Extractive metallurgy of rare earths

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A short account is given on the extraction of rare earths from monazite sand, bastnasite ore, and phosphate rock of igneous origin. This includes mineral beneficiation, leaching methods, fractional crystallisation [of historical interest], ion exchange, solvent extraction, precipitation from solution, and reduction to metals.

On donne un bref compte-rendu de l'extraction des terres rares à partir de sable monazité, de minerai de bastnaésite et de roche phosphatée d'origine ignée. Ceci inclut l'enrichissement du minéral, les méthodes de lixiviation, la cristallisation fractionnelle (d'intérêt historique), l'échange d'ion, l'extraction par solvant, la précipitation à partir de solution et la réduction en métaux.

This paper is part of a special issue on Advances in Rare Earths: From Mine to Materials

Historical introduction

Although most of the rare earth metals were discovered in Sweden, the industrialisation started in the Austrian Empire. This was due to the fact that the Swedish chemist Jons Fridrik Bahr (1815–1875) from Uppsala went to Heidelberg in Germany in 1855 to analyse some rare earth minerals by the spectroscope discovered recently by chemistry professor Robert Bunsen (1811–1899) and his colleague physicist Gustav Kirchhoff (1824–1887). Few years later Carl Auer (1858–1929) from Vienna went also to Heidelberg to study under Bunsen. He was assigned the task to separate the rare earths from these minerals. On his return home, Carl Auer took with him the remaining minerals to continue his studies at the University of Vienna.[1,2]

While in Heidelberg, Carl Auer had noted the remarkable light-emitting powers of the rare earth oxides when they were inserted into the flame of a Bunsen burner. In Vienna he put this observation into practice by inventing the gas mantle, a stocking made of cotton thread and soaked in a solution of the earth metal salts. After the organic matter was burned off, a skeleton of the metal oxide was left. This emitted light when heated in a laboratory Bunsen burner. In 1887, he started a factory at Atzgersdorf, a suburb of Vienna, to separate the rare earths salts necessary for preparing the soaking solution for manufacturing the gas mantles for lighting the streets in Vienna. He also sold the solutions to customers in Germany, England, and USA. The marked

for gas mantle declined later when the Edison lamp was invented at the beginning of the twentieth century.

The second industrial application of rare earths came when Carl Auer recalled the preparation of metallic cerium by his colleagues at Bunsen's laboratory and the sparking of the metal when scratched or drawn over a rough surface. He conceived that this sparking action may be utilised for ignition purposes. However, cerium would be a too costly material. He, therefore, prepared a cerium–iron alloy and found out that when the alloy contained 30%Fe it gave the best sparking effect suitable for ignition of gases. The 'Auer lighter' soon became as famous as his incandescent mantle when it was produced on large scale in 1903. Production reached 1 000 000 kg annually in 1930; it served to prepare 500 million flints which replaced six billion boxes of matches. This work was conducted at his new factory at Treibach in Carinthia which he took possession in 1900 and which is today a successful metallurgical plant known as Treibacher Chemische Werke in Austria.

Rare earths elements

Originally, the term rare earths was only used for the oxides, R_2O_3, which are similar to one other in their chemical and physical properties and are therefore difficult to separate. Within the rare earth group, the elements scandium, yttrium, and lanthanum differ in their atomic structure from the elements cerium to lutetium. The term lanthanides was abbreviated Ln by Chemical Abstracts. Scandium occupies a special position with respect to this classification and its other properties, and therefore does not belong to either of these groups. The rare earth elements always occur in nature in association with each other. The isolation of groups of rare earth elements or of individual elements requires costly separation and fractionation processes owing to the great

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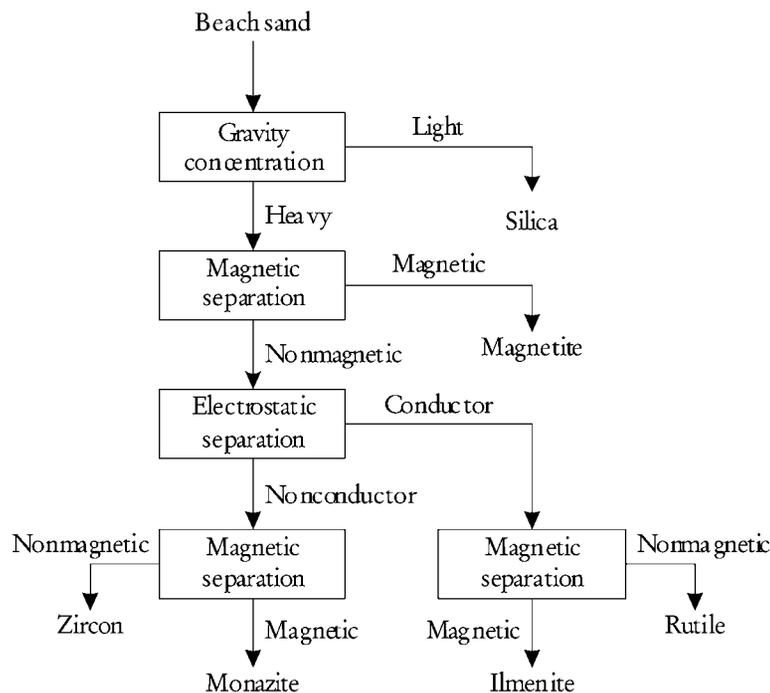
1 Separation of monazite and other valuable minerals from monazite sand by physical methods

similarity of the chemical and physical properties of their compounds, which explains why the history of their discovery has extended over such a long period.

The word 'rare', when used to describe this group of elements, originates from the fact it was thought that these elements could only be isolated from very rare minerals. Considering their abundance in the Earth's crust, the term rare is now inappropriate. These elements are lithophilic and are therefore concentrated in oxidic compounds such as carbonates, silicates, titano-tantalo-niobates, and phosphates.

The abundance of the rare earth elements taken together is quite considerable. Cerium, the most common rare earth, is more abundant than cobalt. Yttrium is more abundant than lead, whereas Lu and Tm are as abundant as Sb, Hg, Bi, and Ag. For all practical purposes promethium does not occur in nature. It forms only in nuclear reactors.

Raw material

The major raw material for rare earths is monazite sand, xenotime, bastnasite, and phosphate rock.

Monazite and xenotime

Monazite derives its name from Γρεεκ μεανινγ *to be alone*. The mineral monazite is a lanthanide phosphate containing some thorium and small amounts of uranium. It is widely distributed in the Earth's crust. It occurs in small proportions in granites. When such rocks are weathered, grains of monazite are carried by waters, then deposited at the mouths of rivers, together with the heavier constituents of the parent rock, to form black sands known as monazite sand. The monazite in these sands is usually present in rounded grains, showing that the grains have previously been rolled to and fro in streams of water. Monazite sands occur mainly in Brazil, India, Australia, and USA. Xenotime is also a lanthanide phosphate but the individual lanthanides occur in a different proportion from that in monazite. It occurs mainly in South East Asia associated with alluvial tin deposits.

Monazite sand and xenotime can be easily concentrated from the sands by physical methods. For example, a monazite sand containing 1% monazite can be concentrated by gravity, magnetic, and electrostatic methods to a concentrate containing 85% monazite (Fig. 1). Some physical properties of monazite and xenotime concentrates are given in Table 1. A chemical analysis of the concentrates is given in Table 2. The composition of the lanthanide fraction in monazite, in xenotime, and bastnasite is given in Table 3. Scandium, although in the same group with yttrium, lanthanum,

Table 1 Physical properties of lanthanide phosphate minerals

	Monazite	Xenotime
Colour	Yellow to red brown	Pale yellow to brownish green
Specific gravity	4·9–5·5	4·45–4·59
Hardness (Mohs)	5	4·5
Crystal structure	Monoclinic	Tetragonal

Table 2   Chemical analysis of lanthanide phosphate concentrates

	Monazite concentrate/%	Xenotime concentrate/%
P_2O_5	24–29	…
Ln_2O_3*	55–65	52–63
ThO_2	5–10	1–3
U_3O_8	0·2–0·4	0·5–3·5
SiO_2	1–3	…
CaO	0·2–0·8	…
Fe_2O_3	1–2	…
Al_2O_3	0·1–0·8	…
ZrO_2	0·7	2–3
SnO_2	…	0–9

*Ln, lanthanide.

and the lanthanides, is not present in any of these minerals.

Monazite and xenotime are the main source of thorium and the lanthanides; uranium is recovered as a byproduct.

Bastnasite

The most important mined rare earth deposit is at the Mountain Pass Mine in California, where up to 40 000 t/a bastnæsite ore concentrate (70% REO) is produced by ore beneficiation. Other important bastnæsite deposits are in Burundi, Madagascar, and in Bayan Obo, near the town of Baotou in Inner Mongolia in China. The bastnasite, with monazite, is associated with magnetite–hematite–fluorspar. Bastnasite is a fluorocarbonate, $Ln_2(CO_3)_3$, LnF_3, or $LnFCO_3$.

Other complex minerals

Minerals of this type are oxidic ores containing titanium, niobium, tantalum, uranium, and thorium; for example:

(i) Euxenite $(Y,Ce)(Nb,Ta,Ti)_2O_6$
(ii) Samarskite $(Y,Ce)_4(Nb,Ta,Ti)_2O_6$
(iii) Fergusonite $(Y)(Nb,Ti,Ta)O_4$
(iv) Betafite $(U,Ca,Y,Ce_2(Nb,Ta,Ti)_2O_6(OH)$

Useful concentrations (up to 5%) of rare earth elements occur in apatite and up to 10% in pyrochlor $(Na,Ca,Ce)_2(NbTa,Ti)_2(O,OH,F)_7$, and loparite (Na,Ca,

Ce)$_2$(Nb,Ta,Ti)$_2$O$_6$ in the Kola Peninsula and also in most uranium minerals as trace substituents.

Scandium occurs in trace amounts in most rare earth minerals. In many minerals, scandium is present in a dispersed state. Wolframite and cassiterite can contain up to 1% scandium, so that scandium is a byproduct of the production of tungsten and tin. Uranium minerals contain much smaller amounts of scandium, but, since uranium is produced in relatively large quantities, scandium is produced in appreciable quantities also.

Phosphate rock

Tonnage wise, phosphate rock is the most important as compared with the other material; about 120 millions tons of rock are treated annually while only 30 000 tons of monazite and xenotime. However, no production of rare earths from this source is actually conducted. Apatite is the principal constituent of phosphate rock. The mineral received its name from the Greek word meaning *I deceive* when it was realised that it was frequently confused with other mineral species, including beryl and tourmaline, prior to the latter part of the eighteenth century. Phosphate rock is the main raw material for the production of phosphatic fertilisers. Phosphate rock is composed mainly of:

(i) Fluorapatite, $Ca_{10}(PO_4)_6F_2$
(ii) Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$
(iii) Carbonato-apatite, $Ca_{10}(PO_4)_6CO_3$

Depending on the proportion of each component, the rock may be frankolite, kunskite, or colophanite (Table 4). Low-grade phosphate rock, may contain appreciable amounts of aluminium phosphate wavellite, $AlPO_4$, and/or calcium–aluminium phosphate, crandallite.

Phosphate rock occurs either as a sedimentary deposit, e.g. in Florida and North Africa, or as igneous rock, e.g., in Kola peninsula, Russia. Sedimentary phosphates supply about 85% of the phosphate rock for the industry. Typical analyses of phosphate rocks are given in Table 5. Phosphate rock is used for the manufacture of fertilisers and elemental phosphorus. Pure phosphoric acid for other uses than fertilisers is prepared from the latter product although attempts are being made to prepare a moderate grade phosphoric acid by leaching the rock.

Table 3   Typical composition of lanthanides in monazite, xenotime, and bastnasite

	Lanthanide oxide	Monazite/%		Xenotime/%		Bastnasite/%	
Light	La_2O_3	23·0		0·5		32·0	
	CeO_2	46·5	93	5·0	8·4	49·0	98·9
	Pr_6O_{11}	5·1		0·7		4·4	
	Nd_2O_3	18·4		2·2		13·5	
Heavy	Sm_2O_3	2·3		1·9		0·5	
	Eu_2O_3	0·07		0·2		0·1	
	Gd_2O_3	1·7		4·0		0·3	
	Tb_4O_7	0·16		1·0		0·01	
	Dy_2O_3	0·52	7	8·7	91·6	0·03	1·37
	Ho_2O_3	0·09		2·1		0·01	
	Er_2O_3	0·13		5·4		0·01	
	Tm_2O_3	0·013		0·9		0·2	
	Yb_2O_3	0·061		6·2		0·01	
	Lu_2O_3	0·006		0·4		0·1	
	Y_2O_3	2		60·8		0·1	
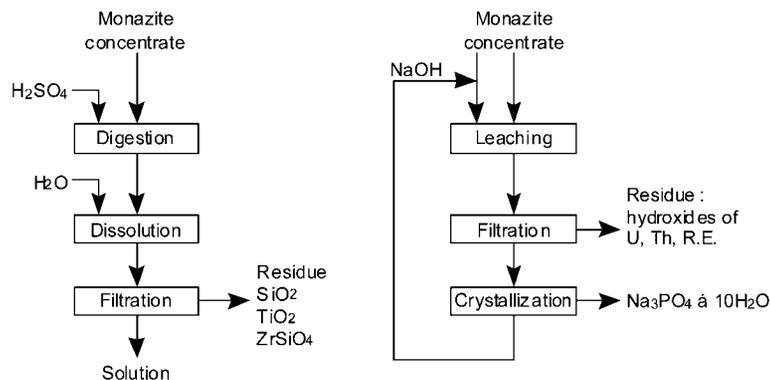
2 Leaching methods for monazite sand

# Recovery methods[3,4]

Monazite/xenotime

There are two methods used for treating these concentrates: the sulfuric acid and the sodium hydroxide methods (Fig. 2). The decision between one and the other is an economic one; for example in Brazil, the NaOH process is used because of a shortage in sulfuric acid. However, the general tendency today is to use the NaOH process because it is possible to recover sodium phosphate as a byproduct.

Sulphuric acid method

This method involves two steps:[5]

Digestion

The concentrate is digested in a closed reactor or baked in a rotary kiln with $93\%H_2SO_4$ at about 200°C for 2–4 h at an acid to concentrate ratio of 2:1. An acid-to-concentrate ratio lower than this, results in incomplete reaction while higher ratio interferes with subsequent operations. Also, with temperatures lower than the above, the reaction will be too slow, and if higher than 300°C, insoluble thorium pyrophosphate is liable to be formed. The reaction is exothermic and can be represented by the equation

$$2LnPO_4 + 3H_2SO_4 \rightarrow Ln_2(SO_4)_3 + 2H_3PO_4$$
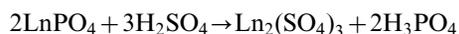
Thorium and uranium are also transformed into sulphates. Due to the high temperature used the product is a thick paste of anhydrous sulphates.
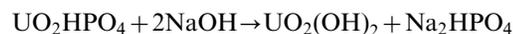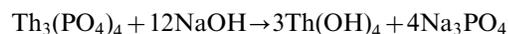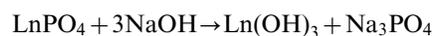
Dissolution of reaction mass

The resulting mass is allowed to cool, diluted with water to allow the insoluble material to settle, and then filtered. Typical analysis of the filtrate is shown in Table 6. The clear leach solution is then subjected to further treatment to separate thorium, uranium, and the

lanthanides. The residue contains most of the radio-active decay products of uranium and thorium.

Sodium hydroxide method

The sodium hydroxide process differs from the acid process in that water soluble phosphates are formed while the lanthanides, thorium, and uranium form insoluble hydroxides

$$LnPO_4 + 3NaOH \rightarrow Ln(OH)_3 + Na_3PO_4$$

$$Th_3(PO_4)_4 + 12NaOH \rightarrow 3Th(OH)_4 + 4Na_3PO_4$$

$$UO_2HPO_4 + 2NaOH \rightarrow UO_2(OH)_2 + Na_2HPO_4$$

Optimum conditions of digestion are 40–50%NaOH, 160°C, NaOH to concentrate 2:1, time of reaction about 3 h. Sodium hydroxide should be free from carbonate otherwise uranium will be lost in solution, since it forms soluble carbonates. The product is a thick paste; it is slurried in water then filtered, washed, and dried. The cake obtained is composed of hydroxides of uranium, thorium, and lanthanides, containing small amounts of phosphate; it is dissolved in acid for further separation. The leach solution contains the unreacted NaOH as well as the phosphorus originally present in the concentrate. When allowed to cool to about 60°C, trisodium phosphate hydrate hydrate ($Na_3PO_4.10H_2O$) crystallises out. After separation, the solution typically analyse 47·4%NaOH, 0·5%Na_3PO_4, 1·5%Na_2SiO_3, and can be recycled.

Thorium problem

The association of thorium with rare earths creates a health hazard problem because of its radioactivity. Thorium disintegrates to radium 224 which in term disintegrates to radon 220 [thoron] which is a gas that

Table 4 Main types of phosphate rock

Type	Composition
Frankolite	Isomorphous mixture of fluoroapatite and carbonate apatite in the ratio 3:1
Kunskite	Isomorphous mixture of fluoroapatite and carbonate apatite in the ratio 2:1
Colophanite	An ultra microcrystalline variety of frankolite
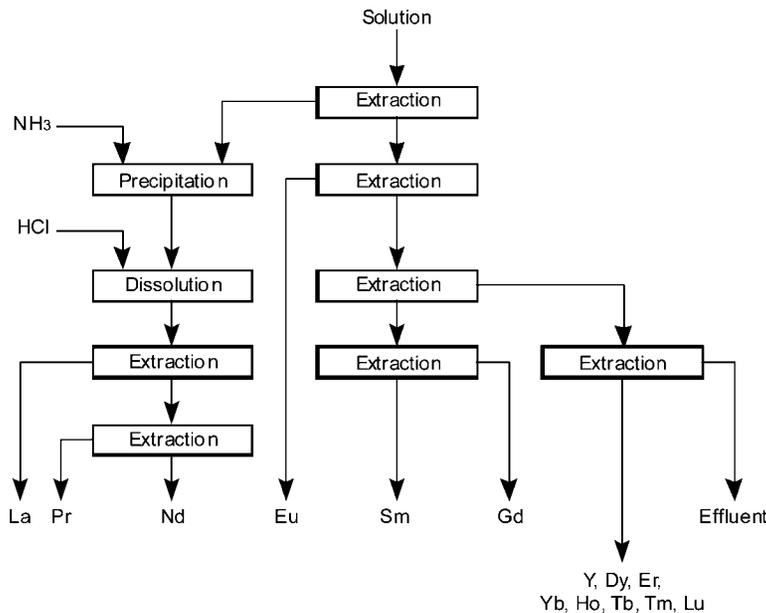
3 Separation of lanthanides from bastnasite by extraction with D2EHPA (Molycop process)

decays to polonium 216 which is a solid. Hence, the possibility of respiration of the gas and the deposition of the radioactive decay product in the lungs.[6] Methods must be devised to avoid this problem.

Bastnasite

In the Molycorp process, the mineral is concentrated to 60% by flotation and then calcined, converting the cerium to the tetravalent state. It is then treated with hydrochloric acid, which causes only the trivalent rare earth elements to go into solution, leaving behind 65–80%CeO_2 (Fig. 3). The individual earths are then separated by solvent extraction (see later).

Phosphate rock

Phosphate rock is insoluble in water, but when treated with acids water soluble monocalcium phosphate, citrate soluble dicalcium phosphate, and phosphoric acid can be obtained. The first two can be used directly as a fertiliser, while the latter is neutralised with ammonia to produce an ammonium phosphate fertiliser. The acids used for treating the rock are the following.

Sulphuric acid

Leaching with sulphuric acid is the most common method for treating phosphate rock. Depending on the amount of acid used, normal superphosphate or phosphoric acid is produced:

- When a small amount of acid is used the product is known as normal superphosphate

$$Ca_{10}(PO_4)_6F_2 + 2H_2SO_4 + 2H_2O \rightarrow$$
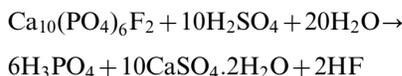$$[3Ca(H_2PO_4)_2 \cdot 2H_2O + 7CaSO_4 \cdot 2H_2O] + 2HF$$
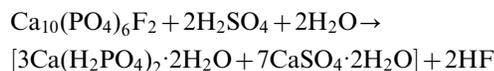
- When a large amount of sulphuric acid is used, phosphoric acid is produced. The reaction is largely complete in few minutes. Three processes are used (Table 7).

Hemihydrate process. Conducted above 80°C and produces 30% acid

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 5H_2O \rightarrow$$
$$6H_3PO_4 + 10CaSO_4.1/2H_2O + 2HF$$
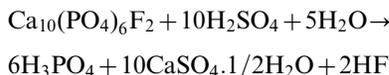
Dihydrate process. Conducted below 80°C and produces 60% acid

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow$$
$$6H_3PO_4 + 10CaSO_4.2H_2O + 2HF$$

More time is needed, about 8 h, to allow for the proper formation of crystals that can be removed easily by filtration.

Table 5   Analysis of typical phosphate rock

	%		%
P_2O_5	29–38	Cl	0·01–0·7
CaO	48–52	CO_2	2–6
MgO	0·2–0·8	SO_3	1–3
Fe_2O_3	0·2–1	SiO_2	0·2–5
Al_2O_3	0·1–1	Organic carbon	0–0·4
Na_2O	1–2	Uranium	0·01–0·02
K_2O	0·1–0·4	Ln_2O_3	0·1–1
F	3·3–4·3		

Table 6   Typical analysis of monazite leach solution, pH=0·05

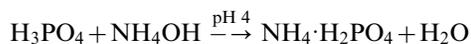|	g L^{-1}		g L^{-1}
Th	5·3	Nd_2O_3	7·0
U	0·2	Sm_2O_3	1·3
Ce_2O_3	16·0	SO_4^{2-}	128·0
La_2O_3	8·5	PO_4^{3-}	26·0
Pr_2O_3	1·7	…	…

Table 7 Production of phosphoric acid by H₂SO₄ route

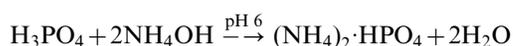|	Hemihydrate process	Dihydrate process	Hemihydrate–dihydrate process
Crystal form	$CaSO_4 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	Initially $CaSO_4 \cdot \frac{1}{2}H_2O$, then $CaSO_4 \cdot 2H_2O$
Crystal size/μm	15–30 (without modifier) 40–60 (with modifier)	40–60	
P_2O_5 losses in crystal/%	3–6	Lower	
Temperature/°C	>80	<80	> 80
Phosphoric acid concentration %P_2O_5–%H_3PO_4	45–54	28–30	
Washing system	Vacuum belt filter (Lurgi)	Counter-current in thickeners (Dorr)	
Phosphoric acid yield/%	91	93	99
Energy requirement	Low	High	
	Because less water to be evaporated later	Because more water to be evaporated later	

Hemihydrate–dihydrate process. Conducted above 80°C to produce the hemihydrate crystals, then slurry is agitated for few hours to allow the crystallization of the dihydrate.

There are two types of wet process phosphoric acid: the 'black acid' and the 'green acid'. The black acid is the one usually produced and its black coloUr is due to the organic matter originally present in the rock. If the organic matter is above certain limits it is usually eliminated by calcining in an oxidizing atmosphere. The acid derived from such treated rock is the green acid because it has a green tint. Both acids are a commercial product, and is shipped to fertiliser producers. It is usually neutralized by ammonia to form ammonium phosphates:
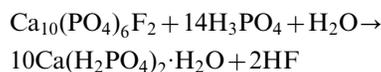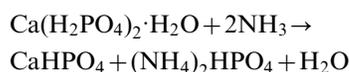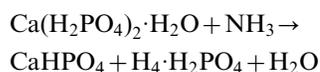
- Monoammonium phosphate (46% P_2O_5, 11% N)

$$H_3PO_4 + NH_4OH \xrightarrow{pH\,4} NH_4 \cdot H_2PO_4 + H_2O$$

- Diammonium phosphate (46%P_2O_5, 18%N)

$$H_3PO_4 + 2NH_4OH \xrightarrow{pH\,6} (NH_4)_2 \cdot HPO_4 + 2H_2O$$

Or, reacted with a fresh batch of phosphate rock in a rotary kiln to produce triple superphosphate (40–48%P_2O_5)

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + H_2O \rightarrow$$
$$10Ca(H_2PO_4)_2 \cdot H_2O + 2HF$$

This in turn is usually treated by ammonia to form ammoniated triple superphosphates

$$Ca(H_2PO_4)_2 \cdot H_2O + NH_3 \rightarrow$$
$$CaHPO_4 + H_4 \cdot H_2PO_4 + H_2O$$

$$Ca(H_2PO_4)_2 \cdot H_2O + 2NH_3 \rightarrow$$
$$CaHPO_4 + (NH_4)_2HPO_4 + H_2O$$

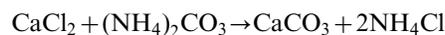### Hydrochloric acid

Hydrochloric acid is used sometimes to leach phosphate rock to produce either monocalcium phosphate fertiliser

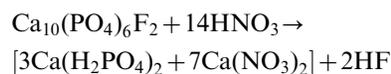$$Ca_{10}(PO_4)_6F_2 + 14HCl \rightarrow 3Ca(H_2PO_4)_2 + 7CaCl_2 + 2HF$$

or phosphoric acid

$$Ca_{10}(PO_4)_6F_2 + 20HCl \rightarrow 6H_3PO_4 + 10CaCl_2 + 2HF$$

Calcium chloride is then removed as $CaCO_3$ by precipitation with $(NH_4)_2CO_3$

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4Cl$$

Nitric acid

Nitric acid is also used to produce a fertiliser known as nitrophosphate

$$Ca_{10}(PO_4)_6F_2 + 14HNO_3 \rightarrow$$
$$[3Ca(H_2PO_4)_2 + 7Ca(NO_3)_2] + 2HF$$

or phosphoric acid

$$Ca_{10}(PO_4)_6F_2 + 20HNO_3 \rightarrow$$
$$6H_3PO_4 + 10Ca(NO_3)_2 + 2HF$$
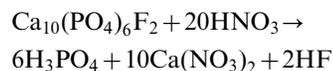
Calcium nitrate is separated by cooling to –10°C then centrifuging the crystals of $Ca(NO_3)_2 \cdot 4H_2O$. It is usually transformed to ammonium nitrate by reaction with ammonium carbonate.

Present tendency

The first fertiliser produced in industry was normal superphosphate. Because of its low concentration in P_2O_5, its production has declined gradually in the past years and its place was taken over by triple superphosphate, and more recently by mono- and diammonium phosphates. Over 70% of the phosphate rock is used in making phosphoric acid by the wet process. Phosphoric acid produced by leaching phosphate rock is impure and cannot be used for manufacturing phosphates needed for the food or detergent industries unless it undergoes extensive purification, e.g. extraction by organic solvents.

Phosphate rock of sedimentary origin contains about 0·5% lanthanide oxides while igneous phosphate, e.g. in Kola Peninsula, contains about 1% lanthanide oxides. During the manufacture of phosphoric acid about 70%

is lost in the gypsum. However, if acidulation is conducted by nitric acid all will go into solution and can be recovered by organic solvents. In Finland, the lanthanides were recovered commercially by Kemira Oy from phosphate rock during 1965–1972 using organic solvents. It is believed that a similar operation is in existence in Russia.

Recovery from leach solution

Separation of thorium and the lanthanides from sulfuric acid leach solution of monazite and xenotime concentrates is based on oxalate precipitation

$$Th^{4+} + 2(C_2O_4)^{2-} \rightarrow Th(C_2O_4)$$

$$Ln^{3+} + 3(C_2O_4)^{2-} \rightarrow Ln_2(C_2O_4)_3$$
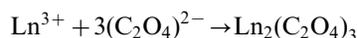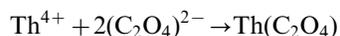
Uranium is not precipitated. The oxalate filter cake is then digested with NaOH solution to convert the oxalates into hydroxides and recover sodium oxalate for recycle

$$Th(C_2O_4)_2 + 4OH^- \rightarrow Th(OH)_4 + 2(C_2O_4)^{2-}$$

$$Ln_2(C_2O_4)_3 + 6OH^- \rightarrow 2Ln(OH)_3 + 3(C_2O_4)^{2-}$$
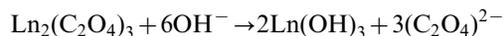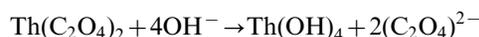
The hydroxides are then calcined, and the resulting oxides dissolved in nitric acid for later separation of thorium by solvent extraction.

Ion exchange

When the acid leach solution containing the lanthanides is allowed to flow through a cation exchange resin bed in hydrogen or ammonium form, they will be sorbed by the resin. However, the resin has no selectivity for one of the lanthanides as compared with the other, and therefore practically no separation can be achieved. In order to separate the different metals, use is made of their different affinities toward complexing agents in solution. When a buffered solution of some negative ion species, which forms a stable complex with the lanthanides, is passed through the column, a competition for the lanthanide ions between the aqueous phase and resin phase will be set up. When equilibrium conditions are maintained, an individual lanthanide ion continuously exchanges between the complexing ion and the resin. The positive ion in the complexing solution replaces the lanthanide ions at the rear edge of the band, so that the lanthanide band is driven down the resin bed. Because the stability constants of the lanthanide complexes differ appreciably from one lanthanide to another, the most stable complex moves faster down the column.
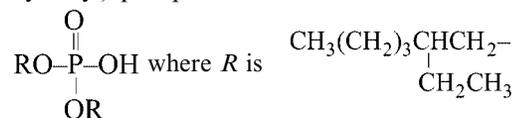
Different complexing agents were used as eluents for example, 5% citric acid adjusted at pH 3 by ammonium hydroxide, 0·1% citric acid adjusted at pH 5–8 by ammonium hydroxide, 1M lactate at pH 3, and 0·26M ethylene diamine tetraacetic acid (EDTA) at pH 3·6. Uniform rate of elution has been obtained by continuously varying the pH of the eluent. The eluent at pH 3·19 was neutralized at a predetermined rate with 1 M lactic acid buffered with ammonia to pH 7 to give a rate of change of pH of +0·1 unit/hour.

In the separation of the lanthanides, the concentrate is dissolved in hydrochloric acid and diluted with water to make up the feed solution for the cation exchange columns 1·5 m long ξ 15 cm diameter in the ammonium form. The solution of the chlorides is loaded on four columns which are connected together in series. The sorbed band is first washed with distilled water then eluted with 0·1% citrate solution at pH 8 at a flow rate of 0·1–1·2 L min^{-1} into a series of six similar columns. Under these conditions, the front of the adsorbed band advances at the rate of about one resin bed per day.

The light lanthanides are sorbed on the first two columns, and the heavy lanthanides are concentrated on the last two columns, while the bulk of yttrium and a considerable portion of terbium and dysprosium are concentrated on the two middle columns. Each set of two columns is further fractioned by elution through a series of eight smaller columns (1·5 m long ξ 10 cm diameter) at a much smaller flowrate of 0·5 L min^{-1}. Each of these small columns is loaded with a pure metal then separately eluted in a container. The pure lanthanide is recovered from the solution by precipitation with oxalic acid. Individual lanthanides up to 99·99% purity from monazite are produced on a commercial scale based on elution with EDTA (Fig. 4).

Solvent extraction

The solvent used for the separation of the lanthanides from leach solution of bastnasite concentrates is di (2-ethylhexyl) phosphoric acid known as D2EHPA

$$RO-\overset{\displaystyle O}{\underset{\displaystyle OR}{\overset{\|}{P}}}-OH \quad \text{where } R \text{ is} \quad \underset{\displaystyle CH_2CH_3}{CH_3(CH_2)_3\overset{|}{C}HCH_2-}$$

Cerium is already separated in the leaching step since it is transformed into soluble cerium(IV) compound and is recovered from the residue. Each extraction step includes numerous stages of contact with the extractant and the stripping agent under certain conditions of organic/aqueous ratio, and extractant and stripping agent concentrations. The plant is computerized and is fully automated (Fig. 5).
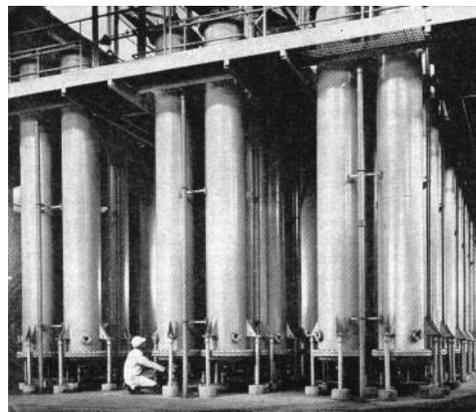
4 Ion exchange columns for separation of lanthanides at Michigan Chemical Corporation, St. Louis, Michigan[5]
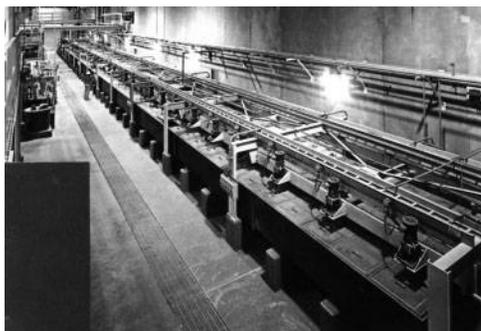
5   **Inside of Molycorp's rare earths extraction plant at Mountain Pass, California**[5]

Cerium salts are produced by liquid–liquid extraction from rare earth cerium containing solutions. Cerium can be extracted out of cerium nitrate–nitric acid solutions in a few steps in the form of a cerium(IV) nitrate complex in tributyl phosphate and therefore separated from the accompanying trivalent rare earth elements, which form less stable nitrate complexes. Purities of 99·99% and better can be achieved.

Fractional crystallisation

This is one of the oldest methods for the separation of rare earths and is now obsolete. It depends on small differences which are magnified by repeated operations. It has been replaced by ion exchange and solvent extraction which are faster and less tedious.
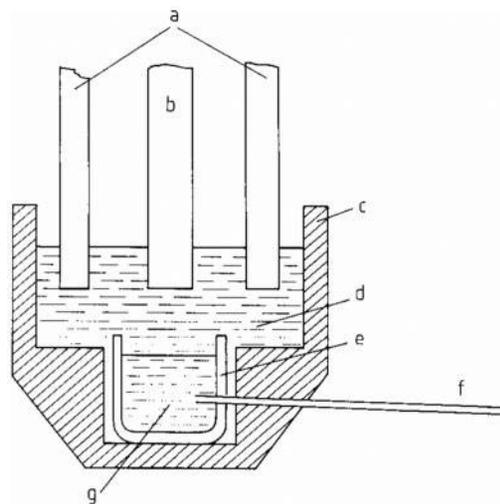
Metal production

Mischmetal

Mischmetal (from German: *Mischmetall* – 'mixed metals') is an alloy of rare earth elements in various naturally-occurring proportions. Monazite-derived Mischmetal typically is about 48% cerium, 25% lanthanum, 17% neodymium, and 5% praseodymium, with the balance being the other lanthanides. Bastnasite derived Mischmetall is higher in lanthanum and lower in neodymium.

Mischmetal is the lowest priced rare earth metal because no expensive chemical separation is needed to produce it. It is produced predominantly by fused salt electrolysis of rare earth chlorides. Mischmetal was first produced industrially in 1908 by Auer von Welsbach, who succeeded in finding an outlet for surplus rare earth in the production of lighter flints. At that time, monazite was used exclusively as the source of thorium needed for the manufacture of incandescent mantles.

Oxide process

A process developed by the US Bureau of Mines and further improved by Santoku Metal Industries in Japan, produces mischmetal from rare earth oxides. The process is similar to Hall–Héroult process for aluminum electrolysis. It avoids emission of chlorine and the consequent expensive purification of off-gas. Rare earth oxides are dissolved in an electrolyte consisting of alkali fluorides (to improve conductivity), alkaline earth fluorides (to reduce melting point), and rare earth fluorides (to improve the solubility of rare earth oxides) and are

a graphite anodes; *b* molybdenum cathode; *c* graphite crucible; *d* liquid electrolyte; *e* molybdenum crucible; *f* tapping pipe; *g* molten mischmetal[4]

6   **Electrolysis cell for production of mischmetal from oxides**

reduced electrolytically to the rare earth metals. The electrolysis cell (Fig. 6) consists of a graphite crucible with graphite anode and molybdenum cathode, working under an inert gas atmosphere to prevent oxidation of the construction materials. The electrolyte is initially melted by resistance heating. Electrolyte and electrodeposited rare earth metals are kept liquid by the joule heat. A cell produces ca. 500 kg of metal per day. If bastnasite is a raw material, it must be specially purified prior to electrolysis.

Individual rare earth metals

The rare earth metals are produced, both on the laboratory and industrial scale, by molten salt electrolysis and metallothermic reduction.

Fused salt electrolysis

La, Ce, Pr, Nd can be produced by molten salt electrolysis of a mixture of anhydrous rare earth chlorides and fluorides with alkali and alkaline earth chlorides and fluorides. This process is made possible by the lower melting points of the cerium earth metals, whereas the yttrium earth metals have higher melting points and therefore do not melt during the electrolysis process. A lower melting point can be achieved by using a cathode (e.g. Cd, Zn) that forms a low melting alloy with the rare earth metal. This alloy can also have a lower density than the fused salt (e.g. Mg), so that it rises to the surface and can be removed from the fused salt. The alloying element can then be removed by distillation. By using molten Cd or Zn as cathode, Sm, Eu, and Yb can also be produced.

The reactivity of the rare earth metals causes problems in the choice of construction materials of the electrolysis furnace. High purity metals can be produced by using molybdenum, tungsten, or tantalum as the crucible and cathode materials. For industrial manufacture, iron crucibles with ceramic or graphite linings are used. If halogens are liberated during the electrolysis, carbon is used as the anode material.
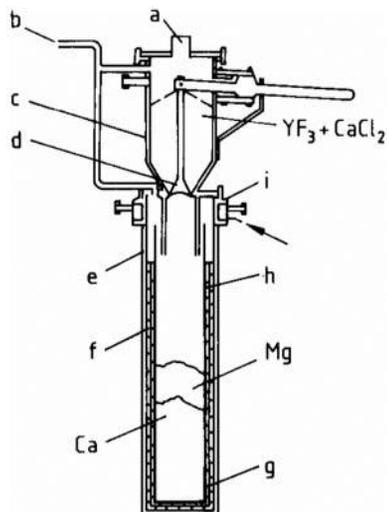
a sight glass; *b* vacuum connection and helium inlet; *c* charging tunnel; *d* charging shut-off mechanism; *e* steel reaction chamber; *f* titanium reaction crucible; *g* graphite insulation; *h* titanium or steel supporting crucible; *i* water cooling[4]

7   Reduction apparatus for production of yttrium

Metallothermic reduction

Metallothermic reduction of the rare earth oxides and anhydrous rare earth chlorides and fluorides can be used to produce high purity rare earth metals, especially Gd to Lu, including Y. Alloys can also be produced by this process. Alkali metals, alkaline earth metals, and aluminium are suitable reducing agents, as are alloys of these elements with each other. Lithium, which forms low melting LiF, is of special importance, as is calcium. The use of Mg or Zn has the additional advantage of producing a low melting alloy with the rare earth metal. The alloying elements can be removed by distillation, yielding the pure rare earth metal.

For the production of La, Ce, Pr, and Nd, the metallothermic reduction of the anhydrous rare earth chlorides is preferred. The reaction is carried out in crucibles lined with MgO at temperatures up to 1100°C. At higher temperatures, reaction takes place between the rare earth metal and the MgO, and the rare earth chlorides vaporize. The process is not suitable for the production of Sm, Eu and Yb, which are merely reduced to the divalent state.

Gd to Lu and Sc, which have higher melting points, are obtained by reduction of the fluorides with Ca at 1500–1600°C. The reduction is carried out in tantalum crucibles under a protective gas or in vacuum. The reaction temperature can be reduced by adding a booster such as iodine, which gives a slag with good flow properties that separates cleanly from the metal. Praseodymium is produced by reduction of the fluoride with lithium. The Carlson–Schmidt apparatus is shown in Fig. 7. This was used between 1957 and 1959 to produce high-purity yttrium metal in 50 kg batches.

Sm, Eu, and Yb can be produced by reduction of the oxides with La or the cheaper cerium mischmetal at
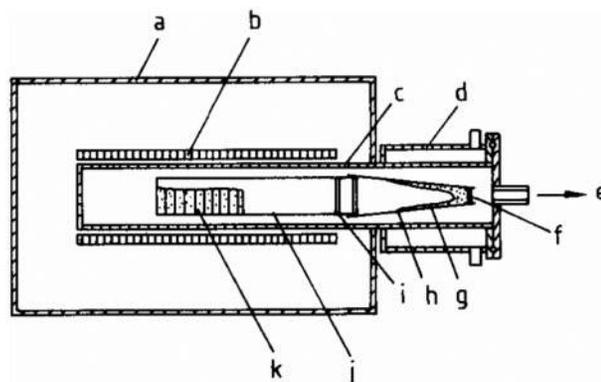
a furnace; *b* heating element; *c* stainless steel container; *d* water cooling; *e* vacuum; *f* baffle; *g* RE metal; *h* molybdenum condenser; *i* heat shield; *j* molybdenum crucible; *k* pelletised reactants[4]

8   Reduction–distillation apparatus for production of samarium, europium, and ytterbium

1000–1300°C. The rare earth oxides and the reducing metal are used in the form of pellets, prepared from chippings or thin disks. Sm, Eu, and Yb are volatile at the reaction temperature under vacuum ($<10^{-4}$ bar), and can be distilled from the reaction space during the reaction and condensed on coolers. Thus, these metals can be separated from rare earth metals that are not volatile under these conditions and obtained in a pure state. Hence, the starting materials can consist of rare earth oxides in which Sm, Eu, and Yb have merely been concentrated. The principle of the reduction distillation apparatus is illustrated in Fig. 8. Further purification can be carried out by a second distillation.

Purification

Production of the pure rare earth metals necessitates the removal of products of the reaction of the metals with the atmosphere, crucible materials, and co-reactants. Suitable methods include melting under a protective gas or in a vacuum. The high boiling rare earth metals can also be purified by distillation. Alloying elements and impurities such as Mg, Cd, Zn, and Ca are distilled off under vacuum. The remaining rare earth metal is then in the form of a sponge, which can be consolidated by fusion in an electric arc furnace. Zone melting, melt extraction, and melt filtration, e.g., through tungsten powder, degassing in a high vacuum, etc., are other recommended purification methods.

USES

The most important uses of mischmetal or cerium are metallurgical. The metallurgical importance of rare earth metals is based on reactions to form solids with oxygen, hydrogen, nitrogen, sulfur, arsenic, bismuth, and antimony, reducing the effects of these elements on the properties of the metals. Mischmetal is added as lumps, rods, or wire. The principal uses for cerium compounds are as polishing agents and as a component in glass. The rare earth metals and their compounds are

used in numerous areas of industry for a wide range of purposes. The most important of these include metallurgy, catalysts in the chemical industry, coloring of glass and ceramics, the production of magnets, and phosphors.[4]

References

1. F. Habashi: 'Researches on rare earths. History and technology', Métallurgie Extractive Québec, Québec City, Canada 2008. Distributed by Laval University Bookstore, www.zone.coop
2. F. Habashi: 'Carl auer and the beginning of the rare earths industry', in 'Rare earths 2012', (ed. J. R. Goode *et al.*), 3–13; 2012, Montreal, Canadian Institute of Mining, Metallurgy, and Petroleum.
3. C. K. Gupta and N. Krishnamurthy: 'Extractive metallurgy of rare earths'; 2005, CRC Press.
4. I. McGill: 'Rare earth metals', in 'Handbook of extractive metallurgy', (ed. F. Habashi), 1695–1741; 1997, Weinheim, WILEY-VCH.
5. F. Habashi: 'A textbook of hydrometallurgy', 2nd edn; 1993, Québec City, Métallurgie Extractive Québec. Distributed by Laval University Bookstore. www.zone.ul.ca
6. F. Habashi: 'Pollution problems in the mineral and metallurgical industries'; 1996, Québec City, Métallurgie Extractive Québec. Distributed by Laval University Bookstore, www.zone.coop