Chapter 4
Mineral Processing and Extractive Metallurgy of the Rare Earths

Abstract This chapter is about mineral processing of the rare earths (making the mined ore into a concentrate of the valuable minerals), and extractive metallurgy of the rare earths (how to get the metals out of the concentrate). The mineral processing of three well-known exploited ore deposits is discussed in more detail.

4.1 Introduction

In Chap. 2, the most important occurrences of the rare earths were described. This chapter will deal with what happens when the rare earths have been mined. It answers the question: how are the ores processed?

Mineral processing (sometimes called mineral dressing or ore dressing) is the preparation of ore from the stage that the material is brought out of the mine (also called "run of mine" or "as-mined") through the production of a mineral concentrate, from which the desired metals can be extracted.

To be able to extract a valuable metal from an ore, the ore as it comes from the mine (usually in fairly large lumps), must be broken down to smaller sizes, and then it must be ground to a finer grain size that is suitable for the separation techniques employed thereafter. The separation step is necessary to separate the valuable minerals from the worthless bulk. Most of the ore is usually worthless. The worthless material is collectively termed "gangue". Gangue must be distinguished from overburden, which is waste material overlying an ore or mineral body. These latter materials are just displaced, not processed (Wills and Napier-Munn 2006). Ores commonly contain just a few percent of the valuable material, although very rich deposits can sometimes contain 5–15 % ore (see Chap. 2). These rich ores, however, may again be located in veins, which cannot be selectively mined, and, as a consequence, a part of country[1] rocks has to be mined too, in order to have an efficient operation.

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[1] Country rocks are the rocks around the ore deposit. They consist of non-valuable material.

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J.H.L. Voncken, *The Rare Earth Elements*, SpringerBriefs in Earth Sciences,
DOI 10.1007/978-3-319-26809-5_4

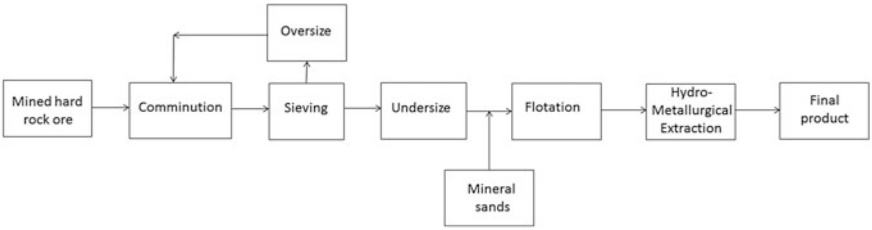

Fig. 4.1 Basic flow sheet of ore processing. Instead of hydrometallurgical processing, pyrometallurgical processing, (involving heat) may be applied (c.f. iron ore processed with a blast furnace)

4.2 Mineral Processing and Extraction of Rare Earths

In this section, it is explained how hard-rock deposits of rare earths are processed. Ores that consist of hard rocks, have to undergo several procedures before the concentration of the valuable material and the extraction of the valuable material from this concentrate can begin. Figure 4.1 gives a basic flow sheet of the process.

4.2.1 Hard Rock Deposits

An intimate knowledge of the mineralogical assembly of the ore is necessary if efficient processing is to take place. Not only the nature of the valuable minerals and gangue must be known, but also knowledge of the texture of the ore is required. The texture refers to the size, dissemination, association and shape of the minerals within the ore. The processing of the ore should always be considered in relation to the mineralogy (Wills and Napier-Munn 2006).

4.2.1.1 Liberation

Liberation of the valuable minerals from the gangue is achieved by comminution.[2] The particles resulting from this process step should be of such as size as to yield relatively clean particles of either mineral or gangue. Grinding is usually the most expensive operation in mineral processing. It may account for up to 50 % of the energy used by the concentrator plant (Wills and Napier-Munn 2006). The relative degree of liberation resulting from a grinding operation is pictured in Fig. 4.2.

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[2] Comminution means crushing or pulverization.

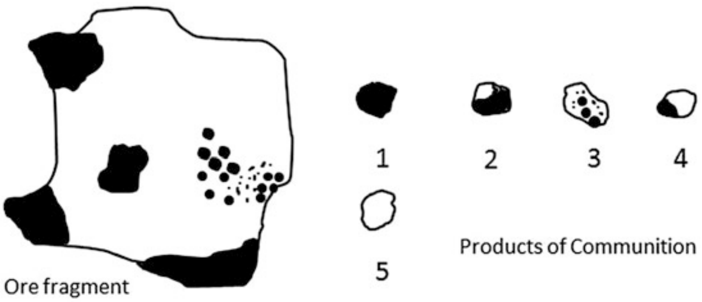

Fig. 4.2 Cross sections of ore particles, before (*left*) and after comminution (*right*). *Black* areas represent valuable mineral

To the left, a large fragment from run of the mine[3] is shown and to the right four fragments resulting from grinding. Black areas represent valuable mineral. The two regions with many small particles of ore and the black spots, within the largest fragment 3, represent highly intergrown areas of ore and gangue. Comminution produces a wide range of particles, varying from completely liberated ore, to completely liberated gangue, and intermediate particles as shown in Fig. 4.2. A particle like particle 1 could be used for metal extraction, particle 3 and 5 would be considered waste (tailings), and particles 2 and 4 might be reground. Regrinding will depend on the relative amounts of different types of particles, and the grade of the ore. If, for instance, the ore would look completely like comminution product 3, one would definitely regrind. If this only a minor proportion of the ore looks like this, the value of the material will play a determining role.

After comminution, sieving operations separate large-, mainly poorly-ground particles from smaller wellground particles. Particles that are too large are reground.

4.2.1.2 Mineral Separation (Flotation)

After comminution, mineral separation will have to take place, to separate the valuable particles from the non-valuable gangue particles. As the ore minerals of the rare earths are hardly magnetic, useful separation techniques would be gravity separation or flotation. For bastnaesite, which does not have an extremely high density, flotation is applied. The principle of flotation is depicted in Fig. 4.3.

Bastnaesite from Mountain Pass ore (hard-rock ore) is processed as follows. After comminution, the ground ore is subjected to hot-froth flotation. However, gangue minerals like calcite, barite or celestite may cause problems in flotation, because they have flotation properties similar to bastnaesite. For this, special treatment has been devised, consisting of six different (steam) conditioning steps

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[3] Run of mine is the raw product that comes from the mine. This may be material like the ore fragment on the left in Fig. 4.2.

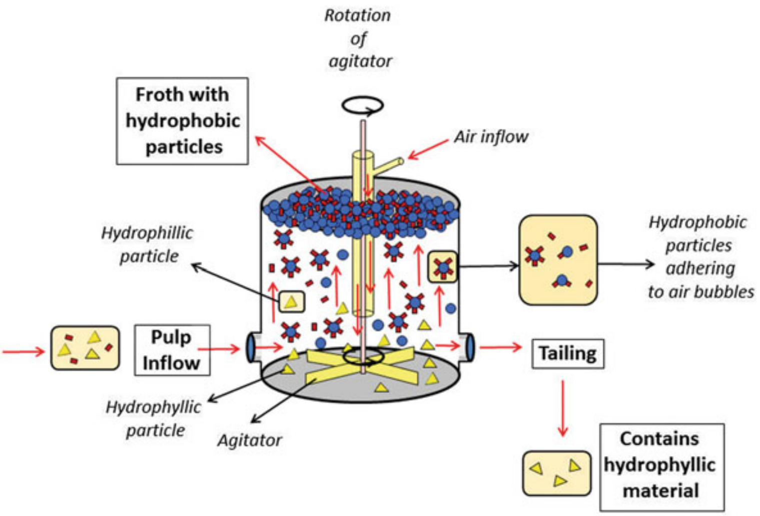

Fig. 4.3 The principle of froth flotation. Redrawn after Encyclopedia Brittanica (2015a)

(Gupta and Krishnamurthy 2005). This yields a slurry containing 30–35 % solids, which is then fed into the flotation process.

In flotation, first a slurry of desired density is formed by adding mineral powder to water. Next, chemicals are added to the diluted slurry in a tank, through which air bubbles are pumped. The slurry is agitated by a stirrer. Due to the added chemicals, the desired mineral(s) become hydrophobic, and adhere to the bubbles, whereas the unwanted minerals become hydrophilic. Also other specific chemicals may be used, which make certain minerals intentionally hydrophyllic, thus preventing them from floating. Such chemicals are termed depressants. The bubbles with the hydrophobic mineral grains rise to the surface, where they form foam, which either overflows the cell or is skimmed off. If more than one mineral must be separated, the process has to be repeated several times. Flotation plants normally perform these separations in several steps, namely rougher, scavenger and cleaner. These comprise the first cells in the bank (rougher), the second set of cells (scavengers), and finally the cleaners, which have diluted pulp, and are designed to take out the last of the valuable mineral (Wills and Napier-Munn 2006).

4.2.1.3 Mineral Processing at Mountain Pass, Bayan Obo, and Mount Weld

At Mountain Pass, a four-stage cleaning takes place, after which the mineral concentrate is thickened, filtered, and dried. The final dried concentrate of Mountain Pass contains 60 % REO (rare earth oxide). The overall recovery is 65–70 %, which means that 65–70 % of the valuable material in the ore ends up in the concentrate.

The quality of the concentrate is expressed as the grade of the concentrate, which gives the pureness of the concentrate (Gupta and Krishnamurthy 2005).

Bastnaesite from Bayan Obo is strongly intergrown with other minerals. These are magnetite (Fe_3O_4), fluorite (CaF_2), hematite (Fe_2O_3), and various niobium oxide minerals (Zhang et al. 2002) and are not waste, but are also valuable. They are recovered as by-products.

The ore is ground to a state where 90 % is smaller than 74 µm. pH is regulated, and depressants are applied for the gangue.[4] A collector is applied to amass the valuable minerals in the foam. Depressed iron oxide minerals and silicate minerals remain at the bottom of the flotation cells and are removed for iron beneficiation and niobium recovery.

After thickening and desliming,[5] selective rare-earth flotation is carried out. In this phase, calcite and fluorite and barite are depressed. The recovery of rare earths as concentrate in this stage is approximately 80 % (Gupta and Krishnamurthy 2005). After this phase, final cleaning is carried out by high-gradient magnetic separation, and two fractions emerge: a 68% REO concentrate and a secondary monazite concentrate, containing 36 % REO. The recoveries are 25 and 36 % respectively. Overall recovery of rare earths from the ore is 61% (Gupta and Krishnamurthy 2005).

At Mount Weld, Australia, physical concentration of the REE minerals is performed as follows: the run of mine material is subjected to crushing, grinding and *flotation* to produce a concentrate with a grade of 40 % REO. The obtained *flotation* concentrate is sent to a thickener, where the resulting pulp is dewatered by applying pressure filtration.

4.2.2 *Placer Deposits*

Heavy mineral sands (placers) in wet environments are mined by dredging techniques, applying bucket line and suction dredges (relatively deep water), or bucket wheel units (relatively shallow water). In dry environments, open pit excavation methods are used. Drilling and blasting are in general not required, but may be applied when the sand is strongly cemented. Mineral sands are processed further as-mined and are ***not*** subjected to any comminution (Gupta and Krishnamurthy 2005).

Heavy mineral sands may differ in composition, depending on the location, and only generalized descriptions of the processing can be given. Monazite and

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[4] Gangue: this is the commercially worthless material that surrounds, or is closely mixed with, a desired mineral in an ore deposit. For instance in so-called Banded Iron Ore, the iron-ore minerals are magnetite (Fe_3O_4) and hematite (Fe_2O_3), and the gangue is quartz (SiO2). Gangue should not be confused with overburden, which is the material that covers a deposit.

[5] Desliming is the removal of the finest fraction, which often may cause difficulties in later processing stages.

xenotime from heavy minerals sands are separated from the other commonly occurring heavy minerals like ilmenite, zircon, rutile, garnet, magnetite and quartz. Techniques used for heavy mineral-sand separation utilize slight differences in specific gravity, magnetic properties, or electrical properties. The specific gravity of monazite is the highest. Ilmenite, garnet, xenotime, and monazite, in decreasing order of magnetisability, behave as magnetic minerals. In electrostatic separation, ilmenite and rutile behave in some instances as conducting minerals, in other instances as non-conducting minerals. Xenotime is more strongly magnetic than monazite and concentrates with ilmenite in magnetic separation. As xenotime is a poor conductor, electrostatic separation is applied to separate it from ilmenite. Leucoxene,[6] when present, may cause problems in the separation of monazite from ilmenite. In that case, separation may be enhanced by roasting under reducing conditions at 600 °C. This converts free hematite in leucoxene into magnetite, which eases the concentration. Flotation is occasionally used (Gupta and Krishnamurthy 2005).

4.2.3 *Chemical Treatment to Decompose the Mineral Concentrates*

In this subsection, the chemical treatment of the rare earths is addressed per ore mineral. The text is largely a summary of chapter three from *Extractive Metallurgy of the Rare Earths* by Gupta and Krishnamurthy (2005).

4.2.3.1 Monazite

Monazite is (Ce, La, Th)PO_4., which is the ideal formula. To extract the rare earths and to remove thorium, a variety of methods are applied after chemically attacking the mineral with either sulphuric acid, or sodium hydroxide.

Acid Treatment

The sulphuric acid method has been used most extensively in the USA. With this method, depending on the ratio of acid to ore, temperature and concentration, the rare earths can either be solubilized, or the thorium can be extracted, or both can be brought into solution (Gupta and Krishnamurthy 2005).

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[6] Leucoxene: an alteration product and mixture of Fe-Ti oxides, including titanite, perovskite, titanian magnetite, but especially ilmenite. Most leucoxene is actually largely anatase, TiO_2, or rutile, TiO_2 (Mindat.org 2015). Fe occurs usually as hematite.

The process of rare earth recovery is based on rare-earth double-salt precipitation. However, yttrium and the heavy rare earths go with thorium. The rare earths are recoverable from the thorium fraction during the solvent extraction[7] step used for the purification of uranium and thorium. Solvent extraction with TBP (tributyl phosphate[8]), from an aqueous 8 N nitric acid solution of thorium and mixed rare earths, enables the recovery of thorium, uranium, cerium and cerium free rare earths (Gupta and Krishnamurthy 2005). Other significant processes involve precipitation of thorium pyrophosphate,[9] or precipitation as basic salts from the leach liquor. After that comes recovery of the rare earths from solution as double sulphates, fluorides, or hydroxides, and also selective solubilisation of thorium itself in the ore treatment stage. The sulphuric acid route does yield impure products, but it is not used anymore (Gupta and Krishnamurthy 2005).

Alkali Treatment

In this process, caustic soda (NaOH) is used. The phosphate part of the ore is recovered as trisodium phosphate. This product is marketable, which is already a major advantage over the acid process, and this process has been very favorable for commercial use. Fine-ground monazite is treated with a 60–70 % NaOH solution at 140–150 °C. The mixed rare earth thorium hydroxide cake resulting from this process is then treated for recovery of thorium and rare earths. A variety of methods is used to accomplish this (Gupta and Krishnamurthy 2005). An effective process for removing thorium completely and in a very pure state is solvent extraction with higher amines. This should preferably be carried out in a sulphate solution. However, leaching of the rare earths from the hydroxide cake with hydrochloric acid is also very effective. The rare earths are recovered from the leachate by solvents extraction.

Several varieties of the alkali treatment method exist, among them the IRE-process (Indian Rare Earths Ltd). These are described in detail in Gupta and Krishnamurthy (2005).

4.2.3.2 Bastnaesite

After physical processing of bastnaesite (ideal formula (Ce, La, Y)CO_3F), a 60 % concentrate is obtained. This can be upgraded by leaching with hydrochloric acid to 70 % REO, while eliminating calcium and strontium carbonates. After calcination, the percentage of REO can be upgraded to 85–90 %. This occurs because calcination removes the carbon dioxide (Gupta and Krishnamurthy 2005).

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[7] Solvent extraction is a separation method in which a substance is separated from one or more others using a solvent. Fundamental to the method is the variation of solubilities of different compounds in different substances.

[8] Tributyl phosphate is an organophosphorus compound with the chemical formula $(C_4H_9)_3PO_4$ (Encyclopedia Britannica 2015b).

[9] A pyrophosphate is a phosphorus oxyanion (Wikipedia 2015a).

U.S. Bureau of Mines Processes

The decomposition of bastnaesite has been intensively investigated. At the U.S. Bureau of Mines at the end of the 1950s, two processes were developed. One involved nitric-acid digestion and solvent extraction, the other involved sulphuric acid and recovery of the rare earths as water soluble sulphates (Gupta and Krishnamurthy 2005).

Molycorp Process-1

Molycorp developed another process, in which the concentrate is roasted in air at 620 °C to drive off CO_2, and oxidize cerium in to a tetravalent state. The resulting material is treated with 30% HCL to dissolve the non-cerium rare earths. This results in a cerium concentrate containing 65–70 % REO with 55–60 % CeO_2. The solution is further processed for the recovery of other rare earths, among them europium. The residue also contains RE-fluorides. The fluorides are decomposed by treatment with caustic soda. The rare earth hydroxides are then leached with HCl (Gupta and Krishnamurthy 2005).

Molycorp Process-2

Another process, developed at Molycorp, consists of the treatment of bastnaesite with HCl, yielding rare earth chlorides. These are subsequently treated with NaOH to convert them onto RE-hydroxides. After separation, are dissolved again in HCl, yielding rare earth chlorides. In the next step, the rare earth fluoride in the solid residue is converted to rare earth hydroxide using NaOH. Next follows neutralisation and purification. This involves hydrochloric acid, yielding a solution with a pH of about 3. By addition of hydroxide, iron precipitates as iron hydroxide. Sulphuric acid is used to precipitate lead sulphate. Then barium chloride is added to precipitate excess sulphate and to act as a carrier for the removal of any thorium daughter products present in the ore. At this pH, thorium hydroxide is insoluble and can be removed. Filtration finally leads to a clear solution of rare earth chlorides. This solution is then either concentrated by evaporation or by evaporation made into a solid form (Gupta and Krishnamurthy 2005).

Processing in China

In China, the rare earths are processed by heating with 98 % sulphuric acid at 500 ° C in a rotary kiln. This results in the release of carbon dioxide and hydrofluoric acid. The rare earths are converted to their sulphates. They are precipitated as a double sodium sulphate by leaching with water and adding sodium chloride. Subsequently, the sulphates are converted to hydroxides by digestion in a strong caustic solution. The separated hydroxides are then dissolved in HCl. After this, separation and purification of the rare earths is done through solvent extraction (Gupta and Krishnamurthy 2005).

Thorium Ltd Process

Bastnaesite is treated with caustic soda to convert the fluoride component into hydroxide. The hydroxide is treated with HCl, which yields a rare earth chloride solution. From this, $RECl_3 \cdot 6H_2O$ is produced, or the solution is processed further for the recovery of the individual rare earths (Gupta and Krishnamurthy 2005).

4.2.3.3 Chlorination

Goldschmidt process
The firm Goldschmidt AG from Germany developed in 1967 a high-temperature chlorination process to directly obtain anhydrous $RECl_3$. From this, metal can be produced directly. The process is suitable for a variety of ore minerals, such as monazite, xenotime, allanite, euxenite, fergusonite and gadolinite.
The ground ore concentrate is thoroughly mixed with a binder and some water. The relative dry brew is compacted into pellets in a briquetting machine, and then passed through a band drier. Eventual fines are screened off, and returned to the mixer. Then the pellets, accompanied by carbon, are fed into the chlorination furnace, where they are converted into chlorides by gaseous chlorine. The chlorides are separated according to their volatility. The rare-earth chlorides are periodically tapped from the bottom of the furnace. Alkali and alkaline earth also collect in the melt chamber. All other reaction products are carried away by the off gases (Gupta and Krishnamurthy 2005).

Baotau Concentrates
Baotau is a city in the REE-rich area of Inner Mongolia in China. The process developed here is similar to the process mentioned above. Ore minerals are mainly bastnaesite and monazite (Gupta and Krishnamurthy 2005).

4.2.3.4 Xenotime

Xenotime (ideal formula YPO_4) is processed differently by using concentrated sulphuric acid. The double sulphate precipitation is not possible, because yttrium and the heavy rare earths are very soluble. The rare earth phosphates are converted into water soluble sulphates by leaching xenotime concentrates in concentrated H_2SO_4 at 250–300 °C for one—two hours. The sulphate solutions are directly used for separation.

In an alternative process, the fine-ground xenotime is treated by fusing it with molten caustic soda at 400 °C, or by mixing it with sodium carbonate and roasting at 900 °C for several hours. The hydroxide residue is dissolved in hydrochloric acid and filtered to remove impurities such as silica, cassiterite etc. The rare earths are precipitated as oxalates by adding oxalic acid. The oxalates are oxidized to rare earth oxides (Gupta and Krishnamurthy 2005).

4.2.3.5 Gadolinite

For processing of gadolinite (ideal formula $(Ce, La, Nd, Y)_2FeBe_2Si_2O_{10}$), the ground ore is leached with nitric or hydrochloric acid. The rare earths are precipitated as oxalates by adding oxalic acid, which makes possible the separation of associated iron and beryllium. Concentrated sulphuric acid or mixtures of sodium hydroxide and sodium peroxide have also been applied to attack the ore (Gupta and Krishnamurthy 2005).

4.2.3.6 Euxenite

Euxenite (ideal formula (Y, Ca, Ce)(Nb, Ta)$_2$O$_6$), is treated by reductive chlorination, which is followed by distillation of the chlorides to separate the rare earths, titanium, niobium and tantalum. Solvent extraction can be used to remove tantalum and niobium chlorides and the rare earths from the chlorination residue (Gupta and Krishnamurthy 2005).

The ore mineral can also be treated by fusing it with ammonium bisulphate or caustic soda, or by digestion with hydrofluoric acid or sulphuric acid, or mixtures of the two (Gupta and Krishnamurthy 2005).

Also digestion in hot sodium hydroxide has been tried. The hydroxides formed are dissolved by dilute hydrochloric acid. Soda ash is added to precipitate a complex carbonate precipitate. This in turn is leached with dilute sulphuric acid, to selectively solubilize the rare earths. The rare earths are then subsequently precipitated as oxalate by adding oxalic acid (Gupta and Krishnamurthy 2005).

4.2.3.7 Loparite, Pyrochlore, Fergusonite and Samarskite

Loparite may be decomposed by chlorination. Pyrochlore decomposition involves use of hydrofluoric acid, followed by solvent extraction of Nb by MIBK (methylisobutylketone). There is also another process, which involves digestion with hot sulphuric acid and precipitation of niobium and rare earths by gradual reduction of acid concentrate and temperature.

Extraction of the rare earths from samarskite and fergusonite is carried out by hot caustic digestion and subsequently acid dissolution. This process is similar to that described for euxenite.

4.2.3.8 Apatite

Apatite may contain significant amounts of rare earths. Examples are apatites from Palabora, RSA (Gupta and Krishnamurthy 2005), Kovdor, Russia (Lapin and Lyagushkin 2014), and Kagankunde, Malawi (Wall and Mariano 1996).

In Palabora, the apatite is decomposed as follows. Apatite is dissolved in a mixture of sulphuric acid and recycled dilute phosphoric acid from the wet process phosphoric acid plant. Most of the rare earths, (70–85 %) contained in the feed, end up in largely in phosphogypsum, which is formed in the dissolution reaction. The rest of the rare earths dissolve in the crude dilute phosphoric acid and eventually precipitate in sludge that forms when the acid is concentrated to commercial-grade phosphoric acid (Gupta and Krishnamurthy 2005).

This sludge contains 2–8 % rare earths. As large amounts of this sludge are produced, they are a valuable source of rare earths. The sludge is washed and leached with dilute nitric acid, to which calcium nitrate has been added. From the leach liquor, the rare earths are recovered by solvent extraction and finally precipitated as rare earth oxalates. The oxalates are calcined in a rotary furnace to yield mixed rare earth oxides of 89–94 % purity.

4.3 Separation Processes

Several processes exist for separation of the naturally occurring rare earths from one another. They all utilize the small differences in basicity resulting from the decrease in ionic radius from lanthanum to lutetium. The basicity differences cause several effects:

- differences in solubility of salts
- differences in the hydrolysis of ions and
- differences in the formation of complex species.

These differences form the basis of the separation procedures by fractional crystallisation, fractional precipitation and ion exchange and solvent extraction.

Also, some trivalent rare earths (Ce, Pr, Tb) may also become tetravalent, and some others (Sm, Eu, Yb) may become divalent. This creates the possibility to use selective oxidation or reduction of these elements to separate them, because the divalent and tetravalent state the elements show marked differences in behavior from the trivalent state (Gupta and Krishnamurthy 2005).

4.3.1 Selective Oxidation

Cerium can be removed from the rare earths mixture after oxidation of naturally occurring Ce(III) to Ce(IV). This valence change occurs, for instance, when bastnaesite is heated in air at 650 °C, or when the rare earth hydroxides are dried in air at temperatures of 120–130°. In aqueous hydroxide suspensions, oxidation can be achieved by chlorination or electrolysis. Also application of ozone is possible for cerium removal. The ozone causes an oxidation precipitation process.

Once oxidized, the Ce(IV) can be removed from the trivalent rare earths in the hydroxide-oxide mixture in two ways:

(1) selective dissolution of trivalent species with dilute acid, or
(2) complete dissolution in concentrated acid

Subsequently, selective precipitation is carried out (Gupta and Krishnamurthy 2005).

However, even the precipitation of 99.8 pure ceric salts does obviously not remove all the cerium from the solution, and additional steps are necessary. A very effective way is air oxidation and solvent extraction. It has become apparent that TBP (tributyl phosphate, see also in Sect. 4.2.3.1) is the best extractant for large scale operations (Gupta and Krishnamurthy 2005).

Although Ce(IV) is stable in aqueous solutions, Pr(IV) and Tb(IV) are not. They cannot be recovered this way. An effective method involves making a solution of rare earth hydroxides in fused potassium hydroxide, and oxidizing this by anodic oxygen or by potassium chlorate (Gupta and Krishnamurthy 2005).

4.3.2 Selective Reduction

It is easily possible to remove Sm(III), Eu(III) and Yb(III) from the trivalent rare earths mixture by reducing them to the divalent state. However, they have to be enriched in the mixture, since they naturally are much less abundant than cerium.

On an industrial scale, a method developed by H.N.McCoy[10] has found acceptance. In a chloride solution, Eu(III) is reduced to Eu(II) by zinc. The divalent Eu is recovered as a sulphate. Zinc does not reduce Sm or Yb (Gupta and Krishnamurthy 2005).

Another method is the reduction of Eu(III) by a photochemical method, followed by the precipitation as a sulphate or chloride. In this method, lanthanide perchlorates and K_2SO_4 (0.05 M) in 10 % isopropanol are used.

Qiu et al. (1991) used also a photochemical method applied to a solution mixture of $SmCl_3$, $EuCl_3$, and $GdCl_3$ in a rare earth saturated ethanol-isopropanol system. Finally $EuCl_2$ was precipitated, which was 92 % pure. Sm(III) and Gd(III) are not reduced (Gupta and Krishnamurthy 2005; Qiu et al. 1991).

Finally, there is a method of separating samarium, europium and ytterbium, based on the fact that the metals Sm, Eu, and Yb cannot be produced by metallothermic reduction[11] of their halides. When a mixture of anhydrous rare-earth halides is reduced with calcium, the halides of Sm, Eu, and Yb are not reduced and remain in the salt slag. They can subsequently be separated from this (Gupta and Krishnamurthy 2005).

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[10] Herbert Newby McCoy (1870–1945) was an American chemist who taught at the University of Chicago and the University of Utah and was the vice-president of Lindsay Light & Chemical Company. He contributed to numerous papers on physical chemistry, radioactivity and rare earths (Wikipedia 2015b).

[11] This is an extraction technology that produces metal by reaction of one of its compounds with a metallic reducing agent through thermal methods.

4.3.3 Fractional Crystallization

Fractional crystallization can be described as follows: a part of a salt in solution is precipitated by a change in temperature or by evaporation of the saturated solution. If the solubility of the various compounds of the solution differs, the composition of the crystalline precipitate will not be the same as the composition of the original solution. The least soluble substance will be the first to crystallize.

This method has been considered the best of the classical separation procedures for producing individual elements in high purity. The most suitable compounds are ammonium nitrates (for La, Pr, and Nd) and double magnesium nitrates (for Sm, Eu, Gd). Manganese nitrates have also been used for separation of lanthanides of the cerium group (La–Nd). Bromates and sulphates have been used in the separation of the yttrium group (being the heavy lanthanides or HREE)

Erbium, thulium, lutetium and yttrium have been separated by application of a rare-earth hexa-antipyrine iodide salt.[12] Other chemicals applied include a sodium rare earth EDTA[13] salt for separating gadolinium, terbium, dysprosium, and yttrium. For these rare earths, a purity of 99% has been reached with this method.

Fractional crystallization works best for the lanthanum end of the series, as there the differences in ionic radius are the largest. Fractional crystallization is very slow for the heavy rare earths and in the Sm(III)–Gd(III)—region, because the differences in properties between the rare earths decrease as the atomic number increases (Gupta and Krishnamurthy 2005).

Fractional crystallization is one of the oldest methods for the separation of rare earths and is now not used anymore for separation of rare earths (Habashi 2013).

4.3.4 Fractional Precipitation

Fractional precipitation means the removal of part of the dissolved elements from solution by adding a chemical reagent to form a new less-soluble compound. In this respect, it is different from fractional crystallisation, where NO other compound is introduced in the solution.

Hydroxides and double sulphate have extensively been used, as well as double chromate. The latter one especially has been used for the separation of yttrium from the other rare earths. The addition of sodium sulphate to the rare earth solution leads to the precipitation of double sulphates. The elements La, Ce, Pr, Nd and Sm form poorly-dissolvable double sulphates, whereas Ho, Er, Tm, Yb, Lu and Y form well-dissolvable double salts. The salts of Eu, Gd and Dy form salts of intermediate solubility. Generally, the use of this method crudely separates the rare earth mixture

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[12] Antipyrine: a white crystalline powder with the formula (CH)(CH)CHNO, which was formerly used to relieve pain and reduce fever.

[13] EDTA is ethylene-diamine-tetra-acetic-acid, $((HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2)$.

into three groups, although separation of La and Y is very well possible (Gupta and Krishnamurthy 2005).

4.3.5 Ion Exchange

This method involves the exchange of ions between two electrolytes or between an electrolyte solution and a usually solid material called an ion exchanger. The latter is often a resin, or it is a mineral substance, like a zeolite[14] (Slater 1991; Zagorodni 2007).

Generally, an ion with a higher charge will replace an ion with a lower charge. When the ions have the same charge, the ion with the larger radius displaces the one with the smaller radius according to the laws of mass action. In ion exchange, there is an adsorption stage and an elution stage. In the first, the ions from the solution get loaded on the exchanger, and in the latter, as a consequence of a change of conditions, the ions desorb from the exchanger and go again into solution (Gupta and Krishnamurthy 2005).

For the rare earths, this was first attempted in the late 19th century (1893) for the separation of yttrium and gadolinium using activated carbon. Later the separation of the rare earths was also tried using other exchangers. At first ion exchange seemed not very promising, as the affinity of the chemically closely related rare earth elements for the applied exchangers was not sufficiently different to result in a satisfactory separation. The separation factors for adjacent rare earths were found to be close to unity (Gupta and Krishnamurthy 2005).

The situation changed with the appearance of complexing agents, which could enhance separation factors. Examples of these are citric acid–ammonium citrate, nitrilotriacetic acid (NTA) or ethylene-diamine-tetra-acetic acid (EDTA). Exchange with the citrate worked, but the application of NTA and EDTA did not lead at first to satisfactory results. Later, after the invention of the so-called band-displacement technique (Spedding et al. 1954), separation improved. The most useful commercial complexing agents are EDTA and HEDTA[15] (Gupta and Krishnamurthy 2005).

EDTA can effectively separate most of the rare earths from each other. Only for the pairs Eu–Gd, Dy–Y, and Yb–Lu does it not work so well. Separation of Dy–Y with HEDTA is, however, possible. HEDTA also shows good results for Tm–Yb–Lu, and for La–Ce–Pr–Nd–Y–Sm, and Ho–Er–Tm–Yb–Lu mixtures.

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[14] *Definition*: A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four O-atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These are usually occupied by H_2O molecules and extra framework cations that are commonly exchangeable. The channels are large enough to allow the passage of guest species (Coombs et al. 1997).

[15] HEDTA is hydroxyethyl-ethylene-diamine-triacetic acid.

In ion-exchange separations, temperature plays a crucial role. Some separations (e.g., Gd–Eu and Eu–Sm) worked very well at, for instance, 92 °C, whereas at room temperature they encountered difficulties (Gupta and Krishnamurthy 2005).

The band-displacement technique with ammonium-ethylene-diamine-tetra-acetate as the complexing agent has made ion exchange the most-used commercial process for rare-earth-element separation since the mid 1950. The advantages are many: separation of a mixture of 15 rare earths into its components with 99.99 % purity in one pass through the system; potential upscaling to multi-ton quantities; the possibility for recovery and recycling of water; and retention of ion and complexant. The technique is still used today, even with the possibility of solvent extraction, which is discussed hereafter (Gupta and Krishnamurthy 2005).

4.3.6 Solvent Extraction

Solvent extraction (SX), also called **liquid-liquid-extraction** (LLE), is the transfer of one or more solutes contained in a feed solution to another, essentially ***immiscible*** liquid (solvent). It takes place with aqueous and organic solutions at ambient temperatures and pressures (Kislik 2012).

The process was first applied to rare earths in the 1930s. Separation of the rare earths by solvent extraction is currently the most favored method to obtain very pure fractions of every rare earth. One of the liquid phases is an aqueous solution and the other is a non-aqueous phase (usually an organic liquid). There are many advantages to the use of solvent extraction for the separation of the rare earths. A major advantage is that the rare earth loading in the solvent or extractant can be very high. Aqueous solutions with up to 140 g of rare earth oxide per liter can be used (Gupta and Krishnamurthy 2005). Another advantage is that, with relatively simple equipment and rather quickly, very high purity can be achieved (Kislik 2012). Purities of >99.999 %, reached almost exclusively with solvent extraction, are reported in Gupta and Krishnamurthy (2005).

The organic phase used in the extraction process usually consists of two or more substances. One is the extractant itself, but very often this is as such a very viscous material, which cannot be applied in practice. It is therefore dissolved into a suitable solvent to ensure that there is good contact with the aqueous phase.

Usually the complete transfer of the metal ions to the organic phase does not proceed to its full extent in one contact. Therefore the process has to be repeated several times. After this, scrubbing and stripping must take place. This means that the loaded organic phase is brought in contact with an aqueous solution to collect the impurities extracted by the solvent. Stripping means that the scrubbed organic phase is brought in contact with an aqueous phase, in order to recover the main extracted substance(s) from the organic phase back to the aqueous phase (Gupta and Krishnamurthy 2005).

4.4 Scandium

Scandium is also extracted by solvent extraction from its resources. These are, however, essentially non-rare earth minerals. The main scandium resource minerals are uranium minerals, and trace amounts occur in iron and magnesium rich rocks.

Therefore, scandium is produced during the extraction of uranium. Initially, it is extracted together with uranium, but it is collected during the subsequent purification of uranium (Gupta and Krishnamurthy 2005).

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