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A REVIEW ON RECYCLING OF RARE EARTH ELEMENTS (REEs)

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Abstract
The rare earth elements are a group of seventeen chemically similar metallic elements which include scandium, yttrium and the fifteen lanthanides. The rare earth elements have gained more importance over the years due to their useful applications. Human activities have been a significant source of rare earth elements which have eventually contaminated the earth's surface. Recycling of rare earth elements is an important part of the global economy, especially considering the large resource demands and negative environmental impact of current rare earth production processes. There is need to develop innovative and environment-friendly recycling technologies that will take care of these issues. This review paper mainly focuses on the various rare earth recycling technologies developed over the years.
Keywords: Rare earths, elements, lanthanides, recycling, technologies, balance problem

Introduction

The International Union of Applied and Pure Chemistry (IUPAC) defines the rare earth elements (REE) as the fifteen lanthanide elements plus scandium and yttrium (IUPAC, 2005). The fifteen lanthanide elements consist of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. The rare earth elements (REEs), contrary to what their name implies, are relatively abundant in the earth crust, with each of them being more plentiful than silver, and four of them (cerium, lanthanum, neodymium, and yttrium) being more plentiful than lead. Their combined crustal abundance is around 200 parts per million (ppm). REE consist of light rare earth elements (LREEs) and heavy rare earth elements (HREEs). Light rare earth elements (LREEs) are known as the cerium group (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd) and the heavy rare earth elements (HREEs) are known as the yttrium group (Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu). The rare earth elements also have distinctive physical and chemical properties that gave rise for their usage in a broad number of technological applications. Rare earth elements (REEs) are generally chemically stable, have excellent thermal conductivity, high ductility and corrosion resistance. Rare earth elements are also found in high concentrations, i.e. higher than 10% in rare earth oxide (REO).The REEs occur in different ratios in ores such as monazite and other minerals which is based on the natural abundance of these rare earth elements.

Despite existing in more than 200 minerals, only three ores are considered suitable for extraction: bastnasite, xenotime and monazite (Gupta and Krishnamurthy, 2005; Weng, Jowitt, Mudd and Haque, 2013, Mudd and Jowitt, 2016). The rare earth elements are widely used in various industrial fields such as electronics, petroleum chemistry, metallurgy, medicine etc. They are becoming increasingly important in the transition to a green, low-carbon economy. This is due to their essential role in permanent magnets, lamp phosphors, rechargeable NiMH batteries, catalysts and other applications (Table 1).

Table 1 **Summary of the rare earth elements (REEs) and their common uses (Jowitt, Werner, Zhehan and Mudd, 2018)**

REEs	Common uses
La	Optics, batteries, catalysis
Ce	Chemical applications, colouring, catalysis
Pr	Magnets, lighting, optics
Nd	Magnets, lighting, lasers, optics
Pm	Limited use due to radioactivity, used in paint and atomic batteries; very rare in nature
Sm	Magnets, lasers
Eu	Lasers, colour TV, lighting, medical applications
Gd	Magnets, glassware, lasers, X-ray generation, computer applications, medical applications
Tb	Lasers, lighting
Dy	Magnets, lasers
Ho	Lasers
Er	Lasers, steelmaking
Tm	X-ray generation
Yb	Lasers, chemical industry applications
Lu	Medical applications, chemical industry applications
Sc	Alloys in aerospace engineering, lighting
Y	Lasers, superconductors, microwave filters, lighting

Effects of demand and Supply on REEs

The increasing popularity of hybrid and electric cars, wind turbines and compact fluorescent lamps is causing an increase in the demand and price of REEs. In its landmark report, Critical Raw Materials for the European Union (2010), the European Commission considers the REEs as the most critical raw material group, with the highest supply risk (European Commission, 2010).The demand and supply of rare earth elements (REE) has become an increasingly important issue both politically and economically. The importance of REEs continues to increase due to its wide technological and industrial application.

Most production of REE takes place in China. With China presently producing more than 90% of the global REE output. China specializes in the extraction of rare-earth oxides from the ores as well as in the downstream processes such as its separation into the individual elements, the processing into rare-earth metals, and the production of rare-earth permanent magnets and lamp phosphors. This makes the supply of REE potentially vulnerable. Faced with its increasingly tight export quota, the rest of the world is confronted with a REE supply risk. Many countries will have to rely on recycling of REEs from pre-consumer scrap, industrial residues and REE-containing end-of-life products due to absence of economical and/or operational primary deposits within their territory.

Effects of human activities on REEs

Human activities have overburdened the ecosystem with large quantities of trace metallic pollutants and contaminants which can be regarded as a main source of recycled REEs. Bioaccumulation of rare earth elements in organisms depends upon their bioavailability. REE waste dumped in water bodies possess health hazardous potentials which have detrimental effects on living organisms. REE affected areas if not properly managed and controlled when exposed to weathering contaminate the air, soil and water which can lead to environmental challenges.

Effect of “balance problem” on REEs

REE recycling is al recommended in view of the so-called “balance problem” (Falconnet, 1985)
For instance, primary mining of REE ores for neodymium generates an excess of the more abundant elements, lanthanum and cerium. Hence the recycling of neodymium can lead to the reduction of the total amount of REE ores that needs to be extracted. The balance problem also explains why countries with large primary rare-earth resources, such as China is considering the recycling of REEs as an important issue (Xu and Peng, 2009). As REE are vital for many important industrial, technological and electronic products such as electric motors, hard drives etc., many nations have started looking for alternative supplies of these elements. One potential source that has attracted much attention in developed regions is REE-containing waste, mainly scrapped electronics. In regions such as the EU, electronic waste cover a significant part of the demand for REE.

Despite a vast, mostly lab-scale research effort on REE recycling, up to 2011 less than 1% of the REEs were actually recycled. This is mainly due to inefficient collection, technological problems and, especially, a lack of incentives. There is need to develop innovative and environmental-friendly recycling technologies, analytical methods and biomarkers with government support. Improved methods of recycling REE is absolutely necessary. With these efforts, an advanced recycling industry can be established. This review highlights the various steps and methods of recycling rare earth elements (REE).

Recycling of rare earth elements (REE)

In considering the large resource demands and supply, “balance problem” as well as the negative environmental impact of current REE production processes, recycling of REE should be an important part of the global economy. Recycling of REE is important in view of the efficient use of natural resources and to ensure a supply of these critical raw materials. Of the numerous methods for REE recycling as shown in Table 2 from various waste fractions, only a few have been tested in a larger scale. These large-scale recycling processes can be hydrometallurgical processes similar to those used in regular REE production or specific recycling methods used to recycle pure waste fractions within a production facility. Most recycling processes that do not use an already pure feedstock aim to produce a REE containing concentrate that can be fed into existing, commercially available REE separation processes. The dominant separation method is multiple stage solvent extraction; another method in commercial use is ion exchange, which is employed where especially high purity is required

The recycling process can be split into three types, namely

a) the direct recycling of manufacturing scrap or residues,

b) the urban mining of end-of life products, and

c) the recycling of solid and liquid industrial wastes (Li and He, 2017)

Recycling of magnets

The majority of current REE is being extracted from recycled permanent magnets, although they are obtained in relatively low amounts. Recycling approaches include

a) Traditional methods of recycling which includes the hydrometallurgical recovery techniques where magnets are dissolved in leaching solutions such as acids (or in the future potentially ionic liquids) before the REE are precipitated out of solution.

b) Pyrometallurgical recovery techniques where REE alloys are heated and remelted. They are separated from alloyed transition melts in a liquid metallic state. They are refined in an electroslag process, or are dissolved out of alloys by reaction with a molten flux, with the REE then supercooling with the flux to form a glass. The approach used depends on the nature of the rare earth elements within the magnets.

c) Gas phase extraction methods where the REE are transferred to a volatile chloride phase. They are separated based on differences in volatility.

Recycling of fluorescent lamps

Recycling approaches for energy-efficient and longer lasting compact fluorescent lamps which contains different amounts of REE in the form of white, red, green and blue phosphors include

a) direct re-use, although this has a very limited approach.

b) individual separation of phosphor components although it does not easily yield pure phosphor fractions.

c) chemical extraction of the REE, an approach that could yield individual REE for reuse in a variety of end-products but one that is much more difficult and intense than the other approaches in terms of energy and chemicals (Kumari, 2018)

The majority of research to date has focused on the extraction of Eu and Y from red phosphors as these elements are relatively easy to recover and are of high value (Van, Binnemans and Van Gerven, 2017). However, the La, Ce and Tb-bearing green phosphors are being targeted as important phosphors for future recycling, even though these phosphors are harder to dissolve, requiring high temperature acid dissolution using molten NaOH or Na_2CO_3 (Van et al., 2017; Wu, Yin, Zhang, Wang and Mu, 2014; Porob, Srivistava, Nammalwar, Ramachandran and Comanzo, 2012)

Recycling of REEs catalysts

The REE are extensively used in catalysts which are employed during hydrocarbon cracking and contain around 3.5% by weight of La with lesser amounts of Cerium, Praseodymium, and Neodymium (Binnemans, Jones, Blanpain, Van Gerven, Yang, Walton, and Buchert, 2013). There has been very little interest to date in recycling the REE within these catalysts with research focusing on acid leaching (Binnemans et al, 2013). These catalysts contain REE that have relatively low value (Weng, Jowitt, Mudd, and Haque 2015). It is difficult to decide whether the recycling of the REE in these catalysts is currently economically viable or not.

Recycling of Ni-MH batteries

Rechargeable nickel metal hydride (Ni-MH) batteries contain around 10% REE that are present in order to impart hydrogen storage capabilities (Binnemans et al., 2013; Ueberschaar, Geiping, Zamzow, Flamme and Rotter, 2017). These batteries use mischmetals, metallic stage LREE (predominantly La, Ce, Pr, and Nd) alloys or alloys of the light rare earths generated by fused chloride electrolysis. Until recently the dominant recycling of these batteries was in stainless steel production as a cheap source of Ni, with the REE deporting to smelter slags and being lost (Binnemans et al, 2013; Muller and Friedrich, 2006). However, the REE within these batteries could potentially be recycled using

a) pyrometallurgical recovery
b) hydrometallurgical routes

Although both approaches are still under research.

Table 2 Summary of the potential sources of REE during recycling (Jowitt et al, 2018).

Source	Targeted REEs	Primary recycling mechanism
Magnets	Nd, Dy and the other REE	Hydrometallurgical processes (solvent extraction, leaching, selective precipitation)
Batteries	La, Ce, Pr, and Nd	Pyrometallurgical or Hydrometallurgical recovery routes
WEEE & 'End of Life' consumer goods, Fluorescent material (phosphor powder, fluorescent lamps, etc.)	La, Ce, Tb, and Y	Pyrometallurgy (calcination, roasting); Hydrometallurgy (solvent extraction leaching, selective precipitation); Gas phase extraction
Other industrial processes and residues	Depending on the source material, the REE recycling process can target different REE	Pyrometallurgical processes (calcination, roasting,); Hydrometallurgical processes (solvent extraction, leaching, selective precipitation); Physical separation & microbial leaching (bioleaching)
Industrial process and residues, Fluid Catalytic Cracking (FCC) catalysts	LREE (La, Ce)	Hydrometallurgical processes (solvent extraction, leaching, selective precipitation); Microbial leaching (bioleaching)

Challenges

The main challenges of REE recycling are

a) The small amount of the REE used in the majority of end-products containing these elements combined with the difficulty of the collection, extraction, and recovery of the constituent materials within end-products hampers the recycling of the REE to date (Li and He, 2017; Kumari, Jha and Pathak, 2018).
b) The presence of contaminants in the feedstock (Tsamis and Coyne, 2015). For example, electronic waste has a very complicated composition with numerous contaminants; common permanent magnets contain 72 weight% Fe, which suggests that REE recovery processes cannot be recycled into an economic product.
c) In many cases, extensive pretreatment is required to extract a fraction from which REE can be recovered efficiently (Schüler, Buchert, Liu, Dittrich, and Merz, 2011)
d) Lack of cost effective and efficient methods to purify the mixtures generated during the recycling of consumer devices that contains these rare earth elements.
e) Most recycling methods demand large amounts of energy and chemicals. They often require the use of hazardous chemicals such as strong acids, NaOH and HF, which often cannot be recovered from the process and instead end up as chemical waste or as pollutants in effluent water (Tsamis and Coyne, 2015).
f) Deficiencies in the waste collection and technical difficulties such as separation of neodymium magnets from devices that contain them.
g) Lack of incentives, strict regulations and high cost of recycling processes (Binnemans et al., 2013; Schüler et al., 2011).
h) Another problem is that much used goods containing REE are exported to developing countries, reducing available feedstock for the countries that have the technical infrastructure necessary for the recovery processes (Schüler et al., 2011).

Recommendations on the recycling of the REE

The future potential for the recycling of the REE depends on the type and nature of material being recycled. The following recommendations are being made on the recycling of REEs

a) Development of significant amount of laboratory and computational based research. The findings of these research are geared towards developing solutions and potential methods that would enable a broader and improved method of recycling REEs. However, recycling of the REE currently requires an extensive development of efficient collection infrastructure.
b) Advances in research in the area of purification of mixtures during recycling is necessary in order to provide insights into approaches that can help in tackling this issue.
c) As the demand and supply of REE increases, research and exploration should focus on the discovery of new mineral and ore deposits, adapting existing mines to process the REEs.
d) Developing process technology which prefers to extract and recycle the heavy REEs.
e) Research into other methods of recycling should be encouraged and promoted; for example Microbial leaching (bioleaching).

f) On the demand side, research and development should focus on finding substitute for the REE in different technologies or finding alternatives for these technologies altogether.

Conclusion

The REE are among the most critical elements yet current efforts to recycle these valuable commodities are seemingly relatively ineffective. There is significant potential to increase the amount of the REE recycled from major end-uses, such as fluorescent lamps, permanent magnets, batteries, and catalysts; however, a significant amount of research is needed in all of these areas to increase the amount of these elements. REE recycling has the potential to play a key role in addressing a number of critical issues about these elements, including meeting increased demand, increasing the security of their supply, overcoming the balance problem between higher and lower demand REE, the concentrations of the REE available from primary mine-derived sources and its health/environmental impact.

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