Separation of uranium and thorium from rare earths for rare earth production – A review

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Abstract
Rare earths play critical roles in the applications of advanced materials. Recently, the recovery of rare earths from a variety of resources has gained much interest. Radiative elements of uranium and thorium are usually associated with rare earth deposits. The separation of uranium and thorium from rare earths is often a big concern in rare earth industry in order to reasonably manage the radioactive nuclides. This paper reviews the technologies used for separating uranium and thorium from rare earths in rare earth production, particularly in China. Some potentially applicable methods, such as precipitation and solvent extraction for the separation of uranium and thorium from rare earths in different media were also reviewed.

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1. Introduction

Recently, the demand for rare earths has increased significantly, driving the development of new processes to recover rare earths from a variety of new resources (Long et al., 2010; Krebs and Furfaro, 2013; Pawlik, 2013). Among a large number of rare earth minerals, only three are mainly used for rare earth production, namely bastnasite with the composition of (RE)(CO₃)F, monazite of (RE)PO₄ and xenotime of YPO₄ (Kanazawa and Kamitani, 2005; Jordens et al., 2013; Xie et al., 2014). Bastnasite and monazite are the main resources of light rare earths including lanthanum,
cerium, praseodymium and neodymium which generally account for more than 90% of the total rare earths (TRE). Particularly in bastnasite, the four light rare earths account for more than 98% of TRE (Gupta and Krishnamurthy, 2005; Jordens et al., 2013).

The main rare earth element in xenotime is yttrium which accounts for about 60% of TRE. Other rare earths in xenotime with relatively high content are gadolinium, dysprosium, holmium, erbium and ytterbium. Due to their similar chemical structures to rare earths, uranium and thorium are often present in rare earth minerals via lattice substitution, resulting in radiation issues in rare earth processing (Kanazawa and Kamitani, 2005). Jordens et al. (2013) reviewed the content of uranium and thorium in the above rare earth minerals (Table 1). Up to 5% of uranium is usually found in xenotime and rarely in monazite although occasionally found very high to 16%. Large amounts of thorium are commonly found in monazite which even can be up to 20%. Bastnasite usually hosts small amount of uranium and often certain amount of thorium. There is another kind of rare earth resources, ion-adsorption clays mainly found in China. These resources contain very small amounts of uranium and thorium to be about 20–30 ppm ThO₂ and U₂O₅ based on total REO (rare earth oxide) (Wang, 2006; Wang and Tang, 2007). These rare earth resources are found in southern China and they are rich in yttrium and other heavy rare earths. They also are the main sources for heavy rare earth production in the world. No measures are taken for the control of the radiation of uranium and thorium due to their low concentrations.

Excluding the ion-adsorption clays, the presence of substantial uranium and/or thorium in the three primary rare earth minerals causes considerable concern due to their radioactivity. Appropriate methods to separate them from rare earths for their proper management are therefore very important in order to avoid environmental pollution and the contamination of rare earth products (Soldenhoff, 2013). Uranium, if it can be recovered economically as a by-product, is saleable as nuclear fuel. However, thorium currently is only a nuclide which could potentially be used in nuclear industry in the future. There is a very small or even no market for thorium at present. Therefore, thorium is usually the main concern in terms of radiation hazard in rare earth production.

A number of reviews on rare earth resources, productions, applications, etc. have been conducted in the last a few years (Anon., 2012; Chakhmouradian and Wall, 2012; Binnemans et al., 2013; Haque et al., 2014; Xie et al., 2014). Some review slightly mentioned the separation of thorium from rare earths (Anon., 2012; Xie et al., 2014). In order to identify the effective measures to control the radiation pollution rising from thorium and uranium during rare earth processing, the separation of thorium and uranium from rare earths has been reviewed in detail in the present paper.

2. Thorium management during rare earth production in China

At present, most of rare earth products are provided by China. Currently, three main rare earth deposits are processed, including Bayan Obo in Inner Mongolia, Liangshan in Sichuan and ion-adsorption clays in southern China. All three rare earth deposits contain very low levels of uranium which is not recovered as a by-product and does not cause serious contamination or environmental pollution. Therefore, no measure has been taken specifically for uranium management. Thorium content in the ion-adsorption clays is also very low as mentioned above. However, the rare earth deposits in Bayan Obo and Liangshan do contain significant amounts of thorium and radiation pollution is of a great concern during rare earth production from their deposits.

2.1. Processing Bayan Obo rare earth concentrates

Bayan Obo rare earth deposit is the largest one in the world and accounts for more than 70% of total rare earth production in China (Wang and Wang, 2006; Du et al., 2010). The ore is a mixture of mainly two rare earth minerals: bastnasite and monazite with a ratio from 1:0.1 to 1:0.5 (Du et al., 2010). The concentrates after ore beneficitation used for rare earth production usually contain about 50–60% REO, 0.18–0.3% ThO₂ and <0.001% U₂O₅ (Wang and Tang, 2007). At present, about 90% of Bayan Obo rare earth concentrates are digested with H₂SO₄ at >500 °C (enhanced H₂SO₄ digestion). Its conceptual flowsheet is shown in Fig. 1 (Huang et al., 2006; Wang and Wang, 2006; Du et al., 2010).

![Fig. 1. Thorium separation during the rare earth production from Bayan Obo concentrates using enhanced H₂SO₄ digestion.](image-url)
Under the high temperature, phosphate reacts with $\text{H}_2\text{SO}_4$ to form $\text{H}_3\text{PO}_4$ which then dehydrates to pyrophosphoric acid. Thorium oxide reacts with $\text{H}_2\text{SO}_4$ first to form thorium sulphate, and then reacts with pyrophosphoric acid to form thorium pyrophosphate which is insoluble even in a strong acid solution. The overall reactions for rare earths, phosphate and thorium during roasting with $\text{H}_2\text{SO}_4$ are expressed in Eqs. (1)–(4).

\[
\begin{align*}
2\text{REPO}_4 + 3\text{H}_2\text{SO}_4 & = \text{RE}_2(\text{SO}_4)_3 + 2\text{H}_3\text{PO}_4 \\
2\text{H}_3\text{PO}_4 & = \text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \quad (200-300 ^\circ \text{C}) \\
\text{ThO}_2 + 2\text{H}_2\text{SO}_4 & = \text{Th}(\text{SO}_4)\text{H}_2 + 2\text{H}_2\text{O} \\
\text{Th}(\text{SO}_4)\text{H}_2 + \text{H}_2\text{P}_2\text{O}_7 & = \text{ThP}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 
\end{align*}
\]

While rare earths are leached from the acid-roasted concentrate with water, thorium remains in the solid residue, resulting in good separation of rare earths from thorium. Thorium left in the leach solution is usually less than 10 ppm, corresponding to a Th/REO ratio of <0.01% (Xu, 1995). In the subsequent step, thorium is further removed from the leach solution by precipitation together with iron and other impurities to obtain purified pregnant leach solution for further rare earth separations (Fig. 1). The thorium discharged in the radioactive waste currently requires special land for storage.

Only about 10% of Bayan Obo concentrates are processed using alkaline method due to its higher cost compared to the acid method. The thorium separation from rare earths in the process is shown in Fig. 2 (Wang et al., 1999; Wang and Wang, 2006; Liu et al., 2012). In the process, rare earths and thorium are converted into their hydroxide by NaOH during caustic digestion at a sub-boiling temperature. Subsequently, both rare earths and thorium hydroxide are leached with HCl. In the following step, the resultant leach solution is neutralised to pH 4–5 to remove thorium and iron by precipitation. The content of thorium oxide in the precipitate can exceed 10% (Cheng and Hou, 2007). As the precipitate contains substantial rare earths, it has been reported to be re-used as the raw material in the acid process (Wang and Wang, 2006). Selective dissolution of rare earths also can be used after the alkaline conversion to separate thorium and iron. The optimised pH range is pH 4.5–5 with rare earth dissolution of >90% and rare earth concentration of about 200 g/L (Xu, 1995). It is reported that the final rare earth chloride products contained 48% REO with less than 0.03% ThO$_2$. After selective dissolution, the residue accounts for about 5% (w/w) of the initial concentrate which contains 30–40% REO, 0.3–0.5% ThO$_2$, 20–25% Fe, ~5% P and ~3% F. The radioactive residue is stored for future thorium recovery or fed to the acid process.

The thorium distribution in the waste and rare earth product in processing Bayan Obo concentrates using acid and alkaline methods is shown in Tables 2 and 3 (Bai et al., 2001). As environmental protection has become more and more stringent for waste discharge, some new processes have been developed in recent years to meet this requirement (Huang et al., 2006; Wang and Wang, 2006; Lang and Yu, 2009; Du et al., 2010). One typical process for the Bayan Obo concentrate involves digesting with concentrated sulphuric acid at a relatively low temperature (<300 °C). Under such low temperature, no thorium pyrophosphate forms and it is leached into the pregnant rare earth leach solution. The resultant leach residue can meet the requirement for non-radioactive solid waste management (Du et al., 2010). The separation of thorium from the rare earths is conducted using solvent extraction with a primary amine (N1923) which has very high selectivity for thorium over rare earths (Zhu et al., 2006). In the process, thorium was supposed to be stored as a by-product in a pure compound such as thorium oxide for future usage. Currently, there is no application of the above proposed process in China.

### 2.2. Processing Sichuan rare earth concentrates

The rare earth deposit in Sichuan province is the second largest for rare earth production in China and the rare earth minerals are bastnasites. After beneficiation, the concentrates for rare earth production usually contain 60–70% REO, 0.2–0.3% ThO$_2$, and 0.002 % U$_2$O$_4$ (Wang, 2006; Wang and Wang, 2006; Huang et al., 2011). Similar to the Bayan Obo rare earth deposits, the small amount of uranium in these deposits has no economic value and presents no significant harm to the environment. However, the separation of thorium from rare earths and its proper management also are of great concern. At present, almost all concentrates containing only bastnasite are processed using hydrochloric acid leaching with the basic flowsheet as shown in Fig. 3 (Liu et al., 2009, 2012; Huang et al., 2011; Wang et al., 2013). After roasting under a temperature of about 500 °C with sufficient air as the oxidant, more than 95% of cerium is oxidised to Ce$^{4+}$ (Xu, 1995). Thorium and cerium are in the forms of ThO$_2$ and CeO$_2$, respectively and will remain in the leach residue, while trivalent rare earths are selectively leached using HCl. Thorium in the leach residue is separated from cerium after caustic attack to convert thorium and cerium oxide to their hydroxide followed by HCl leaching in a reduced environment. In the leach process, tetravalent cerium is reduced to trivalent cerium which can be leached into the solution while thorium remains in the residue (Huang et al., 2011). It is worth noting that part of the cerium enriched residue from bastnasite processing in China is used for ferrosilicon alloy production in the steel industry where thorium is rejected to a smelter slag (Zhang and Huang, 1997; Huang et al., 2011; Jia et al., 2002). It was reported that thorium content in the waste water and rare earth products is higher than that in the processing Bayan Obo concentrate using the enhanced acid digestion method (Schuler et al., 2011).

### Table 2

Distribution of thorium in rare earth production using Bayan Obo rare earth concentrate containing 0.2% Th (based on Bai et al., 2001).

<table>
<thead>
<tr>
<th>Method</th>
<th>Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste residue</td>
<td>96</td>
</tr>
<tr>
<td>Waste water</td>
<td>2–3</td>
</tr>
<tr>
<td>Off-gas</td>
<td>1</td>
</tr>
<tr>
<td>Rare earth product</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Enhanced acid</td>
<td>95–96</td>
</tr>
<tr>
<td>Alkaline</td>
<td>4–5</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
</tr>
</tbody>
</table>
Previously, an old process was used to process the Sichuan bastnasite concentrate consisting of the following steps (1) roasting under oxidative environment; (2) leaching with sulphuric acid; (3) double salt precipitation to recover Ce-depleted trivalent rare earths; (4) reductive leaching and recovery of Ce by double salt precipitation (Zhang and Huang, 1997; Liu et al., 2009). In the process, thorium was first rejected to the cerium concentrate and then was separated from cerium by cerium selective leaching when Ce(IV) was reduced to Ce(III). This process was ceased in China in the early 1990s because it was too complicated and generated too much waste.

Recently, a number of new processes for processing bastnasite have been developed in China (Huang et al., 2006; Liu et al., 2009). These processes mainly focus on the recovery of thorium and fluorine to comprehensively use the resources and reduce environmental pollution. All the newly developed processes involved solvent extraction to separate thorium from rare earths. However, no such process has been commercially practised, probably due to high cost.

2.3. Processing monazite concentrates

There are monazite rare earth deposits in southern China containing uranium and substantial amount of thorium (Yu and Zhang, 1982; Cheng and Che, 2010; Su, 2014). These processes mainly focus on the recovery of thorium and fluorine to comprehensively use the resources and reduce environmental pollution. All the newly developed processes involved solvent extraction to separate thorium from rare earths. However, no such process has been commercially practised, probably due to high cost.

3. Uranium and thorium separation in some rare earth practices outside China

The only large scale rare earth production outside China is currently operated by Lynas Australia in its refinery plant in Malaysia. The rare earth concentrate is from Mount Weld in Australia which contains 40% REO, 0.16% ThO₂ and 0.003% U₃O₈ (Anon., 2010; Lee, 2012). The main rare earth minerals in the concentrate are monazite and xenotime (Haque et al., 2014). Concentrated sulphuric acid is used to digest the concentrate which is very similar to that used for the treatment of Bayan Obo concentrates in Fig. 1. During processing, thorium is separated from rare earths by rejecting to the leach residue as a radioactive waste stored in a waste tailing pond (Lee, 2012). Uranium management in the process is not documented due to its low content.

Before mid 1980s, Molycorp of USA was the major light rare earths and europium producer (Haxel, 2005), but from 2002 rare earth production has been suspended. The rare earth ores were

<table>
<thead>
<tr>
<th>Method</th>
<th>Waste solid</th>
<th>Waste liquid</th>
<th>Waste gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Output (kg/t ore)</td>
<td>Th (%)</td>
<td>Treatment</td>
</tr>
<tr>
<td>Acid</td>
<td>650</td>
<td>0.1</td>
<td>Storage</td>
</tr>
<tr>
<td>Alkaline</td>
<td>150</td>
<td>0.5</td>
<td>To acid process</td>
</tr>
</tbody>
</table>

Table 3
Distribution of thorium in wastes produced during processing Bayan Obo rare earth concentrates (based on Bai et al., 2001).
from Mountain Pass deposit in the USA with the main rare earth minerals of bastnasites. The concentrate containing 60% REO was used for the refinery process. Firstly, the concentrate was further upgraded by leaching with diluted HCl to partially dissolve carbonate gangue minerals, resulting in an increase in REO content to 70%. Thorium and uranium contents in the concentrates are supposed to be about 0.1–0.2% and 0.01–0.001%, respectively, estimated based on the composition of the original ore body (0.0181% ThO₂ and 0.0019%). The major process for rare earth refinery was similar to that used in China to process bastnasite concentrate shown in Fig. 3. Thorium was also locked in the cerium enriched residue first after trivalent rare earths were selectively leached with HCl. Cerium was then recovered and separated from thorium by decomposing and selective leaching with sulphuric acid (Zhang and Huang, 1997; Haxel, 2005). No operation for uranium was reported also due to the very low content. Re-commencement of the rare earth refinery has been planned for the Mountain Pass deposit (Bleiwas and Gambogi, 2013).

A number of practices have also been operated in a very small scale for the production of rare earths by processing monazites in Canada, India, Brazil or elsewhere (Gupta and Krishnamurthy, 2005; Amer et al., 2013) using typical alkaline process mentioned above as in China (Gupta and Krishnamurthy, 2005). Uranium and thorium are concentrated to a thorium-rich residue as shown in Fig. 2. To recover uranium, thorium and rare earths from this kind of residue, nitric, hydrochloric and sulphuric acids can be used for their leaching and subsequent separation. Solvent extraction with TBP or amines is usually used for the separations of uranium and thorium which will be discussed in the later section. The Alwaye project in India uses hydrochloric acid to dissolve the thorium-enriched residue and the resultant solution is treated with sulphuric acid from where most of the thorium is precipitated as sulphate while most of the rare earths and uranium remain in the solution (Gupta and Krishnamurthy, 2005). Thorium sulphate is purified by re-dissolving and re-precipitating with sulphuric acid, and finally it is converted to thorium hydroxide using ammonia. The uranium and rare earths and the remaining thorium in the solution after thorium precipitation are separated by fractional precipitation using hydrofluoric acid.

Due to the increasing demand and reducing export of rare earth products from China, quite a number of new rare earth projects are under development globally, with many novel process routes being developed for these new deposits. Greenland Minerals and Energy Ltd Australia is developing the process for the Kvanefjeld rare earth deposit in Greenland (Krebs and Furfaro, 2013; Furfaro and Krebs, 2014). Rare earths and uranium are mainly hosted in steenstrupine (silico-phosphate based) minerals. A number of other minerals also host rare earths and uranium in the deposit. The ore is beneficiated using flotation to obtain a rare earth concentrate containing about 14% REO, 0.2% U₂O₅ and 0.5% ThO₂. High uranium content is valuable for recovery as a by-product of rare earths. The uranium and thorium separations from rare earths are indicated in Fig. 4. Most of the uranium is leached from the concentrate with a weak acid solution and recovered using solvent extraction with tertiary amine. Following the weak acid leach, a strong acid leach is conducted where most of the rare earths are converted to their double

![Diagram](image-url)

**Fig. 4.** A schematic flowsheet for processing Kvanefjeld rare earth concentrate (HRE denotes heavy rare earth; PLS denotes pregnant leach solution) (based on Furfaro and Krebs, 2014).
salts by maintaining sufficient sodium in the solution. Some of the thorium and uranium are leached and recycled to the weak acid leach step. Rare earth double salts first are converted to the corresponding RE hydroxide, and then are selectively dissolved by HCl, leaving thorium in the solid residue. Very small amounts of thorium and uranium in the rare earth chloride solution are removed by ion exchange (IX). The resin used is not disclosed.

Arafura Resources of Australia has conducted over ten years research for processing the Nolans Rare Earth deposit located in the Northern Territory of Australia. The rare earths are mainly associated with apatite, monazite and allanite with an average grade of 2.8% REO, 0.02% \( \text{U}_3\text{O}_8 \) and 0.27% \( \text{ThO}_2 \). After ore beneficia-
tion, a concentrate containing about 5% REO is supposed to be used for rare earth refining. In the process, most thorium is separated from rare earths and uranium in the rare earth chloride solution are removed by ion exchange (IX). The resin used is not disclosed.

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Fig. 5. A schematic flowsheet for processing Nolans rare earth concentrate (based on Ganser et al., 2014; Lockyer, 2014).

4. Separation of U and Th from rare earths by precipitation

As discussed above, precipitation and selective dissolution of rare earth have been commonly used to separate thorium from rare earths in the industry. This method takes the advantage of different precipitation pH of thorium and rare earths. The precipitation pH of trivalent rare earth hydroxides (except for scandium) is in the range of 6.8–8.0 in chloride and sulphate media and the precipitation pH decreases from light to heavy rare earths (Xu, 1995). Thorium precipitation from chloride solutions essentially occurs in the pH range of 2.5–5.5, and uranium(VI) precipitation occurs in the pH range of 5.5–7.0 (Pawlik, 2013). Kang et al. (2002) studied uranium precipitation in nitrate medium and found that U(VI) formed an insoluble precipitate of \( \beta\)-\( \text{U}_2\text{O}_5\text{(OH)}_2 \) in a pH range of 6–7.5. It is clear that the precipitation of thorium for its separation from rare earths can be achieved efficiently, but it is difficult to separate uranium from rare earths via the same approach due to their close precipitation pH.

A few investigations for uranium and thorium separations from rare earths by precipitation at different pH values are shown in Table 4. It is evident that thorium precipitation from chloride media is almost complete in the pH range of 4.8–5.8 with minor
Uranium and thorium separation from rare earths by hydroxide precipitation.

<table>
<thead>
<tr>
<th>RE solution</th>
<th>Solution generated</th>
<th>Reagent used</th>
<th>Final pH</th>
<th>Precipitation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 g/L RE chloride, U, Th unknown</td>
<td>Complex deposit by caustic digestion, and dissolution by HCl</td>
<td>NaOH</td>
<td>5.5</td>
<td>50 – 100</td>
</tr>
<tr>
<td>22 g/L RE sulphate, U, Th unknown</td>
<td>Complex deposit by H2SO4 digestion, and water leaching</td>
<td>Lime</td>
<td>5.5</td>
<td>–</td>
</tr>
<tr>
<td>50 g/L RE sulphate, 0.1 g/L Th</td>
<td>Bayan Obo concentrate by H2SO4 digestion, and water leaching</td>
<td>MgO</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>RE chloride</td>
<td>Rare earth double salt by caustic digestion, and dissolution by HCl</td>
<td>NaOH</td>
<td>5.8</td>
<td>99.3</td>
</tr>
<tr>
<td>10 g/L RE chloride, 0.05 g/L Th, 0.0007 g/L U</td>
<td>Monazite, by caustic digestion, and dissolution by HCl</td>
<td>Lime</td>
<td>4.8</td>
<td>71.4</td>
</tr>
<tr>
<td>7.25 g/L RE sulphate, 0.3 g/L Th</td>
<td>Xenotime by H2SO4 digestion and water leaching</td>
<td>NH3</td>
<td>1.5</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4
Uranium and thorium separation from rare earths by hydroxide precipitation.

Table 5
Rare earth recovery by double salt precipitation from a sulphate leach solution (based on Xu, 1995).

<table>
<thead>
<tr>
<th>REO</th>
<th>ThO2</th>
<th>Fe</th>
<th>P2O5</th>
<th>[H+] (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leach solution (g/L)</td>
<td>35</td>
<td>0.15</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>Double salt (%)</td>
<td>42–45</td>
<td>0.1–0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Filtrate (g/L)</td>
<td>0.1</td>
<td>0.02–0.04</td>
<td>21–22</td>
<td>11</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>99.7</td>
<td>73.3–86.6</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Therefore, separation of U(VI) and Th(IV) from rare earths, particularly from light rare earths could be achieved. However, the stripping of U(VI) and Th(IV) from D2EHPA and EHEHPA is difficult. Only sodium carbonate is efficient for their stripping (Ritcey, 2006; Zhang et al., 2010; Dinkar et al., 2012). Reasonably good stripping of Th(IV) from EHEHPA may also be obtained by a strong sulphuric acid solution (Muthuchamy et al., 2002; Zhang et al., 2010).

Organophosphinic acids, typically Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid), are widely investigated for rare earth extraction and separation (Nagaosa and Binghua, 1997; Xiong et al., 2005; Belova et al., 2010; El-Hefny et al., 2010). Although the extractant has good separation factors between the adjacent rare earths, no practical application has been found in the rare earth industry probably due to their high price and low metal extraction capacity. It has been reported that Cyanex 272 can strongly extract U(VI) and Th(IV) even in strong HNO₃ solutions up to 4 M. The extraction of RE(III) was less than 5% when the HNO₃ concentration was in the range of 0.5–1.0 N (Es-Nasab et al., 2011). This indicates that organophosphinic acid extractants could be used to separate uranium and thorium from rare earths. The extraction of Th(IV) in H₂SO₄ solutions with organic systems including D2EHPA, EHEHPA and Cyanex 272 was investigated by Tong et al. (2013) as shown in Fig. 6. Thorium extraction became weaker from D2EHPA to EHEHPA then to Cyanex 272. Thorium stripping is supposed to be achieved using sulphuric acid with concentration >1 M based on Fig. 6.

5.2. Neutral organophosphorus extractants

TBP (tri-n-butylphosphate), a neutral organophosphorus extractant, is the first preferred extractant to separate U(VI), Th(IV) and RE(III) from nitrate medium. The extraction of U(VI) by TBP is much stronger than that of Th(IV) and RE(III). Menzies and Rigby (1961) used 5% (v/v) TBP in xylene to extract uranium and separate it from thorium and rare earths in a nitrate leach solution. Subsequently, a higher concentration of TBP (40% v/v) in xylene was used to extract thorium and separate it from the rare earths. Good separations were also achieved by co-extraction of uranium and thorium to separate them from rare earths using 40% (v/v) TBP in xylene at a higher O/A ratio. Uranium and thorium separation was achieved by selective stripping of thorium. Uranium(VI) and thorium can also be extracted by TBP from hydrochloric acid media by forming UO₂Cl₂·2TBP and ThCl₄·3TBP, respectively. However, their extractions require very high hydrochloric acid concentration, e.g. >5 M HCl for essential uranium extraction and >8 M HCl for thorium extraction (Sato, 1966). No practical application was found due to high HCl consumption and its high corrosiveness.

Di(1-Methyl-Heptyl)Methyl Phosphonate (DMHMP) with Chinese brand name of P350 has been developed in China. The uranium extraction reached >80% from 1 to 2.5 M HCl solution with only 1–2% of thorium and rare earths co-extracted (Zhou, 1992). Thorium could be extracted and separated from rare earths in mixed HCl-HNO₃ media. The separations of uranium, thorium and rare earths using DMHMP have been used for the treatment of monazite processing residues in China.

The separation of uranium(VI), thorium and rare earths in a series of acidic solutions with Cyanex 923 (a mixture of tri-alkylphosphine oxides) was investigated (Gupta et al., 2002). It was found that uranium could be separated well from rare earths in HCl...
and possibly H₂SO₄ solutions (Fig. 7). However, it is difficult to separate uranium from thorium. The separation of thorium from rare earths was also not effective using Cyanex 923. Lu et al. (1998) obtained similar conclusion in their investigation.

5.3. Amide extractants

A series of N-alkyl carboxylic acid amides (R–CO–R’) were synthesised by varying the R’ group (Preston and du Preez, 1995). It was found that good separation between uranium and thorium in nitrate solutions could be achieved when R’ group had large steric hindrance. Since these reagents are not commercially available, no practical application has been found.

5.4. Amine extractants

Amine compounds are good for the extraction of U(VI) and Th(IV) and their separation from rare earths in sulphate solutions (Zhu and Cheng, 2011). All amine compounds including primary, secondary and tertiary amines and quaternary amine salts, have been widely investigated. Amongst them, tertiary amine has very high selectivity for the extraction of U(VI) over Th(IV) and RE(III) and has been widely used in the uranium industry. Representative commercial tertiary amine regents include Alamine 336 (tri-octyl/dodecyl amine), Alamine 304 (tri-dodecyl amine), Alamine 308 (tri isooctyl amine) and Adogen 364 (similar to Alamine 336). In contrast, primary amine has high selectivity for the extraction of Th(IV) over U(VI) and RE(III). Mostly used commercial primary amines are Primene JMT (a primary aliphatic amine with amino nitrogen linked to a tertiary carbon consisting of highly branched alkyl groups in the C16–C22 range) and N1923 (a primary aliphatic amine with amino nitrogen linked to a secondary carbon consisting of branched alkyl groups in C19–23 range). Many investigations have been carried out and a number of new processes have been developed using tertiary amines and primary amines to separate uranium and thorium from rare earths in acidic sulphate leach solutions (Li et al., 2004; Amaral and Morais, 2010). Secondary amine compounds may also extract uranium and thorium and separate them from rare earths (Crouch and Brown, 1959). The selectivity of uranium and thorium is significantly poorer with secondary amines than that using tertiary amines. There are other disadvantages such as poor performance resulted from strong association with phosphate and significant adverse effect of alcohol modifier. Therefore, secondary amines have not gained high interest from the industry. As rare earths are also extracted by primary amine from sulphuric acid solutions (El-Yamani and Shabana, 1985; Desouky et al., 2009), high acidity (>1.1 M H₂SO₄) is required to separate thorium from rare earths as shown in Fig. 8 (El-Yamani and Shabana, 1985).

U(VI) was extracted by tertiary amine and quaternary amine salt from high chloride concentration solutions through the reactions shown in Eqs. (7) and (8), respectively (Kojima et al., 1969; Sato, 1972).

\[ xR_2NHCl_{(org)} + UO_{2+} + 2Cl_{(aq)} = (R_2NHCl)_x \cdot UO_2Cl_{2(aq)} \]  
and  

\[ UO_2Cl_{2(aq)} + R_4NCl_{(org)} = R_4NUO_2Cl_{(org)} + Cl_{(aq)} \]  

where x in Eq. (7) is (2) or (3) depending on uranium loading. At around 4 M HCl, uranium extraction could reach high values by tertiary amine or quaternary amine as shown in Figs. 9 and 10, respectively. The extractions of thorium and rare earths by tertiary amines or by quaternary amine salts are much lower due to the lower ability to form complexes with chloride (Hu, 1996; Muthuchamy et al., 2002; Metwally et al., 2005; Belova et al., 2009). Therefore, uranium separation from thorium and rare earth could be achieved in chloride solutions by tertiary amines and quaternary amine salts. Further separation of thorium from rare earths in chloride solutions can be obtained by acidic organophosphorus acid extractants, such as D2EHPA, EHEHPA and Cyanex 272 as mentioned previously. A process to separate uranium by a tertiary amine and separate thorium by EHEHPA from rare earth in chloride leach solutions has been reported (Muthuchamy et al., 2002).

Carboxylic acid extractants, for example naphthenic acid, are usually used for yttrium separation from heavy rare earths in China since the yttrium extraction isotherm by carboxylic acid is located in the light rare earth group (Lu and Ye, 1994; Xu, 1995; Singh et al., 2006). The extraction of rare earths by carboxylic acids occurs usually at pH higher than 4 while that of Th(IV) at lower
than 4 (Ray and Modak, 1981; Singh et al., 2006). Therefore, possible separation of thorium from rare earth can be achieved using solvent extraction with carboxylic acid. Based on this, it has been reported that naphthenic acid was used for the separation of thorium from rare earths (Shao, 1981). Although study on uranium extraction with carboxylic acids was not found, a process has been developed to selectively extract uranium and thorium from rare earth leach solutions using naphthenic acid, indicating that uranium extraction is also stronger than that of rare earths with carboxylic acids (Liu et al., 2013).

5.6. Other extractants

It was reported that other reagents such as Cyanex 302 (Es-Nasab et al., 2011), high molecular crown ethers (Du et al., 1993) could be used for the separation of uranium, thorium and rare earths in different acid solutions. As these reagents have problems such as instability, high cost and non-commercial availability, they are difficult to be used practically.

6. Summary

Large amounts of thorium are commonly associated with rare earth ores. Thorium is rejected into a radioactive solid waste by forming thorium pyrophosphate at high temperature (>500 °C) for processing Bayan Obo ores, the world largest rare earth deposit, using sulphuric acid treatment in China. Selective precipitation of thorium or selective dissolution of rare earths in chloride solutions is also commonly used to separate thorium from rare earths for processing other kinds of rare earth ores. In the pH range of 4–5, thorium is locked in solid precipitates or solid residues while rare earths stay in the solution. Very small amounts of uranium are found in rare earth ores processed in China and no special measures were taken in relation to the uranium control.

Double salt precipitation of rare earths is widely adopted for some new process development. Large amount of thorium co-precipitation but less uranium(VI) co-precipitation is reported. Therefore, double salt precipitation cannot be used to separate rare earths from thorium and uranium(IV), but possibly from uranium(IV). Oxalic acid can be employed to precipitate thorium and rare earths and separate them from uranium in sulphate solutions at high temperatures. Hot sodium carbonate solution can be used to selectively dissolve thorium and to separate it from rare earths.

Solvent extraction is effective to separate uranium and thorium from rare earths. Tertiary amines can be used to selectively extract U(VI) and to separate it from Th(IV) and RE(III) while primary amines are highly selective for Th(IV) extraction over U(VI) and RE(III) in sulphate solutions. TBP can be used to separate U(VI), Th(IV) and RE(III) effectively based on the extraction order of U(VI) > Th(IV) > RE(III). Tertiary amines and quaternary amine salts are effective to extract uranium and separate it from thorium and rare earths in solutions with high HCl concentrations. Organophosphorus acids including D2EHPA and EHEHPA could be used to extract thorium and separate it from rare earths in chloride solutions. Carboxylic acid extractants can be possibly used to separate uranium and thorium from rare earths.

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