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RARE EARTHS: RECENT PERSPECTIVES

Rare earth elements (REE), a group of metals with unique physico-chemical, phosphorescent, and magnetic properties, are used in different strategic technologies. In the last years their importance has spurred a flurry of literature and the present article aims at a concise update concerning main current and future uses, production, resources, and recycling prospects.

Rare earth elements (REE), also known as the lanthanoids, are a group of 17 metals ranging from lanthanum (atomic number 57) to lutetium (atomic number 71). They have similar chemical properties and usually occur together in nature. According to the official definition by the International Union of Pure and Applied Chemistry, yttrium (atomic number 39) and scandium (atomic number 21) are part of the group due to similar properties and frequent association in ores. REE are usually subdivided in two groups, the "light" rare earths or cerium subgroup (LRE) and the "heavy" rare earths or yttrium sub-group (HRE). The classification is not clear-cut, though: for example, the United States Geological Survey calls the elements from lanthanum to gadolinium the LRE and those from terbium to lutetium and yttrium the HRE [1]. A third class, medium high rare earth rich concentrates (MRE), is being introduced because of recent tax rates differentiation among mineral concentrates [2]. Despite its - misleading - name, REE are relatively abundant, but economically minable concentrations are indeed less common than for many other elements.
Most rare earth oxides (REO) are thermally stable as well as chemically active: they are characterized by high values of density, melting point, electrical conductivity, and thermal conductance.
REEs' atomic radii decrease with increasing atomic number (lanthanide contraction) and the radius of the corresponding trivalent ions gradually diminishes by around 25% from lanthanum to lutetium. Consequently, the oxides basicity, depending on the radius/charge ratio of the cation, regularly diminishes in the same order, which influences properties such as solubility, ionic hydrolysis, and complexation [3]. The chemical properties of rare earth elements are a result of the nature of their electronic configuration: lanthanide elements differ from one another by the number of inner-core electrons in the $4f$ subshell (from $f0$ - lanthanum - to $f14$ - lutetium) and these electrons do not contribute to the valence shell. This results in two particular features: first, there are minor differences among the rare earth metals in their chemical properties because of the similar ionic radii and valence states; second, there are major differences in atomic spectra and magnetic properties and each REE shows specific physical characteristics. Furthermore, since some REE atoms have atomic radii similar to rock-forming elements, REE are often found in rocks containing calcium, strontium, thorium and uranium and a specific metallurgy needs to be applied for their separation [4]. In the case of the last two elements, there are obvious issues linked to radioactivity.
As a result of their unique physico-chemical, phosphorescent, and magnetic properties, REE are used today in many advanced technologies related to communications, transports, medicine, energy, surveillance, and defense. In the last years, their importance has spurred a flurry of literature (scientific and non-specialized articles, technical and market reports, monographs) [5-7]: extensive chemical and physical data is provided not only in the established reference literature, such as Lan-

dolt-Börnstein and Gmelin handbooks, but also in specific volume series and journals [8, 9].
The present note aims at a concise update concerning uses and resources.

Uses

The shift from fossil fuels towards clean energy is in full swing and this transition leads to a continuous demand for REE, thus increasing the need for a reliable supply chain [10]. The products list is impressive (Fig. 1). Let's take for example the automobile: Diesel fuel additives contain cerium and lanthanum; UV cut glass, glass and mirror polishing powders contain cerium; LCD screens contain europium, yttrium and cerium; component sensors yttrium; catalytic converters cerium and lanthanum. Hybrid electric motor and generators contain neodymium, praseodymium, dysprosium, terbium; the negative electrode (cathode) in hybrid nickel metal hydrides (NiMH) rechargeable batteries typically contains a mixture of praseodymium, neodymium, lanthanum, and cerium.
In 2020, the largest use of REE on a worldwide basis was in permanent magnets (29%, largely Nd, Pr and Dy, along with other elements used as fillers such as Ce and Gd), catalysts (21%, mainly Ce and La), polishing (13%), glass (8%), metallurgy (8%), batteries (7%) [11]. Geographic differentiation of uses is wide: catalytic applications, for example, dominated the share in the USA with 75%.
The presence of REE may give unique properties to catalysts formulations, like an exotic spice providing a special flavor. Their main use is long established (but not limited to) in three-way-catalysts for automobiles and zeolites for catalytic cracking in the petroleum industry, both applications with high environmental impact.

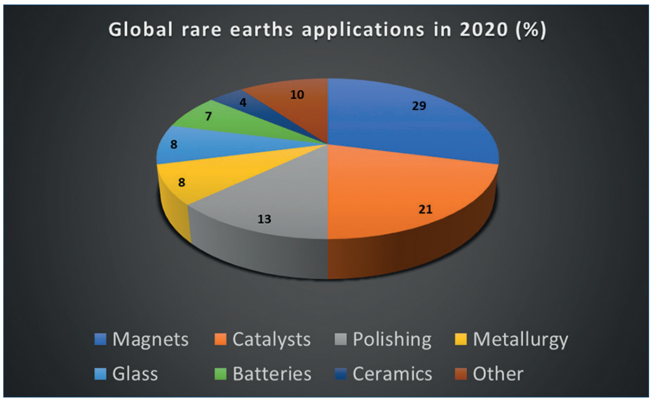

Fig. 1 - Global applications of REE, in % (from Roskill report "Rare Earths - Outlook to 2030" [11])

Catalytic converters, first introduced in the two-way version for cars in California in the mid-1970s, employ rare earth oxides (REO) in their formulation for different purposes, including washcoat stability, platinum metals dispersion, and oxygen storage capacity. The global automotive catalyst market is expected to reach a value of US$ 18 bn in 2024 [12]. The capillarity of automotive diffusion and its aftermarket is self-evident: even in hard-hit 2020, a global production of around 60 million vehicles, conservatively calculated, leads to an estimated 4,000 tons of "deposited" CeO_2 [13] for the specific segment.
Adoption of zeolites in commercial fluid catalytic cracking (FCC) catalysts in the early 1960s was groundbreaking [14] and in 2019, FCC catalysts (with a typical REO content of around 2-4% by weight) cover, by segment, over two-thirds of the global refinery catalysts market estimated at around US$ 4.4 bn [15]. Driving future factors will include regulations for vehicle emissions and rising consumption of petroleum derivatives: products of FCC are used not only in the fuel pool but also in the commercial synthesis of propylene, acrylonitrile, phthalic anhydride, and maleic anhydride. REE addition is known to increase zeolite activity and selectivity with a small loss in octane number, serving as a "bridge" to stabilize aluminum atoms in the zeolite structure and preventing the aluminum atoms from separating from the zeolite lattice when the catalyst is exposed to high-temperature steam in the regenerator. Another role is linked to the skeletal isomerization of olefins favored by Brønsted centers: if these acid centers are moderated with La (or another RE), a catalyst active for double-bond isomerization is obtained.
One major future expansion area for REE will be permanent magnets (Nd, Pr, Sm and Dy), particularly for alternative energies. These will find widespread application in wind turbines, the automotive (electric and hybrid cars) and, most important from a strategic perspective, defense industries (e.g., missile guidance systems). Improving the efficiency of solar energy conversion is another developing area and perovskite type REE mixed oxides are well known as high-temperature superconductors and ferroelectric materials.

Production & Market

Although more than 200 minerals are known to contain REE, the chief sources remain the following three [16]:

a) bastnaesite - (Ce, La) $(CO_3)F$ (Fig. 2);

b) monazite - (Ce, La, Nd, Th)PO_4;

c) xenotime - YPO_4.

Bastnaesite occurs as a primary mineral and over 90% of the economically recoverable REE are found in mineral deposits of this ore. The world's largest mines are Bayan Obo in Inner Mongolia, China, and the Mountain Pass mine in California, USA (Fig. 3). The mineral is a fluoro-carbonate of cerium and yttrium and concentrates may contain 60% (by weight) of REO.

Monazite is a rare-earth phosphate mineral primarily obtained as a by-product of heavy-mineral sands mined for titanium and zirconium minerals. It is mainly found in Australia, Brazil, China, India, and most concentrates contain 55-65% (by weight) of REO.

Xenotime is a phosphate of yttrium: concentrates may be upgraded to 40% (by weight) of REO.

Although generally overlooked by mainstream media, the REE separation process presents severe environmental issues, with tailings harmful to nature and human health. Values reported for the production of 1 ton of REO in China are 60,000 m^3 of waste gases (containing fluoride, sulfur oxides and dust), 200 m^3 of acidified water, and 1.4 tons of radioactive waste [17].

Fig. 2 - Bastnaesite crystal (photograph by Christian Rewitzer, distributed under a CC-BY 2.0 license)

Fig. 3 - 2011 NASA satellite image of Mountain Pass mine (USA) with ponds for wastewater in green areas http://earthobservatory.nasa.gov/IOTD/view.php?id=76880&src=eoa-iotd

For a long time, REE separation has been a complicated operation of inorganic chemistry: the similarity of chemical properties made high-purity separation difficult. Nowadays, liquid-liquid (solvent) extraction is the widely established commercial process and organophosphorus extractants are employed to achieve high efficiency with consecutive steps enabling efficient large volume processing. An aqueous solution containing the metal element to be separated is contacted with an organic phase containing an extractant for the specific element and an organic solvent for diluting the extractant.

Despite advancements, REE separation and purification processes remain challenging: REE are obtained by a series of water-, chemical-, and energy-intensive processes. First, the ores are crushed, milled, and separated through froth flotation into dissolved concentrates. A second processing step occurs via chemical reactions: hundreds of liquid-containing chambers are designed to remove desirable elements using extraction agents (hydrochloric acid) and precipitating agents (ammonium bicarbonate $(NH_4)HCO_3$ or NaOH precipitation), followed by solvent extraction (*e.g.*, with 2-ethylhexyl, 2-ethylhexyl phosphate), and precipitation steps using ammonium bicarbonate and oxalic acid. The precipitated oxalates are filtered and thermally oxidized to form a concentrate of REO [18].

Ion exchange technology is specifically used in order to obtain high purity.

Global REO production data usually refers to REO equivalents by weight as a unit of measurement,

Fig. 4 - Aerial view of Mount Weld mine (Australia) (courtesy of Lynas Corporation Ltd.)

rather than to the chemical nature of the product. Quantitative shares of the single REE are interpolated from specific concentrations in a mined ore. As a result, estimates of overall reserves for a specific element are difficult to calculate. For example, REO content in the bastnaesite of Bayan Obo ore is around 50% (by weight) of CeO_2, 23% (by weight) of La_2O_3 and 18% (by weight) of Nd_2O_3. However, the mineral composition varies according to location. Trade is based on the oxides content expressed in terms of a specific REO or as total REO (TREO).

China is the richest country in REE resources, abundant not only in minerals of LRE (cerium group) but also of HRE (yttrium group). Enormous economic and scientific efforts historically were and are still being exerted in order to support the REE industry and its products. It is today the only country with a complete rare earths industry supply chain. Due to complex economic, regulatory, and environmental factors, between 2010 and 2012, strict export quotas resulted in a temporary global market scarcity and price spikes. In the meantime, trade re-established an apparently calmer state. For 2021, China released its full-year REO quota of 168,000 tons, a 20% year-on-year increase for the so-called “big six” Chinese state-owned companies surviving a radical internal market consolidation. Mining had to be strategically resumed in the USA following years of activity being kept on hold and in 2019 bastnaesite was again the primary product at Mountain Pass in California: a “geo-logical” era had passed since the same mine supplied the world with nearly 100% of the mineral in 1981.

Criticality forced the productive landscape to change significantly within the last few years. In 2019 [19], global mine production was estimated to raise to 220,000 tons of REO equivalents, a 16% increase compared to 2018. China dominated the supply with 132,000 tons of REO equivalents and a productive share of 60% (it was 86% in 2014). In the United States, domestic production of mineral concentrates jumped to 28,000 tons, a 55% rise compared to the previous year. Several other countries, such as Myanmar (25,000 tons) and Australia (20,000 tons, Fig. 4), are joining the race. Estimates for 2020 indicate that global mine production further rose to 240,000 tons of REO equivalents, a 9% increase compared to 2019. China again dominated with 140,000 tons of REO equivalents and a productive share of 58% and the United States production of mineral concentrates rose to 38,000 tons (with a productive share of 16%).

World reserves of REO are ample even considering the current staggering use growth rate (Fig. 5). In 2020, they were estimated to be 120 million tons, of which around 36% in China, 18% in Brazil and Vietnam each, as well as 10% in Russia. These figures are the result of prospective projects launched in recent years and ongoing exploration might detect further deposits worldwide.

Due to strong demand, the value of REE has grown to unprecedented peaks: the market will reach US$ 14.4 bn by 2025 and it was valued at approximately US$ 8.1 bn in 2018 [20]. By product, the cerium segment is expected to dominate in the upcoming years; by application, catalysts and magnets are

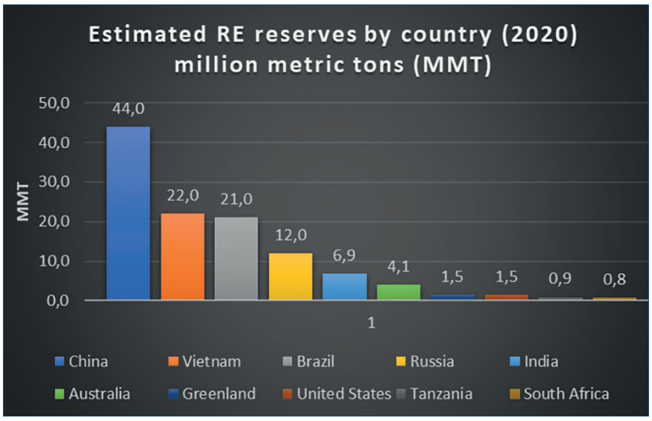

Fig. 5 - Reserves of RE in million metric tons of rare-earth-oxide equivalent (from U.S. Geological Survey, Mineral Commodity Summaries, January 2021)

going to prevail; by region, Asia Pacific will continue its predominance.
Within this framework, the European rare earths scenario is projected to play a more significant role as several initiatives have been launched.
The European Rare Earths Competency Network (ERECON), started in 2013, is a network of excellence comprising REE experts from both industry and academia. Working groups examined challenges and solutions for mining rare earths in Europe, recycling, substituting, and fostering new business models [21].
The European Union funded EURARE project, completed in 2017, focused on establishing the basis for a European rare earths industry by finding ways to supply both raw materials and REE products for industrial use. During the project run, deposits were investigated and identified resources (in Greenland, Sweden, Norway, Denmark, and Greece) were processed with testing of mineral concentrates from laboratory to pilot scale using conventional and innovative metallurgical processes [22].
The EU's Horizon 2020 research and innovation program assigned funding to the industry-based consortium Sustainable Recovery, Reprocessing and Reuse of Rare Earth Magnets (SUSMAGPRO).
More recently, a European call for action was launched in 2021 by the Rare Earth Magnets and Motors Cluster of the European Raw Materials Alliance (ERMA) in order to assess the entire value chain. This involves creating a circular economy around REE by advancing recycling and substitution, as well as all the activities ranging from product development to magnet making and motor design. As usual when the automotive industry takes a certain road, other stakeholders are willing to follow.

Recovery & Sustainability

Less than 1% of REE were recycled in 2011 and, despite increased importance, this rate has not changed significantly in a decade: implementation of a recycling program requiring the collection of radically different items is troublesome and, even in the case of catalysts, the development of a technically feasible and economically acceptable solution for the recycling of REE is still to be accomplished. It is worth noting, though, that the parallel recovery of platinum group metals from spent automotive catalysts is an established technology, such as the process for base metals in other applications.
Reasons lying behind the current state-of-affairs for REE recycling vary [23].
A complication is usually the presence of contaminants in the feedstock. For example, common permanent magnets contain over 70% (by weight) of iron, which in many REE recovery processes cannot be recycled into a salable product. Also, technical issues might be an obstacle, *e.g.* separating neodymium magnets from their containers.
Most suggested recycling methods require large amounts of energy and chemicals, in particular hazardous chemicals such as bases and acids ($NaOH$ and HF), which often cannot be recovered from the process and end up as chemical waste or as pollutants in effluent water [24].
From an economic point of view, regulatory incentives could play a decisive role, or a sufficiently high and stable price level. Scientific breakthroughs in recycling methods need to be promoted: the notion that opening mines is the best way to acquire REE elements is narrow-sighted, especially when considering that new sites would be located in uncontaminated (*e.g.*, Greenland) or populated areas and that the environmental price to pay is high.
Furthermore, price volatility for critical materials is generally low when recycling rates are high, suggesting that recycling is a successful strategy to mitigate price fluctuations linked to geopolitical changes [25].
Contemporary technology has advanced to the extent that recycling can support mining as primary source and different forms thereof can be distinguished.
The first one involves the direct recycling of REE metal scrap generated during the production of REE-based products. At the same time, post-consumer recycling, and landfill mining of REE in historic urban solid waste could deliver additional feedstock.
Additionally, the recycling concept of end-of-life REE products would tackle the so-called balance problem, *i.e.* the discrepancy between the demand for the different REE and the composition available

in mineral deposits. In some cases, wastes containing REE possess simpler chemical compositions than the natural ores, thus also simplifying the separation process [26].
Last but not least, the absence of radioactive elements, nearly always occurring in REE mining, represents a meaningful advantage for recycling.
The most interesting waste streams for REE recycling appear to be catalysts, lamp phosphors, NdFeB permanent magnets, and NiMH batteries [27].
The REE recycling industry is evolving with many of the activities still at development scale: primary constraints seem to be solvable by a combined effort of all stakeholders in the product chain, since only recovery will be able to play a key role to satisfy demand in a sustainable way [28, 29].

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Terre rare: prospettive recenti

Gli elementi delle terre rare (REE), un gruppo di metalli con particolari proprietà fisico-chimiche, fosforescenti e magnetiche, sono utilizzati in diverse tecnologie strategiche. Negli ultimi anni la loro importanza ha stimolato ampia letteratura ed il presente articolo mira a un sintetico aggiornamento su principali usi attuali e futuri, produzione, risorse e prospettive di riciclo.