LEACHING OF RARE EARTH ELEMENTS: PAST AND PRESENT

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Abstract

The recycling of Rare Earth Elements (REE) from mine tailings and REE containing End-of-Life (EoL) scrap, the two main secondary resources, offers great opportunities to secure REE supply in Europe. The relatively low concentration of REE in mine tailings (1000-1500 ppm) and the variety in contaminants in the EoL scrap have made the extraction of REE from these resources very challenging. This paper provides a review of the past and present technologies for REE leaching used in primary REE production and in REE recycling, as an important part of hydrometallurgical REE processing. Detailed studies of existing processes are essential to properly understand and resolve the difficulties in REE recycling from these secondary resources. The known processes range from acid leaching with H\textsubscript{2}SO\textsubscript{4}, HCl or HNO\textsubscript{3} for primary ores, to leaching with NaCl or (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} of ion adsorbed clays and combined base and acid leaching for EoL lamp phosphors. A comprehensive understanding of these processes is the key to applying them to REE recycling from secondary resources.

I. Introduction

The rare earth elements (REE) are a group of 17 chemically similar elements consisting of the lanthanides, Y and Sc. Their unique physical and chemical properties have made them essential in state-of-the-art equipment (e.g. magnets, catalysts, batteries). A potential supply risk of REE, environmental concerns and economic benefits promote research on processing of secondary materials, such as mine tailings or electronic waste, in the EU. Although significant investigations on REE extraction from secondary resources have been carried out and a variety of technologies have been developed or proposed, most of them are still in the stage of research or only suitable for some specific secondary resources. The REE extraction efficiency and selectivity, together with the cost and engineering during process design, still require substantial optimisation before further commercialisation. At the same time, the understanding of interactions between REE minerals in a low concentration and the leaching media, as well as the behaviour of selective leaching of different REE phases in magnet scraps, is still not sufficient. In order to have a better view on the state-of-the-art and to improve engineering possibilities of REE extraction from secondary resources, a review of the most prevailed leaching technologies that are currently in use in REE production is needed.
### Table 1: Summary of leaching technologies in primary REE production

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Process</th>
<th>REE yield</th>
<th>Remarks</th>
<th>Status</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| Bastnaesite | 1) HCl leach to remove non REE carbonate  
2) Calcination of residue to form REO | 85-90% | The oldest way to process bastnaesite concentrates | outdated | [3] |
| | Digestion with HNO$_3$ or H$_2$SO$_4$ | 98% | Acid choice depends on further processing: solvent extraction $\rightarrow$ HNO$_3$ precipitation $\rightarrow$ H$_2$SO$_4$ | outdated | [3] |
| | 1) Roast at 620°C to drive of CO$_2$  
2) 30% HCl leach | -- | Ce$^{III}$ oxidises to Ce$^{IV}$ during roasting $\rightarrow$ will not leach REE fluorides will not leach, residue is marketable | outdated | [3] |
| | 1) Alkaline conversion REF$_3$ $\rightarrow$ RE(OH)$_3$  
2) HCl leach | -- | Process can be preceded with HCl leach to extract REE carbonates before alkaline conversion | In use | [3] |
| | 1) Sulphuric acid roast  
2) NaCl solution leach  
3) Precipitation as Na double sulphates | -- | Precipitates are converted to chlorides for further purification with solvent extraction | In use | [3] |
| Monazite | Digestion in hot H$_2$SO$_4$ | -- | Process conditions determine what is leached: only LREE or LREE+HREE+Th Yields no pure product | outdated | [3] |
| | 1) Digestion in hot 60-70% NaOH  
2) Washing residue with hot water  
3) Leach with mineral acid of choice | 98% | Ce cannot be leached if Mn is present Th is leached together with REE Na$_3$PO$_4$ is marketable by-product | In use | [3-4] |
| | 1) Heat under reducing and sulphidizing atmosphere with CaCl$_2$ and CaCO$_3$  
2) Leach with 3% HCl | 89% | Requires no fine grinding Th does not leach, remains in residue as ThO$_2$ No Mn problem | In use | [5] |
| Ion clay | Salt leach with (NH$_4$)$_2$SO$_4$ | 80-90% | Targets physisorbed REE through cation exchange | In use | [7] |
| | Leach with seawater | 40% | Inefficient but cheap process | R&D | [8] |
| | Acid leach with strong acid (pH<1) | ALL | Dissolves entire clay, incurs significant additional costs | Not used | [7] |
II. Leaching technologies in primary REE production

The main REE minerals used in primary REE production are bastnaesite and monazite. Next to these, ion adsorbed clays are lower grade resources, which due to their easy processing are becoming more popular as a primary resource. Table 1 offers a concise overview of the leaching technologies, both past and present, used in primary REE production.

Bastnaesite

Bastnaesite is a rare earth fluorocarbonate mineral, RE(CO₃)F, which primarily contains light rare earth elements. After physical upgrading, bastnaesite ore concentrates contain between 40 to 60% REE.

One of the main concerns in past bastnaesite processing technologies (see table 1) was the inability to extract the REE fluorides. It has been successfully resolved in the current day technologies in two different ways: pre/post-treatment with alkaline or sulphuric acid roasting. The alkaline treatment, developed by Kruesi and Duker of Molycorp, is a three step process, using the following reactions:

\[ REF_3 - RE_2(CO_3)_3 + 9HCl \rightarrow REF_3 + 2RECl_3 + 3HCl + 3H_2O + 3CO_2 \]  
\[ REF_3 + 3NaOH \rightarrow RE(OH)_3 + 3NaF \]  
\[ RE(OH)_3 + 3HCl \rightarrow RECl_3 + 3H_2O \]

Step I - a mild HCl solution to extract the REE carbonate, step II - reaction with NaOH at 96°C to convert the REE fluorides to hydroxides, which are then dissolved by leaching with HCl in step III. Alternative processes exist, which skip the first leaching step and instead the bastnaesite is first treated with alkaline and then leached with HCl.

Sulphuric acid roasting is the other main process currently used in market to process bastnaesite. In the process, bastnaesite concentrate is heated in a 98% H₂SO₄ solution to 400 to 500°C for several hours. This decomposes the fluorocarbonate matrix of the bastnaesite, leading to the release of the CO₂ and HF gas. The REE are converted to their sulphates and can be selectively precipitated as Na double sulphates by leaching the residue with NaCl containing water. The sulphate process is currently in use at the Bayan Obo mine in China, while the alkaline method was used by Molycorp at the Mountain Pass mine before it closed.

Monazite

Monazite is a rare earth phosphate mineral, RE(PO₄), containing mostly light REE and some heavy REE (more than bastnaesite). Monazite can contain up to 70% REE, primarily Ce and La as well as significant amounts of Nd, Pr and Sm. The Th content is also quite high, ranging from 4 to 12% which is a concern in monazite processing. As shown in Table 1, the alkaline method is currently one of the main leaching technologies for monazite. The reactions during alkaline leaching are:

\[ REPO_4 + 3NaOH \rightarrow RE(OH)_3 + Na_3PO_4 \]  
\[ Th_3(PO_4)_4 + 12NaOH \rightarrow 3Th(OH)_4 + 4Na_3PO_4 \]
After the monazite is digested in 60-70% NaOH at 140-150°C for 4 hours, the residue is dissolved into hot acidic solution, i.e. HNO₃ for solvent extraction using TBP and H₂SO₄ for solvent extraction using amines of the solution. This process requires proper grinding of the monazite ore prior to treatment (particle size below 45 μm) so that extraction rates of 98% can be achieved even with relatively low grade ores (Australian monazite 48.6% REE³). However, Th is leached at the same time, which brings radioactive concern of this process. Another concern is the presence of Mn⁴⁺ during alkaline processing, which oxidises Ce and form CeO₂, which will not dissolve in HCl⁶.

An alternative method has been proposed by Merritt⁵, in which the monazite ore is heated with CaCl₂ and CaCO₃ under a reducing and sulphidizing atmosphere. This leads to the conversion of REE phosphates to REE oxysulphides (REE₂O₂S) and oxochlorides (REEOCl), while creating a stable Th oxide and chloropatite (Ca₅Cl(PO₄)₃). From this mixture, the REE can be selectively leached with 3% HCl. This process has three advantages over the alkaline process: (1) the conversion step is shorter (45 min vs 3-4 h in the alkaline digestion), (2) there is no necessity for fine grinding, and (3) Th is stabilised as ThO₂. However the REE recovery rate is lower than the alkaline method (89% vs 98%) and the Na₃PO₄ by-product is not present.

**Ion adsorbed clays**

Ion adsorbed clays are alumina-silicate clays on which REE ions have been adsorbed. Although these clays have an average REE concentration of only 0.05-0.2 wt%, their ease to process and relatively high heavy REE fraction make them a viable REE resource⁴. These clays require no prior beneficiation process and contain very little radioactive elements, a constant concern with monazite processing.

As given in Table 1, salt or low concentration acidic leaching of these clays to recover REEs is most frequently applied⁷. (NH₄)₂SO₄ and NaCl are commonly used as the leachants and the leaching reaction is as follows⁷:

\[
[Al₂Si₂O₅(OH)₄]^{3+} + 3NH₄^+ \rightarrow [Al₂Si₂O₅(OH)₄]^{2+} + (NH₄^+)₃ + RE^{3+}
\]  

(6)

The kinetics of the leaching process is very fast, equilibrium is achieved in around 10 min and the total REE extraction is between 80-90%. There have also been leaching trials in Madagascar using seawater as a leachant⁸. However, these trials yielded recovery rates of around 40%, vastly inferior to the 80-90% achieved with (NH₄)₂SO₄. The industrial process currently used in China uses an ion clay with an REO concentration between 0.08 and 0.8 wt% and a leachant of 7% NaCl and 1-2% (NH₄)₂SO₄ at a pH of 4. A recovery rate of up to 95% REO is achieved⁹.

**III. Leaching technologies in new and upcoming REE resources**

**REE recovery in the phosphoric acid industry**

The main resource for phosphorous in the phosphoric acid industry is the apatite mineral. This mineral, Ca₅(PO₄)₃(Cl, F, OH), is known to contain 0.1 to 1% REE¹⁰. The REE in apatite are present as either REE³⁺ ions substituted on the Ca²⁺ ion sites of the apatite lattice (balanced with Na⁺ ions) or as REE mineral inclusions, e.g. monazite inclusions. As such many of the
phosphoric acid producers are seeking to extract the REE as a side stream of their process. The REE are most commonly found in the fluorine variant of the apatite mineral, as such Ca$_5$(PO$_4$)$_3$F will be used as the representative formula in this review.

The main reaction in the phosphoric acid production is as follows\textsuperscript{11}:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + xH_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot \frac{x}{5}H_2O \downarrow + HF \uparrow \quad (7)$$

where $x=0$ for calcium sulphate anhydrate, $x=0.5$ for hemihydrate and $x=2$ for dihydrate (most common). As this completely dissolves the apatite, all REE are transferred into the solution. However, 80% of the REE in solution is lost, due to the precipitation of the insoluble CaSO$_4$ (gypsum). Considering the amount of gypsum formed under typical processing conditions where 5 tonnes of gypsum are formed per tonne of P$_2$O$_5$\textsuperscript{12}, it has promoted several different approaches by phosphoric acid producers to recover the REE.

The first approach was to ignore the REE losses to the gypsum and focus on the REE remaining in solution. This method focusses on the purification of the crude P$_2$O$_5$ (27%) to the commercial grade (54%)\textsuperscript{13}. During this process a sludge of CaSO$_4$$\cdot$$\frac{1}{2}$H$_2$O (hemihydrate) forms, which contains the REE. This sludge is leached with HNO$_3$ with a leaching efficiency of around 80%. However, this process is inherently flawed for the production of REE, as most of the REE are lost to the gypsum by-product in the first step. This leads to the second approach, the hemihydrate process\textsuperscript{12}, where the process parameters were adapted in order to minimise the REE losses. Since the REE could be leached from the hemihydrate, the process was adapted such that instead of gypsum the hemihydrate is formed during the digestion of the apatite. It was also found that when precipitating the hemihydrate almost all REE are incorporated in the crystals, instead of 80% in the case of gypsum\textsuperscript{11}. The hemihydrate is filtered and then leached with diluted H$_2$SO$_4$. This dissolves the hemihydrate and brings the REE into solution. The REE in solution inhibit the re-precipitation of gypsum, allowing for them to be removed through solvent extraction\textsuperscript{12}.

Some of the phosphoric acid producers have opted to completely redesign their process in order to make REE recovery easier. Instead of dissolving the apatite using H$_2$SO$_4$, it is dissolved with HNO$_3$\textsuperscript{14}, with Ca(NO$_3$)$_2$ as a by-product. The advantage of this approach is that the solubility of Ca(NO$_3$)$_2$ can easily be controlled, allowing for the REE to be removed from the solution before it is co-precipitated. Also compared to gypsum, Ca(NO$_3$)$_2$ is a marketable product for the fertilizer industry.

Parallel to these developments to extract the REE during the production of phosphoric acid, there have been attempts to process the copious amount of REE containing gypsum already produced by the industry worldwide. In some countries (like Poland\textsuperscript{15}) the dumped gypsum represents the largest national REE resource. The most basic process was by leaching the gypsum with 0.5-1M H$_2$SO$_4$ at room temperature\textsuperscript{10}. This process leaches about 50% of the REE from the gypsum without destroying the gypsum crystal structure. This process was partially improved by mechanical activation through ball milling the gypsum before leaching\textsuperscript{16}. An alternative process uses the following reaction\textsuperscript{10}:

$$\text{(NH}_4\text{)}_2\text{CO}_3 + \text{CaSO}_4 \rightarrow \text{(NH}_4\text{)}_2\text{SO}_4 + \text{CaCO}_3 \quad (8)$$
All REE are incorporated in CaCO₃, which is easily leached with HNO₃, also producing useful Ca(NO₃)₂. Alternatively the CaCO₃ can be calcined to CaO and leached with (NH₄)Cl leaving an REE rich residue.

**Recycling of lamp phosphor**

Fluorescent lamp phosphors are a valuable REE resource, especially for Y, Eu and Tb. The main REE compounds in these lamps are: Y₂O₃:Eu³⁺ (YOX), LaPO₄:Ce³⁺,Tb³⁺ (LAP), (Gd,Mg)B₂O₅:Ce³⁺,Tb³⁺ (CBT), (Ce,Tb)MgAl₁₂O₁₉ (CAT) and BaMgAl₁₀O₁₇: Eu³⁺ (BAM). Some also contain chlorapatite ((Sr,Ca,Ba,Mg)₅(PO₄)₃Cl:Eu³⁺) and halophosphate (Sr,Ca)₁₀(PO₄)(Cl,F)₂.

Among these REE compounds, the leaching of REE from YOX was found to be the easiest, as they dissolve in relatively diluted acids (0.5M H₂SO₄). In comparison, the REE in the other phosphors can only be leached at a sulphuric acid concentration of 18M. This is due to the fact that the REE in YOX are present as oxides, while the REE in the other phosphors have much stronger chemical bonds. It was found that for these compounds the same leaching processes used in monazite processing were relatively effective. Alternatively a leachant of 4M HCl with H₂O₂ also proved moderately effective.

A typical leaching process of REEs from waste phosphor contains three stages. The ground phosphors are leached with 1.5M H₂SO₄ to dissolve Y and Eu. As it also dissolves some impurities (e.g. Ca, P, Mn, etc.), aqueous ammonia is added to the second stage. This keeps the impurities in the solution while converting the remaining undissolved REE into hydroxides, which precipitate out. The precipitates are leached with HCl in the third stage.

A different approach is the process developed by OSRAM A.G. with a patent in 2011. In this process, the multistep leaching targets specific compounds in the phosphors: 1) leaching with diluted HCl below 30°C leaches only the halophosphates; 2) increasing temperature to 60-90°C, the diluted HCl leaches YOX (alternatively dilute H₂SO₄ can also be used); 3) LAP is then dissolved with concentrated H₂SO₄ above 120°C (but below 230°C); 4) CAT and BAM are dissolved in 30% NaOH at 150°C in autoclave or in molten alkali. For acids, H₂SO₄ is preferred as it dissolves fewer impurities (Ca and Sr) compared to HCl or HNO₃. Also ultra sound increases the efficiency, regardless of the leachant.

**Recycling of magnet scrap**

There are two major REE to be recovered from REE magnets: Nd from NdFeB magnets and Sm from SmCo magnets. Most recycling efforts of magnets are currently focused on the production waste (so called swarf). As such the input streams for magnet leaching are relatively pure. The leaching of SmCo swarf is relatively easy. It can completely dissolve in 3M HCl, HNO₃ or H₂SO₄. Processes for SmCo leaching have not been further developed as the magnets have fallen out of favour with the rise of the NdFeB magnets.

For the NdFeB magnets two different leaching routes are established: a total leaching route and a selective leaching route. In the total leaching route the whole swarf is dissolved with the aim to separate the Nd afterwards. Similar to the SmCo swarf, this is relatively straightforward as NdFeB easily dissolves in the three mineral acids. The choice of acid is mostly dependent on the subsequent separation process: H₂SO₄ for selective precipitation and HCl for solvent extraction. HNO₃ is avoided since it produces nitrated waste water.
Note that the solubility of rare earth elements decreases with increasing temperature, leading to lower leaching efficiencies with increasing temperature. As the leaching efficiency is more important than leaching rate in magnet recycling, room temperature is preferred\textsuperscript{22}.

In the selective leaching process, Nd is extracted from the magnets without dissolving Fe and B. This is achieved through roasting and leaching. The roasting is based on the Pourbaix diagram (fig. 1).

A joint stability region of Nd\textsuperscript{3+} and Fe\textsubscript{2}O\textsubscript{3} within the pH range from around 1 to 7 in the diagram can be observed. Using roasting condition of 6 h at 900°C in air and followed by a 0.02M HCl leaching, an extraction rate of 99% of Nd and less than 0.5% of Fe was achieved\textsuperscript{19}, while the same process without the roasting leached over 50% of the Fe.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Pourbaix_diagram.png}
\caption{Pourbaix diagram Fe-H\textsubscript{2}O and Nd-H\textsubscript{2}O system\textsuperscript{19}}
\end{figure}

IV. Recent progress and new leaching technologies for REE leaching

Progress in bastnaesite leaching

The environmental pollution caused by fluorine emissions during H\textsubscript{2}SO\textsubscript{4} roasting of bastnaesite processing in China is becoming an increasing concern\textsuperscript{23}. Due to this, processes have been developed to prevent the emission of fluorine. A first method revolves around only leaching the carbonate REE while leaving the REE fluorides in the residue. This is achieved by thermally activating the ore (400°C for 3 h) and then leaching it with HCl. The thermal activation enables the leaching of the carbonates at conditions in which the fluorides are unaffected. The reported leaching efficiency of this process is 94.6% for the carbonates and 0.07% for the fluorides\textsuperscript{23}.
A different method involves progress in the air roasting process mentioned in section II. This process had already been proven ineffective in leaching the fluoride components, but the oxidation of Ce(III) to Ce(IV) prevented Ce from being leached together with the other REE and led to purification issues. The addition of thiourea24 offered a solution to this problem. Thiourea prevents the oxidation of Ce, keeping it trivalent after roasting and thus allowing it to be leached with HCl together with other REE. This allowed for the recovery of Ce and the non-fluoride bonded REE. These methods are inherently wasteful however, since not all REE present in the bastnaesite are leached.

Another more efficient process involves the mechanochemical activation of bastnaesite by milling it with NaOH powder25. In this process the bastnaesite concentrate is milled together with NaOH powder, followed by washing with water to remove the Na compounds and then leaching with HCl. These steps are performed at room temperature and can lead to a leaching efficiency of around 90%.

**Bioleaching**

The field of bioleaching is being explored for REE extraction from low grade sources. The REE concentration of the sources is often below the 1% level, mostly around 0.5%. These sources include old mine tailings and ion adsorbed clays. As total leaching of these sources, using strong mineral acids and/or bases, leads to large amounts of waste and is very inefficient, alternative low cost routes are being explored. In Egypt the possibility of using ‘*Acidithiobacillus ferrooxidans*’ (a bacteria often used in the bioleaching of copper26) to bioleach low grade Gibbsite ore to recover the REE (0.49%) and U (0.05%) has been investigated27. Their initial results show a leaching efficiency of about 55% for REE and 49% for U. Other bacteria that are tested are ‘*Aspergillus ficuum*’ and ‘*Pseudomonas aeruginosa*’28 leading to slightly higher leaching efficiencies for REE’s, around 75%.

Researchers in Japan have investigated the use of a blue-green algae named ‘*phormidium*’ in combination with (NH₄)₂SO₄ for the extraction of REE from ion adsorbed clays29. In this process the ammonium ions displace the adsorbed REE³⁺ ions in the clays bringing them into solution, as well as several other adsorbed ions, mainly Al, Mn and Si. This solution is then brought into contact with dried and ground algae, which selectively adsorb the REE ions. Leaching efficiencies between 40% (Dy, Gd) and 70% (Nd, Sm), dependent on the REE species, could be obtained. The advantage of this process is that temperature and pH control is easy and the leaching time is relatively short compared to other bioleaches (3 h vs several days). Also, in Japan ‘*phormidium*’ is easily obtained as it needs to be removed from the local reefs to preserve them. The waste of this process is also minimal and easily detoxified.

**Microwave assisted leaching**

Microwave assisted leaching is frequently used for improving mineral leaching efficiency30. For REE extraction however no concrete results have been found yet. The principle of microwave assisted leaching is based on the fact that metal-containing minerals are less transparent for microwaves than gangue minerals such as CaO, CaCO₃ and SiO₂30. This leads to on-site heating at and around the metal-containing mineral, thus locally changing the leaching kinetics. As the leaching kinetics generally increase with increasing temperature this
would lead to increased leaching rates at the metal-containing minerals, allowing the leaching to be finished sooner and with less unwanted dissolved species originating from the gangue. Another effect of the localised and rapid heating is that it can fracture the metal-containing mineral surfaces due to thermal stresses, thereby effectively increasing the surface area. While microwave leaching has not yet been applied to REE leaching, it has been applied to Cu leaching from chalcopyrite and to Au leaching. The effects observed there, e.g. removing reaction product from the surface through convective streams (Cu) or activating finely distribute metal-containing areas (Au), can be beneficial for REE leaching. Considering these current applications there is potential in applying microwave heating to REE leaching, especially for low grade sources where the REE are finely distributed in the material, sometimes in hard to leach compounds (e.g. phosphates), such as in old mine tailings.

V. Conclusions

This brief review shows that there is a variety of leaching technologies that have been developed in the past years, both for primary REE minerals and secondary resources. These in-market technologies were developed according to the mineralogy, REEs occurrence and engineering feasibility. The main features are that these are all multi-step processes and that both acid and alkaline are often interactively used in a single process. In view of the increasing importance of secondary REE resources, this overview of current state-of-the-art technologies can provide a basis for developing more efficient processes for REE recovery from secondary resources, i.e. mine tailings and magnet scraps. For example, old mine tailings often contain a sizeable fraction ofapatite and/or monazite. Drawing inspiration from current monazite processing and phosphoric acid production can lead to a workable process for REE recycling from these tailings. As for WEEE, many individual elements (e.g. lamp phosphors and magnet swarf) of WEEE have been looked at for REE recycling, but not a general WEEE stream. However, knowledge of these individual components will be invaluable to develop a process for a mixed WEEE stream. The main challenges will be overcoming the dilution effect of REE, both in the tailings and in the mixed WEEE, and the variety of contaminants. Here advancements in microwave leaching or bioleaching show promise.

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