LANTHANIDES

1. Introduction

The "lanthanides" is the name given collectively to the 15 elements ranging from atomic number 57 (lanthanum), to 71 (lutetium), also called the "4*f* elements.", atomic number 71. The rare earths constitute the lanthanides, yttrium, (atomic number 39) and scandium, (atomic number 21). The most abundant member of the rare earths is cerium, Ce, atomic number 58). (see CERIUM AND CERIUM COMPOUNDS).

A history of the rare earths can be found in the article by Morral (1). The first rare earth was discovered during the investigation of the mineral now called *gadolinite*. An impure oxide was isolated by Gadolin in 1796 and called yttria. In 1803, another oxide was reported and named ceria. *ceria*. Sir Humphrey Davey demonstrated in 1808 that earths as a class were not elements, but compounds composed of oxygen and a metallic element. Between 1839 and 1901, the rare earths were extensively studied and all were isolated through extensive fractionation processes. Industrial use started in the beginning of the twentieth century, mainly from the works of Auer von Welsbach on incandescent mantles and lighter flints (see section on applications).

2. Occurrence

The lanthanides distributed widely in low concentrations throughout the earth's crust (2), are found as mixtures in many massive rock formations, such as basalts, granites, granites, gneisses, shales, and silicate rocks, where they are present in quantities (10–300 ppm). They also occur in some 160 discrete minerals, most of them rare, but in which the rare-earth content, expressed as oxide, can be as high as 60% (REO). (REO is an abbreviation used in the industry for rare-earth oxide content.) Lanthanides do not occur in nature in the elemental state and they always occur in minerals as mixtures.

Usually lanthanides are divided into two groups the ceric RE (from La to Nd), and the yttric RE (from Sm to Lu plus Y). Alternatively, one can identify the light (from La to Nd), the medium (from Sm to Dy) and the heavy (Ho to Lu) lanthanides.

The relative abundances of certain rare earths in rocks are powerful tools for the study of the formation of rock deposits; geochemists can tell whether they have been molten. Most of the rare-earth-rich minerals were formed deep in the earth's crust. They precipitated from superheated solutions of seawater or molten rock that were subjected to very high pressures. The relative abundances of the rare earths in the earth's crust are listed in Table 1. The abundances of the even-atomic-number lanthanides are considerably greater than the adjacent odd-atomic-number lanthanides, as is true generally for all elements.

Comparing the relative abundance of the rare earth elements and the elements listed in Table 1, it can be concluded that the rare earths are not so rare; cerium, the most abundant of the rare-earth elements is roughly as abundant as tin; and thulium, the least abundant, is more common than cadmium or silver.

Over 200 rare-earth-containing minerals have been identified. Allanite, apatite, bastnaesite, brannerite, cerite, euxenite, fergusonite, fluocerite, gadolinite, monazite, pyrochlore, samarskite, xenotime, and zircon are considered to be the major ones, but only monazite and bastnaesite are processed at a large industrial scale. China has the largest share of the world's reserves of rare earths (>75%). The United States, India, South Africa, and Australia are also significant players in the field (Table 2) (3).

3. Properties

In the sixth row, column three of the periodic table, the binding energies of the $4f$ and $5d$ subshells lie close together, and the electronic configuration of the elements vary from one to the other, as a function of only small factors like for example the filling of the $4f$ subshell. All the lanthanide elements have a $[\mathrm{Xe}]6s^2 4f^{n+1}$ configuration (if n=0 for lanthanum), except lanthanum, gadolinium, and lutetium, which have $[\mathrm{Xe}]6s^2 5d^1 4f^n$. But of most direct interest for the use of rare earths in compounds is the electronic configuration of the ions. Rare-earth ions are generally trivalent with the $[\mathrm{Xe}]4f^n$, configuration; the $4f$ subshell becomes progressively filled from lanthanum to lutetium.

The chemical similarities of the rare earths result from their electronic structure. Consequently, the chemical properties of the trivalent lanthanides vary little if one lanthanide is substituted for another in a given compound or solution. The filling of the $4f$ subshell plays a minor role in the chemical properties of the atom but is of major importance to physical properties, such as the optical and magnetic properties of rare-earth compounds. Energetically, the $4f$ subshell lies inside the already filled $5s^2$ and $5p^6$ subshells, and is thus shielded from interactions with neighboring atoms. This accounts for the original location of the lanthanides in Mendeleev's table (4) and for very specific properties such as the highly ionic character of metal–ligand bonding or the narrow bandwidths for the f–f electronic transitions.

Significant differences thus characterize the rare earths when these are compared, for example, to the transition-metal ions. As a result of the very strong spin-orbit coupling in the rare earths, each electronic state is described by a total angular momentum J and not through L and S quantum numbers. The effect of the crystal field induced by the ligand on the rare-earth ion is much smaller than the one of interelectronic repulsions (see COORDINATION COMPOUNDS). A description of the relative energies of the J states is given in Reference 5. A consequence of the electronic structure is the lanthanide contraction. As the atomic number increases across the lanthanide series, the increasing charge on the nucleus acts on the electrons and tends to pull them closer to the nucleus, leading to a smooth decrease in ionic radius of the trivalent lanthanide cations from lanthanum to lutetium.

Although rare-earth ions are mostly trivalent, lanthanides can exist in the divalent or tetravalent state when their electronic configuration is close to the stable empty, half-filled, or completely filled ones. Thus samarium, europium, thulium, and ytterbium can exist as divalent cations in certain environments.

On the other hand, tetravalent cerium, praseodymium, and terbium are found, even in oxide form, coexisting with the trivalent state.

3.1. Physical Properties. Gschneider has given an overview of the metallurgy and solid-state physics of the rare earths (6) and some properties of the lanthanides are listed in Table 3. The rare earths form alloys with most metals. They can be present interstitially, in solid solutions, or as intermetallic compounds in a second phase. Alloying with other elements can render the rare earths either pyrophoric or corrosion-resistant. It is extremely important, when determining physical constants, that the materials are very pure and well characterized. All impurity levels in the sample should be known. Some properties of the lanthanides are listed in Table 3.

The arc and spark spectra of the individual lanthanides are exceedingly complex. Thousands of emission lines are observed. For the trivalent rare-earth ions in solids, the absorption spectra are much better understood. However, the crystal fields of the neighboring atoms remove the degeneracy of some states, and several levels exist where only one did before. Many of these crystal field levels exist very close to a base level. As the solid is heated, a number of the lower levels become occupied. Some physical properties of rare-earth metals are thus very sensitive to temperature (7).

Above room temperature, the trivalent lanthanide ions are paramagnetic, with the exception of diamagnetic lanthanum and lutetium. Tetravalent cerium and divalent ytterbium are also diamagnetic. For the metals, when the temperature is lowered, the spin and orbital moments line and the metals become antiferromagnetic or even ferromagnetic like gadolinium, terbium, or dysprosium. The magnetism of the rare earths is highly anisotropic and is important in some industrial applications (see section on uses).

3.2. Chemical Properties. Although the chemical properties of the trivalent lanthanides are quite similar, some differences occur as a consequence of the lanthanide contraction (see Table 3). The chemical properties of yttrium are very similar, too, because of its external electronic structure and ionic radius. Yttrium and the lanthanides are typical hard acids, so they bind preferably with hard bases, typically oxygen-based ligands. Nevertheless, they bind with soft bases, typically sulfur- and nitrogen-based ligands in the absence of hard-base ligands.

In aqueous solutions, trivalent lanthanides are very stable whereas only a limited number of lanthanides exhibit a stable divalent or tetravalent state. Practically, only $Ce^{4+}$and Eu^{2+} exist in aqueous solutions. The properties of these cations are very different from those of the trivalent lanthanides. For example, Ce^{4+} is more acidic and cerium(IV) hydroxide precipitates at pH 1. Eu^{2+} is less acidic, and europium(II) hydroxide does not precipitate at pH 7–8.5, whereas trivalent lanthanide hydroxides do. Some industrial separations are based on these phenomena.

The chlorides, bromides, nitrates, bromates, and perchlorate salts are soluble in water and, when their aqueous solutions evaporate, they crystalize as hydrated salts. The acetates, iodates, and iodides are somewhat less soluble. The sulfates are sparingly soluble and exhibit a negative solubility trend with increasing temperature. The oxides, sulfides, fluorides, carbonates, oxalates, and phosphates are insoluble in water. The oxalate, is important in the selective recovery of lanthanides from solutions, this property is used in analytic and industrial applications. The lanthanides readily form double salts, such as $Ln_2(SO_4) \cdot {}_3Na_2SO_4 \cdot 2H_2O$ and $Ln_2(SO_4)_3 \cdot MgSO_4 \cdot 24H_2O$. These salts were used in the fractionation process.

Anhydrous rare-earth salts cannot be prepared by evaporating water. For example, when heated, $LnCl_3 \cdot 6H_2O$ converts partially to the oxychloride. The usual practice has been to heat the lanthanide chloride hydrate slowly while a stream of anhydrous HCl gas is passed over it. Also many binary anhydrous salts can be prepared by combining the metal directly with a more electronegative element; for example, Cl_2 over Ln gives $LnCl_3$ and Ln plus S gives Ln_2S_3.

The lanthanides can form hydrides of any composition up to LnH_3. Lanthanide hydrides can desorb hydrogen reversibly with temperature. Therefore, the lanthanides and some of their alloys are used for hydrogen storage (see applications section). Many of the binary compounds of the lanthanides, such as oxides, nitrides, and carbides, can exist as nonstoichiometric crystals. The lanthanides form many compounds with organic ligands. Some of these compounds are water-soluble, others oil-soluble. Water-soluble compounds have been used extensively in the past for rare-earth separation by ion exchange; examples are complexes with citric acid, ethylenediaminetetraacetic acid (EDTA), and hydroxyethylethylenediaminetriacetic acid (HEDTA). Oil-soluble compounds are used extensively in the industrial separation of rare earths by liquid–liquid extraction.

The rare-earth metals have a great affinity for oxygen, sulfur, nitrogen, carbon, silicon, boron, phosphorus, and hydrogen at elevated temperature and remove these elements from most other metals.

Neutron-rich lanthanide isotopes occur in the fission of uranium or plutonium and are separated during the reprocessing of nuclear fuel wastes (see NUCLEAR REACTORS). Lanthanide isotopes can be produced by neutron bombardment, by radioactive decay of neighboring atoms, and by nuclear reactions in accelerators where the rare earths are bombarded with charged particles.

The rare-earth content of samples can be determined by neutron bombardment and gamma spectrometry, by X-ray spectrometry. The purity of rare-earth products can be determined by spectroscopic techniques [UV, visible, atomic absorption spectrometry (AAS), ICP, ICPMS, arc emission].

4. Mining

A limited number of rare-earth minerals are mined for large-scale rare-earth production: monazite, bastnaesite, loparite, xenotime. In addition, for a decade, rare-earth-containing clays called “ionic ore” are mined in China. Table 4 shows the rare-earth composition of typical bastnaesite, loparite, monazite, and xenotime minerals and ionic ore concentrates.

Monazite contains ∼50 wt% REO, present as phosphates. Monazite is a by-product of titanium ore mining in Australia, Brazil, India, Korea, Malaysia, Thailand, South Africa, and the United States. Extensive deposits of beach sands are dredged, subjected to gravimetric and magnetic separation in order to separate ilmenite [12168-52-4], rutile, zircon, monazite, and xenotime (see MINERAL RECOVERY AND PROCESSING; SEPARATION, MAGNETIC SEPARATION). The monazite and xenotime content of beach sands is generally very low ($<1\%$, average 0.1%) compared with the ilmenite content ($>10\%$). For this reason, the availability of monazite is greatly dependent on the world demand for ilmenite.

There are extensive deposits of the fluorocarbonate mineral bastnaesite in China and near Mountain Pass in southeastern California. The world's largest deposit of rare earths is found at Bayan Obo in Inner Mongolia, China, where bastnaesite is a byproduct of iron ore mining (9). The Bayan Obo deposit contains an estimated 36,000,000 t of rare-earth oxides, $>70\%$ of the estimated world rare-earth reserves. At Mountain Pass typical rock analyses show 50 wt% calcite, 25 wt% baryte, 15 wt% bastnaesite, and 10% silica. The ore, after being crushed and ground, is upgraded first by flotation to 60 wt% (REO) and ≤ 70 wt% REO by leaching with hydrochloric acid. The rare-earth content of this concentrate is as high as 99 wt% in light lanthanides (La to Nd).

Xenotime, like monazite, is a rare-earth phosphate but contains $\leq 60\%$ yttria [1314-36-9], Y_2O_3 and a higher proportion of heavy rare earths than monazite does. Having undergone a concentration process similar to that of monazite, Xenotime occurs with it in beach sand deposits. A second source of xenotime also occurs in cassiterite deposits (tin ore).

Ion-adsorption clay deposits are the result of prolonged *in situ* weathering of REO-rich host rocks, most commonly granitic or volcanic rocks, where erosion has been limited to a low extent. The critical requirements for the formation of such deposits are met in southern China (9). In the Jiangxi Province a large reserve of a rare-earth-containing clay contains over 1,000,000 t of REO. A distinctive feature of the RE distribution pattern in the Chinese ion-adsorption ores is a cerium deficiency (see Table 4). Although ion-adsorption ores are of much lower grade than conventional ones, their mining and processing are straightforward (9).

The ore is mined by open-pit methods and leached by dilute aqueous salt solutions [NaCl, $(NH_4)_2$, SO_4, etc]. Over 90% of the rare-earth content is transferred into solution, then precipitated as oxalates or carbonates and converted to mix RE oxides ready for the separations processing.

A large deposit of *loparite* occurs in the Kola peninsula, Russia. The production reaches 6500 tonnes of REO per year. Loparite contains over 30% of rare-earth oxides from the cerium group. In addition, loparite contains $\leq 40\%$ titanium oxide and $\leq 12\%$ niobium and tantalum oxides.

Apatite and other phosphorites constitute a substantial resource of rare earths. The REO content is highly variable and ranges from trace amounts to 1%. Rare earth rich apatites are found in the Kola peninsula, Russia and Phalaborwa complex in South Africa. In spite of their low REO content apatites could become an important source of rare earths because they are processed in large quantities for the manufacturing of fertilizers.

Commercial mining of rare earth reserves began roughly in the late 1890s. Monazite was the major rare-earth source up until 1965. Thereafter bastnaesite production exceeded monazite production, and presently, bastnaesite is the world's major source of rare earths, constituting almost 75% of world output of rare-earth minerals (see Table 5).

5. Processing

5.1. Digestion of Rare-Earth ores. *Monazite.* The commercial process for monazite treatment is a digestion using caustic soda. The phosphate content of the ore is recovered as marketable trisodium phosphate and the rare earths as RE hydroxide (10). Usual industrial practice is to attack finely ground monazite with a 50% sodium hydroxide solution at 150°C or with a 70% sodium hydroxide solution at 180°C. The resultant mixed rare earth and thorium hydroxide cake is dissolved in hydrochloric or nitric acid, then processed to remove thorium and other non-rare earth elements, then processed to recover the individual rare earths. (see THORIUM AND THORIUM COMPOUNDS).

Bastnaesite. The commercial 60% REO concentrate can be upgraded to 70% REO by leaching with hydrochloric acid then calcining. In the Molycorp process the flotation concentrate is heated in air at 620°C to remove CO_2 and oxidize cerium to the tetravalent state. The resulting solid is treated with 30% HCl to yield a marketable cerium concentrate containing 60–70% CeO_2 and to dissolve the other rare-earth elements (11). In alternative process, which consists of leaching the concentrate with hydrochloric acid, the rare earths become partially dissolved, while a RE fraction combines with the fluorine from the ore. The mixed rare-earth fluoride residue is then decomposed by treatment using caustic soda; the resulting rare earth hydroxides are leached with HCl. Bastnaesite can also be treated with concentrated caustic soda at ~200°C to form rare-earth hydroxides, which are then dissolved in acid.

A sulfuric acid treatment process consists of digesting the bastnaesite concentrate in concentrated sulfuric acid at 400°C and then recovering the rare earths as water soluble sulfates. Impurities such as iron are removed by neutralization.

Loparite. There are two methods used at various plants in Russia for loparite concentrate processing (12). The chlorination technique is carried out using gaseous chlorine at 800°C in the presence of carbon. The volatile chlorides are then separated from the calcium–sodium–rare-earth fused chloride, and the resultant cake dissolved in water. Alternatively, sulfuric acid digestion may be carried out using 85% sulfuric acid at 150–200°C in the presence of ammonium sulfate. The ensuing product is leached with water, while the double sulfates of the rare earths remain in the residue. The titanium, tantalum, and niobium sulfates transfer into the solution. The residue is converted to rare-earth carbonate.

5.2. Separation Processes. The product of ore digestion contains the rare earths in the same ratio as that in which they were originally present in the ore, with few exceptions. This is because of the similar chemical properties of the various RE elements. The various processes for separating individual rare earth from naturally occurring rare-earth mixtures essentially utilize small differences in acidity resulting from the decrease in ionic radius from lanthanum to lutetium. The acidity differences influence the solubilities of salts, the hydrolysis of cations, the formation of complex species so as to allow separation by fractional crystallization, fractional precipitation, ion exchange, and solvent extraction. In addition, the existence of tetravalent and divalent species for cerium and europium, respectively, is useful because the chemical behavior is markedly different from that of the trivalent species.

Fractional precipitation or crystallization used until the early part of this century are now uneconomical.

Selective Oxidation or Reduction. Cerium, the most abundant lanthanide, can be separated easily after oxidation of Ce(III) to Ce(IV). This simplifies the subsequent separation of the less abundant lanthanides. Oxidation occurs when bastnaesite is heated in air at 620°C or when the hydroxides are dried in air at 120–130°C. Once oxidized, Ce(IV) is separated from the trivalent lanthanides either by selective dissolution of trivalent species with dilute acid, or by complete dissolution in concentrated acid followed by selective precipitation of ceric hydroxide [12014-56-1] or solvent extraction of cerium(IV) by tributylphosphate in a nitrate medium. In aqueous solution, the oxidation of cerium(III) to cerium(IV) is carried out by treatment with hydrogen peroxide or sodium hypochlorite or by electrolysis.

In aqueous solution, europium(III) reduction to europium(II) is carried out by treatment with zinc. When reduced to the divalent state, europium exhibits chemical properties similar to those of alkaline-earth elements and can be selectively precipitated as a sulfate, for example. This process is highly selective and allows production of high purity europium (see CALCIUM COMPOUNDS, STRONTIUM AND STRONTIUM COMPOUNDS).

Ion Exchange. Ion exchange has proved to be effective in the separation of high purity rare earths, but generally involves the processing of very dilute aqueous solutions. In the 1950s, the commercial separation of the rare earths was dominated by ion-exchange methods, but technical and economic limitations have restricted its use in present-day industrial-scale separation processes.

Mixed rare-earth cations in aqueous solution are are strongly adsorbed by the organic cation-exchange resin. The rare earths are recovered by elution using a concentrated solution of a monovalent salt, for example, ammonium chloride

If a complexing agent exhibiting significantly different affinities for the various lanthanides is added to the eluant, then a separation occurs. In practice the process uses band-displacement techniques with aminopolycarboxylate eluants, such as ethylenediaminetetraacetate (EDTA) and hydroxyethylene–diaminetriacetate (HEEDTA) among others. Wallace has explained this procedure in Ref. 13. A preliminary charge of a foreign ion (called the "retarding" ion) is adsorbed onto the resin. The foreign ion has a lower affinity for the resin than do the rare-earth elements (REEs). A charge of rare-earth mixture is then adsorbed as a band on the upper part of the resin column. Then band displacement is carried out using an ion that has a greater affinity for the resin than the REE. A possible candidate is NH_4^+ because NH_4^+ has no affinity for the complexing agent, whereas REEs have a great affinity therefore, the eluant used is often an ammonium aminopolycarboxylate aqueous solution. A band of constant length containing the REE moves down through the column, and the concentration of the REE in the band remains constant. The band requires a minimum movement along the column to achieve a constant equilibrium state. Then, the band leaves the column, and the eluant is subjected to fractionation in order to recover each individual rare earth.

Since 1970, small amounts of REE have continued to be separated by ion exchange for specific grades, such as >99.9999% purity. Some new developments have been proposed by using new resins or new equipments, but the main limitation of the ion-exchange process development is the low solubility of RE aminopolycarboxylates in aqueous solution. Ion exchange was largely replaced by liquid–liquid extraction during the 1960s for this reason.

Liquid–Liquid Extraction. The liquid–liquid extraction process for rare-earth separation was discovered by Fischer (14). Extraction of REE with an alcohol, ether, or ketone gives separation factors ≤ 1.5. The selectivity of the distribution of two rare-earth elements, RE_1 and RE_1, between two nonmiscible liquid phases is given by the ratio of the distribution coefficients, D_1 and D_2:

$$D_1 = (RE_1)_o/(RE_1)_a D_2 = (RE_2)_o/(RE_2)_a$$

$$F = D_1/D_2$$

The subscripts o and a stand, respectively, for the organic and aqueous phases, and F is the separation factor. For two neighboring trivalent rare earths, F ranges between 1 and 5. Thus for an effective separation, many single separation operations have to be repeated, batchwise or continuously.

A fully continuous liquid–liquid extraction process in countercurrent flow enables separation into two groups of REE to be achieved. Thus the separation of nREE requires $n + 1$ countercurrent separations carried out using a column or mixer–settler arrangement. A schematic flow diagram of a countercurrent flow extraction plant for the continuous separation of two REE or two groups of REE is shown in Figure 1. The mixture that is to separated is fed to an intermediate stage of the contactor operating in countercurrent flow. The solvent becomes preferentially charged with the REE that form the most stable complex, while the REE that form the less stable REE complex remains in the aqueous phase. The flow extract is further washed by the scrubbing aqueous solution in order to remove traces of the less stable REE complex. The pure extract is then subjected to backextraction in order to recover a high purity aqueous solution. The solvent is then recycled.

The development of a suitable solvent system is important for successful operation. Solvent systems generally consist at least of the following components: extractant, diluent, inorganic salts or acids, and water. The relative optimization of these components yields the best conditions with which to achieve separation. A key factor to success is the choice of the appropriate extractant. Many extractants may be used for REE separation. These groups of extractants—acidic, basic and neutral— have to be considered on the basis of the mechanisms involved.

Acidic Extractants. Acidic Extractants, react with REE according to a cation-exchange reaction, as represented below:

$$RE_a^{3+} + 3\ HL_o \longrightarrow REL_{3o} + 3\ H_a^+$$

The extent of extraction or backextraction is therefore governed by the pH of the aqueous phase. Extraction by carboxylic acids is carried out in a neutral or weakly acidic medium. The most widely used carboxylic acid is $R_1R_2(CH_3)C$–COOH, where $R_1 + R_2$ represents seven carbon atoms. Trade names are Versatic 10 (Shell Chemicals) and Neodecanoic acid (Exxon Chemicals). Naphthenic acids are also used. Carboxylic acids can be used either in chloride or in nitrate media. Many commercial acidic organophosphorus extractants are available: dialkylphosphoric acids, $(RO)_2POOH$; alkyl alkylphosphonic acids, (RO)RÕPOOH; and dialkylphosphinic acids, R_2POOH. The most popular alkyl chains are the 2-ethylhexyl (Albright and Wilson, Bayer, Daihachi commercial extractants) and 2,4,4-trimethylpentyl (Cytec commercial extractants). 2-ethylhexyl 2-ethylhexylphosphonic acid (HEHEHP) is widely used by rare-earth processors. The efficiency of extraction by the organophosphorus acids decreases when the acidity constant decreases, specifically, phosphoric derivatives > phosphonic > phosphinic, whereas the selectivity with respect to the lanthanide series is adversely affected.

Basic Extractants. Only long-chain quaternary ammonium salts, $R_3NCH_3^+X^-$, in which R represents C_8–C_{12} groups and X nitrate or thiocyanate, are effectively used for REE separations. The extractant reacts with REE according to an anion-exchange reaction as follows:

$$\mathrm{RE}_a^{3+} + 3\,\mathrm{X}_a^- + \mathrm{R_4N^+X_o^-} \longrightarrow \mathrm{REX_4^-}, \mathrm{R_4N_o^+}$$

Therefore the extent of extraction or backextraction is governed by the concentration of X^- in the aqueous phase; the distribution coefficients and selectivities depend on the anion. In nitrate solutions, the distribution coefficient decreases as the atomic number of the REE increases, whereas in thiocyanate solutions, the distribution coefficient roughly increases as the atomic number of the REE increases.

The position of yttrium in the lanthanide series is not the same in nitrate and thiocyanate solutions. A combination of extraction by carboxylic acids and by ammonium salts is used for production of high purity yttrium.

Neutral Extractants. Many neutral organophosphorus extractants are presently available: phosphate esters, phosphonate esters, phosphinate esters, and phosphine oxides. The most popular neutral extractant is tributylphosphate (TBP), which reacts with RE elements according to a solvation mechanism as follows:

$$\mathrm{RE}_a^{3+} + 3\,\mathrm{NO}_{3a}^- + 3\,\mathrm{TBP}_o \longrightarrow \mathrm{RE(NO_3)_3}, 3\,\mathrm{TBP}_o$$

The extent of extraction can be increased by a salting-out effect. The selectivity of TBP is very poor compared with HDEHP and is useful only for light rare-earth separation; however, organic phase loadings higher than 100 *g* REO per liter can easily be achieved.

Equipment. The preferred extraction technique in the rare-earth industry uses mixer–settlers. This technology is suitable for the relatively small flow rates in the REE refineries and the large number of stages required for the production of high purity REE. Some difficult separations require batteries of 100 stages and more alone.

5.3. Production. *Salts and Oxides.* The final step in the chemical processing of rare earths depends on the intended use of the product. Rare-earth oxides are obtained by firing at 900°C hydroxides,carbonates, or oxalates first precipitated from the aqueous solution. Rare-earth chlorides are obtained by crystallization of aqueous chloride solutions. Rare-earth fluorides are obtained by precipitation with hydrofluoric acid.

Metal processing. The extraordinarily high electropositive nature of the rare-earth elements precludes their reduction by simple carbon-based pyrometallurgy or by electrolysis from an aqueous solution. Therefore, the industrial production of the rare-earth metals has been carried out only by fused-salt electrolysis or metallothermic reduction.

Fused Salt Electrolysis. Only the light rare-earth metals (La to Nd) can be produced by molten salt electrolysis. The melting points of the medium to heavy rare-earth metals are generally too high and the production elements too low for attractive economics. Alternatively, the rare earth metals can be deposited with a solvent metal (eg, Zn or Mg) and subsequently separated by distillation of the solvent. The light rare earth metals, including mischmetal (which is a mixture of light lanthanide metals), have been produced from a fused chloride bath using an “anhydrous” rare earth chloride as the feed material and from a fused fluoride bath using either the corresponding rare earth oxide or fluoride as the feed material.

The selection of materials of construction for the electrolysis cell is difficult because of the high reactivity of the rare earth metals. The containment crucible is typically constructed of molybdenum, tungsten, tantalum, or even iron with a ceramic or graphite lining. The cathode is usually molybdenum or a soluble transition metal (to produce an eutectic); the anode is frequently carbon.

Metallothermic Reduction. The rare-earth metals from La to Lu and Y, can be produced by metallothermic reduction. Suitable reducing agents are alkali metals, alkaline earth metals, aluminum, or light lanthanide metals, previously obtained by electrolysis. The preferred process involves the reduction of the rare earths from the anhydrous fluoride with calcium at temperatures up to about 1600°C in a tantalum crucible. The volatile metals (eg., Sm, Eu and Yb) can be produced by the reduction of the respective oxide with mischmetal at approximately 1200°C, with the subsequent condensation of the metallic vapor on a chill plate. Rare-earth–transition-metal alloys (eg., samarium-cobalt) can be produced directly by the coreduction or reduction/diffusion process. For example, a mixture of samarium and cobalt oxides is reduced with calcium at about 1000°C to produce a mixture of $SmCo_5$ and CaO, which is subsequently removed by leaching.

6. Economic Aspects

Rare-earth technology is one of the most fascinating and challenging industries in the world. The use of rare earths in many different applications is almost totally ignored by the public and even sometimes by the scientific community. This industry is regularly shaken by big swings in supply and demand, appearance of new applications, entrance of new competitors, and sometimes new raw materials. The rare-earth market can be considered for some segments as a specialty business, while for others it exhibits the characteristics of a commodity business.

In the 1970s and early 1980s rare earths were used mostly in low technology applications [lighter flints, fluid-cracking catalysts (FCC), metallurgy], but now they are widely used in high tech applications (phosphors for lamps and TV sets, high performance magnets, rechargeable batteries, auto catalysts, etc).

6.1. Rare Earth Application Market. The rare-earth application market is split into two distinct segments applications that require nonseparated rare earths (glass, FCC catalysis, metallurgy, rechargeable batteries, polishing powders), and applications that require separated elements (catalysis, magnetism, phosphors, capacitors, ceramics, etc.). In 1970 rare-earth consumption was 15,000 tonnes; it reached 26,000 tonnes in 1983, and 35,000 tonnes in 1990, and in 1997 demand reached approximately 45,000 tonnes (Fig. 1) representing an average growth rate of <5% per year.

In the 1970s the application market was dominated by applications requiring nonseparated elements such as metallurgy, flints, FCC catalysts, and glass. In the eighties the demand for separated elements started to grow mostly in new applications such as phosphors (yttrium and europium) and magnetism (Sm and later Nd). In 1985 the situation started to change as new raw materials became available (ionic ores from China).

At the time, the ionic ore had the best composition to service the needs of the market. It was then possible to increase the output of yttrium and Europium, without generating huge excesses of Cerium and neodymium. In the nineties the demand for cerium and neodymium has been growing, driven by the autocatalyst and magnetism market and the demand for separated rare earths did continue to grow.

The rare-earth market at the salt and oxide level reached about ~45,000–50,000 tons (REO) in 1997. The market (in volume) can be broken down as follows by application and country:

Catalysis	
FCC, automotive, ¼	38%
Electronics	
Phosphors, capacitors, magnets, ¼	30%
Materials	
Glass, ceramics, ¼	22%
Others	
Metallurgy, agrochemicals, ¼	10%
Japan	43%
USA	27%
Europe	18%
ROC	12%

The consumption pattern of rare earths varies significantly between major economic areas. The Japanese, European, and U.S. markets are dominated by high value applications (mostly separated rare earths at approximately 75% of the demand), while the Chinese market is dominated by nonseparated applications (FCC catalysis, mischmetal, cerium concentrates). China has also unique applications for nonseparated rare earths such as fertilizers.

The market for separated rare earths is growing at a rate of approximately 8% per year; however, the situation varies greatly by segment. The demand for cerium compounds is growing at a moderate rate.

Demand for lanthanum and praseodymium is quite flat, while demand for neodymium is growing (>10% per year). The demand for yttrium and europium is quite stable, while samarium demand is flat at best.

Each major application segment is becoming more complex and diverse.

6.2. Metals and Alloys. Around 1985 the metal–alloys segment of the industry was dominated by commodity applications (flints, metallurgy) and the only specialty application was SmCo magnets; the situation has dramatically changed. Since 1992 or so the growth rate in that segment has been staggering (> 15% per year). This growth has been driven by two major markets: *magnetism* (essentially sintered and bonded NdFeB) and *rechargeable batteries*.

Bonded and Sintered NdFeB magnets production worldwide exceeded 7000 tonnes in 1997. Applications are in the computer industry, motors, loudspeakers, and magnetic resonance imaging. The SmCo market remains a niche market. In the rechargeable battery market NiMH has emerged as a major new system since 1995 over; they are now competitive over the alternative NiCd and lithium-ion batteries for applications that require high volumetric energy density (eg., cellular phones). This market is dominated by Japan, which is by far the leading producer of rare-earth-based permanent magnets and rare-earth-based NiMH batteries.

China is also a large producer of medium-grade NdFeB magnets (mostly sintered). While in the past the growth was fueled by the electronic industry (computers, office automation and cellular phones), new applications in new market segments (hybrid vehicles, electric bicycles and scooters, automotive applications, energy-efficient motors for washing machine, air conditioners, etc) should help this market to continue to grow at a healthy pace.

Beside magnetism and rechargeable batteries, there is no other major new development today. Magnetostriction remains a very tiny market highly specialized that does not represent a significant volume.

Magnetooptic applications are growing, but the market is small and the future of rare-earth-based materials compared to other systems (phase-change compounds) is unclear at this stage.

Flints and metallurgy are highly mature markets with almost no growth.

6.3. Catalysis. This market is divided in two major segments: autocatalysts and industrial catalysts, a mature market, and separated rare-earth compounds used in catalysts to improve yields and selectivity in rubber and polymer synthesis.

Cerium-based catalysts are now a major part of the autocatalyst technology used for gasoline emission control. In the late 1990s the market required quite simple compounds (mostly cerium carbonate) with almost no functional properties. Today high performance cerium-based compounds are tailored to meet increasingly stringent gasoline-engine emission regulations. The ACTALYS product range has been launched by Rhodia. The use of these products boosts the efficiency and durability of the catalytic converter and offers a solution for eliminating the pollutants released during the first few minutes after starting the engine.

6.4. Materials. Cerium- and lantanum-based compounds have been used for years in applications such as polishing powders, UV absorption, glass formulation, and opacifiers. In the past pigments represented a very small market for rare earths where relatively small amounts of praseodymium and cerium were used in the ceramics, and plastics industries. This is changing with the new family of inorganic pigments Neolor developed by Rhodia. Cerium sulfide pigments cover the red-orange color spectrum. Cerium sulfide is an ideal substitute for cadmium sulfoselenide and lead molybdenate in plastics, especially in high temperature processed plastics. Developed primarily as a substitute for cadmium sulfoselenide in plastics, it also could be used in coatings.

6.5. Electronics. Phosphors remains the major application market for yttrics (yttrium, europium, terbium etc). These compounds, used in TV, computer monitors, and compact lamps, have evolved from high purity rare earths to complex compounds such as YEu or LaCeTb mixed oxides, mixed phosphates, and other compounds. Functional ceramics for the electronics industry is a growing segment for rare-earth-based compounds. Major applications are oxygen sensors, capacitors, and microwave appliances (ovens, etc).

There is also a great diversity of small niche markets requiring specially tailored compounds, as is the case, for example, for different products used in medical applications (eg, X-ray-contrast agents).

6.6. Principal Producers. Few new producers have entered the market since the late 1980s. The major producers are listed below (Table 1). Rhodia and Molycorp are today the only two major non-Chinese producers that are continuing to run large-scale separation units for both cerics and yttrics.

6.7. Prices of Rare-Earth Products. Rare-earth products are sold either as a single compound (salt, oxide, metal) or as a formulated product (coprecipitate, alloy, etc). Many products are also developed specifically to meet the particular need of a specific customer. As a consequence, there is great diversity of rare-earth-based compounds being sold, and the price range is quite broad.

The (1998) prices of rare-earth oxides depending on quality and volumes, were as follows:

Cerium oxide	\$7–30
La oxide	\$6–15
Nd oxide	\$17–25
Pr oxide	\$6–15
Sm oxide	\$11–18
Y oxide	\$28–50
Dy oxide	\$35–70
Tb oxide	\$200–400
Eu oxide	\$300–600

6.8. Recycling and Disposal. In the existing industrial applications, the rare earths are more often used as additives at a relatively low mass ratio. Thus, in practice there is no recycling industry in the rare-earth industry. But the situation could change in the future with new regulations in the handling and disposal of industrial and domestic residues.

In current practice, the only case of rare-earths recovery is the magnet industry. Rare-earth-rich residues are produced during the production of Nd and Sm magnets. Processes have been developed using classic separation techniques. In the case of NdFeB, a calcination of the scraps make the iron insoluble during the acidic dissolution of neodymium (X).

Projects on the recovery of luminescent material from used TV sets or lamps are also underway.

6.9. Health and Safety Factors. The lanthanides are considered to be only slightly toxic in the Hodge–Sterner classification system and are safety handled with ordinary care (15). Inhalation of rare-earth compound vapors or dust should be avoided, and the skin should be washed thoroughly if it comes into contact with any dust or solution.

Toxic effects of the rare earths on humans have not been reported, but extensive tests of toxicity have been conducted on animals. If the rare earths are administered orally, the toxicity is low. When RE vapors or dusts are inhaled, they are somewhat more toxic and are only slowly absorbed into the body. If injected subcutaneously, most of the injected material remains in place. The most toxic reactions are obtained if the RE are introduced by means of intraperitoneal or intravenous injections. The symptoms of toxicity of the rare-earth elements include writhing, ataxia, labored respiration, walking on the toes with arched back, and sedation.

There is a delayed lethality due to rare-earth exposure; the death rate peaks between 48 and 96 h. Chelating agents, citrate or EDTA, obscure the lethal effects of the rare earths. The effect of atomic weight of rare-earth elements on lethality is difficult to assess, but the medium RE elements appear to have a lesser toxicity than do light or heavy RE elements. The toxicity of neodymium salts increases as follows: chloride < propionate < acetate < sulfate < nitrate (15). Rresults of some acute lethal doses of lanthanide chlorides in mice, by oral or intraperitoneal administration route, are given in Table 7.

7. Uses

Rare earths are used many industrial applications, mainly because of their unique physical properties, but some applications are also due to some of their specific chemical properties.

The rare-earth industry started at the beginning of the twentieth century when Auer von Welsbach developed the incandescent mantle, owing to the candoluminescence of a mixture of thorium and cerium oxides. In the view of getting value of the residues he obtained from this preparation, Auer also developed the lighter flints, taking advantage of the pyrophoricity of iron–mischmetal alloys.

Rare-earth compounds with controlled purity really became available at the industrial scale after World War II, and that corresponded to the development of the applications we know today.

7.1. Applications Linked to Chemical and Structural Properties. *Metallurgy.* This is an old application, which relies on the strong affinity of rare-earth metals for oxygen and sulfur. Small amounts of mischmetal act as a trap for these elements, usually detrimental to the properties of steel or cast iron.

This results in better resistance to high temperature oxidation and thermomechanical properties of several metals and alloys (16,17). Magnetism and electrochemistry are the latest applications of rare earths in metallurgy and are treated later in this article.

Catalysis. Although rare earths are mentioned as active elements in a large number of catalytic reactions (18), only a few areas have reached the industrial level. The oldest one is the structural and chemical stabilization of the zeolites for petroleum cracking applications, where the addition of several percents of rare earths allows the catalyst to remain acidic, essential for the conversion of high weight molecules into lighter species, even in the very agressive conditions of the petroleum industry (19).

Cerium oxide is today extensively used in automotive post-combustion. It is a major component of the three-way catalysts (TWCs) used in all modern gasoline cars. TWCs lower the level of pollutant emissions from the engine through selective reduction of nitrogen oxides (NO_x) and simultaneous oxidation of carbon monoxide and hydrocarbons. As cerium can be either tri- or tetravalent, redox properties of CeO_2 can make it an oxygen buffer, allowing the global stability of the composition of the exhaust gas, particularly to allow the oxidation of CO and hydrocarbons when the medium is globally reducing. The catalyst is made of 100–3000 ppm of precious metal (Pd, Rh or Pt) dispersed on a mixture of alumina and cerium oxide (20 wt%). In addition to its major role in the control of redox conditions of the medium, cerium oxide is highly refractory and allows alumina to keep its surface thermally stable at the elevated temperatures ($>1000^\circ$C) seen by the catalytic muffler (see EXHAUST CONTROL, AUTOMOTIVE).

Finally, it also permits a good, thermally stable, dispersion of the metallic particles, the actual catalyst, preventing them from sintering which would make them inactive (20,21). The development of cerium–zirconium mixed oxides has allowed an increase of the usage properties, in terms of oxygen buffering capacity as well as thermal stability (22).

Based on the industrial development of highly efficient chemical methods, special grades of cerium–zirconium oxides, remaining active at higher and higher temperatures, are now developed for this application (23).

Among the other catalytic applications of rare-earth compounds, one can mention the use of divalent samarium halides in organic synthesis (24). But one other area for rare-earth usage is having a very rapid growth: the use of neodymium salts as diene polymerization catalyst (25). For example, with respect to polybutadiene, the use of neodymium carboxylates (versatates, neodecanoates, octoates, naphtenates, etc) allows the obtention of a high *cis*-polybutadiene content and a very good control of the molecular weight distribution of the polymer. Other advantages of the use of rare-earth salts compared to transition elements are high polymerization temperatures, reducing the cooling stage of the polymer, and substituting toxic aromatic solvents by aliphatic ones. This leads to a significant industrial development of the use of neodymium salts for rubber manufacturing.

7.2. Glass and Ceramics. Rare earths are widely used in the glass industry (26); for instance decolorization of glass is obtained through the oxidation of iron from its deep-blue divalent form to the pale-yellow trivalent one by tetravalent cerium. Furthermore, cerium oxide is the best polishing agent for glass, owing to its natural hardness (due to its compact fluorite structure) and a chemical reaction at the silica–cerium oxide interface. Purity and morphology of the polishing powders made from cerium oxide can be adapted to the polishing quality required (27).

Chemical and structural properties of the rare earths are also used in the ceramics industry. Minute additions of rare-earth oxides stabilize tetragonal or cubic forms of zirconia. Among them yttrium oxide (1–10 mole %) is the best compromise. Stabilized forms of zirconia are used in sensors (for their high ionic conductivity), cutting tools (for their good thermomechanical properties) (see TOOL MATERIALS), or in imitation jewelery (when the cubic form is fully stabilized, for Y_2O_3 content above 7 mol %) (see GEMSTONES, GEMSTONE MATERIALS) (28).

7.3. Applications Linked to Physical Properties. Applications involving physical properties use high purity rare earths (>99,99%), as they exploit the elements' specific electronic configuration.

7.4. Optical Properties. The very low sensitivity to the crystal field effect of the electronic levels for the 4*f* electrons of trivalent rare earths ions results in narrowband electronic transitions. A strong monochromatic character for light absorption or emission is thus observed, of major importance for the applications (29). Sometimes, transitions between 5*d* band and 4*f* levels (Eu^{2+}, Ce^{3+}), or from charge-transfer bands between tetravalent rare earths and anions are observed, for which the color can be modulated by the nature of the crystalline matrix and its composition.

Rare-earth products are used to color glass or ceramics : praseodymium green, neodymium purple, or erbium pink. Zircon ($ZrSiO_4$) doped by tetravalent praseodymium is the strongest and most stable yellow pigment for ceramics with high firing temperatures (30). New pigments for the coloration of plastics and paints are well on the way to being developed, based on the good properties of cerium sulfide derivatives and their nontoxicity. These will come as an alternative to heavy-metal-based pigments like cadmium sulfoselenides (31).

Owing to the doping by alkali or alkaline earths, it as been possible to stabilize a range of colors from orange to bright red and maroon in the form of Ce_2S_3. Besides having good brightness and tinting strength, a good stability in the application media (polymers such as polypropylene, ABS, polycarbonate), and a strong resistance to weathering and UV make the cerium sulfide–based pigments very good candidates as inorganic pigments in a wide range of applications.

Other optical applications involve the use of cerium +IV as an antibrowning agents for glass (eg, in TV faceplates), or lanthanum as a component (40% by weight) of high index borate glasses for microscopes, telescopes, and camera lenses.

Luminescence has been an industrial use for rare earths since europium-activated yttrium oxysulfide ($Y_2O_2S{:}Eu^{3+}$) was used as the red component in color TVs, allowing a twofold increase in brightness compared to ZnS:Ag (32). The outstanding performance of rare-earth-based phosphors (see PHOSPHORS) is also utilized in a wide number of professional applications for cathode ray tubes, such as monitors for computers, instrument panels in planes, or TV projection (33). Rare-earth-based phosphors are also used in fluorescent lamps, where light is obtained from the combination of primary monochromatic emissions at 450, 550, and 610 nm.

Typical phosphors are $Sr_5(PO_4)_3Cl{:}Eu^{2+}$ and $BaMg_2Al_{16}0_{27}{:}Eu^{2+}$ for the blue, $CeMgAl_{11}O_{19}{:}Tb^{3+}$, (Ce, Gd)$MgB_5O_{10}{:}Tb^{3+}$ and (LaCe)$PO_4{:}Tb^{3+}$ for the green, and finally $Y_2O_3{:}Eu^{3+}$ for the red. These highly efficient phosphors have allowed the development of compact fluorescent lamps with an energy consumption 5–8 times lower than that of incandescent lamps, with the same color rendering index (34).

Rare-earth-based phosphors have other industrial applications like X-Ray-intensifying screens where compositions like $Gd_2O_2S{:}Tb$ (green), LaOBr:Tm, and $YTaO_4{:}Nb$ or Tm (blue) have allowed a significant improvement of the picture quality, and a lowering of the patients' exposure time by a factor of (35), and the unique nature of the rare earths' emissions leads to applications in photostimulable phosphors, lasers, dosimetry, or fluorescent immunoassay (36).

7.5. Magnetic Properties. Rare-earth metals have exceptional magnetic properties at low temperature; magnetocrystalline anisotropy constants are 10–100 times higher than for other elements, and absolute saturation magnetization is much higher than in iron, for example. However, magnetic ordering occurs only at low temperatures, as the internal character of the 4*f* orbital induces weak couplings for direct interactions between neighboring atoms as well as for long-range exchange via conduction electrons. Thus, rare-earth metals are paramagnetic or diamagnetic at room temperature; the highest Curie temperature Tc is 293 K for gadolinium, below which it becomes ferromagnetic(see MAGNETIC MATERIALS, BULK).

The Curie temperatures (T_c) of the rare-earth metals are increased to commercially interesting levels by alloying them with elements having higher ordering temperatures, such as the transition metals, iron, cobalt, or nickel. The first really high energy magnetic materials to be industrialized were samarium–cobalt magnets ($SmCo_5$ and Sm_2(Co,Fe,Cu,Zr) (17). These magnets displayed energy products of about 20 MGOe and intrinsic coercivities of >20 kOe, with a T_c of >700°C. These magnetic properties enabled the miniaturization of many electronic devices, such as stepping motors and headphones (Walkman), beginning in the early 1980s (37). The growth of applications was limited only by the relative scarcity and high cost of samarium and cobalt. This limitation was removed by the discovery of the even more powerful neodymium–iron–boron magnets in the mid-1980s (38,39). Anisotropic energy products of almost 50 kOe with intrinsic coercivities of about 12 kOe have been realized. Magnets based on the $Nd_2Fe_{14}B$ structure are produced as 100% dense sintered products using classic powdered metallurgy processes and as bonded materials in epoxy or nylon. Applications range from the hard-disk drive and MRI (magnetic resonance imaging) to innumerable automotive and electronic ones. The average growth of these markets continues to exceed 15% annually.

A new field for the application of rare-earth transition-metal alloys is magnetooptic recording, in which the magnetic (high coercive field and low T_c) and optical (high value of the Kerr rotation angle) properties of (Gd, Tb) (Co, Fe) amorphous alloys are used to obtain high recording densities (20 Mbits/cm^2) in erasable–rewritable laser systems (40).

Hydrogen Storage Properties. Since the ability of rare-earth transition-metal alloys to absorb large amounts of H_2 was discovered in the 1960s, various "alloys" have been studied for bulk H_2 storage, refrigeration and battery electrodes. $LaNi_5$ and its analogs, with mischmetal and various partial substitutions for Ni, have emerged as the preferred negative electrode for NiMH rechargeable batteries. The NiMH battery is competing with rechargeable NiCd and lithium-ion batteries to serve the ever-growing demand for compact consumer cordless devices, such as videocameras, cellular phones, laptop computers, shavers, toys, and tools. The current MM $(Ni, Mn, Co, Al)_5$ electrode's capacity, charge/discharge rate, and corrosion resistance are being improved by new dopants, casting processes, surface treatments, and so on (41).

7.6. Electrical and Nuclear Properties. The use of rare earths as additives to modify the performances of electronic components is well known. Barium titanate is doped by Neodymium in order to stabilize the thermal variation of its dielectric constant over a large temperature range (NPO-type capacitors), or by other trivalent rare earths to get the PTC effect (positive temperature coefficient) used for the realization of sensors or thermal relays for example. Most of the "high T_c" superconductors discovered in the late 1980s involved rare earths, and numerous studies have been undertaken on $YBa_2Cu_3O_7$, for example (42). Finally, gadolinium has the highest cross section for thermal neutrons ever known (46,000 barns — 10^{-28} m^2 — per atom) and is used extensively in the nuclear energy, as a component of the fuel or control rods, where it acts as a consumable poison, a trap for neutrons in the reactor (43).

7.7. Future Applications. Rare earths are now true industrial products available in a wide variety of chemical forms (mixed oxides, metals, alloys, etc) and quality (purity, morphology, reactivity, etc). Their very specific physical and chemical properties, combined with their nontoxicity, and the possibility to adapt their presentation to the needs of the application, are great advantages to think of new areas of applications. For example, the use of gadolinium complexes as contrast agents in magnetic resonance imaging is growing (44). The positive effect of cerium additives on the control pollution from diesel engines (soots, NO_x, etc) has been demonstrated (45), and perovskite $LaTO_3$, (T=Co, Ni, Cu, etc) have been mentioned for oxidation catalysis (46) and electrodes or interconnects for solid oxide fuel cells (47). And last but not least, one can with no doubt expect that rare-earth-based phosphors will be extensively used in the very fast development of flat screens such as plasma display panels, which will replace the venerable cathode-ray tube in the beginning of the twenty-first century (48)

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Table 1. **Rare Earths and Other Elements in the Earth's Crust**

RE elements	Abundance, ppm	Other Elements	Abundance, ppm
lanthanum	18	carbon	320
cerium	46	chromium	200
praseodymium	5.5	manganese	1,000
neodymium	24	iron	50,000
samarium	6.5	cobalt	23
europium	0.5	nickel	80
gadolinium	6.4	copper	70
terbium	0.9	zinc	130
dysprosium	5.0	cadmium	0.3
holmium	1.2	mercury	1
erbium	4.0	silver	0.1
thulium	0.4	gold	0.005
ytterbium	2.7	platinum	0.005
lutecium	0.8	tin	40
scandium	10	lead	16
yttrium	28		

Table 2. **World Reserves of Rare Earths**

Country	Quantity, t × 10^3	Distribution, %
United States	6.471	13.6
Australia	754	1.6
India	1.939	4.1
South Africa	987	2.1
China	36.000	75.6
other	1.463	3.1
Total	*47.614*	*100*

Table 3. **Properties of the Lanthanides**[a]

Parameter	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium
CAS registry number	[7439-91-0]	[7440-45-1]	[7440-10-0]	[7440-00-8]	[7440-12-2]	[7440-19-9]	[7440-53-1]
Atomic number	57	58	59	60	61	62	63
Atomic weight	138.91	140.12	140.907	144.24	145	150.35	151.96
Melting point, °C	918	798	931	1021	1042	1074	822
Boiling point, °C	3464	3433	3520	3074	~3000	1794	1429
Density, g/cm^3	6.1453	6.770	677.3	7.007		7.520	5.234
Heat of fusion, kJ/mol[b]	6.201	5.179	6.912	7.134		8.623	9.221
Heat of sublimation, at 25°C, kJ/mol[b]	431.0	422.6	355.6	327.6	~348	206.7	144.7
Conduction electrons	3	3, 3.1	3	3	3	3	2
Crystal structure	Hcp	Dhcp	Dhcp	Dhcp		Rhombic	Bcc
Radius of atom, nm	0.1879	0.1824	0.1828	0.1821	0.1811	0.180	0.204
Curie point, °C							
Néel point, °C		~ 13				15	90
Valence in aqueous solutions	3	3.4	3	3	3	3	3.2
Color of oxide[c]	white	off-white[d]	black[e]	blue		cream	white, greenish tinge
Color of aqueous solution[e]	colorless	colorless[d]	green	rose	yellow	colorless	colorless
Ionic radius, nm	0.1061	0.103	0.1013	0.0995	0.0979	0.096	0.095

Parameter	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutecium
CAS registry number	[7440-54-2]	[7440-27-9]	[7429-91-6]	[7440-60-0]	[7440-52-0]	[7440-30-4]	[7440-64-4]	[7439-94-3]
Atomic number	64	65	66	67	68	69	70	71
Atomic weight	157.95	158.9254	162.50	164.930	167.26	168.934	173.04	174.97
Melting point, °C	1313	1365	1412	1474	1529	1545	819	1663
Boiling point, °C	3273	3230	2567	2700	2868	1950	1196	3402
Density, g/cm^3	7.9004	8.2294	8.5500	8.7947	9.066	9.3208	6.9654	9.8404
Heat of fusion, kJ/mol[b]	10.05	10.80	10.782	16.874	19.90	16.84	7.657	18.65
Heat of sublimation, at 25°C, kJ/mol[b]	397.5	288.7	290.4	300.8	317.10	232.2	152.1	427.6
Conduction electrons	3	3	3	3	3	3	2	3
Crystal structure	Hcp	Hcp	Hcp	Hcp	Hcp	Hcp	Fcc	Hcp
Radius of atom, nm	0.18013	0.17833	0.17743	0.17661	0.17566	0.17462	0.19392	0.17349
Curie point, °C	292.7	220	86	19	18	32		
Néel point, °C		230	178	133	84	56		
Valence in aqueous solutions	3	3	3	3	3	3	3	3
Color of oxide[c]	white	brown[f]f	yellowish white	yellowish white	pink	white, greenishtint	white	white
Color of aqueous solution[e]	colorless	colorless	yellow tint	yellow	pink	white, greenish tint	colorless	colorless
Ionic radius, nm	0.0938	0.0923	0.0908	0.0894	0.0881	0.0870	0.0858	0.850

[a] All elements are silvery in color.

[b] To convert joules to calories, divide by 4.184.

[c] RE_2O_3 unless otherwise noted.

[d] CeO_2.

[e] Pr_6O_{11}.

[f] Tb_4O_7.

Table 4. **Lanthanide and Yttrium Distribution in Mineral Sources, wt%[a]**

		Common Ores				Ionic Ores (China)		
		monazite[bc]	bastnaésite[d]	xenotime	loparite	ex-Kola-apatite	Xunwu	Longnam
Cerics	lanthanum	23.9	32	0.5	28.0	25.2	30	2.2
	cerium	46.0	49	5.0	57.4	46.3	7.0	1.0
	praseodymium	5.1	4.4	0.7	3.7	3.9	7.5	1.0
	neodymium	17.4	13.5	2.2	8.8	14.2	30	3.5
Yttrics	samayium	2.5	0.5	1.9	0.92	1.72	6.0	2.3
	europium	0.05	0.1	0.2	0.13	0.53	0.5	0.2
	gadolinium	1.50	0.3	4.0	0.22	1.61	4.0	6.0
	terbium	0.04	0.01	1.0	0.07	0.12	0.4	1.1
	dysprosium	0.69	0.03	8.7	0.09	1.15	2.0	7.5
	holmium	0.05	0.01	2.1	0.03	0.11	0.4	1.7
	erbium	0.20	0.01	5.4	0.07	0.15	1.0	4.5
	thulium	0.01	0.02	0.09	0.07	0.02	0.3	1.0
	ytterium	0.12	0.01	6.2	0.30	0.08	0.06	3.5
	lutétium	0.04	0.01	0.4	0.05	0.01	0.3	0.5
	yttrium	2.4	0.1	60.8	0.15	4.90	10.0	64.0

[a] On a basis of 100% REO Content.

[b] Australian monazite usually contains 4–8%thorium and 0.1–0.3% uranium.

[c] Indian monazite contains 8–10% thorium.

[d] Bastnaesite contains 0.1–0.2% thorium.

Table 5. **World Production of Rare-Earth Ores, wt% of REO Content**[a]

Ore	1990	1992	1995
Bastnaesite			
China	8,500	10,000	31,000
USA	22,700	20,700	20,000
Subtotal	31,200	30,700	51,000
Monazite			
Australia	8,000	4,000	3,000
Brazil	1,100	1,100	400
India	2,400	2,500	2,500
Malasiya	1,900	1,000	—
South Africa	1,000	700	400
USA	2,100	800	—
Others (Thailand, Srilanka, Zaire, etc)	600	600	300
Subtotal	*17,100*	*10,700*	*6,600*
Ion adsorption—China	8,000	8,000	9,000
Xenotime—Malasiya	150	100	250
Loparite—Russia	8,500	8,000	2,000
Total	*64,950*	*57,500*	*68,850*

[a] Various sources, Rhodia estimation.

Table 6. **Major lanthanide Producers**[a]

Europe

Rhodia Terres Rares (SO)
Treibacher (MA-SO)
Rare Earth Products (MA)
Norsk Hydro (C)
Silmet, (Estonia) (C-SO)

USA

Molycorp (C-SO-MA)
Rhodia (SO-MA)

Japan

Anan Kasei — joint venture Rhodia and Santoku Metal Industry (SO)
Santoku Metal Industry (MA)
Shinetsu, Mitsui, Nippon Yttrium, Shin Nihon Metal, Showa Denko (SO-MA)

China

More than 50 producers, most of them quite small (C-SO-MA)
Major companies:
- In the North: Baogang, Luxi Rhone (JV with Rhodia), Hangua,Hefa, Gansu and Harbin
- In the south: Zhujiang, Yixing, Yangjiang, Yaolong, Li Yang, AMR (Zibo and Jiang Yin)
- Several producers in Sichuan

Others

Indian Rare Earth (C)
Nuclemon — Brazil (SO - mischmetal)

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[a] C = RE concentrates;SO = salt and oxides; MA = metals and alloys.

Table 7. **Acute Lethal Doses of Lanthanide Chlorides for Mice**

Element	LD_{50}, mg/kg	Administration Route[a]
La	370	Ip
Ce	350	Ip
Pr	360	Ip
	4500	Oral
Nd	600	Ip
	5250	Oral
Sm	585	Ip
	< 2000	Oral
Eu	550	Ip
Gd	550	Ip
	< 2000	Oral
Tb	550	Ip
	5100	Oral
Dy	585	Ip
	7650	Oral
Ho	585	Ip
	7200	Oral
Er	535	Ip
	6200	Oral
Tm	485	Ip
	6250	Oral
Yb	395	Ip
	6700	Oral
Lu	315	Ip
	6700	Oral

[a] Intraperitoneal.

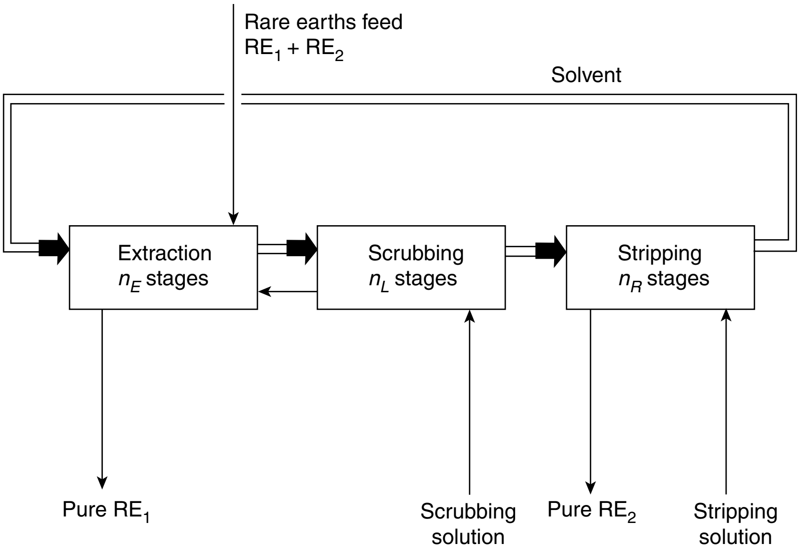

Fig. 1. Liquid & liquid extraction battery.