Titre: Title:	Separation of radioactive elements from rare earth element-bearing minerals
Auteurs: Authors:	Adrian Carrillo Garcia, Mohammad Latifi, Ahmadreza Amini, & Jamal Chaouki
Date:	2020
Type:	Article de revue / Article
Référence: Citation:	Carrillo Garcia, A., Latifi, M., Amini, A., & Chaouki, J. (2020). Separation of radioactive elements from rare earth element-bearing minerals. Metals, 10(11), 1524 (22 pages). https://doi.org/10.3390/met10111524

Document en libre accès dans PolyPublie
Open Access document in PolyPublie

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/9410/
Version:	Version officielle de l'éditeur / Published version Révisé par les pairs / Refereed
Conditions d'utilisation: Terms of Use:	CC BY

Document publié chez l'éditeur officiel
Document issued by the official publisher

The REE are fifteen lanthanide elements in the periodic table with atomic numbers of 57 to 71, including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) as well as scandium (Sc) and yttrium (Y) with atomic numbers of 21, and 39, respectively. There is a fast growth in new applications and demand for the REE, especially in energy, environment, and high technology fields with durability, high efficiency and low carbon emissions [1–5]. These elements are called "rare" owing to their difficult extraction from deposits that is attributed to the similarity in the physical and chemical properties of REE and gangue minerals and to the difficulty to find concentrated deposits. Another challenge for REE production is the heterogeneity of these elements in the deposits [4,6–9], which plays a vital role in configuring the unit operations regarding the geology, versatility, and composition of the minerals [4,6]. The production of REE requires several steps of magnetic, gravity, and electrostatic separations in addition to flotation to efficiently separate the REE from associated gangues with similar physical properties. The individual production of the REE is very challenging owing to their similar chemical properties, and specific extraction techniques are required to recover REE; however, europium and cerium are exceptions, i.e., cerium can be formed as, either trivalent or tetravalent during hydrometallurgical process where the tetravalent cerium can be separated from the trivalent

REE [10,11]. Figure 1 shows a typical REE production process, including geology, mining, physical beneficiation, hydrometallurgy, and separation of individual elements [6].
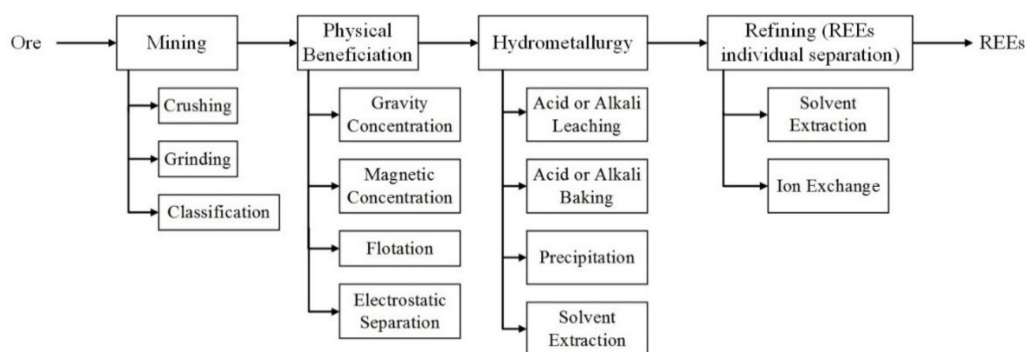

Figure 1. The REE general processing plant.

Since mining and refining of low-grade REE-bearing minerals are technically infeasible owing to a lithophilic nature of the REE [12,13], high-grade REE-bearing minerals, such as bastnäsite, monazite, and xenotime, are used for economic extraction of these elements [4,12,14–16]. Table 1 summarizes both the low-grade and high-grade REE-bearing minerals.

Among various gangues, radioactive elements are a serious challenge in the REE production process, regarding specific regulations for safety management in the processing units (for more details refer to [17–19]). Thorium (Th) and uranium (U) are naturally occurring radioactive materials (NORM), which can be found in the REE deposits (Table 1). Monazite and xenotime are the most known REE-bearing minerals that contain radioactive elements. For instance, the REE-bearing ore at Mountain Pass, i.e., a major bastnäsite resource in California with rare earth oxides (REO) of 8.5 wt.%, contains thorium (Th) and uranium (U) of 0.02, and 0.002 wt.%, respectively [19]. In addition, the Bayan Obo bastnäsite and monazite deposit in China contains minerals such as fluorite, magnetite, barite, calcite and quartz with magnetic susceptibility, specific gravity, electrical conductivity, or floatability similar to REE-bearing minerals [20,21].

The low concentration of radioactive elements in the upstream rare earth ore processing units, e.g., in physical beneficiation, results in quite low emission of radioactivity, whereas the higher concentration of the radioactive elements in downstream separation lines requires safety measurements to be carefully considered. For example, an exposure of a worker to an ore containing 500 ppm thorium and 50 ppm uranium, staying 1 m away from a large mass of the ore for an entire working year, leads to a total exposure of 2.4 mSv that is below the dose limit for a NORM worker, 20 mSv [17]. This exposure is mainly caused by ore dust inhalation (at 1 mg/m^3) and incidentally ore ingestion (at 100 mg/day). Therefore, a step for separation of thorium and uranium is required to minimize risks associated with REE production in terms of safety, environmental hazards, and quality of the final product [22].

In the present paper, various hydrometallurgical techniques applied during REE production process for separating thorium (Th) and uranium (U) are reviewed, including leaching, precipitation, solvent extraction, ion chromatography, and membrane to understand the advantages and limitations of each technique. In addition, the process selection with regards to the feed properties, waste management of the separated radioactive elements, and how they can be treated to produce valuable co-products are also discussed.

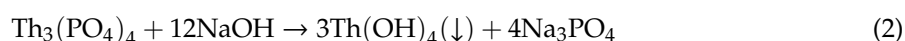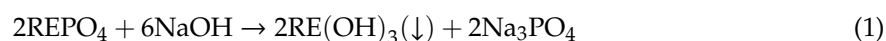**Table 1.** REE-bearing minerals and gangue minerals from deposits.

Type	Mineral	Formula	Average Composition (wt.%)			Ref.
			REE Oxide	ThO$_2$	UO$_2$	
Carbonate	Ancylite	Sr(Ce,La)(CO$_3$)$_2$OH·H$_2$O	46	0–0.4	0.1	[6]
	Bastnäsite	**(Ce,La)CO$_3$F**	**74**	**0–0.3**	**<0.9**	[6]
	Parisite	Ca(REE)$_2$(CO$_3$)$_3$F$_2$	59	0–0.5	0–0.3	[6]
Phosphate	Apatite	Ca$_5$(PO$_4$)$_3$(F,Cl,OH)	19	-	-	[4,6]
	Britholite	(REE,Ca)$_5$(SiO$_4$,PO$_4$)$_3$(F,OH)	56	1.5	-	[4,6]
	Monazite	**(REE,Th)PO$_4$**	**35–71**	**0–20**	**0–16**	[6,23]
	Xenotime	**YPO$_4$**	**61**	**-**	**0–5**	[4,6]
Oxide	Brannerite	(U,REE,Ca)(Ti,Fe)$_2$O$_6$	6	-	-	[6]
	Perovskite	(Ca,REE)TiO$_3$	<37	0–2	<0.05	[6]
Silicate	Allanite	(REE,Ca)$_2$(Al,Fe)$_3$(SiO$_4$)$_3$(OH)	30	0.3	-	[4,6]
	Cheralite	(REE,Th,Ca)(P,Si)O$_4$	5	<30	-	[4,6]

It is worthy of mentioning that recovery of REE from secondary sources such as electronic wastes [24,25], red mud (Bauxite) [26–29], and coal [30] has also been recently investigated. The separation of radioactive elements during these processes is out of the scope of the present review article and requires further study.

2. Separation by Leaching

Leaching is a process based on the different solubility of elements in a leach liquor. To separate the radioactive elements from REE, leaching process is typically applied on, either fresh or concentrated ore [4], in order to maximize the solubility of radioactive elements [31–34] or REE [35] in the liquor.

According to the literature, a one-step leaching process faces technical issues during separation of thorium and uranium from REE owing to the occurrence of undesired reactions and leaching of un-wanted components [36]. For instance, Lapidus and Doyle [33] applied a one-step leaching process to separate radioactive elements from a monazite concentrate using oxalate reagent for leaching out thorium oxalate in the liquid form while rare earth oxalate remains in the solid form. They observed that either Th(HPO$_4$)$_2$ or Th$_3$(PO$_4$)$_4$ is re-precipitated in the liquor at a pH < 3, and oxalate reagent forms stable complexes with other metal impurities, instead of reaction with radioactive elements. To overcome the drawbacks of this process, a two-step cracking-leaching process was proposed. In the first step (cracking), an alkaline reagent, e.g., NaOH, cracks the concentrate of the REE-bearing mineral, either monazite or xenotime, to produce a hydroxide cake containing the REE, thorium, uranium, and some other impurities, reactions 1 and 2 [31,33,35]. This step eliminates the re-precipitation of thorium phosphate resulting in the formation of hydroxide forms of the REE and thorium, which can be separated in the second leaching step [34,37,38],

$$2REPO_4 + 6NaOH \rightarrow 2RE(OH)_3(\downarrow) + 2Na_3PO_4 \tag{1}$$

$$Th_3(PO_4)_4 + 12NaOH \rightarrow 3Th(OH)_4(\downarrow) + 4Na_3PO_4 \tag{2}$$

After the cracking step, acid leaching of the produced hydroxide cake is performed wherein the acidic oxalate reagents are employed to leach the radioactive elements while the REE oxalate is insoluble [34]. If the REE is preferred to be in the liquor solution, other acids such as nitric acid (reaction 3) [35] or hydrochloric acid (reaction 4) [37] can be used instead of oxalate reagents; however, the uranium also tends to leach out with the REE if the pH is not properly controlled,

$$RE(OH)_3 + 3HNO_3 \rightarrow RE(NO_3)_{3(aq)} + 3H_2O \tag{3}$$

$$RE(OH)_3 + 3HCl \rightarrow RECl_{3(aq)} + 3H_2O \tag{4}$$
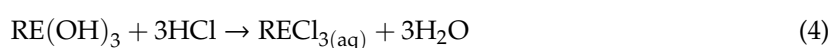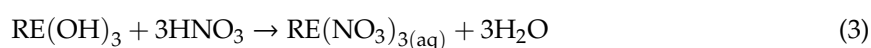
The two-step approach can be improved by employing high-pressure leaching to stabilize products that are unstable at atmospheric conditions. Figure 2 shows an increase in the recovery of thorium by ammonium carbonate (250%), from 13% at atmospheric pressure to 98% at 6.5–10 atm at 70 °C, while no significant change occurs in the recovery of REE [31].
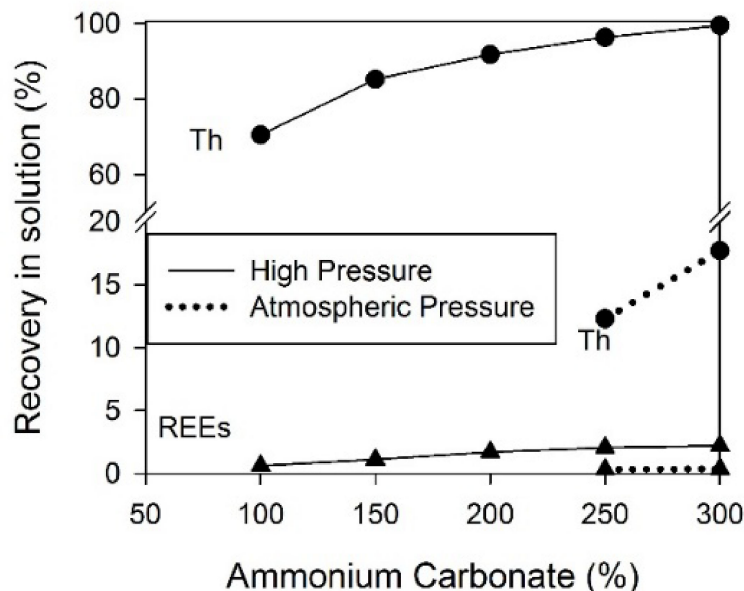

Figure 2. Effect of the pressure on the recovery of thorium (Th) and REE at 70 °C, adapted from [31]. (Reproduced with permission from ref. [31], copyright (2002), Elsevier)

In such a high-pressure leaching process, the ammonium carbonate leaches both the thorium, reaction 5, and uranyl hydroxides, reaction 6, while it produces a solidus complex after reaction with REE, reaction 7 [31,32]. Typically, an excess amount of reagent is employed in either atmospheric or high-pressure leaching owing to the consuming part of the reagent in the secondary reactions,

$$Th(OH)_4 + 5(NH_4)_2CO_3 \rightarrow (NH_4)_6[Th(CO_3)_5] + 4NH_4OH \tag{5}$$

$$UO_2(OH)_2 + 3(NH_4)_2CO_3 \rightarrow (NH_4)_4[UO_2(CO_3)_3] + 2NH_4OH \tag{6}$$

$$2RE(OH)_3 + 4(NH_4)_2CO_3 \rightarrow RE_2(CO_3)_3(NH_4)_2CO_3(\downarrow) + 6NH_4OH \tag{7}$$
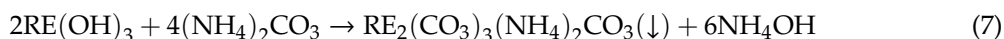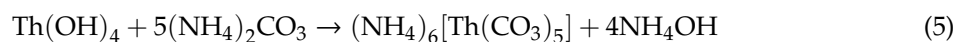
Figure 3 illustrates a flowsheet summarizing the cracking-leaching approaches (two-step leaching process) wherein, either REE or radioactive elements can be extracted in the leach liquor, depending on the leaching reagent. Table 2 summarizes the experimental conditions and the overall recovery of REE, thorium, and uranium in leach liquor for the two-step cracking-leaching process.

Table 2. Uranium and thorium separation from REE by a two-step cracking-leaching process.

REE-Bearing Mineral	Reagent	Operating Conditions			Overall Recovery in Leach Liquor (%)			Ref.
		Pressure (atm)	Time (h)	T (°C)	Th	U	REE	
Xenotime	Nitric acid	1	-	60	<1	-	>98	[35]
Concentrated monazite (87 wt.% REE)	Ammonium carbonate	6.5–10	1–2	80	99	95	2.5	[31]
Monazite (18.5 wt.% REE)	Ammonium oxalate	1	<2	40	100	>40	<1	[33]

Figure 3. Leaching-cracking approaches for separation of REE from radioactive elements.

3. Separation by Precipitation

The REE can be separated from other elements in a liquor via precipitation method using an appropriate reagent such as oxalic acid, reaction 8 [39–42],

$$2RE^{3+} + 3H_2C_2O_4 + 10H_2O \rightarrow RE_2(C_2O_4)_3 \cdot 10H_2O(\downarrow) + 6H^+ \tag{8}$$

To separate the REE from the radioactive elements through precipitation, the most important parameters, include the type of the liquor feed, REE concentration in the feed, the concentration of the precipitation reagent, and the mass rat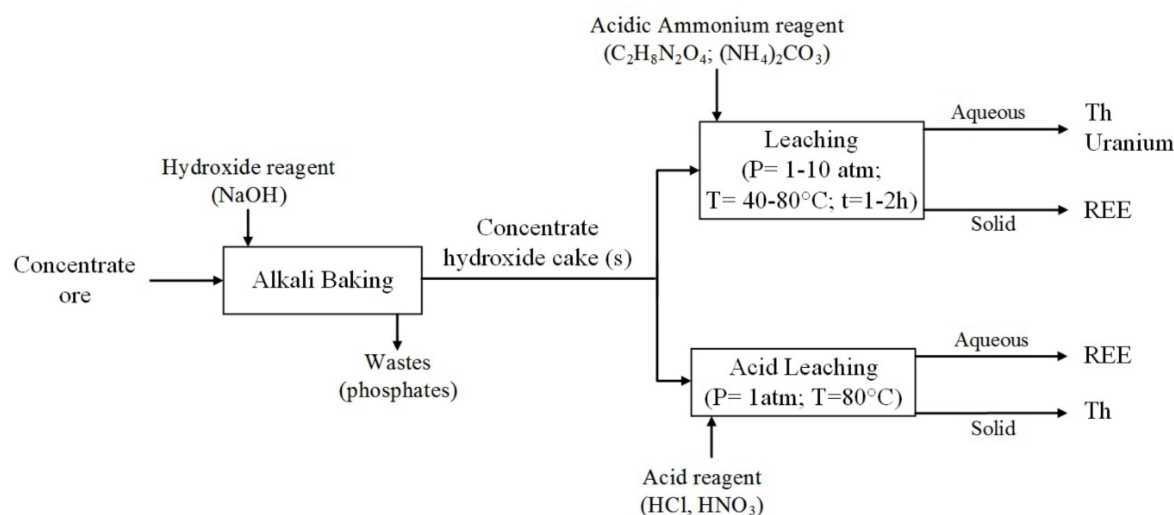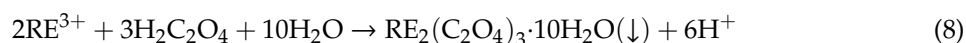io of the reagent to REE. The pH is another parameter that determines the performance of selective precipitation of uranium, thorium, and REE. The ideal case is to find distinct pH values to separate radioactive elements from REE. Uranium and REE precipitate at close pH values with a risk of co-precipitation, whereas a high recovery of thorium is achievable since its precipitation requires a different pH [43–46]. Table 3 presents the pH ranges required for the precipitation of uranium, thorium, and REE in both chloride and sulfate liquors. In an acid liquor, some of alkali precipitation reagents are preferred owing to higher selectivity towards radioactive elements [46–49]. For instance, ammonium hydroxide (NH_4OH) at a pH close to 5 [50], and sodium hydroxide [47] precipitate thorium with a small loss of REE. Whereas, potassium iodate (KIO_3) is inefficient in the precipitation of thorium due to the co-precipitation of REE [50]. In addition, ammonium hydroxide (NH_4OH) precipitates uranium at a pH close to 4.5, which is far enough from the REE precipitation pH of about 6 [51].

Table 3. The pH ranges for precipitation of thorium, uranium and the REE in different liquors.

Elements	Precipitation pH (Approx.)	
	Chloride Liquor	Sulfate Liquor
Th	4.8–5.8	1–2
U	5.5–7	6
REE	6.8–8	3–5.5

3.1. Types of the Liquor and Reagent

Typically, the main liquors produced through the industrial hydrometallurgical processes are chloride and sulfate [4]. In the chloride liquor, precipitation of the radioactive elements is usually achieved by adding an alkali reagent. If the pH is kept close to or below 5.5, the total thorium and a part of uranium are likely precipitated and recovered while the loss of the REE is about 2% [44,45].

A lower pH for precipitation of radioactive elements has been reported in a sulfate liquor compared to the chloride liquor. Table 3 presents the pH range required for precipitating thorium and uranium from chloride and sulfate liquors. For example, 100% thorium is precipitated from sulfate liquor at a pH close to 1 using ammonium hydroxide. However, REE (44.7% La, 63.5% Ce, and 63.2% Nd) are also co-precipitated under such a highly acidic condition [43,46].
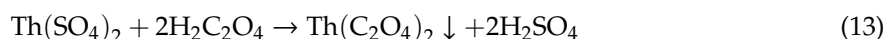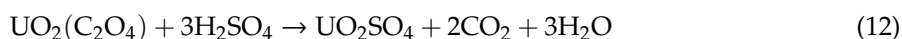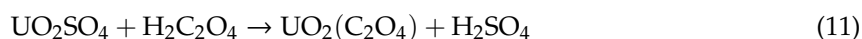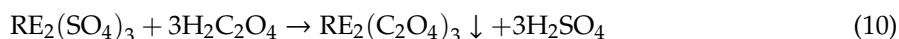
In some cases, nitrate liquor has also been studied for separation of uranium from REE [51,52] wherein the uranium was precipitated by 90% using hydroxide reagents at a pH of 4.5 [51]. Further, a higher efficiency has also been obtained for a precipitation pH between 6 to 8, at which almost total recovery of uranium is achieved in the form of β–$UO_2(OH)_2$ [52].

The type of reagent is another critical parameter that determines which elements, e.g., thorium, uranium, or REE, are precipitated, while the others remain in the aqueous phase. A double sulphate reagent produces the REE precipitate in the form of $MRE(SO_4)_2$ with M representing sodium, potassium or ammonium, leaving radioactive elements in the aqueous phase, reaction 9 [53]. Precipitation of the trivalent REE is attributed to the low solubility of the REE sulfate in water, resulting in the separation from the radioactive elements and tetravalent REE, i.e., cerium (IV):

$$RE(SO_4)_3 + Na_2SO_4 + 2H_2O \rightarrow Na_2SO_4RE_2(SO_4)_3 \cdot 2H_2O \downarrow \tag{9}$$

3.2. Multi- or Single-Step Precipitation

The precipitation for separation of radioactive elements and REE can be conducted in either multi-steps or a single step, regarding the types of the liquor and reagents. A secondary purification step is necessary when the reagent is selective to one of the radioactive elements, while the other one remains with REE. For instance, a 30% concentrated oxalic acid precipitates 99% thorium along with 98% REE at 30 °C, leaving uranium in the solution according to reactions 10 to 13 [35,39,46,54]. Next, a mixed alkali solution of Na_2CO_3 and $NaHCO_3$ selectively leaches and recovers 99% thorium from the oxalate cake, reaction 14, while the REE remains in the solid form as carbonates [39]:

$$RE_2(SO_4)_3 + 3H_2C_2O_4 \rightarrow RE_2(C_2O_4)_3 \downarrow + 3H_2SO_4 \tag{10}$$

$$UO_2SO_4 + H_2C_2O_4 \rightarrow UO_2(C_2O_4) + H_2SO_4 \tag{11}$$

$$UO_2(C_2O_4) + 3H_2SO_4 \rightarrow UO_2SO_4 + 2CO_2 + 3H_2O \tag{12}$$

$$Th(SO_4)_2 + 2H_2C_2O_4 \rightarrow Th(C_2O_4)_2 \downarrow + 2H_2SO_4 \tag{13}$$

$$Th(C_2O_4)_2 + 4Na_2CO_3 + 2NaHCO_3 \rightarrow Na_6Th(CO_3)_5 + 2Na_2C_2O_4 + CO_2 + H_2O \tag{14}$$

Vijayalakshmi et al. [46] also reported a multi-step separation of radioactive elements from REE wherein the thorium is initially precipitated from a sulfate liquor by adding ammonium hydroxide (NH_4OH). Then, REE was separated from uranium in a secondary precipitation step in the form of REE oxalate. They suggested employing an excess amount of oxalic acid to lower the pH of the solution, and adjust it between 1 and 2 to avoid co-precipitation of impurities, e.g., aluminum and iron, with REE [40]. In such a multi-step separation of radioactive elements and REE, control of pH is more comfortable during the process, and the efficiency of the recovery is high. However, a large amount of reagent is required, which is economically infeasible.

To overcome the drawbacks of the multi-step precipitation, various studies were conducted to recover either the REE or both thorium and uranium in a single-step process. Kul et al. [41] applied a double-salt single-step approach and reported 98% recovery of REE in the precipitate while only 15% thorium is co-precipitated. The hydroxide reagents have the potential for a single-step recovery of the radioactive elements from a chloride liquor [48,49,55]. For instance, the hydrated lime, $Ca(OH)_2$, precipitates thorium at a pH of 2.5, while the loss of REE through co-precipitation is minimized [48]. Yu et al. [49] employed the hydrated lime to extract the thorium and uranium from a chloride liquor which was produced from the processing of monazite and REE carbonatite minerals from the Montviel

deposit in the North West of Quebec in Canada. They demonstrated that the addition of hydrogen peroxide (H_2O_2) is necessary to oxidize the iron and facilitate its precipitation. They reported recovery of 99% Th, 80% U, and over 90% iron and phosphate impurities, while minimizing the co-precipitation of REE to less than 2%. The advantage of the single-step separation process is a small amount of reagent required for the precipitation, whereas adjusting a proper pH for selective precipitation is difficult.

The flowsheet in Figure 4 [39,46,48], illustrates various potential precipitation pathways to separate radioactive elements from REE in a sulfate or chloride liquor that would be produced in the upstream hydrometallurgical processes. Table 4 summarizes the recovery yield of the radioactive elements obtained from different precipitation processes.
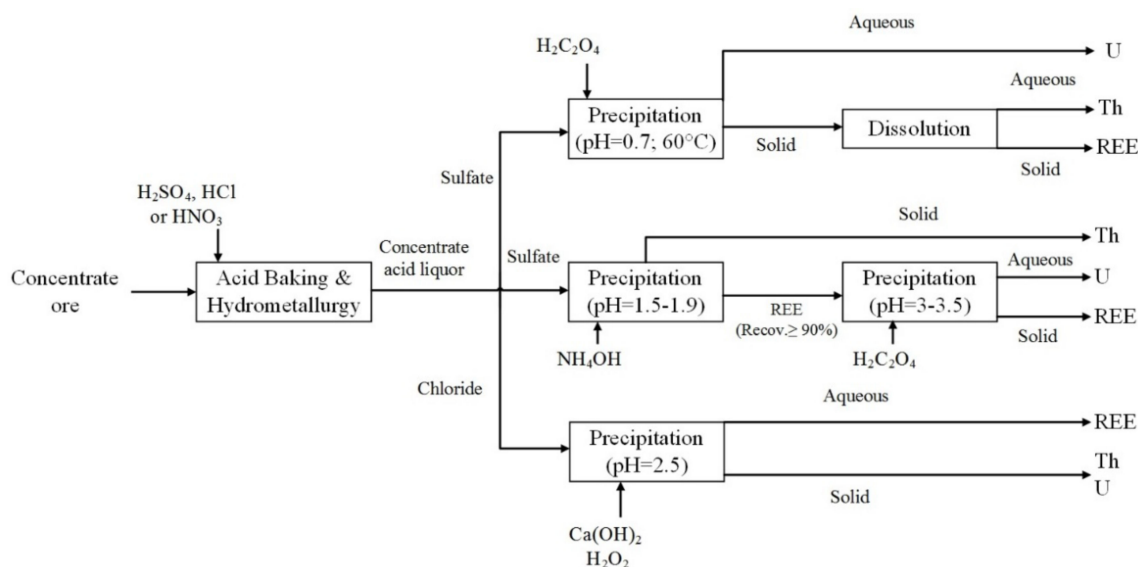

Figure 4. Process flowsheet for separation of Th and U from REE by precipitation.

Table 4. Uranium and thorium separation from REE by precipitation technique.

Original Ore	Upstream Liquor Feed	Precipitation Reagent	Final pH	Precipitation Recovery (%)			Ref.
				Th	U	REE	
Monazite	Sulfate	1st step: Oxalic acid	0.7	98	-	99	[39]
		2nd step: Alkali leaching	-	>99	-	<1	
Synthesized solution	Nitrate	KOH and NH$_4$OH	4.5	-	90	low	[51]
Monazite, Apatite	Chloride	Hydrated lime and NH$_4$OH	2.5	>99	-	5	[48]
Monazite, REE carbonate	Chloride	Lime and H$_2$O$_2$	-	99	>80	<2	[49]
Bastnäsite, Monazite	Hydroxide cake	HCl	5.8	>99	>99	2.3	[56]
Xenotime	Sulfate	1st step: NH$_4$OH	1.5–1.9	>99	-	<6	[46]
		2nd step: Oxalic acid	-	-	-	>98	

4. Separation by Solvent Extraction

The solvent extraction technique has received significant attention for separation of thorium and uranium from REE by using appropriate extractants, which can be dissolved into an organic solvent to provide an immiscible phase and enough interface with the aqueous liquor of the REE.

This process is typically conducted by two main groups of extractants, including amine and organophosphorus extractants. The amine group can be divided into primary and tertiary types where the primary amine is highly selective towards the thorium in either sulfate or chloride liquors,

and the tertiary amine is selective towards the uranium in sulfate liquors. The organophosphorus extractants are usually divided into acid and neutral types, which are applicable to nitrate, chloride and sulfate liquors.

4.1. Solvent Extraction with Amine Extractants

Amine extractants have been employed in the AMEX process, which was developed in the late 1950s, for extracting radioactive elements from REE-bearing minerals. In this process, the amine extractants are mixed with a sulfate leach liquor produced from monazite sands [57]. Thorium is first extracted with a primary amine (reaction 15) followed by a nitric acid stripping step. Then, uranium is extracted with a tertiary amine (reaction 16) and stripped with sodium carbonate,

$$4RNH_2H^+HSO_4^-{}_{(org)} + [Th(SO_4)_4]^{4-}_{(aq)} \rightarrow \left(RNH_2H^+\right)_4[Th(SO_4)_4]^{4-}_{(org)} + 4HSO_4^-{}_{(aq)} \quad (15)$$

$$4R_3NH^+HSO_4^-{}_{(org)} + [UO_2(SO_4)_3]^{4-}_{(aq)} \rightarrow \left(R_3NH^+\right)_4[UO_2(SO_4)_3]^{4-}_{(org)} + 4HSO_4^-{}_{(aq)} \quad (16)$$

Table 5 lists some amines employed for solvent extraction of radioactive elements from the REE [58–60].

Table 5. Performance of amine extractants for uranium and thorium separation from REE.

Amine		Experimental Conditions				Extraction (%)			Ref.
Type	Name	Liquor	Ore	pH	Time (min)	Thorium	Uranium	REE	
Primary	Primene JM-T	Sulfate	Monazite	-	5	95.4	8.8	0.32	[58]
	N_{1923}	Sulfate	Bastnäsite	-	-	>97	-	E_{Ce}: 3–8	[60]
	Octylamine	Sulfate	Monazite	4	15	70–80	50–60	-	[59]
Secondary	N-methylaniline	Sulfate	Monazite	4	15	70–80	5–10	0	[59]
Tertiary	Alamine 336	Sulfate	Monazite	-	5	3.1	82.4	0.02	[58]
	N,N-dimethylaniline	Sulfate	Monazite	4	15	70	15–20	$E_{Ce, Eu, Y}$: 0	[59]
				7	30	0	55	$E_{Ce, Eu, Y}$: 0	[59]
Mixture	Primene JM-T and Alamine 336	Sulfate	Monazite	-	5	45.5	58.8	0.04	[58]

The Primene JM-T is the most applied primary amine to extract thorium, and the Alamine 336 is a tertiary amine that has been employed for uranium extraction from the REE-bearing minerals [58,61,62]. The N_{1923}, i.e., $(C_nH_{2n+1})_2CHNH_2$ ($n = 9$–11), is an alternative primary amine for this process, which has been employed in Baotou and Sichuan in China [60,63–65]. The N_{1923} extractant is characterized by low solubility in water and a high separation factor between thorium and the REE, especially in sulfate liquors [66]. For instance, the selectivity of the N_{1923} for thorium is 600 times higher than for cerium in a sulfate liquor produced from the bastnäsite and monazite concentrates [60,66]. The reaction between the N_{1923} and thorium takes place in the interfacial zone, and it is controlled by the thorium mass transfer [67]. Figure 5 [60] shows a flowsheet for the recovery of thorium from REE-bearing minerals, where a thorium recovery of over 99% is achievable in an organic phase using a primary amine in a multi-step process, including solvent extraction, scrubbing, and precipitation [60].

Employing a mixture of primary and tertiary amines is a promising method for the simultaneous extraction of thorium and uranium from the REE, which is economically and technically favored due to a decrease in the number of steps in the solvent extraction process. For instance, simultaneous separation of Th and U has been reported from sulfate liquor during the processing of monazite using a mixture of Primene JM-T (i.e., a primary amine) and Alamine 336 (i.e., a tertiary amine), wherein the optimized process conditions (concentration of amines, contact time, and pH) resulted in the extraction of 99.9 and 99.5% thorium and uranium, respectively, while the extraction of REE was less than 0.1% [58].
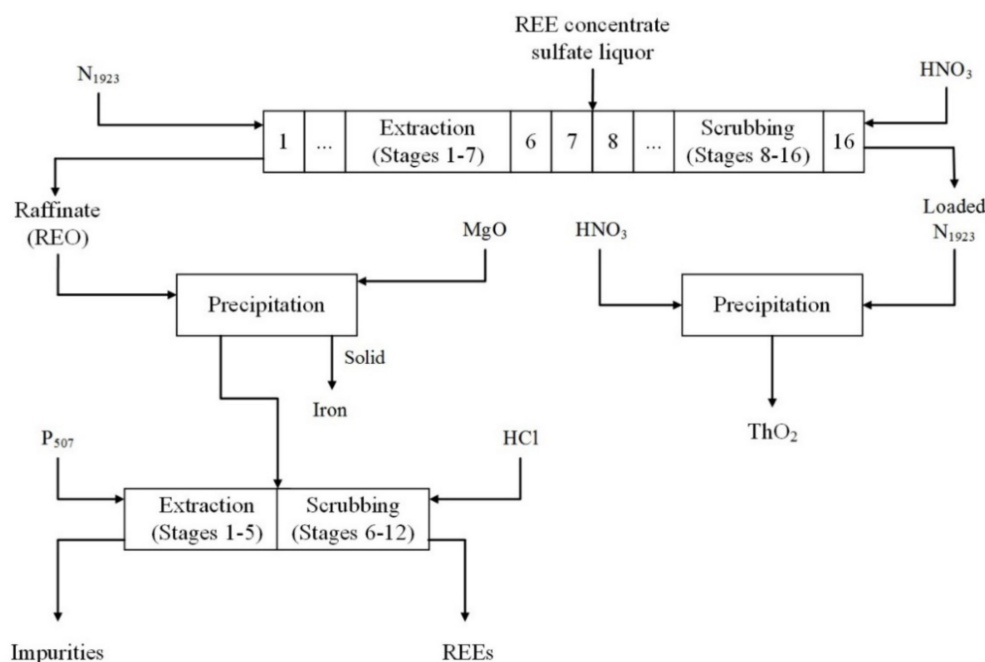
Figure 5. Process of separating Th from REE of Baotou bastnäsite leaching.

*4.2. Solvent Extraction with Phosphorous Extractants*

Phosphorous extractants are alternative for amines to extract the radioactive elements [4,68–72]. This group of extractants includes phosphate esters and amines. Table 6 presents the performance of different types of organophosphorus extractants during the solvent extraction process for separating Th and U from different REE-bearing liquors.

Table 6. Phosphorous extractants for uranium and thorium separation from REE.

Type of Extractant	Feed Liquor	Phosphorous Extractant	Extraction (%)			Ref.
			Th	**U**	**REE**	
Acid	Acidic	Cyanex 272	83	-	12	[69]
	Nitrate	DEHEHP	20		Ce: 95	[65]
	Nitrate	Mixture of HEH and EHP in kerosene	95	-	Ce: 99	[73]
Neutral	Nitrate	TiAP (2 solvent extraction steps)	99	95	<2	[74]
	Nitrate	p-phosphorylated calixarene	99	-	5	[75]
	Nitrate	TEHP in n-paraffin	50–77	2.5	Y: 0.17	[68]
Other	Nitrate	Aliquat 336	97	54	<3	[32,76]
	Nitrate	polyaramide	90	-	>48	[77]

4.2.1. Acid Organophosphorus Extractants

Acidic organophosphorus extractants such as di-(2-ethylhexyl)-phosphoric acid (DEHP), (2-ethylhexyl) 2-ethylhexyl-phosphonic acid (EHEHP), and di-(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP), have been proposed as promising reagents to separate radioactive elements from REE [64,65,78,79]. Reaction 17 shows absorption of thorium during treatment with DEHEHP [64],

$$\mathrm{Th(NO_3)}^{3+} + 3\mathrm{NO_3}^- + \mathrm{L_{(aq)}} \rightarrow \mathrm{Th(NO_3)_4 \cdot L_{2(org)}} \tag{17}$$
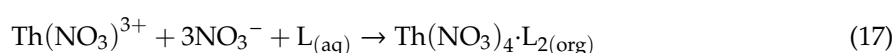
where L is the ligand or extractant. The acid organophosphorus extractants are efficient, especially for the extraction of radioactive elements from highly acidic sulfate solutions. In addition, DEHP, EHEHP, and DEHEHP can be employed for individual separation of the REE [80], since these extractants have a low affinity to extract trivalent REE while cerium(IV) is simultaneously extracted with thorium and

uranium [65]. Nonetheless, to avoid a high loss of the tetravalent cerium, it would be individually recovered in a downstream stripping. Moreover, cerium(IV) can be recovered by applying a second solvent extraction process to the organic phase, owing to a high separation factor of cerium (IV) over thorium, which is 36.

The Cyanex is another type of acid organophosphorus extractant that is widely employed for thorium and uranium separation from REE [69,81–83]. The mechanism of metals extraction by Cyanex is the cation exchange [69], where the strength of the acid determines the performance of the Cyanex extractants. The commonly used Cyanex extractants are the Cyanex 272 (di-2,4,4-trimethyl phosphonic acid), Cyanex 301 (bis-2,4,4-trimethylprntyl phosphonic acid) [84], and Cyanex 302 [69]. The Cyanex 272 shows higher efficiency compared to the Cyanex 302 for separating thorium from lanthanides due to the higher strength of the latter acid [83]. In addition, applying a mixture of extractants, e.g., a mixture of HEH and EHP in kerosene, is a promising approach to increase the efficiency of the solvent extraction for separating thorium from REE (Table 6).

4.2.2. Neutral Organophosphorus Extractants

The tri-n-butyl phosphate (TBP) is the most common neutral organophosphorus extractant for separating thorium and uranium from REE that is especially efficient in a nitrate medium. Tris(2-ethylhexyl) phosphate (TEHP), and tri-iso-amyl phosphate (TiAP) are other neutral organophosphorus extractants, which are usually dissolved in n-paraffin or in xylene [68,74,85–87]. In terms of efficiency, the TEHP has a special affinity to uranium, which leads to the loss of some thorium in the aqueous phase. Therefore, the TEHP should be employed in a two-step solvent extraction (Figure 6) to recover uranium and then thorium [68].
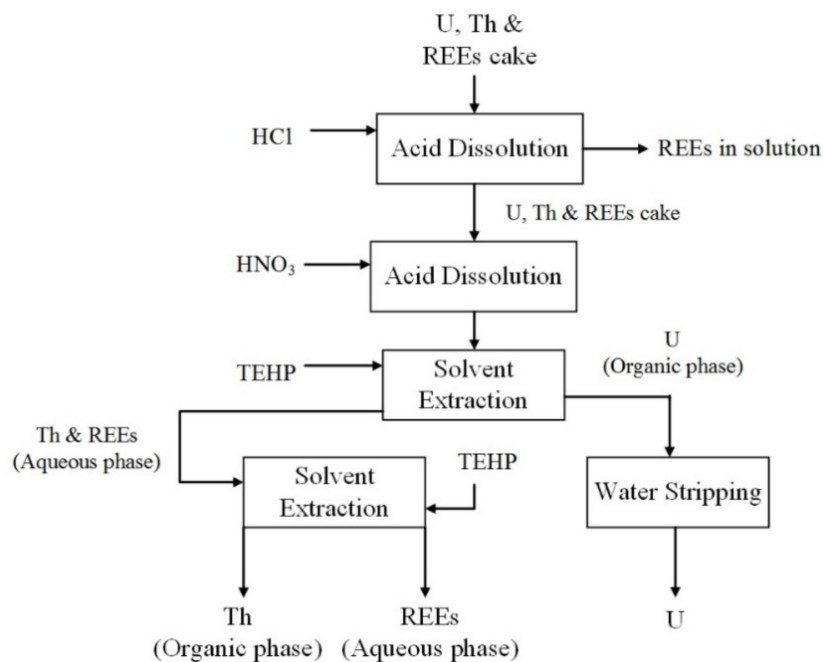

Figure 6. Separation of thorium and uranium from REE by solvent extraction method with TEHP in n-paraffin.

Calixarene is another group of neutral organophosphorus extractants appropriate for recovering radioactive elements from REE [71,73,75,88]. For instance, 5,11,17,23-tetra(diethoxyphosphoryl)-25,26,27,28-tetrapropyloxy calixarene and p-phosphorylated calixarene have been employed, either as a resin in chromatography to concentrate thorium and uranium [88] or as a solvent extractant to recover thorium and uranium from the REE nitrate liquors [71,75]. The efficiency of thorium extraction (reaction 18) would vary with the concentration of nitric acid used in the upstream process. It is

reported that around 85% of thorium is extracted using 2 mol/L nitric acid while the extraction of REE (Gd, La, and Yb) is less than 10% [75],

$$Th^{4+} + 4NO_3^- + 3Calixarene \rightarrow Th(NO_3)_4 \cdot 3Calixarene. \tag{18}$$
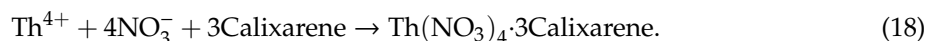
4.2.3. Improvement of Solvent Extraction Process

Although various types of extractants have been applied in the solvent extraction process to separate radioactive elements from REE [32,76,77,89], the selection of an appropriate extractant is a function of its cost, selectivity towards one of the radioactive elements, and the feed liquor (sulfate, nitrate or chloride). For instance, Cyanex extractant shows poor metal extraction, is costly and requires high acidic environments, which make it infeasible for industrial applications.

Employing a mixture of acid and neutral organophosphorus extractants potentially improves the solvent extraction process that would result in a higher separation efficiency than using each extractant separately. For instance, although the selectivity in uranium extraction by acid organophosphorus PC88A (mono (2-ethyl hexyl) ester) showed better performance than the neutral organophosphorus TBP, the best result was obtained with a mixture of both, where the distribution of uranium was 0.1, 1.1, and 2.3 after 20 min treatment with TBP, PC88A, and their mixture (0.15 M TBP and 0.15 M PC88A in xylene), respectively [86,90]. This enhancement in performance is attributed to the role of TBP, which dehydrates uranium, resulting in an enhancement in the hydrophobic nature of the species and improving the extraction by the mixture.

In addition, solvent extraction is typically followed by a stripping step to separate the recovered radioactive element(s) from the accompanying reagent. Recovery of the radioactive elements is usually over 90% after stripping [74,82]. For the stripping step, an appropriate acidic reagent is employed depending on the feed of the solvent extraction [69,74,85,86,90]. For instance, for a feed of sulfate solution, nitric or sulfuric acid is employed as the stripping reagent [58]. For a feed of nitrate liquor, the stripping reagent is usually hydrochloric acid or sulfuric acid [69,76,82].

5. Separation by Ion Chromatography

5.1. Cation Exchange Resin

Cation exchange column has been employed to investigate chromatography principles on the separation of radioactive elements from REE [91–94]. In ion chromatography, it is possible to employ an active stationary phase or an active mobile phase, circulating in a neutral chromatography column. A configuration of a silica gel resin impregnated with ammonium nitrate (NH_4NO_3) in mobile phases of HDEHP (di-(2-ethylhexyl)-dithiophosphoric acid) and HDiBDTP (di-(iso-butyl)dithiophosphoric acid) resulted in the separation of metal ions and the individual REE [94,95]. This method is based on different retention times of thorium, uranium, and REE in the column, which is affected by the employed resin [91]. For this purpose, various resins have been employed such as transUranic-Element Specific (TRU Spec), i.e., a resin composed of TBP and octyl(phenyl)-N,Ndiisobutylcarbamoylmethylphosphine oxide (CMPO) and supported on an inert polymer substrate [93], and the Dionex, i.e., a column for the separation of transition and lanthanide metals from contaminated water [92].

These columns adsorb all the elements of interest and separate them using different eluent. Once adsorbed, the order of elements elution can vary in function of the column resin. By employing appropriate eluents, thorium and uranium can thus be recovered individually with an efficiency of over 90% [91,93]. For instance, Figure 7 [91] shows that the elements of interest, i.e., thorium, uranium, and the REE, are adsorbed in the Ion Pac CS 5 column, then recovered separately with a mixture of hydrochloric acid and ammonium sulfate as eluent. Accordingly, uranium is initially recovered in the form of UO_2Cl^-, then thorium is recovered as $ThSO_4^{2+}$ [91]. Another chromatographic investigation showed over 95% recovery of the light REE, which was adsorbed in a transuranic-element specific resin (TRU Spec), using a LN Spec resin column by a nitric acid elution; later, thorium and uranium

were recovered, respectively, by hydrochloric acid and a mixture of hydrochloric and hydrofluoric acids [93,96].
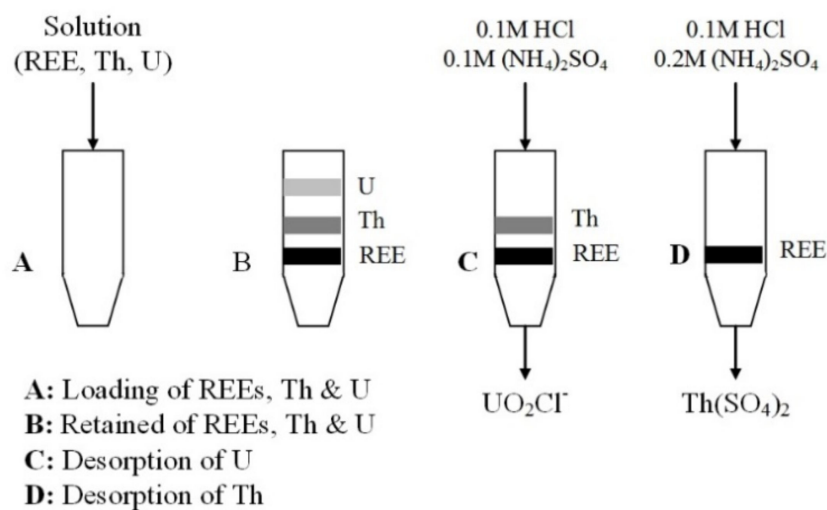

Figure 7. Cation exchange extraction with Dionex Ion Pac CS5 column.

In addition, a combination of different chromatographic columns with different resins can achieve a higher recovery and purity of the products, in addition to the separation of REE from one to another [97,98]. However, the low flow rate of the eluent, e.g., 0.25 to 1.5 mL/min, in the cation exchange resin columns hinder their industrial application. This technique might be suitable in a downstream step where high purity is required.

5.2. Anion Exchange Resin

The anion exchange column is an alternative process for separating metal ions from the contaminating elements where chelating resins such as Dowex [99] and Amberlite [100–106] are employed. The efficiency of the separation depends on both the anion exchange resin and the type of acidic eluent [99–101,106]. A malonic acid eluent in methanol is employed to circulate impurities through the Dowex ion-exchange column, resulting in the adsorption of uranium with an efficiency of over 99%. However, thorium recovery was inefficient, and it remained with REE in the eluate. The Amberlite XAD-4 is another anion exchange resin that is applicable in a wide range of pH [100] and could achieve 99% recovery of uranium [107]. Compared to the XAD-4, the Amberlite XAD-2 has less surface area and larger pore diameter, and extracts uranium when impregnated with Cyanex 302; however, it also partially co-extract thorium (separation factor U/Th = 1.2×10^4) [101]. In some cases, methanol is employed to elute the collected uranium in the column [101,107].

The anion exchange resin column is effective for uranium separation from REE, whereas it is inefficient for thorium separation [108]. Therefore, it can be used as the last step of REE purification. The Amberlite IRA 402 Cl resin was applied as a final purification step in a successive separation of thorium and uranium by precipitation. The low concentration uranium remained with the REE was then separated by anion chromatography, where REE recovery of 99% was achieved by the elution with NaCl. Next, 99% of uranium was recovered by water elution, Figure 8 adapted from [106].

In terms of the potential for the scale-up, in anion exchange resins, similar to cation exchange resins, the small flow rate of the feed solution, e.g., around 1 mL/min, is a significant limitation for an industrial-scale application [99,100,106].
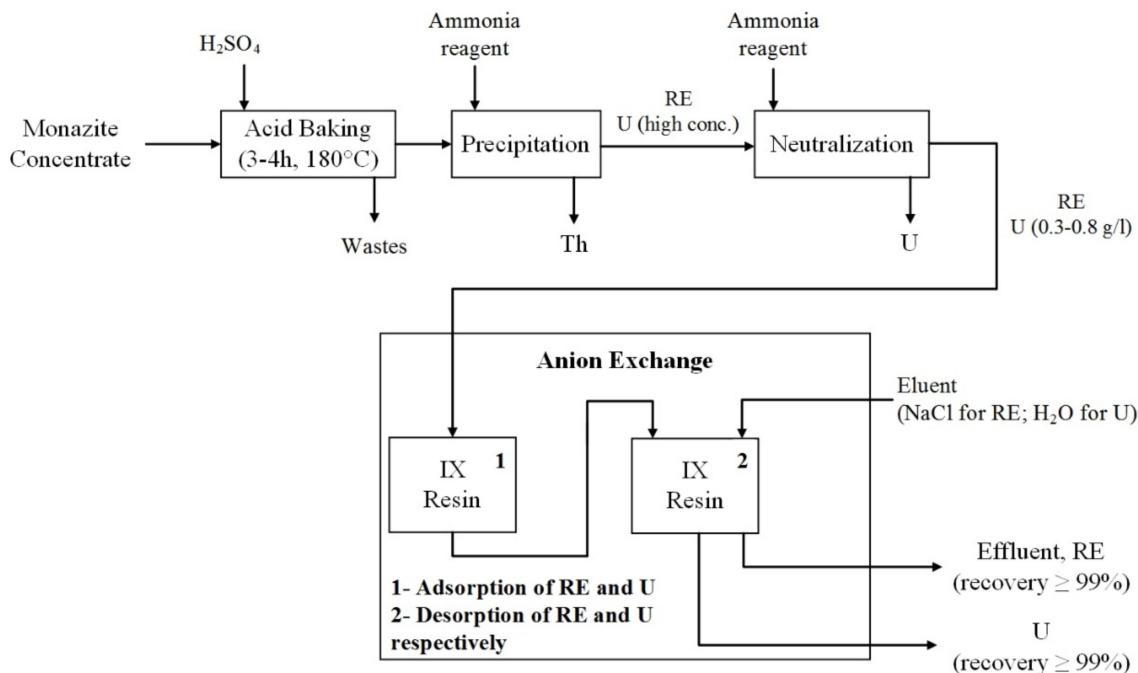
Figure 8. Flow diagram of uranium removal from REE.

6. Separation by Membranes

Membranes have emerged as a new method for recovering thorium and uranium from the REE. At first glance, membranes were used due to their selectivity to individually recover thorium and uranium from other metal ions in liquid solutions [109–111], e.g., recovery of thorium by either graphene oxide (GO) or a silica membrane [112,113]. Such a recovery occurred by the formation of a complex between the element of interest and the membrane. In general, membranes have proved to be efficient and selective in acidic conditions at a pH of 4 to 5.5 for recovery of uranium and lower than 4 to recover thorium. However, to increase the recovery of radioactive elements, it is required to functionalize the membrane using an additive with a higher selectivity towards target elements [114–119]. Membrane functionalization is done by polymer adsorption at the membrane surface. Several functionalization methods are described in detail by Xu et al. [120]. The functionalized membrane has two main purposes, increasing the membrane resistance to the acid media, i.e., at pH lower than 4, and allowing for a better affinity of the membrane toward some ions by modifying some of the membrane parameters, e.g., surface rugosity, conductivity or hydrophobicity [120,121]. In this case, membrane functionalization is thus synonym of a increasing the selectivity of the membrane towards thorium and uranium versus REE (neodymium, europium, and samarium) at ambient conditions and pH below 2. For instance, Li et al. [109] functionalized graphene oxide with PDA (GO-PDA) and showed that, as in Figure 9 adapted from [109], it is more efficient for simultaneous recovery of thorium and uranium as compared with a graphene oxide membrane. The selectivity increase was caused by the surface modification of the functionalization that generated porous channels in the membrane that allowed the REE to pass through at low pH while being impermeable to thorium and uranium [109].

Despite the encouraging performance of the functionalized membranes for simultaneous recovery of radionuclides from the REE, further study is essential to evaluate the effect of various functionalized groups towards selectivity or the regeneration capability of the membranes, especially at high acidic conditions.
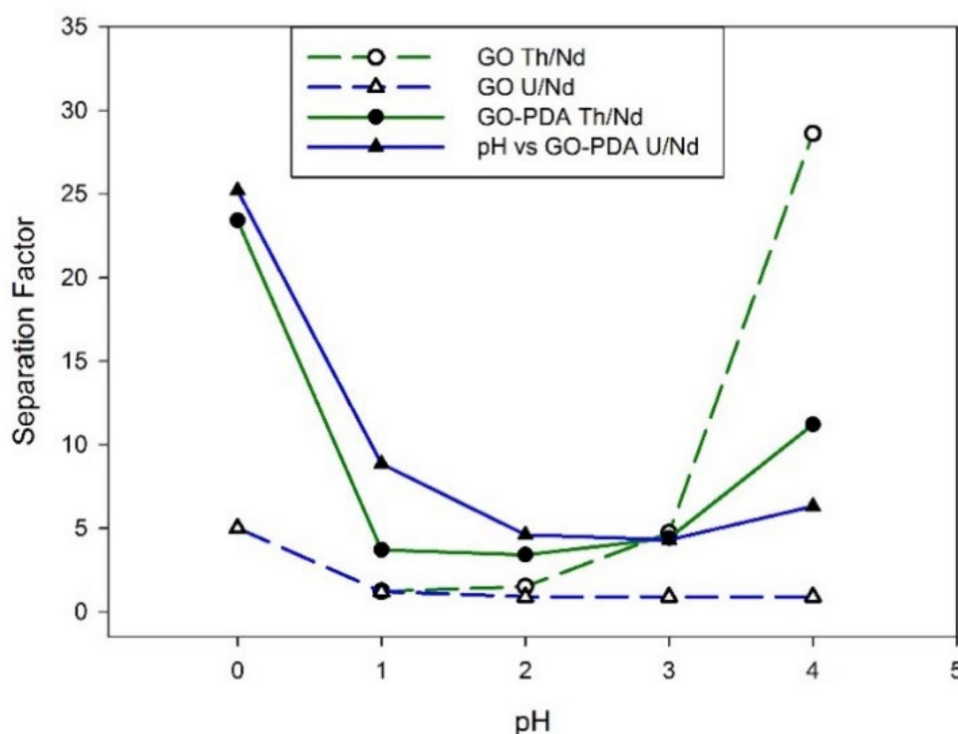
Figure 9. Separation factor of actinides/Nd by graphene oxide (GO) and functionalized graphene oxide with PDA (GO-PDA) membranes. (Reproduced with permission from ref. [109], copyright (2012), Elsevier).

7. Selection of a Separation Process and Potential Waste Management Approaches

Selection of an appropriate process from the presented methods for separating radioactive elements from REE requires various considerations such as the composition of the fresh ore, the applied upstream processes, operating conditions of the reagent, temperature and pH, scale of the process, purification range, and economy of the process, as well as advantages and limitations in each separation techniques. Table 7 summarizes these considerations for leaching, precipitation, solvent extraction, and ion chromatography.

As the separation of the radioactive elements from the REE is required in the REE supply chain, a new problem appears after this step since the presence of radioactive elements in tailings issues a waste management problem. Even though several waste management techniques exist such as water dilution [122], used when thorium and uranium are in the aqueous phase, or the safe storage when they are in the solid phase [123], those seem unreasonable due to high water or space occupation as well as health problem they may generate. One of the most recent propositions was to use thorium as a co-product of the REE industry as it would reduce the waste management problems, and could be used as a feed in the new generation of nuclear reactors [124,125]. As a matter of the fact, thorium is already a co-product of the titanium industry, and its recovery from the REE industry would represent the third most important thorium resource after titanium and uranium [124,126].

Table 7. Advantages and disadvantages of different methods for separating radioactive elements from REE.

Table	Advantages	Limitations	Recovery (%)	Scalability [4]
Leaching	• Simultaneous recovery of Th & U from REE; • Use of cost-effective reagents;	• Must have a particle size of ore/cake similar or smaller than liberation-equivalent size to avoid higher loss of REE [1]; • Feed (REE-radioactive mixture) must be in solid phase;	Th: >98 [3a] U: 65–95 [3a]	+++
Precipitation	• Simultaneous recovery of Th & U from REE; • Being pH dependent, possible individual precipitation of Th or U from REE; • Use of cost-effective reagents;	• Highly dependent on reagent, pH and sometimes temperature; • Possible co-precipitation of REE with Th & U if right pH is not maintained [2]; • Difficult to separate both Th & U simultaneously from REE with high recovery in one single step2 although it can be possible;	Th ≥ 98 U > 80 [3a] Th > 98 U > 90 [3b]	++
Solvent Extraction	• High selectivity towards Th & U; • High recovery of Th & U in individual separation steps;	• Low recovery of Th & U in simultaneous separation; • Multiple separation steps required for individual separation of Th & U; • Use of chemicals: cost of reagents and environmental impact;	Th ≥ 70 U ≈ 55 [3a] Th > 95 U > 95 [3b]	+++
Ion chromatography	• Extraction of Th & U in one step; • High recovery of both radioactive elements;	• Low flow rates; • Selection of the scale-up technology and configuration (batch, column, expanded/fluidized-bed or suspended bed); • Anion exchange only extracts U (with the presence of ppm);	Th: 90–99 U: 90–99	++

[1] Liberation-equivalent size is the optimum size to separate the desired REE minerals off the ore grain, normally found in physical beneficiation steps. [2] Normally pH should be below 6.5 to avoid co-precipitation of REE with radioactive elements, but in fact, pH is dependent on the liquor and reagent. [3a] Simultaneous separation of Th & U from REE; [3b] Individual separation of Th & U from REE; [4] Scalability factors: +++: easy scale-up (process continuous, well-known or developed in other industries); ++: scale-up with some difficulties (process semi-continuous or discontinuous or difficulty to separate two phases). References: ([127,128]); Leaching ([129,130]); Precipitation ([131,132]); SX ([130,133–135]); Ion chromatography ([136–138]).

8. Conclusions

Radioactive elements (thorium and uranium) are commonly associated with REE-bearing minerals, where the concentration depends on the mineral, the formation of the rocks, and the geographical position of the deposit. The presence of radioactive elements causes various problems in the environment and waste management. The extraction of thorium and uranium is necessary to ensure having a low radioactive product, while the loss of REE is minimized. The utilization of conventional hydrometallurgical processes such as selective precipitation, leaching, and solvent extraction for the extraction of radioactive elements is often conducted using complex industrial processes. There is a new trend of investigating new separation processes, such as the ion-exchange chromatography and membrane separation. These processes are yet at lab-scale development stage, but they seem to result in a more selective separation of Th and U from REE. Further research and development activities are required to maturate such processes and to evolve new technologies for economically viable applications at an industrial scale.

The most critical parameters to be controlled in these methods are the operating conditions (pH, and temperature), reagent type, and upstream processes. Depending on the process requirements and limitations, either one- or multi-steps processing would be applied to efficiently separate radioactive elements from REE. Considering the efficiency and the cost of the process, a specific process can be selected with regard to the advantages and limitations in each process.

Author Contributions: A.C.G. reviewed literature, wrote the first draft, and revised the manuscript. M.L. scientifically reviewed and edited the manuscript. A.A. scientifically reviewed and edited the manuscript. J.C. was the supervisor and also scientifically reviewed the manuscript. All authors have read and agreed to the published version of the manuscript.

References

1. Alami, D. Environmental Applications of Rare-Earth Manganites as Catalysts: A Comparative Study. *Environ. Eng. Res.* **2013**, *18*, 211–219. [CrossRef]
2. Bouzigues, C.; Gacoin, T.; Alexandrou, A. Biological applications of rare-earth based nanoparticles. *ACS Nano* **2011**, *5*, 8488–8505. [CrossRef] [PubMed]
3. Chen, L.; Si, Z.C.; Wu, X.D.; Weng, D.; Ran, R.; Yu, J. Rare earth containing catalysts for selective catalytic reduction of NOx with ammonia: A Review. *J. Rare Earths* **2014**, *32*, 907–917. [CrossRef]
4. Gupta, C.K.; Krishnamurthy, N. *Extractive Metallurgy of Rare Earths*; CRC Press: Boca Raton, FL, USA, 2004.
5. Hu, T.; Deng, R.D.; Yang, X.F. Applications and challenges of rare earth resources in China. In Proceedings of the 2013 3rd International Conference on Information Science, Automation and Material System, ISAM 2013, Guangzhou, China, 13–14 April 2013; pp. 159–162.
6. Jordens, A.; Cheng, Y.P.; Waters, K.E. A review of the beneficiation of rare earth element bearing minerals. *Miner. Eng.* **2013**, *41*, 97–114. [CrossRef]
7. Bhargava, S.K.; Ram, R.; Pownceby, M.; Grocott, S.; Ring, B.; Tardio, J.; Jones, L. A review of acid leaching of uraninite. *Hydrometallurgy* **2015**, *151*, 10–24. [CrossRef]
8. Jaireth, S.; Hoatson, D.M.; Miezitis, Y. Geological setting and resources of the major rare-earth-element deposits in Australia. *Ore Geol. Rev.* **2014**, *62*, 72–128. [CrossRef]
9. Clow, G.; Salmon, B.; Lavigne, M.; McDonough, B.; Pelletier, P.; Vallières, D. *Technical Report on Expansion Options at the Niobec Mine, Québec, Canada*; IAMGOLD Corporation: Toronto, ON, Canada, 2011.
10. Bosserman, P.J. *Recovery of Cerium*; Google Patents: Mountain View, CA, USA, 1995.
11. Zou, D.; Chen, J.; Li, D.Q. Separation chemistry and clean technique of cerium(IV): A review. *J. Rare Earths* **2014**, *32*, 681–685. [CrossRef]

12. Simandl, G.J. Geology and economic sifnificance of current and future rare earth element sources. In Proceedings of the 51st Annual Conference of Metallurgists, Niagara Falls, ON, Canada, 30 September–3 October 2012.

13. Mowafy, A.M. Biological leaching of rare earth elements. *World J. Microbiol. Biotechnol.* **2020**, *36*, 61. [CrossRef]

14. Driscoll, M.O. An Overview of Rare Earth Minerals Supply and Applications. In *Materials Science Forum*; Trans Tech Publications Ltd.: Zurich, Switzerland, 1991; pp. 409–420.

15. Jones, A.P.; Wall, F.; Williams, C.T. *Rare Earth Minerals: Chemistry, Origin and Deposits*; Springer: London, UK, 1996.

16. Zhang, J.; Edwards, C. A Review of Rare Earth Mineral Processing Technology. In Proceedings of the 44th Annual Canadian Mineral Processors Operators Conference, Ottawa, ON, Canada, 19–21 January 2010.

17. Chambers, D.B.; Lowe, L.M.; Feasby, D.G. Radiological aspects of naturally occuring radioactive materials (NORM) in the ore processing and production of rare earth element concentrates. In Proceedings of the 51st Annual Conference of Metallurgists, COM, Niagara Falls, ON, Canada, 30 September–3 October 2012.

18. Feasby, D.G.; Chambers, D.B.; Lowe, L.M. Assesment and management of radioactivity in rare earth elements production. In Proceedings of the Rare Earth Elements (COM 2013), West Westmount, QC, Canada, 27–31 October 2013.

19. Park, B.T. Management of thorium and uranium in mining and processing of rare earth minerals. In Proceedings of the 51st Annual Conference of Metallurgists, Niagara, ON, Canada, 30 September–3 October 2012; pp. 171–184.

20. Cheng, J.; Hou, Y.; Che, L. Flotation separation on rare earth minerals and gangues. *J. Rare Earths* **2007**, *25*, 62–66.

21. Fang, J.; Zhao, D. Separation of rare earth from tails of magnetite separation in Bao Steel's concentrator. *Met. Mine* **2003**, *321*, 47–49.

22. Goode, J.R. Thorium and rare earth recovery in Canada: The first 30 years. *Can. Metall. Q.* **2013**, *52*, 234–242. [CrossRef]

23. Kogel, J.E.; Trivedi, N.C.; Barker, J.M.; Krukowsky, S.T. *Industrial Minerals & Rocks: Commodities, Markets and Uses*, 7th ed.; Society for Mining, Metallurgy, and Exploration, Inc.: Littleton, CO, USA, 2006.

24. Dev, S.; Sachan, A.; Dehghani, F.; Ghosh, T.; Briggs, B.R.; Aggarwal, S. Mechanisms of biological recovery of rare-earth elements from industrial and electronic wastes: A review. *Chem. Eng. J.* **2020**, *397*, 124596. [CrossRef]

25. Deshmane, V.G.; Islam, S.Z.; Bhave, R.R. Selective Recovery of Rare Earth Elements from a Wide Range of E-Waste and Process Scalability of Membrane Solvent Extraction. *Environ. Sci. Technol.* **2020**, *54*, 550–558. [CrossRef] [PubMed]

26. Rivera, R.M.; Ulenaers, B.; Ounoughene, G.; Binnemans, K.; Van Gerven, T. Extraction of rare earths from bauxite residue (red mud) by dry digestion followed by water leaching. *Miner. Eng.* **2018**, *119*, 82–92. [CrossRef]

27. Reid, S.; Tam, J.; Yang, M.; Azimi, G. Technospheric Mining of Rare Earth Elements from Bauxite Residue (Red Mud): Process Optimization, Kinetic Investigation, and Microwave Pretreatment. *Sci. Rep.* **2017**, *7*, 15252. [CrossRef]

28. Borra, C.R.; Pontikes, Y.; Binnemans, K.; Van Gerven, T. Leaching of rare earths from bauxite residue (red mud). *Miner. Eng.* **2015**, *76*, 20–27. [CrossRef]

29. Davris, P.; Balomenos, E.; Panias, D.; Paspaliaris, I. Selective leaching of rare earth elements from bauxite residue (red mud), using a functionalized hydrophobic ionic liquid. *Hydrometallurgy* **2016**, *164*, 125–135. [CrossRef]

30. Tuan, L.Q.; Thenepalli, T.; Chilakala, R.; Vu, H.H.; Ahn, J.W.; Kim, J. Leaching Characteristics of Low Concentration Rare Earth Elements in Korean (Samcheok) CFBC Bottom Ash Samples. *Sustainability* **2019**, *11*, 2562. [CrossRef]

31. Abdel-Rehim, A.M. An innovative method for processing Egyptian monazite. *Hydrometallurgy* **2002**, *67*, 9–17. [CrossRef]

32. El-Nadi, Y.A.; Daoud, J.A.; Aly, H.F. Modified leaching and extraction of uranium from hydrous oxide cake of Egyptian monazite. *Int. J. Miner. Process.* **2005**, *76*, 101–110. [CrossRef]

33. Lapidus, G.T.; Doyle, F.M. Selective thorium and uranium extraction from monazite: I. Single-stage oxalate leaching. *Hydrometallurgy* **2015**, *154*, 102–110. [CrossRef]

34. Lapidus, G.T.; Doyle, F.M. Selective thorium and uranium extraction from monazite: II. Approaches to enhance the removal of radioactive contaminants. *Hydrometallurgy* **2015**, *155*, 161–167. [CrossRef]

35. Alex, P.; Hubli, R.C.; Suri, A.K. Processing of rare earth concentrates. *Rare Met.* **2005**, *24*, 210–215.

36. Eyal, Y.; Olander, D.R. Leaching of uranium and thorium from monazite: I. Initial leaching. *Geochim. Et Cosmochim. Acta* **1990**, *54*, 1867–1877. [CrossRef]

37. Panda, R.; Kumari, A.; Jha, M.K.; Hait, J.; Kumar, V.; Kumar, J.R.; Lee, J.Y. Leaching of rare earth metals (REMs) from Korean monazite concentrate. *J. Ind. Eng. Chem.* **2014**, *20*, 2035–2042. [CrossRef]

38. Shaw, K.G. *A Process for Separating Thorium Compounds from Monazite Sands*; Iowa State University: Ames, IA, USA, 1953.

39. Amer, T.E.; Abdella, W.M.; Wahab, G.M.A.; El-Sheikh, E.M. A suggested alternative procedure for processing of monazite mineral concentrate. *Int. J. Miner. Process.* **2013**, *125*, 106–111. [CrossRef]

40. Chi, R.; Xu, Z. A solution chemistry approach to the study of rare earth element precipitation by oxalic acid. *Met. Mater Trans B* **1999**, *30*, 189–195. [CrossRef]

41. Kul, M.; Topkaya, Y.; Karakaya, I. Rare earth double sulfates from pre-concentrated bastnasite. *Hydrometallurgy* **2008**, *93*, 129–135. [CrossRef]

42. Fourest, B.; Lagarde, G.; Perrone, J.; Brandel, V.; Dacheux, N.; Genet, M. Solubility of thorium phosphate-diphosphate. *New J. Chem.* **1999**, *23*, 645–649. [CrossRef]

43. Borai, E.H.; Abd El-Ghany, M.S.; Ahmed, I.M.; Hamed, M.M.; Shahr El-Din, A.M.; Aly, H.F. Modi fi ed acidic leaching for selective separation of thorium, phosphate and rare earth concentrates from Egyptian crude monazite. *Int. J. Miner. Process.* **2016**, *149*. [CrossRef]

44. Krebs, D.G.I.; Furfaro, D. The Kvanefjeld process. In Proceedings of the Alta 2013 Uranium-REE Conference, Perth, Australia, 25 May–1 June 2013.

45. Pawlik, C. Recovery of rare earth elements from complex and low grade deposits. In Proceedings of the ALTA 2013 Uranium-REE Conference, Perth, Australia, 25 May–1 June 2013.

46. Vijayalakshmi, R.; Mishra, S.L.; Singh, H.; Gupta, C.K. Processing of xenotime concentrate by sulphuric acid digestion and selective thorium precipitation for separation of rare earths. *Hydrometallurgy* **2001**, *61*, 75–80. [CrossRef]

47. Bearse, A.E.; Calkins, G.D.; Clegg, J.W.; Filbert, J.R.B. Thorium and rare earths from monazite. *Chem. Eng. Prog.* **1954**, *50*, 235–239.

48. Mackowski, S.J.; Raiter, R.; Soldenhoff, K.H.; Ho, E.M. Recovery of Rare Earth Elements. U.S. Patent 7,993,612 B2, 9 August 2011.

49. Yu, B.; Verbaan, N.; Pearse, G.; Britt, S. Beneficiation and extraction of REE from GEOMEGA resources' Montviel project. In Proceedings of the Rare Earth Elements (COM 2013), West Westmount, QC, Canada, 30 September–3 October 2013.

50. Grimaldi, F.S. The analytical chemistry of uranium and thorium. In Proceedings of the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 8 August 1995; pp. 605–617.

51. Tomazic, B.; Branica, M. Separation of uranium(VI) from rare earths(III) by hydrolytic precipitation. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 377–380. [CrossRef]

52. Kang, M.J.; Han, B.E.; Hahn, P.S. Precipitation and adsorption of uranium (VI) under various aqueous conditions. *Environ. Eng. Res.* **2002**, *7*, 149–157.

53. Abreu, R.D.; Morais, C.A. Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide. *Miner. Eng.* **2010**, *23*, 536–540. [CrossRef]

54. Carter, G.; Everest, D.A.; Wells, R.A. Selective oxalate precipitation of thorium from sulfate leach solutions derived from monazite sands. *J. Appl. Chem.* **1960**, *10*, 149–155. [CrossRef]

55. Sozanski, A. Separation of Trace Quantities of Thorium from Lanthanide Solutions by the Method of Coprecipitation. *Przem. Chem.* **1978**, *57*, 360–362.

56. Chi, R.; Xu, Z.; Zhang, Z.; He, Z.; Ruan, Y. Review on separation and treatment of thorium resources. In Proceedings of the Conference of Metallurgists Proceedings, Vancouver, BC, Canada, 28 September–1 October 2014.

57. Crouse, D.J.; Brown, K.B. The Amex Process for Extracting Thorium Ores with Alkyl Amines. *Ind. Eng. Chem.* **1959**, *51*, 1461–1464. [CrossRef]

58. Amaral, J.C.B.S.; Morais, C.A. Thorium and uranium extraction from rare earth elements in monazite sulfuric acid liquor through solvent extraction. *Miner. Eng.* **2010**, *23*, 498–503. [CrossRef]

59. Borai, E.H.; Shahr El-Din, A.M.; El-Sofany, E.A.; Sakr, A.A.; El-Sayed, G.O. Extraction and Separation of Some Naturally Occurring Radionuclides from Rare Earth Elements by Different Amines. *Arab J. Nucl. Sci. Appl.* **2014**, *47*, 48–60.

60. Li, D.Q.; Zuo, Y.; Meng, S.L. Separation of thorium(IV) and extracting rare earths from sulfuric and phosphoric acid solutions by solvent extraction method. *J. Alloy. Compd.* **2004**, *374*, 431–433. [CrossRef]

61. Crouse, D.J.; Brown, K.B. *Recovery of Thorium, Uranium and Rare Earths from Monazite Sulfate Liquors by the Amine Extraction (AMEX) Process*; Oak Ridge National Laboratory: Oak Ridge, TN, USA, 1959.

62. Cox, J.J.; Ciuculescu, T.; Altman, K.; Hwozdyk, L. *Technical Report on the Eco Ridge Mine Project, Elliot Lake Area, Ontario, Canada*; Roscoe Postle Associates Inc.: Toronto, ON, Canada, 2012.

63. Chunhua, Y.; Jiangtao, J.; Chunsheng, L.; Sheng, W.; Guangxia, X. Rare Earth Separation in China. *Tsingshua Sci. Technol.* **2006**, *11*, 241–247.

64. Wang, Y.L.; Li, Y.L.; Li, D.Q.; Liao, W.P. Kinetics of thorium extraction with di-(2-ethylhexyl) 2-ethylhexyl phosphonate from nitric acid medium. *Hydrometallurgy* **2013**, *140*, 66–70. [CrossRef]

65. Zhao, J.M.; Zuo, Y.; Li, D.Q.; Liu, S.Z. Extraction and separation of cerium(IV) from nitric acid solutions containing thorium(IV) and rare earths(III) by DEHEHP. *J. Alloy. Compd.* **2004**, *374*, 438–441. [CrossRef]

66. Liu, J.J.; Wang, W.W.; Li, D.Q. Interfacial behavior of primary amine N1923 and the kinetics of thorium(IV) extraction in sulfate media. *Colloid Surf. A* **2007**, *311*, 124–130. [CrossRef]

67. Cianetti, C.; Danesi, P.R. Kinetics and mechanism in metal solvent extraction by some organophosphorous extractants. In Proceedings of the International Solvent Extraction Conference, ISEC, Denver, CO, USA, 26 August–2 September 1983.

68. Biswas, S.; Pathak, P.N.; Singh, D.K.; Roy, S.B. Comparative Evaluation of Tri-n-butyl Phosphate (TBP) and Tris(2-ethylhexyl) Phosphate (TEHP) for the Recovery of Uranium from Monazite Leach Solution. *Sep. Sci. Technol.* **2013**, *48*, 2013–2019. [CrossRef]

69. Nasab, M.E.; Sam, A.; Milani, S.A. Determination of optimum process conditions for the separation of thorium and rare earth elements by solvent extraction. *Hydrometallurgy* **2011**, *106*, 141–147. [CrossRef]

70. Gupta, C.K.; Krishnamurthy, N. Extractive Metallurgy of Rare-Earths. *Int. Mater. Rev.* **1992**, *37*, 197–248. [CrossRef]

71. Lu, Y.; Bi, Y.; Bai, Y.; Liao, W. Extraction and separation of thorium and rare earths from nitrate medium withp-phosphorylated calixarene. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 1836–1840. [CrossRef]

72. Rabie, K.A.; Abdel-Wahaab, S.M.; Mahmoud, K.F.; Hussein, A.E.M.; Abd El-Fatah, A.I. Monazite- Uranium Separation and Purification Applying Oxalic- Nitrate-TBP extraction. *Arab J. Nucl. Sci. Appl.* **2013**, *46*, 30–42.

73. Zhang, Y.Q.; Xu, Y.; Huang, X.W.; Long, Z.Q.; Cui, D.L.; Hu, F. Study on thorium recovery from bastnaesite treatment process. *J. Rare Earths* **2012**, *30*, 374–377. [CrossRef]

74. Rakesh, K.B.; Suresh, A.; Rao, P.R.V. Separation of U(VI) and Th(IV) from Nd(III) by Cross-Current Solvent Extraction Mode Using Tri-iso-amyl Phosphate as the Extractant. *Solvent Extr. Ion Exch.* **2015**, *33*, 448–461. [CrossRef]

75. Li, Y.L.; Lu, Y.C.; Bai, Y.; Liao, W.P. Extraction and separation of thorium and rare earths with 5,11,17,23-tetra (diethoxyphosphoryl)-25,26,27,28-tetraacetoxycalix[4]arene. *J. Rare Earths* **2012**, *30*, 1142–1145. [CrossRef]

76. Ali, A.M.I.; El-Nadi, Y.A.; Daoud, J.A.; Aly, H.F. Recovery of thorium (IV) from leached monazite solutions using counter-current extraction. *Int. J. Miner. Process.* **2007**, *81*, 217–223. [CrossRef]

77. He, L.T.; Jiang, Q.; Jia, Y.M.; Fang, Y.Y.; Zou, S.L.; Yang, Y.Y.; Liao, J.L.; Liu, N.; Feng, W.; Luo, S.Z.; et al. Solvent extraction of thorium(IV) and rare earth elements with novel polyaramide extractant containing preorganized chelating groups. *J. Chem. Technol. Biot.* **2013**, *88*, 1930–1936. [CrossRef]

78. Sato, T. The extraction of uranium (VI) from sulphuric acid solutions by di-(2-ethyl hexyl)-phosphoric acid. *J. Inorg. Nucl. Chem.* **1962**, *24*, 699–706. [CrossRef]

79. Sato, T. The Extraction of Thorium from Hydrochloric Acid Solutions by di-(2-ethylhexyl)-phosphoric acid. *Z. Für Anorg. Und Allg. Chem.* **1968**, *358*, 296–304. [CrossRef]

80. Sato, T. Liquid-Liquid Extraction of Rare-Earth Elements from Aqueous Acid Solutions by Acid Organophosphorus Compounds. *Hydrometallurgy* **1989**, *22*, 121–140. [CrossRef]

81. Gupta, B.; Malik, P.; Deep, A. Extraction of uranium, thorium and lanthanides using Cyanex-923: Their separations and recovery from monazite. *J. Radioanal. Nucl. Chem.* **2002**, *251*, 451–456. [CrossRef]

82. Karve, M.; Gaur, C. Extraction of U(VI) with Cyanex 302. *J. Radioanal. Nucl. Chem.* **2007**, *273*, 405–409. [CrossRef]

83. Nasab, M.E.; Milani, S.A.; Sam, A. Extractive separation of Th(IV), U(VI), Ti(IV), La(III) and Fe(III) from Zarigan ore. *J. Radioanal. Nucl. Chem.* **2011**, *288*, 677–683. [CrossRef]

84. Belova, V.V.; Egorova, N.S.; Voshkin, A.A.; Khol'kin, A.I. Extraction of rare earth metals, uranium, and thorium from nitrate solutions by binary extractants. *Theor. Found. Chem. Eng.* **2015**, *49*, 545–549. [CrossRef]

85. Singh, H.; Mishra, S.L.; Vijayalakshmi, R. Uranium recovery from phosphoric acid by solvent extraction using a synergistic mixture of di-nonyl phenyl phosphoric acid and tri-n-butyl phosphate. *Hydrometallurgy* **2004**, *73*, 63–70. [CrossRef]

86. Singh, S.K.; Dhami, P.S.; Tripathi, S.C.; Dakshinamoorthy, A. Studies on the recovery of uranium from phosphoric acid medium using synergistic mixture of (2-Ethyl hexyl) Phosphonic acid, mono (2-ethyl hexyl) ester (PC88A) and Tri-n-butyl phosphate (TBP). *Hydrometallurgy* **2009**, *95*, 170–174. [CrossRef]

87. Sreenivasulu, B.; Suresh, A.; Sivaraman, N.; Vasudeva Rao, P.R. Solvent extraction studies with some fission product elements from nitric acid media employing tri-iso-amyl phosphate and tri-n-butyl phosphate as extractants. *J. Radioanal. Nucl. Chem.* **2014**, *303*, 2165–2172. [CrossRef]

88. Jain, V.K.; Pandya, R.A.; Pillai, S.G.; Shrivastav, P.S. Simultaneous preconcentration of uranium(VI) and thorium(IV) from aqueous solutions using a chelating calix[4]arene anchored chloromethylated polystyrene solid phase. *Talanta* **2006**, *70*, 257–266. [CrossRef]

89. Patil, N.N.; Shinde, V.M. Extraction study of uranium(VI) and thorium(IV) salicylates with triphenylarsine oxide. *J. Radioanal. Nucl. Chem.* **1997**, *222*, 21–24. [CrossRef]

90. Singh, H.; Gupta, C.K. Solvent Extraction in Production and Processing of Uranium and Thorium. *Miner. Process. Extr. Metall. Rev.* **2000**, *21*, 307–349. [CrossRef]

91. Borai, E.H.; Mady, A.S. Separation and quantification of 238U, 232Th and rare earths in monazite samples by ion chromatography coupled with on-line flow scintillation detector. *Appl. Radiat. Isot. Incl. Datainstrumentation Methods Use Agric. Ind. Med.* **2002**, *57*, 463–469. [CrossRef]

92. Jeyakumar, S.; Mishra, V.G.; Das, M.K.; Raut, V.V.; Sawant, R.M.; Ramakumar, K.L. Separation behavior of U(VI) and Th(IV) on a cation exchange column using 2,6-pyridine dicarboxylic acid as a complexing agent and its application for the rapid separation and determination of U and Th by ion chromatography. *J. Sep. Sci.* **2011**, *34*, 609–616. [CrossRef]

93. Pin, C.; Zalduegui, J.F.S. Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: Application to isotopic analyses of silicate rocks. *Anal. Chem. Acta* **1997**, *339*, 79–89. [CrossRef]

94. Soran, M.L.; Curtui, M.; Marutoiu, C. Separation of U(VI) and Th(IV) from some rare earths by thin layer chromatography with di-(2-ethylhexyl)-dithiophosphoric acid on silica gel. *J. Liq. Chromatogr. Relat. Technol.* **2005**, *28*, 2515–2524. [CrossRef]

95. Sivaraman, N.; Kumar, R.; Subramaniam, S.; Rao, P.R.V. Separation of lanthanides using ion-interaction chromatography with HDEHP coated columns. *J. Radioanal. Nucl. Chem.* **2002**, *252*, 491–495. [CrossRef]

96. Ostapenko, V.; Vasiliev, A.; Lapshina, E.; Ermolaev, S.; Aliev, R.; Totskiy, Y.; Zhuikov, B.; Kalmykov, S. Extraction chromatographic behavior of actinium and REE on DGA, Ln and TRU resins in nitric acid solutions. *J. Radioanal. Nucl. Chem.* **2015**, *306*, 707–711. [CrossRef]

97. Ling, L.; Wang, N.H. Ligand-assisted elution chromatography for separation of lanthanides. *J. Chromatogr. A* **2015**, *1389*, 28–38. [CrossRef]

98. Soran, M.-L.; Hodişan, T.; Curtui, M.; Casoni, D. TLC separation of rare earths using di(2-ethylhexyl)dithiophosphoric acid as complexing reagent. *J. Planar Chromatogr. Mod. Tlc* **2005**, *18*, 160–163. [CrossRef]

99. Korkisch, J.; Hazan, I. Anion-exchange behaviour of uranium and other elements in the presence of aliphatic di- and tricarboxylic acids. *Talanta* **1964**, *11*, 523–530. [CrossRef]

100. Dev, K.; Pathak, R.; Rao, G.N. Sorption behaviour of lanthanum(III), neodymium(III), terbium(III), thorium(IV) and uranium(VI) on Amberlite XAD-4 resin functionalized with bicine ligands. *Talanta* **1999**, *48*, 579–584. [CrossRef]

101. Karve, M.; Rajgor, R.V. Amberlite XAD-2 impregnated organophosphinic acid extractant for separation of uranium(VI) from rare earth elements. *Desalination* **2008**, *232*, 191–197. [CrossRef]

102. Merdivan, M.; Duz, M.Z.; Hamamci, C. Sorption behaviour of uranium(VI) with N,N-dibutyl-N'-benzoylthiourea Impregnated in Amberlite XAD-16. *Talanta* **2001**, *55*, 639–645. [CrossRef]

103. Metilda, P.; Sanghamitra, K.; Mary Gladis, J.; Naidu, G.R.; Prasada Rao, T. Amberlite XAD-4 functionalized with succinic acid for the solid phase extractive preconcentration and separation of uranium(VI). *Talanta* **2005**, *65*, 192–200. [CrossRef] [PubMed]

104. Metwally, E.; Saleh, A.S.; El-Naggar, H.A. Extraction and Separation of Uranium (VI) and Thorium (IV) Using Tri-n-dodecylamine impregnated resins. *J. Nucl. Radiochem. Sci.* **2005**, *6*, 119–126. [CrossRef]

105. Prabhakaran, D.; Subramanian, M.S. Extraction of U(VI), Th(IV), and La(III) from acidic streams and geological samples using AXAD-16-POPDE polymer. *Anal. Bioanal. Chem.* **2004**, *380*, 578–585. [CrossRef] [PubMed]

106. Rabie, K.A.; AbdElMoneam, Y.K.; Abdelfattah, A.I.; Demerdahs, M.; Salem, A.R. Adaptation of anion exchange process to decontaminate monazite rare earth group from its uranium content. *Int. J. Res. Eng. Technol.* **2014**, *3*, 374–382.

107. Singh, B.N.; Maiti, B. Separation and preconcentration of U(VI) on XAD-4 modified with 8-hydroxy quinoline. *Talanta* **2006**, *69*, 393–396. [CrossRef]

108. Ang, K.L.; Li, D.; Nikoloski, A.N. The effectiveness of ion exchange resins in separating uranium and thorium from rare earth elements in acidic aqueous sulfate media. Part 1. Anionic and cationic resins. *Hydrometallurgy* **2017**, *174*, 147–155. [CrossRef]

109. Li, Z.; Chen, F.; Yuan, L.; Liu, Y.; Zhao, Y.; Chai, Z.; Shi, W. Uranium(VI) adsorption on graphene oxide nanosheets from aqueous solutions. *Chem. Eng. J.* **2012**, *210*, 539–546. [CrossRef]

110. Li, F.; Yang, Z.; Weng, H.; Chen, G.; Lin, M.; Zhao, C. High efficient separation of U(VI) and Th(IV) from rare earth elements in strong acidic solution by selective sorption on phenanthroline diamide functionalized graphene oxide. *Chem. Eng. J.* **2018**, *332*, 340–350. [CrossRef]

111. Song, W.; Wang, X.; Wang, Q.; Shao, D.; Wang, X. Plasma-induced grafting of polyacrylamide on graphene oxide nanosheets for simultaneous removal of radionuclides. *Phys. Chem. Chem. Phys.* **2015**, *17*, 398–406. [CrossRef]

112. Sadeghi, S.; Sheikhzadeh, E. Solid phase extraction using silica gel modified with murexide for preconcentration of uranium (VI) ions from water samples. *J. Hazard Mater.* **2009**, *163*, 861–868. [CrossRef]

113. Xu, H.; Li, G.; Li, J.; Chen, C.; Ren, X. Interaction of Th(IV) with graphene oxides: Batch experiments, XPS investigation, and modeling. *J. Mol. Liq.* **2016**, *213*, 58–68. [CrossRef]

114. Cheng, W.; Wang, M.; Yang, Z.; Sun, Y.; Ding, C. The efficient enrichment of U(vi) by graphene oxide-supported chitosan. *Rsc Adv.* **2014**, *4*, 61919–61926. [CrossRef]

115. Li, Y.; Wang, C.L.; Liu, C.L. Synthesis and Th(IV) sorption characteristics of functionalised graphene oxide. *J. Radioanal. Nucl. Chem.* **2014**, *302*, 489–496. [CrossRef]

116. Liu, X.; Li, J.; Wang, X.; Chen, C.; Wang, X. High performance of phosphate-functionalized graphene oxide for the selective adsorption of U(VI) from acidic solution. *J. Nucl. Mater.* **2015**, *466*, 56–64. [CrossRef]

117. Pan, N.; Li, L.; Ding, J.; Li, S.; Wang, R.; Jin, Y.; Wang, X.; Xia, C. Preparation of graphene oxide-manganese dioxide for highly efficient adsorption and separation of Th(IV)/U(VI). *J. Hazard Mater.* **2016**, *309*, 107–115. [CrossRef] [PubMed]

118. Shao, D.; Hou, G.; Li, J.; Wen, T.; Ren, X.; Wang, X. PANI/GO as a super adsorbent for the selective adsorption of uranium(VI). *Chem. Eng. J.* **2014**, *255*, 604–612. [CrossRef]

119. Sun, Y.; Shao, D.; Chen, C.; Yang, S.; Wang, X. Highly efficient enrichment of radionuclides on graphene oxide-supported polyaniline. *Environ. Sci. Technol.* **2013**, *47*, 9904–9910. [CrossRef]

120. Xu, Z.; Wan, L.; Huang, X. Functionalization Methods for Membrane Surfaces. *Surf. Eng. Polym. Membr.* **2009**, 64–79. [CrossRef]

121. Li, M.-P.; Zhang, X.; Zhang, H.; Liu, W.-L.; Huang, Z.-H.; Xie, F.; Ma, X.-H.; Xu, Z.-L. Hydrophilic yolk-shell ZIF-8 modified polyamide thin-film nanocomposite membrane with improved permeability and selectivity. *Sep. Purif. Technol.* **2020**, *247*. [CrossRef]

122. Srinivasan, M.; Subba Rao, K.; Dingankar, M.V. The "Actinide Waste" Problem in Perspective. In Proceedings of the Indo-Japan Seminar on Thorium utilization, Bombay, India, 10–13 December 1990.

123. Haridasan, P.P.; Pillai, P.B.M.; Tripathi, R.M.; Puranik, V.D. Operational radiation protection associated with thorium processing in India. In Proceedings of the Naturally Occurring Radioactive Material (NORM VI), Marrakesh, Morocco, 22–26 March 2010.

124. Ault, T.; Krahn, S.; Croff, A. Assessment of the Potential of By-Product Recovery of Thorium to Satisfy Demands of a Future Thorium Fuel Cycle. *Nucl. Technol.* **2015**, *189*, 152–162. [CrossRef]

125. Dekusar, V.M.; Kolesnikova, M.S.; Nikolaev, A.I.; Maiorov, V.G.; Zilberman, B.Y. Mineral reserves of naturally radioactive thorium-bearing raw materials. *At. Energy* **2012**, *111*, 185–194. [CrossRef]

126. Humphries, M. *Rare Earth Elements: The Global Supply Chain*; Diane Publishing: Darby, PA, USA, 2010.

127. Donati, G.; Paludetto, R. Scale up of chemical reactors. *Catal. Today* **1997**, *34*, 483–533. [CrossRef]

128. Dudukovic, M.P. Challenges and Innovations in Reaction Engineering. *Chem. Eng. Commun.* **2008**, *196*, 252–266. [CrossRef]

129. Forbes, L.K. The design of a full-scale industrial mineral leaching process. *Appl. Math. Model.* **2001**, *25*, 233–256. [CrossRef]

130. Arroyo, F.; Fernández-Pereira, C.; Bermejo, P. Demonstration Plant Equipment Design and Scale-Up from Pilot Plant of a Leaching and Solvent Extraction Process. *Minerals* **2015**, *5*, 298–313. [CrossRef]

131. Bałdyga, J. Mixing and Fluid Dynamics Effects in Particle Precipitation Processes. *Kona Powder Part. J.* **2016**, *33*, 127–149. [CrossRef]

132. Marchisio, D.L.; Rivautella, L.; Barresi, A.A. Design and scale-up of chemical reactors for nanoparticle precipitation. *Aiche J.* **2006**, *52*, 1877–1887. [CrossRef]

133. De Santana, A.O.; Dantas, C.C. Scale up of the mixer of a mixer-settler model used in a uranium solvent extraction process. *J. Radioanal. Nucl. Chem.* **1995**, *189*, 257–268. [CrossRef]

134. Geeting, M.W.; Brass, E.A.; Brown, S.J.; Campbell, S.G. Scale-up of Caustic-Side Solvent Extraction Process for Removal of Cesium at Savannah River Site. *Sep. Sci. Technol.* **2008**, *43*, 2786–2796. [CrossRef]

135. Kurniawansyah, F.; Mammucari, R.; Tandya, A.; Foster, N.R. Scale—Up and economic evaluation of the atomized rapid injection solvent extraction process. *J. Supercrit. Fluids* **2017**, *127*, 208–216. [CrossRef]

136. Carta, G. Scale-Up and Optimization in Preparative Chromatography: Principles and Biopharmaceutical Applications. Chromatographic Science Series, Volume 88 Edited by Anurag, S. Rathore (Pharmacia Corporation, Chesterfield, MO) and Ajoy Velayudhan (Oregon State University). Marcel Dekker, Inc.: New York, Basel. 2002. xvi + 342 pp. $150.00. ISBN 0-8247-0826-1. *J. Am. Chem. Soc.* **2003**, *125*, 3398–3399. [CrossRef]

137. Heuer, C.; Hugo, P.; Mann, G.; Seidel-Morgenstern, A. Scale up in preparative chromatography. *J. Chromatogr. A* **1996**, *752*, 19–29. [CrossRef]

138. Rathore, A.S.; Velayudhan, A. Guidelines for optimization and scale up in preventive chromatography. *Biopharm Int.* **2003**, *16*, 1.