

Thorium Extraction Methods

Caroline Williams and Yasin Pourfarjam

March 27, 2017

Introduction

Named after the Norse god of thunder, Thorium is the most efficient nuclear reactor fuel of all the elements. It holds more untapped potential than all oil, coal, natural gas, and uranium combined. With the public's growing desire to have inexpensive, low or no carbon energy sources, abundant thorium is an optimal choice. Thorium-232 is the most common isotope and is not able to undergo nuclear fission in a thermal neutron reactor. Instead when thorium-232 absorbs a neutron, it transmutes to uranium-238, a viable nuclear fuel. Originally, thorium extraction was a process that was high in energy and waste, using large amounts of heat and solvent. Modern science is working to produce thorium more efficiently. In this paper, several common thorium extraction processes are discussed.

Separation of U and Th from Rare Earths by Precipitation

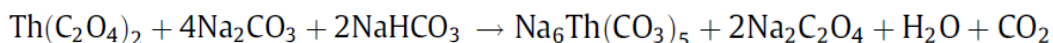
This method uses differences in solubility of rare earth elements in different pH solutions. Trivalent rare earth elements are precipitated in chloride and sulfate media with pH range 5.8-7.0. Thorium is precipitated from chloride solutions in pH range 2.5-5.5. So, because of these significant differences in pH range between thorium and other rare earth elements, separation of thorium from others is done efficiently by precipitation. Table 1 shows results of few investigations on separation of thorium, uranium and other rare earth elements; the precipitation of thorium from chloride is almost perfect in pH range 4.8-5.5.

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)

Table1. Uranium and thorium separation from rare earths by hydroxide precipitation.

In contrast, precipitation of thorium in sulfate media is mostly contaminated with significant amount of phosphate. Phosphate is commonly associated with rare earth ores and forms metal phosphate which is less solvent in sulfate media, reducing the efficiency of precipitation.

Oxalate precipitation is also used to separate thorium from other rare earth elements. In a sulfate 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 are precipitated at pH 0.7 and 60 °C, while uranium is remained in solution. Further dissolving of the precipitant in a solution containing 150 g/L Na₂CO₃ and NaHCO₃ in a ratio of 3:1 at 75 °C results in formation of thorium carbonate which is soluble, while others are not.



Separation of U and Th from Rare Earths by Solvent Extraction

Di(1-Methyl-Heptyl) Methyl Phosphonate (DMHMP) is recently used in industry to separate thorium from other rare earth elements. Thorium is extracted from others in a HCl-NH₃ media

Amine products are also used to separate uranium and thorium from other rare earth elements. Tertiary amine has a greater selectivity for uranium against thorium, while primary amine has high selectivity for the extraction of Th(IV) over U(VI) and RE(III). Mostly used commercial primary amines is 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.

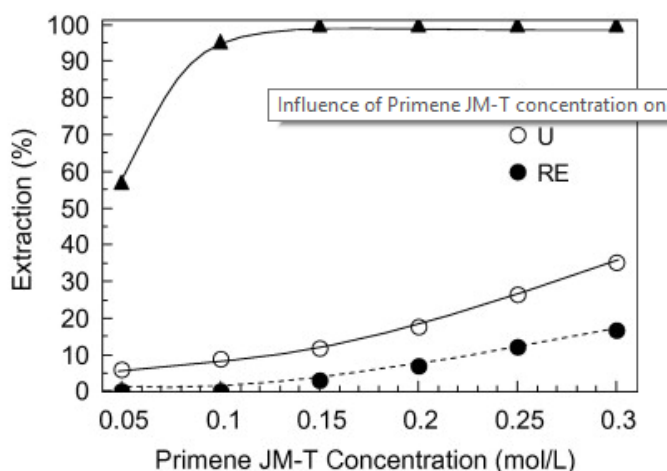
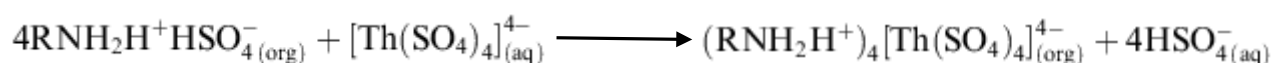


Fig. 1. Influence of Primene JM-T concentration on Th, U and RE extraction.

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. Thorium content in the ion-adsorption clays is very low. 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.

1. Processing Bayan Obo rare earth concentrates

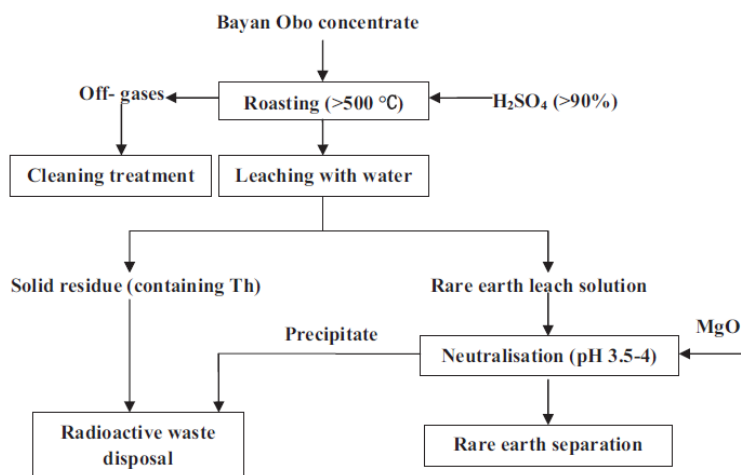


Fig. 2. Thorium separation during the rare earth production from Bayan Obo concentrates using enhanced H₂SO₄ digestion.

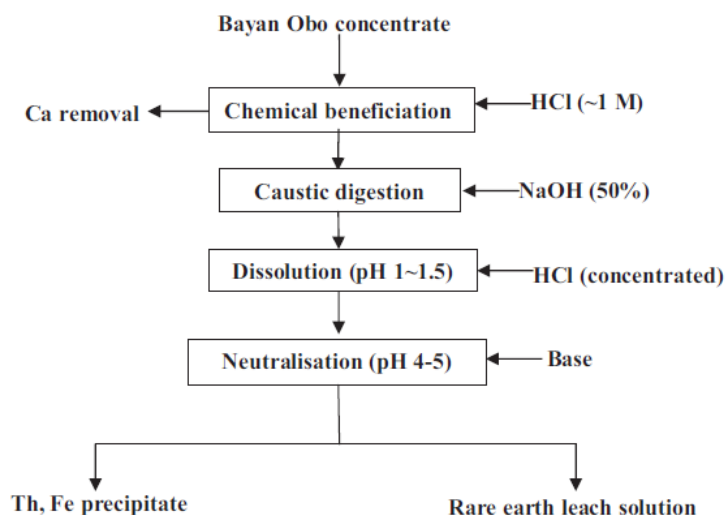
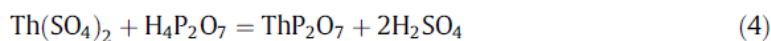
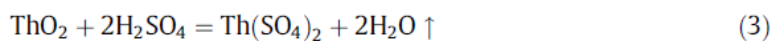
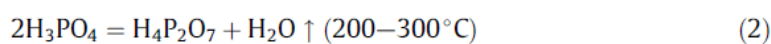
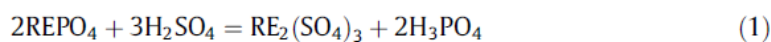


Fig. 3. Separation of thorium from rare earths during processing Bayan Obo concentrates using caustic digestion.

2. Processing Sichuan rare earth concentrates

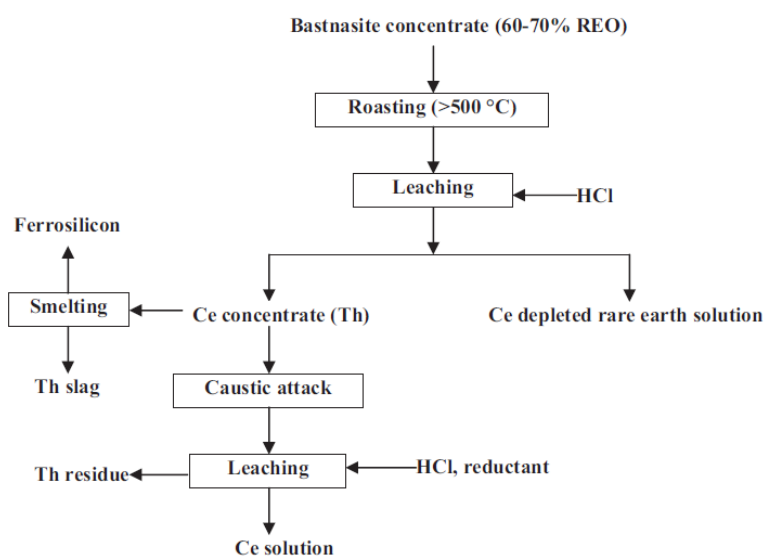


Fig. 4. Thorium separation in rare earth production from bastnasite concentrates.

Bioleaching of Thorium Using Fungi

Thorium can be extracted from monazite and red mud by using several strains of fungus using a process known as bioleaching. Fungi is useful in rare earth element leaching because it can add additional organic acids along with the traditional use of citric acid which was discussed earlier in this paper. The addition of organic acid by fungi is thought to occur by the process of acidolysis. Organic acids serve two purposes in bioleaching, they can dissolve metal ions from leaching materials through chelation of the metals released in solution and weaken the effects metal ions have on microorganisms through chelation or complexation. Studies surrounding bioleaching have been working to perfect the process by altering the fungal strain and vary physical properties such as pulp concentration of the extraction (Figures 5 & 6). Although bioleaching is not efficient enough to compete with traditional extraction methods, this environmentally conscious process could possibly be the future of rare earth element processing.

Organic Acid	<i>A. niger</i>		ML3-1		WE3-F	
	Maximum concentration	Percentage of flasks (%)	Maximum concentration	Percentage of flasks (%)	Maximum concentration	Percentage of flasks (%)
Acetic		0		0	3.8 mM	8
Citric	15.9 mM	78		0		0
Gluconic	5.3 mM	17		0	1.2 mM	67
Itaconic		0	>20 mM	97		0
Lactic		0		0		0
Oxalic	2.0 mM	17		0		0
Succinic	1.6 mM	56	4.0 mM.	28	5.4 mM	11

Figure 5. Max concentrations and percent of identified organic acids produced by fungal isolates during bioleaching.

Radionuclide activity concentration ^a (Bq/kg)	After one-step bioleaching pulp densities (w/v)			After two-step bioleaching pulp densities (w/v)			After spent medium bioleaching pulp densities (w/v)			Untreated red mud
	2%	5%	10%	2%	5%	10%	2%	5%	10%	
²²⁶ Ra	102.4	124.1	220.3	108.6	121.0	164.5	142.7	183.1	245.1	310.3
²³² Th	120.8	136.2	169.2	127.4	132.8	151.6	156.0	171.4	188.9	219.7
⁴⁰ K	114.5	140.0	250.1	122.9	156.8	207.8	190.8	216.2	288.3	423.9
Activity concentration index										
<i>I</i> (Europe) ^b	0.98	1.14	1.67	1.04	1.12	1.38	1.32	1.54	1.86	2.27
<i>I</i> (China) ^c	0.77	0.89	1.31	0.81	0.88	1.08	1.03	1.21	1.46	1.78

^a Values are the means of three experiments; S.D.s < 10%.

^b *I* (European): The activity concentration index calculated using Eq. (1), i.e. protection 112 code formulated by the European Commission.

^c *I* (China): The activity concentration index calculated using Eq. (2), i.e. following the GB 6566–2010 code formulated by the Chinese Government.

Figure 6. Activity concentration in red mud with different bioleaching methods at different pulp densities. Note the more concentrated the pulp, the higher the concentration of rare earth metals.

Electrochemical Leaching of Thorium

Electrochemical leaching is an additional step that can be performed alongside bioleaching. Metal ions can be removed from liquid waste streams via electrodeposition. This process can be used to extract and enrich elements to concentrations that are high enough for conventional methods. A voltage across an electrode generates protons at the anode (oxidation) and electrons at the cathode (reduction). Using a membrane electrolysis, this method is currently the newest process for heavy metal extraction but is aimed at hindering a more reversible, environmentally conscious process.

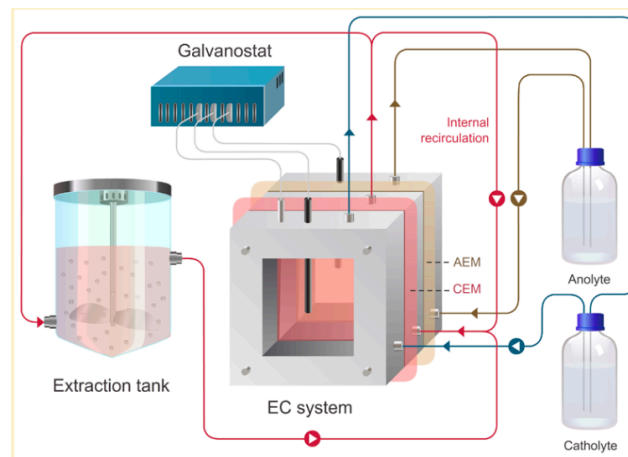


Figure 6. Model setup for electrodeposition extraction of heavy metals.

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Concomitant Leaching and Electrochemical Extraction of Rare Earth Elements from Monazite
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