Rare earths

Several rare earths are used as phosphors in plasma screens, field emission screens and cathode ray tubes

The 15 rare earth metals represent something of an anomaly in the periodic table, because these chemically similar elements have to be theoretically squeezed into a single space. They are shown as a row under the main group, from element 57 (lanthanum) to element 71 (lutetium); they are also called the lanthanides.

In commercial practice, the two metals immediately above lanthanum in the table – scandium (no. 21) and yttrium (no. 39) – are also included in the rare earth group.

The term rare earth – coined in the late 18th century – is also an anomaly, since the metals' abundance in the Earth's crust ranges from 60 ppm for cerium down to about 0.5 ppm for thulium and lutetium. This means that they are all more plentiful than silver, and the four most abundant (yttrium, lanthanum, cerium and neodymium) are more common than lead. The term rare is more a reflection of the past difficulties in separating and identifying these metals from each other.

The one exception in this group is element 61, promethium, which is radioactive and is only found in vanishingly small amounts in nature. It can be isolated from nuclear fission by-products, and has found some uses.

The main sources of the rare earths (RE) are the minerals bastnäsite (RE fluorocarbonate), monazite, loparite and lateritic ion-adsorption clays. The natural concentrations of the ores are such that there are few commercially viable deposits, however. Furthermore, monazite mining and processing has declined markedly because its thorium (and more importantly, by-product radium) content makes it radioactive.

Nevertheless, there is unlikely to be a shortage of rare earths looming. Known reserves are put at 88m tonnes of rare earth oxide (REO) by the US Geological Survey (USGS), while global mine production was 105,000 tonnes (REO content) last year. Undiscovered resources are thought to be very large relative to expected demand, says the USGS.

China's rare earth mining started in the mid-1980s (when global production stood at 40,000 tpy REO) and it now dominates supply with over 93% of world production in 2005 (*see table*). Its main resources are the iron-niobium-RE deposits in Inner Mongolia and the lateritic ion-adsorption ores in southern China. The latter are valuable because of their relatively higher proportions of heavier rare earth elements.

The rare earths

Element	Atomic No	Applications, markets
Scandium (Sc)	21	Cathode ray tubes.
Yttrium (Y)	39	Capacitors, phosphors, microwave ferrites, glass, O_2 sensors, radar, lasers, superconductors.
Lanthanum (La)	57	Glass, electronic ceramics, fuel cells, automotive catalysts, phosphors, pigments, batteries.
Cerium (Ce)	58	Polishing powders, electronic ceramics, phosphors, glass, medicine, catalysts, pigments, UV filters, mischmetal steel refiner, flints.
Praseodymium (Pr)	59	Electronic ceramics, glass, pigments.
Neodymium (Nd)	60	Permanent magnets, electronic components, polymer catalysts, IR filters, glass pigments, lasers.
Promethium (Pm)*	61	β-source for gauges, luminescent paints, miniature nuclear batteries.
Samarium (Sm)	62	Permanent magnets, microwave filters, nuclear industry.
Europium (Eu)	63	Phosphors.
Gadolinium (Gd)	64	Medical imaging, neutron absorption, optical & magnetic recording, electronic ceramics, glass, lasers, crystal scintillators.
Terbium (Tb)	65	Phosphors.
Dysprosium (Dy)	66	Phosphors, ceramics, nuclear industry.
Holmium (Ho)	67	Ceramics, nuclear industry, lasers.
Erbium (Er)	68	Ceramics, nuclear industry, glass colouring, medicine, optical fibres, lasers.
Thulium (Tm)	69	Medical imaging, cathode ray tubes.
Ytterbium (Yb)	70	Metallurgical and chemical research.
Lutetium (Lu)	71	Single crystal scintillators.

*Sources: Rhodia Electronics & Catalysis, Metall Rare Earth, *various.*

PRODUCTION

The relative proportions of RE metals can vary markedly between different ores, and the ratios of metals do not reflect commercial demand. This means that high volumes of the more common metals have to be produced in order to get adequate quantities of rarer, but important, elements.

Run-of-mine ore is generally treated by flotation and separation techniques to produce a concentrate containing 60-70% of mixed rare earth oxides. This can be converted to other intermediates such as mixed RE chlorides, which is the usual starting point for the most common separation technique, solvent extraction. The similarity of the metals means that separation is initially into subgroups, which are then separated into the individual elements by further solvent extraction.

Individual rare earths are normally precipitated as an oxalate which is calcined to the oxide. Very high purity oxides can be made by ion exchange techniques.

While all rare earths have uses as compounds, only some need to be in the metallic form for commercial use (for example, in magnets). The metals can be made from the fluorides by calciothermic or electrolytic reduction, or by metallothermic reduction of the oxide in some cases.

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APPLICATIONS

Rare earths have been steadily growing in importance because of their value in many cutting-edge technologies, including automotive catalytic converters, fibre optics, lasers, oxygen sensors, lighting and imaging phosphors, and superconductors.

Cerium, as the most common and lowest-cost member of the group, has some well-established uses that are quite distinct from the others. Cerium oxide is used for polishing glass, its efficacy depending on both its physical and chemical properties. Virtually all high-quality polished glass is finished by a cerium oxide treatment, including mirrors and precision lenses.

Cerium is the main component of mischmetal, which is a "natural" alloy of the commonest rare earth metals. It may typically contain about 50% cerium, 30% lanthanum, 15% neodymium and 5% praseodymium. Mischmetal is used in steel refining to remove free oxygen and sulphur (as stable oxysulphides) and also impurities such as lead and antimony.

Mischmetal, alloyed with metals such as iron and magnesium, is used for lighter flints and other sparking alloys.

Catalysis. Cerium oxide is used to enhance the performance of automotive emission catalysts, for converting carbon monoxide, unburnt hydrocarbons and nitrogen oxides to carbon dioxide, water and nitrogen. It is said to stabilise the alumina support, enhance certain catalytic reactions and promote the NOx reduction activity of rhodium. It also improves the "cold start" performance of catalysts.

Rare earths are also used to help catalyse various hydrocarbon reactions in the petroleum and plastics industries. Cerium and lanthanum are used in fluid cracking catalysts (FCC) containing zeolites for converting crude oils to petroleum. Rare earths are more resistant to catalyst poisons such as nickel, vanadium and sulphur. Desulphurisation catalysts containing cerium are used to scavenge sulphur from crude oils.

Cerium is also used in catalytic systems for converting methylbenzene to styrene, and rare earths are used to enhance other industrial oxidation, dehydrogenation, hydrogenation and polymerisation catalysts.

Phosphors. The most readily visible rare earth market is in luminescent or phosphor materials, where they are often in both the main matrix and the activating dopant. The electronic structure of rare earth atoms makes them particularly efficient at converting high-energy excitation – gamma-rays, X-rays, cathode rays (electrons) and UV, for example – into visible light of fairly narrow wavebands.

In television cathode ray tubes, yttrium oxysulphide activated with trivalent europium ($Y_2O_2S:Eu^{3+}$) is the standard red phosphor, having replaced ZnS:Ag. Other CRT phosphors include $Gd_2O_2S:Tb^{3+}$ and $Y_3Al_5O_{12}:Ce^{3+}$.

The new generation of compact "triband" fluorescent lamps, which are replacing less-efficient incandescent lamps (*see MBM April*), use three phosphors to convert UV into red, green and blue emissions, resulting in overall white light. Divalent Eu dopant is used for the blue emitter, Ce and Tb for the green emitter and trivalent Eu for the red emitter.

Similarly, flat plasma and field emission screens use rare earth-based phosphors, as do "white-light" LEDs.

World mine production and reserves*

Country	Mine production 2004	Mine production 2005	Reserves
USA	0	0	13,000,000
Australia	0	0	5,000,000
China	95,000	98,000	27,000,000
CIS	2,000	2,000	19,000,000
India	2,700	2,700	1,100,000
Malaysia	250	250	30,000
Thailand	2,200	2,200	n/a
Others	0	0	22,000,000
World total	**102,000**	**105,000**	**88,000,000**

*tonnes of rare earth oxide (REO) content. Figures may be rounded. Source: US Geological Survey

Rare earth markets in the USA*

Automotive catalytic converters	32%
Metallurgical additives and alloys	16%
Phosphors	15%
Glass polishing and ceramics	12%
Permanent magnets	4%
Petroleum refining catalysts	4%
Other	17%

*2004 estimate, by quantity. Total value of RE materials: $1bn. Source: USGS

In medical radiography, rare earth-based phosphors are used to convert X-rays to blue or green light, to which photographic emulsions are far more sensitive.

Yttrium aluminium garnet ($Y_3Al_5O_{12}$ or YAG) is a synthetic crystal which is widely used as the active laser medium in solid-state lasers. It is usually doped to obtain a specific laser wavelength, most commonly with neodymium.

Magnets. Rare earths have revolutionised the permanent magnet sector. Powerful new magnets based on samarium-cobalt were developed from the mid-1960s, the two principal alloys being $SmCo_5$ and Sm_2Co_{17}. Manufacturers have since developed their own refinements, with other rare earths partially substituting samarium, for example. Total production was about 2,400 tonnes last year.

The most powerful hard magnet yet found was introduced in 1984, based on neodymium-iron-boron, $Nd_2Fe_{14}B$. It has a magnetic energy product up to twice that of samarium cobalt and is very resistant to demagnetisation. "Neo" magnets have shown continuing impressive growth and in 2005 comprised the highest market value of any hard magnet material at an estimated $3.7bn, corresponding to over 40,000 tonnes shipped.

The ability of neo magnets to generate a strong field from a small volume has made them an integral part of ongoing electronics miniaturisation.

Other uses. Rechargeable lanthanum-nickel-hydride batteries, usually known as nickel-metal-hydride, are gradually replacing nickel-cadmium because of their superior performance and environmental advantages. Red/orange/brown pigments for plastics and paints based on cerium amd lanthanum have been developed as an alternative to heavy-metal-based colours. Rare earths are added to ceramics to improve their properties. Fibre optic cables transmit signals over long distances because they contain periodically-spaced lengths of erbium-doped fibre which acts as a laser amplifier.

There are various other niche uses for rare earth metals, and with increasing Chinese production tending to hold prices steady, it seems likely that further markets will be developed in future. The generally low toxicity of the group is another factor encouraging their use. ■