



Review on hydrometallurgical recovery of rare earth metals



Manis Kumar Jha ^{a,*}, Archana Kumari ^a, Rekha Panda ^a, Jyothi Rajesh Kumar ^b, Kyoungkeun Yoo ^c, Jin Young Lee ^b

^a Metal Extraction and Forming Division, CSIR-National Metallurgical Laboratory, Jamshedpur 831007, India

^b Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, South Korea

^c Department of Energy & Resources Engineering, Korea Maritime and Ocean University, Busan 606-791, South Korea

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ABSTRACT

Rare earth metals are essential ingredients for the development of modern industry as well as designing and developing high technology products used in our daily lives. Consequently, the worldwide demand of rare earth metals is rising quickly and predicted to surpass the supply by 40,000 tons annually. However, their availability is declining, mainly due to the export quotas imposed by the Chinese government and actions taken against illegal mining operations. This has laid emphasis to exploit and expand technologies to meet the future necessities of rare earth metals. Bastnasite, monazite, and xenotime are their chief mercantile sources, which are generally benefited by flotation, gravity or magnetic separation processes to get concentrates that are processed using pyro/hydrometallurgical routes. To develop feasible and eco-friendly processes, R&D studies are being conducted for the extraction of rare earth metals from leached solutions (chloride, nitrate, sulfate, thiocyanate, etc.) using different cationic, anionic and solvating solvents or ions depending on material and media. Commercial extraction of rare earth metals has been carried out using different extractants viz. D2EHPA, Cyanex 272, PC 88A, Versatic 10, TBP, Aliquat 336, etc. The present paper reviews the methods used for the recovery of rare earth metals from primary as well as secondary resources, with special attention to the hydrometallurgical techniques, consisting of leaching with acids and alkalis followed by solvent extraction, ion exchange or precipitation. The piece of comparative and summarized review will be useful for the researchers to develop processes for rare earth recovery under various conditions.

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1. Introduction

Rare earth elements include the 15 elements of lanthanide group from lanthanum to lutetium, coupled with chemically similar yttrium and infrequently scandium. These elements are split into two sub-groups, the light rare earth elements (LREEs) from lanthanum to europium and the heavy rare earth elements (HREEs), which include the rest of lanthanide elements along with yttrium. Scandium is not included in either of these groups due to its much smaller ionic radius. Rare earth elements are comparatively abundant in the earth's crust than other commonly exploited elements but are not sufficiently concentrated to make them easily exploitable. This is due to the similarity in their ionic radii (Table 1) which makes them interchangeable in most minerals, and are very difficult to separate (Jordens et al., 2013; Gupta and Krishnamurthy, 2005). Rare earths are always found in varieties of minerals viz. silicates, halides, carbonates, phosphates, etc. (Table 2) but never found as pure metal (Jordens et al., 2013; Kumari et al., 2015). Nowadays, more than 250 rare earth minerals have been recognized but in most of them the concentration of rare earths is very low varying from 10 to 300 ppm (Zhang and Edwards, 2012).

The unique properties of rare earth metals is dominantly expanding its application and are needed to supply the required functionality in many high-tech components, green technologies and material industries of high-temperature superconductors, secondary batteries, hybrid cars, etc. The extensive use of rare earth elements is increasing their global demand and was estimated to be 136,000 tons per year, with a worldwide production of 133,600 tons in 2010 (Panayotova and Panayotov, 2012). Bloomberg News (2010) predicted that the demand would reach 210,000 tons per year by 2015, keeping in view the escalating demand of rare earths that is exceeding the industry's ability to produce as the commercial stocks are depleting. The forecast supply and demand of rare earths till 2014 is presented in Table 3 (Seaman, 2010). About, one hundred million tons of rare earth oxide reserves are presently accessible in the world, scattered in more than 30 countries (Chen, 2011). In 1950s, South Africa, India, and Brazil had rare earth mines in operation. Further, during 1960s to 1980s, the Mountain Pass in California became the largest global producer for the same up to 2002 till it closed. Thereafter, China began large scale production and exported rare earths at cheaper rate. Currently, it is the worldwide producer of rare earth elements producing ~97% of the total world supply. But their incessantly increasing requirement has aggravated the Chinese government to drastically limit the export of rare earths up to 35,000 tons while the yearly demand of other countries is estimated to reach 80,000 tons in 2015, thus, confronted with a rare earth supply

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* Corresponding author.

E-mail address: mkjha@nmlindia.org (M.K. Jha).

Table 1
Ionic radii of rare earth elements (Jordens et al., 2013; Gupta and Krishnamurthy, 2005).

Rare earth elements	Ionic radius (nm)
La	1.061
Ce	1.034
Pr	1.013
Nd	0.995
Pm	0.979
Sm	0.964
Eu	0.95
Gd	0.938
Tb	0.923
Dy	0.908
Ho	0.894
Er	0.881
Tm	0.869
Yb	0.858
Lu	0.848
Se	0.66
Y	0.88

risk (Jordens et al., 2013; Panayotova and Panayotov, 2012). According to the U.S. Mineral Commodity Summaries of 2015, the global mine production of rare earth metals (Fig. 1) is 110,000 metric tons while the total reserves is found to be 130,000,000 metric tons. This restriction of supply is being met by the development of many new mining projects or reopening of old mines. Worldwide exploration for economically exploitable rare earth deposit as well as development of indigenous resources and technologies to meet the future requirements of rare earth metals is encouraged.

The objective of the present paper is to explore the current overview of rare earth recovery from various resources with regard to hydrometallurgical processes consisting of leaching, solvent extraction, ion-exchange and precipitation along with their selected environmental impacts and finally the research work further required in these fields.

2. Currently exploited primary and secondary resources

Minerals containing rare earth elements are differentiated into various groups depending upon the content of rare earths present in them. Bastnasite, monazite and xenotime are the three most frequently extracted rare earth minerals. However, ion-adsorbed clays are also very significant source in which 60% of the rare earth oxides comes from the group of HREEs. Rare earth elements are becoming progressively more important in transition to a green economy, due to their vital role in permanent magnets, lamp phosphors, catalysts, rechargeable batteries, etc.

2.1. Primary sources

2.1.1. Bastnasite

Bastnasite, a fluorocarbonate mineral containing approximately 70% rare earth oxide (mainly conquered by LREEs) became the principal source of most rare earth elements and are relatively straightforward to treat (Jordens et al., 2013; Ozbayoglu and Umit Atalay, 2000; Huang et al., 2005). It originates in vein deposits, metamorphic zones, igneous carbonatites deposits and are mainly obtained from the world's largest rare earth mines, the Mountain Pass, USA and the Bayan Obo mine in China (Gupta and Krishnamurthy, 2005). Some of the rare earth distribution present in major deposits of bastnasite minerals is illustrated in Fig. 2 with other metals present in trace amount (Long et al., 2010; Jordens et al., 2013; Chen, 2011). This ore is processed by numerous operations including gravity and magnetic separation to make intermediate rare earth concentrates and are further purified using solvent extraction as well as selective precipitation.

2.1.2. Monazite

A rare earth phosphate mineral, fairly similar to bastnasite as a LREE ore but with slightly more HREEs is known as monazite. Unlike bastnasite, monazite contains a high content of naturally occurring radioactive element, thorium (4–12 wt.%) and a variable amount of uranium which presents a negative aspect of mining and processing, thus eliminating all the monazite production except from southeast Asia and India. It is found throughout the world in placer deposits, beach sands, and is also a component of the Bayan Obo deposit. They are mainly mined as heavy mineral sand from beach deposits and recovered as a byproduct during processing of ilmenite, rutile and zircon (Gupta and Krishnamurthy, 2005; Kumar et al., 2014).

2.1.3. Xenotime

Xenotime is also a rare earth phosphate mineral, containing ~67% rare earth oxides which is rich in yttrium and HREEs, especially the even numbered lanthanides. In spite of its scarcity, xenotime is a vital mineral being a major source of HREEs and ion-adsorbed clays. It occurs in granites of Minas Geraes in Brazil, pegmatite veins at Hittero, Moss as well as in crystalline metamorphic rocks. Xenotime is recovered as a minor ore mineral during heavy sand recovery operations, primarily from monazite in Brazil, India, South Africa and Australia. Limited researches are only focused for the xenotime extraction from monazite using flotation and magnetic separation. Distribution of rare earths in monazite, xenotime and ion-adsorbed clays in some of their major deposits is presented in Table 4 (Long et al., 2010; Jordens et al., 2013; Chen, 2011).

To recover rare earth metals from these ores, various processing routes have been developed. Ores obtained after mining are beneficiated using flotation, magnetic or gravity separation methods. These beneficiated ores (a few successfully exploited minerals is mentioned in Table 2) are usually treated hydrometallurgically or at times by pyrometallurgical operations. However, the ion-adsorbed clays require little or no beneficiation and are directly processed using hydrometallurgical routes.

2.2. Secondary sources

The absence of cost-effective and operational primary deposits is forcing many countries to rely on the recycling of rare earth metals from pre-consumer scrap, industrial residues and end-of-life products. This can reduce the environmental challenges associated with rare earth mining and processing. Rare earth recovery from some of the end-of-life products is discussed in this paper.

2.2.1. Permanent magnets

Neodymium–iron–boron (NdFeB) alloys are the basis of rare earth magnets commonly known as Nd–Fe–B magnets, comprised an $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase surrounded by a neodymium-rich grain boundary with small admixtures of praseodymium, gadolinium, terbium, and especially dysprosium (increases temperature stability against demagnetization) along with other elements such as cobalt, vanadium, titanium, zirconium, molybdenum or niobium (Gutfleisch et al., 2011; Yu and Chen, 1995; Binnemans et al., 2013). This superfluous material is significantly found in hard disk drives (HDDs) along with other electronic goods such as loudspeakers, mobile phones, etc. On global scale, 600 million HDDs are manufactured consuming ~6000 to 12,000 tons of Nd–Fe–B alloys (Binnemans et al., 2013). Rare earth metals are generally recycled from three different magnet materials (1) swarf obtained during magnet manufacturing, (2) small magnets of end-of-life products and (3) large magnets in hybrid and electric vehicles or wind turbines. Direct recycling and re-use is applicable only for the large magnets while further processing is required for other rare earth magnets. A simplified flow sheet as described by Binnemans et al., 2013 for the recycling of rare earth metals from magnets is shown in Fig. 3.

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