

The Extraction and Recovery of some Rare Earth Elements from their Ores: A Review

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ABSTRACT

Rare earth metals, including lanthanum and scandium are being increasingly used in clean energy technologies, coloured phosphors, lasers and high intensity magnets. This is because of their unique physical and chemical properties and has made them essential in state-of -the-art equipment (such as for example, batteries, magnets, catalysts). With the ongoing technological advances in electronics, vehicles and national defense systems, the demand for REEs has increased exponentially. This paper enlarges on the properties of REEs, abundance, economic importance, mining and extraction methods.

Keywords: Rare Earth Metals, abundance, extraction methods, economic uses.

INTRODUCTION

The Rare earth elements (REEs) are lithophile elements (elements enriched in the earth crust) that have similar physical and chemical properties, and therefore occur together in nature in many of the same minerals [1]. Originally the term Rare Earths (REs) was used for the oxides R_2O_3 , which are similar to one another in chemical and physical properties and therefore difficult to separate [2]. The name Rare earth is actually a misnomer as the collection of elements known as "Rare Earths"(REs) are not actually that rare , with some of them more abundant in the earth's crust than Cu or precious metals of Au, Ag and Pt [2]. According to Norman *et al.* (2014)[3], and even the two least common REEs are almost 200 times more abundant than Au .They are never found as free metals in the earth crust and pure mineral of individual rare earths do not exist . It was the very scarcity of these metals that led to the term Rare Earth metals [4].

The term Rare earth elements (REEs) or Rare earths (REs) or rare earth metals (REMs) refer to a group of 17 elements [5] and include the lanthanides series of the periodic table from atomic number 57 to 71 starting with Lanthanum(La) to Lutetium(Lu) and including Scandium(Sc) and Yttrium(Y) [6], [7], [8]. They are grouped together because of their simultaneous presence in minerals that lead to their discovery [9]. Cerium(Ce) and

One of the members of the Lanthanide series Pm is radioactive and exceedingly scarce, and is usually sourced through nuclear transformation [7]. Pm because of its high instability and scandium's limited applications make them irrelevant in our further analysis [9]. The abundance of REEs taken together is quite considerable [12].

- i. Ce, the most common RE, is more abundant than Co and its abundance is almost same as environmentally much more studied elements such as Cu and Zn.
- ii. Y is more abundant than Pb
- iii. whereas Lu and Tm are as abundant as Sn, Hg, Bi and Ag
- iv. the most scarce Lanthanides, Lu and Tm are actually more abundant in the earth's crust than Cd and Se [13].
- v. The most abundant REEs are Ce, Y, La and Ne, they have average crustal abundances that are similar to commonly used industrial metals such as Cr, Ni, Zn, Mo, Sn and W [14].

REE bearing minerals are found scattered in a variety of forms mostly as accessory minerals in igneous and metamorphic rocks, such as granite and gneisses and pegmatite [13]. The minerals Bastnasite, Monazite, Xenotime, allanite, gadolinite, leparite and fergosnite are the sources of REEs [15].

Table 1: Some minerals that contain REEs and occur in potentially exploitable deposits

Mineral	Formula	RED wt 10%
Aeschnyrite	(L, Ca, Fe, Tu (Ti, NB) ₂ (O, H) ₆	36
Allanite	(Ca, Lu) ₂ (AL, Fe) ₃ (SiO ₄) ₃ (OH)	30
Anatase	TiO ₂	3
Apatite	Ca ₅ (PO ₄) ₃ (Fe, Cl, OH)	19
Bastnasite	Lu CO ₃ Fe	76
Euxcenite	(Lu, Ca, U, Tu) (Nb, Ta, Ti) ₂ O ₆	<40
Fergusonite	Lu (Nb, Ti) O ₄	47
Kainosite	Ca ₂ (Y ₁ Lu) ₂ Si ₄ O ₁₂ CO ₃ H ₂ o	38
Laparite	(Lu, Na, Ca) (Ti Nb) O ₃	36
Monazite	(Zn Ln Th) PO _{4,0}	71
Xenotime	YPO ₄	61
Yttrotantacite	(Y, U, Fe) (Ta, Nb) O ₄	<24

Source; Castor and Hedrick, 2006

Bastnasite and monazite contain mostly LREEs, only small amounts of HREEs [16]. Due to their high Th Content, monazite is radioactive [16]. Xenotime is Yttriumphosphate, it contains about 67% REO, mostly the HREEs, but occur less commonly than monazite [16]. In addition REEs are sometimes by-products of mining from iron, copper, gold and other minerals [6]. REEs may also be derived as by-products of phosphate fertilizer production, uranium ore, and aluminum red mud processing. Furthermore REE containing materials are ion absorbing clays which are residues, from alteration products (Zept, 2013)[10]. REEs occur in a wide range of mineral species, such as silicates, carbonates, oxides, phosphates, and clays, however REE content of these minerals are variable and only a few of them are of economic interest [17]. Ores containing REEs are mainly bastnasite, monazite, and ion

adsorption clays [9]. Monazite contains The which is slightly radioactive so that stockpiling and transportation makes it less competent, ion adsorption clays which contains fewer REEs than bastnasite but also needs fewer processing steps (Shirashi, 2010)[9]. About 95% of REs occur in only three minerals: bastnastie, monazite and xenotime [18]. Basnasite is considered the most economic REE mineral and contains approximately 70% REO in its structure [19]. Today several hundred REE containing minerals are known, however only very few have been identified to be of economic importance. Although relatively abundant in the earth's crust, REEs rarely occur in concentrated forms making them economically challenging to obtain [20, [21], [22]. The isolation of groups of REEs or individual elements requires costly separation and fractionation processes owing to the great similarity of the chemical and physical properties of their compounds which explains why the history of their discovery has extended over such along period (Habashi, 2013)[23].. Several factors make their discovery and identification difficult as enumerated by Izatt *et al.*, (2016)[24].

- i. the chemical and physical properties of the different elements are quite similar making their separation from each other challenging
- ii. the element were isolated originally as "earths" or oxides", each of which usually constituted two or more individual elements.
- iii. the methods of separation and purification depend on laborious fractionation, precipitation and crystallization techniques, sometimes requiring thousands of separation processes and;
- iv. difficulties of separation were compounded by lack of good methods of identification, assessment of purity of the separated elements, and lack of knowledge through the 19th century and early 20th century of the number of REEs that existed. The only REEs produced as individual metals are La, Ce, Nd, and Y and together they comprise about a quarter of total production [25].

Technological innovations resulted in manifold applications using REs which led to dramatic increase in their demand [16]. REMs are industrially useful and applied to

advanced technologies in many fields [26]. Because of their unique magnetic, luminescent, and electrochemical properties, these elements help make technologies perform with reduced emissions, and energy consumption, or give them greater efficiency, performance, miniaturization, speed, durability and thermal stability [26]. These properties are useful for magnets, optics, electronics, and other applications [6]. The elements constitute critical components of many important technologies (EPA 2011)[21] and accounts for their usefulness in [27] new technologies such as wind turbines, batteries, lighting or medical techniques. As recounted by Klinger (2015)[28], China produces 97% of the global supply of REs which essentially are used for diverse and ever expanding array of communications, energy, information and military technology. An on this account numerous research and analysis has proliferated enormously. However, in recent years REEs have become strategically critical for developed and developing economies around the world which is primarily due to the shortage of discovered minable resources [29]. Figure 2 shows the many applications of rare earth metals.

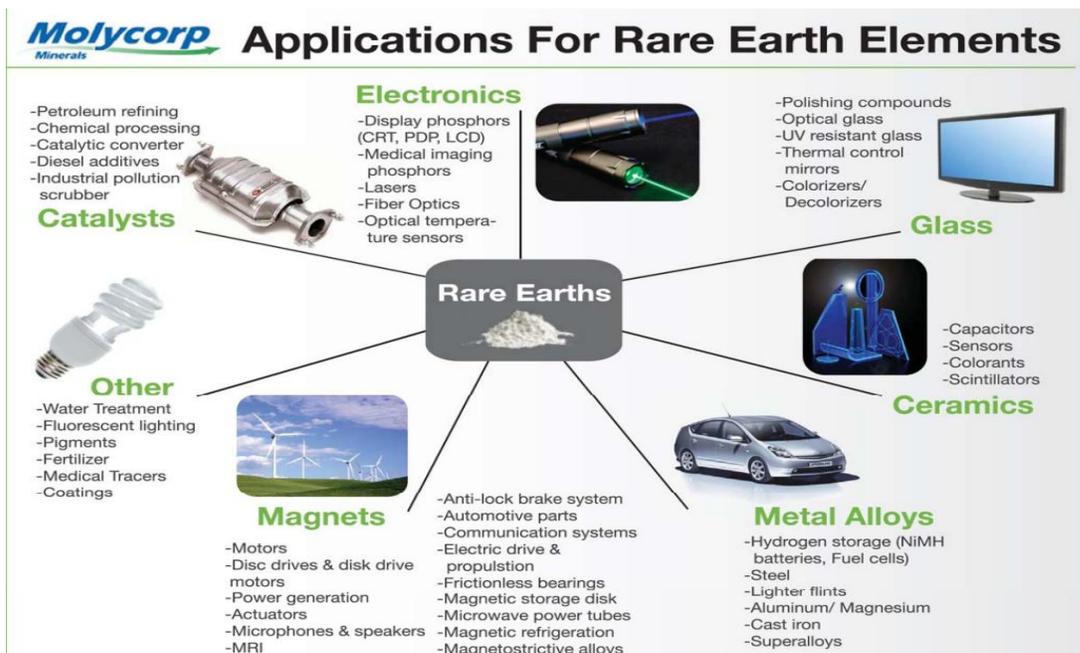


Figure 2: Applications for rare earth elements

Source: MolyCorp minerals. I.I.C. 2010

PROCESSING TECHNOLOGIES OF REES

The production of REs from their ores involve complex processes that is designed according to the nature and mineralogy of each deposit [30]. Extraction methods seek to achieve a Commercially viable separation scheme which employ materials that will economically and selectively bind to the various REEs in the presence of potential interfering ions such as Ca and Fe, and have minimal environmental impact [31]. The production process consists of generally mining, processing and refining [16]. Once mined, the minerals are first separated from non- ore minerals by gravity, floatation and magnetic separation [32]. The generalized extraction and separation scheme is as shown in figure 3 below.

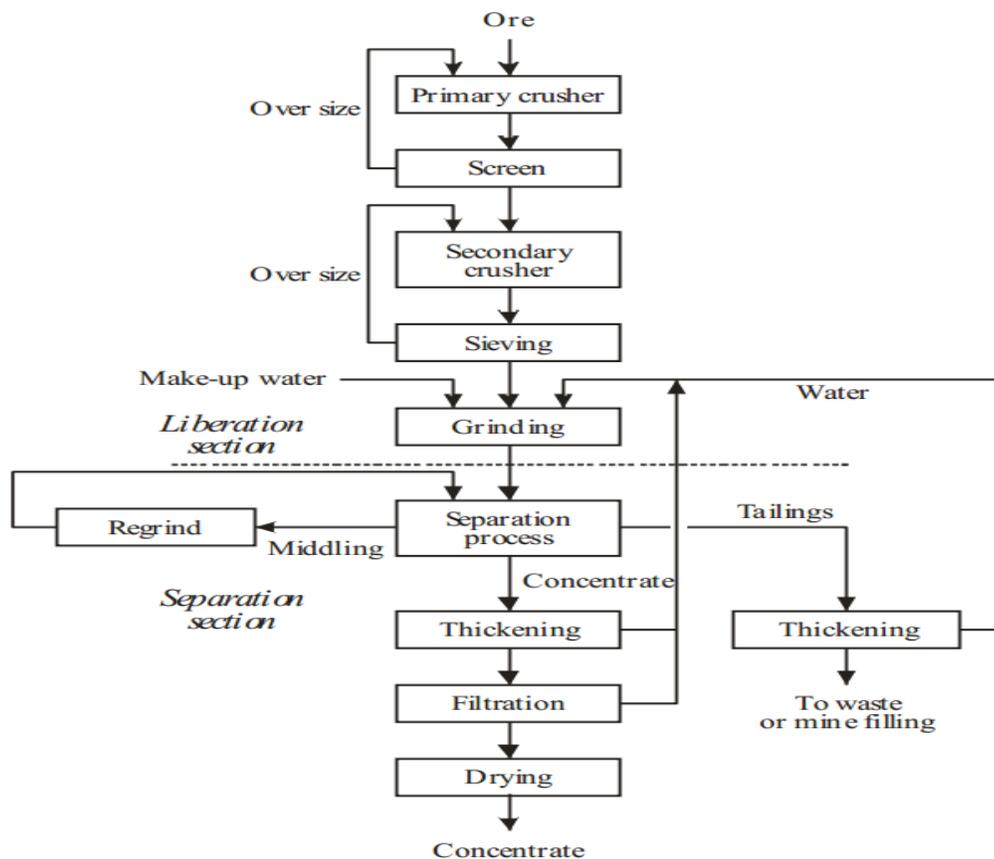


Figure 3: Processing technologies of REES

Source; Habashi, 2015

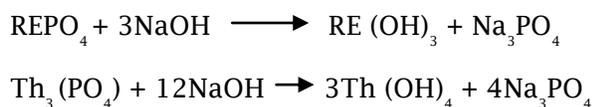
Generally extraction of REE mixture into individual elements is very difficult to achieve, due to the very low separation factors involving the adjacent REE, and because the chemical properties of the individual elements are very similar [33]. It involves mining an area where the REE concentration is high and collecting minerals containing REEs, such as Bastnasite, Loparite, Monazite and Xenotime [34]. Conventional RE production from Bastnasite and Monazite is known to require high material and energy amounts [35].

THE CAUSTIC SODA METHOD

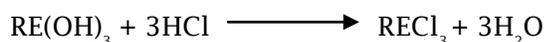
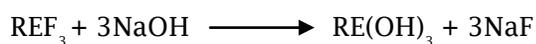
The caustic soda method involves the dissolution of the minerals in concentrated solution of NaOH at 140-150°C converting the REE and Thorium to hydroxides. The phosphate compound is separated by dissolving in water and recovered as trisodiumphosphate. REEs are separated from Thorium using partial dissolution in which REEs are dissolved in concentrated HCl while undissolved material is filtered and forms thorium waste cake [36]. This is the preferred process for chemical treatment as a marketable by-product whereas with acid treatment phosphate is lost.

EXTRACTION FROM MONAZITE AND XENOTIME (CAUSTIC SODA METHOD OR ACIDIC SOLUTION)

According to (Ebner, 2014)[36], REE extraction from Monazite and Xenotime involves the dissolution of the mineral in hot concentrated alkaline (caustic soda method) or acidic solutions (acid treatment). Acid treatment uses hot H₂SO₄ acid digestion then leaching with water to remove the phosphate content. A dilution stage follows whereby a process of selective precipitation deposits the REE as double sulphate. The H₂SO₄ method has been used on a commercial basis in the past but it is no longer in use as it does not yield pure product. The reactions during alkaline leaching according to Peelman *et al.* (2014)[37] are thus:



Bastnasite is a rare earth ferocarbonate mineral, $RE(CO_3)F$, which primarily contains light REE. After physical upgrading, basnaesite concentrates contain between 40 to 60% REE. The alkaline treatment, developed by Kruesi and Duker is a three step process using the following reactions scheme.



SEPARATION OF INDIVIDUAL REES

Selective oxidation or reduction of certain REEs can be useful in the separation process Jacobson (2014)[38]. In general REEs are characteristically trivalent, but Ce, Pr and Te can occur in tetravalent state as well as the trivalent state and Sm, Eu and Tb display divalency. These differences in chemical behaviours can be exploited in the separation of individual REEs. Ce and Eu are generally separated by selective oxidation whilst other REEs can be separated by fractional crystallization, fractional precipitation, solvent extraction and ion exchange. These methods are based on the small differences in basicity resulting in decreasing size in ionic radius from La to Lu.

The demerits of these techniques Jacobson (2014)[38] are:

- i. fractional precipitation and fraction crystallization are however, laborious and inefficient and have consequently been superceded by more effective techniques like ion exchange and solvent extraction
- ii. the solvent extraction method is most appropriate for separating HREE, with the LREE being more difficult to extract using this method
- iii. the ion exchange method produces highly pure REE in small quantities. However it is a time consuming process and only a few HREE are purified commercially on small scale using ion exchange.
- iv. for large scale production solvent extraction is the preferred route. Liquid-liquid extraction is a method used to separate compounds on the basis of their relative solubilities in two miscible liquids, typically water and organic solvent.

Solvent extraction is more convenient than ion exchange because it allows both semicontinuous operation and the use of more concentrated feed solutions. (Tansu *et al.*, 2011)[39]. Solvent extraction methods used have low selectivity for individual REE resulting in the need for using separation stages and carry-over of impurities downstream with the generation of much waste (Rout and Binnemans, 2014)[40]. However, solvent extraction is the most economically viable method of separating REEs [41].

Figure 4 is a typical example of processing routes for the separation of individual REE from the major REE bearing minerals Bastnasite, Monazite/Xenotime.

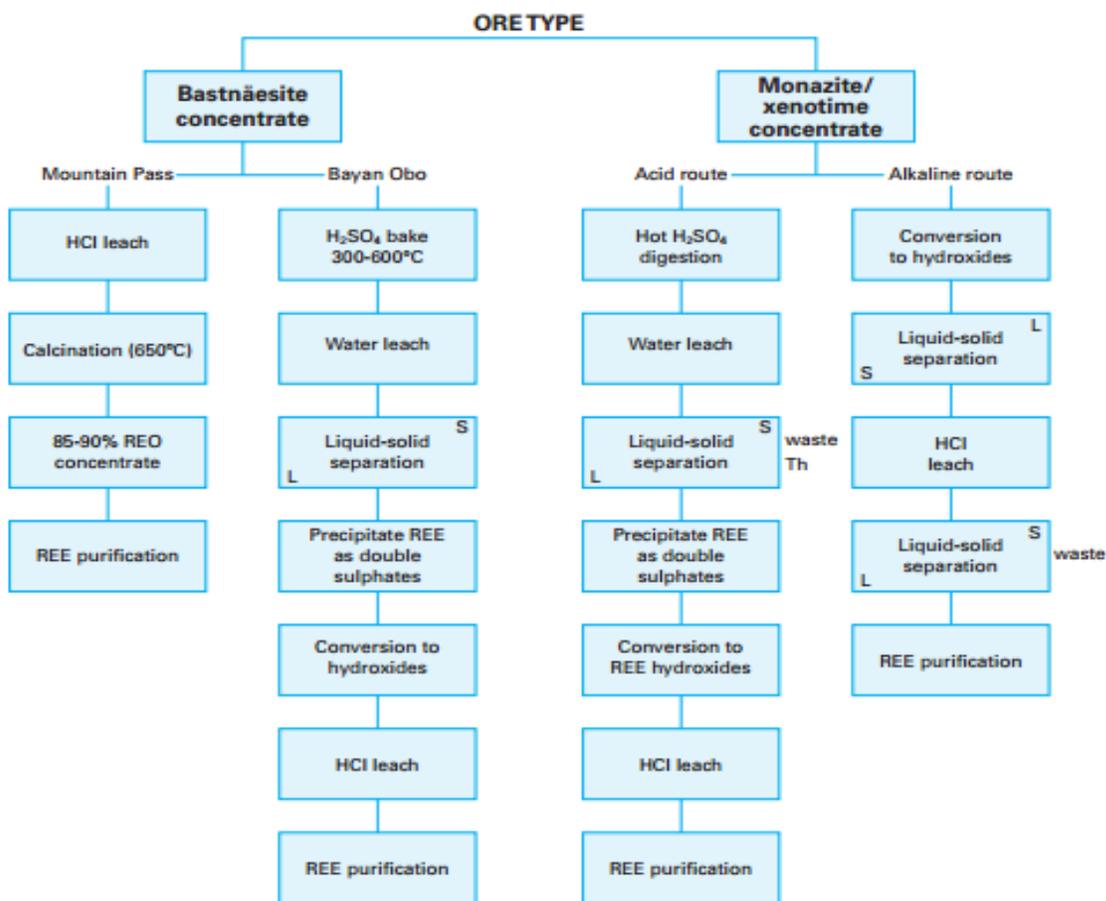


Figure 4: Ore types

Source: British Geological Society, 2011.

CONCLUSIONS

The Rare Earth Metals are an integral input, with little or no substitutes, required in a multitude of industries. These elements are critical to the security of nations, the development of green energy from hybrid cars to wind turbine, and advance in various industries such as petroleum refining, phosphor manufacturing and glass polishing Rare earth minerals are a group of elements that have unique properties. Because of the stable outer shells they have similar chemical properties which present difficulty in their separation during processing. Separation techniques employed to meet increasing demand from 21st century include fractional crystallization ion exchange and solvent extraction among others.

Rare earth metals are a unique family of elements with nearly identical and chemical properties. They account for approximately 1/6th of all naturally occurring elements, but the entire group occupies only one position of the periodic table. REEs receive their name, not only because they are rare in the earth crust, but because they are rarely found in sufficient quantities for practical and economic mining purposes. Rare earths are the Linchpin ingredients of many high technologies for a wide variety of uses-ranging in application from military and medicine to entertainment, communications and petroleum refining, through to lighting and renewable energies. Rare earth elements are also known as Rare Earth Metals (REMs) since they are all metals, and also they are known as rare earth oxides (REOs) because they are traditionally sold or traded in oxide form. REEs most commonly found are Cerium, Yttrium, Lanthanum and Neodymium. The REEs impact nearly everyone in the world. All of the people living in advanced technological countries and almost all living in the third world countries utilize the rare earths in their everyday living.

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