



A Survey on Various Methods of Extraction and Recovery of Thorium

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Abstract: In this survey, some methods of extraction of thorium such as selective extraction of thorium using phosphorodiamidate, selective cloud point extraction of thorium, extraction of thorium from sulfuric acid baking and leaching of monazite, extraction of thorium from chloride solution using Schiff base were discussed. The decomposition of monazite was manifested by sulfuric acid baking and leaching at an elated temperature. The recovery of thorium (Th) from various sources of rare earth and some selective extraction of thorium by using phosphorodiamidate as an extractant was also reported. Using a special synthesized surface-active ionic liquid extractant (SAIL), the cloud point extraction of thorium was analyzed. A synthesized Schiff base was applied for the extraction of thorium in the strategic solvent extraction method. Thorium, using α -amino phosphate extractant from bastnaesite, recovery by using Cyanex 572 and N1923, recovery of Th from industrial residues and recovery of Th from radioactive waste by using IREPO and monazite leached solution were discussed. In this study, the recovery of thorium from the industrial residue as well as from radioactive residue was also discussed.

Keywords: Extraction, Thorium, Monazite, SAIL, Cyanex[®] 572

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INTRODUCTION

The history of human development is often told by the various form of energy. At first, it was muscle, and later when humans learned to control fire, it was heat energy. Eventually using coal and oil, the world was industrialized. With a growing population, the consumption of energy has been increased. This growing energy demand is met when a human entered into this atomic era. The energy harvested from the splitting of a nucleus has made humans the most advanced species on earth. When the demand for nuclear energy increased, the demand for nuclear fuel like thorium (Th) and uranium (U) is also increased. Even though thorium is not fissile, it is referred to nuclear energy since it is three to four times more

abundant on the surface of the earth than uranium and it also provides the most promising options for nuclear power generation in terms of fuel efficiency and economy (1). Lots of researches had been conducted to find a source of energy that would substitute the place of earth's energy resources that has been depleting rapidly day-by-day. The very promising and environment-friendly approach for meeting the ever-growing energy demand is nuclear energy with the least amount of nuclear waste. One of the greenest energy productions is the thorium reactor (2, 3). The possibility of thorium being the nuclear fuel, has given more importance to the production of thorium worldwide and Thorium is a naturally occurring radioactive material (4, 5).

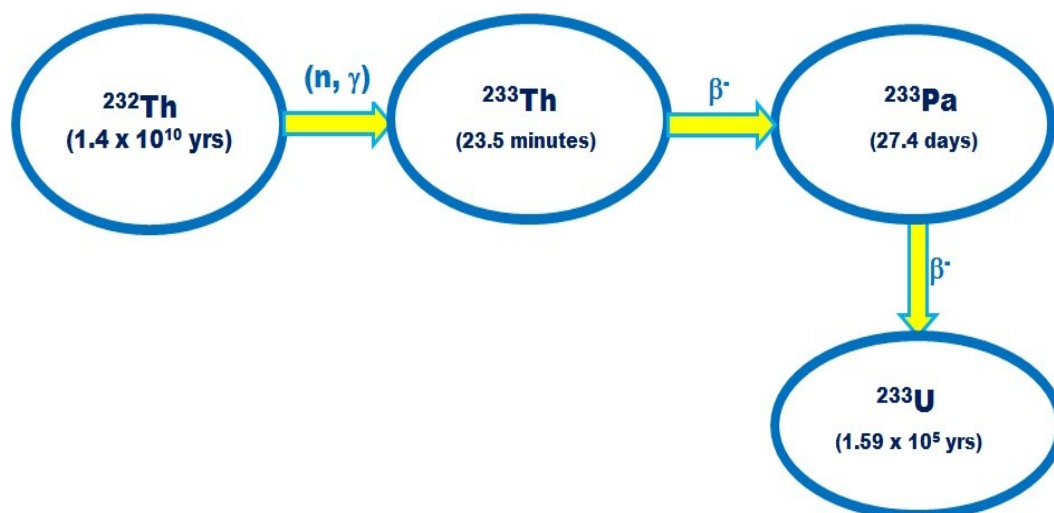


Figure 1: Production of uranium from Thorium (1).

Normally thorium isotopes exist as thorium-232 (^{232}Th) and its half-cycle is around 14 billion years. ^{232}Th is a fertile material that doesn't undergo fission reaction by itself. But a fissile material, i.e., uranium, is produced from its two-beta decay reaction of thorium with a neutron (Figure 1). Out of all nuclear fuels, thorium(IV) oxide (ThO_2) has more advantages compared to uranium because of its lower thermal expansion than uranium(VI) oxide (UO_2) and despite having a similar isometric structure, it is relatively inert (3, 4). The high thermal conductivity of ThO_2 makes it better fuel for nuclear reactors and the thorium fuel is considered an efficient fuel because of its lower hazard nuclear reaction accidents as well as its lower nuclear by-products. In the reactor, there will be no need for fuel reprocessing. The increasing awareness of fuel resources is changing its attitude towards the use of thorium as a fuel resource (5-7). The role of thorium in futuristic green energy production, gives rise to the demand for thorium extraction. There are various methods

for production of Thorium like extraction of thorium by using phosphorodiamidate as extractant, selective cloud point extraction of Th, selective extraction of Th by sulfuric acid baking and leaching of monazite, extraction of Th using a Schiff base etc. (8-12). The extraction behaviors of U(VI) and Th(IV) were investigated by Tan et al. (13) using di(1-methyl-heptyl) methyl phosphonate (DMHMP) as an extractant and kerosene as a diluent. Some novel extractants were synthesized for the separation of thorium and rare earth (RE) by Dong et al. (14). Among the synthesized neutral organophosphorus extractants, n-octyl phosphate diphenyl (ODP) revealed excellent extraction efficiencies and selectivities for Th(IV). The extraction mechanisms of uranium and thorium were studied by Nasab (12). Taguchi's method (12) was used to determine the optimum conditions for the separation of uranium and thorium using neutral extractants. In solvent extraction method, this method has been proposed as powerful method of experimental design (12)

$$(S/N)_i = -10 \left(\frac{1}{n} \sum_i \left(\frac{1}{y_i^2} \right) \right) \quad (1)$$

Where the signal to noise (S/N) ratio is used to determine the best experimental conditions, y_i is the experimental value and n is the number of tests in the experiment. In recent years, the extraction and recovery of thorium ions and their separations from various geological rare earth minerals have gained vital significance due to their wide applications in industries. The different extraction processes of thorium in a single review paper were not found in literatures and thus we have attempted to analyze the processes herewith.

METHODS OF EXTRACTION

Selective Extractions from Rare Earth by Using Phosphorodiamidate as an Extractant

In this method of extraction, an extractant named phosphorodiamidate was synthesized. To separate thorium from rare earth, the medium for the extraction chosen was nitrate medium. The molecular structure for this extractant is given in Figure 2.

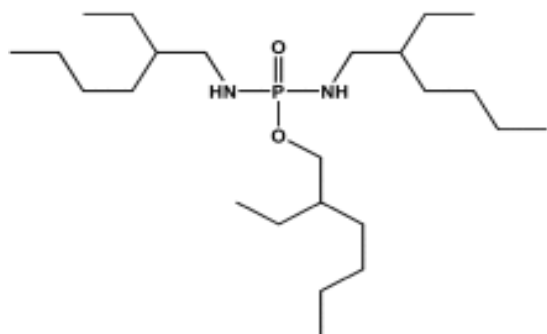


Figure 2: Molecular structure of phosphorodiamidate ligand, designated as **L** (8).

The molecular formula for this extractant is 2-Ethylhexyl-N, N'-di(2-ethylhexyl) phosphorodiamidate. The above extractant was added with a required concentration in n-heptane. The standard solution with concentrated nitric acid was prepared by dissolving corresponding oxides. The prepared solution was diluted with distilled water. The experiment was carried out in a temperature-controlled shaker bath at 298 K. For higher efficiency, nitrate medium with acidity ranging from 0.01 mol/L to 7 mol/L was taken in the extraction process. The extraction of thorium in a different acidic medium generally decreases by the increase in hydration energy of their ions and decrease in hydrophobicity of the extracted complex. The maximum loading capacity of Th in this method was about 48.56 g Th per liter of working solution with 0.69 mol/L of phosphorodiamidate at a 2.1 mol/L concentrated

nitrate medium. The extraction of Th(IV) and U(VI) from dilute nitric acid solution by several neutral phosphorus-based extractants has been studied as a function of temperature in the range of 0–50 °C by Kalina et al. (15). The order of extraction capacity of Th from the different medium: $\text{H}_2\text{SO}_4 < \text{HCl} < \text{HNO}_3$ (16-18). (16-18). In case of phosphoric acid, when the concentration is increased from 1 mol/L to 6.5 mol/L, the thorium stripping becomes 40 % to 70 %. When the concentration of the extractant (L) is increased, the extraction efficiency of thorium has been found more than REs. To reach higher extraction efficiency, the thorium extraction was studied with the acid concentration ranging from 0.01 mol/L to 7 mol/L in different acid medium (8, 16). The stripping of thorium by nitric acid confirmed that the loaded thorium can not be stripped even at high nitric acid concentration. There are maximum value for the stripping efficiency at about 1.5 mol/L for H_2SO_4 and 2.4 mol/L for HCl (8, 16). (8, 16). The higher acid concentration is more helpful for separation of REs. In this method, thorium is extracted in ionic form, Th(IV). The extraction is spontaneous and exothermic.

Cloud Point Extraction (CPE)

It is an eco-friendly method of extraction (9, 19-26). This method of extraction is considered noble because it is inexpensive, fast, selective, precise, and accurate. The procedure is considered green extraction as this method consumes a minimum amount of toxic organic solvents. Figure 3 shows how the cloud point extraction of metal can be done.

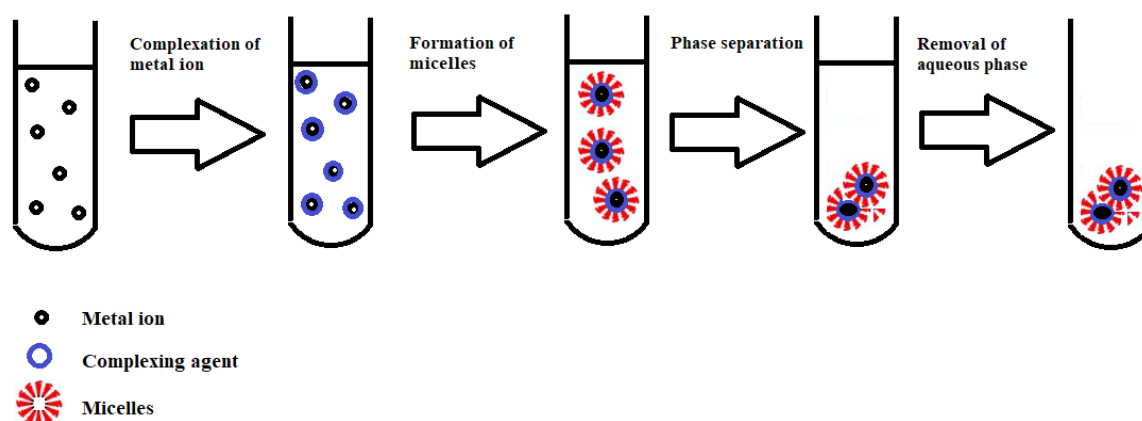


Figure 3: Cloud point extraction method (19).

In the experiment, a known amount of thorium was mixed with an Arsenazo III solution of 0.001 mol/L concentration in a 10 mL centrifuge tube. Then in the Th-Arsenazo III complex, the solutions: 1.0 mL of Triton X-100, 0.5 mL of KI (0.01 mol/L), and 2.5 mL of newly synthesized tetra-cationic surface-active ionic liquid (SAIL)

based on tetraazonia-tricyclodecane derivative (0.001 mol/L) were added respectively with an adjusted pH of 5.0. After taking the solution with deionized water to the mark, it was left in a thermostatic bath (353.15 K) for 30 min to an induced separation. Since the surfactant is denser than water, the solution gets separated into two

phases and the surfactant-rich phase settled through the aqueous phase. Then the tube was cooled down in an ice bath and centrifuged at 6000 rpm for 10 min. Then the aqueous phase was decanted leaving the surfactant-rich phase at the bottom of the tube. The surfactant-rich phase is then diluted with methanol to decrease the viscosity. After that, the extracted sample is moved to the quartz cell for a spectrophotometric determination as shown in Figure 4.

As per the work of Z F Akl and M. A. Hegazy (26), the highest extraction efficiency was achieved at

pH 5.0 with 2.5×10^{-3} mol/L SAIL and 1.0% (v/v) Triton X - 100. At the optimized conditions, the developed method exhibited a linear working range from 10 to 100 ng/mL with a detection limit of 0.77 ng/mL. The temperature also plays a vital role. For efficient extraction, the optimum temperature is 80°C. When the sample is spiked with pre-concentrated Th(IV) by a factor 20, then the extraction percentage of thorium increases more than 98%. This work reported the development of a green, sensitive, selective, and inexpensive method for extraction Th(IV).

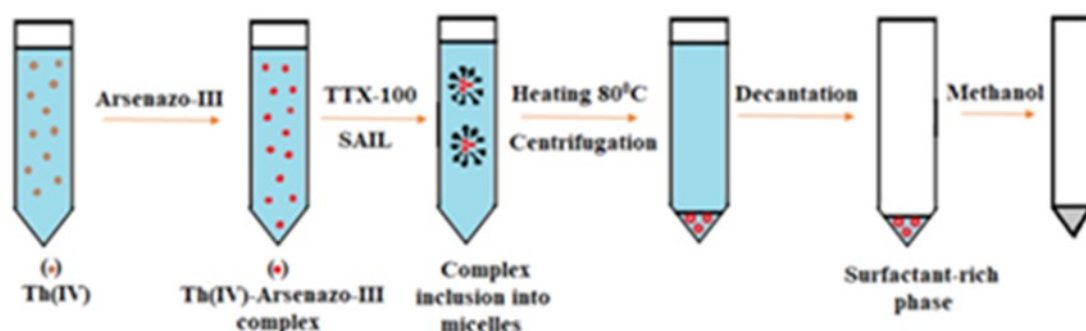


Figure 4: Spectrophotometric determination after cloud point extraction of Th (25).

Selective Extraction of Th by Sulfuric Acid Baking and Leaching of Monazite

Monazite is one of the major sources of thorium and many rare earth elements (REE). In sulfuric acid baking, the rare earth elements were converted into sulfates and those sulfates get dissolved in water leaching process. Monazite was either processed by sulfuric acid baking or alkaline digestion (10). In this process of extraction, at first monazite-sulfuric acid mixture was digested in the stirred reactor at 200 °C to 246 °C. Then the baking was carried out at various temperatures between 200 °C and 800 °C (27). After the baking, the heated sample was removed from the heated furnace and cooled. The cooled sample was ground to a fine powder before it was leached at 40:1 liquid to solid ratio at 20 °C to 29 °C in 0.9 M sulfuric acid for two hours. Then the separation of solid and liquid was done by vacuum filtration. The monazite bearing different concentrates have different bake temperatures. Individual rare earth is not easy to separate from each other because of their similar chemical and physical properties. Before the advancement in industrial solvent extraction, ion exchange techniques were prominent. In environmental and high-tech applications, rare earths are non-replaceable and indispensable because of their unique electro-chemical, luminescent and magnetic properties. To satisfy the diverse application of rare earth, it is mined, screened, and leached for separating it into proper feed materials (28). In this method, one of the influencing factor is precipitation pH. It

is ranging from 2.5 to 5.5 for thorium. But now-a-days solvent extraction is accepted as the most appropriate technique for separating rare earth commercially (29, 30). In this method of extraction, the behaviors of rare earth play a vital role. The separation of uranium and thorium in pure products can be achieved by this method using sulfuric acid liquor and one of the important variables to be considered in the process is the dosage of acid and dilution (31-33). In sulfuric acid baking of rare earth, uranium and thorium get converted into soluble sulfate (34). In the HCl leaching system, the issue of acid consumption is more pronounced. For mineral decomposition in industry, sulfuric acid baking is one of the major processes. This process is responsible for 81% of the world's rare-earth production. There are numerous techniques to investigate the extraction of rare earth metals, but only a few of them are found to be effective and successful. Sulfuric acid baking and leaching are one of them (27, 35-37). The flow chart of sulfuric acid decomposition of monazite is displayed in Figure 5. Various conditions for the baking of minerals, e.g. monazite, have been presented by numerous researchers (27,35-57). This extraction method is exothermic process. The baking of monazite with sulfuric acid gives an enthalpy of -171 kJ/ mol. J. Demol et al. (27) found that the sulfation reaction of monazite with acid resulting in more than 90% solubilization of rare earth elements phosphate and thorium. Their result shows the virtual complete dissolution of rare earth, phosphate, and thorium

during leaching after 250 °C bake. A thorium phosphate type precipitate was formed during leaching after baking at 300 °C and it leads to sharp decrease in extraction of phosphate and

thorium. This method requires high temperature and excessive acids for digestion which involves a number of risk factors while handling the steps.

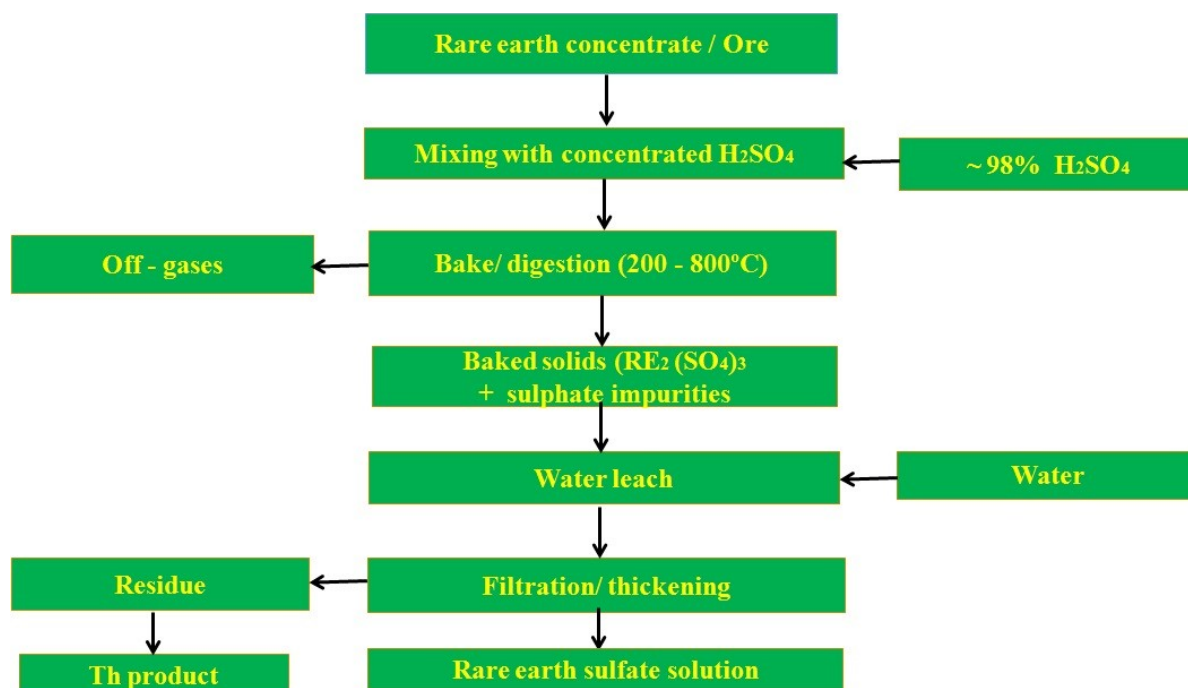


Figure 5: Sulfuric acid treatment of a rare earth mineral concentrate (37).

Extraction of Thorium (IV) from Chloride Solution using Schiff Base

In this strategic method of solvent extraction for thorium selective group extractants such as neutral phosphate (12), amines (12, 58), oximes (59), phosphoric acid (60, 61) and, Schiff base (11, 62, 63) were employed. In this process of extraction,

initially, a synthesized Schiff base (AcPh) was applied for the extraction of thorium from standard solution (1000 mg/L of Th IV) which was prepared by dissolving 2.535 g of thorium nitrate in acidified distilled with 10 mL of concentrated HCl. The preparation of the Schiff base is shown in Figure 6.

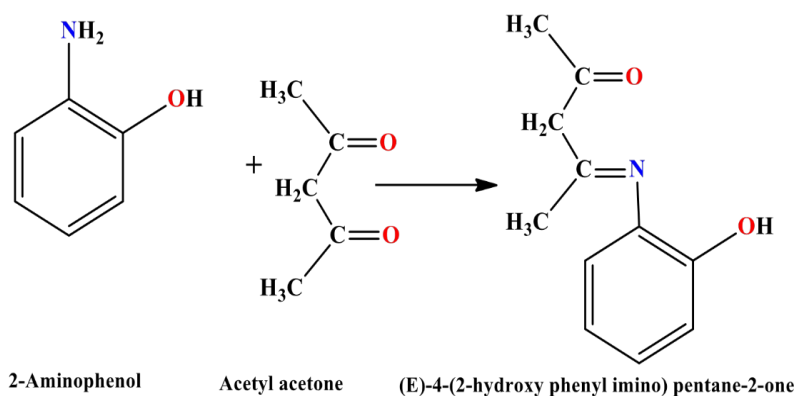


Figure 6: Preparation of the Schiff base (AcPh) (11).

After adding AcPh, then the sample mixture was dissolved in a mixture of diethyl ether and chloroform at the ratio of 2:3. After that sodium malonate was added to the sample containing Th(IV) in chloride form. A dilute solution of HCl/NaOH was added to obtain the desired pH. Then the sample was equilibrated by shaking it for about 7 minutes in a glass with an appropriate

volume of the organic phase. After equilibration, Th in ionic form was separated from its aqueous phase (63, 64). The pH value (≈ 6.5) and concentration of Schiff base are influencing factors for extraction. When the concentration of Schiff base is increased from 0.001 M to 0.002 M, the extraction efficiency of Th(IV) increases from 44% to 96.2% provided the organic phase to aqueous

phase is to be 1:3. M. F. Cheria et al. (11) reported that the maximum extraction efficiency of thorium was obtained at 0.02 M AcPh/chloroform and diethyl ether mixture, 3:1 aqueous to the organic ratio for 5 min contact time at room temperature. The extraction process using Schiff base in chloride medium gives an increased sensitivity of analysis of thorium ions in rock samples. Using this method thorium can be extracted about 330 mg/kg approximately. When phosphorodiamidate extractant used for the extraction, the extraction capacity was found to be 48.55 g per liter of the sample solution. sample solution. The efficiency of stripping decreases gradually with the increase in temperature above room temperature. For efficient extraction the room temperature is considered optimum. This extractant is considered noble as it makes selective extraction of Th from rare earth possible.

RECOVERY OF THORIUM USING DIFFERENT TECHNIQUES, EXTRACTANTS, AND FROM RADIOACTIVE WASTE

Recovery of Thorium(IV) by α -amino phosphate Extractant in Sulfate Medium and from Leach Solution with Cextrant 230

In this process of recovery, α -aminophosphate extractant and Cextrant 230 were used to recovery Th(IV) in sulfate medium and by using leach solution respectively. Here the use of the amine group in phosphate increases the extraction of Th(IV). Bastnasite leaching can be used, in which purities of Th were increased by 98%. Due to the increasing global demand of energy, the recovery

of Th, and U from various sources have drawn great attention at present time (64, 65). Bastnasite ((RE)(CO₃) F), monazite((RE(PO₄), xenotime (YPO₄), and RE-bearing clay have been used as rare earth minerals (65,66). Recently, aminophosphate compounds have drawn the attraction of researchers, and have been extensively used as extractants, herbicides, anticancer agents, etc. It also shows marvelous extractive properties (67-71). Here metals were analyzed using an inductively coupled plasma optical emission spectrometer (72, 73). To determine the pH of an aqueous solution, PHS-3C digital meter was used. The molecular structure of Cextrant 230 is shown in Figure 7.

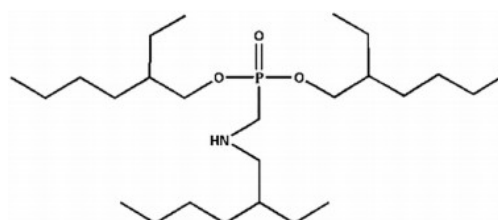


Figure 7: Molecular structure of Cextrant 230 (73).

Cextrant 230 is the most important extractant for the recovery of radioactive elements Th and U from an aqueous solution. It contains aluminium and iron in a sulfate medium. The extraction process of Th and U with cextrant 230 is exothermic (72-74). The flow chart of separating cerium (IV) and thorium (IV) from bastnaesite leaching is shown in Figure 8.

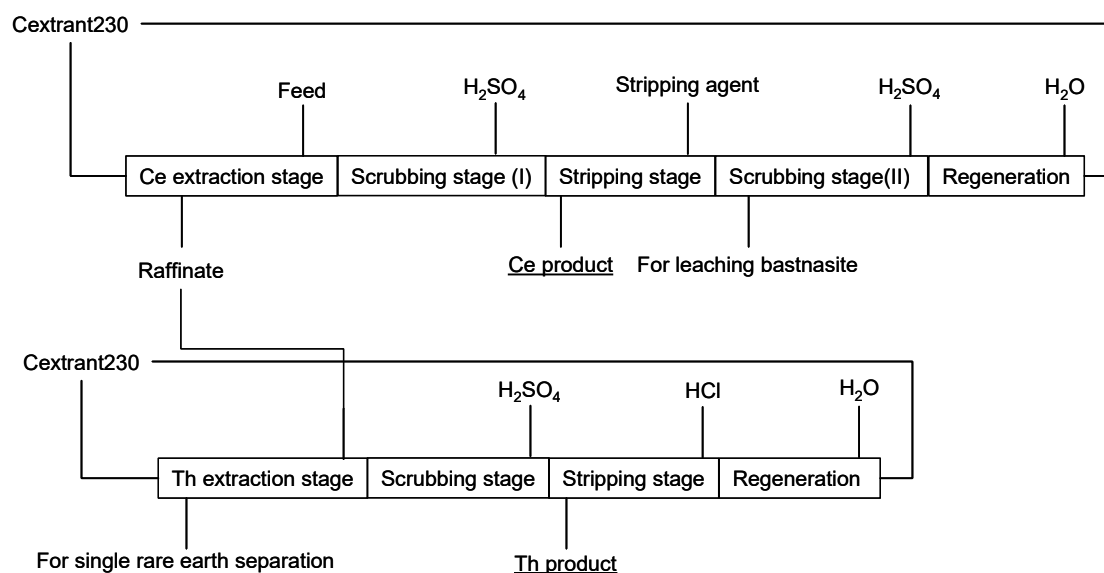


Figure 8: Flow chart of separating cerium(IV) and thorium(IV) from bastnaesite leaching (74).

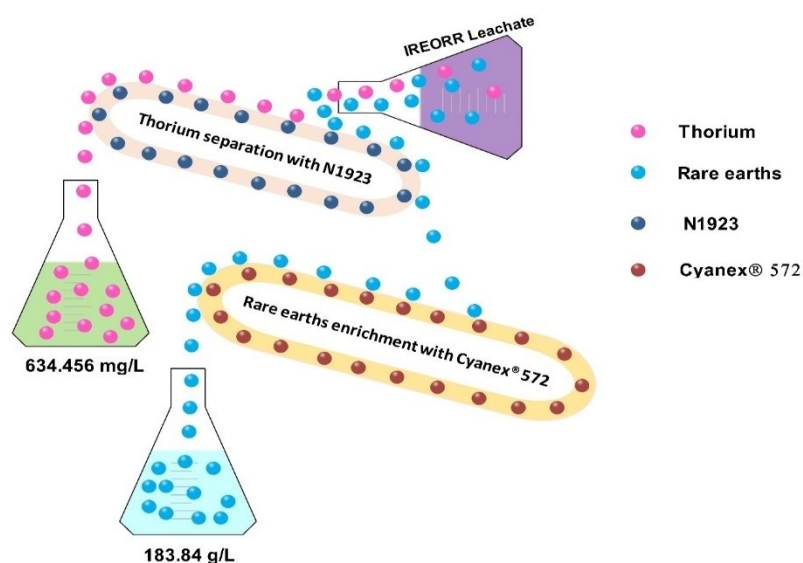


Figure 9: Th separation with N1923 and REE enrichment with Cyanex®572 (75).

Th separation with N1923 and REE enrichment with Cyanex®572 is shown in Figure 9. N1923 and Cyanex®572 can be used for the recovery of thorium using HCl leachate (75). In the method of formulating a high concentration rare earth (RE) feed for individual RE separation, hydrochloric acid is used to dissolve the RE concentrate to reduce the leaching of impurities, about 5% of REEs remains in the dissolved residues (76, 77).

Recovery of Th from Industrial Residues and Monazite Leach Solution

The main chemical used for this process was sulfuric acid digestion followed by water leaching. The lanthanides group as well as the scandium and yttrium group come under a rare-earth group, as the chemical structure of Th and U are similar to REE. They are found in the residues generated in REE processing. In monazite minerals, Th is found in high quantity as compared to U (78, 79). Here the acid digestion is performed with concentrated sulfuric acid and then adds directly to the solid. Sulfuric acid digestion followed by water leaching was found to be the best method to solubilize the metal (80). To recover thorium from monazite, solvent extraction, i.e. liquid-liquid extraction process (80, 81). It is one of the strategic methods and utmost reliable technique to reach out on target metal recovery with enrichment factor. Korean monazite is managed using hydrometallurgical techniques such as water leaching, sulfation, double salt precipitation by using Na_2SO_4 and acidic leaching by HCl (81, 82).

The flowchart for synthesis of thorium-rich residue associated with minor quantities of rare earth elements is shown in Figure 10.

Recovery of Th from Radioactive Waste

There is also removal of thorium using IREPO from radioactive waste (83). In this method, the recovery of Th by using IREOPR was analyzed. In this process, the convenient and effective chemical treatment of IREORR was to dissolve them with a mineral acid before recovering the valuable elements. A process for separating Th and REEs from IREORR leachate using POAA has been designed and illustrated. Here the chemical composition of residues was first analyzed and then the leaching factors such as acid type and acid concentration were noted down. A cost-effective process for recovering thorium and rare earths from radioactive residues is shown in Figure 11.

EXTRACTION AND SEPARATION RESULT WITH THE OPTIMAL CONDITIONAL ANALYSIS

The extraction process follows different steps with response to various diluents, concentration of extractants, pH value, temperature, contact time, acids (HNO_3 , HCl, H_2SO_4) etc. In this study, we have highlighted some important works of different researchers on extraction and separation of thorium from other metals. The parameters studied in the above said processes are calculated by using the following relations (65, 73, 83).

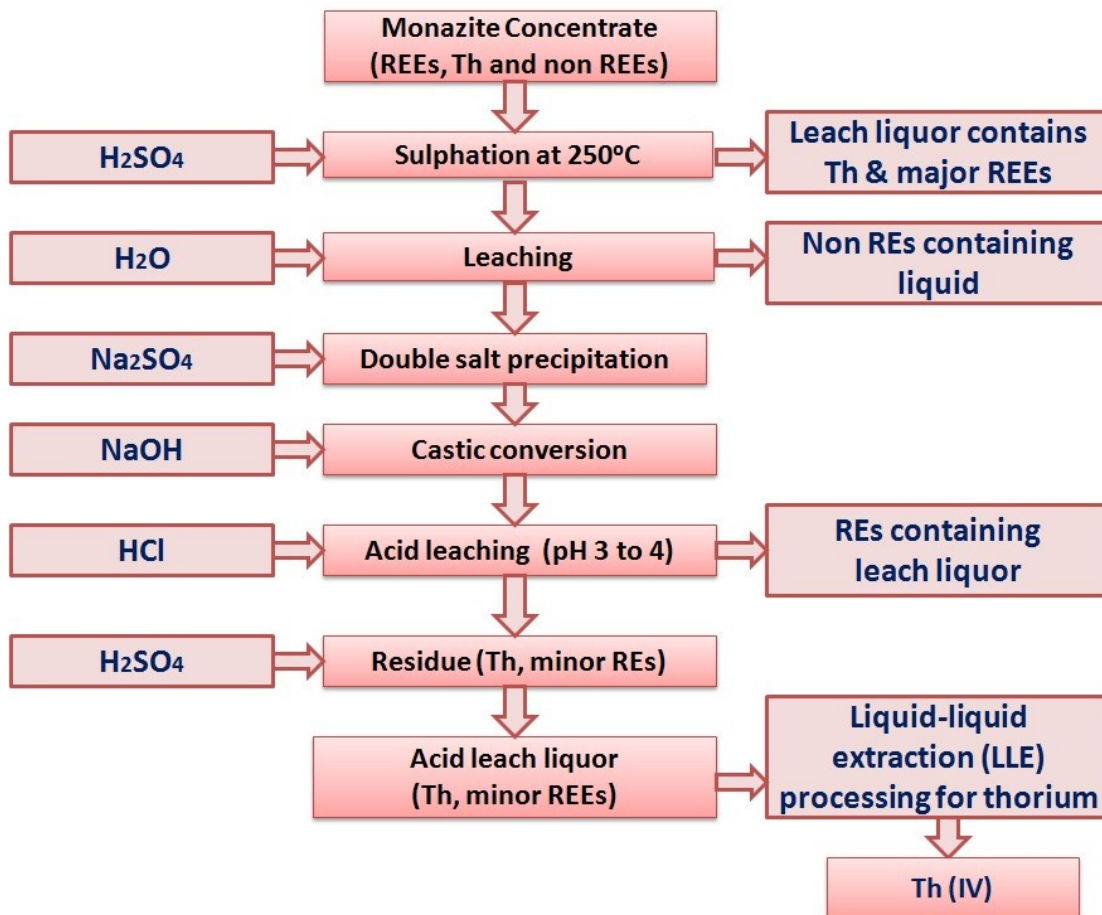


Figure 10: Flowchart for the synthesis of thorium-rich residue associated with minor quantities of rare earth elements (REE) (36).

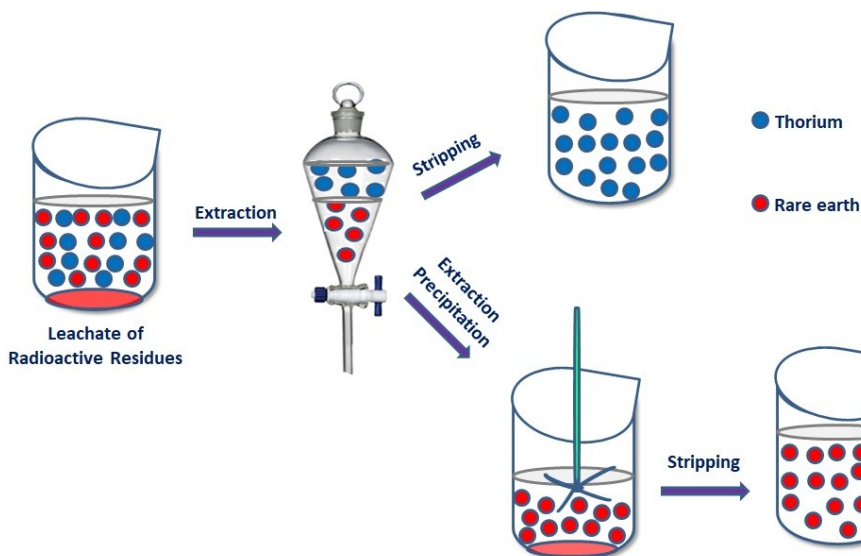


Figure 11: A cost-effective process for recovering thorium and rare earths from radioactive residues.

$$\text{Distribution ratio } (D) = \frac{(M)_O}{(M)_a} \quad (2)$$

$$\text{Stripping percentage (St\%)} = \frac{(M)_a}{(M)_{O,i}} \times 100 \quad (4)$$

$$\text{Separation Factor } (\beta) = \frac{D_1}{D_2}$$

$$\text{Extraction percentage (E\%)} = \frac{(M)_O}{(M)_{a,i}} \times 100 \quad (5)$$

Where $(M)_a$ and $(M)_o$ represent the metal concentrations in the aqueous and organic phases at equilibrium, respectively. $(M)_{a,i}$ and $(M)_{o,i}$ denotes the initial metal ions concentration in the aqueous phase and loaded organic phase respectively.

$$\text{Extraction efficiency} = \frac{C_{M(o)}}{C_{M(o)} \times C_{M(a)}} \times 100\% \quad (6)$$

$$\text{Recovery efficiency} = \frac{C_{M(a)} \times V_{(a)}}{C_{M(a),i} \times V_{(a),i}} \times 100\% \quad (7)$$

$$\text{Stripping efficiency} = \frac{C_{M(a)} \times V_{(a)}}{C_{M(o),i} \times V_{(o)}} \times 100\% \quad (8)$$

Where $C_{M(o)}$, $C_{M(a)}$ are the concentration metal ions in the organic and aqueous phases respectively; $V_{(o)}$ and $V_{(a)}$ are the volume of organic and aqueous phases, respectively; $V_{(a),i}$ is the initial volume of aqueous phase; $C_{M(o),i}$ and $C_{M(a),i}$ are the initial concentration of a metal in organic phase and aqueous phases, respectively.

Y. Lu et al. (74) reported the separation factors between Ce(IV) and Th(IV) at different acidity concentration and their work has shown a recovery of thorium 98% by using a -aminophosphate in acid concentration of H_2SO_4 . X. Yang et al. (73) found the separation factors between Th(IV) and other metal ions (RE, Fe and Al) at different acidity concentrations. The values of separation factor are higher than 160 at 1.0 mol/L of H^+ ion. So, Cextrant 230 can be used as a good extractant for the removal of thorium from a mixed solution of REs and other metals (Fe, Al etc.). The extraction capacity of 5% (v/v) cextrant 230 for Th(IV) was found 4.08 g/L. Again, J. Su et al. (74) reported a fractional extraction experiment for separating thorium and enriching of rare earth elements. They found the yield of Th is higher than 99.9% and the concentration of rare earth elements was 183.89 g/L. Chung et al. (36) reported that 2.5 mol/L acidic conditions was suitable for their work. HCl and H_2SO_4 were tested for recovery of the thorium and HCl showed better results than H_2SO_4 . Higher molar HCl (5 mol/L, 250 °C) appears to be suitable for thorium. As reported by S M Ghag and S D Pawar (84), the separation of Th(IV) and U(VI) from multicomponent mixtures with cyanex®-923 in toluene with specific concentrations with acid, Th(IV) was found to be 99.3% in a 20 µg sample. U (VI) and Th(IV) were extracted in the acid concentration range 5×10^{-5} to 1×10^{-4} M and 5×10^{-5} to 5×10^{-3} M respectively.. J C Amaral et al. (78) proposed a process to recover Thorium, Uranium and REs from an industrial residue. Under the optimized condition, the metal dissolution of 81% (using H_2SO_4) for thorium was obtained. S M

Ibrahim et al. (85), HDEHDGA provides useful selectivity for Th(IV) over light Ln(III) ions, giving new processes for actinides-lanthanides extraction/separation and REs production in the industry. Sulfuric acid digestion followed by water action was found to be the simplest technique to solubilize the metals.

CONCLUSIONS

The different methods of extraction of thorium such as selective extraction of thorium using phosphorodiamidate, selective cloud point extraction of thorium, extraction of thorium from sulfuric acid baking and leaching of monazite, extraction of thorium from chloride solution using Schiff base were discussed. Out of all the discussed methods of extraction, cloud point extraction is considered the best of all as it is more precise, accurate, and cheap as compared with other methods. The method is environmentally friendly as it gives very few toxic by-products. HCl and H_2SO_4 were taken for recovery of the metallic element and the former one is showing better results over latter one. Later on, high molar HCl (5 mol/L) seems to be appropriate for metallic element recovery. The primary aims of all these methods of extractions and recoveries of thorium are for getting an efficient amount of thorium and procedure to get high efficiency of thorium.

CONFLICT OF INTEREST

The authors declared no conflict of interest.

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