LEACHING OF RARE EARTH ELEMENTS: REVIEW OF PAST AND PRESENT TECHNOLOGIES

21

Sebastiaan Peelman, Zhi H.I. Sun, Jilt Sietsma, Yongxiang Yang

Department of Materials Science and Engineering, Delft University of Technology, Delft, The Netherlands

1. INTRODUCTION

The rare earth elements (REE) are a group of 17 chemically similar elements consisting of the lanthanides, yttrium (Y) and scandium (Sc). Their unique physical and chemical properties have made them essential to state-of-the art equipment (e.g., magnets, catalysts, batteries). However, these same properties make them difficult to mine and process, and scarce in the market. The potential supply risk of REE, environmental concerns about the primary REE industry and economic benefits promote the research and development of processing of secondary resources such as mine tailings and electronic waste (waste electrical and electronic equipment (WEEE)) in the European Union. Although significant investigations into REE extraction from secondary resources have been carried out and a variety of technologies have been developed or proposed, most are still in the research stage or only suitable for some specific secondary resources. No technologies currently exist that can extract REE from secondary resources such as mine tailings and WEEE. Rare earth element extraction efficiency and selectivity, together with the cost and engineering during process design, require substantial optimization before further commercialization. In hydrometallurgical processing, leaching is a key step to dissolve REEs in minerals or REE-bearing scrap or waste materials. However, an understanding of interactions between REE minerals at a low concentration and the leaching media, as well as the behavior of selective leaching of different REE phases in WEEE is not yet sufficient to develop a proper hydrometallurgical processing route to extract the REE from the secondary resources. To have a better view on the state of the art and improve the engineering possibilities of REE extraction from secondary resources as well as provide the inspiration to develop new processes, the dominant leaching technologies currently in use in REE production were reviewed and are presented in this work.

2. LEACHING TECHNOLOGIES IN PRIMARY REE PRODUCTION

The main REE minerals used in primary REE production are bastnaesite and monazite. Next to these, despite their substantially lower grade, ion-adsorbed clays are becoming more popular as a primary resource. This is a result of their easy, more environmentally friendly processing and unique REE distribution (Krishnamurthy and Gupta, 2004). Table 1 gives a concise overview of the leaching technologies, both past and present, used in primary REE production.

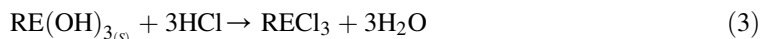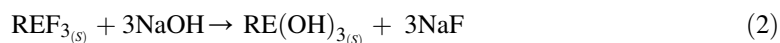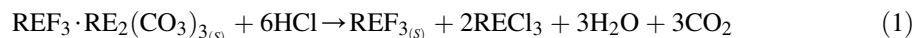**Table 1 Summary of Leaching Technologies in Primary REE Production**

Mineral	Process	REE Yield	Remarks	Status	References
Bastnaesite	1. HCl leach to remove non-REE carbonate 2. Calcination of residue to form REO	85−90%	Oldest way to process bastnaesite concentrates	Outdated	(Krishnamurthy and Gupta, 2004)
	Digestion with HNO_3 or H_2SO_4	98%	Acid choice depends on further processing: Solvent extraction $\rightarrow HNO_3$ Precipitation $\rightarrow H_2SO_4$	Outdated	(Krishnamurthy and Gupta, 2004)
	1. Roast at 620 °C to drive off CO_2 2. 30% HCl leach	−	Ce^{+III} oxidizes to Ce^{+IV} during roasting $\rightarrow$ will not leach REE fluorides will not leach, residue is marketable	Outdated	(Krishnamurthy and Gupta, 2004)
	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	(Krishnamurthy and Gupta, 2004)
	1. Sulfuric acid roast 2. NaCl solution leach 3. Precipitation as sodium (Na) double sulfates	−	Precipitates are converted to chlorides for further purification with solvent extraction	In use	(Krishnamurthy and Gupta, 2004)

Monazite	Digestion in hot H_2SO_4	–	Process conditions determine what is leached: only LREE or LREE + HREE + Th Yields no pure product	Outdated	(Krishnamurthy and Gupta, 2004)
	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_3PO_4 is marketable byproduct	In use	(Krishnamurthy and Gupta, 2004; Kuzmin et al., 2012)
	1. Heat under reducing and sulfidizing 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	(Merritt, 1990)
Ion clay	Salt leach with $(NH_4)_2SO_4$	80–90%	Targets physisorbed REE through cation exchange	In use	(Moldoveanu and Papangelakis, 2013a)
	Leach with seawater	40%	Inefficient but cheap process	Research and development	(Moldoveanu and Papangelakis, 2013b)
	Acid leach with strong acid (pH < 1)	All	Dissolves entire clay, incurs significant additional costs	Not used	(Moldoveanu and Papangelakis, 2013a)

2.1 BASTNAESITE

Bastnaesite is a rare earth fluorocarbonate mineral, $RE(CO_3)F$ (Kanazawa and Kamitani, 2006), which predominantly contains light REEs.[1] After physical upgrading, bastnaesite ore concentrates contain between 40 and 60 wt% REE (Feng et al., 2013; McGill, 2000).

One of the main concerns in past bastnaesite processing technologies (Table 1) was the inability to extract REE fluorides. This has been successfully resolved in current technology in two different ways: pre- and posttreatment with alkaline or sulfuric acid roasting. Alkaline treatment, developed by Kruesi and Duker of Molycorp (Krishnamurthy and Gupta, 2004), is a three-step process, defined by reactions (1)–(3):

$$REF_3 \cdot RE_2(CO_3)_{3_{(S)}} + 6HCl \rightarrow REF_{3_{(S)}} + 2RECl_3 + 3H_2O + 3CO_2 \tag{1}$$

$$REF_{3_{(S)}} + 3NaOH \rightarrow RE(OH)_{3_{(S)}} + 3NaF \tag{2}$$

$$RE(OH)_{3_{(S)}} + 3HCl \rightarrow RECl_3 + 3H_2O \tag{3}$$

Step I is a reaction with a 31.45-wt% HCl solution (1.8 kg/kg of ore) to dissolve the REE carbonate and form REE chlorides; step II is a reaction with NaOH (0.5 kg/kg) at 96 °C to convert the released REE fluorides to hydroxides, which are then dissolved by leaching with HCl in step III. Alternative processes exist that skip the first leaching step, and instead the bastnaesite is first treated with alkaline and then leached with HCl (Krishnamurthy and Gupta, 2004). This consumes more NaOH although it converts all REEs to hydroxides, not only the REE fluorides. Whether this compensates for eliminating a step in the process depends on the economics of the company.

Sulfuric acid roasting is the other main process currently used in industry to process bastnaesite. In the process, bastnaesite concentrate is heated in a 98% H_2SO_4 solution to 400–500 °C for several hours. This decomposes the fluorocarbonate matrix, leading to the release of the CO_2 and HF gas. These emissions are becoming a serious environmental concern. The REEs are converted to their sulfates and can be selectively precipitated as Na double sulfates by leaching the roasted ore with NaCl containing water. The sulfuric acid roasting process is currently in use at the Bayan Obo mine in China, making it the primary method for bastnaesite processing. The alkaline method was used by Molycorp at the Mountain Pass mine before the mine was closed (Krishnamurthy and Gupta, 2004).
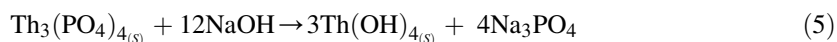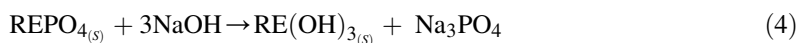
2.2 MONAZITE

Monazite is a rare earth phosphate mineral, $RE(PO_4)$ containing mostly light REE and some heavy REE[2] (more than bastnaesite) (Kanazawa and Kamitani, 2006). Monazite concentrates can contain up to 70% REE after physical upgrading, primarily cerium (Ce) and lanthanum (La) as well as significant concentrations of neodymium (Nd), praseodymium (Pr), and samarium (Sm). The thorium (Th) content is also high, ranging from 4% to 12%; owing to the radioactive nature of Th, it is an ever-present concern in monazite processing.

---

[1]La, Ce, Pr, Nd, Sm, Eu, Gd, and Sc.
[2]Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y.

As shown in Table 1, the alkaline method is currently one of the main leaching technologies for monazite. The main reactions during alkaline leaching are (4)–(5):

$$REPO_{4(S)} + 3NaOH \rightarrow RE(OH)_{3(S)} + Na_3PO_4 \tag{4}$$

$$Th_3(PO_4)_{4(S)} + 12NaOH \rightarrow 3Th(OH)_{4(S)} + 4Na_3PO_4 \tag{5}$$

After the monazite mineral is digested in 60–70% NaOH at 140–150 °C for 4 h, the residue is dissolved into a hot acidic solution. The acid is selected based on the subsequent separation process, i.e., HNO_3 for solvent extraction using TBP or H_2SO_4 for solvent extraction using amines of the solution. Na_3PO_4 is formed as a byproduct that is sold to the fertilizer industry. This process requires extensive grinding of the monazite ore before 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% REE[3]). This process leaches the Th together with the REE, which leads to safety concerns during the separation stage, where the Th can be concentrated up to dangerous levels. Another concern is the presence of Mn^{+IV} during alkaline processing, which oxidizes Ce ($Ce^{+III} \rightarrow Ce^{+IV}$) and forms CeO_2, which will not dissolve in HCl (Kuzmin et al., 2012).

An alternative method was proposed by Merritt (Merritt, 1990), in which the monazite ore is heated with $CaCl_2$ and $CaCO_3$ under a reducing and sulfidizing atmosphere. This leads to the conversion of REE phosphates to REE oxysulfides (RE_2O_2S) and oxychlorides (REOCl) and chlorapatite ($Ca_5Cl(PO_4)_3$) is formed as a byproduct. From this mixture, the REE can be selectively leached with 3% HCl. During the heating process, Th is converted ThO_2, which is stable and does not dissolve in 3% HCl. The ThO_2 can be safely separated and disposed together with the other residue. 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 extensive grinding, and (3) Th is stabilized as ThO_2 in the residue so it is not concentrated in further processing steps. However, the tradeoff is that the REE recovery rate is lower than the alkaline method (89% vs 98%) and the byproduct is not marketable, unlike the Na_3PO_4. Environmental concerns regarding the roosting operation should also be carefully considered.

2.3 ION-ADSORBED CLAYS

Ion-adsorbed clays are becoming increasingly important REE resources in the primary REE industry. These clays have an alumina-silicate matrix onto which REE ions have been adsorbed. Although these clays have an average REE concentration of only 0.05–0.2 wt%, their ease in processing and relatively high heavy REE fraction make them a valuable REE resource (Kanazawa and Kamitani, 2006). These clays require no prior beneficiation process and contain few radioactive elements, a constant concern with monazite processing.

As shown in Table 1, salt or low concentration acidic leaching of these clays to recover REEs is most frequently applied (Moldoveanu and Papangelakis, 2012). $(NH_4)_2SO_4$ and NaCl are the most commonly used leachants, and the leaching reaction (6) (using $(NH_4)_2SO_4$ as an example) is given as follows (Moldoveanu and Papangelakis, 2013a):

$$\left[Al_2Si_2O_5(OH)_4\right] \cdot RE^{3+} + 3NH_4^+ \rightarrow \left[Al_2Si_2O_5(OH)_4\right] \cdot (NH_4^+)_3 + RE^{3+} \tag{6}$$
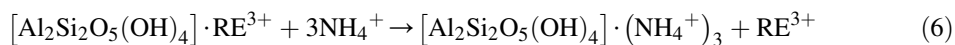
The REEs in reaction (6) are not chemically bound to the alumina–silicate matrix; rather, they are physisorbed. The cations of the leachant (here, (NH_4^+)) displace the RE^{3+} cation from the matrix and transfer them into solution. The kinetics of the leaching process is fast, equilibrium is achieved in around 10 min, and the total REE extraction is between 80% and 90%. There have even been leaching trials in Madagascar using seawater as a leachant (Moldoveanu and Papangelakis, 2013b). However, these trials yielded recovery rates only of around 40%, vastly inferior to the 80–90% achieved with $(NH_4)_2SO_4$. The industrial process currently used in China uses an ion clay with a rare earth oxide (REO) concentration between 0.08 and 0.8 wt% and a leachant of 7% NaCl and 1–2% $(NH_4)_2SO_4$ at a pH of 4. A recovery rate of up to 95% REO is achieved (Shi, 2009).

2.4 DISCUSSION

The main REE resources in the primary industry are high-grade concentrates with REE contents between 60% and 70% after physical upgrading. In both the bastnaesite and monazite minerals, REEs are present in compounds that are difficult to dissolve ($REEF_3$ and $REEPO_4$, respectively). The extraction technologies reflect this because both bastnaesite and monazite treatment are multistep processes with the aim of first converting the REE to a more easily leachable compound before the actual leaching. All of these processes are energy intensive and most are environmentally hazardous. This is part of the reason why the primary REE industry has branched out to low-grade ion clays. The other important reason is, of course, the high fraction of heavy REE in these clays. The understanding of REE extraction behavior originates from these technologies, and it will be from these technologies that the keys to unlocking REE from secondary resources will be found.

## 3. LEACHING TECHNOLOGIES IN NEW AND UPCOMING SECONDARY REE RESOURCES

Next to primary REE production, a range of secondary REE production processes have been established. Among these processes, the recovery of REE in the phosphoric acid industry, the recycling of end of life (EoL) fluorescent lamps, and the recycling of REE magnet production scrap stand out as the most developed processes. All of these processes have in common that they are all hydrometallurgical processes. As such, understanding the leaching behavior of these REE-bearing secondary raw materials is critical to overall REE recovery.

3.1 RARE EARTH ELEMENT RECOVERY IN THE PHOSPHORIC ACID INDUSTRY

The main resource for phosphorous in the phosphoric acid industry is the mineral apatite. This mineral, $Ca_5(PO_4)_3(Cl, F, OH)$, is known to contain 0.1–1% REE (Habashi, 1985). The REEs in apatite are present as either REE^{3+} ions substituted on the Ca^{2+} 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 and valorize the REEs as a byproduct of their process. The REEs are most commonly found in the fluorine variant of the apatite mineral (Preston et al., 1996); as such, $Ca_5(PO_4)_3F$ will be used as the representative formula in this review.

The main reaction in the phosphoric acid production is as follows (Wang et al., 2010):

$$Ca_5(PO_4)_3F + 5H_2SO_4 + xH_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot \frac{x}{5}H_2O\downarrow + HF\uparrow \qquad (7)$$
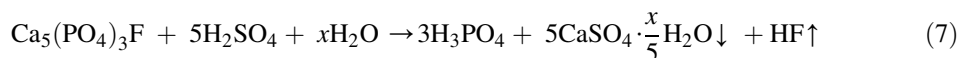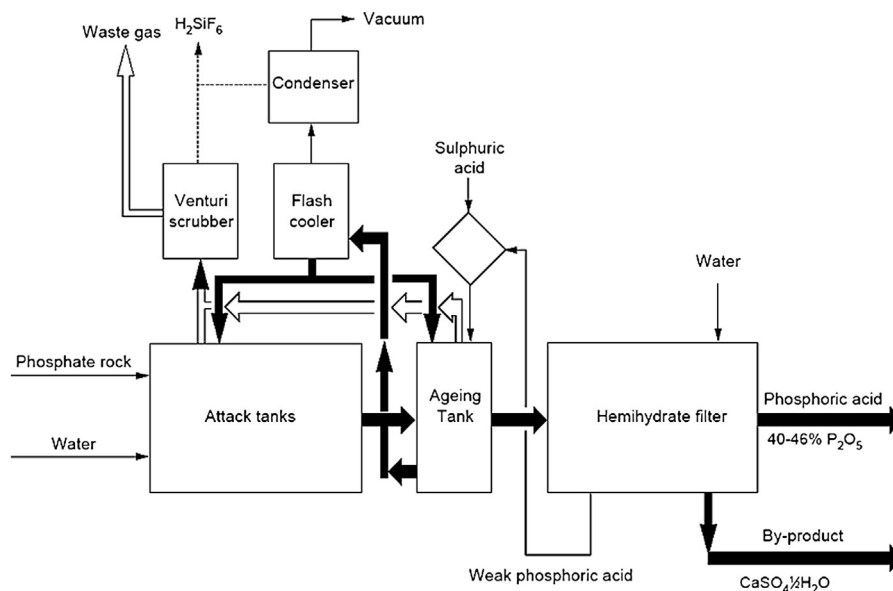
FIGURE 1

Hemihydrate process flow sheet (van Nieuwenhuyse, 2000).

The amount of water in the process determines the nature of the calcium sulfate byproduct. In the conventional process, enough water is present to always form the dihydrate $CaSO_4 \cdot 2H_2O$. This process completely dissolves the apatite, transferring all REE to the solution. However, precipitation of the insoluble $CaSO_4$ (gypsum) formed during this reaction removes 80% of the REE from the solution. This is caused by incorporation of the REE into the $CaSO_4$ crystal lattice during precipitation. Considering the amount of gypsum formed under typical processing conditions (5 tons of gypsum are formed per ton of P_2O_5) (Zielinski et al., 1993) and the chemical stability of gypsum, these REEs are considered lost. This has promoted several different approaches by phosphoric acid producers to recover the REE.

The first approach, proposed back in 1980, was to ignore the REE losses to the gypsum and focus on the REE remaining in solution. This method is applied to the purification process of the crude P_2O_5 (27%) to the commercial grade (54%) (Preston et al., 1996). During this process, a sludge of $CaSO_4 \cdot ½H_2O$ (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 because most of the REEs are lost to the gypsum byproduct in the first step. This has led to the second approach, the hemihydrate process (Zielinski et al., 1993). This process as shown in Figure 1 (van Nieuwenhuyse, 2000) adapts the process parameters (i.e., water content) of the original process so that instead of forming gypsum during the apatite digestion, $CaSO_4 \cdot ½H_2O$ (hemihydrate) is formed and precipitated. The precipitation of the hemihydrate captures nearly all the REE in the solution (unlike gypsum, which captures only 80%), and unlike gypsum the hemihydrate is easily leached to extract the REEs. After precipitation the hemihydrate is filtered and then leached with diluted H_2SO_4. This dissolves the hemihydrate and at the same time brings the REEs into solution. It was found that

under these conditions the REEs in the solution inhibit the re-precipitation of gypsum, allowing for them to be removed through solvent extraction (Zielinski et al., 1993).

Some of the phosphoric acid producers have opted to redesign their process completely to make REE recovery easier. Instead of dissolving the apatite using H_2SO_4, it is dissolved with HNO_3 (Li et al., 2006), with $Ca(NO_3)_2$ as a byproduct. 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 with gypsum, $Ca(NO_3)_2$ is a marketable product for the fertilizer industry. In Brazil (Pereira and Bilal, 2012) the possibility of using HCl is being explored as well. This process has both the advantage and disadvantage of producing $CaCl_2$ as a byproduct. $CaCl_2$ cannot be precipitated from the solution, meaning that no REE can be lost this way. It also means, however, that the solution from which the REE must be separated contains much Ca, which makes it more difficult to achieve a high-purity REE concentrate. Neither the HNO_3 nor the HCl process has seen full-scale implementation in the industry. However, with the rising importance and decreasing availability of the REE, one day these processes could replace the traditional H_2SO_4 process.

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 such as Poland (Jarosiński et al., 1993), the dumped gypsum represents the largest national REE resource. The most basic process was leaching the gypsum with 0.5–1 M H_2SO_4 at room temperature (Habashi, 1985). This process leaches about 50% of the REE from the gypsum without destroying the gypsum crystal structure. This makes the process efficient by limiting chemical consumption and makes the waste easy to handle. This process was partially improved by mechanical activation by ball milling the gypsum before leaching (Todorovsky et al., 1997). An alternative process uses reaction (8) (Habashi, 1985):

$$(NH_4)_2CO_3 + CaSO_{4(S)} \rightarrow (NH_4)_2SO_4 + CaCO_{3(S)} \tag{8}$$

This process produces $(NH_4)_2SO_4$, which is valuable to the fertilizer industry, and $CaCO_3$. All REEs are incorporated into the lattice of $CaCO_3$, which is easily leached with HNO_3, also producing useful $Ca(NO_3)_2$. Alternatively the $CaCO_3$ can be calcined to CaO and leached with $(NH_4)Cl$. This selectively dissolves the CaO, leaving an REE-rich residue.

3.2 EXTRACTING REE FROM RED MUD

Red mud is the characteristic waste product of the Bayer process, in which bauxite ore is converted into alumina. This mud is a hazardous waste that has been troubling the aluminum industry for a long time. There have been many attempts to use red mud as a secondary resource, because the metal content in this mud is high, especially iron (Fe) (up to 60%), but none of these was successful. It has been discovered that the red mud also contains a minor REE fraction, ranging from 500 to 1700 parts per million (ppm) REE. What is especially interesting is that the Sc fraction is considerable, between 130 and 390 ppm (Binnemans et al., 2013b).

Currently, experiments are being carried out to extract the REE from the red mud. Two approaches are being attempted: (1) physical upgrading of the red mud to obtain an REE concentrate before leaching and (2) directly leaching the red mud (Petrakova et al., 2014). The first approach aims to limit the volume of mud that has to be treated so that chemical consumption and additional waste production can be minimized. However, most physical upgrading techniques fail to separate more than 20 wt% of

the REE from the bulk of the mud. The second approach is to treat the red mud directly, so that all REEs can be extracted. An example of such a process is the leaching with low concentration (0.5 M) HNO_3 combined with dissolved SO_2 (Binnemans et al., 2013b). The SO_2 functions to keep the Fe for dissolving together with the REE. Recovery ratios of 80% for Sc and 95% for Y were obtained. Recovery ratios of the light REE were around 30–50%. The problem with this process is the considerable chemical consumption and the large amount of waste that is produced afterward, both solid and liquid. Development of these technologies is ongoing, but as REEs become more critical in our society they could become a solution to solving the REE supply problem.

3.3 RECYCLING OF LAMP PHOSPHOR FROM EoL FLUORESCENT LAMPS

Fluorescent lamp phosphors represent a valuable REE resource, especially for Y, europium (Eu), and terbium (Tb). The main REE compounds in these lamps are Y_2O_3:Eu^{3+} (YOX), $LaPO_4$:Ce^{3+}, Tb^{3+} (LAP), $(Gd,Mg)B_5O_{12}$:Ce^{3+}, Tb^{3+} (CBT), $(Ce,Tb)MgAl_{11}O_{19}$ (CAT), and $BaMgAl_{10}O_{17}$:Eu^{3+} (BAM). Some also contain chlorapatite $((Sr,Ca,Ba,Mg)_5(PO_4)_3Cl$:$Eu^{3+})$ and halophosphate $(Sr,Ca)_{10}(PO_4)(Cl,F)_2$.

Among these REE compounds, the leaching of REEs from YOX was found to be the easiest (Yang et al., 2013), because they dissolve in relatively diluted acids (0.5 M H_2SO_4). In comparison, the REE in the other phosphors can be leached only at a sulfuric acid concentration of 18 M (98 wt%) (Yang et al., 2013). This is because the REEs in YOX are present as oxides whereas 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 (Binnemans et al., 2013a). Alternatively a leachant of 4 M HCl with H_2O_2 also proved moderately effective (Binnemans et al., 2013a).

A typical leaching process of REEs from waste phosphor contains three stages. The ground phosphors are leached with 1.5 M H_2SO_4 to dissolve Y and Eu (from YOX). Because this also dissolves some impurities (e.g., Ca, P, manganese [Mn]), 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 (Tanaka et al., 2013, p. 255).

A different approach is the process developed by Osram A.G. with a patent in 2011 (Otto and Wojtalewicz-Kasprzak, 2012). 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 H_2SO_4 can be used); (3) LAP is then dissolved with concentrated H_2SO_4 above 120 °C (but below 230 °C); and (4) CAT and BAM are dissolved in 30% NaOH at 150 °C in an autoclave or in molten alkali. For acids, H_2SO_4 is preferred because it dissolves fewer impurities (Ca and Sr) compared with HCl or HNO_3 (Yang et al., 2013). Also, ultrasound increases efficiency regardless of the leachant (Tunsu et al., 2014).

3.4 RECYCLING OF MAGNET SCRAP

Two major REEs can be recovered from REE magnets: Nd from NdFeB magnets and Sm from SmCo magnets. Most recycling efforts of magnets currently focus on production scrap (so-called new scrap). As such, the input streams for magnet leaching are relatively pure. The leaching of SmCo scrap is relatively easy. It can completely dissolve in 3 M HCl, HNO_3, or H_2SO_4 (Tanaka et al., 2013).
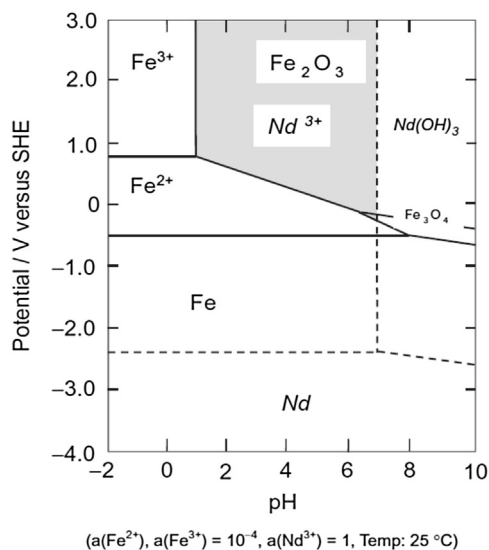
FIGURE 2

Pourbaix diagram: Fe–H_2O and Nd–H_2O system (Tanaka et al., 2013).

Processes for SmCo leaching have not been further developed because these magnets have fallen out of favor with the rise of the cheaper and stronger NdFeB magnets.

For NdFeB magnet scrap, two different leaching routes are established: a total leaching route and a selective leaching route. In the total leaching route, the scrap is fully dissolved with the aim of separating the Nd afterward. Similar to the SmCo scrap, this is relatively straightforward because NdFeB easily dissolves in mineral acids. The choice of acid mostly depends on the subsequent separation process: H_2SO_4 for selective precipitation and HCl for solvent extraction (Lee et al., 2013). HNO_3 is avoided because it produces nitrated waste water. The solubility of REEs decreases with increasing temperature, leading to lower leaching efficiencies at a higher temperature. Because the leaching efficiency is more important than the leaching rate in magnet recycling, low temperatures are preferred (Lee et al., 2013). As such, most of these processes are done at room temperature.

In the selective leaching process, Nd is extracted from the magnets without dissolving Fe and B. This is achieved through a combination of roasting and leaching. The roasting is based on the Pourbaix diagram of Nd and Fe (Figure 2) (Tanaka et al., 2013).

The Pourbaix diagram reveals a joint stability region of solid Fe_2O_3 and dissolved Nd^{3+} at pH 1–7. By exploiting this region, selective dissolution of Nd can be achieved. By using a roasting condition of 6 h at 900 °C in air followed by a 0.02 M HCl leach (eqs (9) and (10)), an extraction ratio of 99% for Nd and less than 0.5% for Fe was achieved (Tanaka et al., 2013). The same process without the roasting leached over 50% of the Fe.

$$Nd_2O_3 + HCl \rightarrow NdCl_3 + H_2O \qquad (9)$$

$$Fe_2O_3 + HCl \nrightarrow FeCl_3 + H_2O \qquad (10)$$
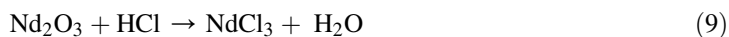
Table 2 Summary of Possible Secondary Rare Earth Resources				
Secondary Resource	REE Content	Extraction Technology	Yield	Remarks
Apatite rock	0.1–1 wt%	Conventional H_3PO_4 process	20% at best	Can be done with no changes to process
		Hemihydrate process	80–85%	Implementable using standard equipment
		HNO_3/HCl process	80%	Still in development
Phosphogypsum	0.3–0.4 wt%	H_2SO_4 leaching	50%	Does not decompose gypsum
		$(NH_4)_2CO_3$ process	–	Valuable byproduct
Red mud	0.05–0.17 wt%	Physical upgrading followed by leaching	<20%	Low yield, low chemical consumption
		Direct leaching	Heavy REE: 80–90% Light REE: 30–50%	Many impurities, a lot of waste
Lamp phosphors	10–28 wt%	Sequential leaching	–	Extraction efficiency varies between steps and compound
SmCo magnets	23–33 wt% (pure)	Total dissolution	100%	Yield after solvent extraction: 70–95%
FeNdB magnets	26.7 wt% (pure)	Total dissolution	100%	Yield after solvent extraction: 96–99%
		Selective dissolution	96–99%	Yield depends on tolerance on Fe dissolution

3.5 DISCUSSION

Countries lacking primary REE resources are turning to what they have and trying to develop it as secondary resources. These potential secondary resources range from production waste and byproducts, such as the gypsum from the phosphoric acid industry and red mud from the aluminum industry, to recycling of EoL REE applications, such as lamp phosphors and magnets. Some producers of phosphoric acid are even considering redesigning their entire production process to be able to valorize the REE present in their feedstock. Extraction technologies for these resources are being developed as either adaptations of the processes in the primary industry (lamp phosphors) or completely new processes (magnets). A summary of possible secondary REE resources and their possible extraction processes is given in Table 2.

4. RECENT PROGRESS AND NEW LEACHING TECHNOLOGIES FOR REE EXTRACTION

The history of primary REE production is mired with environmental pollution in the form of hazardous emissions, copious amounts of both solid and liquid waste and, of course, the presence of

radioactive material. As the primary industry moves forward, eliminating these hazards is becoming increasingly important. Combined with the discovery of new REE resources, whether (very) low-grade waste products from another industry (such as mine tailings or gypsum from the phosphoric acid industry) or recycling of EoL REE-containing appliances (such as magnets or lamp phosphors), this drives the development of new technologies. Some of these developments include the reduction of hazardous emissions during bastnaesite processing, bioleaching, and microwave assistance during leaching.

4.1 PROGRESS IN BASTNAESITE LEACHING

Environmental pollution caused by fluorine emissions during H_2SO_4 roasting of bastnaesite processing in China is becoming of increasing concern (Bian et al., 2011). Because of 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. Thermal activation enables 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 (Bian et al., 2011).

A different method involves progress in the air-roasting process mentioned in Section 2.1. 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 thiourea (Yörükoğlu et al., 2003) 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 nonfluoride bonded REE. These methods are not optimal because not all REEs present in the bastnaesite are being extracted, which leads to a less efficient process. However, considering the abundance of REEs in China, the Chinese REE industry can consider this loss in efficiency an acceptable tradeoff for reducing the environmental impact of the REE extraction processes.

Another, more efficient process involves the mechanochemical activation of bastnaesite by milling it with NaOH powder (Zhang and Saito, 1998). 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%. This process generates no emissions, and the F is bonded with Na as NaF. Ball milling is energy intensive, however, and the process takes several hours.

4.2 BIOLEACHING

The field of bioleaching is being explored for REE extraction from low-grade resources. The REE concentration of the resources is often below the 1% level, mostly around 0.5% even after physical upgrading. These resources include old mine tailings and ion-adsorbed clays. Because total leaching of these resources, using strong mineral acids and/or bases, leads to large amounts of waste and/or pollution and is inefficient, alternative low-cost and clean routes are being explored. In Egypt, the possibility of using *Acidithiobacillus ferrooxidans* (a bacteria often used in the bioleaching of copper) (Nowaczyk et al., 1998) to bioleach low-grade gibbsite ore to recover REE (0.49%) and uranium (U) (0.05%) is being investigated (Ibrahim and El-Sheikh, 2011). 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* (Hassanien et al., 2014) and have led to slightly higher leaching efficiencies for REEs, around 75%. These bacteria are not as harmless to humans as *A. ferrooxidans*, however, and safety can be an issue here.

Researchers in Japan have investigated the use of a blue-green algae named *Phormidium* combined with $(NH_4)_2SO_4$ to extract REE from ion-adsorbed clays (Kim et al., 2011). Like the process used in the primary production, in this process the ammonium ions displace the adsorbed REE^{3+} ions in the clays, bringing them into solution, as well as several other adsorbed ions, mainly Al, Mn, and Si. The difference with the primary industry is the presence of the algae, which selectively adsorbs the REE ions in the solution. Leaching efficiencies between 40% (Dy and Gd) and 70% (Nd and Sm), depending on the REE species, can be obtained and the REE solution is almost devoid of impurities, which makes subsequent separation processes easier. The advantage of this process compared with other bioleaches is that temperature and pH control are easy and the leaching time is relatively short (3 h vs several days). Also, in Japan *Phormidium* is easily obtained because it needs to be removed from the local reefs to preserve them. The waste of this process is also minimal and easily detoxified.

4.3 MICROWAVE-ASSISTED LEACHING

Microwave-assisted leaching is frequently used to improve mineral leaching efficiency (Haque, 1999). However, for REE extraction, concrete results have yet to be found. 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, $CaCO_3$, and SiO_2 (Haque, 1999). This leads to onsite heating at and around the metal-containing minerals, thus locally changing the leaching kinetics. Because the leaching kinetics generally increase with increasing temperature, this leads to increased leaching rates at the metal-containing minerals, allowing the leaching of the metal-containing minerals to be finished sooner and with fewer unwanted dissolved species originating from the gangue. Another effect of localized and rapid heating is that it can fracture the surfaces of the metal-containing minerals owing to thermal stresses, thereby effectively increasing the surface area (Al-Harahsheh and Kingman, 2004), further enhancing the leaching rate. Whereas microwave leaching has not yet been applied to REE leaching, there is a growing interest in doing so. This interest originates from the successful implementation of microwave-assisted leaching in copper (Cu) leaching from chalcopyrite and in gold (Au) leaching (Al-Harahsheh and Kingman, 2004). The effects observed there, e.g., removing reaction product from the surface through convective streams (Cu) or activating finely distributed metal-containing areas (Au), could be beneficial for REE leaching. Considering these current applications, there is potential for applying the microwave technique to REE leaching, especially for low-grade sources in which the REEs are finely distributed in the material, sometimes in difficult-to-leach compounds (e.g., phosphates), such as in old mine tailings.

5. CONCLUSIONS

This brief review shows that a variety of leaching technologies have been developed for both primary REE minerals and secondary resources. These in-market technologies were developed according to the mineralogy of REE ores, REE occurrence, and engineering feasibility. The main features are that these are all multistep processes and that acid and alkaline are often used interactively in a single process.

This proves that REE compounds are challenging to leach, even in the high-grade primary resources. This review also shows that the technologies used in the primary industry can offer a basis for developing technologies for recycling secondary resources, as proven by the recycling of lamp phosphors, which use the same technologies as monazite leaching. However, with the (very) low grade of other prospective secondary resources (such as mine tailings and WEEE), the existing technologies will have to be adapted and refined. One promising method of doing so is microwave-assisted leaching. Technologies from other industries could be also be used, such as bioleaching.

In light of the increasing importance of secondary REE resources, this overview can provide a basis for developing more efficient processes for REE recovery from secondary resources, i.e., mine tailings and WEEE. For example, old mine tailings often contain a sizable fraction of apatite 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 components (e.g., lamp phosphors and magnet scrap) of WEEE have been researched for REE recycling but not for a mixed WEEE stream. However, knowledge of these individual components will be essential to develop a process for extracting REE from a mixed WEEE stream.

The main challenges will be to overcome the low concentration of REE, both in the tailings and in the mixed WEEE, and the variety of contaminants. Here, advancements in microwave-assisted leaching and bioleaching show a promising future for low-grade and difficult-to-leach secondary resources.

ACKNOWLEDGMENTS

REFERENCES

Al-Harahsheh, M., Kingman, S.W., 2004. Microwave-assisted leaching—a review. Hydrometallurgy 73 (3), 189–203. http://dx.doi.org/10.1016/j.hydromet.2003.10.006.

Bian, X., Yin, S.H., Zhang, F.Y., Wu, W.Y., Tu, G.F., 2011. Study on leaching process of activation bastnaesite by HCl solution. Advanced Materials Research 233–235, 1406–1410. http://dx.doi.org/10.4028/. www.scientific.net/AMR.233-235.1406.

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., Buchert, M., 2013a. Recycling of rare earths: a critical review. Journal of Cleaner Production 51, 1–22. http://dx.doi.org/10.1016/j.jclepro.2012.12.037.

Binnemans, K., Pontikes, Y., Jones, P.T., Van Gerven, T., Blanpain, B., 2013b. Recovery of rare earths from industrial waste residues: a concise review. In: In Proceedings of the 3rd International Slag Valorisation Symposium: The Transition to Sustainable Materials Management, pp. 191–205. Leuven, Belgium.

Feng, X., Long, Z., Cui, D., Wang, L., Huang, X., Zhang, G., 2013. Kinetics of rare earth leaching from roasted ore of bastnaesite with sulfuric acid. Transactions of Nonferrous Metals Society of China 23 (3), 849–854. http://dx.doi.org/10.1016/S1003-6326(13)62538-8.

Habashi, F., 1985. The recovery of the lanthanides from phosphate rock. Journal of Chemical Technology and Biotechnology 35A, 5–14.

Haque, K.E., 1999. Microwave energy for mineral treatment processes—a brief review. International Journal of Mineral Processing 57 (1), 1–24. http://dx.doi.org/10.1016/S0301-7516(99)00009-5.

Hassanien, W.A., Desouky, O.A., Hussien, S.S., 2014. Bioleaching of some rare earth elements from Egyptian monazite using *Aspergillus ficuum* and *Pseudomonas aeruginosa*. Walailak Journal of Science and Technology 11 (9), 809–823.

Ibrahim, H.A., El-Sheikh, E.M., 2011. Bioleaching treatment of Abu Zeneima Uraniferous gibbsite ore material for recovering U, REEs, Al and Zn. Research Journal of Chemical Sciences 1 (4), 55–66.

Jarosiński, A., Kowalczyk, J., Mazanek, C., 1993. Development of the Polish wasteless technology of apatite phosphogypsum utilization with recovery of rare earths. Journal of Alloys and Compounds 200, 147–150. http://dx.doi.org/10.1016/0925-8388(93)90485-6.

Kanazawa, Y., Kamitani, M., 2006. Rare earth minerals and resources in the world. Journal of Alloys and Compounds 408–412, 1339–1343. http://dx.doi.org/10.1016/j.jallcom.2005.04.033.

Kim, J.-A., Dodbiba, G., Tanimura, Y., Mitsuhashi, K., Fukuda, N., Okaya, K., Fujita, T., 2011. Leaching of rare-earth elements and their adsorption by using blue-green algae. Materials Transactions 52 (9), 1799–1806.

Krishnamurthy, N., Gupta, C.K., 2004. Extractive Metallurgy of Rare Earths. CRC Press, Boca Raton, FL.

Kuzmin, V.I., Pashkov, G.L., Lomaev, V.G., Voskresenskaya, E.N., Kuzmina, V.N., 2012. Combined approaches for comprehensive processing of rare earth metal ores. Hydrometallurgy 129–130, 1–6. http://dx.doi.org/10.1016/j.hydromet.2012.06.011.

Lee, C.-H., Chen, Y.-J., Liao, C.-H., Popuri, S.R., Tsai, S.-L., Hung, C.-E., 2013. Selective Leaching Process for Neodymium Recovery from Scrap Nd-Fe-B Magnet 44A, 5825–5833. http://dx.doi.org/10.1007/s11661-013-1924-3.

Li, H., Guo, F., Zhang, Z., Li, D., Wang, Z., 2006. A new hydrometallurgical process for extracting rare earths from apatite using solvent extraction with P350. Journal of Alloys and Compounds 408–412, 995–998. http://dx.doi.org/10.1016/j.jallcom.2004.12.119.

McGill, I., 2000. Rare earth elements. In W.-V.V.G., & C. KGaA (Eds.), Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany, Wiley-VCH Verlag GmbH & Co. KGaA.

Merritt, R.R., 1990. High temperature methods for processing monazite: I. Reaction with calcium chloride and calcium carbonate. Journal of the Less Common Metals 166 (2), 197–210. http://dx.doi.org/10.1016/0022-5088(90)90001-Z.

Moldoveanu, G.A., Papangelakis, V.G., 2012. Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism. Hydrometallurgy 117–118, 71–78. http://dx.doi.org/10.1016/j.hydromet.2012.02.007.

Moldoveanu, G.A., Papangelakis, V.G., 2013a. Recovery of rare earth elements adsorbed on clay minerals: II. Leaching with ammonium sulfate. Hydrometallurgy 131–132, 158–166. http://dx.doi.org/10.1016/j.hydromet.2012.10.011.

Moldoveanu, G.A., Papangelakis, V.G., 2013b. University of Toronto – Tantalus Report_January 2013.

Nowaczyk, K., Juszczak, A., Domka, F., Siepak, J., 1998. The use of *Thiobacillus ferrooxidans* bacteria in the process of chalcopyrite leaching. Polish Journal of Environmental Studies 7, 307–312.

Otto, R., Wojtalewicz-Kasprzak, A., 2012. Method for Recovery of Rare Earths from Fluorescent Lamps. U.S. Patent 20120027651A1. Feb. 02, 2012.

Pereira, F., Bilal, E., 2012. Phosphoric acid extraction and rare earth recovery from apatites of the Brazilian phosphatic ores. Romanian Journal of Mineral Deposits 85 (2), 49–52.

Petrakova, O., Klimentenok, G., Panov, A., Gorbachev, S., 2014. Application of modern methods for red mud processing to produce rare earth elements. In: Presented at the ERES 2014: 1st European Rare Earth Resources Conference, Milos, Greece, pp. 222–241.

Preston, J.S., Cole, P.M., Craig, W.M., Feather, A.M., 1996. The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. Hydrometallurgy 41, 1–19. http://dx.doi.org/10.1016/0304-386X(95)00051-H.

Shi, F., 2009. Rare Earth Extraction Technologies, pp. 55–57. Metallurgical Industry Publishing, Beijing.

Tanaka, M., Oki, T., Koyama, K., Narita, H., Oishi, T., 2013. Chapter 255 – Recycling of rare earths from scrap. In: Bünzli, J.-C.G., Pecharsky, V.K. (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 43. Elsevier, pp. 159–211.

Todorovsky, D., Terziev, A., Milanova, M., 1997. Influence of mechanoactivation on rare earths leaching from phosphogypsum. Hydrometallurgy 45 (1–2), 13–19. http://dx.doi.org/10.1016/S0304-386X(96)00065-5.

Tunsu, C., Ekberg, C., Retegan, T., 2014. Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury. Hydrometallurgy 144–145, 91–98. http://dx.doi.org/10.1016/j.hydromet.2014.01.019.

Van Nieuwenhuyse, A.E., 2000. Production of Ammonium Nitrate and Calcium Ammonium Nitrate (vols. 1–8), vol. 4. Fisherprint Ltd, Peterborough, England.

Wang, L., Long, Z., Huang, X., Yu, Y., Cui, D., Zhang, G., 2010. Recovery of rare earths from wet-process phosphoric acid. Hydrometallurgy 101 (1–2), 41–47. http://dx.doi.org/10.1016/j.hydromet.2009.11.017.

Yang, F., Kubota, F., Baba, Y., Kamiya, N., Goto, M., 2013. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system. Journal of Hazardous Materials 254–255, 79–88. http://dx.doi.org/10.1016/j.jhazmat.2013.03.026.

Yörükoğlu, A., Obut, A., Girgin, İ., 2003. Effect of thiourea on sulphuric acid leaching of bastnaesite. Hydrometallurgy 68 (1–3), 195–202. http://dx.doi.org/10.1016/S0304-386X(02)00199-8.

Zhang, Q., Saito, F., 1998. Non-thermal process for extracting rare earths from bastnaesite by means of mechanochemical treatment. Hydrometallurgy 47 (2–3), 231–241. http://dx.doi.org/10.1016/S0304-386X(97)00048-0.

Zielinski, S., Szczepanik, A., Buca, M., Kunecki, M., 1993. Recovery of lanthanides from kola apatite in phosphoric acid manufacture. Journal of Chemical Technology and Biotechnology 56 (4), 355–360.