOX, (Y,Eu)$_2$O$_3$ for new phosphor production or other applications.

Figure 4.7: Proposed flow sheet for recycling of REEs from waste lamps.
CHAPTER 5

1ST STAGE LEACHING FOR APATITE REMOVAL

The dominating phase among the gangue materials in the sieved phosphor powder is apatite (30.13 wt%) and silica (24.42 wt%). Therefore selective separation of apatite and silica would help lower impurity levels in downstream processes. From leaching experiments it was concluded that it is extremely easy to leach the apatite phase from the powder hence eliminating the need for extensive beneficiation steps to make this separation. The common method for apatite \((\text{Ca}_5\text{(PO}_4)_3\text{(Cl,F,OH)})\) dissolution used in the phosphoric acid industry to recover REEs is leaching with \(\text{H}_2\text{SO}_4\) and \(\text{HNO}_3\). The REE in apatite are present as either \(\text{REE}^{3+}\) ions substituted on the \(\text{Ca}^{2+}\) ion sites of the apatite lattice or as REE mineral inclusions. Apatite is known to contain 0.1 to 1% REE. Thus, most phosphoric acid producers extract the REE as a side stream of their process. Leaching apatite with \(\text{H}_2\text{SO}_4\) results in complete dissolution and all REE are transferred into the solution. However, 80% of the REE in solution is lost, due to the precipitation of the insoluble \(\text{CaSO}_4\) (gypsum). Under typical processing conditions 5 tonnes of gypsum are formed per tonne of \(\text{P}_2\text{O}_5\) and thus producers now use \(\text{HNO}_3\) to leach apatite [62].

Due to the formation of gypsum as an insoluble by product, \(\text{HCl}\) and \(\text{HNO}_3\) were investigated for removal of apatite in the sieved powder.

5.1. Phosphor Powder Pre-treatment

The pre-treatment step was carried out at room temperature (RT) with \(\text{HCl}\) and \(\text{HNO}_3\) at low molarity to remove the main impurities such as Ca, P and Fe in the phosphor powder. At low acid molarity (e.g. 0.5 M), pulp density is the driving force of the leaching
process. Therefore, the extraction of both REE and impurities from the dust decreases by increasing pulp density as shown in Figure 5.1.

Extraction of cerium and terbium in the pretreatment step is negligible. However, there is minimum loss of yttrium, europium and lanthanum. It was deduced from Figure 5.1 that acid molarity and leaching time are the important leaching parameters and higher acid concentrations should be investigated.

![Figure 5.1: Extraction of impurities and REEs with HCl at different pulp density. Leaching conditions: 0.5 M HCl, 600 rpm, 30 min, RT.](image)

With higher acid molarity (e.g. 0.7 M), both pulp density and acid molarity are the driving force so the extraction of REE is constant (considering standard deviation) and the extraction of gangue materials or impurities decrease with higher pulp density.

Figure 5.2 to 5.5 gives evidence to this observation. Hydrochloric acid and nitric acid were used for these leaching experiments and the efficiency of both acids was compared.
Figure 5.2: Extraction of impurities with HCl at different pulp density. Leaching conditions: 0.7 M HCl, 600 rpm, 20 min, RT.

Figure 5.3: Extraction of REEs with HCl at different pulp density. Leaching conditions: 0.7 M HCl, 600 rpm, 20 min, RT.
Leaching with nitric acid gave slightly higher extraction of impurities than hydrochloric acid but precipitation and acid recovery is easier with hydrochloric acid. Therefore, hydrochloric acid was used for further optimization of this step. Since calcium
is the main impurity in the dust, its levels dictates how much acid should be added in the pre-treatment step as shown in reaction between calcium halophosphate with HCl:

\[
Ca_5(PO_4)_3 + 10 HCl \rightarrow 5 CaCl_2 + 3H_2PO_4 + H^+
\]

5.2. Optimization of Pre-treatment Step

By using higher acid molarity (e.g. 1 - 3 M), the extraction of impurities is expected to be constant while RE extraction decrease with high pulp density. With this approach higher pulp density such as 300 – 400 g/L can be achieved which will make the process economical. This approach of washing the powder was executed using a design of experiments with two factorials, pulp density (300 – 400 g/L) and time (5 – 40 min).

5.2.1. Effect of Acid Concentration

The pulp density was fixed at 400 g/L and the effect of acid concentration was analyzed. It is evident from Figure 5.6 that higher acid concentration is required to operate at high pulp density.

![Figure 5.6: Effect of acid concentration on extraction of impurities and REE from powder. Leaching conditions: 400 g/L, 600 rpm, 20 min, RT.](image-url)
5.2.2. Effect of Pulp Density

In order to improve acid consumption or usage, the effect of pulp density was monitored at different times. Figure 5.7 shows that 300 g/L is the optimal pulp density and longer leaching time results in higher extraction of the gangue materials (impurities). However, the extraction level of the impurities is low (< 70%).

Figure 5.7: Effect of pulp density on extraction of impurities and REE from phosphor powder. Leaching conditions: 2 M HCl, 600 rpm, and room temperature.

Figure 5.8 shows the extraction level can be improved to over 90% by using higher acid concentration (3 M HCl). However, there is undesirable concomitant effect of higher extraction of total REE (7.57%).
5.2.3. Effect of Leaching Time

In order to decrease the extraction of REE into solution, the effect of leaching time was studied and it is evident that longer time is undesired and thus leaching should be limited to 5 minutes (Figure 5.9).
The results from the pre-treatment optimization study show the pulp density can be increased to 300 g/L and the reaction is mainly chemical controlled than by diffusion. Table 5.1 gives the extraction levels of the main impurities and REEs. Poor results were obtained when the lixiviant was reused to pre-treat or wash another powder.

Table 5.1: Results for pre-treatment of phosphor powder and reuse of acid media.

<table>
<thead>
<tr>
<th>Elements</th>
<th>% Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1ST Wash</td>
</tr>
<tr>
<td>Ca</td>
<td>95.00% ± 4.25</td>
</tr>
<tr>
<td>P</td>
<td>89.49% ± 7.38</td>
</tr>
<tr>
<td>Al</td>
<td>5.85% ± 0.41</td>
</tr>
<tr>
<td>Fe</td>
<td>70.71% ± 6.21</td>
</tr>
<tr>
<td>Y</td>
<td>6.40% ± 1.52</td>
</tr>
<tr>
<td>Eu</td>
<td>8.51% ± 1.45</td>
</tr>
<tr>
<td>Tb</td>
<td>0.83% ± 0.52</td>
</tr>
<tr>
<td>La</td>
<td>4.65% ± 0.56</td>
</tr>
<tr>
<td>Ce</td>
<td>0.72% ± 0.47</td>
</tr>
</tbody>
</table>

5.3. Mass Balance

The mass balance of the process after the pretreatment step is shown in Table 5.2 and the elemental composition of the leach residue after the pretreatment (first leach residue) is given in Table 5.3.

Table 5.2: Mass balance after the pretreatment process.

<table>
<thead>
<tr>
<th>Powder (wt %)</th>
<th>Oversize</th>
<th>Undersize</th>
<th>Leachate</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received feed</td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P200 (75 μm)</td>
<td>47.94% ± 0.06</td>
<td>52.05% ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st Leach Residue</td>
<td></td>
<td>21.3% ± 0.12</td>
<td>30.92% ± 0.19</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3: Chemical composition of the first leach residue and filtrate.

<table>
<thead>
<tr>
<th></th>
<th>As Received</th>
<th>$P_{200}$ (75 μm)</th>
<th>1st Leach Residue</th>
<th>Leach Liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>20.53 ± 3.11</td>
<td>23.15 ± 2.52</td>
<td>6.16 ± 0.04</td>
<td>38.27 ± 0.59</td>
</tr>
<tr>
<td>$P_2O_5$</td>
<td>21.12 ± 3.40</td>
<td>22.54 ± 2.99</td>
<td>6.91 ± 0.12</td>
<td>51.26 ± 0.67</td>
</tr>
<tr>
<td>$Al_2O_3$</td>
<td>8.89 ± 0.92</td>
<td>9.19 ± 0.62</td>
<td>14.62 ± 0.34</td>
<td>1.54 ± 0.02</td>
</tr>
<tr>
<td>$Fe_2O_3$</td>
<td>0.40 ± 0.12</td>
<td>0.39 ± 0.09</td>
<td>0.23 ± 0.02</td>
<td>1.15 ± 0.06</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>24.73 ± 0.85</td>
<td>16.64 ± 2.62</td>
<td>26.64 ± 1.01</td>
<td>2.56 ± 0.05</td>
</tr>
<tr>
<td>CuO</td>
<td>0.32 ± 0.12</td>
<td>0.38 ± 0.13</td>
<td>0.13</td>
<td>1.11 ± 0.03</td>
</tr>
<tr>
<td>$K_2O$</td>
<td>0.43 ± 0.04</td>
<td>0.29 ± 0.04</td>
<td>0.57 ± 0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>Na$_2O$</td>
<td>5.33 ± 0.86</td>
<td>4.18 ± 0.45</td>
<td>7.32 ± 0.35</td>
<td>1.00 ± 0.03</td>
</tr>
<tr>
<td>NiO</td>
<td>0.07 ± 0.12</td>
<td>0.15 ± 0.24</td>
<td>0.02 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.04 ± 0.01</td>
<td>0.09 ± 0.06</td>
<td>0.02</td>
<td>0.20</td>
</tr>
<tr>
<td>MgO</td>
<td>1.11 ± 0.01</td>
<td>0.83 ± 0.06</td>
<td>1.45 ± 0.04</td>
<td>0.51</td>
</tr>
<tr>
<td>Ce$_2O_3$</td>
<td>1.76 ± 0.39</td>
<td>2.41 ± 0.55</td>
<td>3.98 ± 0.13</td>
<td>0.01</td>
</tr>
<tr>
<td>Eu$_2O_3$</td>
<td>0.73 ± 0.29</td>
<td>1.10 ± 0.68</td>
<td>1.30 ± 0.13</td>
<td>0.15</td>
</tr>
<tr>
<td>La$_2O_3$</td>
<td>1.74 ± 1.18</td>
<td>1.98 ± 0.83</td>
<td>4.61 ± 0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>Tb$_2O_3$</td>
<td>0.59 ± 0.22</td>
<td>0.78 ± 0.19</td>
<td>1.37 ± 0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Y$_2O_3$</td>
<td>9.77 ± 1.95</td>
<td>13.33 ± 1.38</td>
<td>24.66 ± 0.74</td>
<td>2.19 ± 0.05</td>
</tr>
</tbody>
</table>

* Values given for the filtrate is the chlorides of the corresponding elements.
CHAPTER 6

2ND STAGE LEACHING FOR YTTRIUM AND EUROPIUM REMOVAL

The phosphor powder used in this research is composed of a mixture of end of life second and third generation lamps. Second generation lamps contain the white halophosphate phosphor, (Sr,Ca)$_{10}$(PO$_4$)(Cl,F)$_2$:Sb$^{3+}$,Mn$^{2+}$ while third generation lamps have trichromatic phosphor made with three main rare earth phosphors and mixed in varying ratios to produce different colors of light. Trichromatic phosphors are transition metal or rare earth compounds of various types. The commonly used REE phosphors are the red phosphor Y$_2$O$_3$:Eu$^{3+}$ (YOX), the green phosphors LaPO$_4$:Ce$^{3+}$,Tb$^{3+}$ (LAP), (Gd,Mg)B$_5$O$_{12}$:Ce$^{3+}$,Tb$^{3+}$ (CBT), (Ce,Tb)MgAl$_{11}$O$_{19}$ (CAT) and the blue phosphor BaMgAl$_{11}$O$_{17}$:Eu$^{2+}$ (BAM). Therefore, the chief rare earth elements in the phosphor powder are yttrium, europium, cerium, lanthanum and terbium. The rare earth elements in the as-received powder were upgraded to 19.6% by sieving to below 75 µm. The -200 Tyler mesh fraction was then used for the leaching experiments. After the sieved powder is pre-treated to remove the gangue materials, the residue undergoes two stages of chemical digestion to solubilize the REEs to produce two pregnant leach liquors – Y and Eu fraction and Ce, La and Tb fraction. The flowsheet is designed to selectively leach Y and Eu first since they occur as oxides in the red and blue phosphors. Cerium, terbium and lanthanum are present in the green phosphor as phosphates and thus those three REEs are targeted in the third leaching step. The higher solubility of the Eu and Y containing phosphor can hence be exploited to increase overall recovery.

Acidic leaching has been a common method of extracting rare earths from naturally occurring minerals due to the tendency of the rare earths to be taken into solution easily at
low pH. Thermodynamic modeling of rare earths on HSC has confirmed that acid leaching of rare earth minerals is not only possible but also relatively easy; therefore it was justified to explore acid leaching on the phosphor powder.

6.1. Thermodynamics of REE Leaching

Thermodynamic modeling was focused on yttrium, europium, and terbium due to the high market price of these particular REEs and thus better extraction and recoveries of these three would ensure maximum profitability. HSC Chemistry 5.1 was used to evaluate the thermodynamics of the leaching reaction. The proposed chemical reaction for the process is:

\[
Y_2O_3 + 6H^+(aq) + 6Cl^-(aq) \rightarrow 2Y^{+3}(aq) + 6Cl^-(aq) + 3H_2O \quad (6.1)
\]

\[
Eu_2O_3 + 6H^+(aq) + 6Cl^-(aq) \rightarrow 2Eu^{+3}(aq) + 6Cl^-(aq) + 3H_2O \quad (6.2)
\]

\[
Tb_2O_3 + 6H^+(aq) + 6Cl^-(aq) \rightarrow 2Tb^{+3}(aq) + 6Cl^-(aq) + 3H_2O \quad (6.3)
\]

It can be seen from the tables that all the reactions in Equation 6.1 to 6.3 are thermodynamically favorable for Y and Eu throughout the entire temperature range because of the large negative Gibb’s free energy values (ΔG) and large positive equilibrium constant values (K). The enthalpies of reaction are also negative meaning that both reactions will be exothermic (Table 6.1 and Table 6.2).

For the terbium reaction in Equation 6.3, the K values are small which means the backward reaction is favored and thus there will be low concentration of Tb\(^{+3}\) in solution (Table 6.3). Therefore different leaching conditions should be explored to improve the susceptibility of leaching Tb from the phosphor powder. The small K values also suggest that the solubility of terbium chlorides in HCl is low and therefore other leaching reagents should be considered to enhance the leaching efficiency of terbium.
Table 6.1: Thermodynamic properties for leaching of yttrium with HCl.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>ΔH (kcal)</th>
<th>ΔS (cal/K)</th>
<th>ΔG (kcal)</th>
<th>K</th>
</tr>
</thead>
<tbody>
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</table>

Table 6.2: Thermodynamic properties for leaching of europium with HCl.

<table>
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<th>T (°C)</th>
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Table 6.3: Thermodynamic properties for leaching of terbium with HCl.

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6.2. **Eh-pH Diagrams for REE Systems**

In order to test the feasibility of acid leaching of the phosphor dust, Eh-pH diagrams were obtained for the most important rare earth systems. Eh-pH diagrams for Y-Cl-Eu-H$_2$O, Eu-Cl-Y-H$_2$O, Tb-Ce-Cl-La-P-H$_2$O, Ce-Cl-P-H$_2$O and La-Ce-Cl-P-Tb-H$_2$O systems at 70°C show that it is thermodynamically feasible to get terbium, europium and yttrium into solution in an aqueous phase (Figure 6.1 to 6.5). The redox state of metals and ligands that may complex them is the critical factor in the solubility of many metals. The Pourbaix diagrams show that rare earths are soluble in HCl at pH less than 4 and Eu and Y dissolves significantly at higher or positive Eh values whereas Tb, Ce and La are mainly soluble at negative Eh values (highly reducing environment) thereby making these metals sparingly soluble in strong oxidizing agents like Cl.

![Figure 6.1: Eh-pH diagram for Y-Cl-Eu-H$_2$O system at 70 °C.](image)
Figure 6.2: $E_h$-pH diagram for Eu-Cl-Y-H$_2$O system at 70 °C.

Figure 6.3: $E_h$-pH diagram for Tb-Ce-Cl-La-P-H$_2$O system at 70°C.
Figure 6.4: $E_h$-pH diagram for Ce-Cl-P-H$_2$O system at 70$^\circ$C.

Figure 6.5: $E_h$-pH diagram for La-Ce-Cl-P-Tb-H$_2$O system at 70$^\circ$C.
Therefore, by thermodynamics strong reducing agent such as sulfite in H$_2$SO$_4$ can improve the dissolution of cerium, terbium and lanthanum from phosphors powder. The Pourbaix diagrams also show that at higher pH; yttrium, europium, cerium and lanthanum form RE-OH, which is insoluble. Therefore oxidative leaching of the phosphor powder is required to solubilize the REEs.

6.3. Speciation Diagrams for REE System

Speciation diagrams were created using a thermodynamic stability program called Stabcal to illustrate the thermodynamically stable species present as a function of pH. Figure 6.6 to 6.10 are the respective speciation diagrams of (Y, Eu) and (Tb, Ce, La) with hydrochloric acid.

![Yttrium (III) speciation diagram (2 M total solution concentration).](image)
Figure 6.7: Europium (III) speciation diagram (2 M total solution concentration).

Figure 6.8: Terbium (III) speciation diagram (2 M total solution concentration).
Figure 6.9: Cerium (III) speciation diagram (2 M total solution concentration).

Figure 6.10: Lanthanum (III) speciation diagram (2 M total solution concentration).
It is evident from the speciation diagrams that in the acidic region, the predominant REE species are chloride cations (RECl$^{2+}$, RECl$_2^+$, RECl$_3$, and RECl$_4^-$). Conversely, in the alkaline region the predominant species present are the hydroxide anions (RE(OH)$_3$, REOH$_2^+$, REO$_2^-$, and REO$_2$H). Thus, as the pH shifts from acidic to alkaline regions, the REEs precipitate out of solution. Therefore leaching should be conducted at low pH to maintain the solubility of the rare earth elements.

6.4. Leaching Parameters

Recent work carried out by Takahashi et al. studied hydrometallurgical separation and recovery of rare earths from phosphors in fluorescent lamp wastes by leaching with sulfuric acid at different conditions [43]. The optimized leaching condition after those series of studies are: 1.5 M sulfuric acid, 70 ºC, 1 hour, and 30 g/L. A feasibility test was performed using Takahashi’s optimized conditions as reference in order to identify the best leaching reagent for extracting the REEs from the phosphor powder. After the type of leaching reagent was established, the effect of leaching parameters was investigated using a modification of Takahashi’s optimized leaching conditions to account for the high pulp density used in this research.

6.4.1. Effect of Leaching Reagent

Different acidic reagents were tested at the reference leaching conditions to determine which medium gives the highest leaching efficiency. The isotonic leaching reagents (1.5 M) used: hydrochloric acid, sulfuric acid, and nitric acid. All the experiments were carried out with the same leaching conditions: temperature of 70ºC, leaching time of 1 hour, and pulp density of 30 g/L.
Figure 6.11 shows that HCl gave the highest Eu and Y extraction and Ce, Tb and La all showed poor dissolution in all acidic leaching systems. H$_2$SO$_4$ and HNO$_3$ leaching systems gave similar results in Ce, Tb, La, Eu and Y extraction but the latter was rejected because red toxic gases of NO and NO$_2$ were generated. HCl was therefore established as the leachate of choice because of the highest leaching efficiency and also it is already being used extensively in most rare earth extraction processes.

Figure 6.11: Extraction of REEs from phosphor powder with different leaching reagent. Leaching conditions: Time = 1.5 M of lixiviant, 1 hr, 70 °C, 30 g/L, 200 rpm.

6.4.2. Effect of Acid Concentration

The reference conditions set up for batch leaching tests were a temperature of 70°C, solid to liquid ratio of 180 g/L, leaching time of 1 hour and agitation of 600 rpm.

Figure 6.12 below shows the variation in extraction of Y and Eu from the powder into solution under different concentration of acid. The extraction of Ce, Tb and La was significantly low and thus not included in the graph. With increasing acid concentration the
extraction increases significantly initially and then plateaus beyond 2 M. Europium and yttrium extraction reaches substantially high values (over 90%) with acid concentrations of 2 M and 99% extraction is achieved with 4 M HCl.

![Figure 6.12: Extraction of Y and Eu as a function of HCl concentration. Leaching conditions: 1 hr, 70 °C, 180 g/L, 600 rpm.](image)

**6.4.3. Effect of Temperature**

The temperature for the experiment was varied from 25°C to 80°C while the other leaching parameters were held constant at the reference conditions.

Figure 6.13 shows that Y and Eu extraction increases by over 30% by increasing the temperature from 25°C to 50°C. The highest extraction of Y and Eu occurred at 80°C
but it wasn’t significantly greater than at 70°C. Thus 70°C was chosen as the optimal temperature for further leaching experiments.

Figure 6.13: Extraction of Y and Eu as a function of temperature. Leaching conditions: 2 M HCl, 1 hr, 180 g/L, 600 rpm.

6.4.4. Effect of Leaching Time

In order to optimize the leaching efficiency for maximum total rare earth extractions, the leaching time was varied while the other leaching parameters were held constant at the reference conditions.

It can be seen from Figure 6.14 that extraction of Y and Eu increases steadily from 15 minutes to 3 hours. Maximum recovery (100%) of Y and 97.73% of Eu was obtained at 3 hour, which represents the optimal leaching time.
Figure 6.14: Extraction of Y and Eu as a function of time. Leaching conditions: 2 M HCl, 70°C, 180 g/L, 600 rpm.

6.4.5. Effect of Pulp Density

The solid to liquid ratio or pulp density is critical for the leachability of metals because it controls acid consumption and the interaction between the leachant and the feed particles. The pulp density was varied between 100 g/L to 180 g/L and the other leaching parameters held at the reference conditions.

It is evident from Figure 6.15 that using 100 g/L resulted in high extraction of Y and Eu. Beyond 100 g/L, the extraction of Y and Eu drops from 100% and 98.9% for Y and Eu respectively to 96.64% and 95.46% respectively at 180 g/L. Since there is a small drop in extraction, 180 g/L was chosen as the optimal pulp density.
6.4.6. Effect of Agitation Speed

Optimum agitation aids in increasing the rate of a heterogeneous reaction. In order to optimize the agitation, the system was agitated to speeds varying from 300 rpm to 750 rpm while the other leaching parameters were held constant at the reference conditions.

Figure 6.16 shows that extractions of Y and Eu didn’t change significantly as a function of agitation speed. However, 600 rpm was selected as the optimal agitation speed to prevent settling of feed particles since high pulp density was used.
6.5. **Leaching Optimization Study**

In order to make the REE recycling process cost-effective and economically attractive it is essential to optimize the extraction of yttrium and europium in the powder. Thus an optimization study was conducted to investigate the optimized conditions for leaching. The parameters explored were leaching time and pulp density, as they had significant effect on the extraction of Y and Eu. They are also key parameters for the process efficiency and profitability. Therefore, hydrochloric acid concentration was fixed at 2.5 M in order to accommodate the variance in REE content of the feed and agitation was also fixed at 600 rpm.

![Figure 6.16: Extraction of Y and Eu as a function of agitation. Leaching conditions: 2 M HCl, 70°C, 1 hr, 180 g/L.](image)
Stat-Ease Design-Expert 9.0.5® software was used for the experimental design, statistical analysis, statistical modeling and optimization of the leaching process. The matrix design of experiment used was a two factor three level full factorial design. The three-level design is written as a $3^k$ factorial design where $k$ is the number of factors. Thus, with two factors the experimental matrix consisted of nine experiments, which is done in replicate to produce a total of eighteen experiments. The variables chosen for investigation were time and pulp density and their lower and upper set points (Table 6.4).

The experimental matrix had three levels and thus the mid-level is the center point. It is important to add center points to the experimental matrix since it permits a statistical check for the goodness-of-fit of the two-level factorial model. Stat-Ease uses the average response value from the actual center point experiments to compare to the estimated value of the center point that comes from averaging all the factorial points. Therefore, if there is curvature of the response surface in the region of the design, the actual center point value will be either higher or lower than predicted by the factorial design points [63].

Although Stat-Ease is user-friendly, it is imperative to understand the statistical information and also properly evaluate of the data in order to create a statistically viable model. Stat-Ease first determines the effects present in the design of experiments. For a two factor three level full factorial design there are eight interaction parameters that must be analyzed in order to determine the significant effects in the process. These interaction parameters are $A$, $B$, $AB$, $A^2$, $B^2$, $A^2B$, $AB^2$ and $A^2B^2$ where $A$ is leaching time (minutes) and $B$ is pulp density (g/L). The absolute value of the effect of each interaction parameter, $\Delta Y$, is determined by subtracting the average of the low response values from the high response values [63].
Table 6.4: Full factorial design of experiments for the leaching optimization study.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Time (min)</th>
<th>Pulp Density (g/L)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<td>150</td>
</tr>
<tr>
<td>2</td>
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<td>18</td>
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<td>175</td>
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</tbody>
</table>

A Daniel probability table is then produced to determine if the effects are significant. For each individual factor, $i$, the cumulative probability, $P_i$, and $\Delta Y$ are determined. The cumulative probability is obtained using the following equation:

$$P_i = \left(\frac{100}{m}\right) \times (i - 0.5)$$

Where $m$ is the total number of factors (eight for two main factors) and $i$ is the number of the individual factor. Stat-Ease then plots $P_i$ versus $\Delta Y$ on a half normal scale to produce the Daniel plot or a Half Normal plot, which determines which factors are significant. Stat-Ease also generates the Pareto chart, which also determines which factors are significant. The software recommends using the Daniel plot or Half-Normal plot for choosing the statistically significant effects but the Pareto chart is a useful tool for showing the relative size of effects. The Pareto chart includes two lines indicating the Bonferroni
limit and the T-Value limit and both of these limit values are adjusted as significant interaction parameters are selected and are used to help distinguish significant and insignificant effects [63].

After the significant interaction parameters are selected on the Daniel plot and/or the Pareto chart, Stat-Ease performs an analysis of variance (ANOVA) to vary the selected interaction parameters statistical significance [63]. First, the sum of squares (SS) for each selected interaction parameter is calculated by the following equation:

$$SS = \frac{N}{4} \times [\Delta Y]^2$$

Where $N$ is the number of experiments performed and $[\Delta Y]^2$ is the absolute value of the effects squared. The SS for both the selected interaction parameters and the residual factors or noise are added to create a table from which the degree of freedom, df is obtained. The degree of freedom values and the sum of squares values are used to calculate mean squares value (MS), which is the model estimate of variance. The MS for the model is then divided by the MS for the residuals to obtain the F value which is the variance of the group mean divided by the mean of the group variances. The p-value is then estimated from the corresponding F tables. The p-value gives the probability of the effect of the interaction parameter occurs due to noise. P-values less than 0.05 indicate that the interaction parameters are significant in the model, i.e. there is a 95% confidence level that the F value is not a result of noise [63].

In addition to these values already discussed, Stat-Ease also calculates various correlation factors to ensure that the model is statistically sound and appropriate for making predictions within the upper and lower set points of each process parameters. The
first correlation factor calculated by ANOVA is the R-squared value ($R^2$) or multiple correlation coefficient. $R^2$ value is calculated by the following equation:

$$R^2 = 1 - \frac{SS_{Residual}}{(SS_{Model} + SS_{Residual})}$$

In the ideal case, $R^2$ has to be equal to 1. The next correlation factor calculated is an adjusted $R$-squared value. This is the $R$-squared value that is adjusted for the number of parameters in the model relative to the number of points in the design of experiments. It is a measure of the amount of variation about the mean explained by the model. The adjusted $R^2$ value is calculated by the following equation:

$$Adj. R^2 = 1 - \left( \frac{SS_{Residual}}{df_{Residual}} \right) \left( \frac{SS_{Model}}{df_{Model}} \right)$$

AVONA also calculates the predicted $R$-squared value, which measures how good the model predicts a response value. It is computed by the following equation:

$$Pred. R^2 = 1 - \frac{PRESS}{SS_{Model} + SS_{Residual}}$$

Where PRESS is the predicted residual sum of squares and is a measure of how well the model fits each point in the design. Lastly, ANOVA calculates the adequate precision term, which compares the range of predicted values at the design points to the average prediction error. Adequate precision terms greater than four indicate adequate model discrimination [63].

6.6. Stat Ease Optimization Results

Table 6.5 shows the results for the two factor three level full factorial experimental design. The maximum percentage extraction obtained in this study was 100% for Y and Eu and the minimum percentage extraction achieved was 98.46% and 95.75% for Y and Eu.
respectively. Therefore, the range of experimental results doesn’t provide an optimal spread of data for statistical analysis and modeling. The chemical analysis of the leached residue after the optimization tests corroborates with the high percentage extraction of Y and Eu.

Table 6.5: Results for yttrium and europium full factorial design of experiments.

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<tr>
<th>Test #</th>
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<th>Pulp Density (g/L)</th>
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<td>200</td>
<td>98.46</td>
<td>95.92</td>
</tr>
<tr>
<td>17</td>
<td>30</td>
<td>150</td>
<td>98.96</td>
<td>97.52</td>
</tr>
<tr>
<td>18</td>
<td>45</td>
<td>175</td>
<td>100.00</td>
<td>99.76</td>
</tr>
</tbody>
</table>

Stat Ease generated an ANOVA table (Table 6.6 and Table 6.7) after the significant interaction parameters were chosen. The overall model F-value of 1 and 0.61 for Y and Eu respectively implies that the model is not significant.

The p-values for all of the interaction parameters chosen are significantly greater than to 0.05, which also indicates that these model terms are not significant. The calculated correlation factors generated in the ANOVA are shown in Table 6.8. All of the R-squared values are low which further indicates the model doesn’t fit well and can’t be used to
predict values within the design space. Furthermore, the adequate precision value is less than four, which indicates noise.

Table 6.6: Stat-Ease ANOVA for yttrium leaching optimization model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1.36</td>
<td>8</td>
<td>0.17</td>
<td>1</td>
<td>0.5000</td>
</tr>
<tr>
<td>A-Time</td>
<td>2.220E-016</td>
<td>1</td>
<td>2.220E-016</td>
<td>1.309E-015</td>
<td>1.0000</td>
</tr>
<tr>
<td>B-Pulp Density</td>
<td>4.441E-016</td>
<td>1</td>
<td>4.441E-016</td>
<td>2.618E-015</td>
<td>1.0000</td>
</tr>
<tr>
<td>AB</td>
<td>0.031</td>
<td>1</td>
<td>0.031</td>
<td>0.18</td>
<td>0.6791</td>
</tr>
<tr>
<td>A²</td>
<td>2.220E-016</td>
<td>1</td>
<td>2.220E-016</td>
<td>1.309E-015</td>
<td>1.0000</td>
</tr>
<tr>
<td>B²</td>
<td>0.000</td>
<td>1</td>
<td>0.000</td>
<td>0.000</td>
<td>1.0000</td>
</tr>
<tr>
<td>A²B</td>
<td>0.010</td>
<td>1</td>
<td>0.010</td>
<td>0.061</td>
<td>0.8105</td>
</tr>
<tr>
<td>AB²</td>
<td>0.28</td>
<td>1</td>
<td>0.28</td>
<td>1.64</td>
<td>0.2368</td>
</tr>
<tr>
<td>A³B²</td>
<td>0.092</td>
<td>1</td>
<td>0.092</td>
<td>0.55</td>
<td>0.4814</td>
</tr>
<tr>
<td>Residual</td>
<td>1.36</td>
<td>8</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>3.08</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.7: Stat-Ease ANOVA for europium leaching optimization model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>10.67</td>
<td>8</td>
<td>1.33</td>
<td>0.61</td>
<td>0.7505</td>
</tr>
<tr>
<td>A-Time</td>
<td>0.67</td>
<td>1</td>
<td>0.67</td>
<td>0.31</td>
<td>0.5947</td>
</tr>
<tr>
<td>B-Pulp Density</td>
<td>4.52</td>
<td>1</td>
<td>4.52</td>
<td>2.06</td>
<td>0.1890</td>
</tr>
<tr>
<td>AB</td>
<td>0.14</td>
<td>1</td>
<td>0.14</td>
<td>0.062</td>
<td>0.8100</td>
</tr>
<tr>
<td>A²</td>
<td>0.16</td>
<td>1</td>
<td>0.16</td>
<td>0.072</td>
<td>0.7946</td>
</tr>
<tr>
<td>B²</td>
<td>0.13</td>
<td>1</td>
<td>0.13</td>
<td>0.058</td>
<td>0.8164</td>
</tr>
<tr>
<td>A²B</td>
<td>1.22</td>
<td>1</td>
<td>1.22</td>
<td>0.56</td>
<td>0.4761</td>
</tr>
<tr>
<td>AB²</td>
<td>0.13</td>
<td>1</td>
<td>0.13</td>
<td>0.059</td>
<td>0.8143</td>
</tr>
<tr>
<td>A³B²</td>
<td>0.64</td>
<td>1</td>
<td>0.64</td>
<td>0.29</td>
<td>0.6040</td>
</tr>
<tr>
<td>Residual</td>
<td>17.52</td>
<td>8</td>
<td>2.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>33.84</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.8: Stat-Ease correlation factors for yttrium and europium leaching model.

<table>
<thead>
<tr>
<th></th>
<th>R-Squared</th>
<th>Adjusted R-Squared</th>
<th>Predicted R-Squared</th>
<th>Adequate precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>0.5000</td>
<td>0.0000</td>
<td>-1.5313</td>
<td>3.4420</td>
</tr>
<tr>
<td>Eu</td>
<td>0.3786</td>
<td>-0.2428</td>
<td>-2.1459</td>
<td>3.073</td>
</tr>
</tbody>
</table>

The Pareto charts, and 3D response surface graphs in the leaching parameter optimization are included in Appendix B. There is minimal difference in percentage.
extraction among the tests for the optimization study. Thus the data wasn’t statistical relevant to compute or formulate a model. However, the high leachability of Y and Eu from the phosphor powder is good for process economics. The optimization test shows optimum extractions of Y and Eu from the phosphor dust were observed at the following conditions: 2.5 M HCl, 175 g/L, 70˚C, 1 hour and 600 rpm. Under these conditions, stage recovery is 100% for Y and Eu.

6.7. Characterization of Second Leach Residue

The leach residue after the second leach was characterized in order to evaluate the best method to concentrate and extract the remaining REEs in the powder. The powder was characterized using FE-SEM and XRD analysis.

6.7.1. Mass Balance

The mass balance of the process after the second leach step is shown in Table 6.9. The weight percent of the powder that goes to the leachate and residue after leaching is calculated and the composition of the leachate is also analyzed with ICP-OES.

<table>
<thead>
<tr>
<th>Powder (wt %)</th>
<th>Oversize</th>
<th>Undersize</th>
<th>Leachate</th>
<th>Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received feed</td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P_{200} (75 μm)</td>
<td>47.94% ± 0.06</td>
<td>52.05% ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1^{st} Leach Residue</td>
<td></td>
<td></td>
<td>21.3% ± 0.12</td>
<td>30.92% ± 0.19</td>
</tr>
<tr>
<td>2^{nd} Leach Residue</td>
<td></td>
<td></td>
<td>8.7% ± 0.17</td>
<td>22.22% ± 0.21</td>
</tr>
</tbody>
</table>

Table 6.10 shows SiO₂, Al₂O₃ and Na₂O are present in higher concentration in the second leach residue. The remaining REEs left in the powder are found in the green phosphor - Ce₂O₃, La₂O₃ and Tb₂O₃. The chemical composition of the leach liquor after the second stage leach is shown in Table 6.11.
Table 6.10: Mass of the leaching process after the second leaching stage.

<table>
<thead>
<tr>
<th></th>
<th>Dry Solid (wt %)</th>
<th>Filtrate* (wt% by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{200}$ (75 μm)</td>
<td>1st Leach Residue</td>
</tr>
<tr>
<td>CaO</td>
<td>23.15 ± 2.52</td>
<td>6.16 ± 0.04</td>
</tr>
<tr>
<td>$P_2O_5$</td>
<td>22.54 ± 2.99</td>
<td>6.91 ± 0.12</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9.19 ± 0.62</td>
<td>14.62 ± 0.34</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.39 ± 0.09</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>16.64 ± 2.62</td>
<td>26.64 ± 1.01</td>
</tr>
<tr>
<td>CuO</td>
<td>0.38 ± 0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.29 ± 0.04</td>
<td>0.57 ± 0.02</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>4.18 ± 0.45</td>
<td>7.32 ± 0.35</td>
</tr>
<tr>
<td>NiO</td>
<td>0.15 ± 0.24</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.09 ± 0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.83 ± 0.06</td>
<td>1.45 ± 0.04</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>2.41 ± 0.55</td>
<td>3.98 ± 0.13</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>1.10 ± 0.68</td>
<td>1.30 ± 0.13</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>1.98 ± 0.83</td>
<td>4.61 ± 0.10</td>
</tr>
<tr>
<td>Tb$_2$O$_3$</td>
<td>0.78 ± 0.19</td>
<td>1.37 ± 0.02</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>13.33 ± 1.38</td>
<td>24.66 ± 0.74</td>
</tr>
</tbody>
</table>

* Values given for the filtrate is the chlorides of the corresponding elements

Table 6.11: Chemical composition of the second leach liquor.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>2nd Leach Liquor (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl$_3$</td>
<td>988.15</td>
</tr>
<tr>
<td>CaCl</td>
<td>700.85</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>457.32</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>185.83</td>
</tr>
<tr>
<td>SiCl$_4$</td>
<td>75.15</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>53.62</td>
</tr>
<tr>
<td>KCl</td>
<td>6.98</td>
</tr>
<tr>
<td>NaCl</td>
<td>274.74</td>
</tr>
<tr>
<td>ZnCl$_2$</td>
<td>3.91</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>12.00</td>
</tr>
<tr>
<td>CeCl$_3$</td>
<td>14.78</td>
</tr>
<tr>
<td>EuCl$_3$</td>
<td>2127.79</td>
</tr>
<tr>
<td>LaCl$_3$</td>
<td>23.02</td>
</tr>
<tr>
<td>TbCl$_3$</td>
<td>14.77</td>
</tr>
<tr>
<td>YCl$_3$</td>
<td>35679.49</td>
</tr>
</tbody>
</table>
6.7.2. X-ray Diffraction Analysis

The phase composition of the second leach residue is shown in Figure 6.17. From the XRD phase identification, it is clear that yttrium oxide present in major amounts in the sieved powder and first leach residue became a minor phase in the second leach residue.

Figure 6.17: XRD pattern for phase identification in second leach residue. F: fluoroapatite; Y: yttrium oxide; V: wakefieldite; C: calcite; M: monazite; Q: quartz.
There is significant reduction in the yttrium oxide peaks which represents the bulk of the REE minerals in the powder. This signifies high leachibility of Y and Eu. There is also significant reduction in the calcite peaks.

6.7.3. FE-SEM EDS Analysis

The morphology of particles in the second leach residue was detected with FE-SEM Secondary Electron Imaging (Figure 6.18) and the elemental composition of the powder at the listed pointed is shown in Table 6.12.

![FE-SEM micrograph showing particles in the second leach residue.](image)

Figure 6.18: FE-SEM micrograph showing particles in the second leach residue.

The micrograph was obtained with a zoom of 500x and the elemental composition of the powder was obtained with EDS. Table 6.12 shows the predominant elements in the second leach residue is silicon and aluminum and there is concentration of lanthanum, cerium and terbium as previous discussed.
Table 6.12: EDS elemental analysis of Veolia feed.

<table>
<thead>
<tr>
<th>Element</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>30.4</td>
<td>27.75</td>
<td>36.25</td>
<td>28.87</td>
<td>28.66</td>
<td>28.61</td>
<td>38.63</td>
</tr>
<tr>
<td>Al</td>
<td>14.55</td>
<td>14.52</td>
<td>10.33</td>
<td>13.73</td>
<td>13.64</td>
<td>13.66</td>
<td>12.45</td>
</tr>
<tr>
<td>Si</td>
<td>24.63</td>
<td>19.67</td>
<td>23.71</td>
<td>20.8</td>
<td>20.92</td>
<td>20.89</td>
<td>34.46</td>
</tr>
<tr>
<td>Y</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>1.1</td>
</tr>
<tr>
<td>P</td>
<td>1.3</td>
<td>2.47</td>
<td>3.08</td>
<td>2.26</td>
<td>2.1</td>
<td>1.65</td>
<td>0.00</td>
</tr>
<tr>
<td>Ca</td>
<td>2.75</td>
<td>1.92</td>
<td>2.14</td>
<td>2.34</td>
<td>2.11</td>
<td>2.3</td>
<td>3.44</td>
</tr>
<tr>
<td>La</td>
<td>9.81</td>
<td>10.46</td>
<td>8.73</td>
<td>8.67</td>
<td>8.73</td>
<td>8.68</td>
<td>0.79</td>
</tr>
<tr>
<td>Ce</td>
<td>8.65</td>
<td>9.41</td>
<td>6.6</td>
<td>9.18</td>
<td>8.77</td>
<td>8.88</td>
<td>3.14</td>
</tr>
<tr>
<td>Eu</td>
<td>0.00</td>
<td>0.62</td>
<td>0.00</td>
<td>0.83</td>
<td>0.83</td>
<td>0.55</td>
<td>1.07</td>
</tr>
<tr>
<td>Tb</td>
<td>2.68</td>
<td>3.57</td>
<td>0.64</td>
<td>2</td>
<td>3.28</td>
<td>3.23</td>
<td>0.24</td>
</tr>
<tr>
<td>Fe</td>
<td>0.11</td>
<td>0.2</td>
<td>0.00</td>
<td>0.53</td>
<td>0.45</td>
<td>0.41</td>
<td>0.29</td>
</tr>
</tbody>
</table>
3RD STAGE LEACHING FOR CERIUM, LANTHANUM AND TERBIUM REMOVAL

Despite the fact that rare earths are reactive metals, cerium, lanthanum and terbium are not easily solubilized with both weak and strong acids. The flowsheet that has been developed for REE recycling from waste lamps is designed to selectively leach yttrium and europium from the sieved powder in the second leach step to produce a cerium, lanthanum and terbium concentrate for the third leaching step. High extraction of terbium is targeted in the third leaching step due to its high market price and thus will ensure maximum profitability. Cerium, lanthanum and terbium are present in the green phosphor as phosphates, which is recalcitrant because rare earth phosphates have high thermal stability. Small amount of $\text{Tb}_2\text{O}_3$ is used to make lamp phosphors but it is locked in the LAP phosphate matrix. LAP is a rare earth phosphate, $\text{LaPO}_4:\text{Ce}^{3+},\text{Tb}^{3+}$ and is the main green phosphor used in lamps. The thermal decomposition of the LAP phosphor and its amenability to acid leaching is thus critical for improving the extraction of terbium.

7.1. Thermal Decomposition of LAP Phosphor

In the industrial processing of rare earth minerals, high temperature treatments such as calcining and roasting is employed to decompose the minerals to allow easy recovery of the rare earth values [5]. The family of rare earth phosphates has been shown to possess high temperature phase stability and high melting point above 1900˚C. Lanthanum phosphate is present in bulk amounts in the LAP phosphor so it was chosen for the thermodynamic modeling using HSC Chemistry 5.1 to determine the conditions
necessary for thermal decomposition of LAP as well as chemical compounds formed during this process.

Equilibrium composition diagram of the thermal decomposition reaction of lanthanum phosphate with sodium carbonate was generated. Figure 7.1 shows that it possible to break down LaPO$_4$ at 200°C during calcination with Na$_2$CO$_3$. Over 80% of LaPO$_4$ decompose to LaO$_2$ (gas) and La$_2$O$_3$, which is soluble in acids and slightly soluble in water. Significant amount of carbon dioxide is also generated and have to be scrubbed with NaOH, which will extra cost to the process.

![Thermal decomposition diagram of LaPO$_4$ by calcination with Na$_2$CO$_3$.](image)

Figure 7.1: Thermal decomposition diagram of LaPO$_4$ by calcination with Na$_2$CO$_3$. Input: 1 kmole LaPO$_4$ and kmole Na$_2$CO$_3$.

Equilibrium composition diagrams of the decomposition reaction of lanthanum phosphate in oxidizing (air), reducing (with CO), sulfidizing (with SO$_2$) and chloridizing...
(Cl₂) atmospheres at temperatures ranging between 500°C and 2000°C were generated (Figure 7.2 to 7.5). This was to model the thermal decomposition of the LAP phosphor at high temperatures. From the equilibrium composition diagrams, it is evident that thermal decomposition of LaPO₄ in air, CO, SO₂ and Cl₂ atmospheres occur at very high temperatures. At temperatures ranging between 1500°C to 2000°C, less than 40% of LaPO₄ break down and that makes the process uneconomical for industrial application.

![Thermal decomposition diagram of LaPO₄ in air. Input: 1 kmole LaPO₄ and kmole O₂.](image)

Figure 7.2: Thermal decomposition diagram of LaPO₄ in air. Input: 1 kmole LaPO₄ and kmole O₂.

From the equilibrium composition diagrams, it is evident that thermal decomposition of LaPO₄ in air, CO, SO₂ and Cl₂ atmospheres occur at very high temperatures. At temperatures ranging between 1500°C to 2000°C, less than 40% of LaPO₄ break down and that makes the process uneconomical for industrial application.
Figure 7.3: Thermal decomposition diagram of LaPO\textsubscript{4} in a reducing environment. Input: 1 kmole LaPO\textsubscript{4} and kmole CO.

Figure 7.4: Thermal decomposition diagram of LaPO\textsubscript{4} in a sulfidizing atmosphere. Input: 1 kmole LaPO\textsubscript{4} and kmole SO\textsubscript{2}.
High temperature processes are expensive to run on the basis of capital and operational cost. Therefore leaching at low temperatures was employed to extract cerium, lanthanum and terbium in order to improve the economics of REE recycling from lamp phosphors.

The leaching parameters investigated were temperature (80 and 90°C), leaching reagent (hydrochloric acid and phosphoric acid), acid concentration (2 and 4.5 M) and pulp density (7.5, 10, 12, and 15 g/L). The entire leaching tests were conducted at an agitation speed of 600 rpm.

The results of the percentage extraction of these three REEs are shown in Table 7.1. Low level of extraction of Ce, La and Tb was attained with H₃PO₄ so HCl was used for further test at higher concentration (4.5 M) and temperature (90°C). However, the
highest extraction of Tb obtained was only 19.25%. The results don’t justify using high concentration of HCl for extracting these REEs from waste lamp phosphors.

Table 7.1: Leaching efficiency of Ce, La, Tb from phosphor in third stage of leaching.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Leaching Conditions</th>
<th>% Extraction</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce</td>
<td>La</td>
<td>Tb</td>
</tr>
<tr>
<td>2 M H$_3$PO$_4$</td>
<td>75 g/L, 80˚C, 1 hr</td>
<td>0.18</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>120 g/L, 80˚C, 1 hr</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>150 g/L, 80˚C, 1 hr</td>
<td>0.19</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>75 g/L, 90˚C, 1 hr</td>
<td>2.12</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>75 g/L, 90˚C, 1.5 hr</td>
<td>5.56</td>
<td>5.58</td>
</tr>
<tr>
<td>2 M HCl</td>
<td>75 g/L, 90˚C, 1.5 hr</td>
<td>7.87</td>
<td>8.12</td>
</tr>
<tr>
<td></td>
<td>120 g/L, 80˚C, 1 hr</td>
<td>1.22</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>150 g/L, 80˚C, 1 hr</td>
<td>1.13</td>
<td>1.25</td>
</tr>
<tr>
<td>4.5 M HCl</td>
<td>75 g/L, 90˚C, 1 hr</td>
<td>17.97</td>
<td>18.56</td>
</tr>
<tr>
<td></td>
<td>100 g/L, 90˚C, 1 hr</td>
<td>11.36</td>
<td>11.66</td>
</tr>
<tr>
<td></td>
<td>120 g/L, 90˚C, 1 hr</td>
<td>13.14</td>
<td>13.63</td>
</tr>
<tr>
<td></td>
<td>150 g/L, 90˚C, 1 hr</td>
<td>9.52</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Further research is required to improve the dissolution of terbium in order to make the process economical. Therefore, the residue after the second stage leach should be stockpiled until the market price of Ce, La, Tb justifies the expensive capital cost for extracting these REEs.

Yamashita et. al have successfully employed magnetic separation to separate different phosphor powders. Phosphors with a high terbium content such as LaPO$_4$;Ce$^{3+}$,Tb$^{3+}$, (Gd,Mg)B$_5$O$_{12}$;Ce$^{3+}$,Tb$^{3+}$ and (Ce,Tb)MgAl$_{11}$O$_{19}$ are substantially more paramagnetic with respect to the europium-based phosphors or the halophosphate phosphors, and thus they are more strongly attracted towards magnetic fields [64]. The green phosphor has high magnetic susceptibility and thus it could be separated by this
method. It is one order of magnitude more magnetically susceptible than red and blue phosphors. They used three series stages of separation with high-gradient magnetic separator (HGMS) with a maximum 2 Tesla field to obtain a purity of 99% of green phosphor from a suspension of synthetic red, blue, green and white halophosphate (cool and warm white) phosphors. They obtained 90% purity of LAP from sieved waste lamp phosphor after two-stage separation.

Therefore, the green phosphor in the second leach residue can be concentrated using wet high intensity magnetic separation (WHIMS) followed by leaching for the extraction of Ce, La and Tb. Another approach is to break the phosphate matrix of the green phosphor using caustic solid conversion with 50% NaOH under high pressure and temperature followed by leaching with 6 M HCl digestion in order improve the dissolution of terbium.

7.2. Acid Recovery and Regeneration Methods

As concentrated acid is needed for a single use in leaching of the phosphor powder, the cost for wastewater treatment will be high. From an economical point of view, the benefits arise from the acid recycling as well as reduction of the consumption of alkali required for neutralization process. Therefore, recovery of acid from the spent acidic leach liquor is of interest. Some of the technologies to regenerate, recover and purify the waste fluid of hydrochloric acid include:

1. Diffusion Dialysis
2. Electrodialysis
3. Membrane Distillation
4. Pyrohydrolysis
7.2.1. Diffusion Dialysis

Diffusion dialysis (DD) has been applied as an industrial membrane process ever since 1984 and has been successfully exploited to recover acids, alkalis and valuable metals from waste solution generated in the steel and non-ferrous metal smelting industries, metal-refining, electroplating and cation exchange resin regeneration [65]. Diffusion dialysis, also known as concentration or natural dialysis is an ion-exchange membrane (IEM) separation process driven by concentration gradient. Diffusion dialysis is also known as a spontaneous separation process because the driving force for the separation process is mainly concentration gradient [66]. As a spontaneous process, the process of diffusion dialysis gives rise to an increase in entropy and decrease in Gibbs free energy, so it is thermodynamically favorable.

The principle of DD is that based on the difference in the diffusivity between an acid and salt through an anion exchange membrane. The acid can be recovered from a solution containing the acid and its corresponding salts. This principle is illustrated by the separation of HCl from a feed solution in Figure 7.6.

HCl and its metal salts in the feed solution tend to transport to the water-side due to the concentration difference across the membrane. Due to the presence of the anion-exchange membrane (AEM), the Cl$^-$ ions (or SO$_4^{2-}$, NO$_3^-$, PO$_4^{3-}$, etc.) are allowed to pass, while the metals in the waste solution are restricted passage. The H$^+$ ions, although positively charged, have higher competition in diffusion than metal ions because of their smaller size, lower valence state and higher mobility. Hence they can diffuse along with the Cl$^-$ ions (or SO$_4^{2-}$, NO$_3^-$, PO$_4^{3-}$, etc.) to meet the requirement of electrical neutrality.
Figure 7.6: Diffusion dialysis process of HCl separation from a feed solution [65].

Some advantages of DD process compared to other methods (neutralization, precipitation, crystallization, and thermal decomposition) include low consumption of energy, low installation and operating cost, higher efficiency in purifying wastewater and no pollution to the environment. However, the concentration of recovered acid or metals is restricted by the equilibrium concentration and the processing capability is relatively low [65]. Furthermore, the long-time running stability of DD process depends largely on the strength and stability of the ion exchange membranes. High acidic resistance of the membranes is especially required for acid recovery, and other requirements such as high proton permeability but strong rejection of salts, relatively high water content but poor water permeability have to be met to make DD process effective [65][66]. Therefore, the membranes satisfying the above specifications are quite limited, which inhibits the further development of DD process.
Presently, commercial or laboratory scale ion exchange membranes are mostly based on organic polymer materials, such as poly(vinyl alcohol) (PVA), perfluorinated materials, polystyrene (PS), polysulphone (PS), poly(ether-ether-ketone) (PEEK), or poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [68]. Due to the inherent characteristics of polymer materials, the membranes may lack in stability and strength and therefore modification through cross-linking, heat-treatment and other methods need to be conducted [66]. A summary of applications of diffusion dialysis systems in the recovery of HCl is shown in Table 7.2.

<table>
<thead>
<tr>
<th>Application</th>
<th>Scale</th>
<th>Membrane</th>
<th>Process characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl recovery</td>
<td>Lab and pilot scale (TSD-2</td>
<td>Neosepta –AFN (Tokuyama Co., Japan)</td>
<td>Membrane area: 16 cm$^2$ for lab scale; membrane area: 200 cm$^2$ for pilot scale; RHCl: 60–80%</td>
</tr>
<tr>
<td>HCl recovery from NiCl$_2$</td>
<td>Lab scale</td>
<td>Neosepta –AFN (Tokuyama Co., Japan)</td>
<td>Membrane area: 62.2 cm$^2$; permeability for HCl: 0.84 x 10$^{-6}$ to 2.4 x 10$^{-6}$ ms$^{-1}$; permeability for NiCl$_2$: two orders of magnitude lower than that for HCl</td>
</tr>
<tr>
<td>HCl recovery from solution containing HCl + FeCl$_2$</td>
<td>Lab scale</td>
<td>Neosepta –AFN (Tokuyama Co., Japan)</td>
<td>The partial flux of FeCl$_2$ &lt; 5.6%; the concentration gradient of has significant effect on the salt flux</td>
</tr>
<tr>
<td>HCl permeability through Neosepta –AFN</td>
<td>Pilot scale</td>
<td>Neosepta –AFN (Tokuyama Co., Japan)</td>
<td>The permeability of HCl apparently increases with acid concentration</td>
</tr>
<tr>
<td>HCl recovery from the waste acid solution</td>
<td>Pilot scale</td>
<td>DF120-I (Shandong, China)</td>
<td>RHCl $&gt;$ 88%, RFe: 89 -77%; RZn $&gt;$ 56%</td>
</tr>
</tbody>
</table>

7.2.2. Electro dialysis

Electrodialysis (ED) is a process where ion exchange membranes are used for removing ions from an aqueous solution under the driving force of electrical potential. It is applied to remove salts from solutions or to concentrate ionic substances. ED is an attractive technique for treating waste acids. Purified and reconcentrated acid can be
obtained and reused and also there is production of lower amounts of salt effluents or sludges. The principle of ED for this application is schematized in Figure 7.7 [67].

![Figure 7.7: The Asahi Glass CS-0 electrodialysis cell. Compartments: D - diluate; C - concentrate; EC, EA - electrodes. Membranes: AEM - anion-exchange; CEM - cation-exchange. V is the applied voltage [67].](image)

The spent acid is circulated in the diluate (D) and the purified and reconcentrated acid is obtained in the concentrate (C). The anion exchange membranes must have a very low permeability to protons and the cation exchange membranes must have a high permeability to protons but a very high rejection of the divalent metallic ions. Both membranes must also have a low permeability to water in order to limit acid dilution in the concentrate [67]. Electro-dialysis is a promising method for purification of electroplating wastewater and extraction of non-ferrous metals from them.

Water-splitting electrodialysis is a special type of electrodialysis that uses bipolar membranes instead of anion exchange membranes. Bipolar membranes are composed of anion and cation exchange layers. Water is split to H⁺ and OH⁻ ions in the interlayer, which is formed by water film. Ions pass through the corresponding layer of the membrane.
Water-splitting electrodialysis has been applied to electroconversion of salts to the corresponding acids [68].

A large number of existing applications of electrodialysis have been described in the literature. Urano et al. proposed electro-dialysis for recovery of hydrochloric acid and sulphuric acid [69]. Wisniewski et al. studied the acid purification using bipolar electrodialysis [70]. This process yielded an acid solution having concentration up to 51-fold (for hydrochloric acid) and 63-fold (for sulphuric acid) as compared to that obtained by conventional electro-dialysis. In recent years, new AEM's with lower proton leakage have appeared in the market. Thus it is now possible to concentrate hydrochloric acid solution using these new membranes [71].

7.2.3. Membrane Distillation

Membrane Distillation (MD) is the process in which a hydrophobic membrane separates the two aqueous solutions at different temperature and composition under the driving force of the partial pressure difference induced by the temperature gradient between the solutions on both sides of the membrane. Therefore, mass-transfer of water vapor in the pores of the hydrophobic membrane is attained by the water-vapor pressure gradient. The principle of separation is that as the liquid evaporates at the feed/air filling pores interface, vapor diffuses through the pores and condenses directly in a cold distillate. Thus the water evaporates from the feed stream (hot side) and then passes through the pores of a hydrophobic membrane to the strip stream (cold side or receiver stream) where it re-condenses [72]. The hydrophobicity of the membrane used, and maintaining a gaseous phase inside the membrane pores, are the necessary conditions of the process. MD can be performed at a feed temperature considerably lower than its boiling point. This permits the
utilization of the waste heat or alternative energy sources [72].

Membrane processes offer a number of advantages over conventional treatment of industrial effluents by its simple operation and low energy requirements, a highly concentrated solution can be treated and valuable products can be recovered and commercially utilized. Another advantage of MD is that pure water is obtained in the receiver stream.

Membrane distillation is classified into four processes based on the different methods of water condensation in the receiver stream – Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Sweeping Gas Membrane Distillation (SGMD) and Vacuum Membrane Distillation (VMD).

Zeng used VMD to recover HCl from rare earth chloride solutions on a laboratory scale. The separation was achieved using the ‘salting-out’ effect of RECl₃, and the partial pressure calculation of H₂O and HCl. The results indicated that HCl separation from rare earth strip solution was possible using VMD method (vacuum membrane distillation) with the recovery ratio of 80% [72]. Tomaszewska et al. have shown, that hydrochloric acid may be separated from the solutions by membrane distillation [73]. Madhumala et. al. also recovered hydrochloric acid and glycerol from aqueous solutions in chloralkali and chemical process industries by membrane distillation [74]

7.2.4. Pyrohydrolysis

Pyrohydrolysis is a roasting process in which acidic ferrous chloride is burned to produce iron oxide and hydrogen chloride gas. Hydrogen chloride gas is then processed in an adsorption column where the hydrogen chloride gas reacts with incoming water (usually rinse water from the pickling process) to form a near-azeotrophic hydrochloric acid.
Hydrochloric acid regeneration using pyrohydrolysis provides total recovery of a metal-free acid solution yielding hydrochloric acid in its free and bonded state and also high quality iron oxide pellets or fine powder as by product.

Iron (II) chloride solution is produced on account of the following reaction of iron oxide and the unused HCl (Equation 7.1 and 7.2):

\[
Fe_2O_3 + 4HCl \leftrightarrow 2FeCl_2 + 2H_2O \quad (7.1)
\]
\[
Fe_2O_3 + 6HCl \leftrightarrow 2FeCl_3 + 3H_2O \quad (7.2)
\]

The water and free acid components in the pickling solution rapidly evaporates at the high temperature of reaction. Thus the roasting gas contains the entire free and bonded acid in a form that can be absorbed. The hydrochloric acid is recovered by the absorption of gaseous HCl in water in the absorber. The pyrohydrolysis process is very energy intensive and thus costly [75].

7.3. Free Acid Determination

It is imperative to prove that acid recovery is technically possible with the spent leach liquor. The best method for acid recovery must be based on economic and operating cost. In order to ascertain the best and practical method to recover or regenerate the spent leach liquor, the free acid or unused acid need to be determined.

Free acidity refers to the “free” amount of hydrochloric acid or the unbound hydronium ions in the metal chloride solution or spent leach solution. Free acidity was measured using the traditional titration method. 5 ml of the spent acidic leach solution was titrated against 1 M NaOH titrant solution (Sigma Aldrich) using phenolphthalein (2 to 3 drops) as indicator. The neutralization reaction end point is known when the solution changes from colorless to fuchsia.
Generally, a complexing agent such as potassium oxalate is added before titration to prevent hydrolysis of metallic ions in solution such as iron and copper. However, these complexing agents form a white precipitate in the solution, which hinders the observation of color change during titration. Therefore, no complexing agent was added before titration and as a result any hydroxide consumption by cupric and ferric ions wasn’t prevented. Consequently, the measurement of free acid (g/L) in the leach solution may be lower than as reported. Free acidity was calculated using the volume of base to reach the end of point of titration using the following equation (Equation 7.3):

\[ HCl + NaOH \rightarrow NaCl \text{ (aq)} + H_2O \quad (7.3) \]

The results of the free acidity measurement of the leach solutions shows over 50% the acid is unused in the leaching reaction. However, they may be hydrolysis of Fe and Cu in the leach liquor, thus the free acidity numbers reported in Table 7.3 might be higher than the actual free HCl in the leach solutions.

<table>
<thead>
<tr>
<th>Table 7.3: Free acidity measurement of spent leach solutions.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NaOH (mL)</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>5 mL 1st Leach Soln.</td>
</tr>
<tr>
<td>8.4</td>
</tr>
<tr>
<td>7.8</td>
</tr>
<tr>
<td>7.6</td>
</tr>
<tr>
<td>5 mL 2nd Leach Soln.</td>
</tr>
<tr>
<td>7.0</td>
</tr>
<tr>
<td>7.1</td>
</tr>
<tr>
<td>6.9</td>
</tr>
<tr>
<td>5 mL 3rd Leach Soln.</td>
</tr>
<tr>
<td>8.6</td>
</tr>
<tr>
<td>8.7</td>
</tr>
<tr>
<td>8.9</td>
</tr>
<tr>
<td>5 mL 3rd Leach Soln.</td>
</tr>
<tr>
<td>15.5</td>
</tr>
<tr>
<td>15.9</td>
</tr>
</tbody>
</table>

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7.4. Rare Earth Recycling Process

The developed recycling technology involves three steps (Figure 7.8). First there is mechanical separation of coarse glass particles from the retorted phosphor powder followed by chemical digestion with HCl to separate halophosphate and aluminates (L1) and solubilize yttrium and europium (L2). The green phosphor left in the residue can then be separated with Wet High Intensity Magnetic Separation (WHIMS) followed by leaching (L3) to extract cerium, lanthanum and terbium. Another approach is that the residue after L2 undergoes caustic solid conversion with 50% NaOH under high pressure and temperature to break the phosphate matrix and improve terbium extraction with HCl digestion. The rare earths in the leach liquor then undergo oxalic precipitation to produce RE oxalate, which is then calcined to produce a mixed REO concentrate. The impurities left in the leach liquor is treated in a wastewater treatment facility via chemical precipitation with lime, coagulation, pressure filtration and ion exchange. The solid waste (residue) remaining is washed with water to remove any entrained HCl and then sent to landfills.

The REO concentrate produced is shipped to a facility for separation of the individual REOs using solvent extraction to produce pure REO, which can then be sold or used to make co-precipitates LaCeT, (La,Ce,Tb)PO$_4$ YOX, (Y,Eu)$_2$O$_3$ for new phosphor production. The phosphor quality has to be validated in lamp tests.
Figure 7.8: Proposed Rare earth recycling flow plan.
CHAPTER 8
KINETICS AND MECHANISM OF LEACHING

Leaching of phosphor dust after pretreatment was carried out using 2 M HCl at 180 g/L pulp density and 600 rpm at different temperature (25, 50, 70 and 80°C) and time (0, 7.5, 15, 22.5, 30, 45 and 60 min). From these experiments, a reaction rate curve was generated by plotting the percentage extraction of yttrium and europium as a function of time at different temperature.

It was observed that the extent of leaching of Y and Eu increased with increase in time and temperature (Figure 8.1 and 8.2). Smaller particles in the powder leach at a faster rate than the larger particles and thus the steep region of the reaction rate curve corresponds to leaching of the smaller particles.

Figure 8.1: Reaction rate curve of leaching of yttrium for kinetic study.

Figure 8.1: Reaction rate curve of leaching of yttrium for kinetic study.
Figure 8.2: Reaction rate curve of leaching of europium for kinetic study.

After the small particles have been dissolved, the larger particles are subsequently leached at a slower rate and this is the region of the curve with a gentle slope. More large particles are leached at higher temperature since an increase in temperature also increases reaction rate. The reaction rate curve was used in a kinetic study to determine the rate-controlling step for the leaching reaction, which is given by the following equations (Equations 8.1 and 8.2):

\[
Y_2O_3 + 6H^+(aq) + 6Cl^-(aq) \rightarrow 2Y^{3+}(aq) + 6Cl^-(aq) + 3H_2O \quad (8.1)
\]

\[
Eu_2O_3 + 6H^+(aq) + 6Cl^-(aq) \rightarrow 2Eu^{3+}(aq) + 6Cl^-(aq) + 3H_2O \quad (8.2)
\]

The proton destabilizes the rare earth oxide crystal lattice by attacking the oxygen to form water. The chloride ion from HCl is a strong complexing ligand and forms an aquo complex with the unbounded rare earth cation to form rare earth chlorides. The reaction can go forward or backwards depending on the concentration of rare earth chlorides and also their solubility.
8.1. Heterogeneous Reaction Kinetics

Heterogeneous reaction kinetics describes the particle-fluid interaction between oxidized Re$_2$O$_3$ particles, and the HCl acidic leach solution. Leaching is a heterogeneous reaction that takes place at the interface between a solid and liquid phase or in some cases a gaseous phase. At the interface or boundary between the two phases, a diffusion layer is formed which is also called stationary aqueous layer in the case of a solid in an aqueous phase. The diffusion layer can never be completely removed but can be made smaller by vigorous stirring (high agitation rate). Typical thickness of the diffusion layer in a well-stirred system ranges from 1-10 μm. Heterogeneous reaction kinetics can be described in the following steps as shown in Figure 9.3 [76] [77]:

1. Diffusion of reagent through the diffusion layer
2. Adsorption of reagent on surface
3. Reaction on the surface
4. Desorption of product from surface
5. Diffusion of product through the diffusion layer

The rate-controlling step is the slowest step in the leaching reaction. Based on which process is rate-controlling, three different types of reactions may occur - chemical controlled, diffusion controlled and intermediate controlled leaching (Figure 8.3). If the chemical reaction at the surface is much slower than diffusion of reagents through the diffusion layer, the leaching becomes reaction controlled and the concentration of reagents at the surface ($C_i$) becomes equal to the concentration in the bulk phase ($C$), i.e. $C_i \approx C$. When the chemical reaction on the surface is much faster than diffusion, leaching becomes diffusion-controlled and $C_i = 0$. When the rate of chemical reaction at the surface is
approximately the same as the rate at which reactants diffuse through the diffusion layer, the leaching becomes intermediately controlled and $0 < C_i < C$ [77].

Figure 8.3: Schematic diagram of the rate controlling steps for leaching models [77].

The most common models considered in leaching are illustrated in Figure 8.4. Figure 8.4a corresponds to the case when the reaction takes place on the exposed surface of the particle and the product completely dissolves in the liquid. Shrinking Spherical Particle model is the case when the reaction takes place on the exposed surface of the particle and the product completely dissolves in the liquid (Figure 8.4a). “Shrinking Core - Constant Particle Size” is the case when the product does not dissolve in the liquid and the particle size does not change but the reacting core shrinks inside the particle (Figure 8.4b).
“Shrinking Core - Shrinking Particle” is the case when as the reaction proceeds, the unreacted core of particle shrinks while a soft gelatinous silica layer forms around the core, which breaks apart when the particles collide (Figure 8.4c). However, a thin layer of silica (ash layer) remains around the core, which forms an exoskeleton around the shrinking particle. Shrinking spherical particle and shrinking-core model were considered as the base kinetic model for the leaching of Y and Eu in this study [78].

Heterogeneous rate expressions for fluid-solid reactions based on the shrinking particle and shrinking core model are listed in Table 8.1 and 8.2. The rate expressions for shrinking spherical particle are considered for a small particle, which corresponds to the small size particles of the first leach residue (4 – 45 μm in diameter) used for this kinetic study. For the rate equations corresponding to both models, $E$ is percentage extraction or fractional conversion of a particle leached at time $t$, $k_c$ and $k_d$ are the rate constants for the chemical and diffusion controlled model respectively.
Table 8.1: Rate expressions for shrinking spherical particle [79].

<table>
<thead>
<tr>
<th></th>
<th>Film Diffusion Control</th>
<th>Ash Diffusion Control</th>
<th>Chemical Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrinking Particle</td>
<td>$1 - (1 - E)^{\frac{2}{3}} = k_d t$</td>
<td>N/A</td>
<td>$1 - (1 - E)^{\frac{1}{3}} = k_c t$</td>
</tr>
</tbody>
</table>

Table 8.2: Rate expressions for shrinking-core model [79].

<table>
<thead>
<tr>
<th></th>
<th>Film Diffusion Control</th>
<th>Ash Diffusion Control</th>
<th>Chemical Control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E = k_d t$</td>
<td>$1 - 3(1 - E)^{\frac{2}{3}} + 2(1 - E) = k_d t$</td>
<td>$1 - (1 - E)^{\frac{1}{3}} = k_c t$</td>
</tr>
</tbody>
</table>

The time dependent behavior of the reaction at different temperatures was then used to plot the left hand side of the various rate equations in Table 8.1 and 8.2 against $t$ and the rate equation that resulted in the most linear function was determined to correspond to the rate-controlling step.

### 8.2. Leaching Model Application

Data obtained in the leaching of Y and Eu at different time and at 25, 50 and 70°C was analyzed in a kinetic study to determine the leaching model, which describes the rate-controlling step. The chemical and film diffusion controlled model for shrinking spherical particle model was not applicable for the kinetic data (Figure 8.5 – 8.8). Chemical, ash diffusion and film diffusion controlled models for the shrinking core models were also tested and they weren’t applicable. These models weren’t applicable because they showed a poor fit at 70°C (Figure 8.9 – 8.12).

The rate of the leaching reaction is very fast. The reaction curve (Figure 8.1 and 8.2) starts to flatten by 7.5 minutes. Therefore, kinetic data should have been taken between 0 and 7.5 minutes to effectively analyze the reaction kinetics and determine the model, which describes the rate-controlling step. Kinetic data after 7.5 minutes measure the
thermodynamic effect since the extent of reaction or percentage extraction didn’t change much with time.

Figure 8.5: Chemical controlled of shrinking spherical particle model for yttrium.

Figure 8.6: Chemical controlled of shrinking spherical particle model for europium.
Figure 8.7: Film diffusion controlled of shrinking spherical particle model for yttrium.

Figure 8.8: Film diffusion controlled of shrinking spherical particle model for europium.
Figure 8.9: Ash diffusion controlled of shrinking core model for yttrium.

Figure 8.10: Ash diffusion controlled of shrinking core model for europium.
Figure 8.11: Film diffusion controlled of shrinking core model for yttrium.

Figure 8.12: Film diffusion controlled of shrinking core model for europium.
The kinetic data were also analyzed using the empirical model of leaching governed by the following logarithmic equation (Equation 8.3) [80][81]:

$$(-\ln(1 - E))^2 = k_t t \quad (8.3)$$

Where $E$ is the percentage of particle leached into the solution at time $t$ and $k_t$ is the specific rate constant for the empirical model.

Table 8.3 shows the kinetic data relatively show a better fit to the logarithmic equation than the shrinking spherical particle and shrinking core models. This is evident from the high $R^2$ values using the empirical kinetic model (Figure 8.13 and 8.14). The kinetic data obtain at 70°C best fits the empirical model as compared to the other models investigated in this study.

![Empirical Model for Kinetics of Leaching of Yttrium](image)

Figure 8.13: Empirical model for kinetics of leaching of yttrium.
Figure 8.14: Empirical model for kinetics of leaching of europium.

Table 8.3: Leaching models with their respective $R^2$ values.

<table>
<thead>
<tr>
<th>°C</th>
<th>Shrinking Particle</th>
<th></th>
<th>Shrinking Core</th>
<th></th>
<th>Empirical Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical Control</td>
<td>Film Diffusion</td>
<td>Ash Diffusion</td>
<td>Film Diffusion</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.8443</td>
<td>0.844</td>
<td>0.8913</td>
<td>0.7892</td>
<td>0.9661</td>
</tr>
<tr>
<td>50</td>
<td>0.9894</td>
<td>0.9826</td>
<td>0.9959</td>
<td>0.9699</td>
<td>0.9873</td>
</tr>
<tr>
<td>70</td>
<td>0.9193</td>
<td>0.9211</td>
<td>0.9409</td>
<td>0.9174</td>
<td>0.9487</td>
</tr>
<tr>
<td>25</td>
<td>0.7879</td>
<td>0.746</td>
<td>0.7857</td>
<td>0.7046</td>
<td>0.8768</td>
</tr>
<tr>
<td>50</td>
<td>0.9969</td>
<td>0.9912</td>
<td>0.9971</td>
<td>0.9817</td>
<td>0.9809</td>
</tr>
<tr>
<td>70</td>
<td>0.9548</td>
<td>0.9521</td>
<td>0.9647</td>
<td>0.9491</td>
<td>0.9678</td>
</tr>
</tbody>
</table>

The activation energy for leaching of Y and Eu from the phosphor powder was calculated using the values of the specific rate constant, $k_t$ to generate the Arrhenius plot (Figure 8.15 and 8.16). Activation energy was calculated to be 77.49 kJ/mol for Y and 72.75 kJ/mol for Eu in the temperature range of 25 to 70°C and these values are within the
range for metal dissolution following the logarithmic relation. Therefore, the empirical model explains the mechanism of leaching of Y and Eu from waste lamp phosphor powder.

![Figure 8.15: Arrhenius plot for empirical kinetic model for leaching of yttrium.](image1)

![Figure 8.16: Arrhenius plot for empirical kinetic model for leaching of europium.](image2)
Himanshu and coworkers investigated the kinetics and mechanism of leaching of rare earth metals from phosphor powder. Their kinetic data followed empirical model of leaching and the activation energy was found to be 76 kJ/mol and 61 kJ/mol for dissolution for yttrium and europium, respectively in the temperature range of 70 to 90°C [81].
CHAPTER 9

PRECIPITATION OF RARE EARTH ELEMENTS

The separation and purification of rare earth elements (REEs) is still a matter of utmost concern and a process to recover significant amount of REEs from acidic solutions without compromising the purity is needed. Individual rare earth elements in high purity can be produced by separation as double nitrates [5]. A widely used and common REE precipitation methods is the formation of sodium double sulphate hydrates (NaRE(SO₄)₂.xH₂O) through the addition of sodium sulphate [5]. Sodium double sulphate hydrates salts are only slightly soluble in acidic solutions and they can be separated from each other by using a metathesis reaction to convert the double sulphate into a rare earth hydroxide, which is highly soluble [5]. These methods are effective but some require many process steps and material handling. One of the most widely used precipitation method to separate rare earth elements from other metals in acidic solutions is by precipitating them with oxalic acid and sodium/ammonium carbonate, since metals such as (Al, Fe, Zn, Ti, Zr, and Mo) remain in solution as soluble oxalate or carbonates complexes [5]. Rare earth oxalates and carbonates have very low solubility, which increases slightly as a function of pH [82].

Precipitation of rare earths from acidic solutions is the most common treatment method used today. Before the industrial use of solvent extraction and ion exchange, rare earths were separated from acidic leach liquor by means of selective precipitations. Selective precipitation is largely preferred due to its cost benefits and thus it has been extensively studied for industrial application. Some of research efforts on this topic include dissolution of the rare earth concentrates with ammonium carbonate and the resultant
complexes treated with hydrogen peroxide for the precipitation of the corresponding peroxicarbonates [83].

Another investigative approach is the precipitation of REEs with alkaline carbonates. Firsching and Mohammadzadel determined the solubility products of rare earth carbonates [84]. Krumholz and his co-workers produced various rare earth concentrates using carbonate as precipitant, some of them for industrial application as a “rare earth carbonate”, “didymium-45 carbonate”, “didymium-50 carbonate”, “neodymium-85 carbonate” and “yttrium-85 carbonate” [85]. Vasconcellos has demonstrated that ammonium carbonate precipitation with the addition of hydrogen peroxide could be used to separate yttrium as a soluble peroxycarbonate from europium as an insoluble peroxycarbonate [86][87].

Researchers have also exploited the different behavior of rare earth chlorides with oxalic acid and the differential precipitation of the corresponding rare earth oxalates. Thus oxalic acid has been used to precipitate rare earth chlorides from acid media as rare earth oxalates, which are then fire refined by calcination to produce rare earth oxides. Large amount of iron tend to inhibit precipitation of the rare earth element and therefore should be removed by either extraction or the rare earths should be separated by fluoride precipitation [88][89]. The proposed reaction for oxalic acid precipitation of rare earths is given by equation 9.1:

$$2RE^{3+} + 3H_2C_2O_4 \leftrightarrow RE_2(C_2O_4)_3 \cdot xH_2O_{(solid)} + 6H^+ \quad (9.1)$$

According to Equation 9.1, the solubility of rare earths decreases as the oxalic acid concentration increases and decreases as the hydrogen ion concentration in solution increases. Low solubility of rare earths at high concentrations of oxalic acid is due to formation of insoluble rare earth oxalate complex. One of the largest expenses involved in
oxalate precipitation process is the high cost of oxalic acid. Therefore, any means of recovering this acid would result in substantial savings [5].

9.1. Precipitation of REEs from Acidic Leach Liquor

The $E_{h}$-$pH$ diagram for Y-Cl-H$_2$O and Eu-Cl-H$_2$O system in Figure 9.1 and 9.2 confirms the ease of precipitation of rare earth hydroxides at room temperature (25°C) at relatively high pH (alkaline environment). The rare earth chlorides in the leach liquor are converted to hydroxides, which are insoluble at high pH.

Chi explored the optimum conditions to precipitate rare earths with oxalic acid. Similar to phosphor leach solution, calcium, magnesium and aluminum impurities consume large 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 the optimum conditions [90].

![Figure 9.1: The Eh-pH diagram for Y-Cl-H$_2$O system at 25°C.](image-url)
The pregnant leach liquor used for the precipitation experiments was obtained by leaching the residue from the wash stage under the following conditions: 2 M HCl, 175 g/L, 70°C, 1 hour, 600 rpm. Precipitation experiments were conducted at room temperature with oxalic acid as precipitant. The solution was then stirred for 2 hours to allow time for the rare earth elements to precipitate (Figure 9.1). The solution was then filtered and the residue (mixed rare earth oxalates) was dried and calcined at 900°C to produce the mixed rare earth oxide powder, which was then analyzed for their rare earth content with XRF.

The parameters investigated in the precipitation experiments are pH, temperature and oxalic acid stoichiometric ratio (SR) to evaluate the best possible precipitation conditions. The experiments were done to improve recovery of Y and Eu from the leach liquor and the grade of the mixed (Y, Eu) oxide. The experimental procedure is shown in Figure 9.3.
The pH was adjusted with sodium hydroxide and stoichiometric amount of oxalic acid was added according to the proposed reaction for rare earth oxalate precipitation. Oxalic acid stoichiometric ratio is defined by Equation 9.2:

\[
Oxalic \text{ Acid Stiochiometric Ratio (SR)} = \frac{3\text{H}_2\text{C}_2\text{O}_4}{2\text{Re}^{2+}} \quad (9.2)
\]

Therefore, oxalic acid stoichiometric ratio of 1.5 and 2.0 means 50% and 100% excess stoichiometric amount of oxalic acid was used for precipitation. The leach liquor used was obtained from the second staged leach in the newly developed process for extracting the chief rare earth elements in waste fluorescent lamps. The results of the precipitation experiments are listed in Table 9.1.
Table 9.1: Precipitation of yttrium and europium from leach liquor.

<table>
<thead>
<tr>
<th>Test #</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Oxalic Acid SR</th>
<th>Grade (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>25</td>
<td>1.0</td>
<td>98.41</td>
<td>89.18</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>25</td>
<td>1.5</td>
<td>98.81</td>
<td>99.18</td>
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<tr>
<td>3</td>
<td>0</td>
<td>25</td>
<td>2.0</td>
<td>98.57</td>
<td>99.59</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>50</td>
<td>1.0</td>
<td>99.18</td>
<td>88.30</td>
</tr>
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<td>5</td>
<td>0</td>
<td>50</td>
<td>2.0</td>
<td>99.00</td>
<td>99.65</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>75</td>
<td>1.0</td>
<td>99.11</td>
<td>91.13</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>75</td>
<td>1.5</td>
<td>99.28</td>
<td>89.20</td>
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<tr>
<td>8</td>
<td>0</td>
<td>75</td>
<td>2.0</td>
<td>99.20</td>
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<td>9</td>
<td>1</td>
<td>25</td>
<td>1.5</td>
<td>72.60</td>
<td>99.34</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>25</td>
<td>2.0</td>
<td>77.35</td>
<td>99.92</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>50</td>
<td>1.0</td>
<td>94.28</td>
<td>89.34</td>
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<td>12</td>
<td>1</td>
<td>50</td>
<td>1.5</td>
<td>82.65</td>
<td>98.77</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>50</td>
<td>2.0</td>
<td>78.46</td>
<td>99.90</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>75</td>
<td>1.0</td>
<td>99.14</td>
<td>92.89</td>
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<tr>
<td>15</td>
<td>1</td>
<td>75</td>
<td>1.5</td>
<td>85.97</td>
<td>98.84</td>
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<tr>
<td>16</td>
<td>1</td>
<td>75</td>
<td>2.0</td>
<td>79.70</td>
<td>99.77</td>
</tr>
<tr>
<td>17</td>
<td>2</td>
<td>25</td>
<td>1.0</td>
<td>95.03</td>
<td>90.96</td>
</tr>
<tr>
<td>18</td>
<td>2</td>
<td>25</td>
<td>1.5</td>
<td>73.64</td>
<td>99.27</td>
</tr>
<tr>
<td>19</td>
<td>2</td>
<td>25</td>
<td>2.0</td>
<td>69.37</td>
<td>99.14</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>50</td>
<td>1.0</td>
<td>90.94</td>
<td>84.70</td>
</tr>
<tr>
<td>21</td>
<td>2</td>
<td>50</td>
<td>1.5</td>
<td>75.96</td>
<td>99.38</td>
</tr>
<tr>
<td>22</td>
<td>2</td>
<td>50</td>
<td>2.0</td>
<td>82.49</td>
<td>99.88</td>
</tr>
<tr>
<td>23</td>
<td>2</td>
<td>75</td>
<td>1.0</td>
<td>95.45</td>
<td>88.15</td>
</tr>
<tr>
<td>24</td>
<td>2</td>
<td>75</td>
<td>1.5</td>
<td>82.73</td>
<td>99.43</td>
</tr>
</tbody>
</table>

The results for recovery were obtained from ICP-OES on the filtrate and the results for grade was obtained by XRF on the mixed oxide. The design of experiments was analyzed by Stat-Ease Design-Expert 9.0.5® software to develop a statistical model for Y and Eu precipitation optimization. The data wasn’t statistically relevant and thus the model wasn’t significant. However, the 3D surface plots generated describe the best operation conditions attained in the precipitation experiments. The parameters investigated are recovery of yttrium and europium from the leach liquor and the grade of mixed (Y, Eu) oxide produced. The desirability of the precipitation process, which is a combination of recovery and grade, was also analyzed.
9.2. Precipitation Optimization for Mixed REO Production

Figure 9.4 and 9.5 shows the influence of the leaching parameters on the grade and recovery of the mixed (Y, Eu) oxide. The effect of oxalic acid SR, temperature and pH on grade, recovery and desirability was investigated.

Figure 9.4: 3D response surface graphs generated by Stat-Ease software for Y and Eu precipitation optimization model showing a) the effect of oxalic acid SR and pH on grade of mixed oxide and b) the effect of temperature and pH on grade of mixed oxide.

Figure 9.5: 3D response surface graphs generated by Stat-Ease software for Y and Eu precipitation optimization model showing a) the effect of oxalic acid SR and pH on recovery and b) the effect of temperature and pH on desirability.
Figure 9.6 shows that the grade of (Y, Eu) mixed oxide is maximized at the lowest pH (0 or native pH of leach liquor), least amount of oxalic acid SR (1.0) and temperature effect is inconclusive, although grade increased with temperature at low pH. Temperature didn’t affect recovery. Figure 9.5 shows that recovery of Y and Eu from the acid leach liquor is maximized with the highest oxalic acid SR and it slightly increases with pH. Figure 9.6 further shows that high oxalic acid stoichiometric ratio improves recovery but decreases grade, which is expected as the excess oxalic acid introduces more impurities to the mixed oxide powder. Standard deviation of the grade and recovery in Figure 9.6 was less than 1% (0.01) and thus wasn’t included in the graph. Thus the optimum conditions for precipitation in this study are at room temperature (25°C) and native pH (pH = 0).
It is evident that it is easy to precipitate the rare earths from the leach liquor using oxalic acid. All the rare earth elements are precipitated as rare earth oxalate even at pH of 0 or without any base added. The main impurities are calcium, aluminum, sodium, silicon, potassium, phosphorus, antimony, copper, manganese, zinc and iron all at trace amount concentration. Most of the impurities were in the leach liquor, which was extracted from the powder, but there were also some impurities from the precipitant media (NaOH and oxalic acid). Over 99% pure mixed rare earth oxide at 99% recovery has been attained from these experiments but further experiments should be conducted to optimize the precipitation conditions to minimize entrained impurities. This will also reduce oxalic acid consumption, which is a major expense in REE oxalate precipitation.

9.3. Characterization of (Y, Eu) Mixed Oxide

A sample of the mixed oxide from Test #5 was characterized to check the morphology of the particles, phases of minerals present and confirm the purity. The morphology of particles in the mixed oxide was detected with FE-SEM SEI with a zoom of 500x (Figure 9.7). The micrograph shows that the mixed oxide contains both single and aggregated crystals of different size and shape.

Elemental composition of the powder was obtained with EDS. Semi-quantitative elemental composition information was determined over the entire area of the mixed oxide under a magnification of 8500 (Figure 9.8). The result of the elemental composition is shown in Figure 9.5, which confirms the high purity of the mixed oxide. The only detectable impurity in the mixed oxide is gadolinium, which is only present in trace amount (0.43 wt %). Consequently the purity of the mixed oxide powder produced is 99.57% and the ratio of yttrium to europium is approximately 1:21 by atomic weight.
Figure 9.7: FE-SEM micrograph showing morphology of particles in the mixed oxide.

Figure 9.8: FE-SEM micrograph showing the mixed oxide at a zoom of 8500x.
Figure 9.9: EDS elemental analysis of mixed (Y, Eu) oxide.

Figure 9.10 shows the phases of the minerals present in the mixed oxide powder corresponds to pure (Y, Eu) oxide.

Figure 9.10: XRD pattern for phase identification in mixed (Y, Eu) oxide.
CHAPTER 10
SCOPING ECONOMIC ANALYSIS

The purpose of this chapter is to highlight the economics of the proposed flowsheet. Three separate process economic scenarios are considered – high (6 year historical average), low (2 year historical average) and base case (current price). The estimated capital and operating cost for each scenario are discussed.

10.1. Material Flows and Assumptions

It was necessary to make several materials flow assumptions in developing capital and operating costs. In an effort to give a reasonably conservative estimate, a 20% contingency was factored into the final capital and operating costs. Material flow assumptions were as follows:

- 300 MWh/year recycling facility.
- Use existing recycling facility for plant.
- Use existing water treatment facility for wastewater treatment.
- 350 days/year in operation.
- 3 shifts/day.
- 2400 tons/year recycled phosphor powder.
- Phosphor powder sieved to 75 μm and shipped to facility for $0.20/Ib freight on board (FOB).
- 50% of total phosphor powder weight is in the 75 μm fraction.
- 1200 tons/year recycled phosphor powder.
- Shipping adds 20% to the equipment cost.
• 10% solution volume increase from phosphor powder or residue addition.

• Electricity cost estimate is $0.112 kWh (the average for Colorado).

• Sieved powder is 20% REO and contains 14% yttrium and europium oxide in 15.5:1 ratio.

• Phosphor powder molar ration is 26:1 yttrium to europium oxide.

• 88% total recovery of yttrium and europium from the sieved powder to calcined mixed oxides.

• Second leach residue is 30% of original phosphor weight.

• Use 1.5 times the stoichiometric ratio of oxalic acid to Y and Eu.

• Recoverables, per year are as follows:
  • 145 tonnes mixed (Y, Eu) oxide, 99% pure
  • 9 tonnes Eu₂O₃
  • 136 tonnes Y₂O₃.

• Shipping adds 20% to the equipment cost

• 10% solution volume increase from phosphor powder or residue addition

10.2. Capital Equipment Cost

Capital equipment cost, power consumption, and capacities were gathered from Alibaba and confidential sources. For each of the three scenarios, an estimate of the necessary major equipment was calculated. From initial primary equipment estimates, final fixed capital costs, including a 20% contingency, were calculated using factors presented in Muller’s (2002), “Factored Capital Cost Estimate Guide”. Equipment power ratings were converted to kWh using Equation 10.1:
Total Power Consumption (kWh) = Power (HP) x 0.746 \left(\frac{kW}{HP}\right) x Daily Use (hr) \ (10.1)

A summary of the factors used in the determination of total fixed capital cost is presented in Table 10.1. In each case, the capital equipment cost was determined using Alibaba.com or confidential source as presented in Tables 10.1. Total capital equipment cost is estimated to be $339,940. The plant required 340,830 kWh power per day. The total fixed capital cost was estimated to be $712,008.

Table 10.1: Capital cost for the REE recycling facility.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Installation</th>
<th>Piping, Instrumentation</th>
<th>Auxiliaries</th>
<th>Engineering</th>
<th>Sub Total</th>
<th>Contingent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Wash</td>
<td>$42,000</td>
<td>$16,800</td>
<td>$17,640</td>
<td>$4,410</td>
<td>$8,820</td>
<td>$72,030</td>
</tr>
<tr>
<td>Filtration</td>
<td>$75,600</td>
<td>$30,240</td>
<td>$31,752</td>
<td>$7,938</td>
<td>$15,876</td>
<td>$129,654</td>
</tr>
<tr>
<td>2nd Leach</td>
<td>$48,000</td>
<td>$19,200</td>
<td>$20,160</td>
<td>$5,040</td>
<td>$10,080</td>
<td>$82,320</td>
</tr>
<tr>
<td>All</td>
<td>$27,000</td>
<td>$10,800</td>
<td>$11,340</td>
<td>$2,835</td>
<td>$5,670</td>
<td>$46,320</td>
</tr>
<tr>
<td>Other</td>
<td>$110,640</td>
<td>$44,256.00</td>
<td>$46,469</td>
<td>$11,617</td>
<td>$23,234</td>
<td>$189,748</td>
</tr>
<tr>
<td>Building (29%)</td>
<td>$87,940</td>
<td></td>
<td></td>
<td></td>
<td>$87,940</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>$391,180</td>
<td>$121,296</td>
<td>$127,361</td>
<td>$31,840</td>
<td>$63,680</td>
<td>$104,011.32</td>
</tr>
</tbody>
</table>

10.3. Detailed Capital Cost

The primary capital cost for the process includes two leach tanks, filter press, tray dryer and powder loaders. Table 10.2 shows the individual equipment costs, the number needed and their power usage. The specifications and the source of the equipment are given as well. The source of some of this information is confidential and therefore cannot be disclosed. There is also an added 20% contingency included in the individual cost.

10.4. Operating Cost

The operating cost includes electricity, hydrochloric acid, oxalic acid, cost of CFL powder, cost of sieving and labor. The labor includes a supervisor, a process engineer, a maintenance supervisor, and 10 technicians. The total labor costs were taken from a
similar, confidential operation. The operating cost summed on yearly basis is shown in Table 10.3.

Table 10.2: Individual equipment cost, number and power consumption.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Equipment</th>
<th>Specifications</th>
<th>Number</th>
<th>kW</th>
<th>Hours/day</th>
<th>kWh/Day</th>
<th>$/Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Wash Leach</td>
<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>Filtration</td>
<td>Plate &amp; Frame Filter Press</td>
<td>10 Ft²</td>
<td>1</td>
<td>1.5</td>
<td>6</td>
<td>9</td>
<td>60000</td>
<td>Confidential</td>
</tr>
<tr>
<td>Filtration</td>
<td>Pan Filter</td>
<td></td>
<td>1</td>
<td>1</td>
<td>6</td>
<td>66</td>
<td>15600</td>
<td>Confidential</td>
</tr>
<tr>
<td>2nd Leach</td>
<td>Glass lined reactor</td>
<td>12000 L, 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>2nd Leach</td>
<td>Boiler for reactor</td>
<td></td>
<td>1</td>
<td>102</td>
<td>6</td>
<td>102</td>
<td>18000</td>
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</tr>
<tr>
<td>Calcination</td>
<td>Tray Dryer oven</td>
<td></td>
<td>3</td>
<td>12</td>
<td>8</td>
<td>288</td>
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</tr>
<tr>
<td>Other</td>
<td>Air Compressor</td>
<td>75 GPM@ 40', CPVC, PP</td>
<td>15</td>
<td>1.1</td>
<td>10</td>
<td>165</td>
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<td>3</td>
<td>7.5</td>
<td>3</td>
<td>22.5</td>
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<td>3</td>
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<td></td>
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<td>3240</td>
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<td>Other</td>
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<td>Total</td>
<td></td>
<td></td>
<td>811.5</td>
<td>339240</td>
<td>+20% energy contingency</td>
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Table 10.3: Yearly operating cost.

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<th>$/Year</th>
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<tr>
<td>Rent</td>
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<tr>
<td>Labor</td>
<td>699000</td>
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<tr>
<td>Phosphor powder</td>
<td>1375000</td>
</tr>
<tr>
<td>Sieved Powder</td>
<td>490000</td>
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<tr>
<td>Energy</td>
<td>38173</td>
</tr>
<tr>
<td>HCl</td>
<td>144316</td>
</tr>
<tr>
<td>Oxalic Acid</td>
<td>307802</td>
</tr>
<tr>
<td>Operating Cost</td>
<td>3174290</td>
</tr>
</tbody>
</table>

10.5. Revenue

The revenue is generated from a salable 99% pure mixed europium/yttrium oxide. The salable value is a 30% discount from Chinese FOB REO prices based on a confidential source. Three revenue scenarios were calculated, current REO prices, 2-year average REO prices and 6-year average REO prices.
10.6. **Major Reagent Cost Estimates**

Reagents utilized during the process are oxalic acid and hydrochloric acid. Concentrated hydrochloric acid is $200 per ton FOB. A total of 554,750 liters per year were used. The cost of oxalic acid is $1140 per ton FOB. 244 tonnes per year of oxalic acid is needed to run the process.

10.7. **Net Present Value, IRR and Payback Period**

An economic analysis was performed for a 7-year project life and capital equipment cost was depreciated using the Modified Accelerated Cost Recovery System (MACRS) 7-year depreciation. The cost of capital was assumed to be 12% and the total operating costs were assumed to increase 3% per year. Operating expenses were deducted in the year incurred. A corporate income tax rate of 35% was assumed.

Three scenarios are as stated: REO 6-year average (Table 10.4 and Figure 10.1), REO 2-year average (Table 10.5 and Figure 10.2), and REO current price (Table 10.6 and Figure 10.3). The cumulative discounted after tax cash flow is also calculated for each case and shown in the figures. The first two scenarios are highly economic with NPVs of $19.3 million and $3.7 million dollars, respectively. In either case, the payback period is less than a year. However, regarding the third scenario, REO current price, it is non-economic because the revenues are less than the operating costs.

The break-even price to make the process economical is 3.65 times the current price of europium oxide and yttrium oxide or $420 and $15.50 per kg respectively. Therefore, the prices of REO would have to increase in order to be able to economically run a facility for this developed process.
Table 10.4: Cash flow using the 6-year average REO price.

<table>
<thead>
<tr>
<th>Base Case REO 6 Year Average</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<td><strong>Production</strong></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Selling Price $/Unit</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Europium oxide $/kg</td>
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<td>1178</td>
<td>1178</td>
<td>1178</td>
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<td>9034</td>
<td>9034</td>
<td>9034</td>
<td>9034</td>
<td>9034</td>
<td>9034</td>
</tr>
<tr>
<td>Yttrium oxide $/kg</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
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<tr>
<td>Yttrium oxide kg/year</td>
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<td>140026</td>
<td>140026</td>
<td>140026</td>
<td>140026</td>
<td>140026</td>
<td>140026</td>
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</tr>
<tr>
<td>Discount Value from China REO FOB</td>
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<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
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<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
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</tr>
<tr>
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<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
<td>10880045</td>
</tr>
<tr>
<td>- Operating Expense($)</td>
<td>(3174290)</td>
<td>(3269519)</td>
<td>(3367605)</td>
<td>(3468633)</td>
<td>(3572692)</td>
<td>(3679873)</td>
<td>(3790269)</td>
<td></td>
</tr>
<tr>
<td>- Depreciation</td>
<td>101746</td>
<td>174371</td>
<td>124530</td>
<td>88930</td>
<td>63511</td>
<td>63582</td>
<td>31756</td>
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</tr>
<tr>
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<td>7784897</td>
<td>7636970</td>
<td>750342</td>
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<td>7263755</td>
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<td>(2724714)</td>
<td>(2672940)</td>
<td>(2625120)</td>
<td>(2579802)</td>
<td>(2542314)</td>
<td>(2492536)</td>
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<td>4964031</td>
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<td>4721441</td>
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<tr>
<td>+ Depreciation</td>
<td>(101746)</td>
<td>(174371)</td>
<td>(124530)</td>
<td>(88930)</td>
<td>(63511)</td>
<td>(63582)</td>
<td>(31756)</td>
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</tr>
<tr>
<td>- Capital Costs:</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Depreciable Equip. Costs</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>(5712008)</td>
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<td>4839501</td>
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<td>4597240</td>
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<td>2,359,816</td>
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<tr>
<td>x (P/F 12%, n)</td>
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<td>0.89</td>
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<td>0.71</td>
<td>0.64</td>
<td>0.57</td>
<td>0.51</td>
<td>0.45</td>
</tr>
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<tr>
<td>= DCFROR (IRR)</td>
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Figure 10.1: Discounted cumulative cash flow using a 6-year REO average price.
Table 10.5: Cash flow using the 2-year average REO price.

<table>
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<tr>
<th>Base Case REO 2 Year Average</th>
<th>Year 0</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
<th>Year 4</th>
<th>Year 5</th>
<th>Year 6</th>
<th>Year 7</th>
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<tr>
<td>Production</td>
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<td>616</td>
<td>616</td>
<td>616</td>
<td>616</td>
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<td>Selling Price $/Unit</td>
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<td>9034</td>
<td>9034</td>
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</tr>
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<td>Europium oxide $/kg</td>
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<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
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<td>140026</td>
<td>140026</td>
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<tr>
<td>Discount Value from China REO FOB</td>
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<td>0.7</td>
<td>0.7</td>
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<td>0.7</td>
<td>0.7</td>
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<tr>
<td>Gross Revenue ($)</td>
<td>5110870</td>
<td>5110870</td>
<td>5110870</td>
<td>5110870</td>
<td>5110870</td>
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<tr>
<td>Net Revenue</td>
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</tr>
<tr>
<td>- Operating Expense($)</td>
<td>(3174290)</td>
<td>(3269519)</td>
<td>(3367605)</td>
<td>(3468633)</td>
<td>(3572692)</td>
<td>(3679873)</td>
<td>(3790269)</td>
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<tr>
<td>- Depreciation</td>
<td>101746</td>
<td>174371</td>
<td>124530</td>
<td>88930</td>
<td>63511</td>
<td>63582</td>
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<td>Taxable Income</td>
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<tr>
<td>- Tax @ 35%</td>
<td>(713414)</td>
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<tr>
<td>= Net Income</td>
<td>1324912</td>
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<tr>
<td>+ Depreciation</td>
<td>(101746)</td>
<td>(174371)</td>
<td>(124530)</td>
<td>(88930)</td>
<td>(63511)</td>
<td>(63582)</td>
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<tr>
<td>- Capital Costs:</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>- Depreciable Equip. Costs</td>
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</tr>
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<td>977857</td>
<td>907895</td>
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</tr>
<tr>
<td>= DATCF</td>
<td>(712,008)</td>
<td>1092,112</td>
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<td>658,606</td>
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</tr>
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<td>= Cumulative DATCF</td>
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<tr>
<td>x (P/F 12%, n)</td>
<td>1.0000</td>
<td>0.89</td>
<td>0.80</td>
<td>0.71</td>
<td>0.64</td>
<td>0.57</td>
<td>0.51</td>
<td>0.45</td>
</tr>
<tr>
<td>= Cumulative DATCF (NPV)</td>
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<td>= DCFROR (IRR)</td>
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</table>

Figure 10.2: Discounted cumulative cash flow using a 2-year REO average price.
Table 10.6: Cash flow using the current REO price.

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<th>REO Current Price</th>
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<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selling Price $/Unit</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Europium oxide $/kg</td>
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<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td>Europium oxide kg/year</td>
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<td>9034</td>
<td>9034</td>
<td>9034</td>
<td>9034</td>
<td>9034</td>
<td>9034</td>
<td>9034</td>
</tr>
<tr>
<td>Yttrium oxide kg/year</td>
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<td>140026</td>
<td>140026</td>
<td>140026</td>
<td>140026</td>
<td>140026</td>
<td>140026</td>
<td>140026</td>
</tr>
<tr>
<td>Discount Value from China REO FOB</td>
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<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
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<tr>
<td>Gross Revenue ($)</td>
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<td>1143812</td>
<td>1143812</td>
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<td>1143812</td>
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<td>- Operating Expense($)</td>
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<td>(3269519)</td>
<td>(3367605)</td>
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<td>(3572692)</td>
<td>(3679873)</td>
<td>(3790269)</td>
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<td>- Depreciation</td>
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<td>88930</td>
<td>63511</td>
<td>63582</td>
<td>31756</td>
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</tr>
<tr>
<td>Taxable Income</td>
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<tr>
<td>- Tax @ 35%</td>
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<td>682968</td>
<td>734742</td>
<td>782562</td>
<td>827879</td>
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<td>915146</td>
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<tr>
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<td>(174371)</td>
<td>(124530)</td>
<td>(88930)</td>
<td>(63511)</td>
<td>(63582)</td>
<td>(31756)</td>
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</tr>
<tr>
<td>Capital Costs:</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>- Depreciable Equip. Costs ($712,008)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>= After-Tax Cash Flow (ATCF) ($712,008)</td>
<td>-1355422</td>
<td>-1442740</td>
<td>-1489051</td>
<td>-1542259</td>
<td>-1601001</td>
<td>-1670693</td>
<td>-1731312</td>
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</tr>
<tr>
<td>= DATCF ($712,008)</td>
<td>1,210,198</td>
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<td>1,059,877</td>
<td>980,134</td>
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<td>846,425</td>
<td>783,157</td>
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<td>1,922,206</td>
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<td>4,132,226</td>
<td>5,112,360</td>
<td>6,020,811</td>
<td>6,867,236</td>
<td>7,650,393</td>
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</tr>
<tr>
<td>x (P/F 12%, n) 1.0000</td>
<td>0.89</td>
<td>0.80</td>
<td>0.71</td>
<td>0.64</td>
<td>0.57</td>
<td>0.51</td>
<td>0.45</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<td>= DCFROR N/A</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PAY BACK PERIOD (years) N/A</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 10.3: Discounted cumulative cash flow using current REO price.
Based on the analysis of the three economic scenarios, two are economic and one is non-economic. At the current REO prices, the recycling of phosphor dust is economically non-viable. However, using historical and recent rare earth prices, the phosphor powder flow plan is highly profitable. Figure 10.3 shows that the economics of the project is most sensitive to phosphor powder throughput in the facility and the total operating cost.

Figure 10.4: NPV sensitivity analysis on the process using 2-year REO average price.
Full phosphor characterization of the waste phosphor powder has been conducted for specific mineralogical and metallurgical parameters. The phosphor powder consists predominantly of quartz (54.30%), apatite (16.64%), Y-bearing minerals (14.98%), calcite (4.75%) and monazite (3.45%) and minor concentrations of xenotime, iron oxide, barite, celestine (Sr), phosphate group, europium and terbium bearing minerals and corundum.

The particle size of the rare earth element-bearing minerals in the phosphor powder are less than 30 µm in size with over 60% being less than 10 µm. These fine particles of the rare earth-bearing minerals make size based separation the most promising physical beneficiation technique in terms of REEs grade and recovery improvements as well as process economics.

Sieving the phosphor powder to below 75 µm helps eliminate most of the coarse glass and some fine glass from the feed. It also led to an REE upgrade of 34.38% with 98.75% recovery. The sieved powder was used for further processing to recover the chief rare earth elements - yttrium, europium, cerium, terbium and lanthanum. Emphasis was placed on yttrium, europium and terbium since these metals have relatively higher market price.

Direct acid leaching or multistage leaching with mild or strong acid reagents isn’t efficient for the extraction of the entire rare earths especially cerium, lanthanum and terbium. Based on experimental work, a new process for extracting the chief REEs from
end of life fluorescent lamps has been developed. The proposed process employs a three-stage leaching and precipitation process for selective extraction and recovery of the REEs.

The first stage leach is the pre-treatment of the sieved phosphor powder to remove significant amount of the gangue materials such as Ca (95.00% ± 4.25), P (89.49% ± 7.38) and Fe (70.71% ± 6.21). The results from the pre-treatment optimization study also shows the pulp density can be increased to 300 g/L and the reaction is mainly chemical controlled rather than by diffusion. The spent hydrochloric acid leach liquor cannot be reused to treat another batch of phosphor powder and therefore acid recovery techniques should be investigated.

The second stage leaching is aimed at removing yttrium and europium. The leaching parameters that were investigated are leaching reagent, acid concentration, temperature, time, and pulp density and agitation speed. Under the optimization study, stage recovery of 100% for Y and Eu were observed at the following conditions: 2.5 M HCl, 175 g/L, 70°C, 1 hour and 600 rpm.

Stat-Ease Design-Expert 9.0.5® software was used for experimental design and analysis to statistically model optimization of the leaching process. The p-values for all of the interaction parameters investigated are significantly greater than 0.05, which indicates the leaching models generated by Stat-Ease are not significant.

The third stage leaching removes the remaining REEs in the powder – Ce, La and Tb. Low levels of extraction of Ce, La and Tb was attained with H₃PO₄ and HCl because the green phosphor that contains these rare earths is recalcitrant and has high thermal stability. Therefore, the residue after the second stage leach should be stockpiled until the market price of Ce, La, Tb justifies the expensive process cost for extracting these REEs.
Kinetic data of the leaching of yttrium and europium showed best fit to the logarithmic rate expression of the empirical model of leaching. Activation energy was calculated to be 77.49 kJ/mol for Y and 72.75 kJ/mol for Eu in the temperature range of 298 to 343 K.

After dissolution of the REEs, the metals were recovered by precipitation with oxalic acid and sodium hydroxide as rare earth oxides. Precipitation tests demonstrate that at least 50% excess the stoichiometric amount of oxalic acid is needed to recover yttrium and europium efficiently and produce a pure (Y, Eu) mixed oxide. Total recovery of the REEs was achieved even at very low pH or without any base added. Over 99% pure mixed rare earth oxide at 99% recovery has been attained from the precipitation experiments but further experiments should be conducted to optimize the precipitation conditions to minimize entrained impurities and also reduce oxalic acid consumption.

An economic assessment of the developed process have been undertaken and based on the analysis of the three economic scenarios, two are economic and one is non-economic. At the current REO prices, the recycling of phosphor powder is economically non-viable. However, using historical and recent rare earth prices, the phosphor powder flow plan is highly profitable.
CHAPTER 12

RECOMMENDATIONS FOR FUTURE RESEARCH

There is still some research that needs to be done before finalizing a full scale recycling technique to recover REEs from spent fluorescent lamp phosphors. The following areas must be examined in greater detail to assess process viability:

1. Evaluate variability of REO content in the phosphor powder from different lamp manufactures on a batch-to-batch basis.
2. Re-investigate mineral processing methods to concentrate and recover REEs.
3. Quantitative evaluation of calcium, phosphor and silica flow throughout the process.
4. Complete mass balance of the entire process.
5. Efficient process for phosphorus and calcium recovery and recycling/disposal.
6. Leaching efficiency should be determined as a function of REE content to ensure better reagent consumption.
7. Determine which acid recovery method is best for the spent leach solutions in the first and second stage leaching steps.
8. Investigate methods to concentrate Tb in the second leach residue and also ascertain the best and cost effective method to selectively increase the solubility of terbium from LAP.
9. Reduce the amount of oxalic acid in REO precipitation to cut cost and also reduce entrained impurities to produce 99.999% mixed (Y, Eu) oxide.
10. Kinetic study of the leaching of Y and Eu using data between 0 and 7.5 minutes leaching time at 25, 50 and 70°C.

11. Demonstrate the viability of the technology to industry by evaluating the process on a pilot scale.

12. Life cycle analysis (LCA) of REEs in phosphors.
Figure A1: Cumulative particle size of sieved powder (75 μm).

Figure A2: Number of particles at different size range for sieved powder (75 μm).
Table B1: Chemical composition of the leach residue for optimization test 1 to 9.

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Figure B1: Normal plot for the leaching optimization model for yttrium.

Figure B2: Normal plot for the leaching optimization model for europium.
Figure B3: 3D response surface graphs generated by the Stat-Ease software showing the desirable conditions for optimized leaching.

Figure B4: 3D response surface graphs generated by the Stat-Ease software for the leaching optimization model for yttrium.
Figure B5: 3D response surface graphs generated by the Stat-Ease software for the leaching optimization model for europium.
REFERENCES CITED


Mei, G.J., Rao, P., Matsuda, M., Fujita, T., 2009a. Separation of red (Y\textsubscript{2}O\textsubscript{3}: Eu\textsuperscript{3+}), blue ((Sr,Ca,Ba)\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2}:Eu\textsuperscript{2+}) and green (LaPO\textsubscript{4}:Tb\textsuperscript{3+},Ce\textsuperscript{3+}) rare earth phosphors by liquid/liquid extraction. Journal of Wuhan University of Technology-Materials Science Edition 24, 418-423.


