



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



Zhaowu Zhu*, Yoko Pranolo, Chu Yong Cheng

CSIRO Mineral Resources Flagship, Australia

ARTICLE INFO

Article history:

Received 29 January 2015

Revised 9 March 2015

Accepted 10 March 2015

Keywords:

Rare earths
Uranium
Thorium
Separation

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. Radioactive 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.

© 2015 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	185
2. Thorium management during rare earth production in China	186
2.1. Processing Bayan Obo rare earth concentrates	186
2.2. Processing Sichuan rare earth concentrates	187
2.3. Processing monazite concentrates	188
3. Uranium and thorium separation in some rare earth practices outside China	188
4. Separation of U and Th from rare earths by precipitation	190
5. Separation of U and Th from rare earths by solvent extraction	191
5.1. Acidic organophosphorus extractants	191
5.2. Neutral organophosphorus extractants	192
5.3. Amide extractants	193
5.4. Amine extractants	193
5.5. Carboxylic acid extractants	193
5.6. Other extractants	194
6. Summary	194
Acknowledgement	194
References	194

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 $(RE)(CO_3)F$, monazite of $(RE)PO_4$ and xenotime of YPO_4 (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,

* Corresponding author.

E-mail address: Zhaowu.zhu@csiro.au (Z. Zhu).

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 ThO_2 and U_3O_8 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 beneficiation used for rare earth production usually contain about 50–60% REO, 0.18–0.3% ThO_2 and <0.001% U_3O_8 (Wang and Tang, 2007). At present, about 90% of Bayan Obo rare earth concentrates are digested with H_2SO_4 at >500 °C (enhanced H_2SO_4 digestion). Its conceptual flowsheet is shown in Fig. 1 (Huang et al., 2006; Wang and Wang, 2006; Du et al., 2010).

Table 1
Uranium and thorium content in rare earth minerals (based on Jordens et al., 2013).

Minerals	Chemical formula	Weight percentage (%)		
		REO	ThO_2	UO_2
Bastnasite	(Ce,La)(CO_3)F (La, Ce)(CO_3)F Y(CO_3)F	70–74	0–0.3	0.09
Monazite	(Ce,La,Nd,Th) PO_4 (La,Ce,Nd,Th) PO_4 (Nd,Ce,La,Th) PO_4	35–71	0–20	0–16
Xenotime-Y	YPO_4	52–67	–	0–5

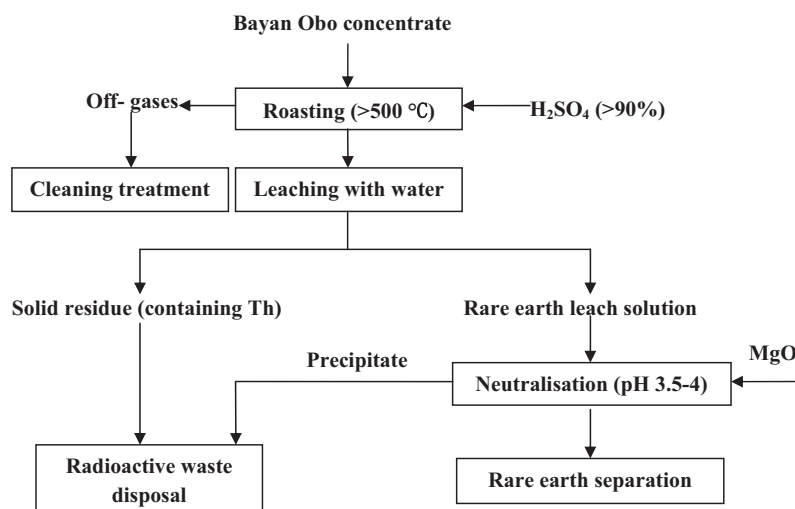
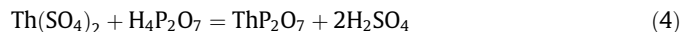
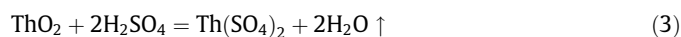
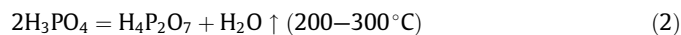
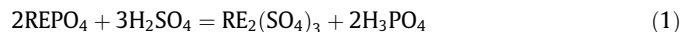


Fig. 1. Thorium separation during the rare earth production from Bayan Obo concentrates using enhanced H_2SO_4 digestion.

Under the high temperature, phosphate reacts with H_2SO_4 to form H_3PO_4 which then dehydrates to pyrophosphoric acid. Thorium oxide reacts with H_2SO_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 H_2SO_4 are expressed in Eqs. (1)–(4).



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_3O_8 (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).

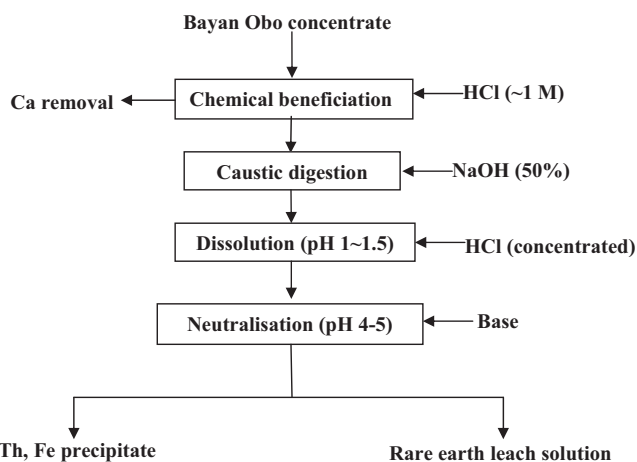


Fig. 2. Separation of thorium from rare earths during processing Bayan Obo concentrates using caustic digestion.

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).

Method	Distribution (%)			
	Waste residue	Waste water	Off-gas	Rare earth product
Enhanced acid	96	2–3	1	<0.02
Alkaline	95–96	4–5	0	0.02

Table 3
Distribution of thorium in wastes produced during processing Bayan Obo rare earth concentrates (based on Bai et al., 2001).

Method	Waste solid			Waste liquid			Waste gas
	Output (kg/t ore)	Th (%)	Treatment	Output (t/t ore)	Th (g/t)	Treatment	Treatment
Acid	650	0.3	Storage	12 (average)	0.1–1 (average)	Discharge	Rinsing with water
Alkaline	150	0.5	To acid process	12	0.1–1	Discharge	No off-gas

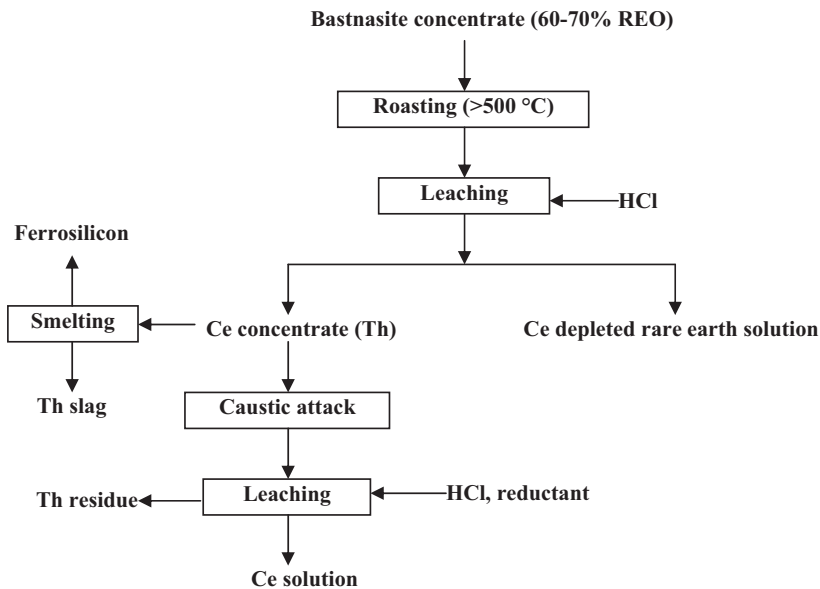


Fig. 3. Thorium separation in rare earth production from bastnasite concentrates.

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). Currently, the exploitation of the deposit containing only monazite minerals is prohibited in China due to high pollution resulting from the high thorium content (Su, 2014). However, some monazites are processed in China as a by product, particularly from zircon and titanium processing. The processes used are typical alkaline method similar to that used for processing Bayan Obo concentrates in Fig. 2. Since phosphorus content is high and no or trace fluorite

is present in the monazite concentrates, phosphorus is usually recovered as a by product of sodium phosphate. Both uranium and thorium are rejected to a solid residue after selective dissolution of rare earths by HCl. As mentioned previously, this residue still contains significant amount of rare earths. In the very early stage from 1950s to 1970s of rare earth industry in China, uranium, thorium and rare earths were recovered from these kinds of residues after dissolving in HNO₃ solution followed by solvent extraction with TBP (tri-n-butylphosphate). The extraction and separation of uranium, thorium and rare earths in HNO₃ solution with TBP will be discussed in the subsequent section. At present, all residues containing thorium are stored as radioactive wastes without further processing (Yu and Zhang, 1982; Su, 2014).

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 concentrate as shown 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

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 (Bleiwass 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 Always 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% U₃O₈ 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

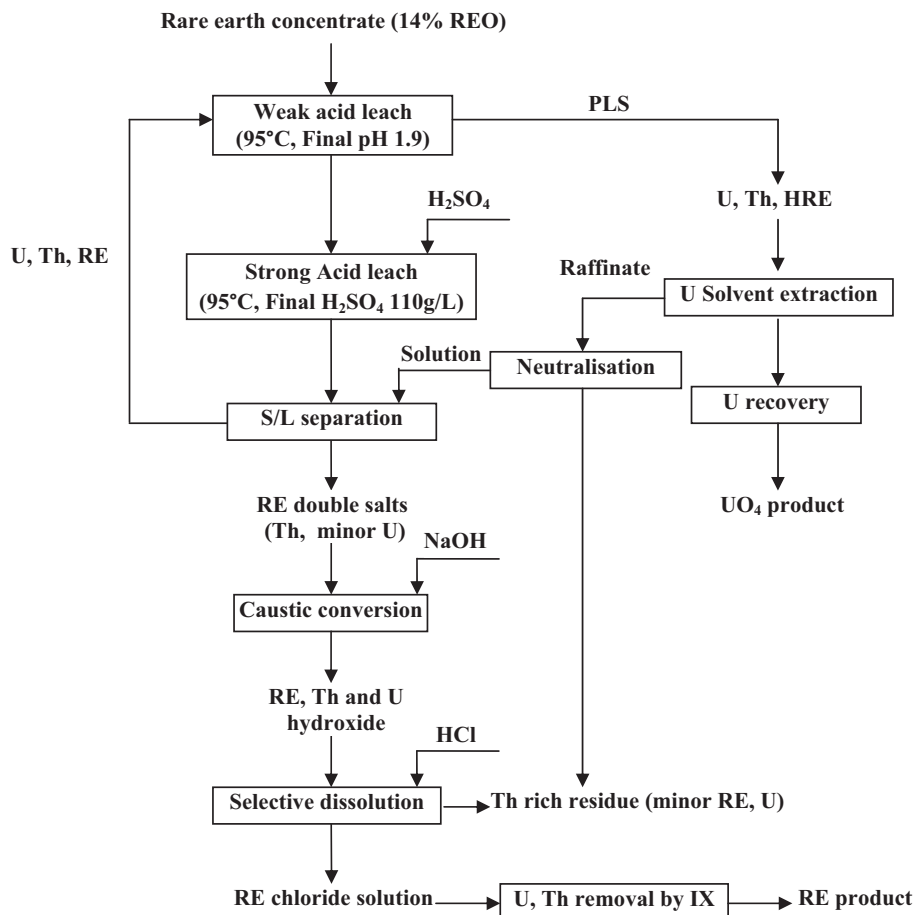


Fig. 4. A schematic flowsheet for processing Kvanefjeld rare earth concentrate (HRE denotes heavy rare earth; PLS denotes pregnant leach solution) (based on Furfaro and Krebs, 2014).

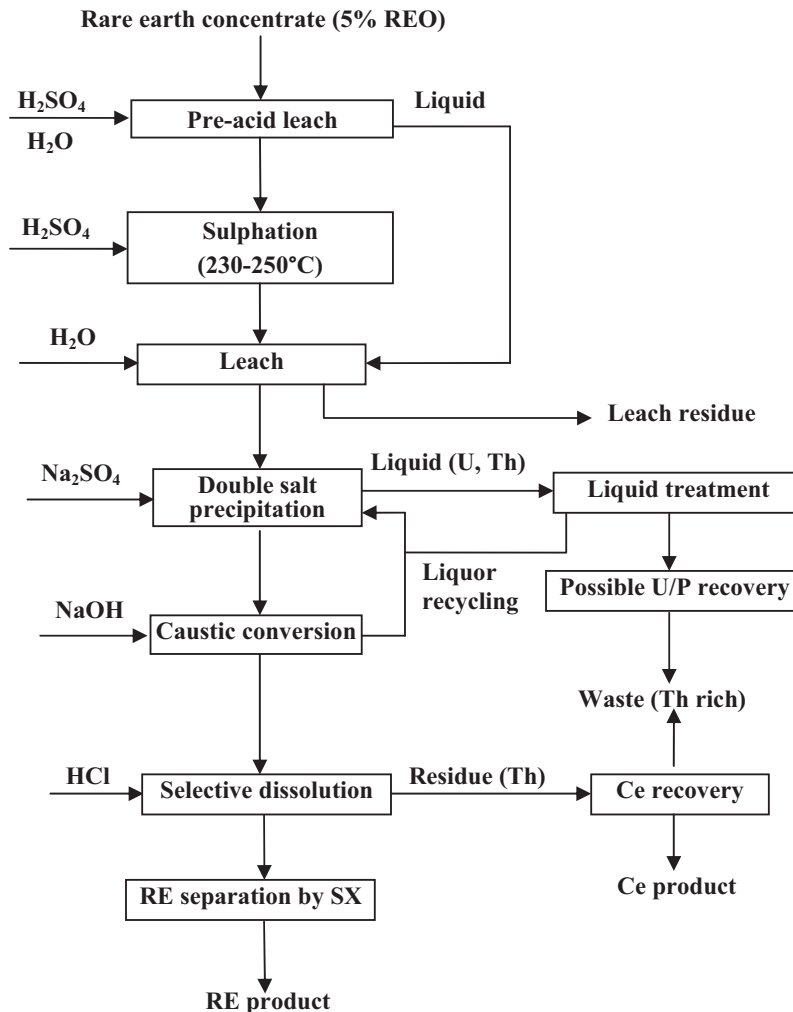


Fig. 5. A schematic flowsheet for processing Nolans rare earth concentrate (based on Ganser et al., 2014; Lockyer, 2014).

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% U_3O_8 and 0.27% ThO_2 . After ore beneficiation, 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 a sulphate leach solution by selective precipitation using MgO for pH adjustment. Uranium separation from rare earths in the sulphate solution is achieved by IX. No detailed test work has been reported for uranium recovery in the process. Most recently, a very different process is under investigation in Arafura with the conceptual flowsheet shown in Fig. 5 (Ganser et al., 2014; Lockyer, 2014). In the process, uranium is principally separated from rare earths during rare earth double salt precipitation as it maintains in the solution. Part of thorium is rejected to the leach liquor together with uranium and eventually is precipitated as a solid waste. A portion of thorium is rejected to rare earth double salts will be separated by the selective

dissolution with HCl just as the same as used in monazite treatment mentioned in Section 2.3. This process is in a very preliminary stage and no detailed test results are available currently.

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 $\beta-UO_2(OH)_2$ 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

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

RE solution	Solution generated	Reagent used	Final pH	Precipitation (%)			References
				U	Th	RE	
20 g/L RE chloride, U, Th unknown	Complex deposit by caustic digestion, and dissolution by HCl	NaOH	5.5	50	~100	2.2	Pawlik (2013)
22 g/L RE sulphate, U, Th unknown	Complex deposit by H ₂ SO ₄ digestion, and water leaching	Lime	5.5	–	~100	80%	Pawlik (2013)
50 g/L RE sulphate, 0.1 g/L Th	Bayan Obo concentrate by H ₂ SO ₄ digestion, and water leaching	MgO	4	–	98	0.4	Zhu et al. (2006)
RE chloride	Monazite, by caustic digestion, and dissolution by HCl	NaOH	5.8	99.3	99.7	2.3	Xu (1995)
10 g/L RE chloride, 0.05 g/L Th, 0.0007 g/L U	Rare earth double salt by caustic digesting, and dissolution by HCl	Lime	4.8	71.4	100	<1%	Krebs and Furfaro (2013)
7.25 g/L RE sulphate, 0.3 g/L Th	Xenotime by H ₂ SO ₄ digestion and water leaching	NH ₃	1.5	–	95	5.8	Vijayalakshmi et al. (2001)

rare earth co-precipitation. In sulphate media, large amounts of phosphate are often present in leach solutions because phosphate is commonly associated with rare earths ores. As a result, the precipitation pH of thorium, uranium and rare earths will shift to lower values due to the formation of metal phosphates which are less soluble (Sandino and Run, 1992; Fourest et al., 1999). Therefore, the precipitation of thorium and co-precipitation of rare earths with pH variation in sulphate medium has been found to be quite variable by different investigations, probably due to differing amounts of phosphate in the solutions as shown in Table 4.

Sulphate double-salt precipitation was widely used in the past in the USA and China to recover trivalent rare earths and separate them from impurities. Some new processes still tend to use this method (Kul et al., 2008; Abreu and Morais, 2010; Furfaro and Krebs, 2014; Ganser et al., 2014; Lockyer, 2014). Trivalent rare earths precipitate as double salts with single valence ions such as NH₄⁺, Na⁺ and K⁺ in sulphate solutions at high acidity based on Eq. (5) (Abreu and Morais, 2010).

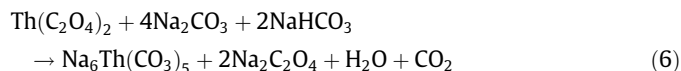


Rare earth double salt precipitation was mainly used for the separation of trivalent rare earths from tetravalent cerium in the early rare earth industry in China (Xu, 1995). Since cerium usually accounts for about half of total rare earths, oxidation of cerium to Ce(IV) and separating it from other rare earths can significantly simplify the overall process and lower the cost. Although thorium does not form double salt with sodium and sulphate, considerable amounts of thorium can also be co-precipitated with rare earth double salts. Kul et al. (2008) reported that 25–30% of thorium was co-precipitated during rare earth double salt precipitation from a bastnasite leach solution containing about 20 g/L RE and 0.3 g/L Th using sodium sulphate. Xu (1995) reported that thorium co-precipitation even reached around 87% during rare earth double salt precipitation as shown in Table 5.

Uranium, if present as U(VI), is less co-precipitated than Th(IV) due to the large difference between UO₂²⁺ and RE³⁺ ions. In the recently developed process for Nolans rare earth concentrate, uranium was essentially separated from rare earths during double salt precipitation (Ganser et al., 2014; Lockyer, 2014). However, if

uranium was present as U(IV), its co-precipitation was very high. For example, it reached 34–97% when 72–99% of Ce(III) was precipitated as double salts (Wyllie, 1947).

A process has been suggested by Amer et al. (2013) to separate uranium, thorium and rare earths using oxalate precipitation for processing a monazite concentrate. In a sulphate solution containing 0.147 g/L U, 2.51 g/L Th and 23.93 g/L RE, 98% of thorium and 99% of rare earths were precipitated at pH 0.7 and 60 °C, respectively, while uranium remained in the solution. Thorium oxalate precipitate was subsequently selectively dissolved in a solution containing 150 g/L Na₂CO₃ and NaHCO₃ in a ratio of 3:1 at 75 °C. It was proved that thorium could form a soluble complex with carbonate via the reaction shown in Eq. (6) (Amer et al., 2013).



Zhang (1982) developed a process to remove thorium from the rare earth carbonate obtained from a sulphate leach solution of Baotou rare earth ore. Using 224 g/L Na₂CO₃ at room temperature (20 °C) to wash the rare earth carbonate, 98% of thorium was redissolved into the solution with ThO₂/REO ratio in the precipitate decreasing from 0.04% to 0.007%. The rare earth loss was less than 3%. This again demonstrates that the separation of thorium from rare earths can be effectively achieved using Na₂CO₃.

5. Separation of U and Th from rare earths by solvent extraction

5.1. Acidic organophosphorus extractants

Solvent extraction is widely used in rare earth separations (Brown and Sherrington, 1979). Di-(2-ethylhexyl) phosphoric acid (D2EHPA, Chinese brand P204) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (EHEHPA, Chinese brand P507) are commonly used extractants which extract heavier rare earths more strongly than lighter ones (Sato, 1989; Zhu, 1991; Yan et al., 2006). D2EHPA can extract rare earths at very low pH and is commonly used for the separation of light rare earths from medium and heavy ones between Nd and Sm, and it is also used to transfer rare earths from sulphate solutions to chloride solutions for further separation in China (Huang et al., 2006; Li et al., 2007). EHEHPA has been commonly used for the separation of adjacent rare earths in chloride solutions to obtain individual rare earth products (Yan et al., 2006). Both D2EHPA and EHEHPA strongly extract U (VI) and Th(IV) even in highly acidic solutions (Sato, 1962; Sato, 1968; Haggag et al., 1976). In moderately acidic solutions, for example, less than 5 M, metal extraction by D2EHPA and EHEHPA is via an ionic exchange mechanism (Sato, 1962, 1968, 1989), and the extraction of U(VI) and Th(IV) is stronger than that of RE(III) (Xu, 1995; Gupta and Singh, 2003; Zamani and Yaftian,

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

	REO	ThO ₂	Fe	P ₂ O ₅	[H ⁺] (mol/L)
Leach solution (g/L)	35	0.15	21	10	1.5
Double salt (%)	42–45	0.1–0.2	0.2	0.3	
Filtrate (g/L)	0.1	0.02–0.04	21–22	11	1.5
Recovery (%)	99.7	73.3–86.6	100	100	

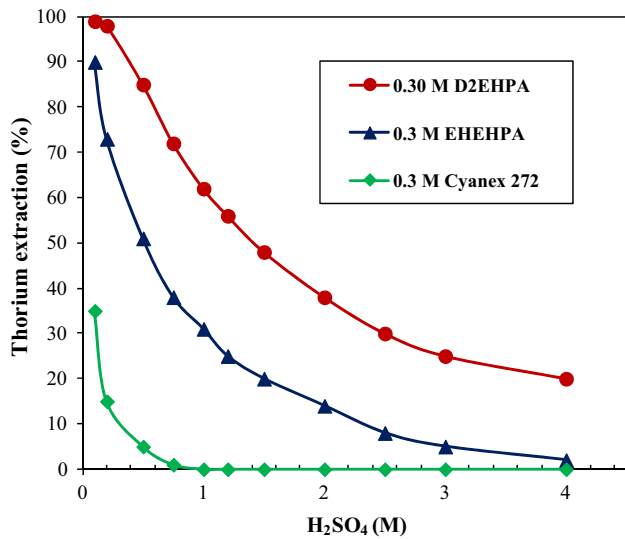


Fig. 6. Thorium extraction with different acidic organophosphorus extractants in H₂SO₄ solutions containing 0.044 M Th at room temperature (based on Tong et al., 2013).

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

2004). 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

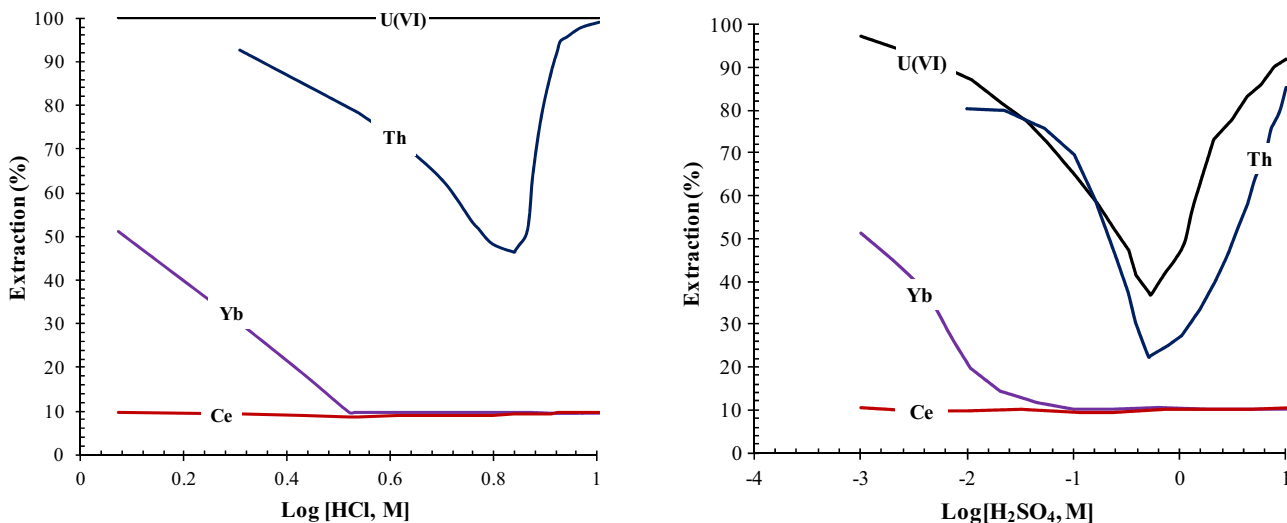


Fig. 7. Metal extraction with Cyanex 923 in toluene from HCl and H₂SO₄ solutions ([Metal ion] = 0.0001 M, [Cyanex 923] = 0.10 M) (based on Gupta et al., 2002).

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.

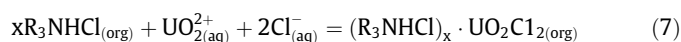
5.3. Amide extractants

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.

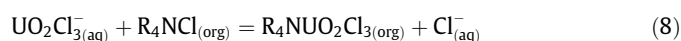
5.4. Amine extractants

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 reagents 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 (Crouse 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).



and



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

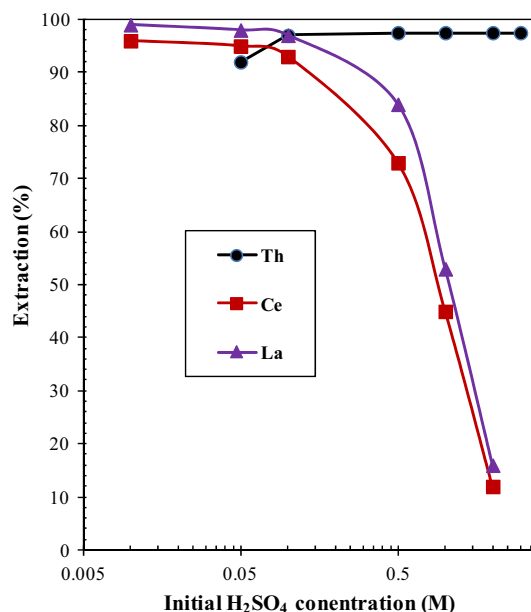


Fig. 8. Extraction of thorium and rare earths with 0.05 M Primene JMT in kerosene (initial metal concentrations: $\sim 10^{-6}$ M) (based on El-Yamani and Shabana, 1985).

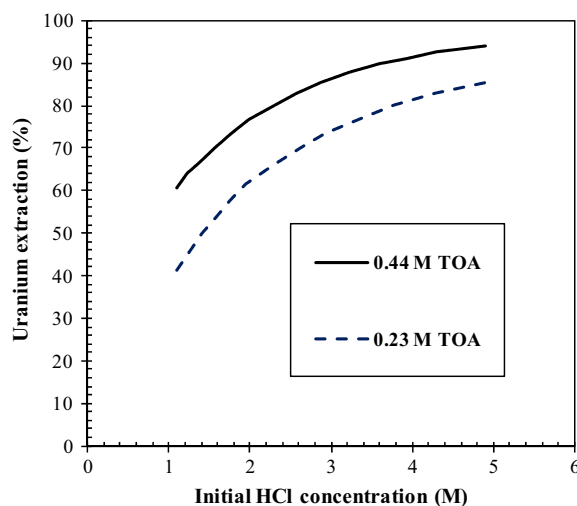


Fig. 9. Uranium(VI) extraction from hydrochloric acid solutions containing 0.5 g/L U by tri-n-octylamine (TOA) in benzene (based on Kojima et al., 1969).

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).

5.5. Carboxylic acid extractants

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

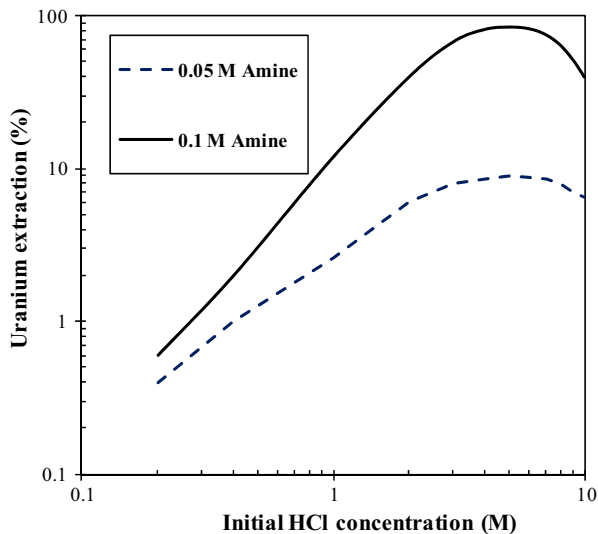


Fig. 10. Uranium(VI) extraction from hydrochloric acid solutions containing 5 g/L U by tricaprylmonomethylammonium chloride in benzene (based on Sato, 1972).

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.

Acknowledgement

The authors would like to thank Dr. Keith Barnard for reviewing this paper and providing valuable comments. The support of Mineral Resource Flagship is gratefully acknowledged.

References

- Abreu, R.D., Morais, Carlos A., 2010. Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide. *Miner. Eng.* 23, 536–540.
- Amaral, J.C.B.S., Morais, C.A., 2010. Thorium and uranium extraction from rare earth elements in monazite sulphuric acid liquor through solvent extraction. *Miner. Eng.* 23, 498–503.
- Amer, T.E., Abdella, W.M., Wahab, G.M.A., El-Sheikh, E.M., 2013. A suggested alternative procedure for processing of monazite mineral concentrate. *Int. J. Miner. Process.* 125, 106–111.
- Anon, 2010. Radiological impact assessment of advanced materials plant Gebeng industrial estate Kuantan, Pahang. <<http://www.loyarburok.com>>.
- Anon, 2012. Rare earth elements: a review of production, processing, recycling, and associated environmental issues. EPA/600/R-12/572, United States Environmental Protection Agency.
- Bai, L., Zhang, L., Wang, L., 2001. Radiation pollution and control measures during processing Baotou rare earth ores. *Chin. Rare Earth* 22 (1), 76–78 (in Chinese).
- Belova, V.V., Voshkin, A.A., Kholkin, A.I., Payrtman, A.K., 2009. Solvent extraction of some lanthanides from chloride and nitrate solutions by binary extractants. *Hydrometallurgy* 97, 198–203.
- Belova, V.V., Voshkin, A.A., Egorova, N.S., Kholkin, A.I., 2010. Extraction of rare earth metals from nitrate solutions with a binary extractant based on Cyanex 272. *Russ. J. Inorg. Chem.* 55 (4), 629–633.
- Binnemans, K., Jones, P.T., Blanpain, B., Gerven, T.V., Yang, Y., Walton, A., Buchert, M., 2013. Recycling of rare earths: a critical review. *J. Clean. Prod.* 51, 1–22.
- Bleivas, D.I., Gambogi, J., 2013. Preliminary estimates of the quantities of rare-earth elements contained in selected products and in imports of semimanufactured products to the United States, 2010, U.S. Geological Survey Open-File Report 2013-1072, p. 14. <<http://pubs.usgs.gov>>.
- Brown, C.G., Sherrington, L.G., 1979. Solvent extraction used in separation of industrial rare earths. *J. Chem. Technol. Biotechnol.* 29, 193–209.
- Chakhmouradian, A.R., Wall, F., 2012. Rare earth elements: minerals, mines, magnets (and more). *Elements* 8, 333–340.
- Cheng, J., Hou, Y., 2007. Comprehensive exploitation of Bayan Obo rare earth resources. In: Proceedings of the conference for Chinese rare earth comprehensive exploitation and environment protection. 6–10 June, Haikou, Hainan China, 22–40 (in Chinese).
- Cheng, J., Che, L., 2010. Current mining situation and potential development of rare earth in China. *Chin. Rare Earth* 31 (2), 65–69 (in Chinese).
- Crouse, D.J., Brown, K.B., 1959. Recovery of thorium, uranium and rare earths from monazite liquors by the amine extraction (AMEX) process. Report of Oak Ridge National Laboratory, ORNL-2720, USA.
- Desouky, O.A., Daher, A.M., Abdel-Monem, Y.K., Galhoum, A.A., 2009. Liquid-liquid extraction of yttrium using primene-JMT from acidic sulfate solutions. *Hydrometallurgy* 96, 313–317.
- Dinkar, A.K., Singh, S.K., Tripathi, S.C., Verma, R., Reddy, A.V.R., 2012. Studies on the separation and recovery of thorium from nitric acid medium using (2-ethyl hexyl) phosphonic acid, mono (2-ethyl hexyl) ester (PC88A)/n-dodecane as extractant system. *Sep. Sci. Technol.* 47, 1748–1753.
- Du, C., Li, M., Liu, S., Chang, H., Hu, Y., 2010. Present situation and suggestions for treatment of Baotou's rare earth concentrate. *Hydrometall. China* 29 (1), 1–4 (in Chinese).
- Du, H.S., Wood, D.J., Elshani, S., Wai, C.M., 1993. Separation of thorium from lanthanides by solvent extraction with ionizable crown ethers. *Talanta* 40 (2), 173–177.

- El-Hefny, N.E., El-Nadi, Y.A., Daoud, J.A., 2010. Equilibrium and mechanism of samarium extraction from chloride medium using sodium salt of CYANEX 272. *Sep. Purif. Technol.* 75, 310–315.
- EL-Yamani, I.S., Shabana, E.I., 1985. Solvent extraction of lanthanum(III) from sulphuric acid solutions by primene JMT. *J. Less-Common Metal* 105, 255–261.
- Es-Nasab, M., Milani, S.A., Sam, A., 2011. Extractive separation of Th(IV), U(VI), Ti(IV), La(III) and Fe(III) from zarigan ore. *J. Radioanal. Nucl. Chem.* 288, 677–683.
- Fourest, B., rard Lagarde, G., Perrone, J., Brandel, V., Dacheux, N., Genet, M., 1999. Solubility of thorium phosphate-diphosphate. *New J. Chem.* 23, 645–649.
- Furfaro, D., Krebs, D.G.I., 2014. Continuous leaching of Kvanefjeld concentrate. ALTA 2014 Uranium-Rare earth conference, May 24–31, Perth, Australia.
- Ganser, J., Napier, A., Kyle, J., White, D., Jayasekera, S., 2014. The Nolans rare earth project-an update. ALTA 2014 Uranium-Rare earth conference, May 24–31, Perth, Australia.
- Gupta, C.K., Malik, B.P., Deep, A., 2002. Extraction of uranium, thorium and lanthanides using Cyanex-923: their separations and recovery from monazite. *J. Radioanal. Nucl. Chem.* 251 (3), 451–456.
- Gupta, C.K., Singh, H., 2003. Uranium Resource Processing: Secondary Resource, Heidelberg 2003. Springer-Verlag Berlin, Germany.
- Gupta, C.K., Krishnamurthy, N., 2005. Extractive Metallurgy of Rare Earths. CRC Press.
- Haggag, A., EL-Fekey, S.A., Yehia, M.E.M., Sanad, W., 1976. Solvent extraction studies on thorium sulphate and halides. *J. Radioanal. Chem.* 33, 139–152.
- Haque, N., Hughes, A., Lim, S., Vernon, C., 2014. Rare earth elements: overview of mining, mineralogy, uses, sustainability and environmental impact. *Resources* 3, 614–635.
- Haxel, G.B., 2005. Ultrapotassic mafic dikes and rare earth element- and barium-rich carbonatite at mountain pass, Mojave desert, Southern California: summary and field trip localities. USGS Report-2005-1219, <<http://pubs.usgs.gov>>.
- Hu, H., 1996. Study of extraction of uranium with tertiary amine for the separation from Th and rare earths. *Rare Metal Cem. Carbides* 124, 4–7 (in Chinese).
- Huang, X., Li, H., Xue, X., Zhang, G., 2006. Development status and research progress in rare earth hydrometallurgy in China. *J. Chin. Rare Earth Soc.* 24 (2), 130–133 (in Chinese).
- Huang, X., Zhang, Y., Li, H., 2011. Status and trend of development of exploitation and usage of rare earth resources in China. *Chin. Acad. Fund* 3, 134–137 (in Chinese).
- Jia, Y., Zhang, X., Bai, B., Guo, Y., 2002. Differences of Sichuan rare earth concentrate from Baotou rare earth concentrate in processing ferrosilicon. *Chin. Rare Earth* 23 (1), 24–26 (in Chinese).
- Jordens, A., Cheng, Y.P., Waters, K.E., 2013. A review of the beneficiation of rare earth element bearing minerals. *Miner. Eng.* 41, 97–114.
- Kanazawa, Y., Kamitani, M., 2005. Rare earth minerals and resources in the world. *J. Alloy. Compd.* 408–412, 1339–1343.
- Kang, M.J., Han, B.E., Hahn, S., 2002. Precipitation and adsorption of U(VI) under various conditions. *Environ. Eng. Res.* 7 (3), 149–157.
- Kojima, T., Fukutomi, H., Kakiana, H., 1969. Extraction of uranium (VI) from hydrochloric acid solution by tri-n-octylamine in benzene. *J. Nucl. Sci. Technol.* 6 (2), 81–89.
- Krebs, D.G.I., Furfaro, D., 2013. The Kvanefjeld process. In: ALTA 2013 Uranium-REE Conference. May 25–June 1, Perth, Western Australia.
- Kul, M., Topkaya, Y., Karakaya, I., 2008. Rare earth double sulfates from pre-concentrated bastnasite. *Hydrometallurgy* 93, 129–135.
- Lang, X., Yu, X., 2009. The latest development of Chinese mixed rare earth concentrate processing. *Rare Metal Cem. Carbides* 37 (3), 43–47 (in Chinese).
- Lee, B., 2012. Rare earth and radioactive waste – a preliminary waste stream assessment of the Lynas advanced materials plant, Gebeng, Malaysia. Lynas Quarterly Report September 30, 2011. National Toxic Network, 2012. <<http://www.ntn.org.au>>.
- Li, D., Zuo, Y., Meng, S., 2004. Separation of thorium(IV) and extracting rare earths from sulfuric and phosphoric acid solutions by solvent extraction method. *J. Alloy. Compd.* 374, 431–433.
- Li, J., Huang, X., Zhu, Z., Long, Z., Peng, X., Cui, D., 2007. Extracting rare earth by D₂EHPA-HEHEHP-H₂SO₄ system. *J. Chin. Rare Earth Soc.* 25 (1), 55–58 (in Chinese).
- Liu, H., Ao, B., Luo, X., 2009. Development status and research progress in rare earth hydrometallurgy for Sichuan bastnasite. *China Nonferr. Metall.* 2009, 33–37 (in Chinese).
- Liu, J., Luo, M., Ping, A., Jiang, X., Yuan, Z., 2012. Progress in extraction technology of thorium from rare earth concentrate. *Chin. J. Rare Metal* 36 (4), 651–658 (in Chinese).
- Liu, Z., Qiu, X., Zhu, W., Guo, Q., 2013. A method to extract uranium and thorium from the rare earth leach solution of ionic type of rare earths ore from southern Chinese. Chinese patent, CN 102943183A (in Chinese).
- Lockyer, G., 2014. Bridging the rare earths gap. In: Rare Earths North America 2014 Conference, June 11, 2014, New York City, USA.
- Long, K.R., Gosen, B.S.V., Foley, N.K., Cordier, D., 2010. The principal rare earth elements eeposits of the United States – a summary of domestic deposits and a global perspective. Scientific Investigations Report 2010–5220. U.S. Geological Survey.
- Lu, Y., Ye, Z., 1994. New technology for rare earth extraction by naphthenic acid. *Chin. Rare Earth* 15 (1), 14–16 (in Chinese).
- Lu, J., Wei, Z., Li, D., Ma, G., Jiang, Z., 1998. Recovery of Ce(IV) and Th(IV) from rare earths (III) with Cyanex 923. *Hydrometallurgy* 50, 77–87.
- Menzies, I.A., Rigby, F., 1961. Separation of thorium from uranium and rare-earth elements by solvent extraction with tri-n-butylphosphate-xylene. *J. Appl. Chem.* 11, 104–113.
- Metwally, E., Saleh, A.S., El-Naggar, H.A., 2005. Extraction and separation of uranium (VI) and thorium (IV) using tri-n-dodecylamine impregnated resins. *J. Nucl. Radiochem. Sci.* 6 (2), 119–126.
- Muthuchamy, S., Nair, V.R., Matharana, L.N., 2002. Application of solvent extraction technique for the separation of rare earths, thorium and uranium. In: Proceedings of International Symposium on Solvent Extraction. September 26–27, Bhubaneswar, India.
- Nagaosa, Y., Binghua, Y., 1997. Solvent extraction of rare-earth metals with bis(2-ethylhexyl)phosphinic acid. *Fresenius' J. Anal. Chem.* 357, 635–641.
- Pawlik, C., 2013. Recovery of rare earth elements from complex and low grade deposits. ALTA 2013 Uranium-REE Conference. May 25–June 1, Perth, Western Australia.
- Preston, J.S., du Preez, A.C., 1995. Solvent extraction of uranium(VI) and thorium(IV) from nitrate media by carboxylic acid amides. *Solvent Extr. Ion Exch.* 13 (3), 391–413.
- Ray, U.S., Modak, S.C., 1981. Solvent extraction of thorium with Versatic 911. *Sep. Sci. Technol.* 16 (1), 87–96.
- Ritcey, G.M., 2006. Solvent extraction-Principles and applications to process metallurgy, Uranium. Vol. 2, G.M. Ritcey & Associates Incorporated, Ottawa, Canada (Chapter 3.25).
- Sandino, A., Run, J., 1992. The solubility of (UO₂)₃(PO₄)₂·4H₂O (S) and the formation of U(VI) phosphate complexes: their influence in uranium speciation in natural waters. *Geochim. Cosmochim. Acta* 56, 4135–4145.
- Sato, T., 1962. The extraction of uranium (VI) from sulphuric acid solutions by di-(2-ethylhexyl)-phosphoric acid. *J. Inorg. Nucl. Chem.* 24, 699–706.
- Sato, T., 1966. Extraction of uranium (VI) and thorium from hydrochloric acid solutions by tri-n-butyl phosphate. *J. Appl. Chem.* 16, 53–57.
- Sato, T., 1968. The extraction of thorium from hydrochloric acid solutions by di-(2-Ethylhexyl)-phosphoric acid. *Z. Anorg. Allg. Chem.* 19 (8), 296–304, 358.
- Sato, T., 1972. The extraction of uranium(VI) of from hydrochloric acid solutions by long-chain alkyl quaternary ammonium. *J. Inorg. Nucl. Chem.* 34, 3835–3843.
- Sato, T., 1989. Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. *Hydrometallurgy* 22, 121–140.
- Schuler, D., Buchert, M., Liu, R., Dittrich, S., Merz, C., 2011. Study on rare earths and their recycling. Report for The Green/ERF Group in the European Parliament. Öko-Institut e.V. Freiburg, Germany. <<http://www.oeko.de>>.
- Shao, Y., 1981. Leaching and separation with solvent extraction and ion exchange of thorium and rare earths. *China Nonferr. Metall.* 11, 46–49 (in Chinese).
- Singh, D.K., Singh, H., Mathur, J.N., 2006. Extraction of rare earths and yttrium with high molecular weight carboxylic acids. *Hydrometallurgy* 81, 174–181.
- Soldenhoff, K., 2013. Challenge in rare earth processing. In: ALTA 2013 Uranium-REE Conference. May 25–June 1, Perth, Western Australia.
- Su, Z., 2014. Research status on the comprehensive exploration of monazite resources. *World Nonferr. Metal* 8, 31–33.
- Tong, H., Wang, Y., Liao, W., Li, D., 2013. Synergistic extraction of Ce(IV) and Th(IV) with mixtures of Cyanex 923 and organophosphorus acids in sulfuric acid media. *Sep. Purif. Technol.* 118, 487–491.
- Vijayalakshmi, R., Mishra, S.L., Singh, H., Gupta, C.K., 2001. Processing of xenotime concentrate by sulphuric acid digestion and selective thorium precipitation for separation of rare earths. *Hydrometallurgy* 61, 75–80.
- Wang, G., 2006. Suggestion to reduce the environment pollution during rare earth mining, beneficiation and metallurgy in China. *Sichuan Rare Earth* 3, 2–8 (in Chinese).
- Wang, G. and Tang, J., 2007. Pollution and suggestions for controlling measurement of the three types of waste in rare earth production. In: Proceedings of the Conference for Chinese Rare Earth Comprehensive Exploitation and Environment Protection. June 6–10, Haikou, Hainan China, 147–153 (in Chinese).
- Wang, J., Fan, Y., Zhou, L., 1999a. Study on the technologic conditions for rare earth chloride production using alkaline method. *Inner Mong. Petrochem. Ind.* 25 (3), 15–17 (In Chinese).
- Wang, J., Wang, X., 2006. Comprehensive exploitation and cleaning production technology of Bayan Obo rare earth ore. *Chin. Rare Earth* 27 (1), 103–105 (in Chinese).
- Wang, M., Zeng, M., Wang, L., Zhou, J., Cui, D., Wang, Q., Weng, R., Chen, X., 2013. Catalytic leaching process of bastnasite with hydrochloric acid after oxidation roasting pretreatment. *J. Rare Earths* 23 (2), 148–154 (in Chinese).
- Wang, Z., Li, J., Yu, C., 1999b. Performance of extractant Cyanex 272 and Cyanex 274 for separating rare earths. *Chin. Rare Earth* 20, 15–18 (in Chinese).
- Wylie, A.W., 1947. Coprecipitation of uranium sulphate with rare-earth double sulphates. *Nature* 160, 830.
- Xie, F., Zhang, T.A., Dreisinger, D., Doyle, F., 2014. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* 56, 10–28.
- Xiong, Y., Wang, X., Li, D., 2005. Synergistic extraction and separation of heavy lanthanide by mixtures of Bis(2,4,4-trimethylpentyl)phosphinic acid and 2-ethylhexyl phosphinic acid mono-2-ethylhexyl ester. *Sep. Sci. Technol.* 40, 2325–2336.
- Xu, G., 1995. Rare earths, second ed. Metallurgical Industry Press, Beijing, China (in Chinese).
- Yan, C.H., Jia, J.T., Liao, C.S., Wu, S., Xu, G.X., 2006. Rare earth separation in China. *Tsinghua Sci. Technol.* 11 (2), 241–247.

- Yu, X., Zhang, B., 1982. The status and prospect of comprehensive exploitation of Hunan monazite resources. *Chin. Rare Earth* 04, 53–57 (in Chinese).
- Zamani, A.A., Yafian, M.R., 2004. Solvent extraction of thorium, lanthanum and europium ions by bis(2-ethylhexyl)phosphoric acid using 2-nitrobenzo-18-crown-6 as ion size selective masking agent. *Sep. Purif. Technol.* 40, 115–121.
- Zhang, C., 1982. Mixed rare earth production from Baotou rare earth ore by roasting with concentrated sulphuric acid and thorium removal from carbonate precipitate. *Chin. Rare Earth* 01, 27–32 (in Chinese).
- Zhang, G., Huang, X., 1997. Review on metallurgical technology for bastnasite. *Chin. J. Rare Metal* 21 (3), 195–199 (in Chinese).
- Zhang, Y., Hu, F., Huang, X., Long, Z., Cui, D., Xu, Y., 2010. Stripping behaviour of thorium from HEH/EHP. *J. Chin. Rare Earth Soc.* 28 (6), 660–664 (in Chinese).
- Zhou, D., 1992. Extraction-separation process for U, Fe, Th and rare earth elements in monazite. *J. Guang Dong Non-ferr. Metal* 2 (1), 16–22 (in Chinese).
- Zhu, T., 1991. Solvent extraction in China. *Hydrometallurgy* 27, 231–245.
- Zhu, Z., Han, Y., Luo, X., Long, Z., Huang, X., 2006. Enrichment and recovery of thorium from Baotou rare earth concentrate. In: *Proceedings of 5th Academic Conference for Chinese Rare Metals*, 18–19 November, Hunan Changsha, China (in Chinese).
- Zhu, Z., Cheng, C.Y., 2011. A review of uranium solvent extraction: its present status and future trends. *ALTA 2011 Uranium Conference*, May 26–27. Burswood Convention Centre, Perth, Australia.