ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

N-butyl methyl amine as a new extracting reagent for uranium from monazite sulphuric acid leaching liquor

Laila.A.Guirguis(1), Lely.H.Khalifa(2), Hesham.K.Foad(3), Basma.T.Mohamed(4)
(1, 3, 4) Nuclear Materials Authority
(2) Chemistry Dep., Faculty of science, Ain shams university

Manuscript Info

Manuscript History:

Received: 15 April 2014
Final Accepted: 23 May 2014
Published Online: June 2014

Key words:
Monazite, acid leaching, N-butyl methyl amine, phosphoric acid, uranyl peroxide.

***Corresponding Author**

Laila.A.Guirguis

Abstract

Sulphuric acid leaching of 97% monazite is subjected to hydrophobic / hydrophilic solvent extraction in one step to separate the high quality phosphoric acid produced from uranium residue. Uranium residue extracted by N-butyl methyl amine (1M) in kerosene at an aqueous / organic phase ratio 1:3. Optimum mixing time is 15 minutes while settling time is 5 minutes at room temperature.

Uranium stripping is carried out by 8M HCL at an organic / aqueous 1:2 and a mixing time of 5 minutes at room temperature and settling time of 5 minutes. The obtained strip liquor is concentrated and uranium is precipitated as uranyl peroxide. Total process recovery is more than 90%.

INTRODUCTION

Monazite, one of the most economic minerals of the Egyptian black sand deposits which are distributed along the Mediterranean coast from Abo-Quir in the west to Rafah in the east is the starting material for this investigation. The purity of monazite sample is 97% and it is kindly given by the Physical Processing Dept. at Nuclear Materials Authority.

Several methods for monazite breakdown have been studied; these include, mainly, the acid treatment, the alkali opening methods, beside chlorination and treatment with calcium carbonate.

Some other method has also been applied as NH_4F powdered monazite **(1).**

Chendrayan (2) dissolved thorium from monazite by bacterial action using thiobacillus-thio oxidants. Beside sulphuric acid, which is commercially used for monazite opening, other acids have been studied; these involve nitric acid (3)**,** per chloric acid (4) and pyro phosphoric acid (5)**.**

In the present investigation sulphuric acid route is follows according to the equation

$2Ln\,(PO_4) + 3H_2SO_4 \rightarrow Ln_2\,(SO_4)_3 + 2H_3PO_4$……………(1)

$Th_3\,(PO_4)_4 + 6H_2SO_4 \rightarrow 3Th\,(SO_4)_2 + 4H_3PO_4$……………..(2)

Extraction of uranium from phosphoric acid residue by N-butyl methylamine which is a secondary amine straight chain of a molecular formula $C_5H_{13}N$ and molecular weight 87.16.

Structure of N-butyl methylamine appears in **Figure (1)**.

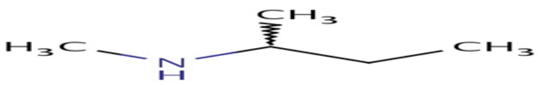

Fig. 1. N-butyl methylamine structure

2. Experimental

2.1Complete chemical analysis

Complete chemical analysis of the input 97% monazite sample as well as the acid leaching products and the solvent extraction follow up has been undertaken by a variety of analytical techniques.
Sulphuric acid breakdown of monazite, sulphuric acid leaching of monazite (grade 97%). The mineral is treated with concentrated sulphuric acid at controlled temperature of 230-250 ºC for 10-12 hrs, and leached with hot purified water at 45 ºC and then after precipitated at pH 1.1. The residual, un-dissolved REEs and/or monazite is moreover processed with concentrated H_2SO_4 at 300 ºC and leached with cold water and precipitated at pH 2.3.The remained acid insoluble residue is mainly a refractory material **(6).**

2.2 Separation of phosphoric acid from sulphuric acid leached liquor of monazite

Extraction of phosphoric acid from sulphuric acid leached liquor of monazite was carried out in a magnetic stirrer in a thermostat to control temperature. Monazite 97% contains 24.5% P_2O_5 , 100 ml of the leached liquor with 24.5% P_2O_5 and mixture of 100 ml ethanol and 700 ml MIBK were mixed for 20 minutes and were allowed to separate for 5 minutes in a separating funnel , after settling scrubbing of organic phase with 27% ortho-phosphoric acid by ratio (1:1), while shaking for 15 minutes . Stripping for P_2O_5 from organic phase is done by distilled water of organic aqueous phase ratio (3:1) and shake for 5 minutes, and then after settling take the strip solution which is clear purified $H_3PO_{4.}$ Complete chemical analysis of the produced H_3PO_4 is shown in **Table (2.1).** Uranium residue recovered by solvent extraction using (1M) N-butyl methylamine in kerosene.

Table (2.1). Ultra-pure phosphoric acid obtained, complete chemical analysis relative to the acid leached liquor

% Element	**P_2O_5 Before purification**	**P_2O_5 After purification**
P_2O_5	**24.5**	**22.5**
Fe_2O_3	**0.43**	**0.20**
Na_2O	**0.0082**	**0.003**
K_2O	**0.0048**	**.00009**
CaO	**.34**	**U.D.L**
Al_2O_3	**0.00092**	**U.D.L**
MgO	**U.D.L**	**U.D.L**
Cl^-	**U.D.L**	**U.D.L**
SO_4^{-2}	**2.4**	**0.20**
TiO_2	**0.25**	**U.D.L**
MnO	**U.D.L**	**U.D.L**
SiO_2	**2.57**	**U.D.L**
Zn (ppm)	**4.088**	**U.D.L**
Ni (ppm)	**28.0125**	**U.D.L**

The process of solvent extraction, as a separation method is divided into three main steps namely extraction, scrubbing and stripping besides solvent regeneration **(7).** All these steps can be identified as follows; Scrubbing process is the washing of the organic phase after extraction and is carried out to eliminate metal impurities. Stripping process is the removal of the extracted solute from organic phase, where the solute is obtained in an enriched and purified form and the solvent is simultaneously prepared for re-use. The basic equations in the process of solvent extraction coefficient (D_E) which is the ratio of the concentration of the element in the solvent to that of the concentration on the aqueous phase.

$$D_E = \frac{\text{Conc. Of the extracted element in the organic phase}}{\text{Conc. Of the extracted element in the aqueous phase}}$$

Extraction % (E %) can be obtained from the following equation..

%E = 100 D_E (P)/(HP) D_E …………………….. (3)

When P is the phase ratio = vol. of organic / vol. of aqueous, and D_E is the extraction coefficient. All the solvent extraction process is carried out in a separating funnel.

3. Study of relevant factors of the uranium extraction process

3.1 Effect of concentration of solvent on extraction of uranium

By using different concentrations of solvent and make all other factors like temperature, diluent, phase ratio, etc…fixed concentration of solvent from (0.25M to 1M) was used. Maximum extraction occurred at (1M) concentration of solvent; above 1M concentration of solvent the two phases make emulsion, as obtained in **Figure (2)**

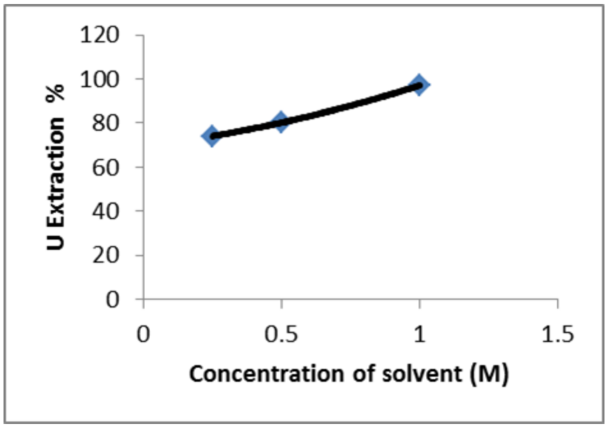

Fig. (2). Effect of concentration of solvent on uranium extraction

3.2 Effect of different diluents on the extraction process

The extraction of uranium has been studied using different types of organic diluents namely carbon tetrachloride, O-Xylene, Kerosene and chloroform. The other studied factors were fixed. It was found that the effective diluent used is Kerosene for maximum extraction of uranium using N-butyl methylamine as shown in **Figure (3).**

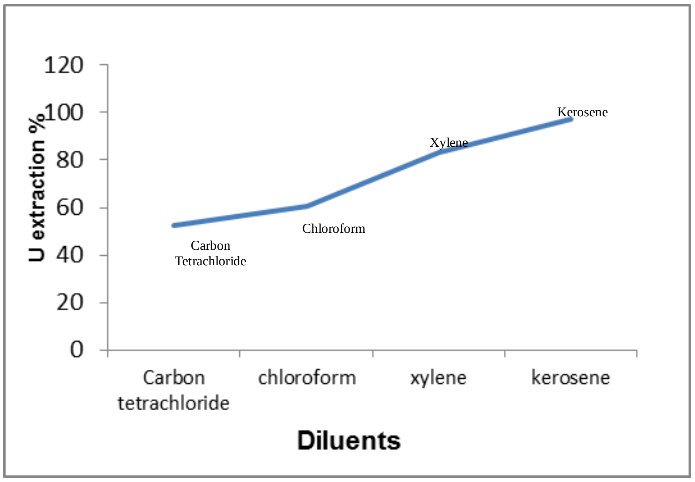

Fig.(3).Effect of different diluents on uranium extraction

3.3 Effect of A/O phase ratio on extraction process

The aqueous/organic phase ratio has a significant effect on the extraction of uranium. This effect was studied by changing the aqueous: organic phase ratio from 1:1 to 1:3. The results obtained are shown in **Figure (4);** it is clear from the results that the aqueous: organic phase ratio 1:3 is the best ratio as it gives the best extraction process of uranium.

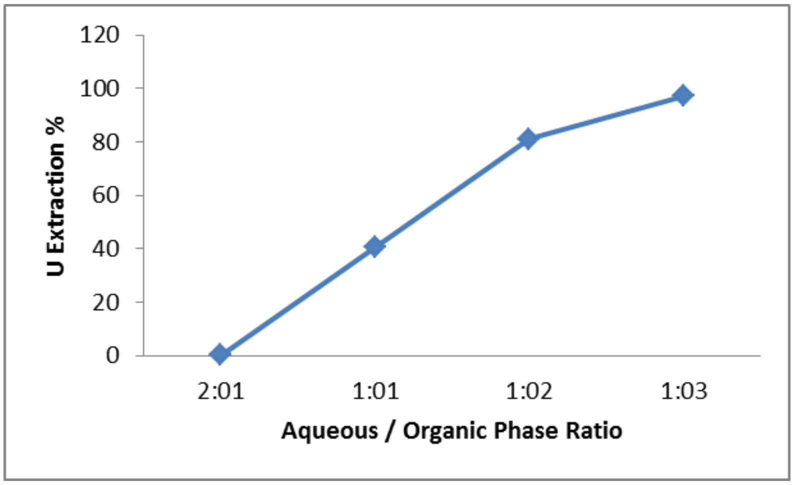

Fig (4). Effect of A/O phase ratio on extraction process

3.4 Effect of mixing time on extraction process

The effect of time of mixing (contact time) on the extraction process was investigated. The extraction was carried out at optimum previously determined values and at room temperature. The mixing time was varied from 5: 20 minutes. The results are given in and are represented in **Figure (5);** since the optimum mixing time was of 15 minutes, this mixing time was adopted for further experiments.

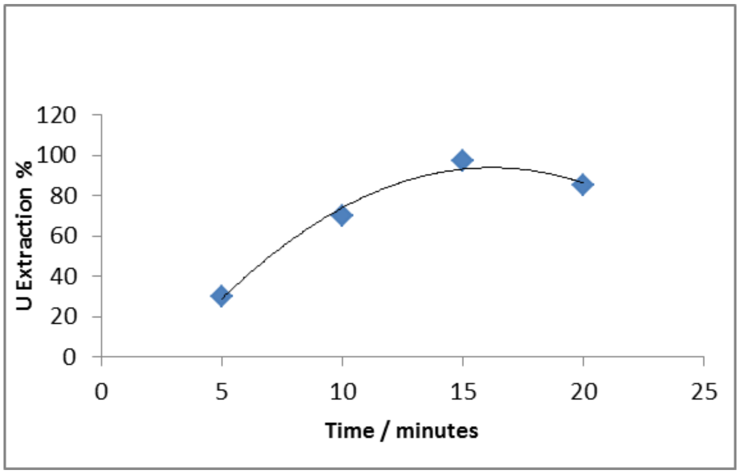

Fig.(5). Effect of mixing time on extraction process

3.5 Effect of settling time on extraction process

The effect of settling time on the extraction process was investigated. The extraction was carried out at optimum previously determined values and at room temperature. The settling time was varied from 1: 10 minutes. The results are given in **Figure (6)**

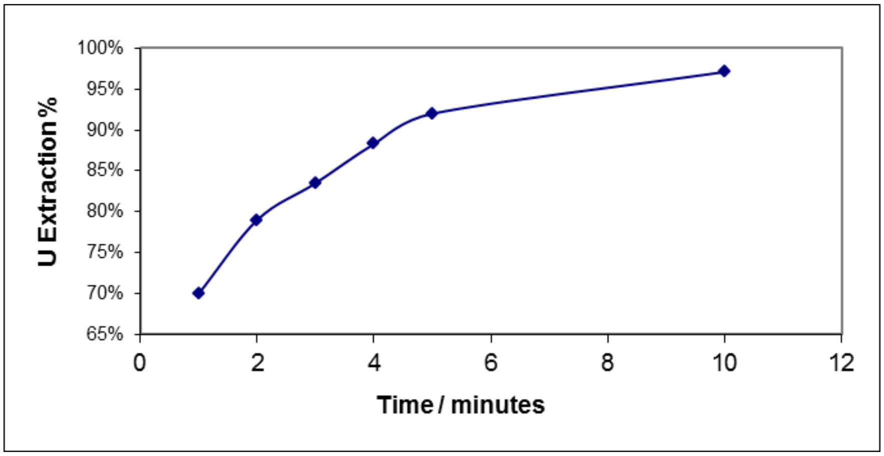

Fig.(6). Effect of settling time on extraction process

3.6 Effect of temperature and calculation of activation energy on extraction process

The effect of temperature on the distribution coefficient reflects its results on the percentage extraction of uranium. Experiments were carried out, other factors kept constant, where the temperature is regulated from 10 to 60 ^{0}C and shaking time 15 minutes. The results obtained are shown in **Figure (7).** Results show that the best extraction carried out at room temperature. The relation between the equilibrium constant K and the temperature are given by Van Hoff's equation:

D Ln K/ dt = DH/RT2............(1)
By integration
Ln K= (-DH/R) (1/T) + a…………..(2)

And since the distribution ratio D is related by definition to the equilibrium constant K the previous equation could be written

Ln D = (-DH/R) (1/T) + a………… (3)

The results fit a straight line equation with slope equals

DH=-10946J/mol.-DH/2.303R extraction……….. (4)

The negative values of enthalpy change (DH) indicate that the process with an increase in randomness of the system shown by the high value of entropy change, the negative value of ΔG indicates that the reaction is spontaneous on the other hand, the observed decrease in the negative value of ΔG with elevated temperature implies that the extraction reaction becomes more favorable at room temperature.

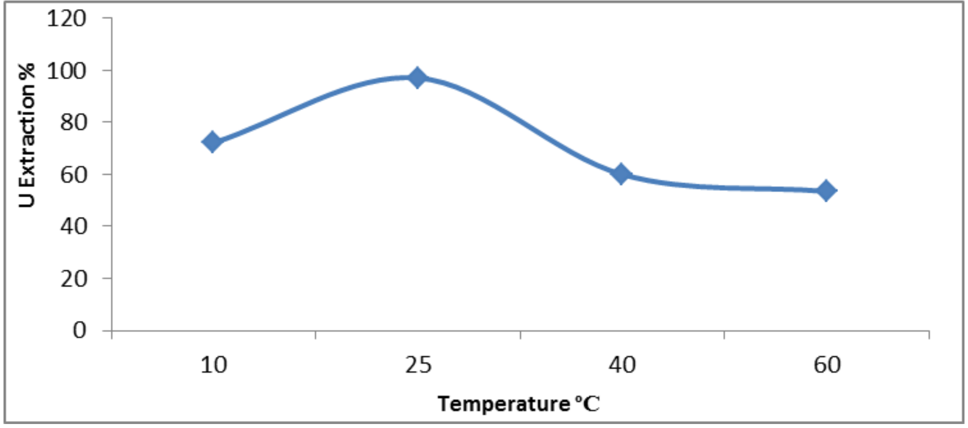

Fig.(7). Effect of temperature on U extraction

3.7 Stripping process

A general procedure for this technique is as follows, the loaded solvents contacted with a suitable strip solution, at an appropriate phase ratio until equilibrium is attained. . The aqueous phase is then removed and analyzed for uranium. Stripping process depends on a number of factors which have to be studied in order to obtain the best stripping efficiency that takes at the same time economic consideration.

3.7.1 Effect of organic / aqueous phase ratio on the stripping process

This effect on the stripping process was studied by changing the organic/aqueous phase ratio from 1:2 to 2:1. The best ratio was found to be 1:2 O/A phase ratio. The other factors were kept as mentioned before. The results are represented in **Figure (8)**

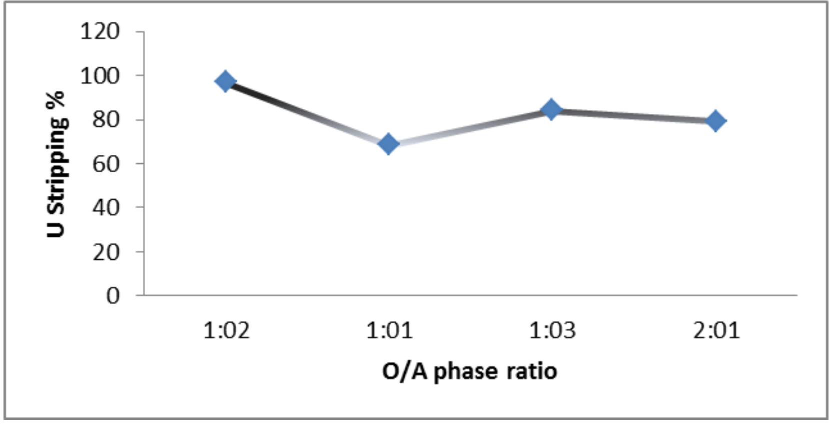

Fig (8). Effect of organic / aqueous phase ratio on the U stripping process

3.7.2 Effect of different concentrations of stripping agent on stripping process

Different concentration of the stripping agent used were 3, 5,6, 7,8, 10 molar of HCL,in all cases, the volumetric phase ratio of organic solvent to stripping solution was 1:2 and operating temperature was 25^0C and 5 minutes contact time. Stripping results are shown in **Figure (9)**

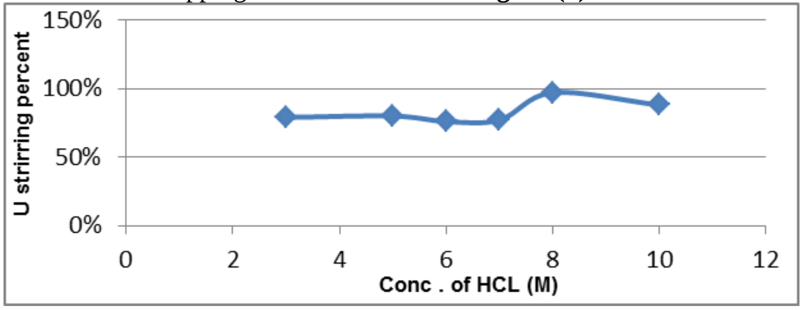

Fig (9) Effect HCL concentrations on U stripping process

3.7.3 Effect of mixing time on stripping process

The effect of time of mixing (contact time) on the U stripping process was investigated. The extraction was carried out at optimum previously determined values and at room temperature. The mixing time was varied from 2: 10 minutes. The results are given in **Figure (10).**Since the plateau region starts at mixing time of 5 minutes; this mixing time was adopted for further experiments.

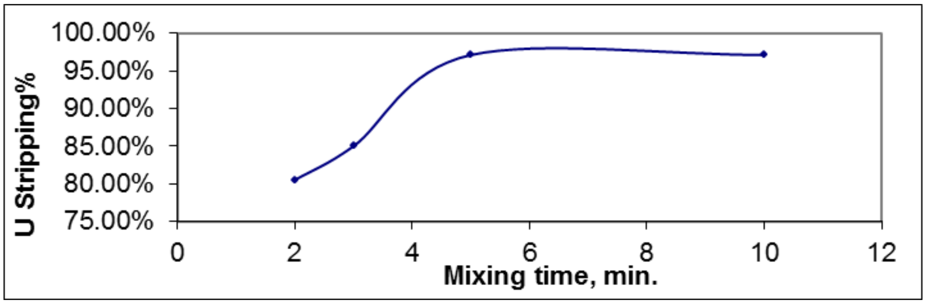

Fig (10) Effect of mixing time on stripping process

3.7.4 Effect of settling time on Stripping process

The effect of settling time was studied at different time intervals for maximum phase separation of both phases. After mixing (shaking) of both phases for 5 minutes as previously optimized, the latter is left for complete settling after a period of time. This time was studied as a function of maximum stripping percentage where the results are show in **Figure (11).** It was found that maximum settling of both phases was obtained after 5 minutes.

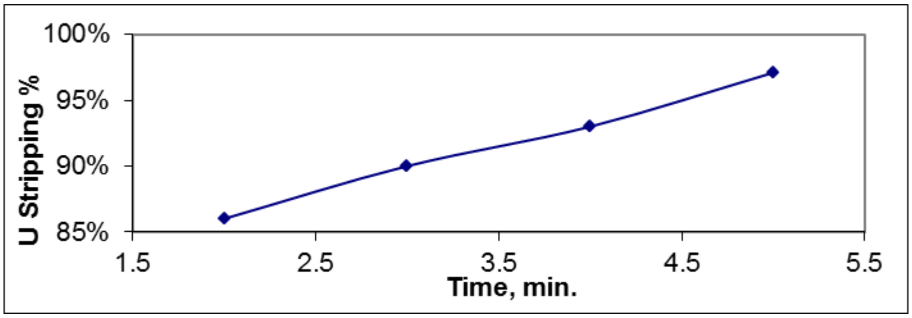

Fig (11) Effect of settling time on U Stripping process

3.7.5 Effect of temperature on stripping process

The effect of temperature on maximum stripping of uranium from loaded N-butyl methylamine was studied from 10^o C up to 60^o C and other factors were kept constant. It was observed from **Figure (12)** that maximum stripped uranium was performed at 25^o C, i.e. room temperature.

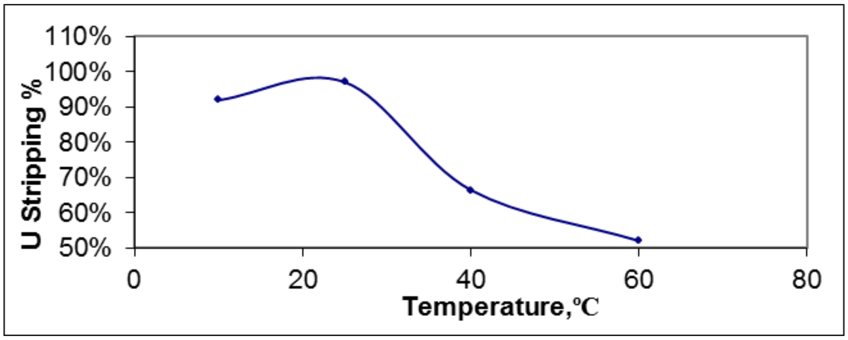

Fig (12) Effect of temperature on stripping process

3.8 Precipitation of uranium from the strip solution

The strip solution containing uranium from the loaded N- butyl methylamine was precipitated using hydrogen peroxide as an efficient selective precipitating agent. The strip solution, adjusted to pH 1, was mixed with 30% H_2O_2 (0.2g per gram of uranium) at room temperature. The stoichiometric requirements are 0.126g H_2O_2/g of U_3O_8 precipitated. In practice, about 1.5 times this amount is required for complete precipitation. The whole solution was stirred for 5 to 10 minutes and ammonium hydroxide was added to attain a pH 2 (reaction pH). After a specified reaction period of two hours, the precipitate was filtered, washed with 0.2% solution of hydrogen peroxide and dried.

4. Conclusions

1. The suggest method is very maliable as different monazite grades at different grain size can be treated.
2. One step extraction using 1 M, N-butyl methylamine in kerosene is used.
3. The negative value of enthalpy change (DH) indicate that the process increase in randomness of the system shown by the high value of entropy change, the negative value of (ΔG) indicates that the reaction is spontaneous, on the other hand, the observed decrease in the negative value of ΔG with elevated temperature implies that the extraction reaction becomes more favorable at room temperature.
4. The present technique is very useful as one can get H_3PO_4 which upon concentration using reduced pressure in a rotary evaporator can get pharmaceutical grade H_3PO_4 acid. While uranium can be separated in a nuclear grade uranyl peroxide.
5. On the basis of the achieved results a technological flow- sheet is adopted **Figure (13).**

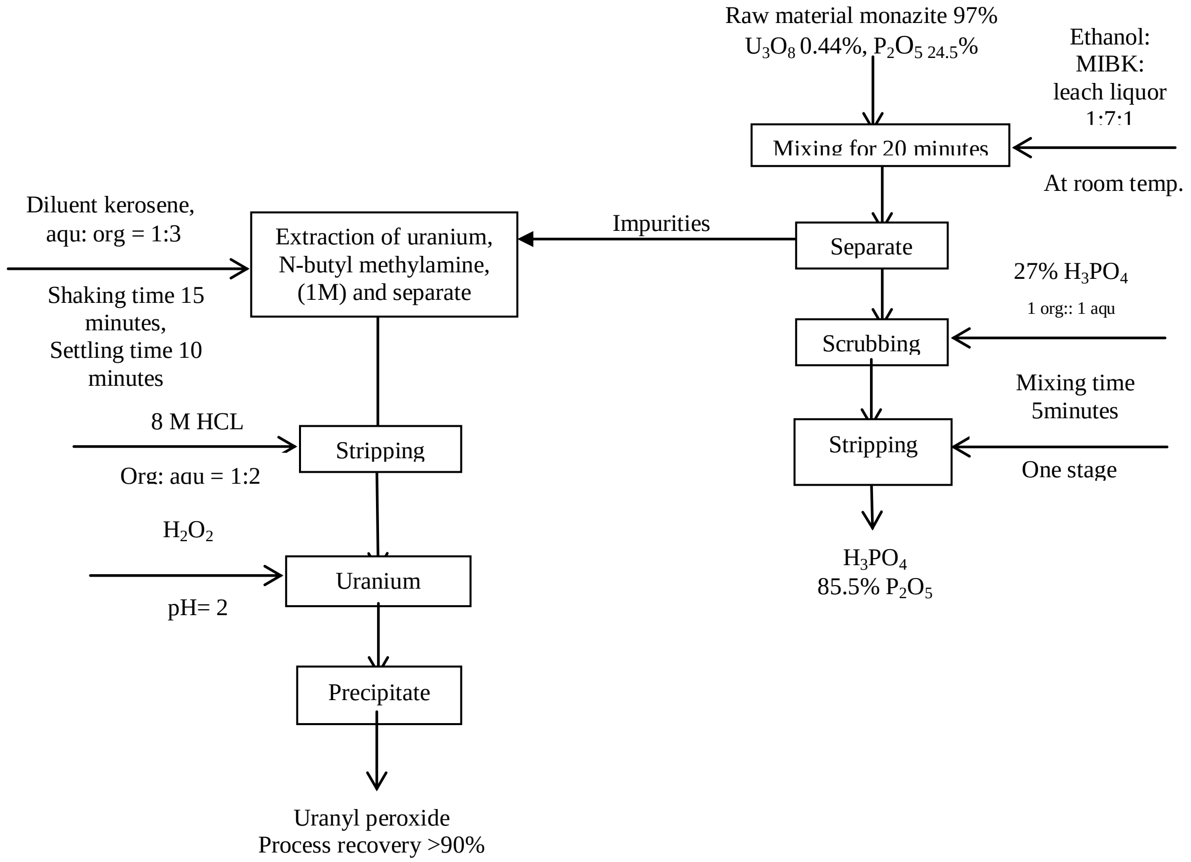

Fig (13), Technological flow sheet for the suggested method of uranium extraction as byproduct of phosphoric acid

5. References

1 **Joseph, P.,** and **Mony, C. N.,** Chem. Ind. London, 50, 1400, (1968)

2 **Chendrayan, K., Francis, A.J., and Moorthy, A.,** " Microbial Dissolution of Thorium from Monazite", Bhabha Atomic Research Center, Bombay, P.216, 1987

3 **Farag, A.Kh.,** M.Sc. Thesis, "Recovery of Thorium, Uranium and Cerium from Egyptian Monazite Sands", Fac. Sci., Cairo University, Egypt, (1972).

4 **Cuthbert, F.,** "Thorium production Technology", Addison Wesly Publishing Co., New York, 1958

5 **Marchand ,B., Atomkernen Energie, 7, 371 (1962)**

6 **Moneir. A . Abdel hameid, Hisham K.Fouad,Fathi A. Ammar, Mohamed I.Moustaf and Mohamed El-Shankary,** the 6th international conference on Geochemistry, Alexandria university, Egypt, 15-16 September (2004), P.1-11

7 **Rydberg, J., Coy, M. Musicans,c and Chappin, G.,** "Solvent extraction principles and practice" , Marcel Dekker, Inc, New York 2nd edition p.1 (1992)