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Liquid- Liquid Extraction Studies on Th (IV) and U (VI) from Egyptian Monazite Using Tertiary Amine

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Abstract: *The present work deals with separation of Th (IV) and U (VI) from Th –U concentrate obtained from alkaline leaching of Egyptian monazite pilot plant. The liquid–liquid extraction of Th (IV) and U (VI) from sulfate medium using tertiary amine is investigated with regard to extractant concentration, diluents type, equilibration time, pH, temperature, and extraction isotherm. Aliphatic diluents were preferred compared to aromatic diluents for their higher extraction, shorter equilibration time and good phase separation. Increasing temperature had a negative effect on Th (IV) and U (VI) extraction. Quantitative Th (IV) and U (VI) extraction efficiency was achieved at room temperature within 10 min, using three stages of extraction with 0.06 M trioctyl amine, pH 0.8 at a phase ratio of 1:1 and* ΔH *value for U (VI) was (-26.04 kJ/mol) and for Th(IV) was (-27.76), this value of* ΔH *for U(VI) and Th(IV) was used to obtain the corresponding free energy (*ΔG_U *= -3994.09 kJ/mol and entropy* ΔS_U *= 13.31 J/mol.K) and (*ΔG_{Th} *= -4222.33 kJ/mol, and* ΔS_{Th} *= 14.07 J/mol.K) at 298°K.*

Keywords: *monazite, trioctyl amine, Th –U cake, extraction isotherm, diluents.*

I. Introduction

The Egyptian beach sand deposits usually contain mainly heavy economic minerals; ilmenite, rutile, magnetite, zircon, and monazite. The mean relative frequency of monazite in the beach deposits in some samples collected from Damietta and Rosetta (Egypt) attains 0.3 to 1.5%. Therefore, the Egyptian black sand beach deposits are considered as the chief thorium ore in Egypt due to the presence of monazite **[1].** The process of extraction of thorium and uranium from the sulfuric acid liquor generated from the chemical monazite treatment through a solvent extraction technique. Amaral and Morais, **[2]** indicated the possibility of extracting, thorium and uranium simultaneously 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 ThO_2 and 1.27 g/L of U_3O_8 was obtained. The metals content in the raffinate was below 0.001 g/L, indicating a thorium extraction over 99.9% and a uranium extraction 99.4%. The rare earths content in the raffinate was 38 g/L of RE_2O_3.

The production of uranium concentrate from sulfuric acid liquor typically adopts solvent extraction and chemical precipitation techniques. The most commonly used extractant at uranium extraction stage is the Alamine -336, a long-chain tertiary amine, diluted in purified kerosene. A modifier, usually a long-chain alcohol, is also added to the organic solution to prevent the formation of third phase and emulsion. Stripping of uranium was done by some aqueous solutions, like sodium chloride (NaCl), ammonium sulfate ($(NH_4)_2SO_4$), and sulfuric acid (H_2SO_4) solutions **[3].** Stripping of uranium from a loaded Alamine-336 solution by sulfuric acid and its precipitation as uranium peroxide from the pregnant strip solution (PSS) was investigated. Stripping studies were carried out in batch as well as in continuous scale. Before the uranium peroxide precipitation study, the sulfate content reduction was carried out through its precipitation as hydrated calcium sulfate ($CaSO_4\ xH_2O$) by adding lime milk. Uranium peroxide precipitation experiments were carried out by hydrogen peroxide (H_2O_2) addition and reaction pH control by the addition of magnesium oxide/magnesium hydroxide ($MgO/Mg(OH)_2$) mixture.

II. Materials and methods

Trioctyl amine (TOA) was obtained from Merk, Germany. Odorless kerosene (non-aromatic) was obtained from Misr Petroleum Co., Egypt. Arsenazo III (A.R grade) was obtained from Fluka and all other chemicals were Prolabo products and were used as received. For the equilibration experiments, a good mixing for the two phases was achieved using a magnetic stirrer. Complete phase separation of the two phases was attained by using separation funnel. All measurements were carried out at laboratory temperature. Uranium and thorium was determined spectrophotometrically using the colorimetric determination (Marczenko, 1976) and a “Metertech Inc” model SP-8001, UV–Visible spectrophotometer. All measurements were carried out in Nuclear Materials Authority Lab.

2.1. Characteristics of input thorium- uranium cake

The main material for thorium- uranium cake is nearly 97% monazite sands. This monazite concentrate is obtained from Egyptian Black Sand. It was upgraded by ore dressing techniques at the Nuclear Materials Authority. The mineral monazite is primarily composed of rare earth phosphates especially those of low atomic numbers (Cerium group) along with numerous other minor constituent among which thorium and uranium are the most interesting elements **[4].** A typical analysis for Egyptian monazite concentrate obtained from Egyptian black sands is given in **Table (1)**. The preliminary operation in any process for the recovery of thorium and uranium from monazite sand concentrates involves its decomposition and dissolution. Such process has to be so designed in a manner to separate the entire valuable components from the present phosphate and silica gangue in a form suitable for further processing. For economic considerations, this process should be performed by inexpensive chemical and be able to provide a high rate of recovery for thorium, uranium and rare earths. The following methods can be used for the breakdown of monazite; sulfuric acid process, treatment with nitric acid, treatment by alkali fusion, chlorination of monazite sample and aqueous caustic soda breakdown process. At Egyptian N.M.A. the aqueous caustic soda breakdown process was found to be the most suitable method for the pilot plant separation of thorium- uranium cake from the physically upgraded monazite from black sand **[5].**

2.2. Caustic soda reaction

In order to avoid the complications brought out by sulfuric acid process and for economic consideration, the aqueous caustic soda breakdown process was found the most suitable for the recovery of these valuable elements. The most satisfactory conditions for the decomposition of Egyptian monazite sand concentrate with caustic soda solution and which are compatible with economic consideration would be particle size of monazite sand(grinding) -325 mesh size, reaction temperature 140ºC, caustic soda to sand weight ratio 1:1, concentration of sodium hydroxide solution 50% and time of reaction 3 hours **[5]**. The reaction of monazite with hot concentrated solution of caustic soda can be represented by the following Equations (1,2) :

$2Ln(PO_4) + 6NaOH \rightarrow Ln_2O_3.3H_2O$ or $Ln(OH)_3 + 2Na_3PO_4$ (1)

$Th_3(PO_4)_4 + 12NaOH \rightarrow 3ThO_2.2H_2O$ or $Th(OH)_4 + 4Na_3PO_4$ (2)

The dry hydrous oxide cake was treated by hot HCl and using 20% NaOH to adjust pH of the chloride solution of Th/U and REEs cake, at pH 5.8. The obtained Th–U concentrate which have a chemical composition shown in **Table (2)**, and we emphasize the chemical results by ESEM analysis for the same sample which gives the following results in **Figure (1)**, and at pH= 8 we have REEs concentrate which have the chemical composition as 20.75%La_2O_3, 34.71%Ce_2O_3, 6.78% Pr_2O_3, 14.98% Nd_2O_3, 2.42% Sm_2O_3, 2.69% Gd_2O_3, 1.11% Tb_2O_3 and 2.34% Y_2O_3. In addition to, P_2O_5, Fe_2O_3 and loss of ignition(LOI) which presented in percentages 4.20%, 3.13% and 6.89% respectively.

III. Results and discussions

3.1. Effect of trioctyl amine (TOA) on extraction of U(VI) and Th(IV)

The results are shown in Fig (2). The extraction percent of U(VI) and Th(IV) increased gradually with increase in (TOA) concentration until 0.06M. After that the decrease of extraction will be happened for U(VI) and Th(IV). In increasing the extraction may be due to the more available sites of extractant for the extraction of U (VI) and Th (IV). But further increase in extractant concentration did not result in any significant increase in extraction percentage of U(VI) and Th(IV). The decrease on the extraction percent above 0.06M probably due to the increase in the viscosity of extractant TOA that causes a decrease in the mass transfer of U(VI) and Th(IV) from aqueous to organic phase.

3.2. Effect of diluents

In solvent extraction, the term diluent refers to the organic liquid in which the extractant and modifier are dissolved to form the solvent. In the majority of cases, the diluent comprises the major portion of a solvent. The general requirements of a diluent are, in no particular order of preference, that it be mutually soluble with an extractant or modifier, have high solvency for an extracted metal species, thus minimizing both the problem of third phase formation and low loading capacity of a solvent, have low volatility and a high flash point, thus decreasing losses due to volatility as well as fire hazards, be insoluble in the aqueous phase, have low surface tension, be cheap and readily available. Many of the extractants used in solvent systems are surface-active, and high concentrations tend to emulsify, especially with high agitation, so dilute concentration was recommended **[6]**. Diluents influence the extraction of metals by amines due to the aggregation of the amine in the organic phase **[6,9]**. The incomplete extraction of ions by some diluents may be due to the formation of non extractable complex species in the organic phase, which produce a low concentration of a free extractant for the metal extraction with a consequent decrease in the extraction percentage **[7]**. Therefore, various aromatic and aliphatic solvents were tested as diluents for the extraction of U(VI) and Th(IV) with 0.06 M TOA in all diluents (**Figure 3**). The extraction of U(VI) and Th(IV) were maximum with kerosene, n-hexane, chloroform and carbon tetrachloride as diluents but benzene, pxylene and toluene proved to be poor diluents. It is obvious that from **Figure (3)**, short equilibrium time and good phase separation was achieved when aliphatic diluents were used compared to aromatic diluents. Considering several factors like cost, environmental and safety aspects and maximum U(VI) and Th(IV) ions extraction efficiency, aliphatic kerosene was preferred as the diluent for further studies **[9]**.

3.3. Effect of equilibration time

The effect of contact time on the attainment of an equilibrium state has been studied for the time interval 1-20 minutes, while the other factors kept as mentioned before. The results obtained are shown in **Figure (4).** It is obvious that contact time of 10 minutes is quite adequate for efficient U(VI) and Th(IV) extraction. It is clear from the **Figure (4)**, the extraction percent was increased from 1- 10 minutes and after that there is a slight decrease in the U (VI) and Th (IV) extraction with increase the interval time, probably due to the entrainment of some organic droplet into the aqueous phase, which causes a slight decrease in the extractive power of TOA⁄ kerosene.

3.4. Effect of pH value

The extraction process has been studied by varying the pH values of the studied sulfate liquor from 0.1 to 2, using either sulfuric acid (1M) or sodium hydroxide (2M). Other factors were fixed at 1:1 (v/v) organic to aqueous phase ratio, 0.06 M TOA dissolved in kerosene as a diluent, contact time of 10 minutes and experiments were carried out at room temperature. The results obtained are given in **Figure (5)**. The extraction of U(VI) and Th(IV) increase with increase pH until pH =0.8, above pH 0.8, the extraction efficiency decreased, which may result from the formation of non–extractable metal species as result of complication with component of aqueous phase. The lower values obtained at higher acid concentrations (pH <1) are due to competition between the extractable U(VI) and Th(IV) species and $HSO_4^{\,-}$ which predominates in sulfate media at low pH **[8, 9]**.

3.5. Effect of temperature

For studying the effect of temperature on the distribution coefficient and extraction percent experiments were carried out in oil bath using electric thermostat of which regulated from $25^{o}C$ to $50^{o}C$. The other studied factors were kept constant at 1:1(v/v) organic to aqueous phase ratio, pH=0.8, contact time of 10 minutes and 0.06M TOA in kerosene. From the obtained results in **Figure (6)**. It is obvious that the extraction percentage of U(VI) and Th(IV) decreases, by increasing temperature from $25^{o}C$ to $50^{o}C$. This behavior is inagreement with that reported by previous investigators **[10],** which mean that the extraction process is exothermic. Then, the room temperature can be considered as the best temperature for extraction.

3.6. Construction of McCabe-Thiele diagram for U (VI) and Th (IV) extraction

In practice, the number of stages for extraction of an element could be properly determined by using McCabe-Thiele diagram. The latter necessitates the plotting of an equilibrium curve together with a suitable operating line. The equilibrium curve is generally obtained by shaking samples of different ratios of aqueous leach liquor and the chosen organic phase. The operating line whose slope represents the optimum O/A phase ratio to be used in the continuous counter current solvent extraction is then drown. The operating line is based on the mass balance of the system and therefore the metal concentration in the solvent entering and in the aqueous raffinate leaving any stage are co-ordinates of metal points on the operating line. Similarly, any concentration in the aqueous feed entering and in the solvent leaving any stage are the co-ordinates of such points on the equilibrium curve. The theoretical stages are stepped off by extending a horizontal line from the upper end of the operating line to intersect the extraction isotherm and then drawn vertically downwards to intersect the operating line. This is continued until the lower end of the operating line is intercepted. Each step is called a theoretical stage. In the present work, the corresponding McCabe -Thiele diagram was then constructed using A/O volume ratio of (1:1) for the operating line. The practical number of stages was stepped off as shown in **Figures (7,8)**. From the latter it is evident that three stages are quite adequate to almost saturate the organic phase and to deplete the mother leach liquor of U (VI) and Th (IV).

3.7. Re-extraction process (stripping)

A general procedure for this technique is as follows: The loaded solvent is contacted with suitable strip solution, acid or base, at an appropriate phase ratio until equilibrium is attained. The aqueous phase is then removed and analyzed for U(VI) and Th(IV). Stripping process depends on number of different factors which have to be studied in order to obtain the best stripping efficiency that matches at the time with economic consideration are, effect of different reagents (strip solution) acid or base, effect of reagent concentration, effect of contact time and effect of organic/aqueous phase ratio.

3.7.1. Acidic stripping

Different acidic stripping reagents namely HCl, HNO_3, H_2SO_4, H_3PO_4 and CH_3COOH of the same concentration(4M) was used, the aqueous phase with an A/O phase ratio of 1:1, equilibration time of 10 minutes and at room temperature. It is clear from the obtained result that H_2SO_4 is the best reagent for stripping of U (VI) and Th (IV), as it shown in **Figure (9)**.

3.7.2. Alkaline and neutral stripping

Sodium carbonate, sodium hydroxide and sodium sulphate (0.01M) were chosen for the present work at contact time of 10 minutes and aqueous/organic phase ratio of 1:1, a precipitate took place as soon as the solutions were added to the loaded solvent. This must probably due to the precipitation of U (VI) and Th (IV) hydroxide at higher pH. But the precipitate was not formed at very dilute solution (0.01M) from NaOH and Na_2CO_3. For this reason 0.01M was used from the results as shown from **Figure (10)**, it is clear that U(VI) and Th(IV) stripping efficiency are not good enough for these elements. From the studies of the type of the stripping agents it was found that the mineral acids are suitable for stripping of U (VI) especially 4M H_2SO_4. The following factors were studies to define the optimum conditions for stripping of U (VI) process with sulfuric acid as stripping agent. For simultaneous Th (IV) and U (VI) stripping, HCl, NaOH, Na_2SO_4, Na_2CO_3, HNO_3, CH_3COOH and H_3PO_4. H_2SO_4 showed a satisfactory performance. In this case, Th/U separation can be achieved by selective precipitation **[2].**

3.7.3. Effect of different sulfuric acid concentrations.

A series of stripping experiments were carried out, using H_2SO_4 solution of concentration ranging from 0.5 to 5 M. The obtained results for U (VI) and Th (IV) are shown in **Figure (11)**. It is clear from the obtained results that stripping by H_2SO_4 decreases after 4M H_2SO_4. The best U(VI) and Th(IV) re-extraction percent was given by 4M H_2SO_4, while contact time was 10 minutes and phase ratio (1:1) (v/v) organic / aqueous phase ratio at room temperature.

3.7.4. Effect of contact time on the stripping process

The effect of contact time on the attainment of an equilibrium state has been studied at the time intervals 1-20 minutes, while the other factors were kept at 4M H_2SO_4 and 1:1(v/v) aqueous: organic phase ratio. The experiments were carried out at room temperature. The results obtained are shown in **Figure (12)**. It is obvious that contact time of 15 minutes is sufficient for high stripping efficiency of U(VI) and Th(IV) from the loaded solvent.

3.7.5. Construction of Mc Cabe Thiele diagram on U(VI) and Th(IV) stripping

Fresh loaded solvent is added to the funnel containing the remainder of the aqueous phase for the operating line. The practical number of stages was stepped off as shown in **Figure (13,14)**. It is obvious that five stages are quite adequate to almost saturate the aqueous phase and to deplete the mother leach liquor of U (VI) and Th (IV). The corresponding McCabe -Thiele diagram was then constructed using A/O volume ratio of (1:1) and 15 minutes until the equilibrium is obtained.

IV. Effect of temperature

The extraction of a metal complex into an organic phase involves large changes in enthalpy (solvation processes) and in entropy (solvent orientation and restructuring), leading to considerable temperature effects. To study the effect of temperature on extraction of U(VI) and Th(IV) ions, experiments were carried in the range 298–323°K. The results obtained showed that the extraction of U(VI) and Th(IV) decreased from 298°K to 333°K. The results are shown in **Figure (15)** as a function of Log D versus 1000/T, K^{-1} gives a straight line whose slope equals (-ΔH / 2.303R) for the extraction of U (VI) and Th (IV) by TOA in kerosene from sulfate medium. From **Table (3)** the ΔH value for U (VI) was (-26.04 kJ/mol) and for Th(IV) was (-27.76) as calculated from the slope using the Van't Hoff equation (Equation (3)).

$$\text{Log D} = \frac{-\Delta H}{2.303\,RT} + C \qquad (3)$$

Where D is the distribution coefficient, ΔH the enthalpy change for the extraction reaction, R is the universal gas constant (8.314 J/mol k) and C is an integration constant which includes the equilibrium constant for the extraction. This value of ΔH for U (VI) and Th (IV) was used to obtain the corresponding free energy (ΔG_U = -3994.09 kJ/mol and entropy ΔS_U = 13.31 J/mol.K) and (ΔG_{Th} = -4222.33 kJ/mol, and ΔS_{Th} = 14.07 J/mol.K) at 298^oK using Equations (4,5), respectively:

$$\Delta G = -\,2.303RT \log D \qquad (4)$$

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

The negative value of ΔH indicates that the extraction of Th(IV) and U(VI) in this system is an exothermic process, with an increase in the randomness of the system shown by the high positive value of the entropy change (ΔS)**.** The negative value of ΔG indicates that the extraction reaction is spontaneous, and the observed decrease in the negative values of ΔG with elevated temperature implies that the extraction reaction becomes more favorable at room temperatures **[11].**

V. Recovery and precipitation of U (VI) and Th (IV)

U(VI) and Th(IV) precipitation was performed by ammonium hydroxide and 10% oxalic acid solutions. The attained U(VI) and Th(IV) precipitations efficiency were about (90%) as a thorium oxalate and ammonium diuranate crystals precipitated from the concentrated stripping solution. The obtained U(VI) and Th(IV) precipitation was subjected to characterization by using Environmental Scanning Electron Microscope**.**

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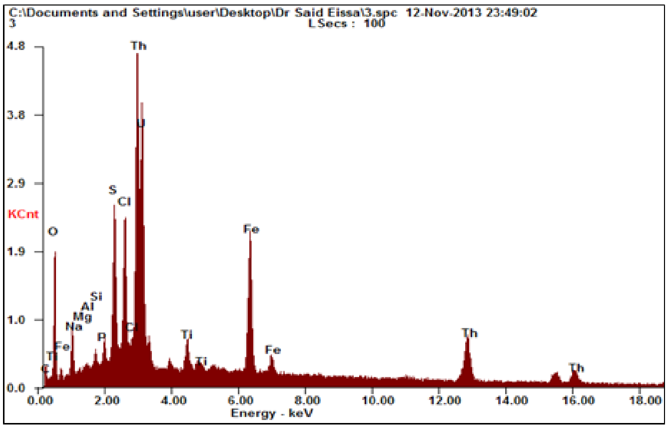


Fig (1): EDAX of pure Th/U concentrate at pH= 5.8

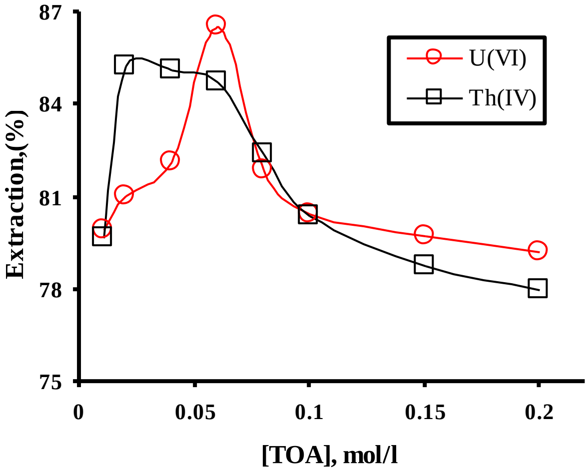
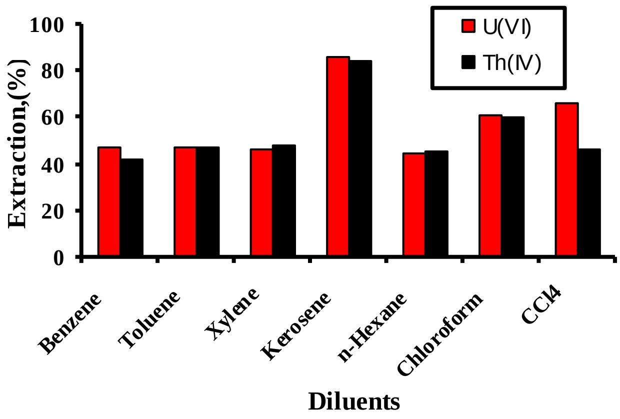


Fig. (2): Effect of TOA conc. on U(VI) and Th(IV) extraction.



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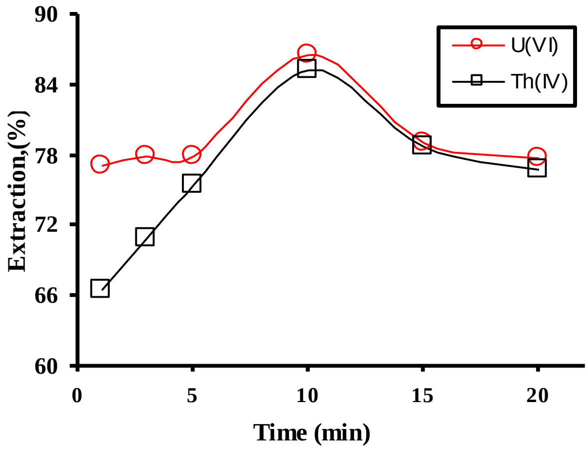

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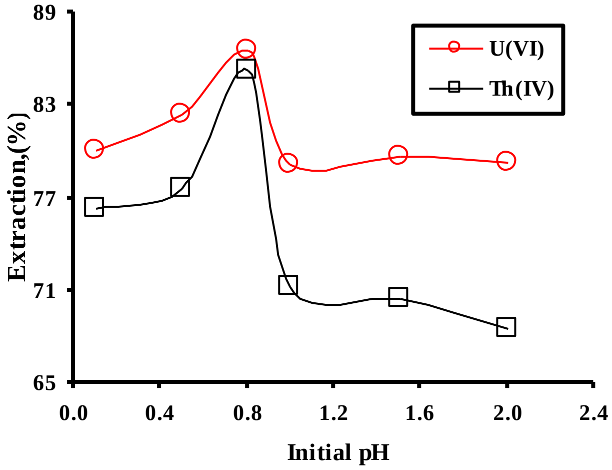
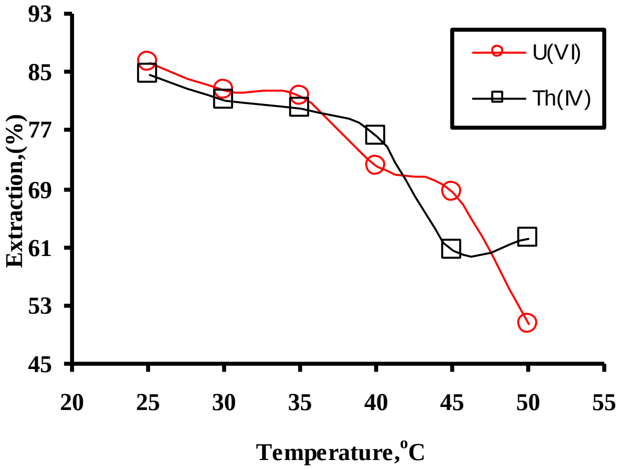


Fig. (5): Effect of pH on U (VI) and Th (IV) extraction.



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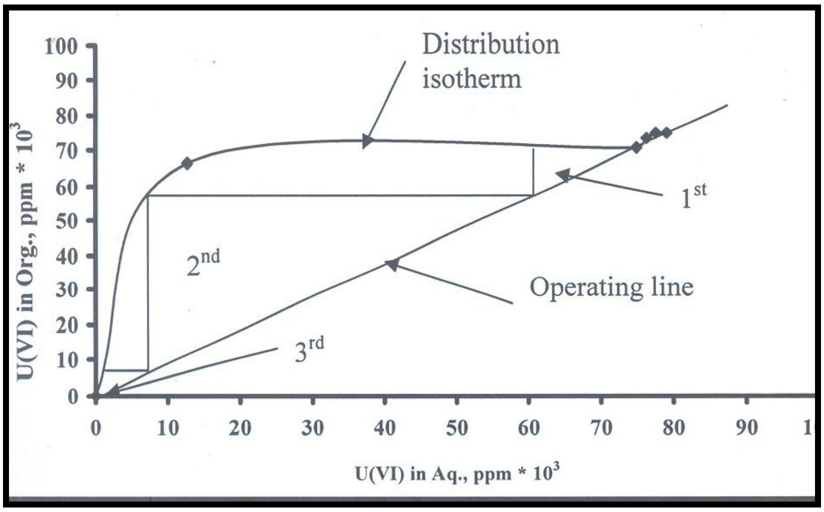
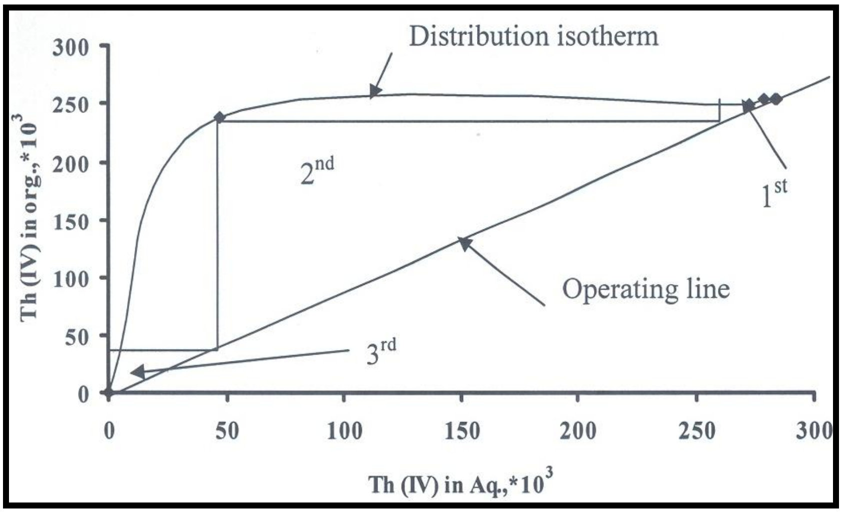


Fig.(7): Mc Cabe Thiele of diagrame of U(VI).



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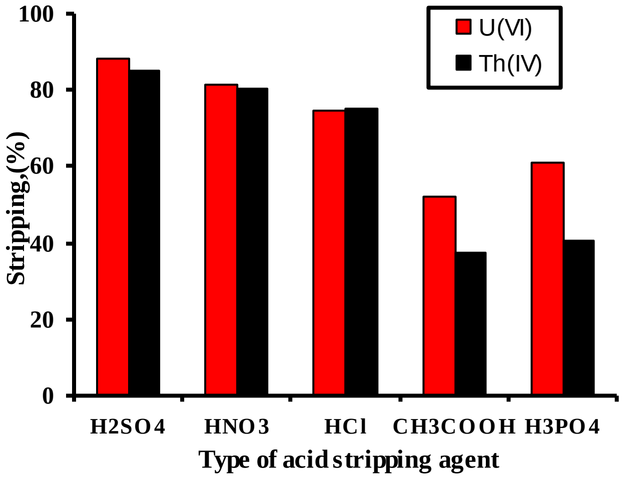
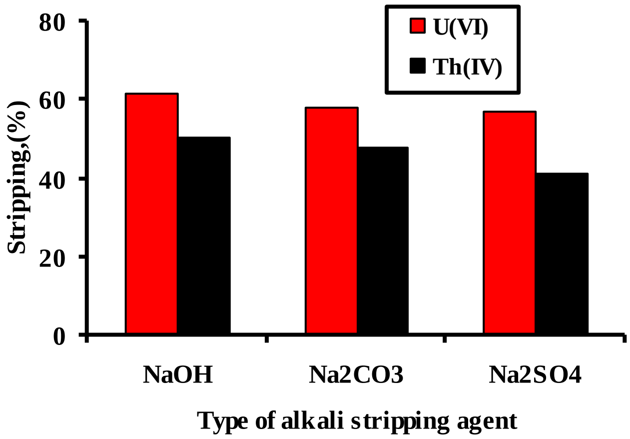


Fig. (9): Effect of different types of acidic stripping agent on U (VI) and Th (IV) stripping.



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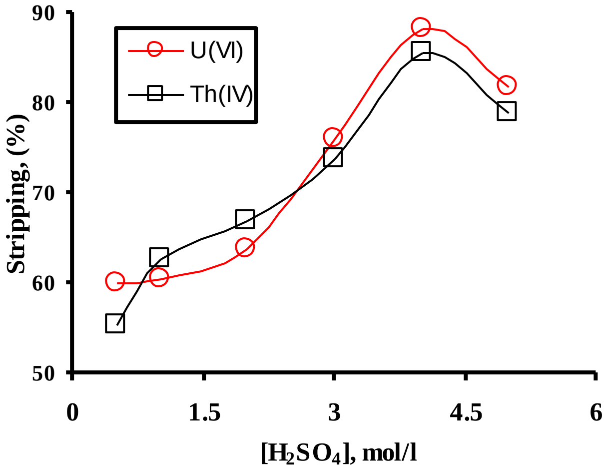

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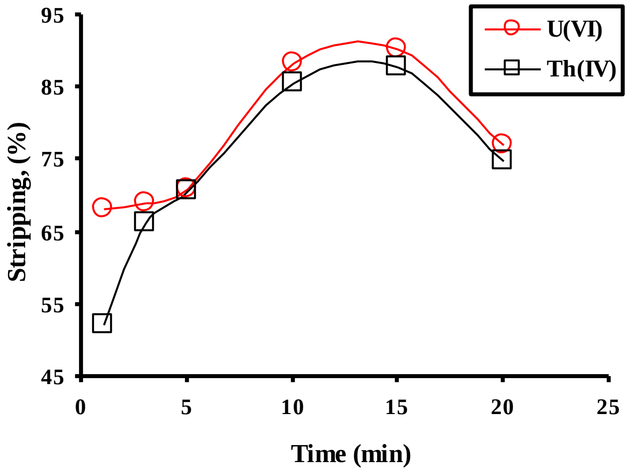


Fig. (12): Effect of equilibration time on U(VI) and Th(IV) stripping

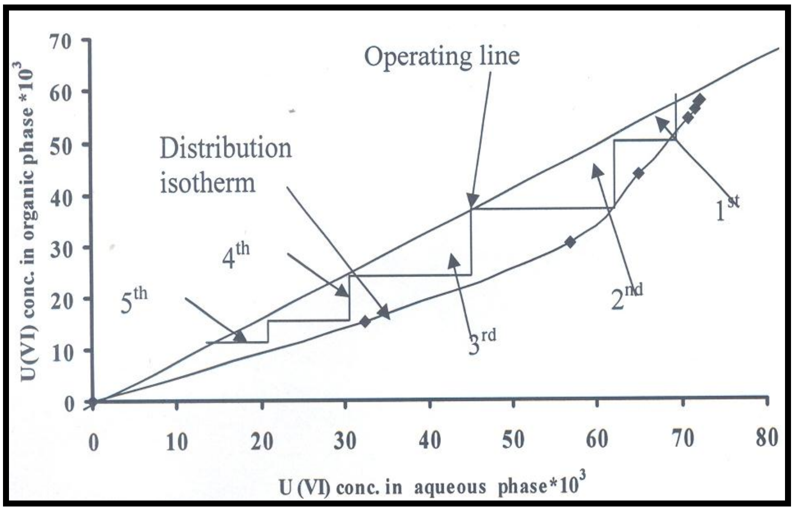
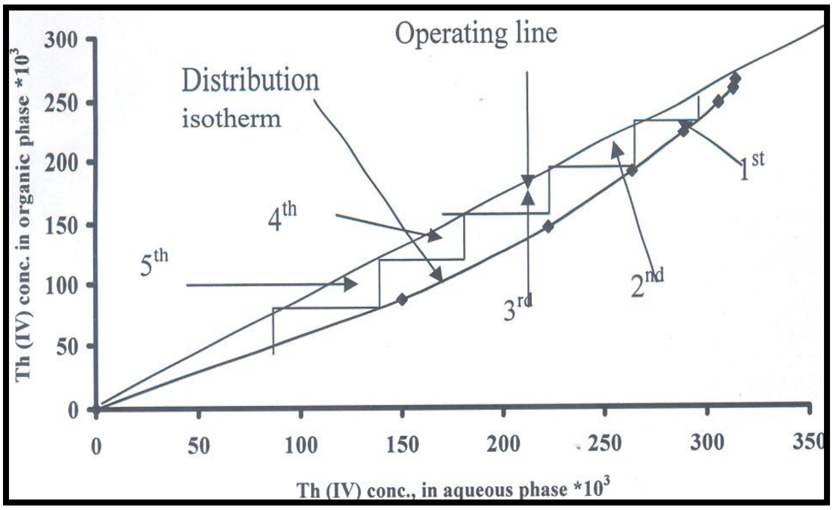


Fig. (13): Mc Cabe Thiele diagram of U (VI)



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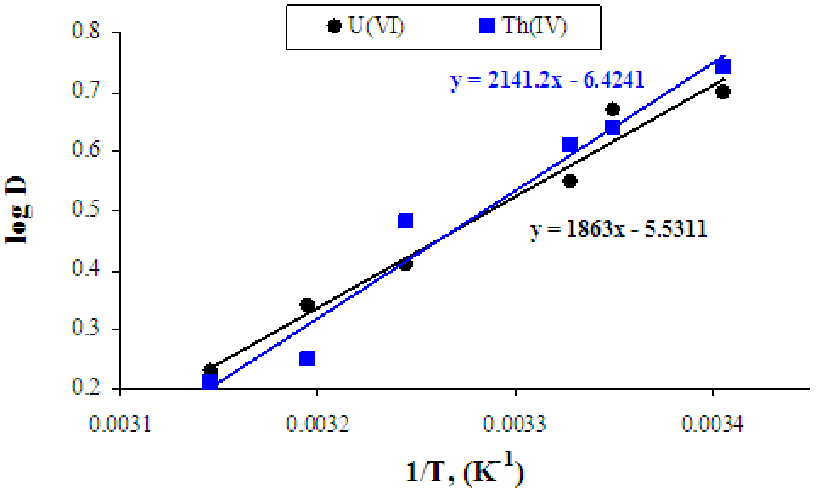

Fig. (15): Van't Hoff plots of ln log D against 1/T, K^{-1} of U(VI) and Th(IV) ion.

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Table (1): Chemical composition of Egyptian monazite

Constituents	%	Constituents	%
Monazite content	96.87	Eu_2O_3	0.055
Total REEs(RE_2O_3)	58.79	Gd_2O_3	1.15
U_3O_8	0.41	Iron(Fe_2O_3)	1.910
ThO_2	4.89	Tm_2O_3	0.01
P_2O_5	27.73	Yb_2O_3	0.039
La_2O_3	13.35	Y_2O_3	1.43
CeO_2	26.26	Tb_4O_7	0.17
Pr_6O_{11}	3.42	Dy_2O_3	0.37
Nd_2O_3	12.00	Ho_2O_3	0.075
Sm_2O_3	2.43	Er_2O_3	0.095
Lu_2O_3	0.01	Moisture content	6.5

Table (2): Chemical compositions of Th/U concentrate

Constituents	%	Constituents	%
ThO_2	54.04	TiO_2	0.68
U_3O_8	7.88	CaO	1.41
RE_2O_3	4.42	MgO	0.75
Fe_2O_3	0.89	Moisture content	29.21
TiO_2	0.72		

Table (3): Thermodynamic parameters and values of R^2 for U(VI) and Th(IV) extraction.

Metal ion	T, K	1000/T, K^{-1}	log D	ΔH, KJ/mol	ΔG, KJ/mol	ΔS, J/mol	R^2
U(VI)	298	3.36	0.7	-26.04	-3994.09	13.31	0.9653
	303	3.30	0.67		-3887.06	12.75	
	305	3.29	0.55		-3243.53	10.45	
	313	3.19	0.41		-2457.15	7.76	
	318	3.14	0.34		-2070.19	6.43	
	323	3.10	0.23		-1422.44	4.32	
Th(IV)	298	3.36	0.74	-27.76	-4222.33	14.07	0.9759
	303	3.30	0.64		-3713.01	12.16	
	305	3.28	0.61		-3597.36	11.59	
	313	3.19	0.48		-2876.66	9.10	
	318	3.14	0.25		-1522.19	4.70	
	323	3.10	0.21		-1298.75	3.93	

VI. Conclusion

This study presents a rapid and selective method for the recovery of U (VI) and Th (IV), existing in economically interesting concentrations, from Egyptian monazite, liquid- liquid extraction and separation of U(VI) and Th(IV) from REEs and co-leached main elements such as iron, and purification and enrichment, the use of lower concentration of TOA and D2EHPA encourages the commercial use of this extractant for the recovery of U (VI) and Th (IV), TOA and D2EHPA extract U(VI) and Th(IV) nearly quantitavely from Egyptian monazite sample solutions and thus offer a potential commercial applicability in the U(VI) and Th(IV) recovery from metal strip solutions, TOA and D2EHPA extract U (VI) and Th(IV) quantitavely unlike, tributyl phosphate and tri octyl phosphine oxide which require the use of salting-out agent for low result conditions of extraction, TOA and D2EHPA is successfully used to separate U (VI) and Th(IV) from some commonly associated metal ions like Fe (III), Ca (III), P_2O_5, Y (III) and other REE's, extraction and separation of U (VI) and Th(IV) with TOA and D2EHPA proves commercially economic because both of them can be regenerated and reused several times.

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