

Thorium and uranium extraction from rare earth elements in monazite sulfuric acid liquor through solvent extraction

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ABSTRACT

This paper describes the process of extraction of thorium and uranium from the sulfuric liquor generated in the chemical monazite treatment through a solvent extraction technique. The influence of the extractant type and concentration, contact time between phases, type and concentration of the stripping solution and aqueous/organic volumetric ratio were investigated. The results indicated the possibility of extracting, simultaneously, thorium and uranium from a solvent containing a mixture of Primene JM-T and Alamine 336. The stripping was carried out with a hydrochloric acid solution. After selecting the best conditions for the process, a continuous experiment was carried out in a mixer-settler circuit using four stages in the extraction step, five stages of stripping and one stage of the solvent regeneration. A loaded stripping solution containing 29.3 g/L of ThO₂ and 1.27 g/L of U₃O₈ was obtained. The metals content in the raffinate was below 0.001 g/L, indicating a thorium extraction of over 99.9% and a uranium extraction of 99.4%. The rare earths content in the raffinate was 38 g/L of RE₂O₃.

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1. Introduction

Of the 200 best known minerals containing rare earth (RE) elements, only three contain significant amounts – bastanite, monazite and xenotime, monazite being the second most important source of rare earths (Thompson, 1980). Monazite is a rare earth phosphate also containing thorium and uranium as associated metals (Abrão, 1994; Loureiro, 1994; Miyawaki and Nakai, 1996; Sundaram, 1987; Wall and Mariano, 1996). Its structural group consists of arsenate, phosphate and silicate, having the general formula ABO₄, where A corresponds to RE, Th, U, Ca, Bi, etc. and B corresponds to As⁵⁺, P⁵⁺ or Si⁴⁺ (Fleischer et al., 1990; Toledo and Pereira, 2003). The processing of monazite leads to the generation of RE concentrates containing thorium (Th), uranium (U) and phosphate (PO₄³⁻). Monazite is cracked through one of the two following methods: (i) the basic process with a sodium hydroxide solution where Th and U are separated during the process as a hydroxide; (ii) the acid process with concentrate sulfuric acid (H₂SO₄) where a liquor containing the RE elements, Th and U is generated (Thompson, 1980; Deqian et al., 2004; Habashi, 1997; Vijayalaskhmi et al., 2001; Silva et al., 1995).

The recovery of mixed rare earths and the removal of thorium and uranium from monazite are accomplished through a variety of methods after chemically attacking the mineral with sulfuric

acid or sodium hydroxide (Gupta and Krishnamurthy, 1992). The purification of chemically similar substances through techniques involving repeated transitions between solid and liquid phases has been replaced by a technologically simpler liquid–liquid extraction. The successful development of the solvent extraction processes using alkyl amines for recovering uranium from ore-leach liquors led naturally to the adaptation of these extractant for use in the recovery of other metals, e.g., thorium. Thorium is of particular interest because of its potential usefulness as a fertile material for breeder reactors. Technological processes for the extraction of thorium from sulfate solutions with amines date back to 1958–1959 (Crouse and Brown, 1959). Since then, a large number of papers on the selective separation of thorium and uranium using solvent extraction have been published. The Amex process, which is the core of most of the processes utilized in the industry, was first described in 1959 (Crouse and Brown, 1959; Shimidt, 1971). Crouse and Brown (1959) describe a process where thorium and uranium are extracted in two solvent extraction cycles. In this process, thorium is extracted in the first cycle with a primary amine, while uranium is extracted in the second cycle using secondary or tertiary amine.

A novel method for the separation of thorium and uranium from RE elements has been devised by the authors and in the process, thorium and uranium are simultaneously extracted from the sulfuric liquor generated in the monazite process with the use of a mixture of Primene JM-T (primary amine) and Alamine 336 (tertiary amine). Studies involving discontinuous and continuous solvent extraction experiments have been carried out, in which

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the parameters required for the extraction of thorium and uranium were determined.

2. Experimental

2.1. Reagents and solutions

The extractants used in this study included: Primene[®]JM-T (primary amine), Primene[®]81-R (primary amine), Alamine[®]336 (tertiary amine), Aliquat[®]336 (quaternary ammonium salt) and a mixture of Primene JM-T and Alamine 336. Both Primene JM-T and Primene 81-R were supplied by Hohm and Haas Company. Alamine 336, Aliquat 336 and tridecanol (used as modifier) were supplied by Cognis do Brasil Ltda. Exxsol[®] (purified kerosene) used as diluent was supplied by Exxon Química. Extractant solutions were prepared at the specified concentration plus 5% v/v of tridecanol and diluted in Exxsol.

The sulfuric liquor from the chemical monazite treatment, containing 36.2 g/L RE₂O₃, 3.25 g/L ThO₂, 0.17 g/L U₃O₈, 94 g/L SO₄²⁻ and 15.1 g/L P₂O₅, was supplied by Indústrias Nucleares do Brasil S.A. – INB/Caldas plant in the state of Minas Gerais. All reagents used in the stripping study were of analytical grade and their respective solutions were prepared with distilled water.

2.2. Discontinuous experiments

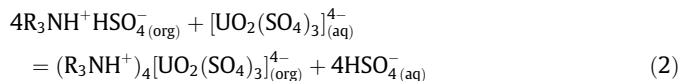
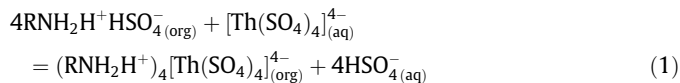
The extraction and stripping experiments were carried out in beakers under mechanical agitation (330 rpm), at room temperature (25 ± 2 °C) and contact time between phases of 5 min. Following contact, the aqueous and organic phases were separated by means of a separation funnel and then analyzed. Unless otherwise specified in the experiment, the volumetric ratio between phases was equal to 1. Th, U and RE were determined by energy X-ray spectrometry (Kevex system), neutronic activation (Th) and delayed neutrons (U).

2.3. Continuous experiments

After selecting the best conditions for the process, two continuous extraction and stripping experiments were carried out. The continuous counter-current experiments were carried out in a sequence of mixer-settler stages, with mixers of 70 mL and settlers of 260 mL. In the first experiment, four stages for extraction and five for stripping were used. The experiment was carried out using a mixture of 0.15 mol/L Primene JM-T and 0.05 mol/L Alamine 336 without recycling the solvent. In the second experiment, the Alamine 336 concentration was modified to 0.15 mol/L and a solvent regeneration stage was introduced. The experiment was conducted with the recycling of the solvent. The control of the system stability was evaluated through the determination of the thorium and uranium in the exit flows every hour. During the development of the process, the thorium and uranium concentrations were measured by means of energy-dispersive X-ray spectrometry (Kevex system).

3. Chemical process

Metal extraction by amines depends on the capacity of the metallic ions to create anionic or neutral species in the aqueous phase; these species are then extracted through an anion exchange mechanism or by adduct formation, respectively. In sulfuric medium, thorium is extracted preferably by primary amines, while uranium is extracted by tertiary amines, especially Alamine 336 (Crouse and Brown, 1959; Morais et al., 2005; Morais and Gomiero, 2005). Mechanisms for thorium and uranium extraction by amines were proposed by Shimidt (1971), according to Eq. (1) and (2).



According to Crouse and Brown (1959), the extraction coefficient of the thorium obtained from the sulfuric medium can be as high as 1000 for 0.1 mol/L primary amine solutions and practically null for tertiary amines.

4. Results and discussion

4.1. Extraction step

In the choice of the solvent composition to be used in the extraction study, extractant solutions were prepared at a concentration of 0.1 mol/L. For the extractant mixture, the final concentration of each was 0.05 mol/L. Extraction percentages for different extractants are shown in Table 1. As indicated, and complying with literature, Primene JM-T and Primene 81-R extract thorium preferably. The basic difference between such extractants is the number of carbons composing their respective aliphatic chains. The Primene 81-R aliphatic chain is composed of 12–14 carbons, while the Primene JM-T aliphatic chain is composed of 16–22 carbons. Primene JM-T was selected for the thorium extraction studies because it displayed a better phase separation and a lower REE extraction coefficient as compared to Primene 81-R (Table 1). Alamine 336 extracts preferably uranium. Aliquat 336 also prefers uranium, but it is less efficient than Alamine 336. The REE extraction was lower than 1% for all extractants investigated at the specified concentration. It can also be noted that it is possible to extract Th and U simultaneously by using a mixture of Primene JM-T and Alamine 336.

This paper reports selective extraction of thorium and uranium from a rare earth sulfuric liquor using a mixture of Primene JM-T and Alamine 336. The effect of the concentration of Primene JM-T and Alamine 336 on Th, U and RE extraction was investigated. The influence of the concentration of Primene JM-T was evaluated for the 0.05–0.30 mol/L interval. Results of such experiments are shown in Fig. 1. As expected, the thorium distribution coefficient increases as the extractant concentration increases. An increasing percentage of uranium and REE extraction can be noticed. REE extraction becomes significant at a Primene JM-T concentration 0.15 mol/L, being higher than 17% for a concentration of 0.3 mol/L. However, REE extraction is of no interest in this case, as it implies a reduced recovery of such elements after thorium extraction and also contaminates the Th and U products. Results indicate the inconvenience of using Primene JM-T at concentrations higher than 0.15 mol/L (Fig. 1).

The effect of the concentration of Alamine 336 was also investigated for the 0.05–0.30 mol/L interval. Results are shown in Fig. 2. Across the investigated interval, uranium extraction per-

Table 1
Influence of the extractant on Th, U and RE extraction.

Extractant	Extraction (%)		
	Th	U	REE
Primene 81-R	93.1	5.9	0.85
Primene JM-T	95.4	8.8	0.32
Alamine 336	3.1	82.4	0.02
Aliquat 336	1.5	11.8	0.02
^a P. JM-T/A. 336	45.5	58.8	0.04

^a Mixture of Primene JM-T and Alamine 336 at the volumetric ratio of 1:1.

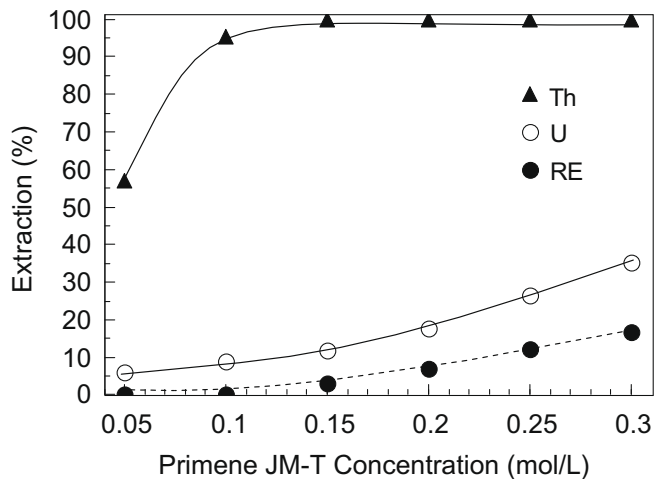


Fig. 1. Influence of Primene JM-T concentration on Th, U and RE extraction.

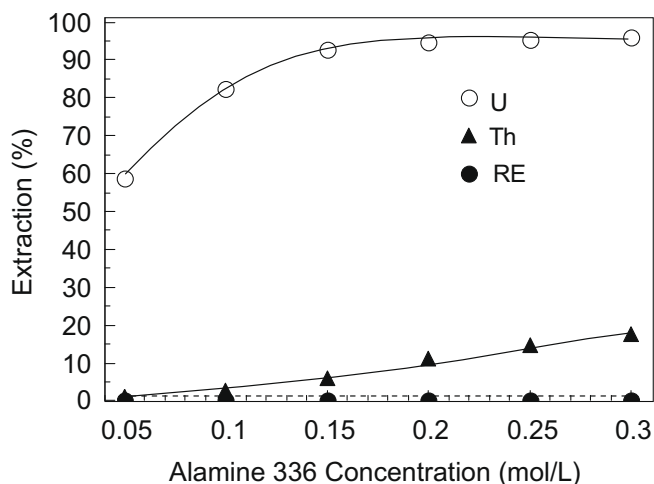


Fig. 2. Influence of Alamine 336 concentration on Th, U and RE extraction.

centage increases from 59 to 96. Above 0.15 mol/L, there was practically no increase in the U distribution coefficient. An increase in the Th extraction was perceived, which was negligible (1%) for 0.05 mol/L and as high as 17.5% at a concentration of 0.3 mol/L Alamine 336. In the investigated concentration interval, the REE extraction percentage was below 0.1, suggesting that the REE extraction is not a restricting factor in the determination of the concentration of Alamine 336 to be used in the process (Fig. 2).

Residual uranium in the aqueous phase (~ 0.01 g/L), even for higher Alamine 336 concentrations, may be attributed to the high sulfate content in liquor (94 g/L). According to Merritt (1971), for a solution containing 0.1 mol/L SO_4^{2-} , the distribution coefficient for uranium extraction by tertiary amines is around 1000, whereas for a solution containing 1.0 mol/L, this coefficient drops to values below 100, which indicates the need for using a relatively concentrated Alamine 336 solution comparable to the U content in the liquor. It can be due the competition of the ion sulfate and bisulfate with the uranium sulfate complex.

Another process variable investigated was the aqueous/organic phase ratio (A/O). This study was carried out with a mixture of Primene JM-T/Alamine 336, both at the concentration of 0.15 mol/L. The A/O ratio ranged between 1/1 and 4/1. The volumetric feeding ratio of the aqueous and organic phases for a solvent extraction process was obtained through the McCabe–Thiele

diagram. The study of this variable aims at evaluating the behavior of the REE extraction. The REE extraction of 0.67% (0.21 g/L RE_2O_3) at A/O ratio = 1 dropped to 0.11% (0.04 g/L RE_2O_3) at A/O ratio = 2, maintaining the same percentage for A/O ratio = 3 and 4. The thorium extraction fell significantly from 99.4% to 48% when the A/O ratio increased from 1 to 4 and the uranium extraction dropped from 93.5% to 74.1%.

In the next step of the study, an extraction isotherm (equilibrium curve) was constructed and a McCabe–Thiele diagram was drawn to determine the number of theoretical stages and the volumetric feeding ratio of the liquor and type of solvent for continuous experiments (Merritt, 1971). The equilibrium curve was constructed according to the successive contacts technique for organic phase loading and aqueous phase depletion. The Primene JM-T and Alamine 336 concentrations of the solvent were 0.15 mol/L. The thorium extraction isotherm and McCabe–Thiele diagram are shown in Fig. 3. The uranium diagram is not shown because the solvent saturation for that metal was not achieved. To achieve saturation, a greater number of experiments would be required as 0.15 mol/L Alamine 336 solution loads approximately 8 g/L U_3O_8 (Morais et al., 2005; Morais and Gomiero, 2005). With respect to U, the objective was to observe the metal depletion efficiency in the liquor, which was achieved in the second successive depletion contact. For Th depletion, three contacts were necessary. As shown in Fig. 3, for a volumetric feeding liquor/solvent ratio of 1.5, obtaining a Th-free raffinate requires three mixer-settler stages. Under such condition, it would be possible to obtain a loaded solvent containing 5 g/L ThO_2 .

4.2. Stripping step

In preliminary experiments aimed to select the Th and U stripping agent some mineral acids and salt solutions were tested. The efficiencies of hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium chloride (NaCl), ammonium fluoride (NH_4F), ammonium bifluoride ($\text{NH}_4\text{F}\cdot\text{HF}$) and sodium carbonate (Na_2CO_3) were investigated. In such experiments, a mixture of Primene JM-T and Alamine 336 previously loaded with thorium and uranium was used. The characterization of this loaded solvent is demonstrated in Table 2.

The stripping results are shown in Table 3. As observed, the investigated reagents do not display a selective Th and U stripping. For simultaneous Th and U stripping, HCl, NaCl, Na_2CO_3 and $\text{NH}_4\text{F}\cdot\text{HF}$ showed a satisfactory performance. In this case, Th/U separa-

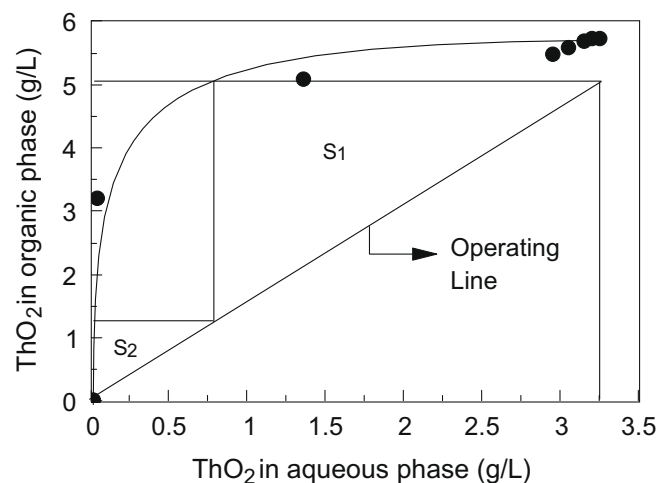


Fig. 3. Thorium extraction isotherm and McCabe–Thiele diagram for solvent containing 0.15 mol/L Primene.

tion can be achieved by selective precipitation. In experiments using NH_4F and $\text{NH}_4\text{F}\cdot\text{HF}$, a precipitation of thorium fluoride occurred in the aqueous phase.

The effect of the hydrochloric acid concentration was investigated from 0.5 mol/L to 3.0 mol/L using a volumetric organic/aqueous phase ratio of 1:1. The contact time was 5 min and the

Table 2

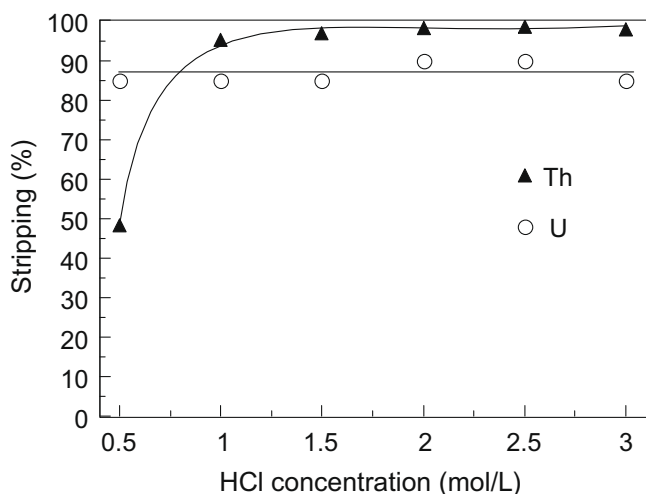
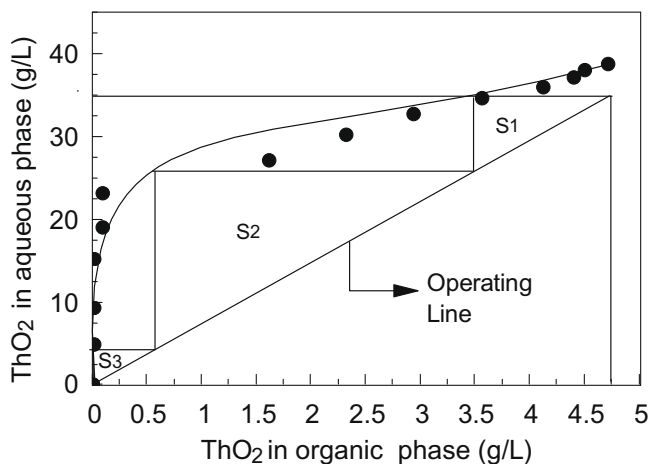
Chemical characterization of the loaded solvent.

Species	ThO_2	U_3O_8	RE_2O_3
Content (g/L)	5.33	0.37	0.054

Table 3

Stripping percentage of Th, U and RE for investigated reagents.

Stripping agent		Stripping (%)		
Name	Concentration (mol/L)	Th	U	RE
HCl	2.0	89	77	44
H_2SO_4	2.0	17	32	72
NaCl	2.0	95	91	32
Na_2CO_3	2.0	95	99	74
NH_4F	1.0	31	49	26
$\text{NH}_4\text{F}\cdot\text{HF}$	1.0	79	60	63

**Fig. 4.** Influence of the concentration of hydrochloric acid on Th and U stripping.**Fig. 5.** Thorium stripping isotherm and McCabe–Thiele diagram for 2 mol/L hydrochloric acid solution.

separation time was less than 30 s. The loaded solvent (mixture of Primene JM-T 0.15 mol/L and Alamine 336 0.05 mol/L) used in the stripping experiments contained 5.33 g/L ThO_2 , 0.20 g/L U_3O_8 and 0.054 g/L RE_2O_3 . This loaded solvent was obtained through successive discontinuous contacts with the liquor.

As shown in Fig. 4, the thorium stripping percentage increased from 48.5% to 98%. For levels above 1.5 mol/L, there was practically no increase in Th stripping. At the investigated interval, the uranium stripping was practically constant at 98%.

Based on laboratory experimental results, the stripping isotherm (equilibrium curve) was constructed and a McCabe–Thiele diagram was drawn to determine the theoretical number of stages and the volumetric feed ratio of the liquor and solvent for the continuous experiments. The equilibrium curve was constructed according to the successive contacts technique using phase ratios of 1. The McCabe–Thiele diagram is shown in Fig. 5.

5. Continuous experiments

Two continuous experiments were used to optimize the extraction of Th and U. They were carried out using a mixture of extractants (Primene JM-T and Alamine 336), in a counter-current system using a sequence of mixer–settler units, with mixers of 70 mL and settlers of 260 mL. In the continuous experiments, the variables studied were: number of stages in the extraction and stripping steps; organic/aqueous ratio in all steps, HCl concentration in the stripping. The experimental set-up comprised two steps: extraction and stripping (Fig. 6) and the regeneration of the organic in experiment 2. The variables were progressively adjusted. Table 4 shows the chemical composition of the monazite liquor. Fig. 6 shows the distribution of the products obtained in a continuous counter-current circuit for the thorium and uranium recovery in the experiment.

Experiment 1 was carried out in four extraction stages and five stripping stages for 30 h, when approximately twenty liters of liquor were processed and four organic cycles were run. The contact time in the mixer for the extraction stages was 4 min and 8.4 min for the stripping stages. The efficiency of the extraction process for the continuous experiment 1 is depicted in Figs. 7a and 7b. The profiles of the thorium and uranium concentration are shown in Figs. 7a and 7b, respectively. The ratios of the aqueous/organic phase in the extraction were 1.4 and 7 for the stripping step. As shown in Fig. 7a, practically all the thorium is extracted in the first and second stages. In the extraction step, the thorium and uranium concentrations in the organic were 5.1 g/L ThO_2 and 0.18 g/L U_3O_8 and in the raffinate were 0.10 g/L ThO_2 and 0.05 g/L U_3O_8 . In the stripping step, the concentration in the loaded strip liquor was 34.3 g/L ThO_2 and 1.29 g/L U_3O_8 .

As can be noted in Figs. 7a and 7b, the extraction of metals was not complete. In this case, the extraction of thorium and uranium was 97.2% and 70.6% respectively. This fact can be attributed to the lack of regeneration of the solvent, low concentration of the Alamine 336 used, or the relationship between the ratio of the aqueous and organic phases (A/O).

The objective of the continuous experiment 2 was to improve the uranium extraction process. The experimental set-up encompassed extraction, stripping and regeneration of the solvent with 1.0 mol/L Na_2CO_3 . Contact with Na_2CO_3 removes the chloride ions, thereby regenerating the solvent (Morais et al., 2005; Morais and Gomiero, 2005). Experiment 2 was carried out in four extraction stages and five stripping stages for 32 h. The contact time in the mixer for the extraction step was 5 min and 9.8 min in the stripping step. The ratios of the aqueous/organic phases in the extraction and stripping were 1.25 and 7, respectively. Figs. 8a and 8b shows the profiles of the products obtained in a continuous counter-current circuit. As shown in Figs. 8a and 8b, in the extraction

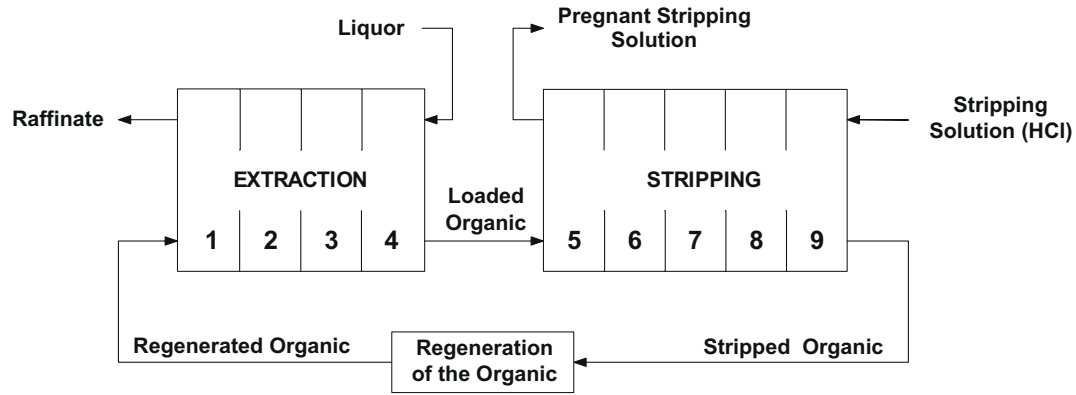


Fig. 6. Proposed flow diagram illustrating the successive extraction and stripping stages.

Table 4
Chemical composition of the monazite liquor.

Component	Concentration (g/L)
RE ₂ O ₃	36.2
ThO ₂	3.60
U ₃ O ₈	0.17
P ₂ O ₅	15.1
SO ₄ ²⁻	94.0

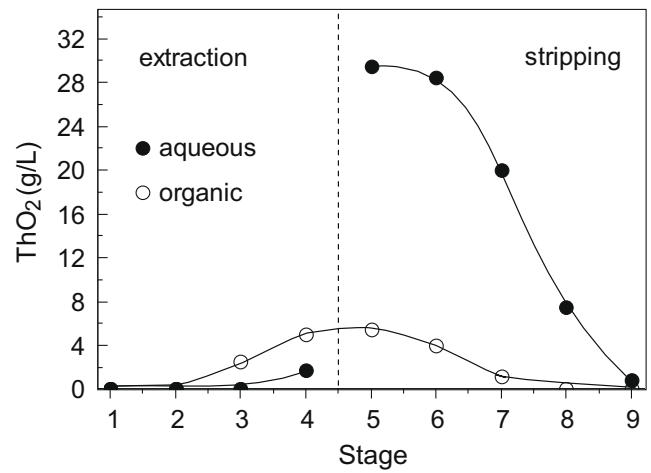


Fig. 8a. Profile of thorium concentration in experiment 2.

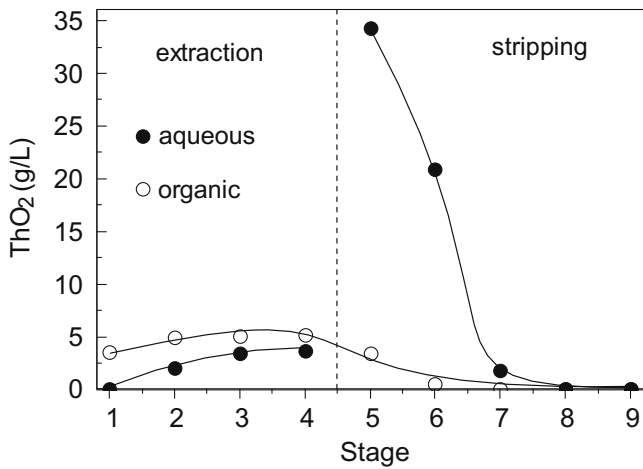


Fig. 7a. Profile of thorium concentration in experiment 1.

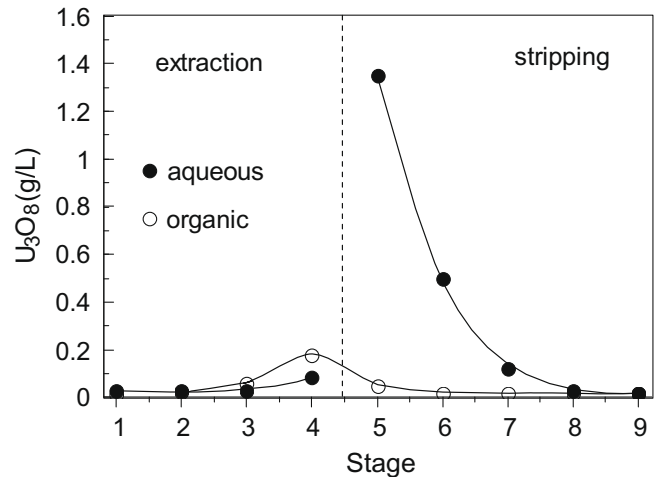


Fig. 8b. Profile of uranium concentration in experiment 2.

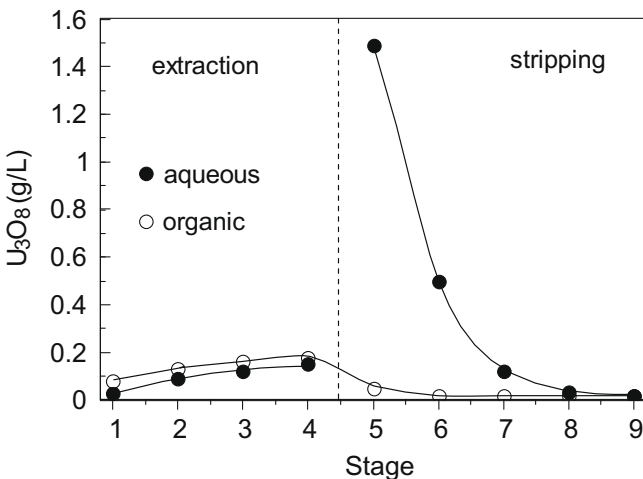


Fig. 7b. Profile of uranium concentration in experiment 1.

step the concentration of metals in the organic was 5.0 g/L ThO₂ and 0.20 g/L U₃O₈, and raffinate concentrations were below 0.001 g/L for both ThO₂ and U₃O₈. In the stripping step, the concentration was 29 g/L of ThO₂ and 0.94 g/L of U₃O₈ in the loaded strip liquor. In this case, the extraction yield was higher than 99.9% for Th and 99.5% for U, indicating that the changes in experiment 2 solve the problem observed in experiment 1.

6. Conclusion

The study presents the possibility of simultaneous extraction of thorium and uranium from sulfuric liquor generated in the chemical monazite treatment. For the mixture of extractants investigated, Primene JM-T preferably extracts thorium, while Alamine 336 preferably extracts uranium. The Primene JM-T concentration in the solvent may not exceed 0.15 mol/L. Increased concentration of Primene JM-T in the solvent will cause an increased extraction of rare earth elements, which is not desirable in the process. This fact was not observed for Alamine 336 in the concentration range investigated. The selection of the stripping agents will depend on more experiments as well as on economic factors. For simultaneous stripping, a study of metal separation through a selective precipitation technique should be carried out.

After the process optimization, the extraction yield was higher than 99.9% for Th and 99.5% for U. In both experiments, the extraction of rare earth elements was below 0.1%.

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