Chapter 2
Rare Earth Beneficiation and Hydrometallurgical Processing

Prior to individual REE separation, the rare earth ore will go through a series of physical separation and hydrometallurgical processing. In this chapter, the rare earth ore beneficiation, mineral concentrate decomposition, and rare earth leaching are introduced briefly.

2.1 RE Mineral Processing Technology

Each rare earth deposit is unique and is always composed of a variety of minerals. For example, the Baiyun Obo deposit, the largest rare earth mine in production in China, contains bastnaesite, monazite, fluorite, magnetite, barite, calcite, quartz, feldspar, etc. (Cheng et al. 2007a, b). In order to make a rare earth project economically feasible, a series of ore beneficiation techniques are always employed to concentrate the rare earth minerals. The commonly used ore beneficiation technologies include gravity separation, flotation, and magnetic separation.

2.1.1 Gravity Separation

The successful application of gravity separation depends on the difference of specific gravity between the rare earth minerals and the major gangue materials. The particle size is also very important in gravity separation. The hinder-settling ratio as defined in Eq. (2.1) can be used to determine the suitability of gravity separation. In Eq. (2.1), $SG_{RE}$ is the specific gravity of rare earth minerals, $SG_{M}$ is the specific gravity of media, for example, water or heavy liquid, and $SG_{G}$ is the specific gravity of associated gangue materials.

\[ \text{Hinder-settling ratio} = \frac{SG_{RE} - SG_{M}}{SG_{G}} \]
Hinder settling ratio = \( \frac{(SG_{RE} - SG_M)}{(SG_G - SG_M)} \) \hspace{1cm} (2.1)

When the hinder-settling ratio is no less than 2.5, gravity separation will be effective; when the hinder-settling ratio is between 1.75 and 2.5, gravity separation can be used to separate those particles coarser than 0.15 mm; when the hinder-settling ratio is between 1.5 and 1.75, gravity separation can be used to separate those particles coarser than 1.6 mm; when the hinder-settling ratio is below 1.25, gravity separation is not recommended.

### 2.1.2 Flotation

Flotation is one of the most common beneficiation technologies in rare earth processing due to the fine liberation size of rare earth minerals. The development of rare earth flotation technology is always associated with the development of rare earth flotation reagents. Since the 1960s, extensive efforts have been devoted to the development of high efficiency rare earth flotation reagents. The rare earth flotation reagents include depressant, collector, and frother. Sodium silicate is the most common used gangue depressant in rare earth flotation. The major rare earth flotation collectors include hydroxamates, phosphonic acid, and carboxylates. The major rare earth collectors are shown in Table 2.1.

### 2.1.3 Magnetic Separation

Magnetic separation utilizes the difference of magnetic susceptibility between rare earth minerals and associated gangue materials. Materials can be classified into paramagnetic material and diamagnetic material based on the form of magnetism by an externally applied magnetic field.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Collector</th>
<th>General formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxamate</td>
<td>C5-9 alkyl hydroxamate</td>
<td>RCONHOH</td>
</tr>
<tr>
<td></td>
<td>C7-9 alkyl hydroxamate</td>
<td>RCONHOH</td>
</tr>
<tr>
<td></td>
<td>Aromatic hydroxamate</td>
<td>C₆H₅CONHOH</td>
</tr>
<tr>
<td></td>
<td>Salicylic hydroxamic acid</td>
<td>C₆H₅OHCONHOH</td>
</tr>
<tr>
<td></td>
<td>H₃O₅</td>
<td>C₆H₃NO₃</td>
</tr>
<tr>
<td>Phosphonic Acid</td>
<td>Styrene phosphonic acid</td>
<td>C₆H₅O₂P</td>
</tr>
<tr>
<td></td>
<td>Alky phosphate</td>
<td>RH₂PO₄</td>
</tr>
<tr>
<td>Carboxylate</td>
<td>Oleic acid</td>
<td>C₁₈H₃₄O₂</td>
</tr>
<tr>
<td></td>
<td>Phthalate</td>
<td>C₆H₄(COOCH₃)₂</td>
</tr>
<tr>
<td></td>
<td>Paraffin oxide soap</td>
<td></td>
</tr>
</tbody>
</table>
In magnetic separation, the magnetic force needs to be larger than the mechanical force such as gravity force or centrifugal forces to achieve separation. This requires an uneven magnetic field with high intensity and large gradient. Also, the magnetic susceptibility difference between rare earth minerals and gangue materials must be sufficient. The ratio of magnetic susceptibility \( K \) as defined by Eq. (2.2) is often used to determine the suitability of magnetic separation, where \( x \) and \( x' \) are the magnetic susceptibility of magnetic material and non-magnetic material, respectively. When \( K > 1 \), magnetic separation can be an effective separation method.

\[
K = \frac{x}{x'}
\quad (2.2)
\]

Due to the existence of other mechanical forces, for magnetic material separation, the magnetic force must be higher than the overall mechanical forces to achieve separation. For non-magnetic material separation, the magnetic force must be less than the overall mechanical forces to achieve separation.

Based on the magnetic susceptibility of minerals, they can be classified into: (1) high magnetic materials \((x \geq 3000 \times 10^{-9} \text{ m}^3/\text{kg})\), (2) low magnetic materials \((15 \times 10^{-9} \text{ m}^3/\text{kg} < x < 600 \times 10^{-9} \text{ m}^3/\text{kg})\), and (3) non-magnetic materials \((x < 15 \times 10^{-9} \text{ m}^3/\text{kg})\).

### 2.2 Rare Earth Ore Beneficiation

Besides the rare earth minerals, the ore always contains other minerals such as fluorite, magnetite, barite, calcite, quartz, and feldspar. These minerals have similar floatability, magnetic susceptibility, specific gravity, and electrical conductivity. The similarity of these physical properties poses significant challenges in separating the rare earth minerals. Often, more than one valuable mineral is present in a rare earth deposit. In addition to monazite and xenotime, other minerals such as ilmenite, rutile, zircon, and wolframite are also considered for recovery.

Even though more than 250 rare earth minerals have been identified, only a few of them have industrial value. Currently bastnaesite, monazite, xenotime minerals, and ion-adsorbing type rare earth clays are the major sources of rare earth production.

#### 2.2.1 Bastnaesite

Bastnaesite is the most industrially important rare earth mineral, containing 67–73 % REO. It is the major source of light rare earth elements. Well known bastnaesite deposits are Mountain Pass in California, Baiyun Obo in Inner Mongolia, Eastern China Weishan (WS), and Western China Mianning (MN). Baiyun Obo
is a complex rare earth deposit of bastnaesite and monazite. The others are bastnaesite deposits.

The chemical composition of bastnaesite is relatively simple in comparison with other rare earth minerals. A bastnaesite deposit is relatively easy to concentrate. The key is to manage the separation between bastnaesite and calcium and barium minerals. Flotation is the most common concentration process. A collector with good selectivity for bastnaesite and an effective depressant for other ore minerals are required. Bastnaesite concentrate can also be obtained through a combination of gravity-flotation or magnetic-flotation processes.

### 2.2.1.1 Eastern China WS Rare Earth Deposit

The WS rare earth deposit mineral veins contain bastnaesite, parisite, Ce-apatite, monazite, arfvedsonite, chloropyrite, pyrite, molybdenite, galena, sphalerite, magnetite, and perovskite. The intergrown gangue includes carbonatite, barite, limonite, quartz, fluorite, and some muscovite. The major rare earth mineral is bastnaesite. It is easier to separate bastnaesite from silicate minerals than from barite and limonite because the latter have similar specific gravity and floatability to bastnaesite. In the WS rare earth deposit, bastnaesite is intimately associated with barite and limonite. Limonite is a weathered clay which makes the separation even harder. A gravity-flotation process can produce a rare earth concentrate, while avoiding the interference of clays in flotation. However, the gravity separation process is complex. A simple flotation process for the WS rare earth deposit is shown in Fig. 2.1.

The WS rare earth flotation process uses oleic acid and kerosene as collectors. Sulfuric acid is used to adjust the pH to 5.5–6. Oxidized paraffin soap (RCO₂Na) is used as the barite collector. Barite flotation is performed at pH 11.

Zeng (1993) has done extensive investigation of flotation of the WS rare earth ore. A modified reverse flotation process, shown in Fig. 2.2, was proposed to upgrade the rare earth from 3 to 7% to 60% rare earth oxide (REO) and barite from 25 to 92–95%. Overall, rare earth recovery is 77–84% and barite recovery is 61–68%.

### 2.2.1.2 South West China MN Rare Earth Deposit

The South West China MN rare earth deposit is a bastnaesite deposit containing an average of 2.8% REO. The major minerals include aegirine-augite, barite, biotite, and bastnaesite. Aegirine-augite has been weathered to a black–brown clay-type powder. Bastnaesite exists as chips with large grain sizes. There are more than 20 associated minerals including galena, molybdenite, pyrite, wulfenite, limonite, goethite, magnetite, arfvedsonite, quartz, and feldspar. De-sliming is required to remove clays to improve concentrate grade. The feed can be pre-concentrated
Two methods of de-sliming have been investigated extensively (Wang and Chi 1996):

1. Attrition-scrubbing using water to wash clays from the feed before flotation.
2. Shaking table to remove clays as well as other low density gangue minerals.

Two processes have been developed for the MN rare earth deposit. One is a gravity-flotation separation process shown in Fig. 2.3. The flotation uses sodium silicate (Na$_2$SiO$_3$) as the depressant, soda ash (Na$_2$CO$_3$) as a modifier, and sodium alkyl hydroxamic acid as the rare earth collector. RE recovery is 53–67 % at a concentrate grade of 68–69 %.

The other is a de-sliming-flotation process. As shown in Fig. 2.4, the feed is washed using water to remove clays and then fed to flotation where Na$_2$SiO$_3$ is added as the depressant, Na$_2$CO$_3$ as the modifier, and sodium alkyl hydroxamic acid as the rare earth collector. Rare earth recovery is 40–67 % with a concentrate grade of 66–67 %.
2.2.2 Monazite

Monazite is one of the most important rare earth minerals and it was the first rare earth mineral recovered for industrial application. It is widely distributed across the world. Australia, Brazil, India, and China are all important monazite producers. There are a variety of endogenic and exogenic monazite mineral deposits. Monazite placers are exogenic mineral deposits. The China Baiyun Obo deposit and South African monazite deposits are endogenic mineral deposits.

2.2.2.1 Monazite Placers

Monazite exists mainly in placers, especially coastal placers. Many other minerals are commonly found in a monazite placer deposit. They are listed in Table 2.2. The separation of monazite from coastal placers is a complex process involving gravity separation, magnetic separation, electrostatic separation, flotation, and chemical separation. Magnetic and gravity separations are the major concentrating technologies for monazite. The usual equipment includes magnetic separators, shaking tables, spirals, and sluices. In a monazite separation process, there are typically several by-products, such as ilmenite, zircon, rutile, garnet, tinstone, and tungsten.

Fig. 2.2  Easter China WS rare earth reverse flotation process
Figure 2.5 shows a general separation process for monazite placers. It removes the +1.00 mm gravels and \(-0.025\) mm clays in the first step using attrition-scrubbing and settling to obtain the preliminary concentrate. Then, a series of magnetic separators with various magnetic intensities are utilized to separate the rare earth minerals and by-products.

2.2.2.2 Weathered Crust Monazite Deposit

Monazite is also found in weathered crust deposits. As listed in Table 2.3, many intergrown minerals can be found in a weathered crust deposit. The monazite separation process from a weathered crust deposit is more complicated in comparison to a monazite placer deposit. Figure 2.6 shows a general separation process for monazite from a weathered crust deposit. The first step is to remove coarse grain minerals and clay minerals, and then to remove light minerals such as silica, feldspar, and mica. After acid treatment, magnetic and gravity separation are used to separate the other minerals.
2.2.3 Xenotime

Xenotime is a rare earth phosphate mineral with its major component yttrium orthophosphate (YPO₄). It is one of the important sources of heavy rare earth elements. Occurring as a minor accessory mineral, xenotime is found in coastal placers, pegmatites, weathered crust, and igneous rocks. Associated minerals include zircon, magnetite, ilmenite, leucoxene, limonite, epidote, tourmaline, topaz, and scheelite. Major intergrown gangue materials are feldspar, silica, kaolin, and mica.

Yttrium is the major rare earth element in the xenotime. The total rare earth oxide content is higher than 42 % and yttrium accounts for 50–70 % of this.

The separation of xenotime uses a combination of gravity separation, electrostatic separation, and strong magnetic separation. However, it is difficult to separate fine grain ores through these separation processes, so flotation is always used for fine grain xenotime.

Fig. 2.4 MN desliming and flotation rare earth separation process
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Color</th>
<th>Magnetic susceptibility (m³/kg)</th>
<th>Density (g/cm³)</th>
<th>Abrasive hardness</th>
<th>Conductivity (s/m)</th>
<th>Sorting voltage (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>Brown</td>
<td>8,000</td>
<td>4.9–5.2</td>
<td>5.5–6.5</td>
<td>2.78</td>
<td>7,800</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>Iron black</td>
<td>1,800–3,997</td>
<td>5.5–6.0</td>
<td>5.5–6.0</td>
<td>2.51</td>
<td>7,050</td>
</tr>
<tr>
<td>Garnet</td>
<td>Glass red</td>
<td>63</td>
<td>3.5</td>
<td>8.0</td>
<td>6.48</td>
<td>18,000</td>
</tr>
<tr>
<td>Monazite</td>
<td>Yellow to brown</td>
<td>14</td>
<td>4.9–5.5</td>
<td>5.0–5.5</td>
<td>2.34</td>
<td>6,552</td>
</tr>
<tr>
<td>Zircon</td>
<td>Purple or colorless</td>
<td>0.19</td>
<td>4.7</td>
<td>7.5</td>
<td>4.18</td>
<td>11,700</td>
</tr>
<tr>
<td>Rutile</td>
<td>Blood red, bluish, brownish yellow, brown red, violet</td>
<td>Nonmagnetic</td>
<td>4.2–4.3</td>
<td>6–6.5</td>
<td>&lt;10⁻⁸</td>
<td>8,000–25,000</td>
</tr>
<tr>
<td>Quartz</td>
<td>Colorless</td>
<td>0–10</td>
<td>2.7–2.8</td>
<td>7.0</td>
<td>3.57–5.30</td>
<td>8,890</td>
</tr>
<tr>
<td>Mica</td>
<td>Black</td>
<td>40</td>
<td>1.0–2.0</td>
<td>1.0–1.5</td>
<td>1.73</td>
<td>14,820</td>
</tr>
</tbody>
</table>

Table 2.2  Common monazite placer deposit minerals and their physical properties
2.2.3.1 Xenotime Separation from Coastal Placers

Coastal placers are exogenic mineral deposits containing many intergrown minerals. As shown in Table 2.4, a coastal placer deposit in southeastern China contains 0.0107% xenotime, 0.0516% monazite, and many other associated minerals. SiO$_2$ is the major component of the deposit and total rare oxide content is 0.086%. The applicable separation process is shown in Fig. 2.7.

Fig. 2.5 General monazite separation process for a coastal placer deposit

2.2.3.1 Xenotime Separation from Coastal Placers

Coastal placers are exogenic mineral deposits containing many intergrown minerals. As shown in Table 2.4, a coastal placer deposit in southeastern China contains 0.0107% xenotime, 0.0516% monazite, and many other associated minerals. SiO$_2$ is the major component of the deposit and total rare oxide content is 0.086%. The applicable separation process is shown in Fig. 2.7.
2.2.3.2 Xenotime Separation from Weathered Crust

Xenotime is also found in weathered crust deposits. The content of clay minerals is relatively high in a weathered crust type of xenotime deposit. If soluble rare earths are adsorbed on the clay, the recovery of the adsorbed rare earth must be considered as well in the separation process. This type of rare earth deposit is normally found in south China. REO content is 0.05–0.3 %. Figure 2.8 shows a recommended xenotime concentrating process from a weathered crust type of rare earth deposit in south China.

2.2.4 Ion-Adsorbed Type Rare Earth Deposits

An ion-adsorbing type rare earth deposit was first found in China’s Jiangxi Province in 1969. The REEs are adsorbed on the surface of clays in the form of ions. The REEs are not soluble or hydrolyzed in water but follow ion-exchange laws. The grade of the ion-adsorbing type clay is 0.05–0.3 % rare earth oxide. Of the total rare earth up to 60 % are heavy rare earth elements including yttrium. The ore composition is relatively simple in comparison to the coastal placers. Sand content is low. The major components are clay minerals, quartz, and other rock-forming minerals. The clay minerals include halloysite, illite, kaolinite, and small amount of montmorillonite.

The separation process is relatively simple, including leaching, precipitation, and calcination. An alumina removal circuit can be installed to reduce the reagent consumption. The clarified solution can be precipitated by either oxalic acid or ammonium carbonate. Figure 2.9 shows an rare earth oxide (REO) production process from an ion-adsorbed type rare earth ore (Zhao et al. 2001).

<table>
<thead>
<tr>
<th>Industrial minerals</th>
<th>Associated minerals</th>
<th>Large amount</th>
<th>Minor amount</th>
<th>Trace amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monazite</td>
<td>Feldspar</td>
<td>Hematite</td>
<td>Columbite</td>
<td></td>
</tr>
<tr>
<td>Xenotime</td>
<td>Silica</td>
<td>Limonite</td>
<td>Fluorite</td>
<td></td>
</tr>
<tr>
<td>Fergusonite</td>
<td>Mica</td>
<td>Tourmaline</td>
<td>Apatite</td>
<td></td>
</tr>
<tr>
<td>Columbite-tantalite</td>
<td>Clay minerals</td>
<td>Pyrosluise</td>
<td>Aechynite</td>
<td></td>
</tr>
<tr>
<td>Microlite</td>
<td></td>
<td>Psilomelanle</td>
<td>Cassiterite</td>
<td></td>
</tr>
<tr>
<td>Zircon</td>
<td>Topaz</td>
<td>Beryl, rutile</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Arsenopyrite</td>
<td>Ferrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrite</td>
<td>Polycrase</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wolframite</td>
<td>Thorium</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Epidote</td>
<td>Gadolinlite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2.6 General monazite separation process for a weathered crust deposit

Table 2.4 Common minerals in Chinese coastal placer deposits

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Content (%)</th>
<th>Minerals</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenotime</td>
<td>0.0107</td>
<td>Ilmenite</td>
<td>0.1722</td>
</tr>
<tr>
<td>Monazite</td>
<td>0.0516</td>
<td>Marcasite</td>
<td>0.0730</td>
</tr>
<tr>
<td>Zircon</td>
<td>0.1355</td>
<td>Tourmaline</td>
<td>0.1663</td>
</tr>
<tr>
<td>Rutile and anatase</td>
<td>0.0280</td>
<td>Maghemite</td>
<td>0.0044</td>
</tr>
<tr>
<td>Topaz and staurolite</td>
<td>0.6758</td>
<td>Quartz, Feldspar, Mica</td>
<td>98.68</td>
</tr>
</tbody>
</table>
Baiyun Obo Rare Earth Deposit

Baiyun Obo rare earth is a multi-metal mineral intergrown deposit. It is now the largest rare earth production mine in the world. It is located in Inner Mongolia, China. There are 71 elements and over 170 minerals in the Baiyun Obo ore. Fifteen rare earth minerals have been identified (Yu and Deng 1992; Xiang et al. 1985). However, bastnaesite and monazite are the dominant rare earth minerals. The valuable minerals are closely associated with each other with small grain sizes between 0.010 and 0.074 mm.

The processing of Baiyun Obo rare earth has gone through many stages of development (Zhang et al. 2002b; Yang 2005; Fang and Zhao 2003; Cheng et al. 2007a, b; Zhao et al. 2008; Cai et al. 2009). Milestones include: (1) Calcination-magnetic separation-flotation process; (2) Flotation-low magnetic separation process; (3) Low magnetic separation-flotation-high magnetic separation process; (4) Low magnetic separation-high magnetic separation-flotation process.
2.2.5.1 Calcination-Magnetic Separation-Flotation Process

Ore is calcined at 650 °C with reducing reagents. The product is sent to magnetic separation. Iron minerals are recovered as magnetic materials. The rare earth and niobium minerals are left in the magnetic tails. The magnetic tails are sent to flotation to separate the rare earth minerals and niobium minerals. The process diagram is shown in Fig. 2.10 (Yu and Deng 1992). Of the total rare earth, 49.5 % can be recovered in the concentrate at a grade of 36 % rare earth oxide.
2.2.5.2 Flotation-Low Magnetic Separation Process

As shown in Fig. 2.11, ore is ground to 95 % passing 74 μm and sent to flotation. At pH 11, polymerized sodium silicate is added to suppress rare earth minerals and iron minerals. Fluorite is floated first. Addition of an activator and pH adjustment to 8.5–9.0 floats rare earth minerals. Iron minerals are floated in an acidic environment using H₂SO₄ as activator and pH modifier. Low intensity magnetic separation is applied to recover magnetite from the iron flotation tails. Of the rare earth, 37.3 % can be recovered at a grade of 24.8 % rare earth oxide. Of the iron 80.8 % can be recovered at an iron grade of 56.0 %.

Fig. 2.9 Rare earth recovery from an ion-adsorbed type of clay deposit
2.2.5.3 Low Magnetic Separation-Flotation-High Magnetic Separation Process

Low intensity magnetic separation is used to separate iron-rich minerals. The magnetic separation tails are sent to flotation to separate fluorite and rare earth products. The flotation tails are fed to high intensity magnetic separation to recover hematite. The flow sheet is shown in Fig. 2.12.

A permanent magnet magnetic separator is used in the high intensity magnetic separation circuit with the magnetic field intensity 5500–6000 G. The rare earth recovery is between 20 and 30 % at a grade of 14–18 % REO. Of the iron, 65.4 % can be recovered at a grade of 55 %.

2.2.5.4 Low Magnetic Separation-High Magnetic Separation-Flotation Process

Yu and his colleagues developed the low magnetic-high magnetic-flotation process (Yu and Deng 1992; Yu and Che 2006). As shown in Fig. 2.13, the ore is ground to 95 % passing 0.074 mm and then separated into three fractions based on the
2.2 Rare Earth Ore Beneficiation

![Diagram of flotation and low magnetic separation process](image1)

**Fig. 2.11** Flotation and low magnetic separation process

![Diagram of low magnetic separation, flotation, high magnetic separation process](image2)

**Fig. 2.12** Low magnetic separation, flotation, high magnetic separation process
The ferromagnetic fraction is recovered using low intensity magnetic separation and the martite as well as primary hematite are recovered through high intensity magnetic separation. The rare earth minerals are preliminarily concentrated in the middlings of high intensity magnetic separation. The amounts of minerals such as fluorite, barite, and apatite, which have similar floatability to the rare earth minerals, are reduced significantly through high intensity magnetic separation. This enables more efficient flotation of the rare earth minerals. Sodium silicate is used as a depressant and H$_2$O$_5$ as collector. H$_2$O$_5$ is a kind of hydroxamic acid with amide as the polar end and aromatic hydrocarbon as the non-polar end. The flotation pH is controlled at 9.5, temperature at 35–45 °C, and feed solids at 35–45 wt%. The process with one stage of rougher flotation, plus one scavenger flotation as well as two cleaner flotation stages produces a primary rare earth concentrate and a secondary rare earth concentrate. In this process, 12.6 % of rare earth is recovered at a REO grade of 55.6 and 6.0 % is recovered at a REO grade of 34.1 %, respectively.
2.2.6 WS Rare Earth Deposit

The WS rare earth deposit is one of three big light rare earth sources in China. It is located in Shandong Province in eastern China. The deposit is composed of rare earth minerals, iron minerals, barite, carbonatite, quartz, feldspar, mica, amphibole, and other minor minerals. Its main feature is NW-trending bastnaesite-baryte-carbonate veins associated with a quartz-syenite complex emplaced in Archaean gneisses (Jones et al. 1996). Bastnaesite is the only mineral of interest, although monazite, allanite, pyrochlore, aeschynite, chevkinite, columbite, and thorite are also present.

Flotation has been used dominantly in the processing of the WS rare earth deposit (Zeng et al. 1992). As shown in Fig. 2.14, the ground ore is first fed to the rougher flotation. The first cleaner tails and scavenger concentrate are recycled. The third cleaner tails are recovered as secondary rare earth concentrate to ensure the quality of primary rare earth concentrate and maintain overall rare earth

![Fig. 2.14 Weishan rare earth flotation process](image_url)
recovery. Reverse flotation is performed on the fourth cleaner concentrate to remove gangue minerals such as barite to ensure the quality of primary concentrate (Pan and Feng 1992).

The flotation is performed in an alkaline environment with sodium silicate and alum as depressants and \( \text{H}_2\text{O}_5 \) as collector. Of the total rare earth, 59.6 % can be recovered at a REO grade of 61.2 % in the primary concentrate and 23.8 % at a REO grade of 33.5 % in the secondary concentrate.

### 2.2.7 MN Maoniuping Rare Earth Deposit

The MN Maoniuping rare earth deposit is located in Sichuang Province, south western China. It is NNE-trending bastnaesite-baryte-carbonate vein associated with nordmarkite intruding a granite batholith (Pu 1988). Major minerals include bastnaesite, barite, celestine, fluorite, aegirine, quartz, feldspar, arfvedsonite, biotite, pyrite, galena, magnetite, hematite, limonite, and calcite. In addition to bastnaesite, barite, fluorite, and galena can be recovered as by-products. The disseminated grain sizes of the bastnaesite vary between 0.03 and 2.0 mm (Li and Zeng 2003a, b).

A combination of gravity separation, magnetic separation and flotation processes are used for the separation of the Maoniuping rare earths (Xiong 2002; Li and Miu 2002; Li and Zeng 2003a, b; Lin 2005, 2007; Yu and Che 2006; Cheng et al. 2007a, b). As shown in Fig. 2.15, the run of mine ore is ground to 65 % passing 0.150 mm and sent to a shaking table where the coarse grain bastnaesite concentrate is recovered. The shaking table middlings are fed to the magnetic separation circuit to remove iron minerals and recover the magnetic rare earth concentrate. The shaking table tails and the magnetic tails are combined and classified to remove coarse grain tails. The classified products are ground to 75 % passing 0.074 mm and mixed with water. The clay is removed by de-sliming. Flotation is performed at the end of the rare earth separation process to obtain a flotation concentrate.

Starting with REO ore grading 5.46 %, the shaking table produces concentrate grading 57.7 % REO. Magnetic and flotation concentrates are 73.2 % REO and 64.3 % REO, respectively. The overall REO recovery is 83.1 %.

A relatively simple flotation process for the MN Maoniuping rare earth ore was reported by Xiong and Chen (2009). As shown in Fig. 2.16, a closed flotation circuit was tested. REO recovery was 87.0 % at a grade of 62.1 %.

### 2.2.8 Mountain Pass Rare Earth Deposit

The Mountain Pass mine in California used to be the largest rare earth concentrating facility in the world. However it was closed in 2003 due to environmental restrictions and international competition. The ore body contains bastnaesite rich in
Fig. 2.15 MN Maoniuping rare earth concentrating process
cerium group REEs as well as monazite. Associated with the bastnaesite are barite, calcite, strontanite, and silica as well as small amounts of apatite, hematite, galena, talcum, and phlogopite.

Flotation was used to separate the Mountain Pass rare earth ore. As shown in Fig. 2.17 (Johnson 1966), the ore was crushed and ground to minus 100 mesh and sent to conditioning at 55 % solids slurry. The staged conditioning was done in four stages of agitated tanks. Steam was injected to the first stage tank to raise the slurry temperature to 60 °C. Soda ash was added to control the pH at 8.95. Orzan, a kind of lignin sulfonate, was added as depressant in the second stage where temperature was raised to 80 °C using steam. The third stage was used to raise the slurry to boiling and to add N-80 oleic acid as collector and promotor. The fourth stage conditioner was used to cool the slurry to 60 °C for pumping to rougher flotation. One stage of rougher flotation, four stages of cleaner flotation, and one stage of scavenger flotation were used to concentrate the REO to 60 %. The overall REO recovery was between 65 and 70 %. The flotation concentrate could be sent to leaching using 10 % HCl. Lime was leached out and the bastnaesite stayed in the solids. Thickening and filtration were then used to remove excess water. REO at 70 % grade was produced after drying the leached solids. Calcination was also used to decompose the carbonate and obtain 90 % grade REO product.

**Fig. 2.16** Flowsheet of a simplified flotation circuit for the MN Maoniuping rare earth deposit
The Mount Weld deposit is located in Western Australia and is a deeply weathered volcanic carbonatite structure that contains approximately two million tons of rare earth oxides at an average grade of 20% (Guy et al. 2000). Two main types of ore are identified as limonitic siltstone (CZ) and nodular limonitic ironstone (LI). The lower grade LI-type ore overlies the higher grade and more extensive CZ-type ore. The deposit contains a complex association of carbonates, phosphates, and iron oxides. The rare earth minerals include monazite, cheralite, cerianite, rhabdophane, florencite, and bastnaesite.

Two processing options for treatment of CZ-type ore were explored by Lynas Corporation Ltd. for pilot plant consideration. Option 1 includes gravity concentration and flotation. Option 2 includes finer grinding and four stages of open

**Fig. 2.17** Mountin pass rare earth concentrating process

### 2.2.9 Mount Weld

The Mount Weld deposit is located in Western Australia and is a deeply weathered volcanic carbonatite structure that contains approximately two million tons of rare earth oxides at an average grade of 20% (Guy et al. 2000). Two main types of ore are identified as limonitic siltstone (CZ) and nodular limonitic ironstone (LI). The lower grade LI-type ore overlies the higher grade and more extensive CZ-type ore. The deposit contains a complex association of carbonates, phosphates, and iron oxides. The rare earth minerals include monazite, cheralite, cerianite, rhabdophane, florencite, and bastnaesite.

Two processing options for treatment of CZ-type ore were explored by Lynas Corporation Ltd. for pilot plant consideration. Option 1 includes gravity concentration and flotation. Option 2 includes finer grinding and four stages of open
circuit cleaner flotation. The Option 1 flowsheet is shown in Fig. 2.18. Typical metallurgical results are a final concentrate grade of 49% with recovery of about 35%.

The Option 2 flowsheet is shown in Figure 2.19. The Option 2 process has similar metallurgical results. The Mount Weld mine officially opened in 2011. The process used is not public information. It is probably a hybrid of the two process schemes, incorporating the best features of each. Mount Weld intends to supply 11,000 ton REO in phase I and 22,000 ton REO in phase II. Full capacity production from phase I is expected in 2012 (Latimer 2011).

### 2.2.10 Summary of the Rare Earth Beneficiation Processes

The unit operations used in rare earth mineral processing are well-known and conventional. However, the above flowsheets demonstrate that for rare earth mineral processing these are employed in unusual and often complex arrangements. In addition, the rare earth mineral processing reagents tend to be specific to this industry and, as always, the optimal unit operations and reagents are specific to each mineral deposit, so their selection requires skilled testwork. Increasing demand for rare earth minerals, coupled with uncertainties over the reliability of supply from China, are expected to drive an increased effort to discover and process rare earth minerals around the world. However, a significant portion of the new discoveries belongs to challenging low grade deposit which will need the development of innovative processing technologies including specialized equipment and selective reagents.

### 2.3 Hydrometallurgical Processing of Rare Earth Mineral Concentrate

The processes for rare earth extraction include the decomposition of rare earth minerals, and the concurrent or subsequent leaching of the rare earth elements from the decomposed minerals. Ore beneficiation concentrate can be decomposed by, for example, acid roasting, caustic cracking, and chlorination. The rare earth elements can be selectively extracted. The nature of the rare earth extraction process depends on the type of minerals in the concentrate, the grade of the concentrate and the targeted products. This section reviews rare earth element extraction from the major rare earth minerals, including bastnaesite, monazite, xenotime, ion-adsorption clay, allanite, cerite, and eudialyte.

Different with the physical beneficiation introduced in Sect. 2.2, rare earth extraction is chemical processing, which converts the rare earth mineral concentrate to a rare earth compound which is either an end product or an intermediate product.
2.3 Hydrometallurgical Processing of Rare Earth Mineral Concentrate

Fig. 2.18 Option 1 flowsheet development for CZ-type of ore

Fig. 2.19 Option 2 flowsheet development for CZ-type of ore
for the subsequent production of individual rare earth elements or other compounds. The rare earth extraction process uses one or more reagents to decompose the minerals and to leach the rare earth elements into solution. The rare earth element separation process uses solvent extraction, ion-exchange, or chemical precipitation to produce either mixed rare earth oxides or individual rare earth oxides. The varieties of rare earth extraction methods use many different reagents. These reagents are mainly inorganic acids, alkalis, electrolytes, and chlorine gas. The commonly used acids include sulfuric acid (H₂SO₄), hydrochloric acid (HCl), and nitric acid (HNO₃). Sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) are the most common alkalis. Electrolytes include ammonium sulfate ((NH₄)₂SO₄), ammonium chloride (NH₄Cl), and sodium chloride (NaCl). HCl, HNO₃, and H₂SO₄ are commonly used to extract RE from silicate ore minerals such as gadolinite, eudialite and allanite. The alkalis and H₂SO₄ are mainly used to leach rare earth elements from phosphate ore minerals like monazite and xenotime. The carbonatite rare earth minerals such as bastnaesite are treated using either H₂SO₄ or alkalis. HNO₃ is mainly used to leach eudialyte and apatite. The extraction of rare earth elements from ion-adsorption clay deposits uses electrolyte solutions. Chlorine gas (Cl₂) is exclusively used in the chlorination process which can be used to treat most of the rare earth minerals. In the following sections, the decomposition and leaching of rare earth mineral concentrates are described.

2.3.1 H₂SO₄ Acid-Roasting and Water Leaching

Acid-roasting is a major RE mineral decomposition process, classified into low-temperature roasting (<300 °C) or high-temperature roasting (>300 °C). The low-temperature process, formerly used in the 1970s to treat low-grade RE concentrates, is normally followed by long and complex processes to remove impurities from the leach solution. To inhibit the generation of soluble impurities, the high-temperature acid roasting process was developed in the 1980s to treat high-grade RE concentrates (Shi 2009). Currently, the majority of acid-roasting RE extraction operations use the high-temperature process. The high-temperature acid-roasting process is relatively simple but generates potentially hazardous exhaust gases such as hydrogen fluoride (HF), sulfur dioxide (SO₂), sulfur trioxide (SO₃) and silicon tetrafluoride (SiF₄). Normally, a water scrubber is used initially to capture most of the exhaust gases. A mixed acid containing HF, H₂SO₄, and H₂SiF₆ can be recovered in this initial scrub. A second scrubber using diluted sodium carbonate solution is used to purify the exhaust gas before it is released.

A general acid-roasting and leaching process for bastnaesite and monazite is shown in Fig. 2.20. It consists of grinding, mixing, roasting, leaching, and solid–liquid separation. The RE mineral concentrate is normally ground to less than 100 μm (150 mesh) before mixing with concentrated acid. A rotary kiln is employed for the acid roasting. Either a filter or thickener can be used to separate the leach solution from the residue. At higher acid/ore ratio more REEs plus
Thorium are solubilized. A lower ratio permits selective dissolution. With the increase in temperature higher than 300 °C, the decomposition rate is compromised but the leaching of thorium is also reduced due to the formation of insoluble ThP₂O₇. This is utilized to leave the thorium in the residue in some rare earth processing plants.

The REEs, thorium, and uranium are converted to soluble sulfates during H₂SO₄ acid-roasting. The major reactions include (Chi and Wang 1996):

\[
2\text{RECO}_3\text{F} + 3\text{H}_2\text{SO}_4 = \text{RE}_2(\text{SO}_4)_3 + 2\text{HF} + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (2.3)
\]
\[
2\text{REPO}_4 + 3\text{H}_2\text{SO}_4 = \text{RE}_2(\text{SO}_4)_3 + 2\text{H}_3\text{PO}_4 \quad (2.4)
\]

**Fig. 2.20** General acid-roasting and leaching process for bastnaesite and monazite
ThO₂ + 2H₂SO₄ = Th(SO₄)₂ + 2H₂O \uparrow \quad (2.5)

2U₃O₈ + O₂ + 6H₂SO₄ = 6UO₂SO₄ + 6H₂O \uparrow \quad (2.6)

RE₂O₃ + 3H₂SO₄ = RE₂(SO₄)₃ + 3H₂O \uparrow \quad (2.7)

The major side reactions include:

CaF₂ + H₂SO₄ = CaSO₄ + 2HF \uparrow \quad (2.8)

Fe₂O₃ + 3H₂SO₄ = Fe₂(SO₄)₃ + 3H₂O \uparrow \quad (2.9)

SiO₂ + 2H₂SO₄ = H₂SiO₃ + H₂O \uparrow + 2SO₃ \uparrow \quad (2.10)

4HF + SiO₂ = SiF₄ \uparrow + 2H₂O \uparrow \quad (2.11)

H₂SiO₃ = SiO₂ + H₂O \uparrow \quad (2.12)

2H₃PO₄ = H₄P₂O₇ + H₂O \uparrow \quad (2.13)

Th(SO₄)₂ + H₄P₂O₇ = ThP₂O₇ + 2H₂SO₄ \quad (2.14)

At the Saskatchewan Research Council, numerous H₂SO₄ roasting and leaching tests have been conducted. Normally the acid/concentrate mass ratio is between 1/1 and 2/1 depending on the grade of the rare earth mineral concentrate and the gangue minerals occurring in the concentrate. When the grade is high, the acid consumption is relatively low. Acid consumption will increase if the content of carbonate, fluoride and/or iron minerals is high. As well, the acid consumption is affected by roasting time and temperature. A higher roasting temperature and shorter roasting time can be used to reduce acid consumption while maintaining the same decomposition efficiency. However, higher roasting temperature may reduce the conversion of rare earth elements to soluble sulfates and reduce the rare earth recovery. A white or reddish color of roasted sample is one of the indicators of over-roasting. However, a dark green color indicates under-roasting. Roasting between 180 and 300 °C for 2–4 h is often successful.

The solubility of rare earth sulfates will also drop with an increase in leaching temperature. Therefore, water leaching is normally performed at ambient temperatures. To reduce dissolved rare earth loss from adsorption in the leach residue, the leach is relatively dilute, at a water/concentrate mass ratio between 7 and 15.

In addition to bastnaesite and monazite, the acid-roasting and water leaching process can also be used to process xenotime, aeschynite, and RE silicates.

### 2.3.2 HCl Acid Leaching

Dilute HCl is used to dissolve calcium carbonate and concentrated HCl is used to decompose bastnaesite. The major reaction of the latter type is shown by Eq. (2.15).
The equation for the reaction is:

$$3\text{RECO}_3\text{F} + 6\text{HCl} = 2\text{RECl}_3 + \text{REF}_3 \downarrow + 3\text{H}_2\text{O} + 3\text{CO}_2 \uparrow$$  \hspace{1cm} (2.15)

RE fluorides remain in the residue after HCl decomposition. After an initial solid–liquid separation, NaOH is used to convert them to RE hydroxides as shown by Eq. (2.16).

$$\text{REF}_3 + 3\text{NaOH} = \text{REOH} \downarrow + 3\text{NaF}$$  \hspace{1cm} (2.16)

After a second solid–liquid separation, the RE hydroxides are combined with the RECl$_3$ solution from the major reaction and are dissolved by the excess HCl. This process is diagrammed in Fig. 2.21.
Concentrated HCl is also often used to decompose allanite, cerite, and gadolinite. The reaction between concentrated HCl and gadolinite is expressed by Eq. (2.17).

\[
\text{RE}_2\text{FeBe}_2\text{SiO}_4 + 12\text{HCl} = 2\text{RECl}_3 + \text{FeCl}_2 + 2\text{BeCl}_2 + 2\text{SiO}_2 + 6\text{H}_2\text{O}
\]  

HCl can also be used to dissolve rare earth oxide, rare earth carbonate and other rare earth intermediate products in subsequent process stages.

### 2.3.3 HNO\textsubscript{3} Acid Leaching

Eudialyte is a rare earth silicate. A eudialyte mineral concentrate can be decomposed using 30–50 % nitric acid (HNO\textsubscript{3}). In addition to rare earth elements, zirconium (Zr), tantalum (Ta), and niobium (Nb) can also be recovered from eudialyte.

REEs can enter the crystal matrix of apatite through isomorphous replacement. The rare earth content in apatite is normally very low. However, apatite is one of the important rare earth element sources because it is a relatively common and widely occurring mineral. Apatite can be decomposed by HNO\textsubscript{3}, HCl, or H\textsubscript{2}SO\textsubscript{4}, releasing rare earth elements into the leach solution. Apatite readily dissolves in 50–60 % HNO\textsubscript{3} acid at 60–70 °C as shown in Eq. (2.18).

\[
\text{Ca}_5\text{(PO}_4)_3\text{F} + 10\text{HNO}_3 = 3\text{H}_3\text{PO}_3 + 5\text{Ca(NO}_3)_2 + \text{HF}
\]  

### 2.3.4 Na\textsubscript{2}CO\textsubscript{3} Roasting

Low grade (20–30 % REO) bastnaesite and monazite concentrate can be decomposed through 350–550 °C roasting with sodium carbonate at a mass ratio of concentrate to sodium carbonate from 6:1 to 3:1. The reactions during roasting include (Huang 2006):

\[
\text{RECO}_3\text{F} = \text{REOF} + \text{CO}_2 \uparrow
\]

\[
2\text{CeCO}_3\text{F} + \frac{1}{2}\text{O}_2 = \text{Ce}_2\text{O}_3\text{F}_2 + 2\text{CO}_2 \uparrow
\]

With an increase in roasting temperature to 600–700 °C, the following additional reactions will occur.
2REOF + Na₂CO₃ = RE₂O₃ + CO₂ ↑ + 2NaF \hspace{1cm} (2.21)

Ce₂O₃F₂ + Na₂CO₃ = 2CeO₂ + 2NaF + CO₂ ↑ \hspace{1cm} (2.22)

2REPO₄ + 3Na₂CO₃ = RE₂(CO₃)₃ + 2Na₃PO₄ \hspace{1cm} (2.23)

2REPO₄ + 3Na₂CO₃ = 2RE₂O₃ + 3CO₂ ↑ + 2Na₃PO₄ \hspace{1cm} (2.24)

CaF₂ + Na₂CO₃ = CaCO₃ + 2NaF \hspace{1cm} (2.25)

BaSO₄ + Na₂CO₃ = BaCO₃ + 2Na₂SO₄ \hspace{1cm} (2.26)

Ca₃(PO₄)₂ + 3Na₂CO₃ = 3CaCO₃ + 2Na₃PO₄ \hspace{1cm} (2.27)

After roasting, the soluble salts can be washed out using water or dilute acid. The rare earth oxide will stay in the solids and the grade can be increased from 20–30 % to 50–60 %.

2.3.5 NaOH Decomposing

Concentrated NaOH solution (>50 % by weight) can be used to decompose rare earth mineral concentrates. When it is used to decompose bastnaesite and monazite, the following reactions occur (Chi and Wang 1996):

\[
RECO₃F + 3NaOH = RE(OH)₃ + NaF + Na₂CO₃ \hspace{1cm} (2.28)
\]

\[
REPO₄ + 3NaOH = RE(OH)₃ + Na₃PO₄ \hspace{1cm} (2.29)
\]

At 140 °C and a mass ratio of NaOH/rare earth concentrate of 1.2–1.4, over 90 % rare earth elements can be extracted within 5 h. The concentration of NaOH solution has significant effects on the extraction kinetics and alkali consumption. For example, the reaction time can be reduced from 5 h to less than 1 h with NaOH concentration increased from 50 to 60 %. Concurrently, the NaOH consumption is reduced from 1,200–1,400 to 800–900 kg/t concentrate. Particle size and agitation can also play important roles. For example, in monazite decomposition 100 % passing 325 mesh or 43 μm and sufficient agitation are necessary due to the fact that the produced RE hydroxide attaches to the surface of the concentrate particles and forms a layer around the reacting core thus increasing the mass transfer resistance and the reaction time. Furthermore, the increase in reaction temperature improves the subsequent RE(OH)₃ dissolution in hydrochloric acid.

Rare earth mineral concentrate can also be decomposed with fused NaOH at higher temperatures of approximately 350 °C or higher. However, the rare earth products of fused NaOH decomposition are difficult to dissolve. For this reason, this process has been abandoned by the rare earth industry.

To reduce cost and improve operational safety, an alternating electric field NaOH decomposing process was developed in 1980s by the Beijing General Research Institute of Nonferrous Metals. The major improvement with this process
is using electrode heating to replace steam heating of NaOH. The decomposition reaction time is reduced from 6–12 h to 2 h. As well, the alkali consumption is low in comparison with the traditional NaOH decomposing process.

### 2.3.6 Chlorination

The chlorination process uses chlorine gas (Cl₂), at high temperatures (600–1200 °C) in the presence of carbon (C), to decompose RE mineral concentrates. The REEs and some other elements are converted to chlorides. SiCl₄ is used as required to remove fluorine through the formation of gaseous SiF₄. The major RE mineral decomposition and chlorination reactions during chlorination include (Zhang et al. 2002a; Zeng et al. 2007):

\[
\text{RECO}_3\text{F} = \text{REOF} + \text{CO}_2 \uparrow \quad (2.30)
\]

\[
\text{REOF} + C + \text{Cl}_2 + \frac{1}{4} \text{SiCl}_4 = \text{RECl}_3 + \frac{1}{4} \text{SiF}_4 \uparrow + \text{CO} \uparrow \quad (2.31)
\]

\[
\text{REOF} + \frac{1}{2} C + \text{Cl}_2 + \frac{1}{4} \text{SiCl}_4 = \text{RECl}_3 + \frac{1}{4} \text{SiF}_4 \uparrow + \frac{1}{2} \text{CO}_2 \uparrow \quad (2.32)
\]

\[
\frac{1}{3} \text{REO}_4 \downarrow + C + \text{Cl}_2 = \frac{1}{3} \text{RECl}_3 + \frac{1}{3} \text{POCl}_3 \uparrow + \text{CO} \uparrow \quad (2.33)
\]

\[
\frac{1}{3} \text{REO}_4 \downarrow + \frac{1}{2} C + \text{Cl}_2 = \frac{1}{3} \text{RECl}_3 + \frac{1}{3} \text{POCl}_3 \uparrow + \frac{1}{2} \text{CO}_2 \uparrow \quad (2.34)
\]

As well, some gangue minerals also undergo chlorination reactions.

\[
\frac{1}{3} \text{Fe}_2\text{O}_3 \downarrow + C + \text{Cl}_2 = \frac{2}{3} \text{FeCl}_3 + \text{CO} \uparrow \quad (2.35)
\]

\[
\frac{1}{3} \text{Fe}_2\text{O}_3 \downarrow + \frac{1}{2} C + \text{Cl}_2 = \frac{2}{3} \text{FeCl}_3 + \frac{1}{2} \text{CO}_2 \uparrow \quad (2.36)
\]

\[
\text{BaSO}_4 \downarrow + C + \text{Cl}_2 = \text{BaCl}_2 + \text{CO}_2 \uparrow + \text{SO}_2 \uparrow \quad (2.37)
\]

\[
\text{CaF}_2 + \frac{1}{2} \text{SiCl}_4 = \text{CaCl}_2 + \frac{1}{2} \text{SiF}_4 \uparrow \quad (2.38)
\]

The resulting chlorination products have a range of melting and boiling points. The lower boiling point products, such as FeCl₃, will exit the process in the exhaust gases, while the higher melting point products will remain in the solid residue. The chlorides of rare earth elements, Ca, Ba, and other alkali earth metals are collected as melts, which go through impurity removal, separation, and purification to produce rare earth products.
The major stages of the chlorination process are feed preparation, chlorination, and separation of chlorides. The reaction rate of chlorination increases with temperature.

Chlorination can also be performed using ammonium chloride as shown by the following equation (Shi and Zhou 2003).

\[
\text{RE}_2\text{O}_3 + 6\text{NH}_4\text{Cl} = 2\text{RECl}_3 + 6\text{NH}_3 + 3\text{H}_2\text{O}
\]

(2.39)

Chlorination can be used to treat a variety of rare earth minerals like bastnaesite, monazite, xenotime, allanite, cerite, euxenite, fergusonite, and gadolinite. The REO grade of chlorination products is relatively high. However, rare earth mineral concentrate chlorination products still require subsequent extraction and separation processes. Currently, there is no industrial application of the rare earth chlorination process.

### 2.3.7 Leaching of Ion-adsorbing Type of Rare Earth Clay

An ion-adsorbing type rare earth deposit is normally the weathered crust of a magmatic-type primary deposit. The rare earth elements are adsorbed on the surface of clays in the form of ions. The rare earth elements are not soluble or hydrolyzed in water but follow ion-exchange laws (Lu et al. 1997; Tian and Yin 1996; Li 1993; Chi 1989).

\[
[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]_m \times n\text{RE} + 3n\text{Me}^+ = [\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]_m \times 3n\text{Me} + n\text{RE}^{3+}
\]

(2.40)

where, Me could be Na$^+$ or NH$_4^+$.

The ion-adsorption type of rare earth deposit has unique features: (1) Mining is simple due to the shallowness of the deposit; (2) No grinding is required since the rare earth elements are adsorbed and concentrated on the surface of the silicate clays; (3) Rare earth element grade is low from 0.05 to 0.3 %; (4) Almost all of the rare earth elements can be found in the ion-adsorbing type of deposit and HRE accounts for approximately 40 % of the TRE; (5) There is a low concentration of radioactive impurities. These features of the ion-adsorbing type of deposits make them a very important and an economical REE source, especially as a HREE source.

The processes for REE extraction from the ion-adsorption type of deposits include heap leaching, agitated leaching and in situ leaching (or direct leaching). In heap leaching, the ore is stacked to about 1.5 m in height on a solution collection membrane. An electrolyte solution such as NaCl or (NH$_4$)$_2$SO$_4$ is sprayed onto the stack and trickles down through the stack to the collection membrane. In the stack Na$^+$ or NH$_4^{+}$ exchanges the RE$^{3+}$ to the solution. Temperature and pressure have no
significant impact on the ion exchange efficiency. The ion exchange rate is affected by the concentration of the electrolyte solution, pH, and solution wash rate. The ion exchange rate between Na\(^+\)/NH\(_4\)^+ and RE\(^{3+}\) increases with electrolyte concentration and wash rate. A pH4 electrolyte solution is normally employed. A higher pH causes RE hydrolyzation thus decreases the leaching rate while a lower pH will dissolve more impurities such as aluminum and iron.

If the deposit is mined by a wet process, the permeability of the ore required for heap leaching will be destroyed. In this case, agitated leaching will be used as the extraction process. Because ion exchange is a reversible process, the extraction efficiency with agitated leaching is normally lower than with heap leaching. However, both agitated leaching and heap leaching involve mining a large amount of material and producing large amount of tailings, which pose a serious environment protection challenge. In-situ leaching was developed and implemented as the second generation leaching process to reduce the environmental impacts associated with the development of ion-adsorption type of rare earth deposits. The overall resources utilization was also improved from no more than 50 % in agitated leaching and heap leaching to over 70 % in in situ leaching (Tang and Li 1997).

### 2.3.8 Summary

The decomposition and leaching of rare earth mineral concentrates involve the use of relatively large amounts of reagents and highly specific, relatively high cost reaction conditions. Except for the leaching of ion-adsorbing type of clay, the lack of selectivity of decomposition and leaching of RE minerals makes the subsequent impurity removal and rare earth element separation from the leaching solution of low grade rare earth mineral concentrate with higher reagent consumption than the processing of high grade concentrate. Therefore, the rare earth mineral concentrate grade plays a significant role in the economics of a rare earth extraction process.

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