CHAPTER 12.32

Rare Earth Elements

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The International Union of Pure and Applied Chemistry (IUPAC) defines the lanthanoids as the 15 elements with atomic numbers of 57–71 inclusive: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). The rare earth elements (REE) are defined as the lanthanoids plus yttrium (Y) and scandium (Sc) (Connelly et al. 2005). Pm is an unstable element and not found in nature, so in practical terms there are 16 REE.

The abbreviation Ln is sometimes used to signify the lanthanoids or the entire group of REE. Didymium, sometimes abbreviated as Dd or NdPr, is an unseparated, and therefore lower cost, mixture of Pr and Nd, usually at the natural Pr:Nd ratio of approximately 1:3.4 and often used in NdFeB magnets. The REE industry uses other abbreviations as follows:

- LREE = light REE
- MREE = medium REE
- HREE = heavy REE
- TREE = total REE
- CREE = critical REE
- SEG = Sm, Eu, and Gd

IUPAC does not refer to LREE, MREE, and HREE, but the terms are in common use although defined in different ways by different parties. The U.S. government agencies only use LREE and HREE and define LREE as the elements from La to Gd inclusive, all of which have unpaired electrons in the 4f electron shell. The HREE, with paired 4f electrons, are the elements from Tb to Lu plus Y. Y usually behaves like an HREE with properties between those of Ho and Er. IUPAC includes Sc as a REE, but this element does not fit comfortably into either the LREE or HREE group.

Actinium, particularly ^{227}Ac, which is a radioactive decay product of ^{235}U and found in most REE deposits, behaves like La and tends to report to separated La products where it can concern end users.

The U.S. Department of Energy (U.S. DOE 2010) and European Union (European Commission 2014) have defined the critical rare earth elements (CREE) as those for which there is a serious risk of assured supply and that are important to the present way of life. The DOE report identified Dy, Nd, Tb, Y, and Eu as critical through the year 2025. The European Union defined the HREE (Gd to Lu plus Y) as being particularly critical, the LREE (La to Eu) as being somewhat less critical, and Sc being noncritical. The criticality matrices are changing as REE uses and production levels change.

When rare earth oxides are being referenced, common with product prices and analytical data, the abbreviation REO is used as well as LREO, MREO, HREO, TREO, and CREO. REM is occasionally used to signify the metal.

The REE are usually encountered in the trivalent state, so most of the oxides are written as La_2O_3, Y_2O_3, and so on. However, Ce, Pr, and Tb do not ignite to trivalent oxides and their oxides are CeO_2, Pr_6O_{11}, and Tb_4O_7, respectively.

Certain fundamental data and oxide–metal conversion factors for the REE are presented in Table 1. Selected properties of the REE, which govern the way in which the REE behave in minerals and in solution, are presented in the following sections.

VALENCY

The REE are generally trivalent. However, Nd, Sm, Eu, Dy, Tm, and Yb can be reduced to the divalent state and Ce, Pr, and Tb can be oxidized to the quadrivalent state.

IONIC RADIUS

The ionic radii of the trivalent REE get smaller as the atomic mass increases (the “lanthanoid contraction”), except for those of Y and Sc. The Y ionic radius falls between that of Ho and Er and, consequently, the solution chemistry of Y is often intermediate to that of Ho and Er. The lightest REE, Sc, has the smallest ionic radius and often, but not always, behaves as an HREE. Ac, a progeny of ^{235}U and ^{232}Th, has an ionic radius similar to that of La and behaves in a similar way to La. The ionic radii of the REE, expressed in picometers (1 pm = 10^{-12} m) are plotted in Figure 1.

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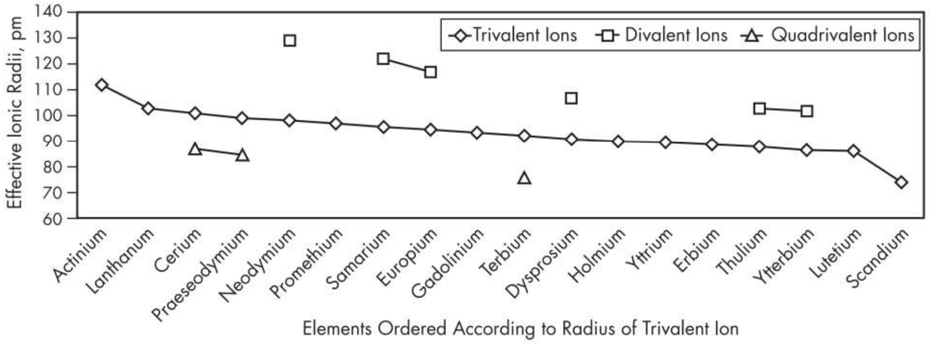
Table 1 Fundamental REE data and oxide–metal conversion factors

	Light REE							Heavy REE
Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Atomic number	57	58	59	60	62	63	64	65
Atomic mass	138.905	140.116	140.907	144.242	150.360	151.964	157.250	158.925
Oxide formula	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7
Conversion Factors								
Element to oxide	1.17277	1.22837	1.20816	1.16638	1.15961	1.15792	1.15261	1.17617
Oxide to element	0.85268	0.81408	0.82770	0.85735	0.86235	0.86361	0.86759	0.85021
	Heavy REE							–
Element	Dy	Ho	Er	Tm	Yb	Lu	Y	Sc
Atomic number	66	67	68	69	70	71	39	21
Atomic mass	162.500	164.930	167.259	168.934	173.054	174.966	88.906	44.956
Oxide formula	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3	Sc_2O_3
Conversion Factors								
Element to oxide	1.14768	1.14551	1.14348	1.14206	1.13867	1.13716	1.26993	1.53383
Oxide to element	0.87131	0.87297	0.87451	0.87560	0.87820	0.87938	0.78743	0.65196



Data from Shannon 1976

Figure 1 Effective ionic radii of the REE and Actinium

DISCOVERY AND DEVELOPMENT

Swedish Army Lieutenant C.A. Arrhenius discovered an unusual mineral near Ytterby, Sweden, in 1787. Seven years later, Johan Gadolin, a chemist at the University of Abo (now Turku) in Finland, separated a previously unknown metal oxide from a sample of the mineral. The mineral was later dubbed gadolinite and the oxide named yttria after the discovery location.

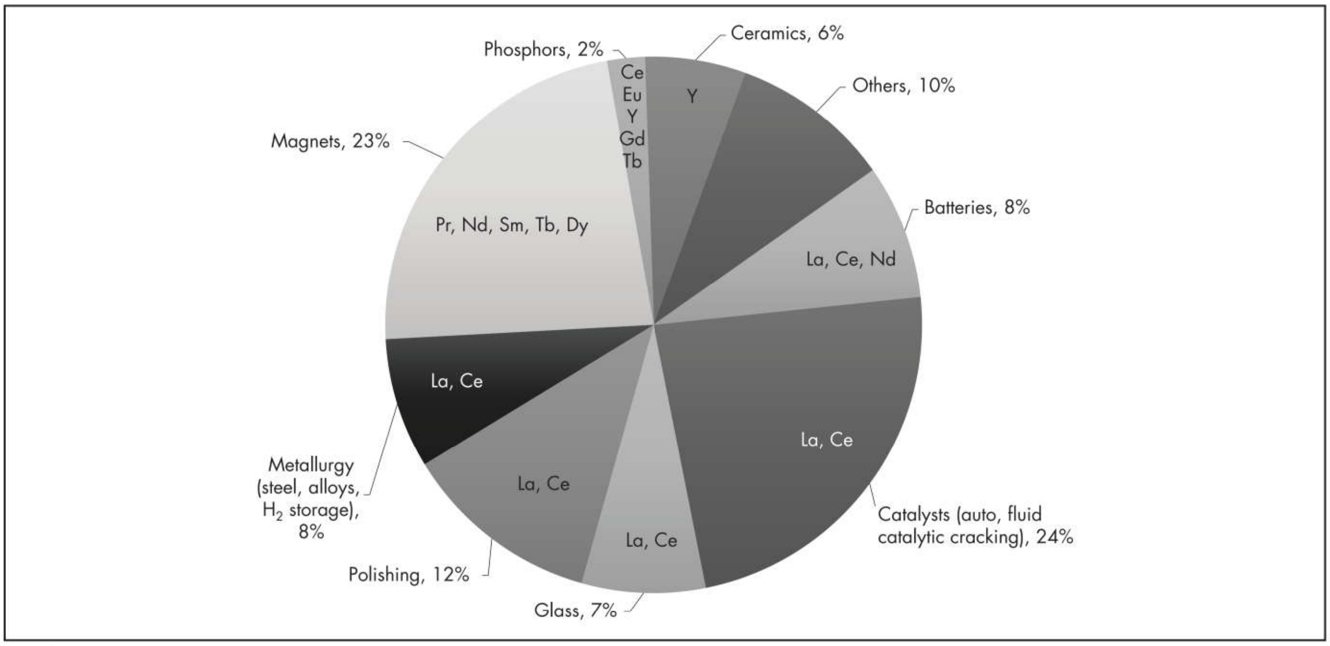
In 1803, Jöns Jacob Berzelius and Wilhelm Hisinger in Sweden studied a heavy mineral discovered at Bastnas in Sweden and extracted a metal oxide that they named ceria. Martin Klaproth independently separated ceria at about the same time in Germany.

The crude metal oxides, yttria and ceria, isolated from these minerals were studied, and it became evident that both were mixed oxides of other elements. A Swedish chemist, Carl Mosander, extracted La_2O_3 and didymia, a mixture of Pr and Nd oxides, from ceria in the late 1830s. A couple of years later, he separated oxides of Y, Tb, and Er from yttria.

Between 1869 and 1900, work by Paul-Émile Lecoq de Boisbaudran, Eugène-Anatole Demarçay, and Carl Auer von Welsbach had produced compounds of Sm, Eu, Gd, Pr, and Nd from ceria. Several chemists contributed to the further separation of the HREE in yttria after Mosander's pioneering work. The Swiss chemist Jean Charles Galissard de Marignac isolated Gd, Tb, and Yb in the late 1870s. Lars Nilson of Sweden discovered Sc in 1879, and his countryman, Per Cleve, identified Ho and Tm the same year. Georges Urbain, Charles James, and Welsbach independently discovered Lu in 1907.

Separation of the REE during the pioneering years was achieved using oxidation–reduction reactions, double salt formation, and fractional crystallization or precipitation procedures. As an illustration of the time-consuming nature of these methods, Urbain performed 15,000 sequential nitrate crystallization operations to separate Lu from a crude Yb product.

The earlier separation processes satisfied the low demand for individual REE through the first half of the 20th century. During the 1950s, separation by ion exchange (IX), with chromatographic elution, was developed and commercial plants were constructed in the United States, United Kingdom, former Union of Soviet Socialist Republics, and France (Spedding and Powell 1954). These plants operated until the 1960s when they were replaced by more efficient solvent extraction systems similar to those still used today (Kaczmarek 1981).



Data from Roskill 2016

Figure 2 Distribution of REE use

USES

In the 1880s, Welsbach discovered that the REOs emit a brilliant light when heated in a gas flame, and he went on to develop a lighting system using gas mantles incorporating La and Y (Habashi 2012). A much-improved formulation using ThO_2 with about 1% CeO_2 was extensively employed for street lighting and in kerosene-burning lanterns known as Petromax or Tilley lamps in much of the world and as Coleman lanterns in North America. Welsbach factories in Germany and France produced Th from monazite and made a bulk REE by-product. In 1903, seeking a market for the REE, Welsbach developed a cerium–iron alloy, mischmetal, that sparked when struck. It became widely used as lighter flints and is still used today.

After these earliest commercial applications, further REE uses were developed for mixed and separated REE, including glass polishing, ultraviolet (UV) cut glass (which reduces UV light transmission), Al and Mg alloying, high refractive-index lenses, and catalysts. The demand for REE increased dramatically after 1955 with the use of red phosphors incorporating Eu and Y in television cathode ray tubes. Permanent magnets comprising an alloy of Sm and Co with a formula of $SmCo_5$ (about 34% Sm by mass) were developed in about 1970, followed by NdFeB magnets in 1982. The latter are nominally $Nd_2Fe_{14}B$ alloys, but in addition to about 30% Nd they also contain between 2% and 9% Dy and Tb. A mixture of Pr and Nd, which is less expensive since the difficult Pr–Nd separation is avoided, can be used instead of pure Nd. NdFeB magnets remain the most important end use for REE and largely control the present demand and production of REE. The distribution of REE uses is illustrated in Figure 2.

REE deposits contain each of the REE in certain proportions and, as a general rule, the percentage recovery of each REE is similar. Therefore, to produce a given mass of a particular REE, say Nd, a given mine will incidentally produce certain quantities of the other REE in the deposit. There are exceptions to this depending on exact mineralogy and process methods. However, it is generally true that some high-demand REE are relatively valuable, whereas others, for which supply exceeds demand, command low prices or are not marketable.

The history of REE demand has changed as new uses are developed and older technologies discarded. A recent example is a reduction in demand for Y and especially Eu and Tb as compact fluorescent lamps are replaced by longer lasting, more energy-efficient LED lights.

MINERAL DEPOSITS

The most common REE (Ce, La, Y, and Nd) are more abundant than Li, Cu, Mo, Sn, W, Pb, and U. Furthermore, REE minerals can occur in mineable deposits with grades as high as 50% REE—far higher than most other elements. REE are usually found in deposits in which they are the most valuable elements, although they are also found in deposits that are primarily deposits of Fe, niobium (Nb), U, Cu, or other elements.

The U.S. Geological Survey (USGS) divides REE deposits into nine types: peralkaline igneous rocks, carbonatites, iron oxide copper–gold, pegmatites, porphyry molybdenum, metamorphic, stratiform phosphate residual, paleoplacer, and placer. The USGS identifies various REE deposit types within each association and provides examples (Long et al. 2010).

The British Geological Survey (2017) classifies REE deposits into four primary deposit types: carbonatite associated, associated with alkaline igneous rocks, iron–REE deposits, and hydrothermal deposits; and five secondary deposit types: marine placers, alluvial placers, paleoplacers, lateritic deposits, and ionic clays, for a total of nine types.

Table 2 lists the main deposit types, typical examples, and general characteristics of each deposit type. Figure 3 presents grade and tonnage data for REE deposits and identifies important deposits.

Currently, almost all primary REE production comes from four mining areas (Goode 2016c):

Table 2 Main REE deposit types

Deposit Type	Examples	Typical REE-Bearing Minerals	Typical Non-REE Minerals	Average in Situ REO Distribution	By-Products or Co-Products
Carbonatites	Mountain Pass[*] and Bear Lodge, USA Bayan Obo[†] and Mianning[†], China Niobec and Ashram, Canada	Bastnaesite, parisite, synchysite, monazite, xenotime, aeschynite	Calcite, dolomite, ankerite, aegerine, riebeckite, biotite, magnetite, hematite, fluorite, barite	HREO 2.8% CREO 23.6%	Fe, Nb, CaF_2
Weathered carbonatites (laterites)	Mt. Weld, Australia[†] Ngualla, Tanzania Kangankunde, Malawi Morro de Ferro, Brazil	Bastnaesite, apatite, monazite, synchysite, cerianite, churchite	Goethite, gibbsite, magnetite, mica, kaolinite	HREO 4.4% CREO 24.9%	None
Intrusive peralkaline complexes (nephaline syenites)	Bokan Mountain and Pajarito Mountain, USA Weishan, China[†] Lovozero, Russia[†] Strange Lake, Thor Lake, Kipawa, Canada Norra Karr, Sweden Dubbo, Australia Illimaussaq, Greenland	Eudialyte, loparite, bastnaesite, steenstrupine, synchysite, allanite, fergusonite, gadolinite, mosandrite, britholite, monazite, xenotime	Feldspars, nepheline, sodalite, pyroxene, amphibole, quartz, arfvedsonite	HREO 26.5% CREO 38.4%	Nb, Ta, Zr, U, Zn, phosphates
Hydrothermal deposits	Lehmi Pass, USA Steenkampskrall, South Africa[*] Hoidas Lake, Canada Lofdal, Namibia Browns Range, Australia	Monazite, xenotime		HREO 27.3% CREO 41.8%	None
Volcanic	Foxtrot, Canada	Allanite, chevkinite, fergusonite, monazite, zircon	Quartz, K-feldspar, amphibole/pyroxene, plagioclase, Fe-oxides, biotite	Only two examples, so average is meaningless	None
	Brockman, Australia	Bertrandite, bastnaesite, parisite, synchysite	Quartz, mica, albite		
Iron-REE deposits	Olympic Dam, Australia[‡] Pea Ridge and Minesville, USA Kiruna, Sweden[‡]	Monazite, apatite		Limited data but generally dominantly LREO	Cu, U, Fe
Placers	Chavara, India Richards Bay, South Africa[‡] Aksu Diamas, Turkey	Monazite, zircon, allanite, chevkinite		HREO 12.9% CREO 30.4%	Ilmenite, zircon, garnet, magnetite, Nb
Paleoplacers	Bald Mountain, USA Elliot Lake, Canada[*]	Monazite		Limited data but generally dominantly LREO	U, Th, pyrite
Ionic clay deposits	Longnan[†], Xunwu, etc. China Serra Verde, Brazil Tantalus, Madagascar	REE on clays, residual primary monazite, bastnaesite, etc.	Clay, granites	Variable but Ce in deposits usually relatively insoluble, so low Ce in product	None

Note: Distribution by author. Numerical assay data from company releases collated from public sources in TMR 2015 with analysis by author.

[*] Past REE producer.

[†] Current REE producer.

[‡] Currently producing but not REE.

1. **Bayan Obo, Inner Mongolia Autonomous Region, People's Republic of China.** Carbonatite with bastnaesite and monazite, three large open pits, beneficiation by magnetic and flotation methods with REE recovered as a co-product of iron concentrate, acid bake to process REE concentrate.
2. **Mianning–Dechang District, Sichuan Province, People's Republic of China.** Carbonatite with bastnaesite; several widely spaced open pits; beneficiation by gravity, magnetic, and flotation methods; roast and leach or acid bake to process concentrate.
3. **Southern China: Jiangxi, Guangdong, Fujian, and Hunan provinces and Guangxi Zhuang Autonomous Region, People's Republic of China.** Ionic clay deposits; heap or in situ leaching with weak electrolyte, such as $(NH_4)_2SO_4$.
4. **Mt. Weld, Western Australia.** Weathered carbonatite, single open pit, beneficiation by flotation, acid bake to process concentrate.

Originally operated in about 1950, Molycorp's Mountain Pass rare earth mine in California (United States) included an open pit mine, and flotation and hydrometallurgical plants. Molycorp closed the operation in 1998 because it was not profitable at the prevailing prices and because of environmental issues. With improving REE prices in about 2010, and under new ownership and management, the plant was redesigned and refurbished and restarted in 2013. However, prices for the REOs produced by Molycorp were far lower than projected and there were severe technical issues limiting REO production that together rendered the operation unprofitable. Molycorp declared bankruptcy in June 2015 and placed the plant on a care-and-maintenance basis.

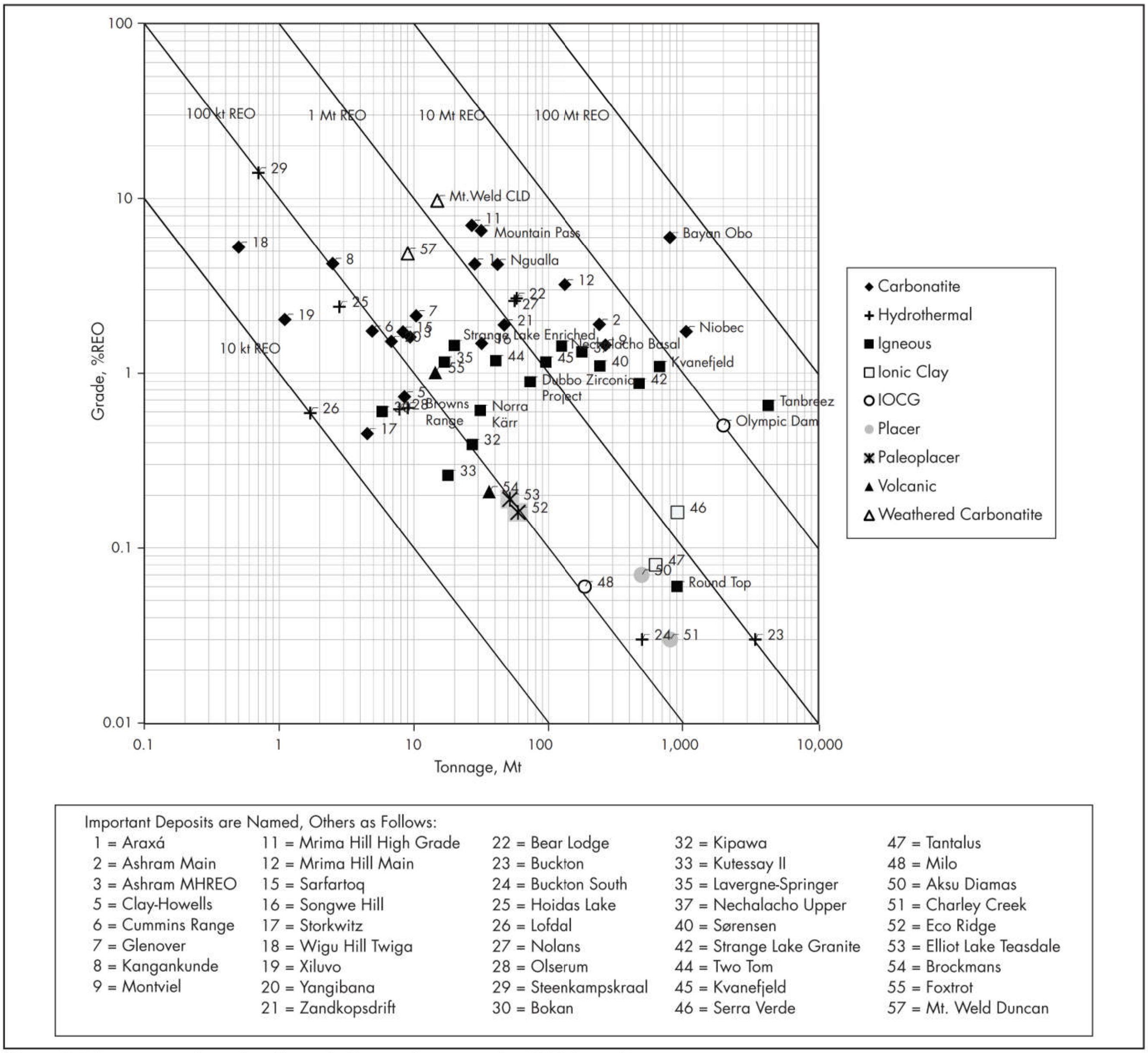


Figure 3 Tonnage and grade of producing and prospective REE deposits

The elemental distribution of the REE within each deposit varies widely according to the deposit type and within the deposit type. The minerals in the carbonatite deposits are frequently bastnaesite, monazite, and other LREE-bearing minerals, so the carbonatites and weathered carbonatites are generally very low in HREE content. The placer and paleoplacer deposits also tend to be poor in HREE.

In contrast, the intrusive peralkaline deposits tend to be relatively rich in HREE. The products from the ionic clay deposits also tend to be rich in HREE largely because the weathering and ion exchange processes cause the Ce to be oxidized and precipitated as cerianite, $Ce(Th)O_2$, a refractory mineral, rather than being sorbed on the clay. Thus, the product obtained by elution of REE from the clays with a weak electrolyte generally contains little Ce, leading to a high-HREE product.

The distribution of REE within selected deposits, and available Sc, U, and Th assays are presented in Table 3. This table also includes an indicative value for the mixed oxide that would be produced from each deposit using projected 2020 REO prices (Roskill 2016). This way of calculating relative value is deceptive since several REE, including La and Ce, cost more to separate than they can be sold for. The relatively low value of the carbonatite deposits is evident.

MINERALOGY

There are several hundred REE-bearing minerals. The REE minerals that are most commonly encountered and typical gangue minerals are listed with formulae and important properties in Table 4.

Table 3 REO distribution; REO, Sc, U, and Th content; and nominal product value for selected deposits

			Carbonatite				Ionic Clay (distribution in products, not ore)			Intrusive Peralkaline	
			Bayan Obo	Mianning	Mountain Pass	Mt. Weld	Longnan	Xinfeng	Serra Verde	Dubbo	Strange Lake
	Oxide	Price, US$/kg oxide*	China	China	USA	Australia	China	China	Brazil	Australia	Canada
REO Distribution as %TREO in Carbonatite and Intrusive Alkaline Ore in Product from Ionic Clay	La_2O_3	1	25.6	29.5	32.9	25.6	2.5	26.2	33.7	19.6	10.4
	CeO_2	1	48.5	47.6	49.7	46.9	0.5	1.9	4.2	36.9	25.0
	Pr_6O_{11}	65	5.7	4.4	4.5	5.3	1.0	6.0	6.3	4.0	2.7
	Nd_2O_3	71	16.8	15.2	12.0	18.6	5.1	21.1	20.4	14.1	9.7
	Sm_2O_3	1	1.6	1.2	0.6	2.4	3.9	4.5	3.3	2.2	2.5
	Eu_2O_3	48	0.12	0.23	0.10	0.44	0.30	0.71	0.20	0.08	0.14
	Gd_2O_3	10	0.31	0.65	0.03	0.10	6.62	4.80	3.20	2.17	2.71
	Tb_4O_7	377	0.20	0.12	0.02	0.07	1.34	0.77	0.50	0.31	0.63
	Dy_2O_3	205	0.19	0.21	0.02	0.12	8.83	4.10	3.00	2.02	4.58
	Ho_2O_3	0	0.02	0.05	0.02	0.07	1.60	0.80	0.60	0.39	1.04
	Y_2O_3	4	0.7	0.7	0.0	0.1	58.3	25.1	20.7	15.8	32.6
	Er_2O_3	21	0.02	0.06	0.02	0.07	5.10	2.00	1.90	1.16	3.40
	Tm_2O_3	0	0.10	0.04	0.02	0.07	0.66	0.20	0.30	0.16	0.56
	Yb_2O_3	0	0.01	0.05	0.02	0.07	3.94	1.60	1.60	1.01	3.54
	Lu_2O_3	0	0.13	0.01	0.02	0.07	0.51	0.20	0.20	0.16	0.49
Ore Assay†	REO, %	—	5.5	7	8.5	15	0.06	—	0.148	0.9	1.1
	Sc, %	—	—	—	—	—	—	—	~0.0003	—	—
	U, %	—	—	—	0.002	0.003	—	—	0.001	0.012	0.007
	Th, %	—	0.04	—	0.02	0.069	—	—	0.011	0.038	0.037
Value of Mixed Oxide, $/kg REO			17.4	15.3	12.3	17.9	31.6	32.6	28.5	19.5	23.0

*Prices from Roskill 2016 for 2020, allowing for inflation. Prices for individual REE can and will change, and relative values might also change.

†Ore assays for Sc, U, and Th are generally not available.

Table 4 Common REE-bearing minerals and associated gangue minerals

Mineral*	Ore–Gangue†	Class‡	Formula§	Typical REE%	Density, g/mL	Hardness, Mohs scale	Electrostatic Response**	Magnetic Response (USGS)††	Acid Leach Response‡‡	Caustic Crack Response§§
Bastnaesite	O	C	$(Ce,La)CO_3F$	64	5.0	4–5	N	0.7–0.9	2, 3	2, 3
Huanghoite	O	C	$BaCe(CO_3)_2F$	34	4.6	5	—	0.7–0.8	3	2
Parisite	O	C	$Ca(Ce,La)_2(CO_3)_3F_2$	52	4.4	4–5	—	0.7	3	2
Synchysite	O	C	$Ca(Ce,La)(CO_3)_2F$	44	4.0	4–5	—	—	2, 3	2,3
Ankerite	G	C	$Ca(Fe^{2+},Mg,Mn)(CO_3)_2$	0	3.1	3–4	N	0.4–0.5	1	—
Calcite	G	C	$CaCO_3$	0	2.7	3	N	>1.7	1	—
Dolomite	G	C	$CaMg(CO_3)_2$	0	2.8	3–4	N	>1.7	1	—
Siderite	G	C	$Fe^{2+}CO3$	0	4.0	3.5	N	0.2–0.3	1	—
Fluocerite	O	F	$(Ce,La)F_3$	71	6.1	4–5	—	0.6–0.7	2, 3	2
Fluorite	G	F	CaF_2	0	3.1	4	N	>1.7	2, 3	2
Fergusonite	O	N	$YNbO_4$	36	5.1	5–6	—	0.4–0.6	3	3
Pyrochlore	O	N	$(Na,Ca)_2Nb_2O_6(OH,F)$	0	5.3	5–6	C	0.9–>1.7	3	2
Aeschynite	O	O	$(Ce,Ca,Fe,Th)(Ti,Nb)_2(O,OH)_6$	20–28	4.8–5.2	5–6	—	0.7–0.8	3	—
Cerianite	O	O	$(Ce^{4+},Th)O_2$	53	7.2	—	—	—	2	—
Euxenite	O	O	(Y,Ca,Ce)(Nb,Ta,Ti)2O6	19	4.8	6–7	C	0.5–0.6	—	2
Loparite	O	O	$(Ce,Na,Ca)_2(Ti,Nb)_2O_6$	25	4.8	5–6	—	—	—	—
Uraninite	O	O	UO_2	Varies	8.7	5–6	N	0.5–>1.7	2	—
Goethite	G	O	$Fe^{3+}O(OH)$	0	3.8	5–6	N	0.4–0.5	1	—
Hematite	G	O	Fe_2O_3	0	5.3	6–7	C	0.1–0.3	2	—
Ilmenite	G	O	$Fe^{2+}TiO_3$	0	4.7	5.6	C	0.2–0.3	—	—

(continues)

Table 4 Common REE-bearing minerals and associated gangue minerals (continued)

Mineral[*]	Ore–Gangue[†]	Class[‡]	Formula[§]	Typical REE%	Density, g/mL	Hardness, Mohs scale	Electrostatic Response[**]	Magnetic Response (USGS)[††]	Acid Leach Response[‡‡]	Caustic Crack Response[§§]
Magnetite[***]	G	O	$Fe^{2+}Fe^{3+}{}_2O_4$	0	5.2	5–6	C	0.01	2	—
Muscovite	G	O	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	0	2.8	2–3	N	0.6>1.7	—	—
Quartz[†††]	G	O	SiO_2	0	2.6	7	N	>1.7	4	2
Brockite	O	P	$(Ca,Th,Ce)PO_4{\cdot}H_2O$	6	3.9	3–4	—	—	—	2
Churchite	O	P	$(Nd,Y)PO_4{\cdot}2(H_2O)$	40–54	3.3	3–4	—	—	3	2
Monazite	O	P	$(Ce,La,Nd,Th)PO_4$	55	5.2	5–6	N	0.5–0.8	2, 3	2, 3
Steenstrupine	O	P	$Na_{14}Ce_6Mn^{2+}Mn^{3+}Fe^{2+}{}_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7{\cdot}3(H_2O)$	27	3.4	4	—	—	—	2
Xenotime	O	P	YPO_4	48–65	4.8	4–5	N	0.4–0.5	2, 3	2, 3
Apatite	G	P	$Ca_5(PO_4)_3(OH,F,Cl)$	0	3.1	5	N	>1.7	2, 3	—
Allanite	O	S	$(Ce,Ca,Y,La)_2(Al,Fe^{3+})_3(SiO_4)_3(OH)$	18–32	3.8–3.9	5–6	—	0.4–0.5	2, 3	2, 3
Britholite	O	S	$Ca_2(Ce,Ca)_3(SiO_4,PO_4)_3(OH,F)$	28–41	4.1–4.5	5–6	—	0.4	—	—
Cerite	O	S	$(Ce,La,Ca)_9(Mg,Fe^{3+})(SiO_4)_6(SiO_3OH)(OH)_3$	55–62	4.7–4.9	5–6	—	0.6–0.7	—	2
Chevkinite	O	S	$(Ce,La,Ca,Th)_4(Fe^{2+},Mg)_2(Ti,Fe^{3+})_3Si_4O_{22}$	36	4.5	5–6	—	0.4–0.5	3	—
Eudialyte	O	S	$Na_{15}Ca_6(Fe^{2+},Mn^{2+})_3Zr_3SiO(O,OH,H_2O)_3(Si_3O_9)_2(Si_9O_{27})_2(OH,Cl)_2$	8	2.9	5–6	—	—	1, 2	—
Gadolinite	O	S	$(Ce,La,Nd,Y)_2FeBe_2Si_2O_{10}$	38–50	4.2	6–7	—	0.2–0.4	2	3
Mosandrite	O	S	$Na(Na,Ca)_2(Ca,Ce,Y)_4(Ti,Nb,Zr)(Si_2O_7)_2(O,F)_2F_3$	28	3.3	4	—	—	2	—
Stillwellite	O	S	$(Ce,La,Ca)BSiO_5$	51	4.6	6–7	—	—	—	—
Zircon	O	S	$ZrSiO_4$	4	4.7	7.5	N	>1.7	3	3
Kainosite	O	S	$Ca_2(Y,Ce)_2Si_4O_{12}(CO_3){\cdot}(H_2O)$	30	3.5	5.5	—	—	2	—
Albite	G	S	$NaAlSi_3O_8$	0	2.6	7	N	>1.7	—	—
Augite	G	S	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$	0	3.4	5–7	V	0.4–0.9	—	—
Biotite	G	S	$K(Mg,Fe^{2+})_3[AlSi_3O_{10}(OH,F)_2$	0	3.1	2–3	N	0.3–0.8	3	—
Chlorite	G	S	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$	0	2.6–3.3	2–3	N	0.2–0.5	—	—
Diopside	G	S	$CaMgSi_2O_6$	0	3.4	6	N	0.4–0.6	—	—
Microcline	G	S	$KAlSi_3O_8$	0	2.6	6	N	>1.7	—	—
Orthoclase	G	S	$KAlSi_3O_8$	0	2.6	6	N	>1.7	—	—
Titanite	G	S	$CaTiSiO_5$	4	3.5	5–6	—	0.8–>1.7	4	4
Barite	G	Su	$BaSO_4$	0	4.5	3–4	N	>1.7	4	4
Pyrite	G	Su	FeS_2	0	5	6–7	C	>1.7	4	1
Wakefieldite	O	V	$(La,Ce,Nd,Y)VO_4$	30–56	4.2–4.8	4–5	—	—	—	—

[*] Mineral characteristics and response to acid or caustic attack varies depending on exact composition of mineral and conditions of attack.

[†] Ore–gangue abbreviations: O = ore, G = gangue.

[‡] Class abbreviations: C = carbonate, F = fluoride, N = niobate, O = oxide, P = phosphate, S = silicate, Su = sulfides/sulfate, V = vanadate.

[§] Formulae and mineral properties generally from Webmineral (2016) and Outokumpu Technology (2006).

[**] Electrostatic abbreviations: N = nonconductor; C = conductor; V = variable; — = no data.

[††] Magnetic response data from Rosenblum and Brownfield (1999) of the USGS and showing best range amperage data determined using a Frantz isodynamic magnetic separators, Model L-1.

[‡‡] Leach response scale:

1 – Readily attacked by dilute acid at ambient temperature
2 – Attacked by strong acids at elevated temperature
3 – Responds to concentrated sulfuric acid baking
4 – Not attacked by simple mineral acids

[§§] Alkali treatment scale:

1 – Attacked by weak caustic solution
2 – Attacked by strong (>50%) hot (>100°C) caustic solution
3 – Responds to caustic fusion or alkali fusion
4 – Not attacked by strong caustic solution

[***] Magnetite is ferromagnetic and gives a positive response in the Frantz separator at 0.01 A.

[†††] Quartz gives no response, even at Frantz separator currents exceeding 1.7 A.

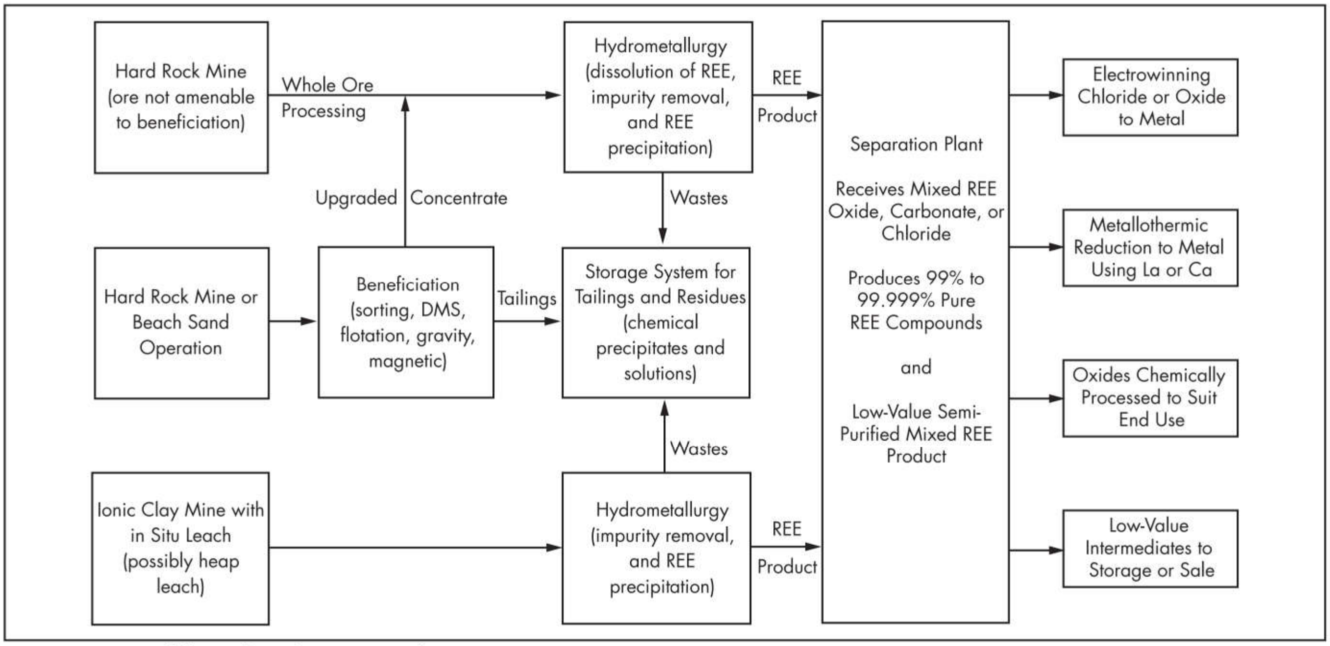


Figure 4 Overall flow sheet for REE production

PROCESSING

Process details for operating REE facilities are usually not published. Although companies are often legally required to state ore reserves, there are no requirements to provide details of how the ore is being processed. Furthermore, the REE industry is competitive and there is nothing like the sharing of technical information between producers of gold, copper, and other REE. Often, there is copious information on what has been tested in the laboratory but no reliable information on plant practice.

More information is available regarding proposed operations, especially for companies listed on stock exchanges in Canada, Australia, and the United States. In these cases, information can be obtained from company websites and also from SEDAR (System for Electronic Document Analysis and Retrieval, www.sedar.com), EDGAR (Electronic Data Gathering Analysis and Retrieval, www.sec.gov/edgar), or the ASX website (www.asx.com.au).

Overall Process Flow Sheet

REE ore deposits contain between a few hundred parts per million to as high as 50% REE. The ultimate end uses of REE typically require high-purity separated products. The general path from ore to end product is illustrated in Figure 4.

The beach sands and hard rock ores that are presently being processed are beneficiated using gravity, flotation, and/or other beneficiation methods to reject low-grade or waste material. The upgraded concentrate, usually containing between 40% and 60% REO, is then processed hydrometallurgically to “crack” the REE minerals, and the REE are then dissolved. Leach solutions are treated for the removal of impurities, including specific radionuclides, and processed to generate a purified bulk rare earth product. This product is often a solid oxide, carbonate, or chloride that is low in impurities and suitable for separation into the individual REE. If the hydrometallurgical plant and separation plant are closely coupled, then the product of the hydrometallurgical plant could be a purified solution suitable for separation. Some REE ores now under investigation are not amenable to beneficiation, and the developers are proposing to hydrometallurgically process the whole ore.

The ionic clay deposits in China are the dominant source of HREE, and although heap and vat leaching have been used, they are generally exploited by in situ leaching. Leach solutions are purified and a high-grade REE product recovered by precipitation and sent to separation plants.

Regardless of the ore type and manner of hydrometallurgical processing, the mixed REE product of the hydrometallurgical plant requires separation into the REE products of interest. The separated products will then be further processed (e.g., reduced to metal) before being used.

Less than 5% of the REE consumed is recycled and most of the mined REE contained in scrap fluorescent lamps, electronics, and automobiles end up in landfills. When reprocessing is practiced, it typically starts with physical upgrading, sometimes a thermal treatment, followed by hydrometallurgical processing to remove impurities or other products such as Hg, Ni, or Co, to yield a pure solid or solution containing REE ready for separation or for direct recycle as a mixed REE product. At least one proposed mining operation intends to incorporate scrap phosphor in the feed to its hydrometallurgical plant.

BENEFICIATION

Table 4 presents data on the density, magnetic response, and conductivity of common REE minerals and associated gangue. The density of most of the REE minerals is substantially higher than most of the gangue minerals with averages of 4.7 for the REE minerals (range 2.9–7.2) and an average of 3.5 for the gangue minerals, although the more common gangue minerals have densities of less than 3. Gravity separation can be an effective means of beneficiating REE ores and is used at some operations and proposed for some projects under development.

Several of the REE-bearing minerals respond well to magnetic separation, and this process is used in, or proposed for, several REE beneficiation plants. Some REE minerals have different conductivities to other REE minerals or accompanying gangue minerals, and electrostatic separation is used at beach and riverine sand processing operations.

The present REE producers and most potential producers are using some form of beneficiation to upgrade the ore before hydrometallurgical processing. However, some ores cannot be effectively beneficiated because the REE minerals are too fine, poorly liberated, or simply not amenable. In such cases, the whole ore is subjected to hydrometallurgical processing. Examples of such proposed projects include Alkane Resources' Dubbo Zr-REE project; Search Minerals' Foxtrot project; Frontier Rare Earths' Zandkopsdrift project; the Chuktukon and Tomtor REE projects in Russia; Texas Rare Earth Resources Corp.'s Round Top project; and all ionic clay deposits.

Beneficiation is discussed in more detail in the following section. Additional information can be obtained from the literature (Zhang and Edwards 2012; Jordens et al. 2013; Goode 2016c; Li and Yang 2014).

Coarse Ore Beneficiation

Ore sorting and dense media separation (DMS) are coarse ore beneficiation processes that operate on material in the approximate size ranges of 300 mm down to 20 mm, and 150 mm down to 0.5 mm, respectively. Both techniques have been, and continue to be, widely used in industries other than the REE industry.

Automated ore sorting has been used since the 1950s, and there are presently hundreds of machines sorting industrial minerals and ores of gold, uranium, and base metals. Many more machines are used for sorting glass cullet, metallic scrap, and seeds are used in other nonmining applications. Sorting machines can process rock particles as large as 300 mm and as small as 5 mm. However, the capacity of sorting machines decrease as the feed size becomes finer, and the sorting of particles finer than 20 mm is generally not economical. DMS is widely used for processing coal and base metal ore.

A 2016 review of the application of coarse ore beneficiation to REE ores prepared for Natural Resources Canada (Goode 2016a) indicated that there were no REE production facilities using ore sorting or DMS. The review also showed that few potential REE mine developers had examined the possibility of coarse ore beneficiation. However, three junior companies, Ucore Rare Metals, Quest Rare Minerals, and Namibia Rare Earths, had conducted tests and were planning to include dual energy X-ray transmission (DEXRT) ore sorting in their flow sheets. With more favorable ores, 50% mass rejection and >95% REE recovery were indicated.

The 2016 review showed that Great Western Minerals Group, Arafura Resources, and Northern Minerals had all tested DMS on their REE ores, but all three had decided not to include this process in their flow sheets.

The 2016 sorting study examined economics and concluded that coarse ore beneficiation could offer significant advantages on amenable ores (Goode 2016a). This was particularly true for remote processing sites using relatively expensive diesel electric power. Sorting or DMS substantially reduced the amount of material to be ground ahead of fine ore beneficiation (flotation, etc.) and thereby reduced power demand and costs.

Coarse ore beneficiation tests are simple to perform, and this option should be examined by anyone considering development of a REE deposit.

Flotation

Except for the ionic clay and beach/riverine sand operations, all five current and recent REE recovery facilities include flotation upgrading and exhibit the following common features.

- Deposit types: Carbonatite; Mt. Weld is weathered carbonatite.
- REE minerals: Dominantly bastnaesite (with associated monazite at Bayan Obo and Mountain Pass) and other minor REE minerals.
- Non-REE minerals: Carbonates, iron oxides, barite, fluorite.
- Grind—Relatively fine: 95% passing 75 µm (Bayan Obo), 80% passing 43 µm (Sichuan), 75% passing 74 µm (Shandong), and 38 µm at Mt. Weld.
- Beneficiation flow sheet:
  - Bayan Obo: Grind, LIMS (low-intensity magnetic separation) for magnetite recovery, WHIMS (wet high-intensity magnetic separation) for hematite+REE recovery, then a lower intensity WHIMS to separate hematite and REE, reverse flotation to upgrade magnetite+hematite concentrate, flotation upgrading of REE, concentrate transport to Baotou process plant.
  - Sichuan: Grind, gravity, flotation, concentrate transport to process plant.
  - Mt. Weld: Grind, float, concentrate bagged and containerized, ship to process plant in Malaysia.
  - Mountain Pass: Grind, float, leach to dissolve carbonates, concentrate to on-site process plant.
- REE collectors: Hydroxamates, except Mountain Pass, which used fatty acid.
- Depressants: Sodium silicate, except Mountain Pass, which used sodium lignin sulfonate.
- Flotation temperature: Typically elevated (near 90°C at Mountain Pass), except Sichuan.
- Overall metallurgical performance: As shown in Table 5.

All plants target high-grade REE concentrates at the expense of REE recovery. The reason is the high operating cost of the typical hydrometallurgical process, and because mineral resources are generally large, and mining and beneficiation costs are relatively low.

Most of the REE projects under development include beneficiation by flotation. With few exceptions, the grade of concentrate achieved is far lower than the 40% REO or greater concentrate grade of the producing operations. These low-concentrate grades are a detriment to good economics.

Gravity Concentration

The REE minerals generally have high density values and, if the mineralized particles are coarse enough (say, >10 µm) and liberated, could be separated from lighter gangue minerals by density-based processes. Beach and riverine sands are processed for REE recovery by a combination of gravity, magnetic, and electrostatic methods. Spirals, shaking tables, and jigs are variously used for the gravity separation step. A few hard rock REE beneficiation plants in Sichuan and Shandong in China use gravity concentration on shaking tables either alone or in combination with flotation or magnetic separation.

Table 5 Overall performance of REE beneficiation plants

		Non-REO Streams*		REO Concentrates		
Operation	Feed Grade, % REO	Grade, % REO	REO Distribution, % Feed	Mass, % Feed	Grade, % REO	REO Recovery, % Feed
Bayan Obo	5.5	3.7	64	4	49	36
Mianning	7.0	1.7	22	11	61	78
Mountain Pass	8.5	3.2	35	8	68	65
Mt. Weld	15.0	6.1	30	26	40	70

*Non-REO streams for Bayan Obo include Fe concentrate (44% mass, grading 61% Fe at 80% Fe recovery) and tailings. REO concentrate is blend of 61% REO and 40% REO concentrates.

Several potential REE projects under investigation have included gravity separation at various stages of the development process. Avalon Advanced Materials proposed to use a Mozley multi-gravity separator, essentially a centrifugal shaking table, in its flotation circuit. Arafura Resources is proposing gravity separation in the beneficiation of its Nolans REE-U-P project. AMR Minerals Metals proposes to employ gravity concentration using spirals followed by magnetic separation to eliminate magnetite, then further upgrading on shaking tables ahead of flotation at its Aksu Diamas REE project in Turkey. Rare Element Resources has included gravity concentration with magnetic separation for certain ore types from the Bear Lodge deposit.

Magnetic Separation

The Bayan Obo plant in China uses LIMS to extract magnetite from the ground ore, then two stages of WHIMS to first recover hematite and REE minerals (bastnaesite, monazite, huanghoite, etc.) and then separate the hematite and REE minerals, followed by flotation upgrading of the separated hematite and REE streams. Some of the Sichuan operations also use LIMS and WHIMS as part of their beneficiation processes.

Regarding potential REE operations, Leading Edge Materials Corp. is considering development of the Norra Kärr project in Sweden in which eudialyte is the dominant REE mineral. Matamec Explorations is similarly considering development of the Kipawa project in Canada, which contains eudialyte, mosandrite, and britholite. Both companies propose to use LIMS to eliminate magnetite, and similar minerals, ahead of WHIMS for the recovery of the REE minerals. Tanbreez Mining Greenland A/S is proposing to use magnetic separation to upgrade its eudialyte-bearing ore in Greenland. Commerce Resources Corp. is studying the Ashram REE deposit in Quebec and proposes to make a flotation concentrate, leach it with hydrochloric acid (HCl) to remove carbonates, regenerate the HCl, and use WHIMS to recover the monazite, bastnaesite, and xenotime from the leach residue. The nonmagnetic fraction could be marketed as metallurgical-grade fluorspar and the REE concentrate subjected to sulfuric acid baking (Commerce Resources Corp. 2014).

Electrostatic Separation

Mineral sand deposits in Australia, India, and elsewhere are typically wet processed using spirals, or Reichert cones and other gravity devices to produce a heavy mineral concentrate (HMC) and tailings. The HMC is usually dried and separated into the constituent minerals. Commonly, a first electrostatic separation is used to separate a rutile/ilmenite/leucoxene conducting concentrate from a zircon/monazite/garnet/sillimanite nonconducting concentrate. The two concentrates are further separated using magnetic, additional electrostatic, and dry gravity methods.

MINERAL “CRACKING” AND LEACHING

Most REE minerals are refractory (inert to chemical attack) and need “cracking” using aggressive methods, such as baking with strong sulfuric acid or treatment with strong alkali. These processes can be capital intensive and expensive to operate but are viable with certain ores. The ionic clay deposits are more readily processed since they only need contacting with a weakly acidic electrolyte to displace the REE from the exchange sites on the clay. REE ore bodies dominated by silicate minerals, such as allanite, eudialyte, mosandrite, and britholite, are also an exception since the silicates are generally easy to leach. Reference material includes the various company websites, Verbaan et al. (2015), Goode (2016c), Buchanan et al. (2014), Gupta and Krishnamurthy (2005), Sadri et al. (2017), Zhang and Edwards (2013), and publicly available company reports from SEDAR, EDGAR, and ASX.

REE deposits usually contain more than one REE-bearing mineral, and occasionally one leach or cracking system needs to be followed by a second cracking operation to extract all of the REE from the ore. In other cases, the main mineral can be cracked, but part of the REE might be re-precipitated requiring a second crack/leach stage for full recovery. Examples include Molycorp’s Mountain Pass operation where fluoride re-precipitation occurs (SRK Consulting 2010) and Greenland Minerals and Energy’s Kvanefjeld project where a sulfuric acid leach of a high-sodium material leads to the formation of an insoluble double sulfate (Krebs 2014). Both issues are solved using caustic metathesis and releaching.

Low-Temperature Acid Leaching

Some REE minerals are amenable to low-temperature (<100°C) acid leaching. If all the REE in a given material are contained entirely in such minerals, then low-temperature acid leaching can be effective.

Fluorocarbonate Minerals

Dilute mineral acids readily attack bastnaesite and synchysite, but these minerals contain fluorine and the REE fluorides are insoluble. Accordingly, low-temperature acid processing of ores and concentrates containing bastnaesite and/or synchysite can be challenging because the REE can enter solution but immediately re-precipitate as fluorides.

In its early operations, Mountain Pass produced a flotation concentrate that was leached in weak HCl to remove calcite and strontianite and produce a 60%–70% REO grade concentrate dominantly containing bastnaesite. In the pre-2010 flow sheet, the concentrate was roasted at 650°C to crack the bastnaesite, volatilize the contained fluorine, and oxidize the Ce to Ce(IV). The resulting calcine was cooled and leached in cold, weak HCl, which dissolved all the REE except for the Ce(IV). The leach residue was further processed and marketed as a glass-polishing agent with some upgraded to high-grade CeO_2.

The Mountain Pass flow sheet operated after 2010 subjected the preleached bastnaesite to a strong HCl leach that extracted most of the REE, except for about 30%, which combined with the F released from the bastnaesite and reprecipitated as fluorides (SRK Consulting 2010). To get high overall leach extraction, the leach residue was metathesized with NaOH and releached in the pregnant leach solution (PLS) obtained in the first leach in a process similar to that operated in the 1950s by Molycorp at its York, Pennsylvania (United States) facility. However, severe difficulties were encountered with the new Mountain Pass leach system that, with issues elsewhere in the operation including the chlor-alkali plant for reagent regeneration, resulted in unprofitable operations and closure of the plant in 2015 (Thompson Reuters 2015).

Chinese researchers have investigated ways of avoiding the F precipitation effect and otherwise improving the environmental aspects of its REE operations processing F-bearing concentrates. Zhou and Liu (2015) describe pelletizing a mixture of Baotou flotation concentrate and soda ash, roasting at 600°–700°C, washing the calcine with water or weakly acidified water to remove sodium fluoride and other contaminants, then HNO_3 leaching to extract the REE and Th. The process avoids the loss of fluorine and/or the adverse effects of F on REE dissolution. It also oxidizes Ce(III) to Ce(IV), which is extracted with a solvent along with Th, leaving the trivalent REE free of Ce and Th and ready for separation. In 2000, Zhu et al. (2000) described a similar process to remove F from a Sichuan bastnaesite ore using a Na_2CO_3 roast for 30 minutes at 650°C followed by chlorination roasting using NH_4Cl for 1 hour at 325°C to render the REE water soluble.

Peak Resources is developing the Ngualla REE project in Tanzania, which will produce a flotation concentrate containing bastnaesite and assaying about 40% REO. This will be treated by a selective alkaline roast with soda ash at 700°C followed by a water wash to remove the solubilized fluoride and avoid REE re-precipitation. The water wash is followed by a weak (<1%) HCl leach at 80°C to dissolve the REE. The Ce is oxidized to Ce(IV) during roasting such that Ce leach extraction is low. This is seen as an advantage given low Ce prices (Peak Resources 2016).

Silicate Minerals

Eudialyte, a silicate mineral, is readily leached with dilute sulfuric acid, and potential producers, including Leading Edge Minerals Corp. (Norra Kärr project) and Matamec (Kipawa Zeus project), are proposing this leach system. Although much of the REE is dissolved from the silicate mineral, a significant amount of silica also enters the solution and can cause filtration and SX issues.

Leading Edge Minerals determined that its eudialyte concentrate could be effectively leached at pH 1, 30°C, a low pulp density of 15% to avoid silica precipitation, and a 2-hour leach time to give 90% REE extraction. Silica in solution is later removed by raising the pH and filtration followed by reheating the solution and re-acidification ahead of solvent extraction (SX). Matamec found that with a 150-µm grind, a 5-hour leach with 20 g/L free acid, ambient temperature, and 35% solids, its eudialyte-bearing concentrate would yield REE extractions of about 90% and a leached slurry that could be handled through normal liquid–solid separation equipment.

Ucore proposes to upgrade its Bokan Mountain ore using DEXRT sorting and magnetic concentration to produce a 25% mass concentrate containing the silicate minerals allanite and kainosite, as well as bastnaesite. The concentrate is ground to 100% passing 40 µm and then leached for 8 hours at 90°C in two stages using 30% nitric acid. Ucore proposes to recover excess HNO_3 from the PLS using diffusion dialysis.

Sulfuric Acid Baking

Almost all the REE-bearing minerals respond well to baking with concentrated sulfuric acid at temperatures greater than 200°C. An exception is zircon, which is generally not affected by acid baking and can carry significant levels of HREE. In this case, the residue from an acid bake can be caustic cracked to access the REE and Zr in the zircon. Fergusonite, samarskite, and other Nb-bearing REE minerals do not respond well to low-temperature acid baking.

A simple acid bake of REE minerals using excess sulfuric acid at 200°–300°C leads to the following reactions (Xu 1995) for REE minerals and common accessory minerals, using La as a surrogate for all the REE.

Bastnaesite:

$$2La(CO_3)F + 3H_2SO_4 \rightarrow La_2(SO_4)_3 + 2HF\uparrow + 2H_2O\uparrow \quad \textbf{(EQ 1)}$$

Monazite:

$$2LaPO_4 + 3H_2SO_4 \rightarrow La_2(SO_4)_3 + 2H_3PO_4 \quad \textbf{(EQ 2)}$$

and $Th(SO_4)_2$

Hematite:

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O\uparrow \quad \textbf{(EQ 3)}$$

Fluorspar:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 3HF\uparrow \quad \textbf{(EQ 4)}$$

Calcite:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2\uparrow + H_2O\uparrow \quad \textbf{(EQ 5)}$$

Silica:

$$SiO_2 + 6HF \rightarrow (H_3O)_2SiF_6\uparrow \quad \textbf{(EQ 6)}$$

and $SiO_2 + 4HF \rightarrow SiF_4\uparrow + 2H_2O\uparrow$

At progressively higher temperatures through the range of 300° to 800°C, other reactions take place, including

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O\uparrow \quad \textbf{(EQ 7)}$$

$$Th(SO_4)_2 + H_4P_2O_7 \rightarrow ThP_2O_7 + H_2SO_4 \quad \textbf{(EQ 8)}$$

$$H_2SO_4 \rightarrow SO_3\uparrow + H_2O\uparrow \quad \textbf{(EQ 9)}$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O(SO_4)_2 + SO_3\uparrow \quad \textbf{(EQ 10)}$$

$$H_4P_2O_7 \rightarrow 2HPO_3\uparrow \quad \textbf{(EQ 11)}$$

$$Fe_2O(SO_4)_2 \rightarrow Fe_2O_3 + 2SO_3\uparrow \quad \textbf{(EQ 12)}$$

$$La_2(SO_4)_3 \rightarrow La_2O(SO_4)_2 + SO_3\uparrow \quad \textbf{(EQ 13)}$$

$$La_2O(SO_4)_2 \rightarrow La_2O_3 + 2SO_3\uparrow \quad \textbf{(EQ 14)}$$

A low-temperature acid bake, say at 220°C, will convert most of the REE into water-soluble forms, allowing a simple water leach of the baked material to dissolve the REE. Th, Fe species, and other gangue components are also largely or completely sulfated. These reactions consume acid and solubilize Th and Fe, resulting in a PLS containing high impurity levels.

A high-temperature bake, or a high-temperature second-stage bake of a low-temperature baked residue, will, depending on the temperature, cause Reactions 7 to 14 to occur, with Sc sulfate decomposition starting at 700°C and the other REE at about 800°C (Borra et al. 2016). Thorium pyrophosphate and Fe_2O_3 are sparingly soluble, so baking at a higher temperature leads to a PLS that is low in impurities. Depending on the minerals in the feed, a high-temperature bake (>500°C) can also lead to reduced extraction of Zr, Nb, and Al. Finally, much of the acid consumed in sulfation reactions at the lower temperature is released as sulfur oxides at higher temperatures, and these can be used to reconstitute sulfuric acid from the off-gas stream.

Although there are positive aspects to the high-temperature operation, REE recovery can suffer at the higher temperatures. Additionally, the thermal demand of the system is increased and the design and installation of the high-temperature baking equipment, its refractory lining, and the peripheral equipment all become more complex and expensive.

Acid baking is typically achieved by mixing concentrated acid and REE-bearing feed and then placing the mixture into a horizontal rotating kiln for heating to the desired temperature and holding for the necessary time—often between 2 and 4 hours. The high-temperature (>500°C) acid baking process is used to process concentrates obtained from Bayan Obo, Mianning-Dechang, and Mt. Weld. Kilns are typically direct fired and lined with acid-proof refractory. Accretion can be an issue, and scrapers, calcine recycle, and other devices and strategies are used or proposed to reduce such problems. Off-gases need to be scrubbed for the capture of fluorine and sulfur compounds.

Acid baking in rotary kilns is common in Chinese REE recovery plants where the kilns have been operating trouble-free for many years. Initial operations were low tonnage and kilns were small. For example, a processing rate of 3 t/d concentrate could be handled by a kiln that was 0.7 m internal diameter by 11 m long (Xu 1995). As demand and production increased, kilns as large as 1.3 m diameter by 25 m long, and greater, were in use and capable of processing 15 t/d to produce about 2,500 t/yr of REO. Mixing of acid and concentrate, kiln feeding, kiln detailed design, off-gas handling, and so on, are all well established.

Large-scale acid baking of REE concentrates has only recently been applied outside of China. Lynas Corporation's LAMP (Lynas Advanced Materials Plant) operation at Kuantan in Malaysia is designed to process 66,000 t/yr of flotation concentrate containing 40% REO produced at Mt. Weld in Australia. Four 60-m-long kilns have been installed at the LAMP site, each nominally processing about 55 t/d of concentrate at 600°C. The Lynas kilns, and associated mixing and feeding systems, are far larger than the equivalent plants in China. First feed to two Phase 1 kilns was made late in 2012, but serious issues in the baking systems took time to resolve and full design production was only attained in September 2017 (Lynas Corporation 2017). Clearly, high-capacity acid mixing–transfer–bake systems are difficult to design correctly.

Outotec has proposed the use of a high-intensity mixer to contact concentrated sulfuric acid and REE concentrate to form pellets in the 0.1–2 mm size range. Although sulfation in a rotary kiln frequently needs 2–4 hours, Outotec claims 15 minutes is sufficient for complete sulfation in a fluidized bed roaster operating at about 250°–300°C. The sulfated product can then be transferred into a second fluidized bed roaster operating at about 700°C for the selective decomposition of the Fe, Al, and other sulfates (Guentner et al. 2016). Off-gas from the two-stage roasting system can be processed for the regeneration of sulfuric acid, capture of fluoride species, and so on. The Outotec two-stage roasting system forms an integral part of Frontier's proposed Zandkopsdrift project (Venmyn Deloitte 2015).

Several proposed REE projects would include sulfuric acid baking, including Strange Lake in Quebec, Canada (REE silicates); Ashram (monazite); Steenkampskraal in South Africa (monazite); Browns Range in Western Australia (xenotime); and Eco Ridge in Ontario, Canada (monazite). Sulfuric acid baking at high temperature has been proposed and tested for recovering REE from bauxite residue (Borra et al. 2016). In some cases, a preleach, often using HCl, is proposed ahead of the acid bake to eliminate undesirable elements or reduce the feed mass going to the kiln feed.

Agitated Leaching with Concentrated Sulfuric Acid

Concentrated sulfuric acid can be used in an agitated leach system at temperatures up to the boiling point of concentrated acid, which is 287°C for 93% acid. This form of leaching has been referred to as SAAB (strong acid agitated bake) or concentrated acid "pot digestion." Test results have been reported by Commerce Resources (2014) and Rainbow Rare Earths (2016).

The strong acid agitated leach approach typically gives about the same REE extraction as acid baking, but it avoids the difficulties associated with kilns. However, the high-acid addition of the strong acid agitated leach necessitates the recovery of the excess acid, which presents difficult process challenges that have yet to be solved on an industrial scale.

Caustic Cracking

Fusion with pure alkali (NaOH, KOH, etc.) in the absence of water or agitation with strong caustic solutions (e.g., 50% NaOH or greater) at elevated temperatures will crack most REE-bearing minerals, leading to the formation of hydroxide-like compounds that can be leached with a weak-acid solution. Typical reactions for selected REE minerals and typical gangue minerals include the following:

Bastnaesite:

$$La(CO_3)F + 3NaOH \rightarrow La(OH)_3 + NaF + Na_2CO_3 \qquad \textbf{(EQ 15)}$$

Monazite:

$$LaPO_4 + 3NaOH \rightarrow La(OH)_3 + Na_3PO_4 \qquad \textbf{(EQ 16)}$$

and $Th(OH)_4$

Fergusonite:

$$YNbO_4 + 3NaOH \rightarrow Y(OH)_3 + Na_3NbO_4 \qquad \textbf{(EQ 17)}$$

Apatite:

$$Ca_{10}(PO_4)_6F_2 + 20NaOH \rightarrow 10Ca(OH)_2 + 20Na^+ + 6PO_4^{3-} + 2F^- \qquad \textbf{(EQ 18)}$$

Feldspar:

$$KAlSi_3O_8 + 6NaOH \rightarrow K^+ + 6Na^+ + Al(OH)_4^- + 3SiO_3^{2-} + H_2O \qquad \textbf{(EQ 19)}$$

Fluorite:

$$CaF_2 + 2NaOH \rightarrow Ca(OH)_2 + 2Na^+ + 2F^- \qquad \textbf{(EQ 20)}$$

Silica:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \qquad \textbf{(EQ 21)}$$

The preceding reactions show the use of NaOH, but KOH and mixtures can also be effective, although there are differences between NaOH and KOH. For example, the fusion temperature of NaOH is 318°C, whereas that of KOH is 360°C. Another example concerns the solubility of the reaction products. If niobium is present, it could be important that Na_3NbO_4 is soluble in water but insoluble in strong NaOH solution, whereas the K equivalent is soluble in KOH solutions.

Fusion cracking has been, and is, used industrially for the cracking of tungsten concentrates (NaOH, or Na_2CO_3), niobium concentrates (NaOH, with soda ash; or KOH), and zircon (NaOH). Fusion cracking of REE minerals has not been practiced, although development companies have investigated the process in the laboratory. Typically, fusion involves mixing excess alkali with the mineral of interest, heating the mixture on a batch basis to above the fusion point, and holding at that temperature for a required period, often 2–4 hours. When fusion is complete, the melt is allowed to cool or else granulated, then mixed with water, the excess alkali solution filtered off, and the hydroxides processed for metal recovery.

Caustic cracking with strong NaOH solutions (60%–70%) was commonly used for cracking monazite. The process was employed in Brazil, by Rhone Poulenc (now Solvay) at La Rochelle in France, and by REE and Th producers in India. The monazite was generally ground to –40 µm, mixed with an excess of NaOH as a ~50% solution, and held with agitation at 140°C or greater for several hours. At the end of the cracking period, the slurry was diluted with water and agitated, solution was recovered by filtration, the filter cake washed to remove residual caustic solution, the solution cooled for crystallization and recovery of trisodium phosphate (TSP) recovery and then recycled, and the hydroxide-bearing filter cake leached for REE and Th recovery. This was usually done by an initial HCl leach to a pH of about 3.4 to dissolve the REE hydroxides followed by liquid–solid separation, then a strong HCl leach to dissolve Th (Krumholz 1957; Kaczmarek 1981).

One of the key aspects of the caustic cracking process is the removal of excess NaOH and its recovery for reuse, and elimination of soluble cracking products, such as TSP, aluminates, and silicates, without crystallization of the TSP. The solubility of TSP is a strong function of NaOH strength and temperature (Youtz et al. 1950), and test and plant designs need to recognize this issue.

Caustic cracking is not now being used. Of 18 REE development projects summarized by Verbaan et al. (2015), only three are proposed with caustic cracking. Along with Mountain Pass, discussed earlier, the proposed REE caustic crack operations are as follows:

- The Kvanefjeld project in Greenland will use caustic cracking to treat a preleach residue containing REE-Na double sulfates. Details of the cracking step are not provided.
- Lofdal in Namibia will batch process a preleached concentrate containing xenotime. A 50% NaOH solution, 20% solids, and 140°C for 4 hours are proposed followed by hot water washing, then HCl leaching.
- Mkango's Songwe Hill deposit in Malawi contains REE in apatite and synchysite with calcite as the dominant gangue mineral. The proposed flow sheet includes a pH 3.5 HCl preleach to remove calcite with HCl regeneration from the preleach PLS. The preleached concentrate is then leached at ambient temperature with 30% HCl for 0.5 hours, which gives about 80% extraction of LREE and >90% extraction of HREE. A caustic crack applied to the REE leach residue (50% NaOH, 100°C for 4 hours) releases REE from fluoride precipitates and any minerals not cracked by the 30% HCl leach. The NaOH crack step is followed by a 5% HCl releach, which increases overall recoveries for all REE (excluding Ce, Yb, and Lu) to >92% (MSA Group 2015).
- Mountain Pass included caustic cracking of an HCl leach residue to recover insoluble fluorides formed during HCl leaching of the bastnaesite in the preleached concentrate.

Other Cracking Systems

Numerous alternative roasting and baking systems for REE ores and concentrates have been proposed, and some have been used commercially. The roasting of bastnaesite concentrate with a sodium salt ahead of hydrochloric acid leaching has been mentioned earlier as a means of allowing the elimination of fluorine and oxidizing Ce.

The Kashka REE plant in Kyrgyzstan processed a complex ore, high in HREE content, from the Kutessay II mine. Concentrate containing 6%–7% REE was cracked by reaction with Na_2CO_3 at elevated temperature in a rotary kiln. The calcine was ground in a ball mill and dewatered; then the REE was dissolved in nitric acid, purified, and separated using tri-n-butyl phosphate (TBP) SX and IX (Stans Energy 2017; Danilov 2011).

Roasting at 700°C for 1 hour with 15% CaO and 15% NaCl-$CaCl_2$ has been proposed as a means of decomposing the bastnaesite in a Mianning REE concentrate while preventing HF formation (Bian et al. 2006). The bastnaesite was 94% decomposed during the roast. The calcine from this process would be acid leached to dissolve the REE compounds formed during roasting. Similar experiments on a sample of Bayan Obo concentrate, containing bastnaesite and monazite, gave 70% decomposition with CaO alone and 90% decomposition, and almost total retention of F, with CaO-NaCl-$CaCl_2$ mixture (Bian et al. 2010). The NaCl-$CaCl_2$ becomes molten at about 520°C and facilitates the reactions.

Investigators have studied fixing fluorine by mixing bastnaesite-bearing concentrate containing 67% REO and 7% F with MgO (0.1 to 0.3 t/t concentrate) followed by chlorination roasting at ~325°C for 1 hour using about 1:1 mass ratio of NH_4Cl (Chi et al. 2004).

Chinese investigators working with Baotou concentrate and Peak Resources propose to add sodium carbonate to bastnaesite concentrate to promote the formation of NaF during roasting, which can then be water-washed from the calcine to eliminate fluoride precipitation issues.

Avalon Advanced Materials obtained promising results from a mixed alkali cracking pilot plant in which REE concentrate was pelletized with Na_2CO_3 and $CaCO_3$ and then fed to a rotary kiln, the product water leached to remove excess alkali and then acid leached (Avalon Advanced Materials 2013).

Chlorination

Up to 13,000 t/yr of loparite concentrate recovered from mines in the Kola Peninsula are processed by chlorination at the Solikamsk Magnesium Works in the Urals. Loparite concentrate contains about 9% Nb+Ta oxides, 36% TiO_2, and 29% REO; it is processed to yield mixed REE carbonates and oxides, and Nb and Ta products. In 2015, Solikamsk processed 8,509 t loparite and produced 2,312 t REO, 2,014 t Ti, 628 t Nb_2O_5, and 32 t Ta_2O_5 (JSC Solikamsk Magnesium Works 2016).

Zelikman et al. (1964) described chlorination in which loparite was mixed with coke and a binder, briquetted, "coked" at 700°C, then chlorinated at about 800°C in an electric shaft furnace, 4.5–5 m internal diameter by up to 8-m-high partially filled with carbon cylinders as the resistive heating elements. The off-gas was fractionally condensed with a solid containing $NbOCl_3$, $NbCl_5$, $TaCl_5$, and $FeCl_3$ collected first and further processed for Nb and Ta recovery. $TiCl_4$ was then recovered in a packed tower irrigated with cooled liquid $TiCl_4$. REE, Ca, and Na chlorides were not volatilized at the furnace operating temperatures and were removed as a molten salt and refined to yield mixed REE carbonates and oxides.

The Australian Mineral Development Laboratory described the chlorination of briquettes made from a carbon–monazite mixture at temperatures greater than 900°C. Thorium and phosphate were volatilized, while the REE chlorides were collected as molten anhydrous chloride with a recovery exceeding 85% (Hartley 1952).

Th. Goldschmidt AG also developed a process in which finely ground concentrate was mixed with carbon and a binder such as starch or sugar, briquetted, dried, then chlorinated using chlorine gas at 1,000–1,200°C. A special furnace was designed for the aggressive system with heat generated by passing electricity through a bed of coke upon which the carbon–REE concentrates were supported (Brugger and Greinacher 1967).

If the REE concentrate is a phosphate or niobate, the REE are converted to chlorides that are removed as a molten salt mixture, and many of the other chlorides, including $ThCl_4$, are volatilized and leave with the off-gas. If the REE concentrate is bastnaesite, at least part of the REE report as fluorides and part of the Th and U will similarly be converted to fluorides and not volatilized.

Several researchers have developed solutions for the bastnaesite chlorination problem by the addition of fluorine complexing reagents. Wang and Zhang (2002) propose a first bake of the carbon–concentrate mixture with the addition of a silicon, phosphorous, or boron-containing material at between 400° and 700°C to remove F as well as Fe and P. A second-stage roast with Cl at 700°–900°C removes U and Th and chlorinates the REE, which are separated as molten salts from solid residues by filtration at 700°–1,000°C to yield a pure REE chloride melt. The work is described in detail by Zhang et al. (2004). The preferred agent for F removal is revealed as being $SiCl_4$. $AlCl_3$ is used to enhance Th removal.

In 2015, Niobec was granted a patent covering the chlorination of bastnaesite (Bergeron et al. 2015). The patent discusses the fluoride issue and identifies boron-containing Lewis acids, such as $B(OH)_3$, BF_3, BCl_3, B_2O_3, and $Na_2B_4O_7$, as being useful for eliminating the adverse effect of fluorine. Using La to represent the REE, the reactions are

$$\text{LaFCO}_3 \rightarrow \text{LaFO} + \text{CO}_2 \qquad \textbf{(EQ 22)}$$

$$3\text{LaFO} + \text{Lewis acid-Cl}_3 \rightarrow 3\text{LaClO} + \text{Lewis acid-F}_3 \qquad \textbf{(EQ 23)}$$

In the proposal, bastnaesite concentrate is mixed with a carbonaceous reductant, the Lewis acid, and a binder, pelletized to a 10-mm top size, screened at 1 mm, and then dried before being chlorinated. Off-gases are fractionated to remove volatilized chlorides of Fe, Al, P, Ti, Si, Nb, Zr, and Hf, and excess Cl and BF_3 are recycled. Th and U are eliminated by distillation from the molten chloride at 900°C. Gaseous reductants, such as CO, can be used instead of solid reductants.

Elution of Ionic Clay

The ionic clay deposits of Southern China are the main source of HREE (Goode 2016c). Undeveloped deposits are found in Madagascar, Africa, Brazil, and Chile. The genesis, prevalence, mineralogy, and exploitation of such deposits have been discussed by Chi and Tian (2008); Rocha et al. (2014); Moldoveanu and Papangelakis (2013); Goode (2016c); and Vossenkaul et al. (2015).

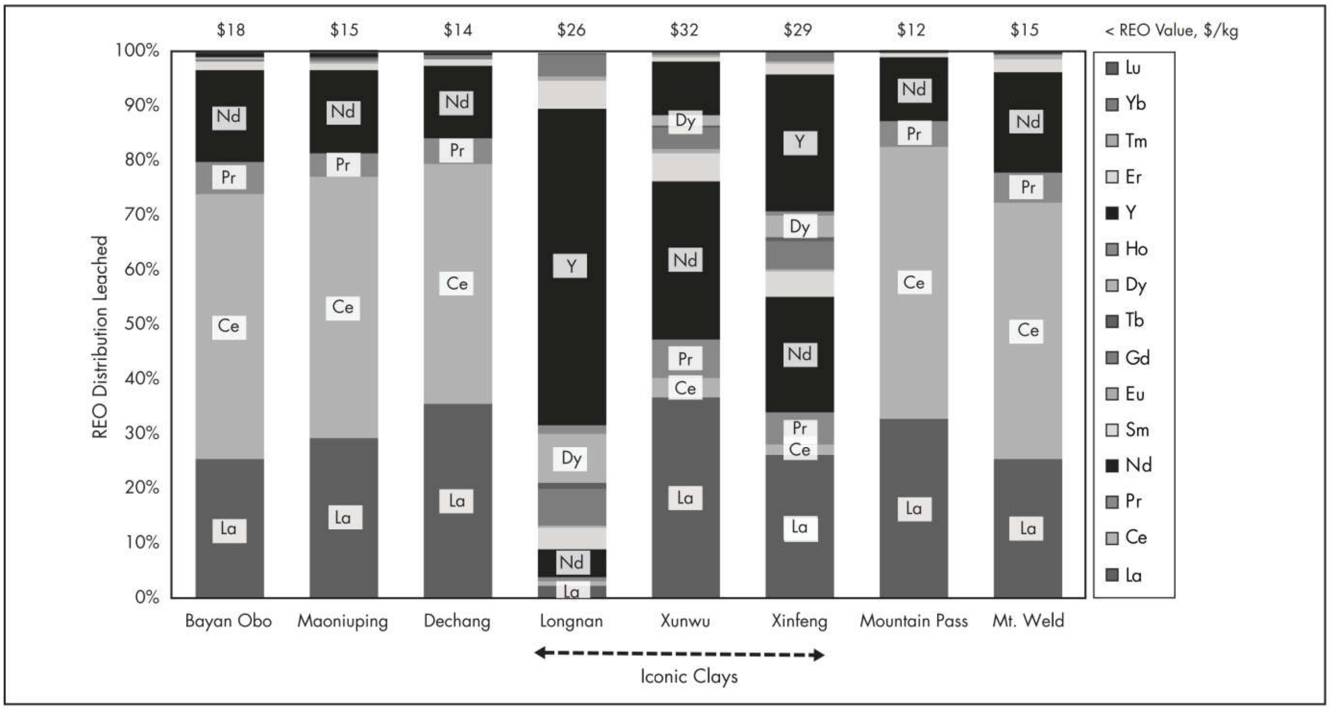
The ionic clay deposits, also known as "weathered crust elution-deposited" and "saprolite" deposits, that are in production are located in China's Jiangxi, Fujian, Guangdong, Yunnan, Hunan, and Zhejiang provinces and Guangxi Zhuang Autonomous Region. They are low grade, typically 0.1% REO, but are economical to process and usually deliver products that are low in Ce. Typical REE distributions and in situ values are shown in Figure 5 with corresponding data for selected operating hard rock deposits.

The ionic clay deposits were formed by intensive weathering in which REE-bearing bedrock was altered into clay-rich saprolite, often for tens of meters from present surface. The original REE minerals, typically xenotime and monazite, were decomposed to an extent between 50% and almost 100%. The dissolved REE were then sorbed through IX processes by the clays of the saprolite. The extraction of the REE sorbed on the clay is readily achieved by contacting the ore with an electrolyte solution such as 0.5 M NaCl or 0.2 M $(NH_4)_2SO_4$.

During deposit formation, cerium was usually oxidized to Ce^{4+} and precipitated with any dissolved Th as cerianite $(Ce^{4+},Th^{4+})O_2$. Cerianite is not dissolved by the leach solutions employed, hence the low Ce of the products.

When ionic clay deposits were first exploited in 1969, REE were extracted from the ore by mining and vat leaching or by heap leaching. However, environmental issues were evident in the form of massive destruction of forests and land, landslides because of the removal of vegetation, and surface water and agricultural land polluted by leach reagents. Eventually, in situ methods of recovery were adopted, particularly for the hilltop deposits that are typical of the area, and are now mandated for new operations.

In situ leach sites in China are often small and might produce just a few hundred tons annually of REO over a couple of years. Larger operating complexes might produce 1,000 or 2,000 t/yr. Preparation for in situ leaching is minimal with vegetation left in place, injection wells drilled on roughly 10-m center around the hilltop, and a low-cost plastic pipe distribution system installed. PLS is collected in tunnels or



Note: Prices from Roskill 2016; distributions from various sources.

Figure 5 Distribution and basket value of in situ hard rock and recovered ionic clays

ditches at the base of the hill. Some recirculation of solution can be practiced to increase grades, but eventually the solution is processed by batch neutralization to pH 5.3 and filtration to remove impurities, then batch precipitation of REE using either oxalic acid or ammonium bicarbonate, followed by filtration and ignition of the precipitate to yield a mixed REO product. Equipment at the smaller operations is rudimentary, with in-ground excavations lined with plastic sheet used as precipitation tanks and plate-and-frame filters for liquid–solid separation.

Some are concerned about the in situ process since lixiviant or PLS can be lost to bedrock fractures or inadequate solution retrieval systems, leading to contaminated aquifers. The recovery of REE from the resource can be low if there is a loss of lixiviant or PLS or if there are extensive areas of low permeability in the deposit. The injection of leach solution into the clay and subsequent rinse water injection and/or rainfall can cause swelling of the clays, leading to landslides.

Much has been said about the illegal production of REE in China, perhaps 40,000 t/yr REO in recent years (China State Council 2012; Roskill 2016). Small, in situ, ionic clay operations are inconspicuous; would readily escape detection; are cheap to build and operate; and are undoubtedly a significant source of illegal material. Illegal REE mining is seen as a cause of environmental damage, health issues, and depressed prices, and the Chinese government is attempting to eliminate such activity.

Development companies with ionic clay deposits in Brazil, Chile, and Madagascar have proposed large-scale operations using mining and either heap or agitation leaching. Although the developers occasionally mention in situ leaching, it does not appear to be a high-priority option. This might be because of the difficulty of demonstrating bedrock impermeability to the satisfaction of the regulators.

HYDROMETALLURGICAL PROCESSING OF REE-BEARING PREGNANT SOLUTION

The cracking and leach processes produce a PLS containing REE and impurity elements such as Fe, Al, Th, and U. The PLS must be treated to eliminate the impurities and produce the REE in an intermediate solution or solid amenable to separation into individual REE products that are typically 99.9% pure or greater. Non-REE impurities complicate the task of the separation plant, and a typical specification for a mixed REE feed to a separation plant will require that it contain very low levels of U, Th, Al, Ca, Fe, Al, Zn, Cd, Pb, SO_4, and U and Th progeny.

Specifications will generally be agreed upon between the producer of the intermediate REE product and the separation plant. Published standards are generally not freely available; however, a Chinese Standard, GB/T 20169–2015, gives standards for "mixed rare earth oxide of ion-absorbed type rare earth ore."

Impurity Removal

Various techniques are being used or have been proposed for the removal of impurities from REE pregnant solutions (Lucas et al. 2015; Verbaan et al. 2015; Yahorava et al. 2013; Zhu et al. 2015; Zhang and Edwards 2013).

Selective Dissolution

Caustic cracking produces a mixture of the hydroxides of those metals that were released during the mineral cracking process. Thus, the solid residue produced by cracking monazite will comprise hydroxides and similar compounds of the REE, Th, Fe, U, and whatever other metals might be converted during the cracking process. Just as Fe and Th hydroxides are precipitated earlier than the REE during selective hydrolysis, so too can REE be dissolved from a mixed hydroxide while leaving

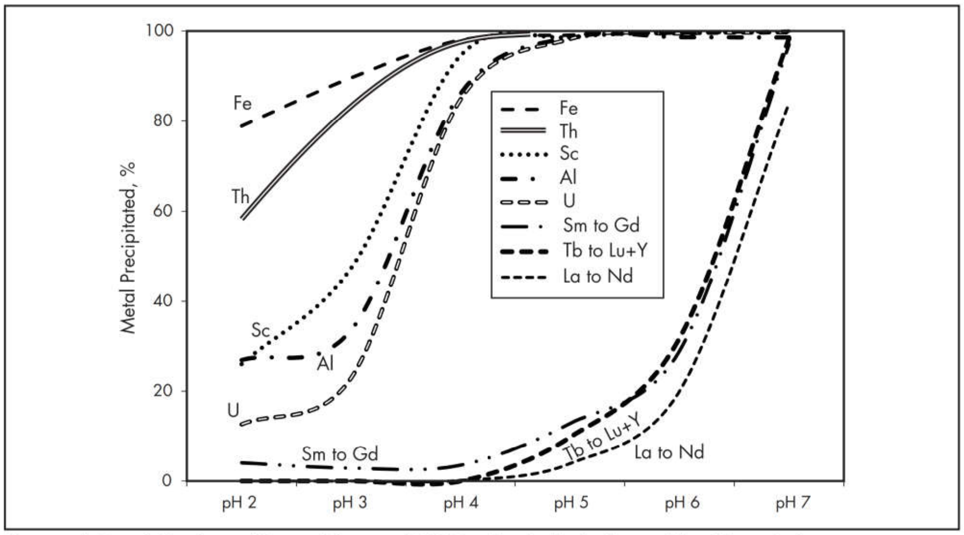


Figure 6 Precipitation of impurities and REE by hydrolysis from chloride solution

the Fe and Th in the residue. Selective dissolution by adding HCl to a pH no lower than 3.5 has long been part of the process for recovering REE from monazite by caustic cracking. When practiced on Brazilian monazite containing 64% REO and 6% ThO_2, the residue from selective leaching contained 60% ThO_2 and 4% REO (Krumholz 1957). Rhone Poulenc practiced selective dissolution from cracked monazite at its La Rochelle plant (Kaczmarek 1981) as did the Indian monazite processors (Pillai 2008; Swaminathan et al. 1988).

Selective dissolution can also be employed if an intermediate REE product is precipitated as a carbonate or hydroxide and then redissolved for further processing.

Fe, Al, and Th Removal by Selective Hydrolysis

PLSs commonly contain Fe, Al, and Th, and these elements can be removed as hydroxides by a careful partial neutralization process in which the pH is raised to between 3 and 5. At the optimum pH, the REE remain in solution, but Fe^{3+}, Al, and Th are precipitated as indicated in Figure 6 for chloride solution. Depending on the starting solution analysis and the operation details, more than 95% of many contaminants can be precipitated with REE losses of well under 5%. Fe^{2+} is only hydrolyzed at about pH 6, so removal of iron will only be complete if the iron has been oxidized.

The precipitation trends shown in Figure 6 do not radically change with the choice of neutralizing agent (e.g., NaOH, MgO, NH_4OH, etc.) except in the case of carbonates (e.g., $CaCO_3$, Na_2CO_3, etc.), in which case the precipitation curves are displaced by about 2 pH units lower and the sharpness of separation is considerably reduced.

The use of CaO or $CaCO_3$ to precipitate impurities from sulfate solutions causes the precipitation of gypsum as well as the impurities. The gypsum precipitate tends to carry down some REE, and clean separations with low-value losses are difficult to achieve. The use of NaOH or Na_2CO_3 as an impurity precipitant from sulfate solutions is not appropriate, especially at higher solution grades, since a part of the LREE will likely be precipitated as the double sulfate salts, typically $La_2(SO_4)_3{\cdot}Na_2SO_4{\cdot}2H_2O$. For the partial neutralization of sulfate solutions, with low REE losses, the preferred reagent is either MgO or $MgCO_3$.

Kim et al. (2014) present data on the speciation of REE and common impurity elements across a range of pH values, which is very much in accordance with the aforementioned observations.

In work conducted for Natural Resources Canada, SGS Canada demonstrated that a phosphate addition equimolar to Fe to a sulfate solution led to 99% elimination of Th at pH 2 (and enhanced Fe and Sc removal), whereas without phosphate, the same level of elimination was not obtained until a pH of 4.5 (SGS Canada 2017).

Although Cu, Zn, and Pb are not commonly encountered in REE solutions, they can be eliminated by sulfide addition. This approach has been used to eliminate radiogenic Pb from PLS. Similarly, sequential additions of $BaCl_2$ and Na_2SO_4 will precipitate $BaSO_4$, which will carry down Ra (Pillai 2008). A simple sulfate addition to a Ba-containing HCl-based PLS will precipitate $BaSO_4$, which will also precipitate Ra.

Solvent Extraction and Ion Exchange

SX or IX is useful for the extraction of U and Th away from REE, and this has been reviewed by Zhu et al. (2015) and Xie et al. (2014).

Li et al. (2013) operated a pilot-plant campaign using a primary amine SX circuit on a solution containing 30–50 g/L of REE and 0.1–0.2 g/L Th obtained by a sulfuric acid bake operation on Bayan Obo concentrates. Using seven loading, eight scrubbing, and eight HNO_3 stripping stages, they achieved REE-bearing raffinates containing about 0.0001 g/L Th and made a Th product that was 98% pure. The raffinate from this operation was contacted with a phosphonic acid extractant (P507), which extracted the REE away from Zn, Mg, Ca, and SO_4, yielding a 223-g/L chloride strip stream immediately ready for separation.

The Kvanefjeld project in Greenland will process ore containing about 1% REO and about 300 ppm of U. The ore will be beneficiated and the concentrate will then be sulfuric acid leached to recover most of the uranium, with the REE reporting to the residue as double sulfates. The leach residue will be metathesized to destroy the double sulfates, then HCl leached to take the REE and remaining U into solution. Selective hydrolysis, $BaCl_2$, and NaHS will be used to eliminate most impurities from the chloride leach solution, followed by IX to remove U immediately ahead of REE precipitation using Na_2CO_3 (Krebs 2014).

A mixture of a tertiary amine (Alamine-336) and a primary amine (Primene-JMT) has been shown to be effective at simultaneously extracting U and Th from sulfate leach solution (SGS Canada 2017).

An industrially used approach is to extract the REE, Th, and U using a mixture of di-(2-ethylhexyl)phosphoric acid (DEHPA) and TBP, and sequentially and selectively strip the elements. This approach was used to recover REE from the barren solution of uranium plants in the Elliot Lake mining camp (Goode 2013).

Double Sulfates

The addition of Group 1 ions, such as Li, Na, K, or the ammonium ion to a sulfate solution of the REE causes the formation of variously soluble double sulfate salts. The formulae for these are commonly written as $La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$ (Kul et al. 2008), but Bickerdike (1937) recorded a wide variety of compositions.

Kul et al. (2008), working with a solution containing about 26 g/L of mostly LREE, showed that precipitation efficiencies greater than 95% could be obtained for the LREE at about 1.5 times the stoichiometric demand for the REE. However, the HREE and Y are only partially precipitated, perhaps 75%. Temperatures up to about 55°C promote the formation of double sulfates, but higher temperatures provided little benefit. Thorium precipitation from the solution, which contained 0.3 g/L Th, increased with the Na addition from 30% at 1.25 times REE stoichiometric to 64% at 3 times stoichiometric demand.

Abreu and Morais (2010) showed that the yield of double sulfates was essentially the same whether NaOH or Na_2SO_4 was the source of Na and that excellent Fe elimination was obtained unless NaOH was used. LREE recovery of 98% was possible at about 2 times stoichiometric Na addition, but Y recovery was only 31%. Y recovery of 99% was obtained at a Na addition of 8.5 times stoichiometric. The authors suggested an optimum temperature of 70°C for maximum Y precipitation and reaction times of 2 hours. They reported the double sulfates as having formulae such as $LaNa(SO_4)_2 \cdot H_2O$ and containing about 44% REO.

Formation of the double sulfate is a useful way of getting a high yield of reasonably pure REE from solution, especially if HREE are not at high levels, but the double sulfates need to be converted to other forms to become commercial commodities or further processed. This is usually done by metathesis using NaOH, which results in the following reaction:

$$LaNa(SO_4)_2 \cdot H_2O + 3NaOH \rightarrow La(OH)_3\downarrow + 2Na_2SO_4 + H_2O \qquad \textbf{(EQ 24)}$$

After filtration, the hydroxide can be dissolved in a weak acid as a reasonable pure and high-strength REE solution and further processed. The sodium sulfate solution can be recycled back to the double sulfate precipitation step. Abreu and Morais (2010) showed that metathesis was best achieved at 70°C with 1.1 times stoichiometric demand.

Abreu and Morais (2010) showed how, after metathesis and dissolution of double sulfate, the Ce could be oxidized from Ce(III) to Ce(IV) by adding about 30% excess permanganate ion, which leads to the precipitation of Ce(IV) hydroxide at a pH of about 3. The precipitate contained Mn, which was removed by releaching the hydroxide in HCl, reprecipitating the Ce with oxalic acid, and calcining it to give a 99.5% CeO_2 product.

Double sulfate precipitation from REE solutions containing low-HREE values can be a useful and economical way of processing since it allows high recovery of the REE from an acidic solution to a high-grade, reasonably pure precipitate.

Precipitation

After the REE have been obtained in a relatively pure solution through processes of mineral cracking, leaching, and impurity removal, it is generally necessary to precipitate the REE from solution to facilitate downstream processes such as separation of the individual REE.

Hydroxides and Carbonates

The REE are readily precipitated from purified solutions as hydroxides by neutralizing to about pH 8 using a suitable base such as CaO, MgO, NH_3, or NaOH. With chloride solutions, any base should be considered. However, if precipitating a REE hydroxide from a sulfate solution is required, MgO or ammonia could be the preferred base since gypsum precipitation and double sulfate salt formation are avoided.

CaO, MgO, NaOH, and NH_3 are relatively expensive, hydroxide precipitates generally do not filter well, and neutralization is not very selective. For these reasons, hydroxide precipitation of the REE is not practiced to any significant degree, although the process has been proposed by some development groups. Carbonate precipitants such as $MgCO_3$, Na_2CO_3, $(NH_4)_2CO_3$, or NH_4HCO_3 are relatively inexpensive and have been used in REE operations and proposed by several project developers. Luo et al. (2013) present data for the ammonium bicarbonate precipitation of REE from low-grade solutions obtained from ionic clay solutions. The work showed that a 3.5:1 molar ratio of NH_4HCO_3 to REE was required and that crystal size and settling rates improved with aging.

Oxalate Precipitation

The REE oxalates are insoluble, oxalate precipitation is quite selective for the REE, and REE oxalates can be calcined at about 900°C to give oxides. For these reasons, oxalic acid is commonly employed in the REE industry for both mixed REE solutions and the highly refined REE solutions produced in separation plants. The reaction is as follows, using La as an example:

$$2La^{3+} + 3H_2C_2O_4 + 10H_2O \rightarrow La_2(C_2O_4)_3 \cdot 10H_2O\downarrow + 6H^+ \qquad \textbf{(EQ 25)}$$

Chi and Xu (1999) provide information on the efficiency of precipitation from solutions produced by leaching ionic clay and containing about 4 g/L REE, 0.1 g/L Al, and 0.3 g/L Fe. The oxalic acid addition for 95% REE recovery was 2.5–3 mol/mol REE or 170%–200% stoichiometric. A residence time of 1 hour was satisfactory and a pH of <2 avoided the precipitation of impurities.

With very pure, higher-grade solutions, such as those produced in separation plants, an oxalate excess of about 10% over stoichiometric is normal for complete precipitation (Liao et al. 2013).

Oxalate precipitation is very selective for REE and against many impurities, but Th co-precipitation is nearly complete and Ca, Sr, and Ba oxalates are partially precipitated along with the REE and consume oxalic acid.

Normally, oxalic acid is added as a solution containing 10% oxalic acid. The precipitated REE oxalates are then recovered by filtration or centrifugation. The high-grade products (>99.9% pure) made in separation plants are washed with copious amounts of water to eliminate dissolved impurities before being calcined. Calcining can be done using a rotary dryer followed by a rotary calciner and cooler, as at Molycorp, or using crucibles that are conveyed through a tunnel furnace, as used by Lynas and most of the Chinese producers.

As an alternative to calcining REE oxalate, the precipitate can be metathesized using NaOH or Na_2CO_3, the resulting $Na_2C_2O_4$ recycled back to precipitation and the REE product calcined.

Early Separation of Cerium as Ce(IV)

Ce makes up about 40% of the REE in the mixed product of most deposits. Ce does not command a high price, yet it consumes essentially the same mass of chemicals as more valuable REE, such as Nd or Dy, in the separation plant. Hence there has been much interest in removing Ce from the main REE stream before the separation plant is reached. Ce in solution is normally trivalent and therefore behaves much as the other REE. However, Ce(III) can be oxidized to the quadrivalent state, Ce(IV), after which it is readily separated from the other REE through selective dissolution or precipitation or SX.

Molycorp roasted its concentrate at 650°C in a multiple-hearth roaster that drove off fluorine and oxidized Ce(III) to Ce(IV). A cold dilute HCl leach solubilized all the REE except for the Ce(IV), which reported to the leach residue. The leach residue was sold as a glass polishing powder, although a portion was purified to give a carbonate of 96% CeO_2 purity. Leach recovery of the trivalent REE was not complete, and the Ce(IV) product, which contained about 60% Ce, did carry about 10% non-Ce REE. The Ce-depleted HCl leach solution went on to impurity removal and the separation of individual REE (Molycorp 1996).

When Molycorp upgraded its plant, it replaced roasting with a process in which all the REE were dissolved in HCl, impurities removed by hydrolysis and sulfide precipitation, and the Ce(III) chemically oxidized to Ce(IV), which precipitated from solution. Data are not given, but it is reasonable to assume that hypochlorite was used as the oxidant (SRK Consulting 2010; Goode 2016c).

Ho et al. (2014) researched the effect of dose, temperature, and pH on the oxidation of Ce using hypochlorite. In a mixed REE solution, 99% oxidation was obtained at 2.5 times stoichiometric hypochlorite addition. A pH of 4 appeared to give best separation of Ce from other REE with poor selectivity at higher pH values. A temperature of 60°C was optimal. Significant co-precipitation of other REE, especially the heavier REE, occurred at all levels investigated. For example, with 1.9 times stoichiometric NaOCl addition, 60°C, and pH 4, levels of co-precipitation were about 30% HREE, 20% medium REE, 12% Nd, 9% Pr, and 5% La.

In 1968, Bauer and Lindstrom reported on the separation of Ce by ozone oxidation from sulfate, nitrate, and chloride solutions containing REE in the proportions of 50% CeO_2, 36% La_2O_3, 10% Nd_2O_3, and 4% Pr_6O_{11} and others. High recovery of high-purity Ce precipitate was obtained from all three solutions at ambient temperature. A pH range of 4 to 5 was recommended. Variations on the basic chemistry were explored. The reaction was

$$2CeCl_3 + O_3 + 3H_2O \rightarrow 2CeO_2\downarrow + 6HCl + O_2 \qquad \textbf{(EQ 26)}$$

Bauer reported co-precipitation of other REE, especially the heavier REE, and investigated a process to redissolve and reprecipitate Ce(IV) to purify Ce and isolate a pure La stream.

Zou et al. (2014) developed a wet oxidation process for Ce starting with a mixed REE hydroxide precipitated from a nitrate medium. They obtained 97% oxidation of Ce to Ce(IV) by first precipitating the mixed hydroxides and then blowing air through the hydroxide slurry at 80°C at pH 13. It was determined that F had little effect on the extent of oxidation, but PO_4^{3-} had an adverse effect on oxidation. The oxidation reaction was given as

$$2Ce(OH)_3 + 0.5O_2 + H_2O \rightarrow 2Ce(OH)_4\downarrow \qquad \textbf{(EQ 27)}$$

Although not detailed in the work by Zou et al., dissolution of the oxidized hydroxides in a weak acid would lead to dissolution of the REE except for $Ce(OH)_4$. Possibly there would be some residual non-Ce hydroxides left with the $Ce(OH)_4$ leading to some losses of the other REE, as experienced by Molycorp and indicated by researchers.

Abreu and Morais (2010) oxidized Ce(III) in a pH 3 solution using potassium permanganate.

Electrolysis of chloride solutions leads to the formation of hypochlorous acid (HClO), chlorite ion (ClO^-), and chlorate ion (ClO_3^-). Vasudevan et al. (2005) oxidized Ce(III) through the in situ electrolytic generation of such oxidants. A temperature of about 30°C, a pH of about 6.7, and concentration of 130 g/L $CeCl_3$ were found to be optimum. The cathode of the electrolytic cell was rotated to prevent the formation of a coating. Using a solution containing a typical LREE mixture, cell electrochemical efficiency was reported as 60% and the purity of the precipitated $Ce(OH)_4$ was 95%. The impurities appear to be other REE, which implies significant losses.

Martin and Rollat (1986) patented a system in which Ce(III) in a mixed REE nitrate solution was electrolytically oxidized to Ce(IV) in the anode compartment of a cell. Ce(IV) was then selectively extracted away from the other REE by, preferably, TBP. The loaded organic was then stripped by placing it, with nitric acid, in the cathode compartment of the same electrolytic cell where it was reduced to Ce(III) and simultaneously stripped from the solvent. In an alternative stripping process, nitric acid was reduced in the cathode compartment to form NO and NO_2 gases, which were mixed with the loaded solvent to form Ce(III), which was then water stripped.

Oxidation of Ce can be achieved through the drying of hydroxide precipitates produced by caustic cracking monazite. Using hydroxide containing about equal proportions of Ce and other REE, Swaminathan et al. (1988) showed that a drying temperature of 160°C was optimal with higher temperatures leading to difficulty in subsequent HCl leaching. The Ce in a 5-mm-thick layer of hydroxide attained 95% oxidation to Ce(IV) after 6 hours and 99% after 12 hours. The dried and oxidized hydroxide was leached with HCl at 50% solids at pH 3 and produced a solution containing 95% of the trivalent REE and CeO_2/REO of about 7%. The CeO_2 in the leach residue was selectively dissolved away from the Th and gangue materials using HCl at pH 1.5 with a sulfite reductant leading to a product containing up to 85% CeO_2.

Ce(IV) in acidic solution is preferentially extracted by solvents away from other REE. TBP and Cyanex 923 are effective from nitrate solutions, carboxylic and organophosphate solvents from sulfate, or chloride solutions (Xie et al. 2014; Lucas et al. 2015; Zhou and Liu 2015).

SEPARATION OF INDIVIDUAL RARE EARTH ELEMENTS

The REE recovery operations described earlier produce a mixed REE solution or solid. The REE distribution in these intermediate products is similar to those indicated in Table 3. However, the manufacturers of magnets, phosphors, and so on, require separated products of individual elements with little or no adjoining REE and with purities ranging from 99% to as high as 99.9999%; therefore, separation plants are necessary.

Large-scale separation was performed using IX until the advent of SX methods in the mid-1960s (Kaczmarek 1981). A typical SX-based production plant separating all the REE will include up to 1,500 mixer-settlers, extensive product precipitation, liquid–solid separation and washing systems, and calcining equipment. Such plants are expensive to build and operate. Capital and operating costs for any separation system can be reduced by not separating all the individual REE. The following can be considered:

- La, Ce, and Y are often high-mass components of the separation plant feed, but they can be removed from the feed (or partway through the separation process) using classic chemistry procedures or more advanced methods. Ce can be oxidized to the Ce(IV) state and isolated as noted earlier. Alternatively, La, Ce, and Y can be extracted away from the other REE using certain solvents as explained later. In another option, the LREE and HREE can be separated through double sulfate precipitation.
- NdFeB magnets can be effectively made using a NdPr mixture (didymium) instead of pure Nd. The Lynas LAMP operation produces much of its output as a NdPr product, thus avoiding the costs of separating these elements.
- Several REE are not in high demand, or their content in the intermediate REE product is low, so they are not worth separating but best made as a bulk product. Bulk products might comprise Sm+Eu+Gd, or Ho+Er+Tm+Yb, or the entire HREE suite (Sm to Lu, including Y).

These strategies can reduce the capital and operating costs of a separation plant by as much as 50%.

Chloride-Based SX Separation Systems

All commercial REE separation plants currently use SX and almost entirely from a chloride-based aqueous phase. Prior to 2015, there were about 100 REE separation plants in China with a combined capacity of more than 400,000 t/yr of REO (Roskill 2016). Most of these are now closed due to market conditions and government regulations intended to consolidate the industry and reduce illegal production. The Chinese separation plants are generally based on the use of a phosphonic acid extractant, H(EH)EHP, at 1.5 molar concentration (50% v/v) in an aliphatic diluent. The reagent is known as P507 in China and as PC88A and Ionquest 801 elsewhere. Separation plants in Japan and Vietnam also use chloride chemistry and H(EH)EHP.

The plants that process Bayan Obo flotation concentrates and the Lynas LAMP operation use sulfuric acid baking to crack the REE minerals and therefore generate a sulfate-based PLS. This is partially neutralized and filtered, and then contacted with DEHPA to extract the REE. HCl is used to strip the REE, which can then be separated using P507.

Although P507 or equivalent is the main extractant in most chloride-based separation plants, certain plant sections might use other extractants, such as naphthenic acid or IX, for special tasks (Li et al. 2013; Huang et al. 2015). Europium is readily reduced to the divalent state, and this fact is exploited in many separation plants to separate Eu from the trivalent REE.

The separation factors (abbreviated as β) between adjacent rare earths are generally small, meaning that many sequential separations are required to obtain a high-purity product from a mixture of rare earths. If all 15 REE are separated to high-purity products (>99.9% pure), the separation plant might contain 1,500 or more mixer-settler units arranged in approximately 15 different circuits. Each circuit would accept a feed solution containing mixed REE and generate two or three outlet streams containing partially or fully refined individual REE. These circuits would be cascaded with partially separated streams directed to other circuits for separation.

A simplified block diagram for a P507-based separation plant producing separated LREE, Sm, Eu, Gd, Tb and Dy, and a bulk concentrate of the heavier REE is provided in Figure 7.

A single circuit, say for the separation of the Sm-Dy group from the heavier REE (Ho-Lu including Y), might contain 50 extraction stages, 30 scrub stages, 15 strip stages, and 5 stages for water washing and saponification for a total of 100 mixer-settlers.

The number of stages needed in a separation circuit is a function of the composition of the feed, the desired REE purity in the scrubbed solvent and the raffinate (aqueous phase leaving the extraction section), and the β for the two REE at which a split is being made. The β for P507 varies from 6.8 for the separation of Ce and La to as low as 1.4 for the separation of Er and Y. A given Er–Y separation will need at least five times as many stages as the equivalent Ce–La separation because of the differences in β. Much research effort is being expended on searching for solvent systems offering improved β.

In many situations, for example, SX using P507, Y acts as an HREE lying between Ho and Er. However, under some circumstances, Y can behave as an LREE (Collier 2012). Figure 8 shows how Y behaves with different SX reagents. Naphthenic acid is commonly used for the separation of Y from the other HREE after a Nd–Sm separation but is also practiced or proposed for the separation of Y (and La+Ce) from other REE before the main separation circuits (Li et al. 1994; Griffith et al. 2016).

Separation plants using an extractant such as P507 typically use HCl to dissolve the incoming oxide feed and to scrub and strip the REE from the loaded solvent. NaOH is used to regulate pH by partially converting the P507 to the sodium form in the saponification step. The use of HCl and NaOH leads to the production of a NaCl brine solution as a separation plant effluent. A conventional P507 separation plant uses about 3 t HCl (100% basis), about 2.5 t NaOH (100% basis), and up to 20 t water, much of it for washing the REE products, to fully separate 1 t mixed REO into purified oxalates (Liao et al. 2013). This water, and the contained NaCl, forms the main plant effluent.

The Chinese have pioneered new plant configurations, such as hyperlinking, that reduce the reagent consumption

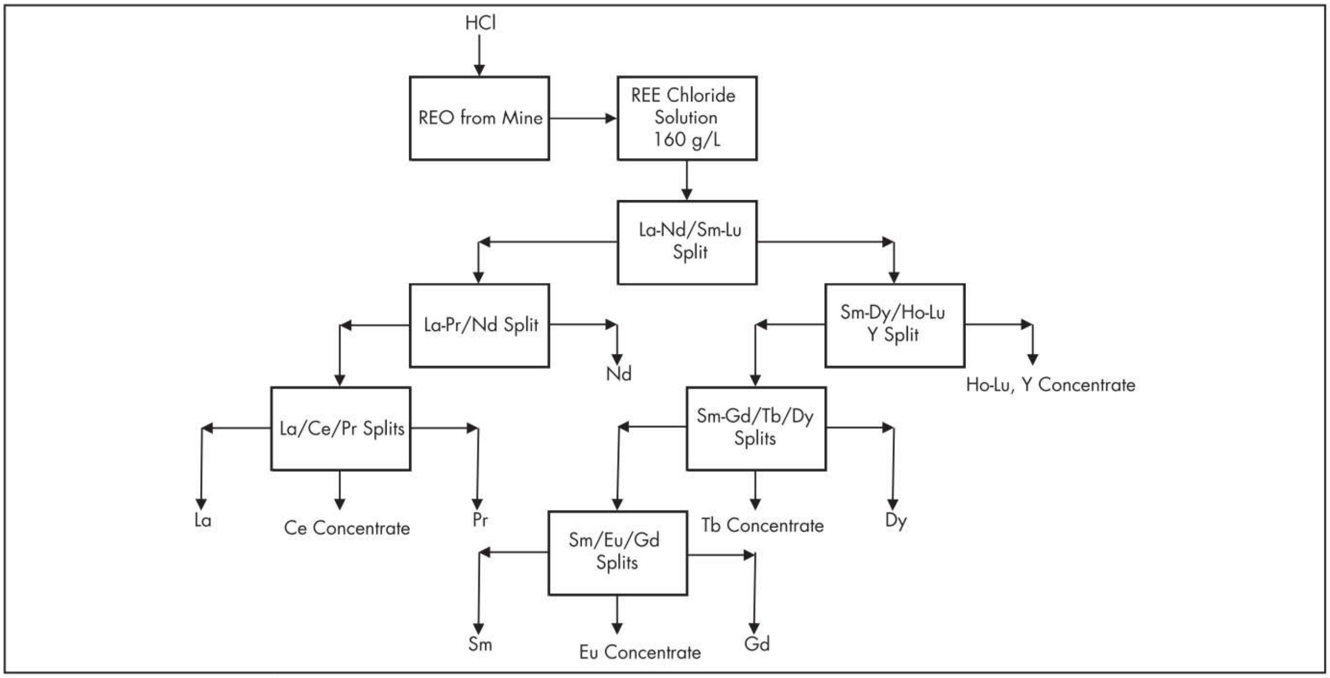


Figure 7 Block diagram of typical P507 separation plant

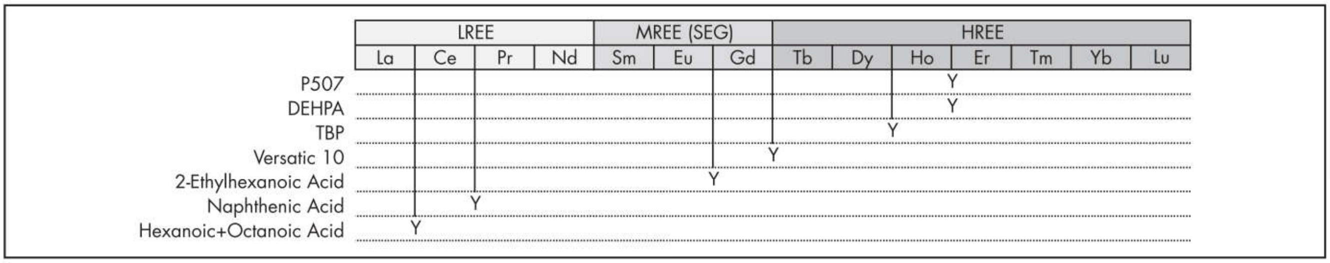


Figure 8 Behavior of Y with different SX reagents

by at least 30% (Liao et al. 2013; Huang et al. 2015). This process, which uses REE in the saponification step instead of NaOH, has been widely adopted in China and is mandated for new plants as a means of reducing environmental impact. The Chinese have also developed saponification processes using slurries of $Ca(OH)_2$, or MgO, or REE carbonates, all aimed at reducing costs and mitigating environmental issues (Huang et al. 2015).

An alternative means of reducing new reagent demand is to operate a chlor-alkali plant on the brine waste stream to regenerate HCl and NaOH. Given low power costs, a chlor-alkali plant might economically regenerate the reagents while also eliminating the costs associated with disposing of the waste brine effluent. Molycorp attempted to operate a chlor-alkali plant at its refurbished Mountain Pass plant, but it appears that the preparation of suitable feed brine from the plant effluents was problematic. The company was forced to buy reagents at a higher-than-projected cost and had to dispose of wastewater at a significant cost, both contributing to its bankruptcy (Molycorp 2015).

Another alternative for the reduction of acid and alkali demand is the use of SX reagents such as Cyanex 272, a phosphinic acid, or Cyanex 572, a chelating extractant. These extractants are weaker than P507, so they extract at a slightly higher pH and are easier to strip, leading to acid savings of about 30% (Soderstrom et al. 2014). REE separation factors are about the same as for P507, so these new reagents do not reduce stage requirements.

In China, a great deal of development activity is aimed at better modeling and optimizing separation circuits; improving separation factors through different reagents; and reducing the environmental impact and operating costs through hyperlinking, online analysis, and other strategies. Chinese law limits the export of technology concerning advanced REE separation plants.

Nitrate-Based SX Separation Systems

Solvay's La Rochelle separation plant uses nitric acid dissolution and TBP for extraction and separation of the LREE (Kaczmarek 1981). TBP is effective for the separation of the dominantly LREE in monazite but is not suitable for separating the HREE. Solvay uses several other solvent extractants, including a quaternary amine such as Aliquat 336, for separating the HREE (Lucas et al. 2015).

Molycorp's Silmet plant in Estonia, which was originally designed and constructed by the Soviets for processing a

LREE-bearing loparite concentrate from the Kola Peninsula, also uses a nitrate-TBP system. Similarly, the Kashka REE plant in Kyrgyzstan used TBP to separate LREE into finished products. The HREE were separated using IX with chromatographic elution (Stans Energy 2017; Danilov 2011).

The plants using nitrate-TBP systems typically dissolve a REE-bearing material in nitric acid; concentrate the solution to typically 200–300 g/L REE; add a "salting-out" reagent such as ammonium, calcium, or sodium nitrate; and then extract the REE with TBP in mixer-settlers arranged in a load-scrub-strip configuration. One such SX battery makes a single separation just as in the chloride systems. Stripping is done with water rather than acid. Although this reduces reagent demand, the dilute strip solution, perhaps containing 100 g/L REE, must be evaporated to a higher concentration before it can be fed to the next separation battery.

TBP circuits consume relatively small amounts of HNO_3 and NH_3 and generate an ammonium nitrate solution as the effluent. After purification, this material can be crystallized and sold as a fertilizer. The reagent consumption in a nitrate-TBP separation plant is less than that of a chloride-P507 plant; however, energy costs are higher because of the evaporation required between SX batteries. Separation factors in the nitrate separation system for the LREE are similar to those in the chloride system, so the number of stages required for a given set of separations is similar. With appropriate extractants for the HREE, separation factors similar to those for P507 can be obtained, so stage requirements are similar.

Alternative Separation Systems

A 2016 review (Goode 2016b) of new separation systems examined the development of non-SX systems and improved SX systems. The SX developments fell into two general categories: (1) replacement of the conventional mixer-settler with more compact devices and (2) new SX chemistries. The new devices include microfluidic contactors, centrifugal contactors, and membranes. The new SX chemistries include the use of novel extractants, precipitative stripping, and ionic liquids.

The non-SX options under investigation included molecular recognition technology by Ucore Rare Metals; free-flow electrophoresis by Geomega Ressources; high-precision liquid chromatography by REEtec AS; electrolytic systems developed by Rare Earth Salts; and new IX systems, for example, those developed by K-Technologies.

In the absence of any large-scale operation using such new systems, the review concluded that several developments held promise but only conventional SX separation could be financed.

POST-SEPARATION PROCESSING

Product Handling

Separation systems produce solutions of highly refined or partially refined individual REE or mixtures of REE. These are precipitated, usually as oxalates but frequently as carbonates, or evaporated to give chloride salts. Precipitates are separated from mother solutions and washed using centrifuges or filters.

REE oxalates are calcined to oxides at temperatures of about 1,000°C in rotary kilns or tunnel furnaces. Carbonates can be marketed as is or calcined to oxide depending on the intended use. Co-precipitates (e.g., of Y and Eu) are frequently produced for special applications. These and other products are often needed with specific physical properties (particle size, etc.) and therefore require carefully controlled precipitation and calcining conditions.

Metal Production

Magnet makers require metallic REE, such as NdPr, Pr, Nd, Sm, Dy, and Tb. Metals are used in the production of nodularized iron, magnesium alloys, and aluminum alloys. Mischmetal, a mixture of the LREE metals, is used in alloying but also in lighter flints. Nickel–metal hydride (NiMH) batteries include an intermetallic negative electrode incorporating LREE with Ni, Co, and Al.

REE metals are produced by electrowinning or by metallothermic processing using calcium, magnesium, or lanthanum metal as the reductant. Electrowinning can be from molten NaCl-REE chloride at about 1,000°C, leading to the production of molten metal at the cathode and Cl_2 at the graphite anode. Alternatively, an REO, such as La_2O_3, can be fed into a molten La/Li/Ca/Ba fluoride electrolyte with molten metal formed at the cathode and O_2 at the graphite anode. Electrowinning is used to produce several pure REE metals and, through co-reduction, various REE-REE, REE-Fe, REE-Cu, and REE-Mg alloys.

Some of the REE metals and their halide salts, particularly Sm, Eu, Tm and Yb, have high vapor pressures at the temperatures used for electrowinning. These have been recovered by metallothermic reduction using La or Ce metal with simultaneous sublimation of the metal. These reactions are highly exothermic, and operating temperatures of 1,200°–1,500°C are common (Songina 1964; Riedemann 2011; Lucas et al. 2015).

ENVIRONMENTAL ISSUES

The rapid development of the REE industry has led to some environmentally unsatisfactory situations (Keith-Roach et al. 2014; Wall et al. 2017). Molycorp's earlier operations at Mountain Pass were curtailed because of environmental issues. Concerns over the massive tailings storage facility near Baotou led to new milling and tailings facilities at the Bayan Obo mine. Concerns remain over radionuclide storage. The earlier ionic clay development projects in China were carried out, often illegally, with little regard for the environment, leading to long-term problems with high projected remediation costs.

The radionuclides that generally occur in REE deposits not only have caused issues at Mountain Pass and Baotou, but have also triggered strong opposition to future REE developments. Concern over the fate of thorium contained in the concentrate processed at the Lynas plant in Malaysia resulted in a commissioning delay of about a year while the International Atomic Energy Agency (IAEA) undertook a third-party review. Local concerns about the Lynas plant were sparked by major Th-based radiological problems resulting from earlier REE operations in Malaysia.

Radionuclides

The regulations covering working with and transporting radionuclides, their incidence in REE processing, concerns, and methods of management have been discussed by Feasby et al. (2013). Concerns include Th and U and their progeny but also the natural radioactivity of some of the REE. ^{147}Sm is particularly radioactive such that the transport of natural Sm can exceed IAEA transport regulation exemption limits. Feasby et al. concluded that radionuclides can be safely handled within process plants and during transportation through proper process and repository design supported by test work to demonstrate environmental stability.

The ways in which radionuclides deport during processing are discussed by several authors (Feasby et al. 2013; Pillai 2008; Anvia 2015).

Overall Environmental Footprint

Haque et al. (2014) discuss various aspects of REE production, sustainability, and environmental impact. The authors reported on the greenhouse gas (GHG; expressed as CO_2) during the production of a mixed REE oxide from a deposit similar to the Bayan Obo operation in China. The total was estimated at 1.4 kg CO_2 equivalent/kg of REO with the main contributors being due to HCl (38%) and steam (32%) usage. The GHG generated during the production of separated products ranged from about 9 kg CO_2 equivalent/kg of REO for La to about 56 kg CO_2 equivalent/kg of REO for a mixed Sm-Eu-Gd (SEG) product. Even higher emissions would be expected for the heavier REE.

In contrast to the GHG data for REE production, Rankin (2012) reported that copper generates between 3 and 6 kg CO_2/kg metal, nickel 11–16 kg CO_2/kg metal, and aluminum 22 kg CO_2/kg metal.

Haque et al. (2014) noted the high water consumption incurred during the production of the REE. Values range from 330 L/kg oxide for La to 1,750 L/kg oxide for SEG. These can be compared with values of 38 L/kg Cu metal for heap leaching, SX, and electrowinning; 110 L/kg for Ti metal; and 377 L/kg for Ni recovery by pressure acid leaching and SX-electrowinning (Norgate and Lovel 2006).

Koltun and Tharumarajah (2014) have analyzed the life-cycle impact of the REE and present data for the consumption of electrical and thermal energy and water, and the GHG emissions for each of the individual REOs. The authors used a price-based method of distributing consumption across the REE production chain. A large range is evident for each parameter using this method. For example, water consumption ranges from 11 m^3/kg REO for CeO_2 to 7,068 m^3/kg Sc_2O_3; electrical energy ranges from 24 mJ/kg REO for CeO_2 to 11,630 mJ/kg Sc_2O_3.

Wall et al. (2017) also published a paper on the responsible sourcing of critical minerals with an emphasis on REE.

Recycling

The level of REE recycling is not well documented but is undoubtedly low, probably less than 5%. Noteworthy recycling efforts include the Showa Denko operation in Vietnam (800 t/yr of REE from magnets), Solvay's recovery of REO from scrap fluorescent lamps (1,000 t/yr capacity), and efforts in Japan to recycle magnet material from scrap motors (e.g., Mitsubishi and Panasonic) and from NiMH batteries (e.g., Toyota) (Roskill 2016).

Although the level of REE recycling was low in 2017, there are signs that recycling will become more important in the future. Research is being conducted in Europe, China, Japan, Korea, and the United States (Binnemans et al. 2013; Bedrossian et al. 2016; Dutta et al. 2016).

CHARACTERIZATION, TESTING, AND ANALYSIS

Because REE ores are typically highly complex, the development of a workable process flow sheet for a new REE deposit can be a long, drawn-out, and expensive affair. An example is the Strange Lake deposit that was discovered in 1980 and subjected to metallurgical test work starting in 1982, for which a final flow sheet has yet to be selected. Allowing for periods of inactivity, test work has probably taken up at least 10 years.

Potential REE by-products, such as Zr, Nb, and Sc, can be a distraction and must be considered pragmatically. Understanding and controlling the deportment of radionuclides is usually more important. The logical steps to developing a viable metallurgical process are described in the following sections.

Geology of the Deposit

The geology of the deposit must be understood in terms of ore types, REE grades, non-REE grades, and mineralogy of REE and gangue. The variability of the analytical grades and suite of minerals must be understood.

Mineralogy

Exploration and metallurgical samples should be thoroughly characterized using QEMSCAN (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) and similar techniques. EMPA (electron probe microanalysis), laser ablation ICP-MS (inductively coupled plasma mass spectrometry), and other techniques can be used to determine the elemental composition of the minerals (Grammatikopoulos et al. 2016).

Composite and Variability Sample Selection

The project team, which should include geologists, mining engineers, and metallurgists, needs to select material suitable for the preparation of one or more master composites representing important ore types, locations, or production periods. Several variability samples covering different locations, lithologies, and grades should also be prepared and tested after the main processing route has come into focus.

Comminution

Crushing and grinding tests must be conducted on appropriate samples using basic methods such as the Bond comminution tests. Bond ball mill tests should be performed using a closing screen size that matches the intended grind size. Tests aimed at determining design parameters for semiautogenous grinding and high-pressure grinding rolls will probably be needed and should be undertaken by experienced testing laboratories.

Beneficiation

Tests should examine the response of ore samples to coarse ore sorting, DMS, and the full range of beneficiation processes. The test program can be guided by geological and mineralogical information. Testing of coarse ore beneficiation processes, such as ore sorting and DMS, requires samples of coarse ore for thorough testing

Hydrometallurgy

Tests should be guided by the mineralogy of the REE mineral and could include roasting, with or without reagent addition, followed by acid dissolution, sulfuric acid baking, caustic cracking followed by acid dissolution, and direct acid attack. These processes will produce an acidic solution containing the REE along with impurities such as Th, U, Fe, and Al. Tests aimed at removing impurities could include partial hydrolysis, SX, IX, and other methods.

The liquid–solid separation characteristics of REE-based slurries are often challenging, and the preferred process flow sheet is often driven by the thickening and filtration characteristics of different process options. Liquid–solid separation characteristics should be monitored at all stages of the test work.

Acid regeneration or recovery is a common requirement in REE circuits. Nanofiltration, reverse osmosis, acid springing (e.g., HCl regeneration through H_2SO_4 addition), electrodialysis, pyrohydrolysis, distillation, and other techniques will need to be examined as appropriate.

Environment

The various waste streams from the REE operation will require characterization to allow effective environmental systems to be designed. Waste characterization is typically obtained through comprehensive elemental analysis using low detection system packages, X-ray diffraction studies, and radionuclide analysis. Environment-specific tests including toxicity characteristic leaching procedure, acid–base accounting, net acid production and net acid generating, shake flask extraction, humidity cell tests, and others will probably be needed.

Geotechnical tests will be needed to allow proper design of tailings facilities. These could include settling tests, consolidation/percolation tests, and others.

The ore likely will include radionuclides, and the way that these are handled must be carefully considered. Ideally, the radionuclides will be produced in a chemically inert form and combined with the main tailings stream. Alternatively, the radionuclide stream would require isolation and special handling.

Pilot-Plant Operations

After bench-scale test work has determined a series of process steps needed to recover a commercially acceptable intermediate mixed REE product, it is essential to combine the operations in an integrated pilot plant. The pilot plant must operate at a scale, and for a duration, that will demonstrate that the selected process will work, confirm its operability, examine materials of construction, and generate or confirm process design criteria needed for engineering design.

The pilot plant will also serve to generate large volumes of slurry needed to allow effective liquid–solid separation testing. It is common to have liquid–solid separation equipment specialists or vendors attend the pilot plant to independently generate reliable data for plant design. Pilot plants are also useful to produce enough product for evaluation of intermediate products by potential toll processors or customers.

The failure to adequately demonstrate a process frequently results in a catastrophic failure of a production plant to attain design throughput, recoveries, and operating costs (McNulty 2004; Verbaan et al. 2014).

Separation

It is possible to demonstrate in a pilot operation that a given intermediate REE product is amenable to separation. This might be useful for the investment community, but in the author's view, this is not necessary since the separation factors between adjacent REE for a given separation system are totally independent of the feed source.

A separation pilot plant is an expensive undertaking. Each separation circuit will require several kilograms of REE to fill and then operate for the several weeks needed to reach equilibrium and deliver the required purities—and there are several separation circuits. To reach equilibrium faster, the circuit could be preloaded with organic and aqueous solutions containing estimated equilibrium compositions, but the validity of the demonstration is then questionable.

The demonstration of a single circuit of a conventional SX separation plant will add about $1 million in costs and significant additional time to the development of a project. The newer separation processes under development might not need such long times and mass of feed material to come to equilibrium. However, as of the time of publication, their industrial-scale viability has not been demonstrated.

Analysis

In the evaluation of a REE deposit, a complete analytical suite should be commissioned, particularly in the initial phase of evaluation. A whole rock assay (WRA = Al_2O_3, CaO, Cr_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, Fe_2O_3, SiO_2, TiO_2, and V_2O_5) is usually obtained by X-ray fluorescence (XRF) and is economical and essential. Analytes that can be important and should not be overlooked include Sr, Ba, Sc, U, Th, Zr, Nb, F, $S_{sulfide}$, S_{total}, and CO_2.

Some of the analytes can be obtained as part of an inductively coupled plasma optical emission spectrometry scan, others using Leco-based methods.

The individual REE, including Y, Sc, Th, and U, can be analyzed by ICP-MS REE scan. For mixed REE samples with a REE content of >80%, the determination of La, Ce, Nd, Sm, and Y is best performed using XRF rather than the normal ICP-MS method.

Analysis of the radionuclides will be necessary and requires the services of specialized analytical laboratories.

ACKNOWLEDGMENTS

The author acknowledges mentors and colleagues, many no longer with us, associated with REE-Th operations at Rio Algom and Denison; good friends from Molycorp, in China, at various laboratories around the world; and development companies in Canada, Brazil, and Russia. Massoud Aghamirian, Kevin Bradley, D. Grant Feasby, Mike Robart, and Niels Verbaan are thanked for reviewing a draft. Parts of Goode 2016b are included in the section titled "Separation of Individual Rare Earth Elements" and are reproduced with permission from the Canadian Institute of Mining, Metallurgy and Petroleum. Special thanks to Ev King for her support and patience.

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