

## **Monazite- Uranium Separation and Purification Applying Oxalic- Nitrate- TBP Extraction**

**\*Rabie. K. A.; \*\*S. M. Abdel-Wahaab; \*K. F. Mahmoud; \*A. E. M. Hussein and Abd El-Fatah. A. I. L. \*\*\***

*\*Nuclear Materials Authority*

*\*\*Faculty of Sciences, Ain -Shams University*

*\*\*\* The author to home all correspondence should be addressed at the following email [nuclis\\_science @ yahoo.com](mailto:nuclis_science@yahoo.com)*

**Received: 5/6/2012**

**Accepted: 20/6/2012**

### **ABSTRACT**

**This paper describes the process of uranium extraction from the sulfuric liquor generated in the chemical monazite treatment through a solvent extraction technique. The influence of the solvent concentration, effect of precipitating agent, effect of temperature, effect of stirring time and effect of pH were investigated. The results indicated the possibility of extracting completely, uranium by using tri-butyl phosphate (TBP) as an extractant from leach liquor produced after sulfuric acid monazite digestion. The stripping was carried out with cold water. After selecting the best conditions for the process, which was 40-50% TBP/ kerosene (diluent) extractant concentration, 1.5-2M oxalic acid concentration as a precipitant for thorium (extracted with uranium), 45-60 minutes stirring time and temperature was 40-50 °C. A loaded stripping solution containing 0.1986g of U<sub>3</sub>O<sub>8</sub> from the starting 0.21 g with more than 99% purity and 99.3% recovery was obtained.**

***Keywords: monazite / uranium / separation / solvent extraction***

### **INTRODUCTION**

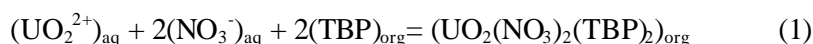
Of the 200 best known minerals containing rare earth (RE) elements, only three contain significant amounts – bastanite, monazite and xenotime, monazite being the second most important source of rare earths (1). Monazite is a rare earth phosphate also containing thorium and uranium as associated metals (2- 6). Its structural group consists of arsenate, phosphate and silicate, having the general formula ABO<sub>4</sub>, where A corresponds to RE, Th, U, Ca, Bi, etc. and B corresponds to As<sup>5+</sup>, P<sup>5+</sup> or Si<sup>4+</sup> (7, 8). The Egyptian black sand beach deposits are the chief thorium ore in Egypt due to the presence of monazite (9). Gupta (10) studied the description of monazite breakdown via. acid and alkali digestion and discussed the composition of the concentrates and their effect on solvent extraction processes. These authors reported that TBP-nitrate system is the most industrially attractive system. The processing of monazite leads to the generation of RE concentrates containing thorium (Th), uranium (U) and phosphate (PO<sub>3</sub><sup>-4</sup>). 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 (H<sub>2</sub>SO<sub>4</sub>) where a liquor containing the RE elements, Th and U is generated (1, 11- 14). 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 (15). 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.

A novel method for the separation of uranium from RE elements and thorium has been devised by the authors and in the process; uranium is simultaneously extracted from the sulphuric liquor generated in the monazite process with the use of Oxalic- Nitrate- TBP extraction method. Studies involving discontinuous and continuous solvent extraction experiments have been carried out, in which the parameters required for the extraction of uranium were determined.

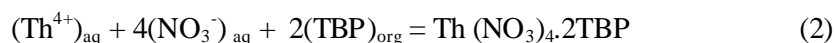
The solvent extraction technique is actually well established for the recovery of nuclear pure uranium and since thorium has certain chemical properties similar to those of uranium, recovery of nuclear pure thorium by solvent extraction has quickly been achieved. In the same manner, cerium in its tetravalent state has to some extent- certain similarities in chemical properties to those of uranium and thorium.

Solvent extraction appeared therefore to be an excellent method adapted to the present situation which is aimed to obtain a continuous production of highly pure uranium. By this method, the required elements are allowed to be extracted from an aqueous nitrate solution into an organic solvent while the impurities would be left behind in the aqueous phase.

Uranium is extracted from nitric acid leach liquors of concentrates by the following reaction (1):

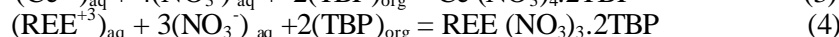
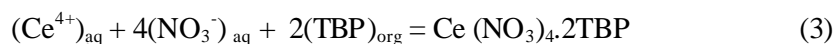


Regarding thorium, it is mainly extracted as  $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TBP}$  from dilute nitric acid solutions with dilute TBP, according to the following equation (2):



However, in extraction at increasing acidities, there is evidence that 3 and even 4 moles of TBP to 1 mole of thorium may be presented in the complex (16).

Finally cerium is also extracted as its tetravalent nitrate (which may be present) and trivalent rare earth elements complex according to the following equations (3, 4):



Since a high concentration of nitrate radical in the aqueous solution derives the above reaction to the right, the loaded organic phase can be easily stripped with either water or dilute nitric acid solutions whereby low nitrate concentration will drive the reaction to the left.

As a matter of fact uranium is actually much more readily extracted by TBP than thorium. This is due to the great different between their respective distribution coefficients which can be advantageously made use of strip selectively thorium from the solvent. Thus by using nitric acid solutions, thorium could be stripped from the TBP extract leaving the uranium behind, which can later be recovered by a simple strip with water.

Along the present experimental work which directed to preserve and attain most of uranium contents of monazite in one purified concentrate and decontaminate the other monazite separated main constituent from it with most available, economic and applicable procedures for up-scaling, an invented process was adapted for such targets. The process summarized in combining a classical uranium- thorium separation methods involving oxalate and tri-butyl phosphate separation methods in an accurate, fast and in one step separation and simultaneous purification of uranium from other contaminants e.g., thorium (major) and REEs (minor) as will be demonstrated and discussed here in after.

During the present work there has been a great need for obtaining maximum separation of thorium from uranium after separating them from REEs. It is therefore an object of the present part to overcome the shortcomings from the prior common solvent extraction processes for recovering and separating uranium from mixtures with thorium. It was also an object of the following work to provide

an improved and highly efficient process for effectively recovering and separating thorium from mixtures with uranium.

## **EXPERIMENTAL**

### **Chemicals and reagents**

The chemicals and reagents in the present work were used as received. Kerosene (nonaromatic) was supplied by Misr Petrol Ltd., Egypt. Tri-butyl phosphate, nitric acid was supplied by BDH, England and sodium hydroxides and oxalic acid and sulphuric acid and ammonia were ADWIC products. The monazite was supplied by the Nuclear Materials Authority, Egypt, as 50% concentrate.

### **Procedure**

According to Cuthbert (17), a suitable pretreatment of TBP solvent consist of the following: A wash with 0.2 vol. of 1.5 M nitric acid. Two washes with 0.2 vol. of 1 M sodium hydroxide. Washes with water until the latter is neutral.

The process of the present section started after monazite mineral acid digestion and dissolution at optimum conditions. The clear sulphate solution (liquor) is treated with sodium hydroxide after precipitation with ammonia solution to prepare the mixed hydrous oxides of the three main mineral cationic components namely rare earth elements as a group, thorium and uranium. The cake was washed thoroughly to be free from excess soda and dried. The cake was dissolved completely in nitric acid 1N with gentle stirring avoiding suspension for easier further filtration processes (filterable raffinates). The aqueous acid solution was then precipitated at pH 5.5 with 10% sodium hydroxide. The filterable mixture was then filtered of for clean pure rare earth nitrates and hydrated thorium & uranium concentrate.

The produced precipitate contains mainly all thorium and uranium constituent of the mother sulphate starting liquor with a minor rare earth percent. The precipitate was washed carefully then redissolved again after drying in a slight excess of stiochiometric nitric acid and then heated till near dryness. The applied separation process comprises and aims to selectively and simultaneously extracting and precipitating thorium from uranium, where both elements are dissolved as their nitrates in the organic solvent, and by contacting the organic solvent solution, containing the thorium and uranyl nitrates dissolved therein, with an aqueous solution of an agent which selectively precipitates the thorium as a crystalline compound which is insoluble in, but transferred to the aqueous phase. Most of the uranium and trace of REEs remains in the organic phase, and can be recovered from it by conventional methods e.g., stripping selectively with water or alkali carbonate solution followed by diluted nitric acid stripping for the minor REEs contents. The small amount of uranium extracted together with the thorium into the aqueous phase can be easily recovered by solvent extraction after or before the filtration of thorium precipitates. The common selective precipitating agent useful for application in the practice of the present process is oxalic acid. The free oxalic acid is preferred than its water soluble salts (oxalates) as selective precipitating agent since it doesn't introduce any foreign cations which might contaminate the separated elements in addition to the possibility of recovering the released nitric acid( after thorium nitrate precipitation as oxalate) into the aqueous phase.

The employed organic solvent, in which the mixed thorium and uranyl nitrates can be dissolved, is tri-butyl phosphate (TBP) as alkyl phosphate (ester of phosphoric acid diluted with kerosene as available petroleum aliphatic solvent). The organic solvent and the organic solution should desirably possess a specific gravity less than that of the aqueous extracting and precipitating agent, otherwise the

precipitate of thorium produced in the process remains in the organic phase and doesn't pass into the aqueous phase. For each 100 gm sample batch of monazite mineral(-125 mesh ~ 50%), the Th &U nitrate mixture produced after the aforementioned procedures contains 2.66 g thorium calculated as ThO<sub>2</sub>, 0.21g uranium calculated as U<sub>3</sub>O<sub>8</sub> and 3.58g rare earth elements calculated as RE<sub>2</sub>O<sub>3</sub>. The mixture was dissolved in different solvent concentrations and treated with different precipitant concentration at different temperatures and stirring time to find the effect of each parameter beside the pH effect. The study of each previous parameter separately while keeping the others constant was fulfilled to find the optimum precipitation and separation parameter which attain the higher possible purity and recovery percents for uranium.

For the rare earth elements present percents in the original nitrate mixture and transferred to the organic solvent a pre-treatment steps for the solvent were carried out. The pre-treatment procedures concised in contacting the solvent with 2M nitric acid solution containing H<sub>2</sub>O<sub>2</sub> with ratio 1 H<sub>2</sub>O<sub>2</sub>: 5 HNO<sub>3</sub> (0.2 aqueous: 1 organic phase ratio) in one contact to remove the co-extracted trivalent rare earth elements and tetravalent cerium which may be present.

After scrubbing (washing) of the loaded solvent the aqueous raffinate was analyzed for Th, U and total rare earth elements. It was found that the solvent elemental components lost are 0.03 g, 0.01 g and 3.51g of ThO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub> and RE<sub>2</sub>O<sub>3</sub> respectively. In other words the starting solvent elemental components were 2.63g, 0.20g and 0.07g (700 ppm) of thorium as ThO<sub>2</sub>, uranium as U<sub>3</sub>O<sub>8</sub> and rare earth elements as RE<sub>2</sub>O<sub>3</sub> with scrubbing percent of REEs exceeded 98% and 4.7 % of uranium and 1.1% of thorium lost from the solvent starting composition. 3. Analytical Procedures. Analytical procedures for thorium, rare earths and uranium are summarized as follows, gravimetric methods analysis, spectrophotometric methods of analysis (JASCO V530) and titration method (18-22).

## **RESULTS AND DISSCUSIONS**

From general overview on the effect of solvent concentration, precipitating agent concentration, time of stirring and temperature on the extraction of thorium and uranium and the percent of recovery of each in addition to their purity (decontamination of each from the other one), one can judge that, a noticed increase in thorium values with solvent concentration, temperature, stirring time and precipitant concentration till certain limit. While the case was reserved with uranium concentration values in most cases. The noticeable variation in the experimental results will be declared separately with the variation of each factor after presentation of the data here in after with probable interpretation of the results. Before going to discuss the results, separation of thorium from uranium and vise versa is made effective for their purification (via selective and simultaneous precipitation and extraction of thorium oxalate) from each other and from the other co-existing elements such as few hundreds of part per millions REEs which may be existed.

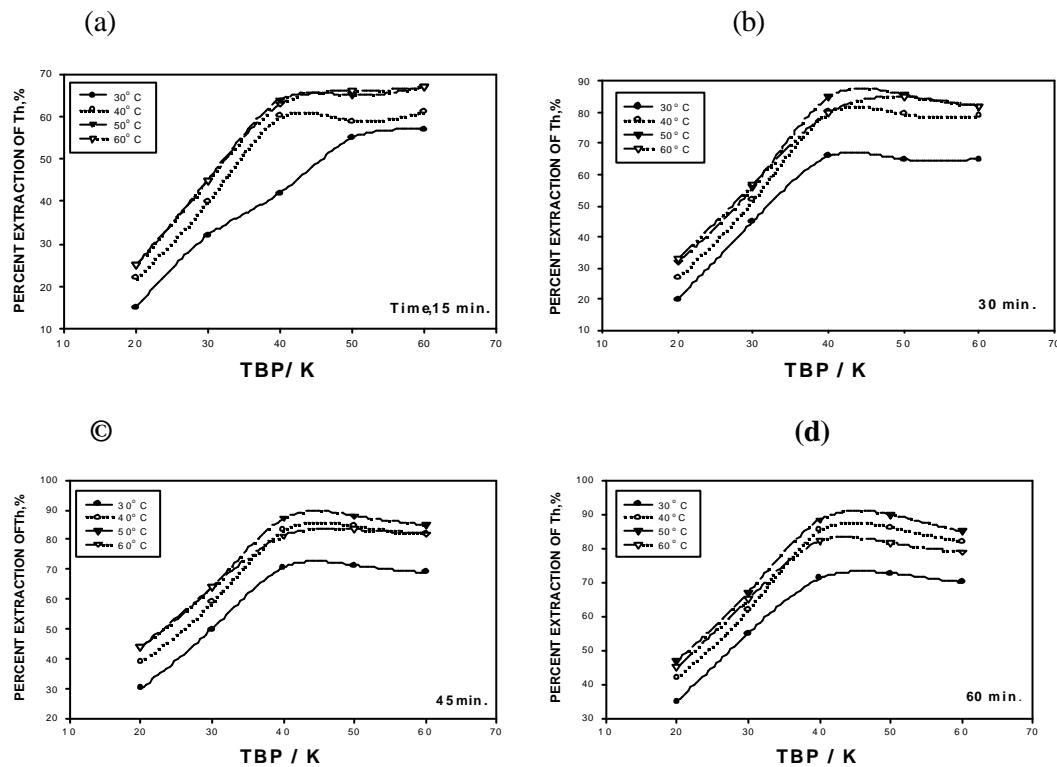
Since the use of the precipitating agent in the aqueous extracting phase makes it possible to minimize the volume ratio of the aqueous to organic phases, and at the same time provide a high acidity and / or concentration of nitrates in the aqueous extracting phase, this influences the distribution of uranium nitrate is favor of the organic phase. This assists in the effectiveness of the separation of the thorium from uranium, since the latter remains predominantly in the organic solvent, thereby reducing the amount of uranium contaminating the thorium oxalate which is transferred to aqueous phase.

All thorium and uranium recorded values were obtained after analysis of both elements in their produced concentrates. In other words, thorium was determined in its crystalline oxalate precipitate easily while uranium was determined in the final aqueous raffinate of stripping contact between water and TBP after oxalate separation. At the same time the lower values of each element inside the other

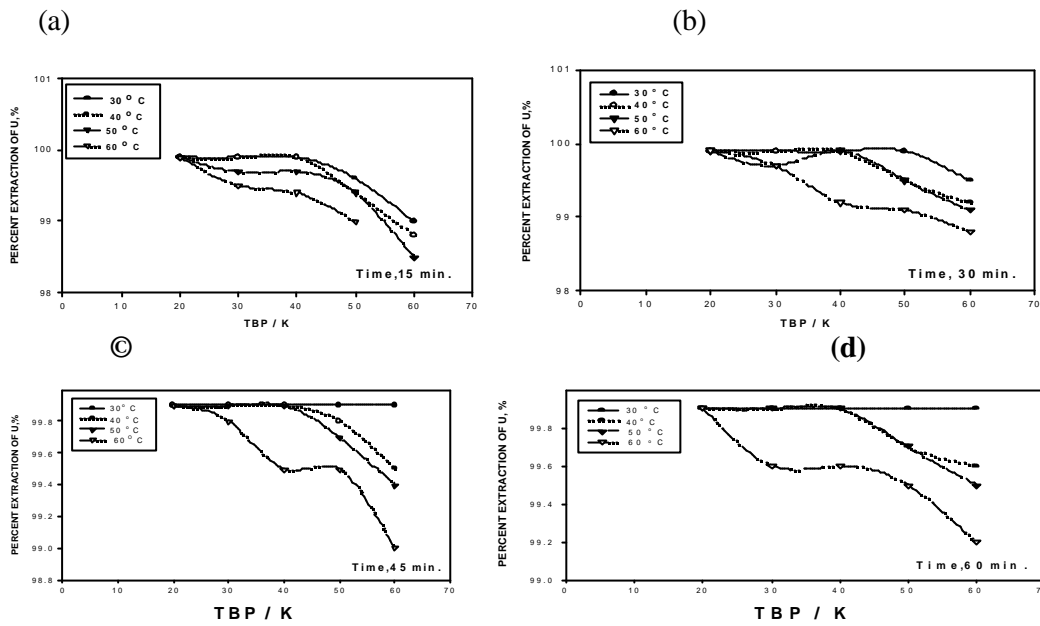
after the process application were determined by subtraction ( $C_i - C_f$ ) where  $C_i$  represent the initial element concentration inside the solvent and  $C_f$  is the final concentration of the element inside its concentrate after the process completion.

The process results make it possible to recover thorium without co-extracting more than 1% of the original uranium present in the organic solvent starting solution. It is possible under certain circumstances to recover up to 99.9% of the thorium originally present in the organic solvent starting solution while, up to 99% of the initial uranium remains in the organic phase and is effectively separated from the thorium.

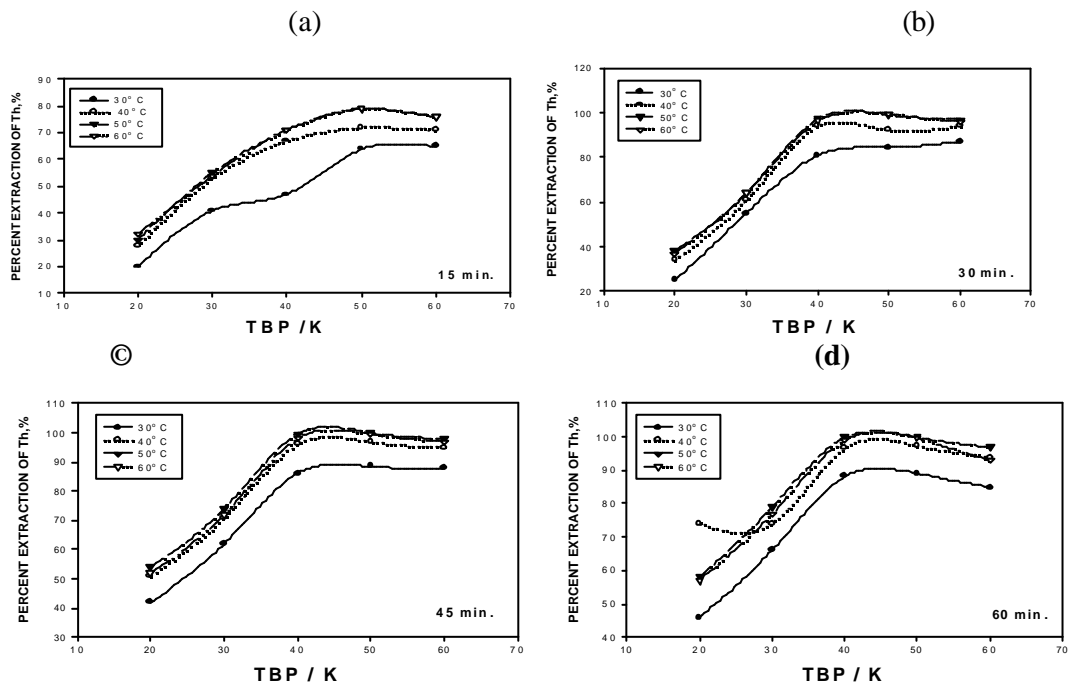
The selected region of the applied conditions is dependent on the target whether thorium or uranium preservation and purification. Experiment was carried out by contacting 25 ml solvent (TBP/ kerosene) of different concentrations containing nitrate salts of Th & U with 25ml aqueous oxalic acid solution of different concentration and stirring was carried out for different time intervals and at different temperatures which adjusted first for the oxalic acid solution then adapted via external hot plate with stirrer to the desired temperature and keep it constant during the time of the experiment by thermometer. The effect of each studied parameter will be demonstrated clearly through the discussion of the experimental results in figures (1-8) for uranium and thorium extraction percents as will be seen below.



**Figure (1):- Effect of solvent concentration (TBP/ kerosene) on 0.5M of oxalic acid on the extractability of thorium at**  
**a= stirring time 15 minutes                      b= stirring time 30 minutes**  
**c= stirring time 45 minutes                      d= stirring time 60 minutes**



**Figure (2):-** Effect of solvent concentration (TBP/ kerosene) on 0.5M of oxalic acid on the extractability of uranium at  
 a= stirring time 15 minutes      b= stirring time 30 minutes  
 C= stirring time 45 minutes      d= stirring time 60 minutes



**Figure (3):-** Effect of solvent concentration (TBP/ kerosene) on 1M of oxalic acid on the extractability of thorium at  
 a= stirring time 15 minutes      b= stirring time 30 minutes  
 C= stirring time 45 minutes      d= stirring time 60 minutes

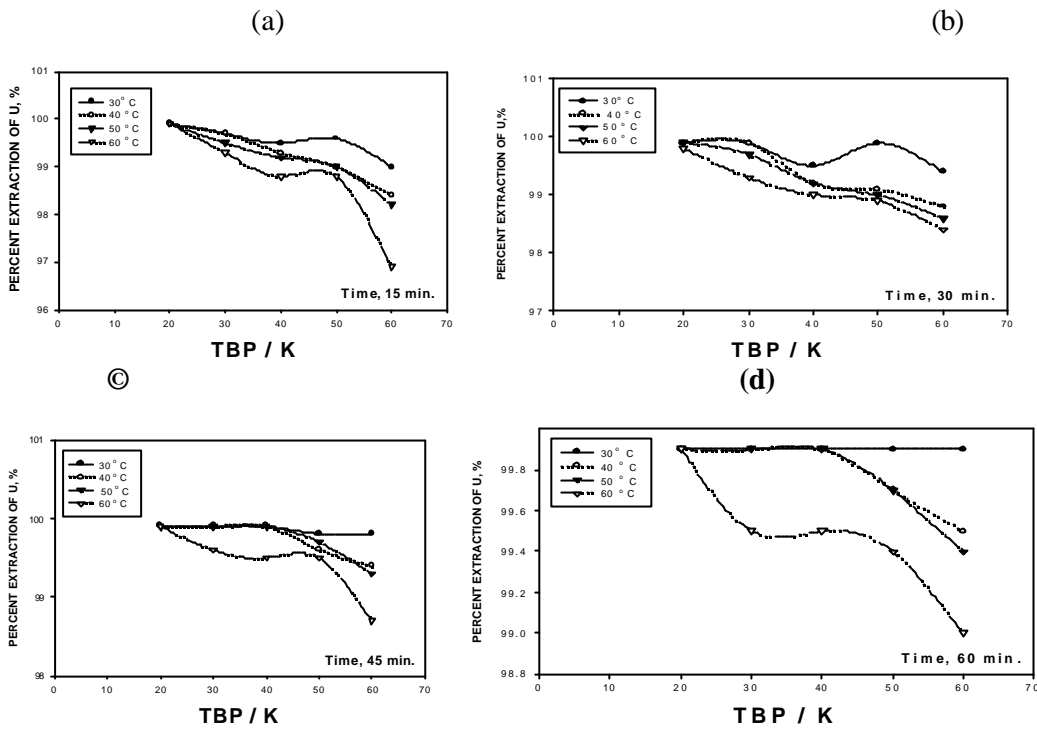


Figure (4):- Effect of solvent concentration (TBP/ kerosene) on 1M of oxalic acid on the extractability of uranium at  
 a= stirring time 15 minutes      b= stirring time 30 minutes  
 C= stirring time 45 minutes      d= stirring time 60 minutes

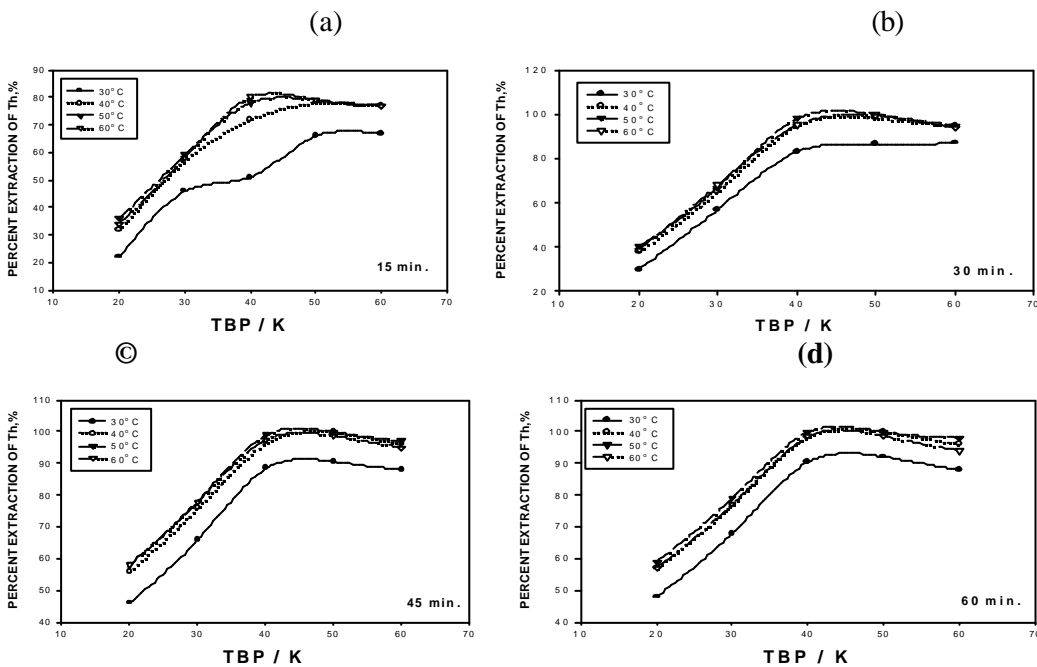
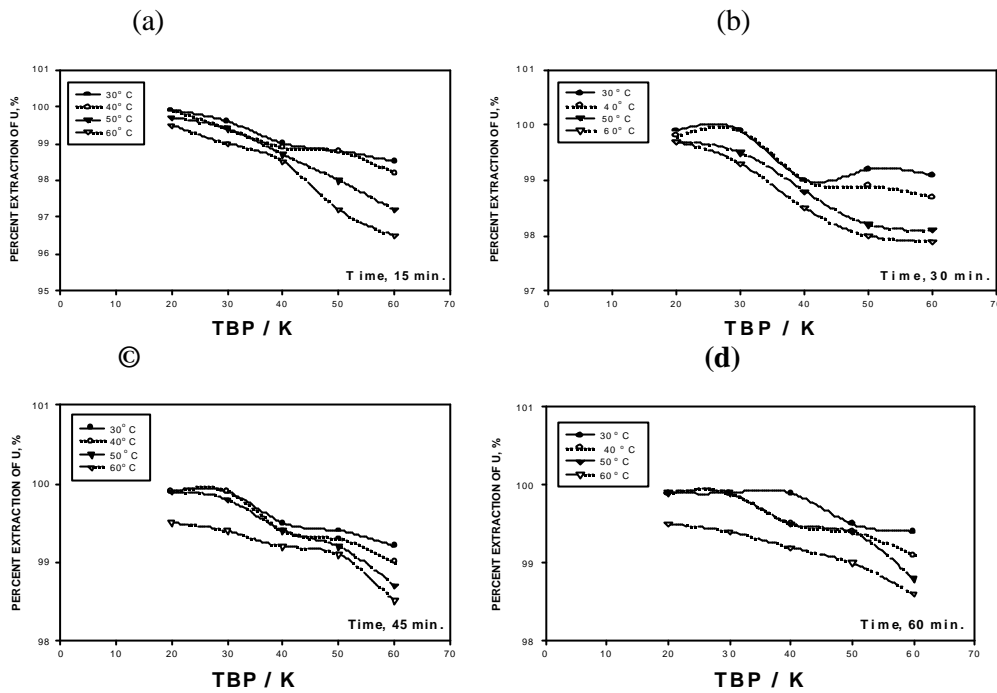
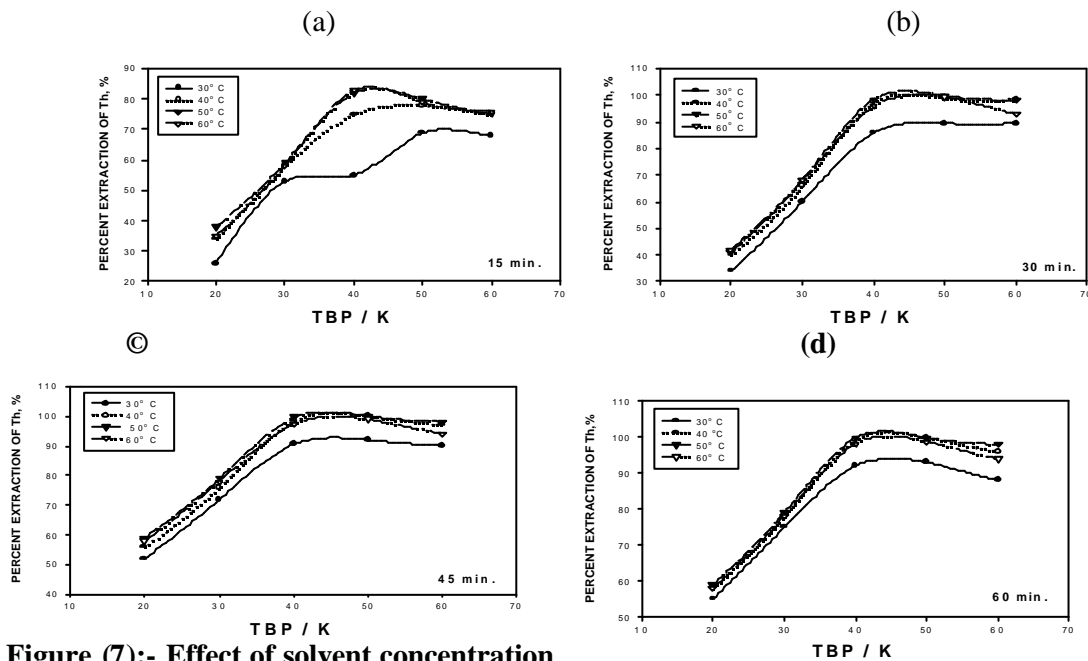


Figure (5):- Effect of solvent concentration (TBP/ kerosene) on 1.5M of oxalic acid on the extractability of thorium at  
 a= stirring time 15 minutes      b= stirring time 30 minutes  
 C= stirring time 45 minutes      d= stirring time 60 minutes

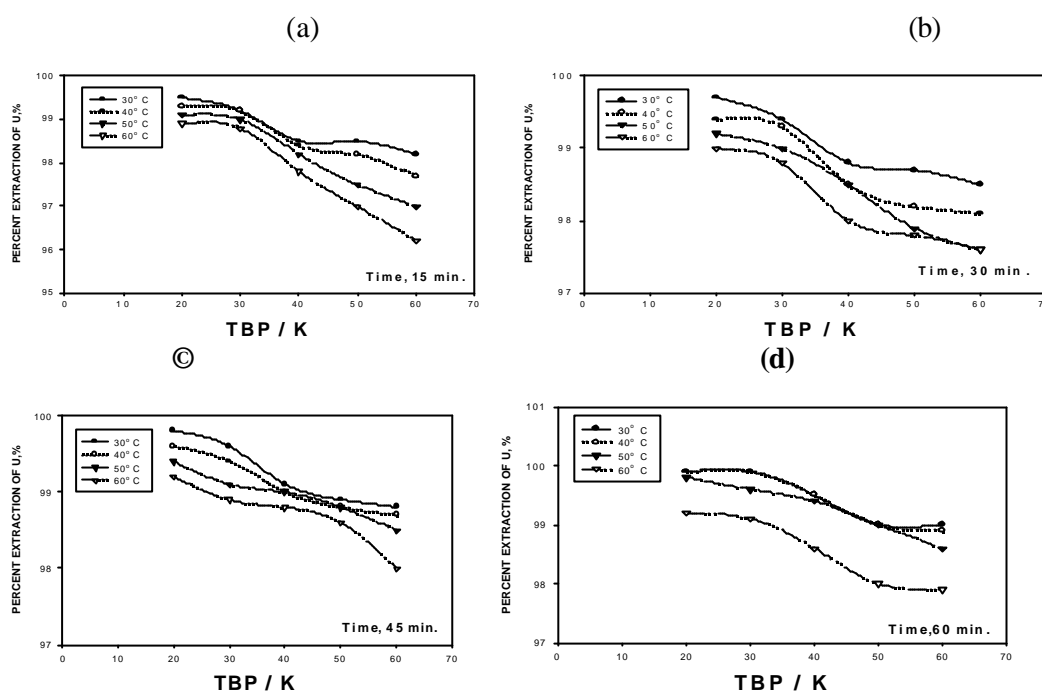


**Figure (6):-** Effect of solvent concentration (TBP/ kerosene) on 1.5M of oxalic acid on the extractability of uranium at  
 a= stirring time 15 minutes      b= stirring time 30 minutes  
 C= stirring time 45 minutes      d= stirring time 60 minutes



**Figure (7):-** Effect of solvent concentration (TBP/ kerosene) on 2M of oxalic acid on the extractability of thorium at  
 a= stirring time 15 minutes      b= stirring time 30 minutes  
 C= stirring time 45 minutes      d= stirring time 60 minutes





**Figure (8):- Effect of solvent concentration (TBP/ kerosene) on 2M of oxalic acid on the extractability of uranium at**  
**a= stirring time 15 minutes                      b= stirring time 30 minutes**  
**c= stirring time 45 minutes                      d= stirring time 60 minutes**

The starting solvent concentration was 20% TBP in kerosene, from the data it's clear that partition of thorium was carried out by solvent and precipitating agent (oxalic acid) with different values starting from 15% at 30°C, 0.5M oxalic acid and 15 minutes stirring time, ended with 58-59% at 45-60 minute stirring time, 50-60°C and 1.5-2M oxalic acid. At the same time uranium was recovered completely in the organic phase under most of the different applied separation conditions. It was evident from all the results of 20% TBP/K extraction experiments, that uranium can be collected in one step but not pure while thorium may need many processes which mean the unsuitability of solvent concentration for complete thorium recovery and for uranium purification targets.

For 30% solvent concentration experiments thorium separation results were enhanced to reach 79% in some circumstances while uranium recorded more than 99% recovery under most applied conditions for thorium and uranium percent extraction respectively. From these results, one can judge that uranium final recovery is not hardly affected with stirring time, oxalic acid concentration and temperature change while recorded thorium percents extraction was increased in all cases by increase in solvent concentration, precipitating agent concentration increase, time of stirring increase and temperature increase till 50 °C then started to decrease again which may be attributed to the harmful effect of higher temperature on the composition of solvent. In spite of the higher attained extraction values for uranium and thorium, the worked solvent concentration under all mentioned conditions did not give the highest desired uranium purity and thorium recovery and purity. In other word uranium can be recovered completely but with high thorium contamination percents.

Tri-butyl phosphate with 40% concentration gave higher extraction percents for thorium than the previous concentration (30%). thorium recovery when using such concentration (40%) reach to more than 99% under some experimental conditions such as, 1-2M oxalic acid, 50° C and 45-60 minute time of stirring figure. At the same time the highest uranium recovery and purity under the

aforementioned conditions (best for Th recovery) was gained with only 1M oxalic acid, 50° C and 45 minute time of stirring. Complete uranium recovery can be attained in many experimental points through most of working conditions but the problem was the suspicious of the decontamination of uranium with thorium. The same case was observed for thorium recovery and products, one can obtain complete thorium recovery along many experiments but little points gave free thorium from uranium. In general the case of thorium and uranium complete or near complete separation with highest recovery and purity of each was close starting from 40% TBP/ Kerosene concentration. The final conclusion was that more than 99% uranium content can be recovered nearly free from thorium contamination with 40% TBP / K and 1-2 M oxalic acid concentration at 50° C with 60 minute stirring time, while more than 99% thorium content can be recovered nearly free from uranium contamination with 40% TBP.

In spite of obtaining a good thorium extraction and purification from uranium in addition to the better uranium recovery and purification percents during 40% TBP group of experiments and measurements it was necessary to complete to the higher solvent concentration to obtain many probable and promising experimental conditions to facilitate their separation and purification during many points more than the previous concentration. 50% of solvent concentration group of extraction experimental data prevails that, more than 99.9% of the thorium content can be recovered in the region 1-2M oxalic acid, 45-60 minutes stirring time under 40-50°C with more than 99.5% uranium recovery. One can obtain pure uranium concentrate free completely from any thorium contamination in the same time; one can obtain thorium concentrate nearly free from uranium except from 5 to 15 ppm U. These experiment results were recorded for thorium and uranium, from the figures it was obvious that, the collapse in all recovery and as a result mutual purity percents for both elements. This may be attributed to the higher viscosity of the organic phase and the adverse effect of temperature especially at higher concentrations. Collecting the total effect of the organic concentration over the whole experimental groups for thorium extraction and uranium recovery through figures (1-8), one can judge that, a general positive increase in the thorium extraction and uranium recovery percents till 40-50% solvent concentration over any particular experimental condition is evident.

Oxalic acid concentration effect as precipitating agent for thorium was discovered through collecting the data in the previous different figures under various conditions of organic concentration, time of stirring and temperature and to demonstrate the most active concentration of the precipitating agent for the present thorium concentration separating by precipitation from various TBP concentrations. Extraction of thorium was increased during the same temperature with oxalic acid increase with all solvent concentration nearly except for high organic concentration. The same trend of increase was observed when increasing the time of stirring under the same temperature and particular organic concentration, till nearly a constant value which attained after about one hour. Moving from one temperature to the next higher one, and comparing with preceding extraction percent, it was clear that, the effect of increasing oxalic acid with temperature increase. In other words, at higher temperatures the increasing in precipitating agent concentration was more effective in separating thorium from uranium with different stirring time and organic concentration.

In the same time oxalic acid concentration increase was not so effective for uranium recovery during most of variable experimental conditions. This may be attributed to the definite oxalic acid rule in uranium recovery, (only reduce uranium inside organic phase leaving it and searching for thorium to precipitate). In other words it affect uranium purity more than recovery via complete or near complete thorium recovery. Increasing temperature effect on each extraction experiment was observed from the figures, it is clear that, extraction of thorium increased with temperature increase within the same experiments till 50°C then the stop and the starting decrease again which may be attributed to the solvent nature as mentioned before. Increasing the stirring time enlarge temperature effect within the same experiment under particular TBP and oxalic acid concentration.

In other words one can say, the effect of temperature increase on the thorium extraction was enhanced with increasing stirring time during most of experiments. The same effect and correlations were noticed under all tried organic concentration till 60% in addition to all precipitant concentrations. Uranium recovery percents were slightly changed with temperature change or increase during most experimental conditions and the decreasing effect in its recovery was observed specially with organic condition increase. In other words, and in general, temperature increasing effect, affect only thorium recovery in most cases and in turn uranium purity.

Stirring time increasing effect can be noticed through all previously presented thorium extraction data and figures. Within the same experiment of the same temperature, it was found that a noticed increase in thorium extractability while a very slight uranium recovery change was observed under the experimental precipitating conditions. The change in thorium extraction behavior with increase of stirring time was nearly the same as temperature increase, under all experimental data of 60% solvent and 50°C. Uranium recovery discussion is more or less similar to the previous discussion. Some selected experiments at different working regions were repeated at different pH values. The results of all pH variation experiments gave no pronounced effect in thorium separation from uranium over the normal experiment without pH control i.e., the pH of the medium is the most suitable pH for each experiment without any further adaptation.

## CONCLUSION

From the previous results and discussions for extraction and recovery of uranium in their highest possible purity and recovery percents applying TBP/K extraction thorium oxalate precipitation – uranium water stripping is a new adapted scheme, where uranium can be extracted with more than 99.5% percent recovery and more than 99.9% purity. The best experimental extraction-precipitation stirring condition to obtain the aforementioned recovery and purity percents for uranium were:-

Opening: - conc.  $H_2SO_4$  (W /V) (acid / ore ratio) 1: 1.6  
Dissolution: - ice water 1:20  
First Precipitation: -  $NH_4OH$  1:1  
Caustification: - 10% excess of 18% NaOH  
Dissolution: 1M  $HNO_3$   
Second precipitation: 10% NaOH at pH 5.5-6  
Dissolution: 7M  $HNO_3$   
Drying  
Organic concentration: - 40-50% TBP/K  
    Scrubbing: - scrub solution 5 (2M  $HNO_3$ ): 1 ( $H_2O_2$ )  
    Aqueous: organic ratio: - 1:5  
Precipitant concentration: - 1.5-2 M oxalic acid  
Stirring time: - 45-60 minutes  
Temperature: - 40-50 °C  
Stripping: - strip solution cold water (1:1)  
Last precipitation: - 10% NaOH, pH 6

The previous conclusion and optimum results and parameter for the whole process from the starting monazite mineral was collected and summarized in the schematic diagram (figure 9) representing the partially mass balanced flow diagram for 100 gm mineral (un-ground~ 50%) digested by  $H_2SO_4$  (98%) and dissolution with cold water (1 : 20) then precipitated with ammonia (1:1) solution. The precipitate was treated as mentioned before till starting our new adapted extraction-precipitation- stripping scheme.

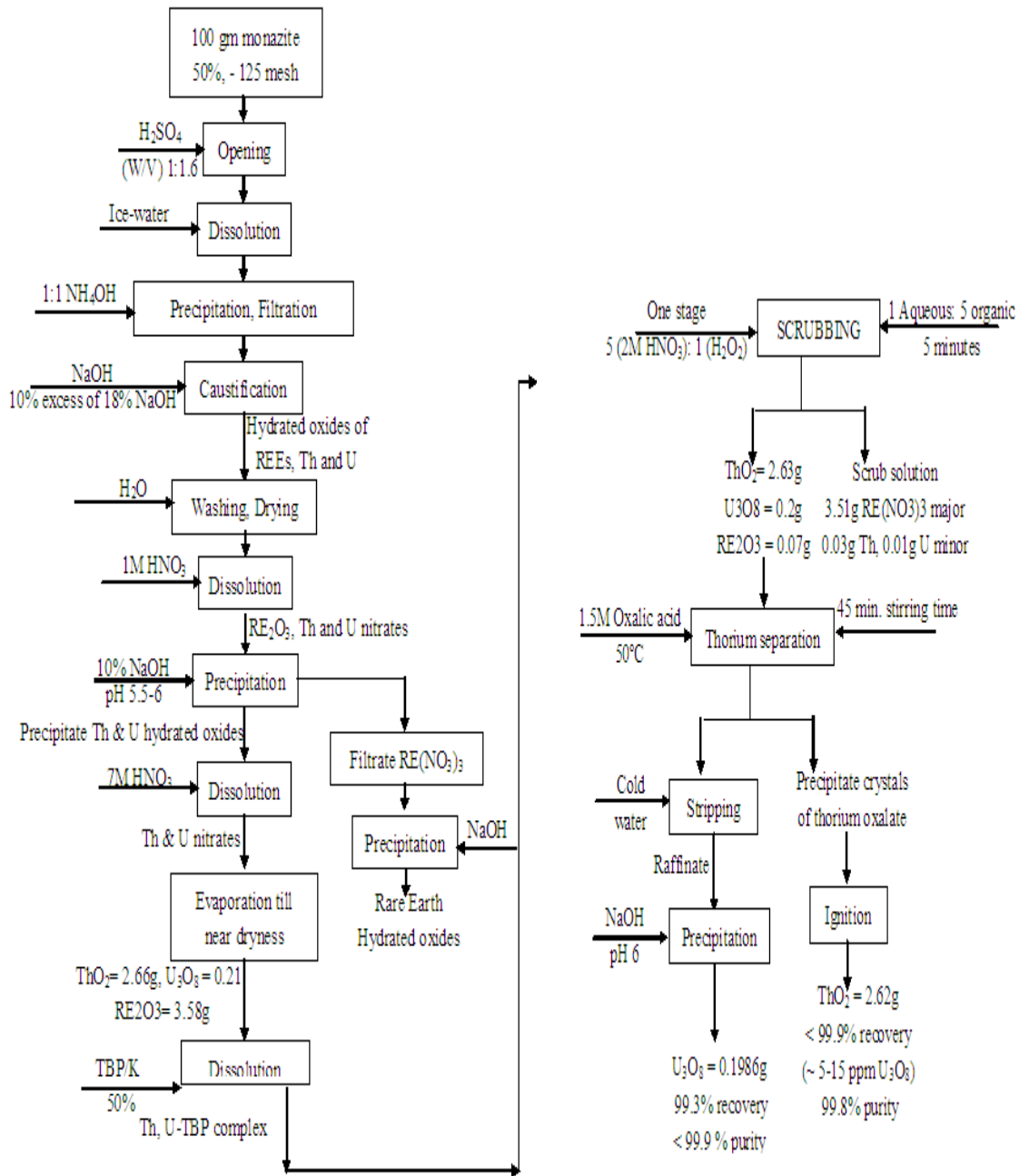


Figure (9):- schematic flow diagram for complete uranium and thorium separation and purification from native Egyptian monazite mineral after sulfuric acid opening process.

### REFERENCES

- 1- Thompson, R., Speciality Inorganic Chemicals. University of Salford, September Special Publication; 40, 403–443 (1980).
- 2- Abro, A., Qu? mica e tecnologia das terras raras. Série Tecnologia Mineral, 66, Rio de Janeiro: CETEM/CNPq.; 212 (1994).
- 3- Loureiro, F.E.V.L., Terras raras no Brasil; depósitos, recursos identificados, reservas. Rio de Janeiro: CETEM/CNPq/MCT, (Estudos e documentos, 21).; 183 (1994).

- 4- Miyawaki, R., Nakai, I., Crystal chemical aspects of rare earth minerals. In: Jones, A.P., Wall, F., Williams, C.T. (Eds.), Rare Earth Minerals: Chemistry, Origin and Ore Deposits, The Mineralogical Society Series, vol. 7. Chapman and Hall, London; 21–40 (1996).
- 5- Sundaram, C.V., Chemistry and metallurgy of rare earth metal extraction and applications. Transactions of the Indian Institute of Metals; (40), 457–477 (1987).
- 6- Wall, F., Mariano, A.N., Rare earth minerals in carbonatites a discussion centre the Kangankunde carbonatite, Malawi. In: Jones, A.P., Wall, F., Williams, C.T. (Eds.), Rare Earth Minerals Chemistry, Origin and Ore Deposits. London Chapman and Hall; 193–226 (1996).
- 7- Fleischer, M., Rosenblum, S., Woodruff, M., The distribution of lanthanides and yttrium in the minerals of the monazite family. Geological Survey Professional Paper, File Report; 91, 125 (1990).
- 8- Toledo, M.C.M., Pereira, V.P., 2003. Ocorrência e variabilidade de composição dos fosfatos do grupo da monazita em carbonatitos. Pesquisas em Geociências; 30(1), 83–95 (2003).
- 9- Farrag, A.K., PhD thesis, Ain Shams University (1979).
- 10- Gupta, V.V., Keni, V.S., Ghosh, S.K., Thorium purification by solvent extraction. Symposium on Solvent Extraction of Metals, Bombay, India, (1–2 Feb.) (1979).
- 11- Deqian, L., Yong, Z., Shulan, M., Separation of thorium(IV) and extracting rare earths from sulfuric and phosphoric solutions by solvent extraction method. Journal of Alloys and Compounds 374, 431 (2004).
- 12- Habashi, F., Hand Book of Extractive Metallurgy. Wiley-VCH.; 1649–1684 (1997).
- 13- Vijayalaskhmi, R., Mishra, S.L., Singh, H., Gupta, C.K., Processing of xenotime concentrate by sulfuric acid digestion and selective thorium precipitation for separation of rare earths, India. Hydrometallurgy; 75–80 (2001).
- 14- Silva, A.S., Almendra, E.R.E., Ogasawara, T., Andrade, M.C., Lixiviação sulfúrica da monazita em autoclave: análise termodinâmica. Anais do III Encontro de Metalurgia, Mineração e Materiais, vol. 1. UFMG, Belo Horizonte/MG, Brasil ; 223–234 (1995).
- 15- Gupta, C.K., Krishnamurthy, N., Extractive metallurgy of rare earths. International Materials Reviews; 5 (37), 204–207 (1992).
- 16- Kolthoff, I. M., and Elving, P. S., "Treatise on analytical chemistry", Part II; Inter-science Publishers, New York; 5 (1961).
- 17- Cuthbert, F.L., "Thorium production technology" Addison- Wesley Publishing Co., Inc., U. S. A.; (1958).
- 18- Marczenko." Spectrophotometric determination of elements". John Wiley and sons Inc. New York; (1986).
- 19- Marczenko, Z., Spectrophotometric determination of elements Ellis Harwood. U.K, 643 (1976)
- 20- Moneir Adel Hamed et. Al, "Internal Scientific Report, Nuclear Materials Authority, under Publication.
- 21- R. W. URIE, J. SOC. Chem. Ind. (London); 66,437 (1947).
- 22- Rabie, K. A. studies on the Separation of some Rare Earth Elements From Egyptian Monazite sand, Ph.D., Cairo University, faculty of science, A. R. Egypt; (1996).