Research Article

Extraction of Uranium from the Raffinate of Egyptian Phosphoric Acid Purification Using Aliquat336 Extractant in One Step

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Abstract This paper describes the extraction of uranium from raffinate phosphoric acid purified using aliquatR336 in kerosene as a selective extracting agent of uranium, Several factors were studied for the maximum extraction of uranium. mainly aliquatR336 concentration, shaking time, aqueous/organic phase ratio, the diluents effect and temperature on the extraction, Effect of different stripping agents were investigated , High uranium extraction yields 98.4% were obtained ,The uranium is finally converted to a high purity using precipitation with hydrogen peroxide, Finally a technological flow sheet is elucidated on the basis of the obtained results.

Keywords Uranyl Peroxide; Phosphoric Acid; Organic Solvents; Aliquatr336

Introduction

During acidulation of phosphate rock with sulphuric acid to produce phosphoric acid for fertilizer application, the uranium values contained in the rock also become solubilised. The phosphoric acid produced by the 'di-hydrate' process, containing 26–30% P_2O_5, called the 'weak phosphoric acid' (WPA), is concentrated to >50% P_2O_5 grade, known as 'merchant grade acid' (MGA). The 'hemi-hydrate' process directly yields acid of high P_2O_5 content. The uranium concentration varies with acid concentration, provided oxidizing conditions are maintained so that selective precipitation of uranium does not take place. Depending on the rock used, the acid produced can contain 0.0050–0.05 g U_3O_8 / L. Separation of uranium by solvent extraction employing a novel synergistic combination of organo-phosphorus reagents is reported [1]. In particular, the solvent mixture of di-nonyl phenyl phosphoric acid (DNPPA) with di-butyl butyl phosphonate (DBBP) in an aliphatic diluent has been found to be a stronger extractant than the commonly used combination of di-(2-ethylhexyl) phosphoric acid (DEHPA) with tri-n-octyl phosphine oxide (TOPO). The DNPPA–TOPO mixture is an even stronger extractant. Results on extraction from both WPA and MGA are reported. Stripping of uranium from the organic phase was achieved with concentrated phosphoric acid in the presence of Fe^{+2} reducing agent at elevated temperature. Stripped uranium was subjected to a second cycle of extraction-stripping and recovered as a peroxide precipitate of high purity. Brief results on allied areas of acid pre-treatment and post-treatment are included.

In the Uranium Corporation of India Limited, Jaduguda Mines in India, the yellow cake is precipitated from eluted solution as magnesium diuranate using magnesia. Because of the stringent specifications set by the Nuclear Fuel Complex, studies were implemented to produce uranium peroxide in place of magnesium diuranate. All the parameters such as precipitation, pH, quantity of hydrogen peroxide required, duration of precipitation and temperature of precipitation were studied in detail [2].

A new efficient extractant of polyalkyl phosphazenes, PN-1200 (supplied by All-Russian Research Institute of Chemical Technology), was used for the separation of uranium from wet process phosphoric acid (PA) in a batch process at a laboratory scale. Solvent extraction of uranium from 29% P_2O_5 phosphoric acid using PN-1200 was

compared with uranium extraction from phosphoric acid using synergistic mixtures of D2EHPA+TOPO and D2EHPA+TRPO. All the extractants were diluted in normal aliphatic kerosene. It is concluded that PN-1200 has some good properties, such as high uranium distribution coefficient, good stability, acceptable kinetics, good phase separation, and simultaneous extraction of U^{4+} and U^{6+} [3]. The extraction of uranium from AR [analytical grade] ortho phosphoric acid by D2EHPA [di-2 ethyl hexyl phosphoric acid] only and D2EHPA-TOPO [tri-n-octyl phosphine oxide] mixture. The influence of various factors affecting the extraction mechanism such as phosphoric acid, D2EHPA and TOPO concentrations have been investigated. The effect of temperature on extraction process was studied and the activation energy of the reaction was calculated and found to be equal 23.1 KJ/mol. Finally, the uranium extraction mechanism by using D2HEPA and D2EHPA/TOPO synergism was suggested [4].

The hydrophilic residue obtained during the purification of industrially produced phosphoric acid to food grade quality in a single stage was the starting material in the work [5]. The residue is fused with sodium hydroxide at ratio of 1:5 and leaching the fused cake with 5M HCl, Uranim was extracted using trioctylamine (TOA) as a selective extractant for uranium. Several factors were studied for the maximum extraction of uranium where shaking time of 20 minutes, aqueous/organic phase ratio(1 :3), the diluents is xylene and temperature on the extraction, the effect of different stripping agents were investigated, high uranium extraction yields 92%**.**

Extraction of uranium from fertilizer grade phosphoric acid with a novel synergistic mixture of di-nonyl phenyl phosphoric acid(DNNPA) and tri butyl phosphate(TBP), the effects of varying the concentration of phosphoric acid, (DNNPA) and(TBP) on the distribution ratio of uranium, batch counter current extraction testes have carried out. The extracted uranium in organic phase was efficiently stripped at 65 °C using concentrated phosphoric acid containing ferrous iron .the stability of the solvent was investigated by extended contact testing as well as cyclic extraction and stripping tests. The data on the effect of temperature on the extraction showed that the enthalpy change is-24KJ/mol when DNNPA and TBP is used as the extractant, more than double when DNNP alone was used. Uranium extracted by DNNP-TBP is further subjected to ascend cycle of extraction using D2EHPA-TBP and scrubbing impurities. The uranium is finally converted to a high purity UO_3 product using precipitation with hydrogen peroxide and heat treatment at 200 °C [6].

Experimental
Materials
- The starting materials of this work is the raffinate of the industrially produced wet process phosphoric acid (U 74 ppm, 43 % P_2O_5,) [5] which is kindly supplied by Polyserve for Fertilizer Company, Cairo, Egypt (from the evaporator unit after filtration).
- AliquatR336.
- The reagents used in this work were of analytical grade quality. Double distilled water was used in all preparations.

Instrumentations
- A Shimadzu 160 A Double beam UV spectrophotometer having a wave length range of 200-1100 nm was used for spectrophotometric determination of sulphate, phosphate, total rare earth elements and uranium.
- An atomic absorption spectrophotometer Unicam 969 supplied with acetylene and nitrous oxide burner heads, regulators and integrated reading in absorbance, was used for the determination of most of the impurities.
- Sherwood 410 flame photometer was used for the determination of sodium and potassium.
- A centrifuge Nf 815 was used to separate aqueous and organic phases during the solvent extraction work.
- A Jenway pH meter is applied satisfactorily in the present work and calibrated daily using two successive buffer solutions (pH 4 and 7 or 7 and 10).
- FT-IR measurements were performed in KBr discs using Nexeus-Nicolite-640-MSA FTIR. Energy dispersive X-ray measurements were measured using The philipsis X-ray diffraction unit PW-3710 with generator PW-1830 scientilation-counterPW-3020, target tube PW 2233,Ni filter at 40 Kv and 30 mA are used and EDAX.

Result and Discussion

Extraction of uranium from impurities of phosphoric acid by aliquatR336

Different concentrations of the aliquatR336 used were 0.1, 0.2, 0.3, 0.4, 0.5 molar, the best concentration of aliquatR336 is 0.2 molar.
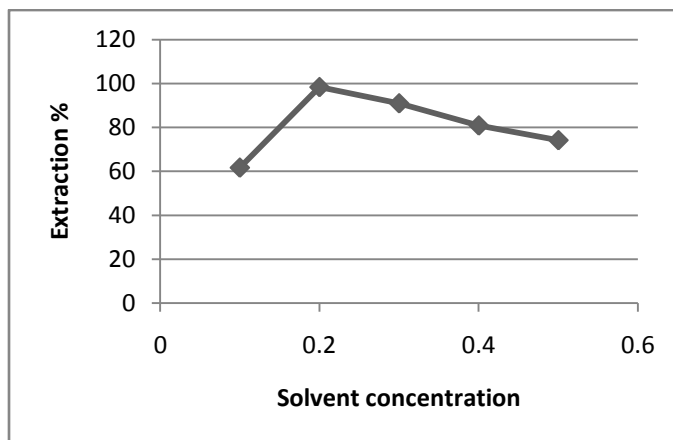

Figure 1: Effect of different concentration from solvent (aliquatR336).

Aqueous/organic phase ratio on the extraction process

Different aqueous to organic phase ratio namely 1/1, 1/2, 1/3, 2/1, 3/1 and 4/1were used to get the optimum phase ratio for extraction uranium while the other extraction factors are kept as before. From the results illustrated in **Figure (2)** the best organic to aqueous phase ratio could be taken as 1 Org: 3 Aq.
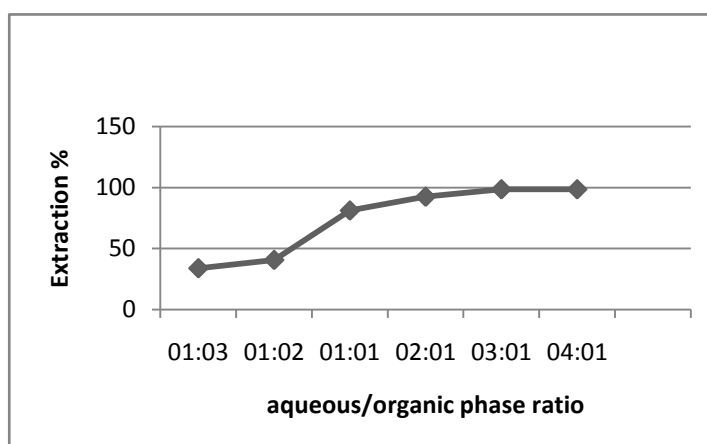

Figure 2: Aqueous/Organic phase ratio on the extraction process

Effect of different types of diluents on the extraction process

The extraction of uranium has been studied using different types of organic diluents namely carbon tetrachloride, *p*-Xylene, Kerosene, toluene and chloroform. The other studied factors were fixed. It was found that the effective diluent used is Kerosene and carbon tetra chloride for maximum extraction of uranium using aliquatR336 as shown in Table (1).

Table1: Effect of different types of diluents on the extraction process.

Diluent	U Extraction %
Carbon tetra chloride	98.3
Chloroform	96.4
Kerosene	98.3
Xylene	86.7
Toluene	57.8

The Pharmaceutical and Chemical Journal

Mixing time on the 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 represented in Figure (3). Since the plateau region starts at a mixing time of 15 minutes, this mixing time was adopted for further experiments.
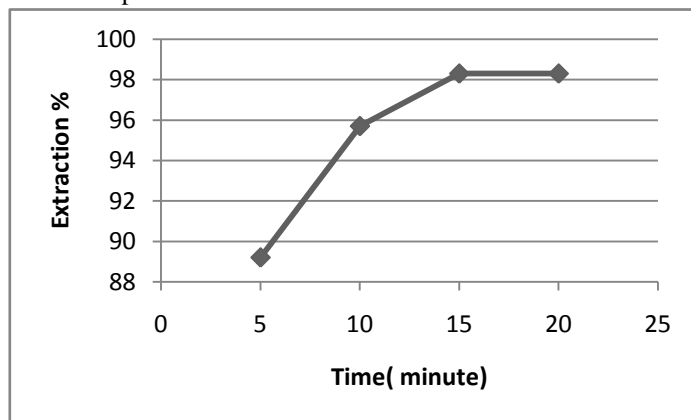

Figure 3: Effect of contact time on the extraction process.

Effect of temperature on extraction:

The effect of temperature on the distribution coefficient reflects its results on the percentage extraction of uranium. Experiments were carried out, where the temperature is regulated from 10 to 60 °C and other factors are kept constant and shaking time 15 minutes. The results obtained in Figure (4) show that the best extraction carried out at room temperature. The relation between the equilibrium constant K and the temperature is given by Van Hoff's equation:

D Ln K/ dt = DH/RT2

By integration

Ln K= (-DH/R) (1/T) + a

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

the results fit a straight line equation with slope equals

DH = - 5946 J/ mol. -DH/2.303 R extraction

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.
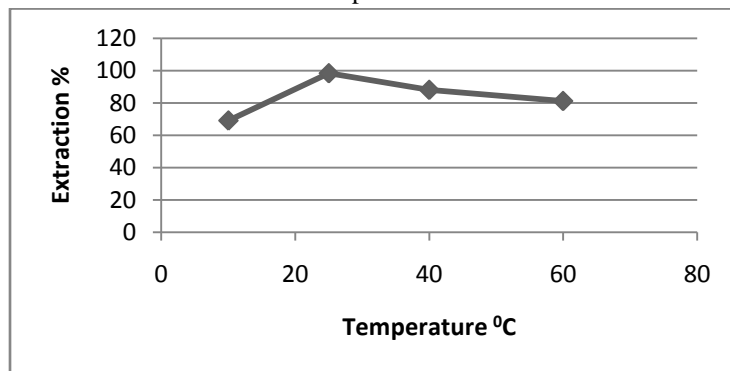

Figure 4: Effect of temperature on the extraction process.

Effect of settling time on the 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 3: 15 minutes. The results are given in Figure (5).
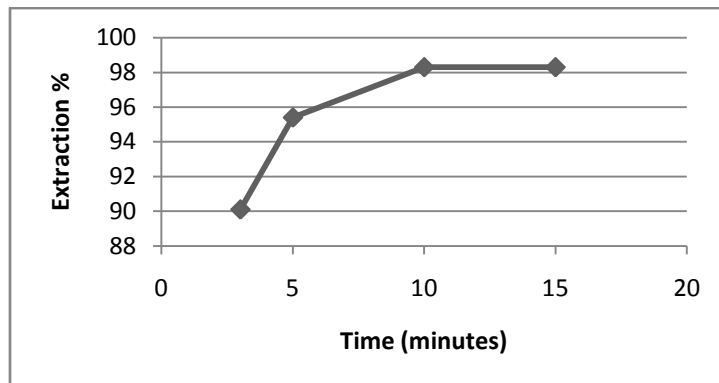

Figure 5: Effect of settling time on the extraction process.

Extraction Isotherm and Construction of McCabe-Thiele diagram for the extraction process

An extraction isotherm is a plot of the equilibrium concentration of the extracted species in the extracted phase against its concentration in the raffinate layer at a given temperature. Data for the extraction isotherm could be easily obtained from either single contacts of a fixed volume of impurities of phosphoric acid with different volumes of organic feed (aliquatR336) (i.e. the phase ratio variation method) or else by repeated contact of one and the same aliquot of the aqueous feed with several aliquots of the fresh organic feed of equal volume.

In this study we use the phase ratio variation method for construction of the extraction isotherm of uranium with organic mixture of aliquatR336 and ,the phase ratios range from 3: 1 (aqueous : aliquat R336). The extraction carried out at the same previous conditions. The results are shown in Figure (6). Uranium concentration in the solvent is plotted versus uranium concentration in the raffinate. The obtained data were used to construct the McCabe-Thiele diagram which is a composite plot of the extraction isotherm and the operating line. The latter could be established by only one point, which corresponds to the final raffinate composition and the ratios of the aqueous to organic phases that determines the slope of the line as it is a straight line. The ideal stages are stripped off by extending a horizontal line from the vertical extremely of the operating line to intersect the isotherm, then a vertical intercept to the operating line to intersect the isotherm, and so on until the other extremely of the operating line is intersected. The saturation curve (equilibrium line) is then constructed as in Figure (6) the next step in construction of McCabe-Thiele diagram was to try a number of operating lines. The slope equal to the ratio of aqueous/organic volumes. The theoretical number of stages could be stepped off upon the diagram in Figure (6). It is clear that one theoretical stage is quite adequate for uranium recovery, if the operating line is at an O/A phase ratio equal to 1:3
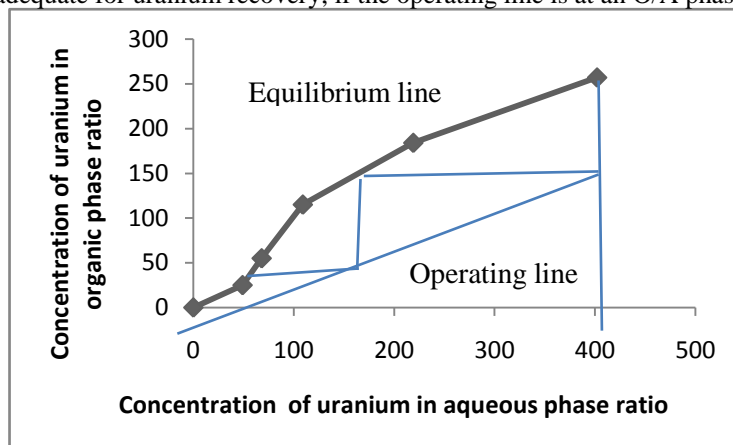

Figure 6: Mc Cabe Thiele diagram on the extraction process.

Stripping Process

Having determined the optimum conditions for the extraction process of uranium from impurities of phosphoric acid a stock solution about five liters was prepared for stripping at optimum condition extraction for A/O ratio 3:1 at room temperature and contact time 15 minute).

Different Reagents on the Stripping Process

Different reagents are used on the stripping of uranium from aliquatR336. The best reagent is sodium carbonate as shown from the results represented in table (2).

<center>Table 2: Effect of different reagents on the stripping process</center>

Reagent	U Stripping %
Na_2CO_3	98.3
NaCL	91.2
HNO_3	33.8
HCL	72.9

Effect of different concentration of the stripping agent

Different concentration of the stripping agent used were 0.5, 1, 2, 3and 4 molar of Na_2CO_3 in all cases, the volumetric phase ratio of organic solvent to stripping solution was 1:1 and operating temperature was 25 °C and 10 minutes stripping results are shown in Figure (7).
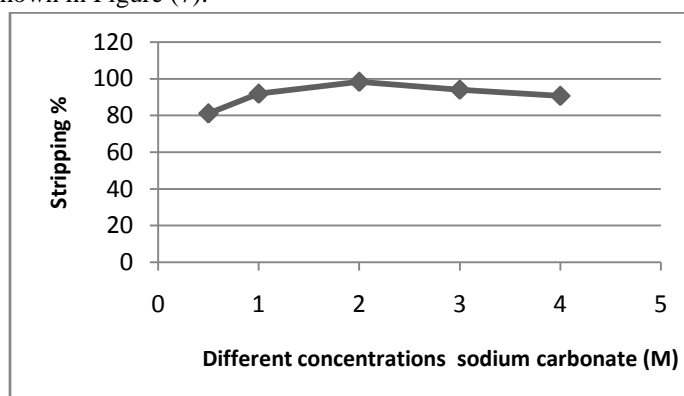

Figure 7: Effect of different concentration from Na_2CO_3 on the stripping process.

Effect of aqueous/ organic phase ratio on the stripping process

This effect on the stripping process was studied by changing the aqueous/ organic phase ratio from 1:1 to 4:1. The best ratio was found to be 1:1. The other factors were kept as mentioned before. The results are represented in Figure (8) showed that 1:1 is the best ratio.
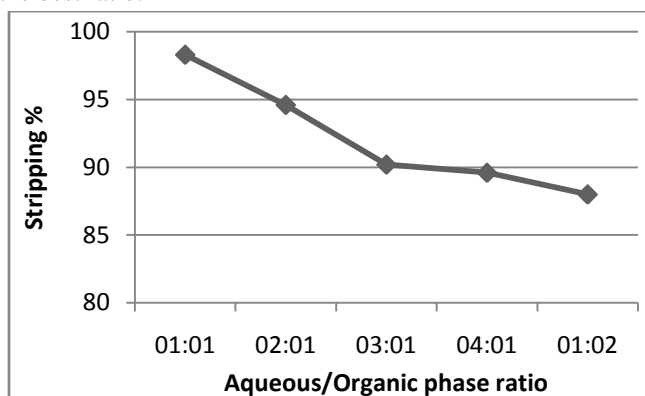

Figure 8: Effect of aqueous/organic phase ratio on the stripping process.

Effect of mixing time on the stripping process

The effect of time of mixing (contact time) on the stripping process was investigated. The stripping was carried out at optimum previously determined values and at room temperature. The mixing time was varied from 5: 15 minutes.

The results are represented in Figure (9). Since the plateau region starts at a mixing time of 10 minutes, this mixing time was adopted for further experiments.
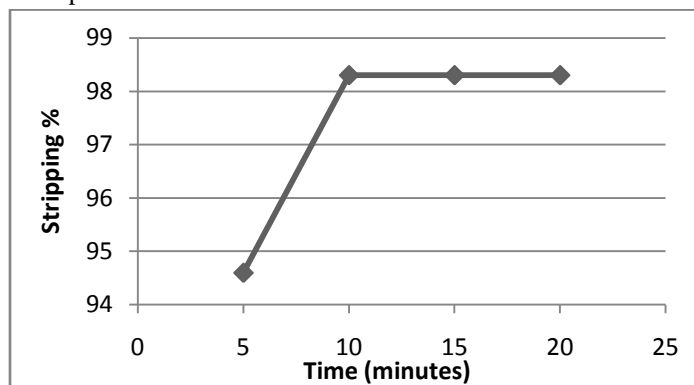

Figure 9: Effect of contact time on the stripping process

Effect of temperature on the stripping process

The effect of temperature on maximum stripping of uranium from loaded aliquateR336 was studied from 10 ^{o}C to 60 ^{o}C and the other factors were kept constant. It was observed from Figure10 that maximum stripped uranium was performed at 25 ^{o}C, room temperature.
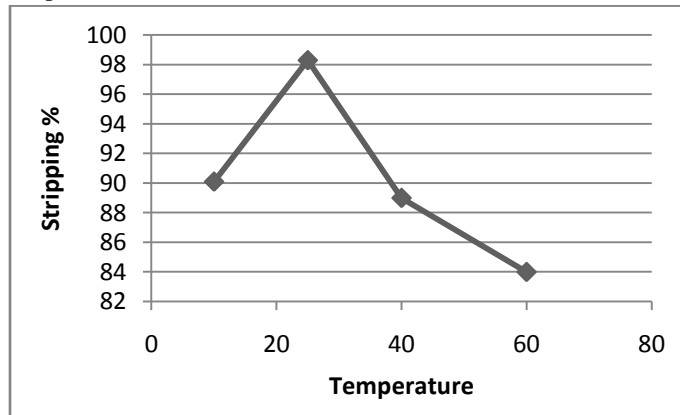

Figure10: Effect of temperature on the stripping process.

Effect of settling time

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 10minutes 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 represented in Figure 11. It was found that maximum settling of both phases was obtained after 10 minutes.
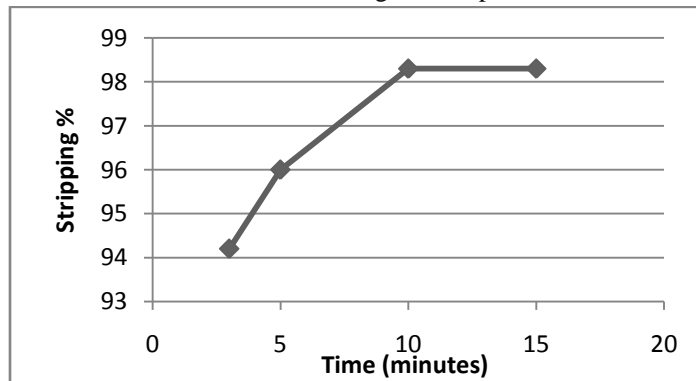

Figure11: Effect of settling time on the stripping process.

Equilibrium line and construction of McCabe-Thiele diagram for the stripping process

Mc Cabe-Thiele diagram is a composite plot of the distribution isotherm and the operating line. The letter coulee readily is established by only one point, which corresponds to the final raffinate composition and the ratio of the aqueous to organic phases that determines the slope of the line, as it is a straight line. The diagram can be used to approximate the number of theoretical stages required for the given process. Another importance of the Mc Cabe-Thiele diagram is in evaluation the results. In this study, 10 gm of loaded organic (al iquatR336) and 10gm of 2 molar of Na_2CO_3 stripping reagent) are contacted for 30 minutes at the previously determined optimum stripping condition until equilibrium is attainted. The phases are allowed to separate (10 minutes). A measured portion of the aqueous phase is taken for analysis. Fresh loaded aliquatR336 is added to the separation funnel containing the remainder of the aqueous phase, in amount to give the same phase ratio as the originally used. The phases are again contacted until the equilibrium is attained and the same procedure is carried out. This process is carried out until saturation of the aqueous phase with uranium is obtained. Figure (12) illustrate the obtained results where one stage was found sufficient for the stripping of uranium from the loaded organic/aqueous phase ratio 1: 1.
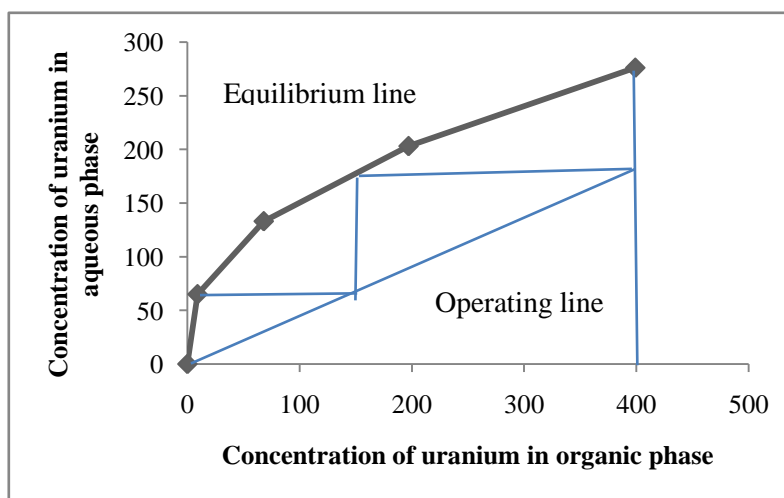

Figure 12: Mc Cabe Thiele diagram on the stripping process.

Precipitation of uranium from the strip solution

The strip solution containing uranium from the loaded aliquatR336 was precipitated using hydrogen peroxide [7] 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 0.126 gm 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, dried and then subjected to several confirmation analyses such as IR and XRD.

IR Spectroscopy

The infrared absorption spectrum of uranyl peroxide Figure (13), infrared absorption peaks are as follows, the bands at 3415.31, 3164.61 cm^{-1} which are designed as hydrogen head OH group stretching vibration where as the peak at 1630.32 cm^{-1}, is assigned as OH bending vibration of coordination water (∂H_2O), the band at 1402 cm^{-1} is assigned to$\mu_5(UO_2)^{-2}$ where as the band at 1050.05 cm^{-1} could be assigned as asymmetric stretching vibration. The band at 559.255 cm^{-1} is assigned as U-X bending vibration [8]. Its absorption data is shown in Table (3).
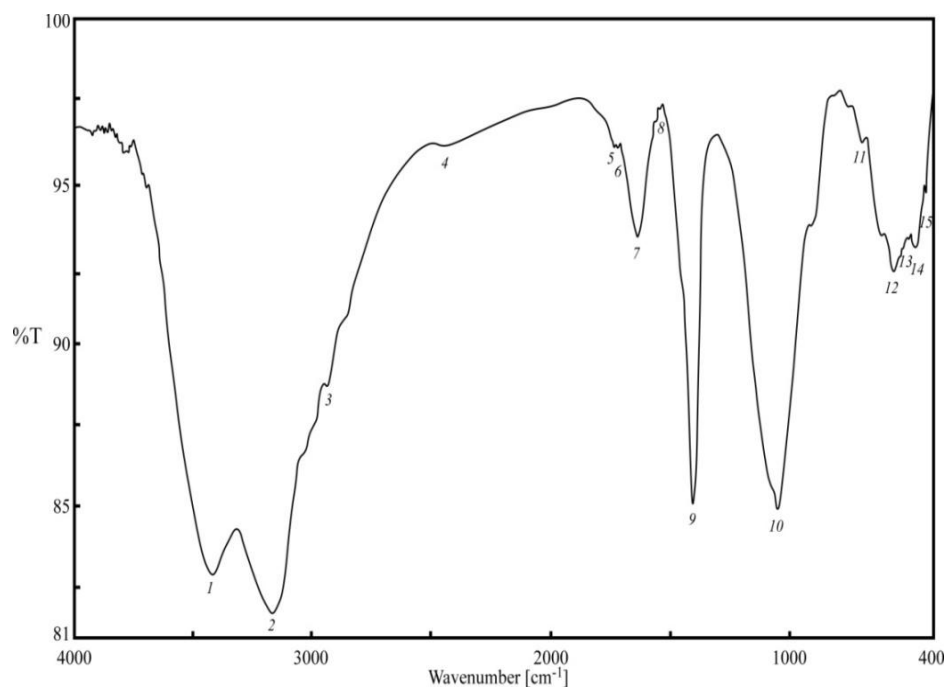
Figure 13: IR spectrum of uranyl peroxide

Table 3: Infrared absorption data of UO_4 sample prepared.

Sample	Peak number	Peak position wave number cm^{-1}	Intensity	Half band width cm
Uranyl peroxide	1	3415.31	82.8842	4.5
	2	3164.61	81.7518	4.9
	3	2929.34	88.733	2.45
	4	2442.4	95.9972	
	5	1728.87	96.0141	
	6	1712.48	95.9445	
	7	1630.52	93.1926	1.2
	8	1539.88	97.1708	
	9	1402	85.0891	3.95
	10	1050.05	84.8936	4
	11	692.32	96.193	0.5
	12	559.255	92.2583	1.85
	13	496.58	93.2435	1.5
	14	465.725	92.9571	1.55
	15	423.298	94.522	1

Table 4: The X-ray diffraction of uranyl peroxide which matches with ASTM card No.10-0309.

		Identified Minerals	
	Sample	Uranyl peroxide ASTM Card No. (10-0309)	
dA°	I/I$_o$	dA°	I/I$_o$
5.09	67	5.11	100
3.43	72	3.445	80
3.42	100	3.426	100

2.85	27	2.857	60
2.55	9	2.557	40
2.48	26	2.487	60
2.14	12	2.138	40
2.13	3	2.053	
2.05	9	1.986	40
1.98	20	1.971	60
1.97	17	1.817	40
1.85	0.3.	1.782	
1.82	5	1.740	30
1.78	12	1.721	40
1.74	10	1.712	40
1.72	7	1.641	20
1.71	8	1.632	30
1.52	4	1.528	30
1.48	22	1.481	30

Conclusion

The present work is a quick, accurate, economic method for the extraction and precipitation of uranium as uranyl peroxide from the raffinate of phosphoric acid purification after one stage solvent extraction by four parts of a mixture synergism using one part TBP and one part buatnol to one part raffinate phosphoric acid.
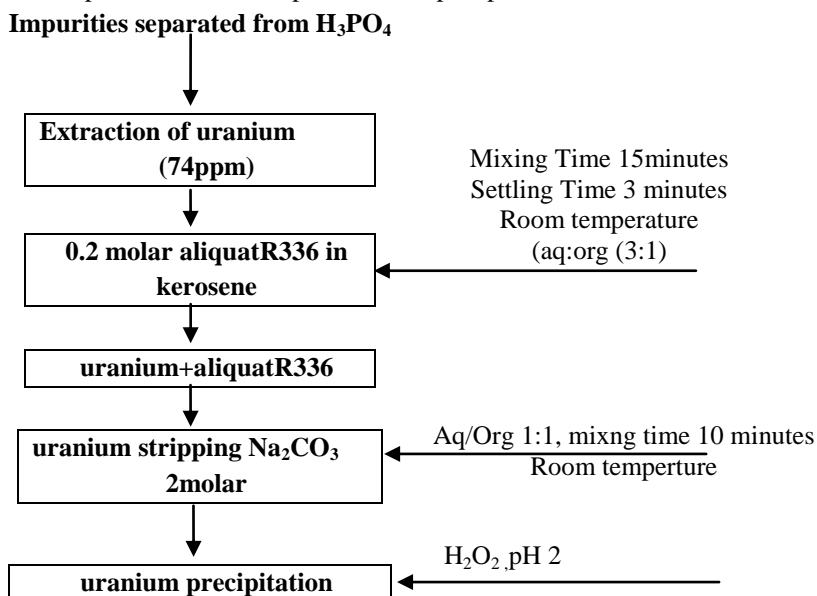
Impurities separated from H₃PO₄

Figure 14: Technical flow sheet for suggested process

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