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# 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. 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.

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### Contents

1.	Introduction				
2.	. Thorium management during rare earth production in China				
	2.1.	Processing Bayan Obo rare earth concentrates	186		
	2.2.	Processing Sichuan rare earth concentrates	187		
	2.3.	Processing monazite concentrates	188		
3.	Urani	ium and thorium separation in some rare earth practices outside China	188		
4.	Separ	ration of U and Th from rare earths by precipitation	190		
5.	Separation of U and Th from rare earths by solvent extraction				
	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		nary	194		
	Acknowledgement				
	References				

#### 1. Introduction

Recently, the demand for rare earths has increased significantly, driving the development of new processes to recover rare earths

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http://dx.doi.org/10.1016/j.mineng.2015.03.012 0892-6875/© 2015 Elsevier Ltd. All rights reserved. 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<sub>3</sub>)F, monazite of (RE)PO<sub>4</sub> and xenotime of YPO<sub>4</sub> (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 ThO<sub>2</sub> 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

#### Table 1

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

Minerals	Chemical formula	Weight percentage (%)		
		REO	ThO <sub>2</sub>	UO <sub>2</sub>
Bastnasite	(Ce,La)(CO <sub>3</sub> )F (La, Ce)(CO <sub>3</sub> )F Y(CO <sub>3</sub> )F	70-74	0-0.3	0.09
Monazite	(Ce,La,Nd,Th)PO4 (La,Ce,Nd,Th)PO4 (Nd,Ce,La,Th)PO4	35-71	0–20	0-16
Xenotime-Y	YPO <sub>4</sub>	52-67	-	0–5

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 ionadsorption 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<sub>2</sub> and <0.001% U<sub>3</sub>O<sub>8</sub> (Wang and Tang, 2007). At present, about 90% of Bayan Obo rare earth concentrates are digested with H<sub>2</sub>SO<sub>4</sub> at >500 °C (enhanced H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> digestion.

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