12. Rare Earth Elements

The rare earth elements (REEs) are a group of 17 chemical elements comprising the lanthanoids[*] plus scandium and yttrium. This group of elements has become almost synonymous with critical raw materials on account of its high concentration of supply and tremendous variety of uses, coupled to a suggestive name arising from the scarcity of the ores originally used to obtain rare earth elements from.

Though the rare earth elements are not rare in the earth's crust - cerium, the most abundant of the rare earths, is more abundant than copper and lead - they are difficult to recover in a pure form because of their chemical similarity. Moreover, this chemical similarity also means that rare earth deposits contain a mixture of rare earth elements that have to be mined and processed together as co-products. Sometimes, the rare earth ores themselves are a by-product, as in the case of the Bayan-Obo mine—the largest single source of rare earths.[1] Needless to say, the composition of the ores available for mining does not necessarily match current market needs.

The rare earth elements are prominently associated with green energy technologies such as wind power (magnets) and electric vehicles (batteries).[2–4] However, they are also renowned for having extremely low recycling rates and with environmental pollution; the latter on account of the extensive processing required to obtain them in the required purity and the association of (some of) the ores with radioactive uranium and thorium.[5]

Currently, the primary production of rare earths is clearly dominated by Chinese producers, though this may change to an extent through the (re-)opening of mines outside of China (e.g. in the USA and Australia) and the intention of some mining companies of reclaiming REE from their tailings. Chinese export restrictions on rare earths—which lead to a price peak of rare earth metals and their oxides in 2011 (see Figure 2)—are currently being contested in a World Trade Organisation (WTO) dispute filed by the USA[6], EU[7] and Japan[7].

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[*] Lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. These are commonly divided into "light" (lanthanum through europium) and "heavy" rare earths, though sometimes an intermediate term ("middle") is introduced to denote the elements between europium and dysprosium.[1]

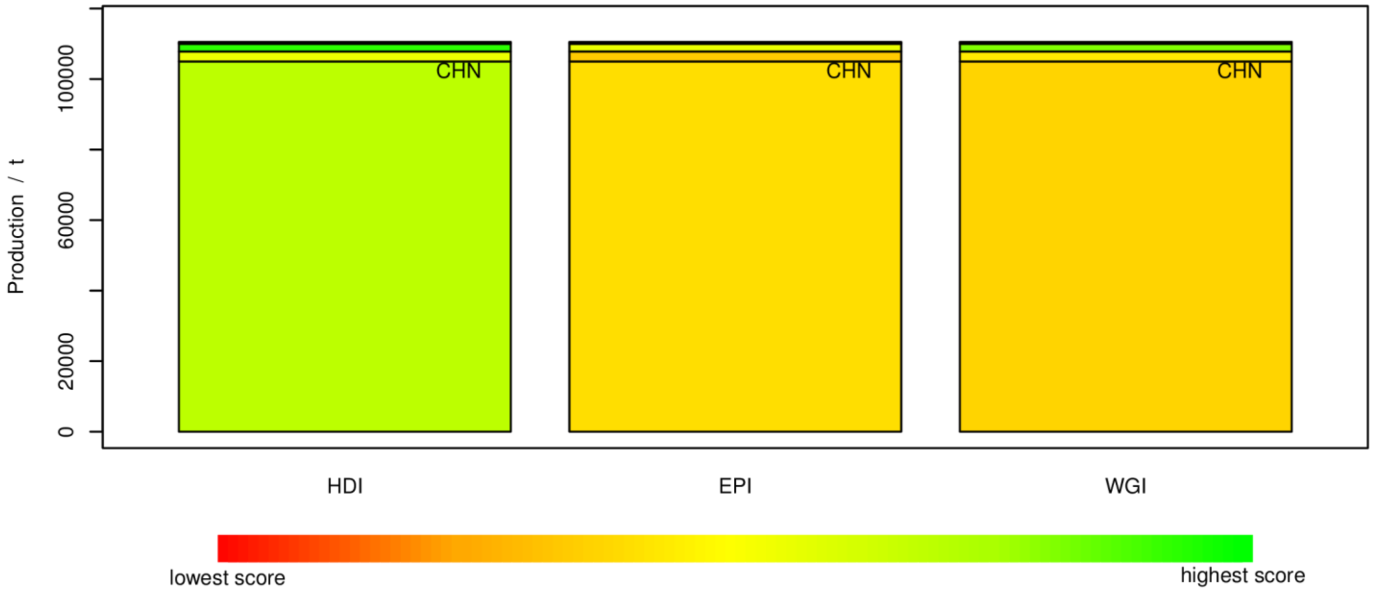

Figure 1: Distribution of rare earth production [8] and corresponding scores of the producing countries in the Human Development Index (HDI)[9], Environmental Performance Index (EPI)[10], and World Governance Indicators (WGI)[11]. Both the EPI and WGI are used to assess supply risks with the EU methodology for determining critical raw materials.[12] CHN = China.

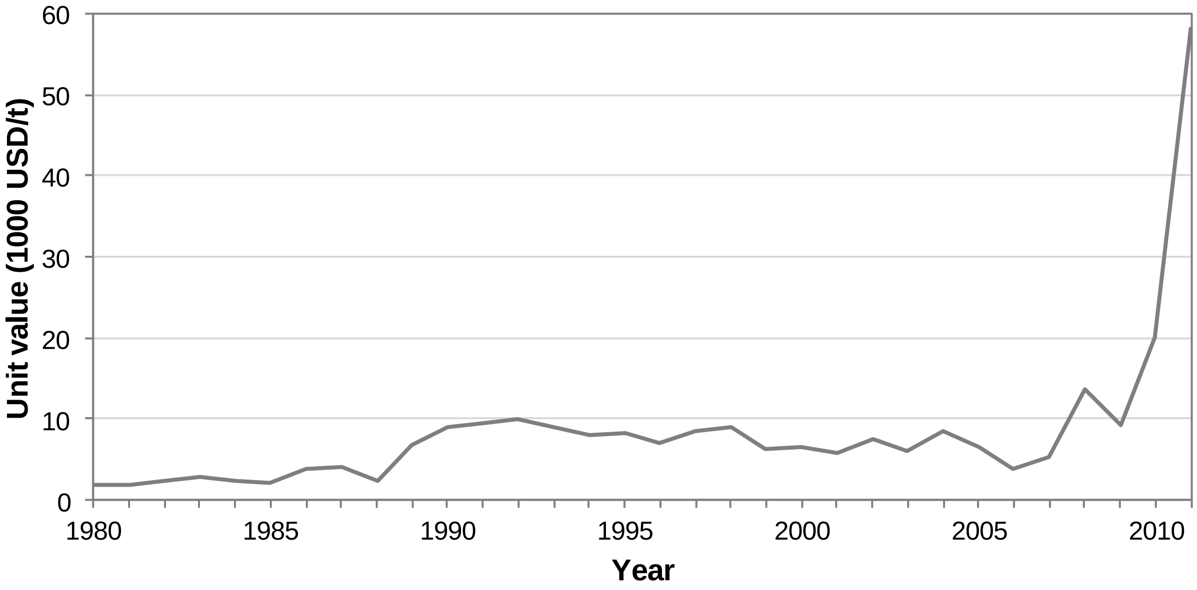

Figure 2: Rare earth oxides (REO) price development during 1980 – 2011. The unit value is the value in dollars of 1 metric ton (t) of REO apparent consumption (estimated).[13] Prices have gone back substantially since their peak in 2011.

Uses and substitutability

Magnets

Permanent magnets have fascinated people for millennia and account for close to 30% of rare earth consumption. Today they play a key role in many emerging applications, most importantly in the production of energy devices such as generators (wind turbines) and motors (cars), in addition to the established markets in magnetic resonance imaging (MRIs) technology, hard disc drives, speakers etc.

In terms of value, two-thirds of the permanent magnet market is dominated by those containing rare earths. Neodymium-iron-boron (NdFeB) magnets have energy products[†] close to the theoretical maximum.[15,16] The outstanding magnetic properties of rare earth based permanent magnets are due to the combination of the high magnetic moments of the transition metals (iron, cobalt) and the exchange coupling between these magnetic moments with those of the rare earths. This coupling results in a high magnetocrystalline anisotropy and thus the potential to achieve a coercivity that is comparable to the magnetisation. No material with superior qualities to NdFeB has been discovered yet. Only an incremental improvement in the record energy product of permanent magnets has been seen during the last 20 years. It is worth noting that neodymium-iron-boron magnets also contain small amounts of dysprosium and terbium, which are added in order to improve confer the ability to remain magnetized when confronted with other magnetic fields or high temperatures (at the cost of a reduced magnetisation).

There is considerable economic potential for the substitution of rare earths permanent magnets, as can be highlighted by the example of off-shore wind farms: Many major suppliers of wind turbines have opted for employing permanent magnet synchronous machines (PMSM) due to advantages in terms of dimension, weight and maintenance. This type of windmill contains an average of 400 to 600 kg of rare earths in up to two tons of permanent magnets (365 kg/MW), implying that price fluctuations of Nd and Dy have significant impacts on production costs and profit margins. For example, the Chinese manufacturer, Goldwind, reported that the price hikes in 2011 lowered its gross profit margin from 20% to 7%. Goldwind has since then opted for fabricating a family of windmills without permanent magnet (rare earth) technology for lower-cost markets and other manufacturers are developing novel wind generators with new designs, for example superconducting materials.

In 2010, the production of permanent magnets consumed 26000 t of rare earth elements (neodymium/praseodymium, dysprosium and terbium) while for 2015 the estimated demand is 48000 t.[17] This expected increase in demand explains the need to develop substitute materials, which can be used in some target applications, albeit not necessarily in those which require the strongest magnet material possible. In fact, the market potential for magnetic materials with properties between rare earth based permanent magnets and the much weaker ferrites is considered extremely positive.[16]

One main approach is the minimization (as opposed to substitution) of rare earth use in permanent magnets. There are promising ways to radically reduce the amount of the costly heavy REEs in NdFeB magnets by optimizing the magnets microstructure, for example by exploiting grain boundary diffusion processes.[18,19]

The other main approach focuses on the identification of completely new kinds of rare-earth-free magnetic materials. One such strategy under research in order to produce hexaferrite powders is mechano-activated

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[†] The energy product is a measure of the magnetic energy stored in a permanent magnet. A small magnet with a large energy product and a large magnet with a small energy product may serve the same use [14].

self-propagating high-temperature synthesis.[20] Fabricating soft and hard magnets by combustion synthesis is an easy-to-handle process, which uses inexpensive oxides and achieves acceptable magnetic properties, which can be further improved by spark plasma sintering. These techniques can then be further improved by combining combustion synthesis and spark plasma sintering (SPS) as method of fabrication of dense β-SiAlON, iron nitride and iron-based composites. This process is highly versatile and scalable with respect to chemistry, size and morphology. It is furthermore possible to influence the characteristics of the magnetic field during the combustion process by aligning the particles. Fibre orientation and alignment are considered two essential features of novel materials to be derived from hexaferrite fibres. Nanocomposite materials, which could potentially be the basis for new substitute magnetic materials, include mixtures of hard magnetic barium ferrite and soft magnetic nickel zinc ferrite (Patent Number KR20080055485 (A), Korea 2008-06-19). Further progress in this research field is expected to derive from advanced analytical tools, which improve the researchers' understanding of the processes taking place on the nano-scale.

Other materials under research to produce substitute magnetic materials are cerium (Ames Laboratory, US), manganese (Pacific Northwest National Laboratory), as well as cobalt-based and samarium-based compounds as substitute for dysprosium (Chiba Institute of Technology, Japan). From this list of potential substitutes, notice that cerium and samarium are themselves rare earth elements and that cobalt is also considered a critical raw material.

Metallugy: Al and Mg alloys[21]

REEs, primarily scandium, are used in aluminium alloys to control grain size. Scandium forms an Al_3Sc phase which has a threefold influence on the alloy: The Al_3Sc phase particles can serve as a grain refiner in the Al melt, a dispersoid for controlling the grain structure of the alloy and a strengthening precipitate. Although there has been a great amount of research conducted on the topic, these alloys have not been commercialized in large scale applications. Compounds that can control the grain size like titanium boride are widely available.

Rare earths are also used in some commercial magnesium alloys—these alloys have the letter "E" in their designation. Up to 3% of cerium and neodymium is added to sand cast magnesium to provide a low melting eutectic phase which increases the castability. In other alloys, REE are used to improve age hardening. These alloys with high REE are only used for advanced applications like aerospace. The REE containing alloys can be substituted with other Mg-alloys at the cost of some performance.[22]

Polishing

Nano/micron-sized cerium-oxide powder is a hard material which can be used for polishing. It has a hardness between that of garnet (silicates) and Green Rouge (chromium oxide).

Cerium-oxide has been used in polishing since the 1930s, and until the late 1990s, growth was driven by demand from the production of CRT display faceplates. Demand has grown since the 1990s with the rapid growth of electronic products containing glass or glass-like components, many of which require polishing to a high standard. In 2010, demand for rare earths in polishing applications was estimated to be around 15,750 t, of which, around 75% were consumed in traditional glass applications (including display panels, flat glass and optical glass) and around 25% in electrical components. Following high prices since 2010, there has been a trend towards reducing the amount of cerium-oxide in polishing slurries accompanied by shorter polishing times, smaller amounts of slurry and slurry re-use where possible. Different types of medium hard alumina can also be used for the same purpose.[23]

Pigments[24]

Because of their unique electronic configuration, the REEs show unusual magnetic and optical properties. Many trivalent lanthanide ions are strikingly coloured, both in solid state and in aqueous solutions. The colour developed depends on the number of unpaired electrons. The pigments derived from rare earths show their characteristic intense colour due to charge transfer interactions between a donor and an acceptor, with the metal ion generally playing the role of an acceptor. Selection of REEs and appropriate donor atoms for achieving the best spectral bandwidth and intensity forms the leading edge of knowledge in this area. Dopants based on rare earths in mixed oxide systems offer an opportunity to tune in colour response through manipulation of energy gaps and delocalization phenomena in conduction and valence bands. However, the cost of separation of the rare earth metal ions makes these pigments economically unattractive, restricting them to niche applications, limiting the economic incentive for substitution.

Metallugy: Iron and Steel[25,26]

Rare Earth Elements are used as alloying elements in cast-iron and steels.

In cast iron, cerium and lanthanum are used to tranform the morphology of graphite from flake to nodule (nodularisers). Since REEs are strong sulfide formers, they form stable compounds in the melt. These compounds nucleate graphite nodules which give the cast iron good mechanical properties. The use of REEs in foundry alloys has been well established but alternative nodularisers based on magnesium (also a critical raw material) are available.

Cerium is required in some special stainless steel grades. Cerium combined with silicon improves the oxidation resistance, erosion corrosion resistance and oxide spallation resistance.

Glass

Traditionally, cerium oxide additives used in the production of CRT faceplates made up the majority of demand in this sector. As CRTs have given way to FPDs, consumption for this application has been in decline because the glass in FPDs is thinner. Cerium oxide is also used to prevent solarisation in sunglasses, bottles (to protect the contents) and in the growing market of luxury vehicles (small market).[23]

Lanthanum has been used to increase the refractive index of glass (for use in lenses) for over 30 years. This use has seen strong growth through security cameras, digital cameras and mobile phones with small fisheye lenses, many of which are 50% La_2O_3.[23]

Catalysts

The dominant usage of rare earths for catalysts is lanthanum, cerium, praseodymium and neodymium for fluid catalytic cracking in the petroleum industry. During the cracking process, the catalyst becomes contaminated with carbon. Although the contaminated catalyst is regenerated and reused, ultimately spent rare earth oxide catalysts become unusable and are disposed of as a waste product.[27] Rising rare earth prices have prompted companies to market services to optimise the amount of rare earth content in catalysts for a particular process[28] or develop rare earth-free alternatives.

The automotive industry generates the other major use for rare earth elements as catalysts, where rare earth oxides (cerium, lanthanum, praseodymium and neodymium) are part of the catalytic converters. Recycling processes for catalytic converters focus on recovering the valuable platinum and palladium and the rare earths are generally not recovered. Since cerium is the primary rare earth element used in catalytic converters (90% by weight[29]) and cerium is the most abundant of the rare earth elements, there is little incentive to research substitutes in this particular application.

Batteries[30,31]

Nickel Metal Hydride (NiMH) batteries contain a mixture of REEs that are incorporated into the negative electrode. The role of the electrode is to reversibly form a mixture of metal hydride compounds. The "metal" M in the negative electrode of a NiMH cell is actually an intermetallic compound. The most common is AB_5, where A is a rare earth mixture of lanthanum, cerium, neodymium, praseodymium and B is nickel, cobalt, manganese, and/or aluminium. Very few cells use higher-capacity negative electrode materials based on AB_2 compounds - where A is titanium and/or vanadium and B is zirconium or nickel, modified with chromium, cobalt, iron, and/or manganese - due to the reduced life performances. Research is currently being conducted into developing alternative Mg-Ni-Ti-Al-based electrode materials. Though rare earths are not satisfactorily substitutable in this type of battery, NiMH batteries face strong competition from lithium ion batteries.

Phosphors

Lanthanum, cerium, europium, yttrium, erbium, terbium are rare earth oxides (REOs) used for lighting phosphors and are vital component in energy efficient fluorescent lamps.[32‡] Lighting accounts for approximately 20% of electricity use in European buildings, second only to space heating. Modern technologies provide opportunities to significantly reduce energy demand from lighting: Fluorescent lighting, light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs) and halogen incandescent require much less energy than the traditional incandescent bulbs, now limited or prohibited in many European countries. This transition away from incandescent bulbs has strengthened demand for phosphors and prompted companies like Osram and Philips to search both for improvements and alternatives, in particular the reduction of the required amounts.[33]

At this moment, there are no clear substitutes for the use in compact fluorescent light (CFL) bulbs. Costs for LED bulbs are much higher than those of CFL bulbs, and LEDs also depend on rare earth based phosphors. Organic LEDs (OLEDs) are a plausible rare earth free alternative, but their lifetime is too short in relation to their costs—a problem that is not expected to be solved in the near future. Finally, rare earth free phosphors for LEDs currently under development include silicon-based nanoparticles (1-5 nm), BCNO phosphors[§] and GaZnON (gallium is also a CRM) are potential substitutes.[34–38] However, there are still issues to be solved concerning costs, colour and thermal stability.

Ceramics

Rare earths are used in two major types of advanced ceramic applications: structural/wear-resistant ceramics (including yttrium-stabilised zirconia, the largest use for yttrium after phosphors) and electronic components (including dielectric ceramics). Ceramics are a small but high value market for rare earths.[23] REE cannot be substituted in most of these materials.

Summary

A summary of the uses of different rare earths in the fields of use described above is given in Table 1. At the moment, substitution of REE in phosphors, glass, catalysts and ceramics is not possible. Substitution in magnets, batteries, polishing, pigments and as alloying elements in iron and steel can only be done through

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[‡] Fluorescent lamps contain halo and triphosphors. Triphosphors use rare earth oxides in their phosphor mix.[32]

[§] BCNO = boron, carbon, nitrogen, oxygen.

the loss of performance. The use of REE as alloying elements in Al and Mg can be avoided through substitution of these alloys with other structural materials at the cost of a minor decrease of performance.

Table 1: Summary of end uses of rare earth elements (both as metals and oxides). The uses with the largest share(s) for each element are marked in bold. [23,39,40] When examined as a group, the end uses of rare earths tend to be dominated by the end uses of the four most abundant elements (lanthanum, cerium, praseodymium and neodymium; all four are “light” rare earth elements).

Rare earth element	End use
Lanthanum (more abundant)	**Batteries**, metallurgy, **catalysts** (catalytic converters, petroleum refining), polishing powders, glass additives, phosphors, ceramics, hybrid engines
Cerium (more abundant)	Batteries, metallurgy, **catalysts** (catalytic converters, petroleum refining), **polishing powders**, **glass additives**, phosphors, ceramics, hybrid engines
Praseodymium (more abundant)	**Magnets**, batteries, metallurgy, catalysts (catalytic converters), polishing powders, glass additives, ceramics
Neodymium (more abundant)	**Magnets**, batteries, metallurgy, catalysts (catalytic converters), glass additives, ceramics
Dysprosium	**Magnets,** laser dopant, neutron radiography, semiconductors
Gadolinium	Magnets, diagnostics, phosphors
Europium	**Phosphors**, red color for TV and computer screens, medical X-ray units
Samarium	Batteries, magnets
Scandium	Aerospace components
Terbium	**Phosphors**, permanent magnets
	Magnets, hybrid engines, ceramic capacitors
Erbium	Phosphors
Holmium	Glass coloring, lasers
Thulium	Medical X-ray units
Lutetium	Catalysts in petroleum refining
Ytterbium	Lasers, steel alloys
Yttrium	Red color, **phosphors**, **ceramics**, metal alloys, glass additives

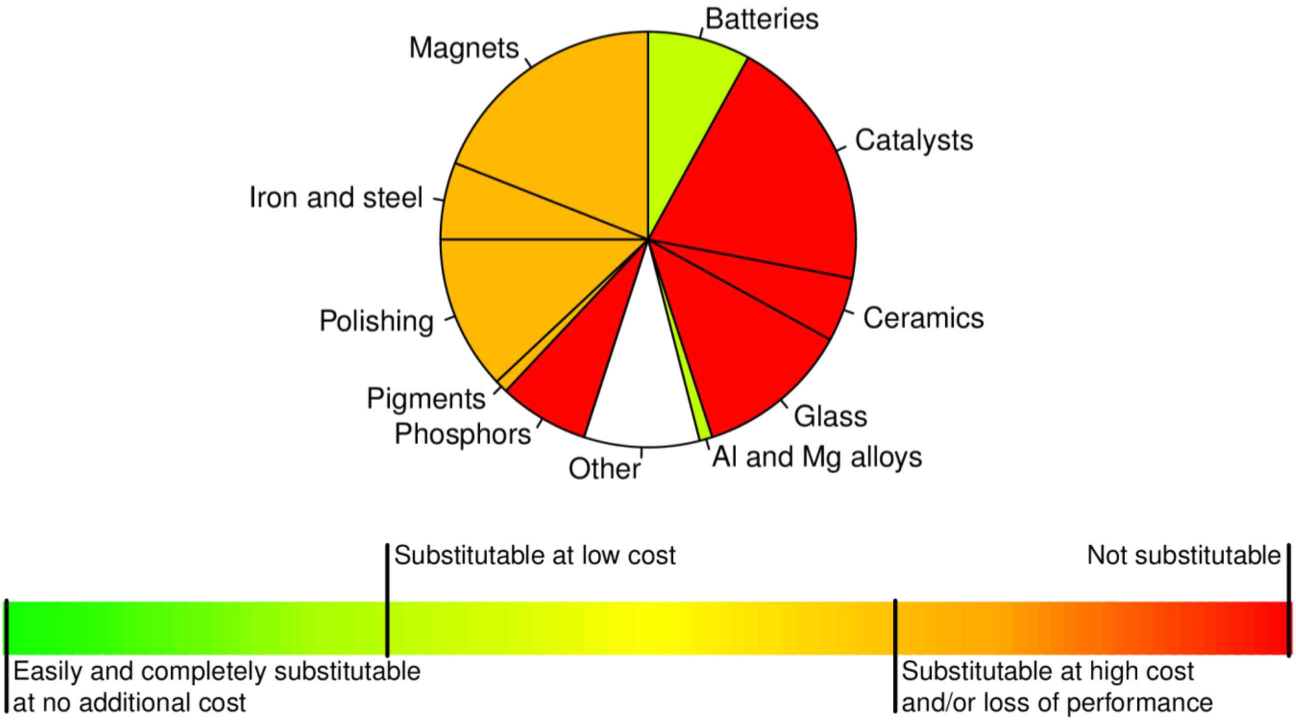

Figure 3: Distribution of end-uses and corresponding substitutability assessment for the rare earth elements (taken as a group). The manner and scaling of the assessment is compatible with the work of the Ad-hoc Working Group on Defining Critical Raw Materials (2010).

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