

Recovery of Uranium from Hydrophilic Phosphoric Acid Residue Using Trioctylamine

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ABSTRACT

The hydrophilic residue (P_2O_5 48.10%, 500ppm uranium and impurities) obtained during the purification of industrially produced phosphoric acid to food grade quality in a single stage was the starting material in this work. In fact, the complete analysis revealed that the sample was composed of U, P, Fe, Na, K, Ca, Mg Al, Mn, Si, Ti, Zn, Ni, Cd, Pb and Cu. The residue was fused with sodium hydroxide at a ratio of 1:5 (residue:NaOH) and leaching the fused cake with 5M HCl, uranium was extracted using trioctylamine (TOA) as a selective extractant for uranium. Several factors were studied for the maximum extraction of uranium, where an aqueous to organic phase ratio (A/O) of 1:3, xylene as a diluent, mixing or shaking time of 20 minutes at room temperature gave a maximum extraction percentage of 92%. Maximum stripping of uranium from the loaded solvent was obtained by studying different factors affecting the process where an A/O phase ratio of 1:1 using 10M hydrochloric acid as a stripping agent for two stages were found sufficient for maximum stripping of uranium with a percentage efficiency of 92%.

KEYWORDS: Hydrophilic residue, Extraction, Trioctylamine, precipitation, uranyl peroxide

INTRODUCTION

In a previous study (paper under press) by the present authors, industrial phosphoric acid was purified to the food grade quality by a single stage extraction using ethanol (hydrophilic) and MIBK (hydrophobic) extractants. Rotary evaporator was used to recover ethanol leaving the hydrophilic residue which was the starting material in the present work.

Natural white silica sand as an adsorbent has been developed to reduce the concentration of iron and uranium ions as inorganic impurities in crude Egyptian phosphoric acid. Several parameters such as adsorbate concentration, adsorbent dose, volume to weight ratio and temperature, were investigated. Equilibrium isotherm studies were used to evaluate the maximum sorption capacity of adsorbent. Thermodynamic parameters showed the exothermic nature of the process and the negative entropy reflected the affinity of the adsorbent material towards each metal ion [1].

During acidulation of phosphate rock with sulphuric acid to produce phosphoric acid for fertilizer application, the uranium values contained in the rock was also solubilized. The phosphoric acid produced by the 'dihydrate process, containing 26–30% P_2O_5 , called the 'weak phosphoric acid' (WPA), was concentrated to >50% P_2O_5 grade, known as 'merchant grade acid' (MGA).

The 'hemi-hydrate' process directly yielded acid of high P_2O_5 content. The uranium concentration varies with acid concentration, provided oxidizing conditions were maintained so that selective precipitation of uranium does not take place. Depending on the rock used, the acid produced can contain 0.0050–0.05g U_3O_8/L . Separation of uranium by solvent extraction employing a synergistic combination of organophosphorus reagents. In particular, the solvent mixture of di-nonyl phenyl phosphoric acid (DNPPA) with di-butyl butyl phosphonate (DBBP) in an aliphatic diluent was found to be a stronger extractant than the commonly used combination of di-(2-ethyl hexyl) phosphoric acid (DEHPA) with tri-n-octyl phosphine oxide (TOPO). The DNPPA–TOPO mixture was an even stronger extractant.

Results on extraction from both WPA and MGA were reported. Stripping of uranium from the organic phase was achieved with concentrated phosphoric acid in the presence of Fe^{+2} as a 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 pretreatment and posttreatment were included [2].

Batch counter current extraction of uranium from fertilizer-grade phosphoric acid with a synergistic mixture of di-nonyl phenyl phosphoric acid (DNPPA) and tri-*n*-butyl phosphate (TBP) was reported. The effect of varying the concentrations of phosphoric acid, DNPPA and TBP on the distribution ratio of uranium were studied.

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The extracted uranium in the organic phase was efficiently stripped at 65°C using concentrated phosphoric acid containing ferrous iron. Uranium extracted by DNPPA-TBP was further subjected to a second cycle of extraction using D2EHPA-TBP and scrubbing impurities. The uranium was finally converted to a high purity UO₃ product using precipitation with hydrogen peroxide and heat treatment at 200°C. [3].

An efficient extractant of polyalkyl phosphazenes, PN-1200, was used for the separation of uranium from wet process phosphoric acid (PA) in a batch process at laboratory scale. Extraction of uranium from 29% P₂O₅ phosphoric acid using PN-1200 was compared with uranium extraction from phosphoric acid using synergistic mixtures of D2EHPA+TOPO and D2EHPA+TRPO. All extractants were diluted in normal aliphatic kerosene. It was 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 U⁴⁺ and U⁶⁺ [4].

In the present work, uranium was extracted from the solid hydrophilic residue separated during the purification of phosphoric acid to reach the food grade quality. The residue was decomposed by alkaline fusion then leached with 5M hydrochloric acid. Extraction of uranium was performed with TOA where optimum conditions were studied for its maximum extraction. It was found that hydrochloric acid was the optimum stripping reagent for uranium from the loaded TOA, where different concentrations were studied to select the most effective one. It was found that 10M HCl has the ability for maximum stripping of uranium from the loaded solvent.

EXPERIMENTAL

Methods

Sample Dissolution

- 1) A weight of 5g residue was ignited at 550°C in a porcelain crucible for four hours.
- 2) A 0.5g of the ignited impurities was fused with sodium hydroxide and sodium peroxide in a nickel crucible. The fused cake was leached with 5M HCl.
- 3) The uranium concentration in the hydrophilic residue was found to be 500ppm.
- 4) Consequently, a weight of 15g of the dried residue was fused sequentially in order to recover the uranium from the hydrophilic residue using Trioctylamine (TOA) as an extractant.

Instrumentations

Philips X-ray diffraction unit (PW 3710/31) with generator PW1830 scintillation counter (PW 3020), Cu target tube PW 2233, Ni filter at 40kV and 300mA was used for the identification of minerals.

An atomic absorption spectrophotometer model Unicam 969 supplied with acetylene and nitrous oxide burner heads, regulators and integrated reading in absorbance, was used for the determination of the impurities.

RESULTS AND DISCUSSIONS

Extraction of Uranium

Several factors for the maximum extraction of uranium from the decomposed hydrophilic residue (containing uranium) in 5M HCl were studied namely; type of the diluent, A/O phase ratio, mixing or contact time, and temperature.

Type of Diluent

Different types of organic diluents have been studied to increase the efficiency of the solvent for maximum extraction of uranium, namely; carbon tetrachloride, p-xylene, Kerosene and chloroform, where the A/O phase ratio was 1:1, mixing time of 15 minutes, settling time 5 minutes at 25°C. From the data gathered in Table (I), it was found that the most effective diluent used is xylene as it gave the maximum extraction of uranium using trioctylamine.

Table I. Effect of different diluents on the extraction of uranium

Diluent	% U Extraction
Xylene	90
Kerosene	85
Chloroform	66
Carbon tetra chloride	46

Effect of concentration of solvent

After optimizing xylene as the proper diluent for TOA, the concentration of the latter in xylene was studied for maximum extraction of uranium. From results obtained in Table (II), it was found that 30% TOA dissolved in xylene obtained the maximum extraction of uranium.

Table II. Effect of concentration of TOA in xylene on extraction of uranium

Concentration of solvent (%)	% U Extraction
10	70
20	85
30	93

Effect of Aqueous / Organic Phase Ratio on the Extraction Process

The aqueous to organic phase ratio has a significant effect on extraction of uranium. This effect was studied by changing the aqueous/organic (A/O) phase ratio from 1:1 to 1:4. The results obtained were presented in Table (III). It was clear from the results that an aqueous / organic phase ratio of 1:3 was the optimum ratio as it gave the highest percentage extraction of uranium.

Table III. Effect of aqueous organic phase ratio on the extraction of uranium

(A/O) Phase Ratio	U Extraction (%)
1:1	20.2
1:2	52
1:3	92
1:4	88

Effect of mixing time on the extraction process

The effect of mixing time was studied from 10 minutes to 30 minutes for maximum extraction of uranium, using 30% TOA in xylene and an aqueous to organic phase ratio of 1:3 at room temperature. Results illustrated in Figure (1) have shown a plateau region starting after a mixing time of 20 minutes, where it was the optimum for further experiments.

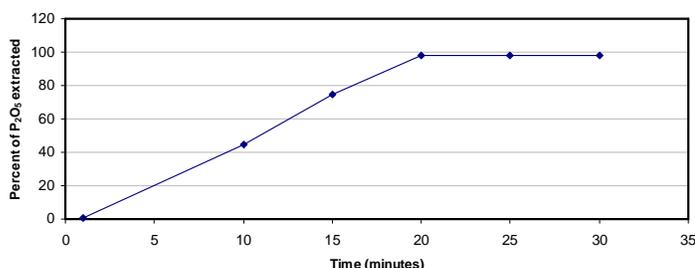


Figure (1): Effect of mixing time on the extraction of uranium

Effect of settling time

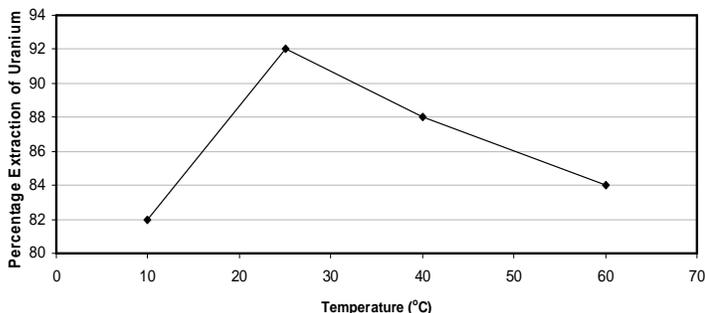
The effect of settling time was studied from 2 minutes to 5 minutes using 30% TOA in xylene at an A/O phase ratio of 1:3 and mixing both phases for 20 minutes. Results obtained in Table (IV) have shown that optimum settling time of both phases reached after 4 minutes.

Table IV. Effect of settling time after extraction of uranium

Time (minutes)	U Extraction (%)
2	83
3	88
4	92
5	92

Effect of temperature on the extraction process

The effect of temperature on the distribution coefficient reflects the results on the percentage extraction of uranium. Uranium extraction from its impurities was carried out and the temperature was regulated from 10°C to 60°C while the previous studied factors were kept constant. The results illustrated in Figure (2) showed that the best extraction process was carried out at 25°C.



**Figure (2): Effect of temperature on the extraction of uranium
Extraction Isotherm and Construction of Mc Cabe-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. In this study the phase ratio variation method will be used for the construction of extraction isotherm of uranium with organic mixture (TOA) and the phase ratios will range from 1:1 to 4:1 (O/A) where the extraction process will be carried out at the same previous optimum conditions. The obtained data were used to construct the Mc Cabe-Thiele diagram. Figure (3) was a composite plot of the extraction isotherm and the operating line.

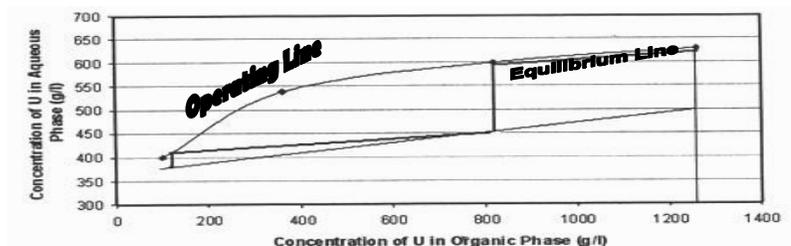


Figure (3): Mc Cabe-Thiele diagram for the extraction process

It was clear that one theoretical stage was quite adequate for uranium recovery.

Stripping process

After optimizing the maximum extraction of uranium using TOA in xylene as an efficient extracting solvent, re-extraction or stripping process was applied for the loaded uranium in order to perform its maximum recovery. Several factors were studied namely; concentration of stripping agent, A/O phase ratio, mixing time, temperature and settling time.

Effect of different concentrations of stripping agent

Hydrochloric acid was used as a stripping agent for uranium from the loaded TOA solvent [5]. Different concentrations of the stripping agent (3, 5, 7, 10, 11M) were used with A/O phase ratio of 1:1 at room temperature. From the results obtained in Table (V) it was found that 10M HCl is the optimum stripping reagent for maximum stripping of uranium from the loaded TOA solvent.

Table V. Effect of different concentrations of stripping agent

HCl concentration (M)	U stripping (%)
3	58
5	72
7	86
10	92
11	91

Effect of aqueous /organic phase ratio on the stripping process

This effect was studied by changing the aqueous / organic phase ratio from 1:1 to 2:1 keeping the other factors constant. From the data gathered in Table (VI). It was found that 1:1 phase ratio gave the highest percentage stripping for uranium.

Table VI. Effect of A / O phase ratio on the stripping process

(Aq/Org)	U stripping (%)
1:1	92
1:2	88
1:3	74
2:1	63

Effect of mixing time

The effect of mixing time (contact time) was studied from 2-10 minutes for maximum stripping of uranium from the loaded TOA using 10M HCl as the optimum stripping agent while the other studied factors were kept constant. Results gathered in Table (VII) showed that maximum stripping of uranium was obtained after mixing for 5 minutes and hence it was adopted as the best time for further experiments.

Table VII. Effect of mixing time on the stripping process

Mixing Time (minutes)	U Stripping (%)
2	88
3	90.1
5	92
10	92

Effect of settling time

The effect of settling time was studied after mixing both phases for 5 minutes, as previously optimized. The phases were left for complete settling after a period of time. This time was studied as a function of maximum stripping percentage. From Table (VIII), it was found that optimum settling time of both phases was 4 minutes.

Table VIII. Effect of settling time on the stripping process

Time (minutes)	U Stripping (%)
2	89
3	91.2
4	92
5	92

Effect of temperature

The effect of temperature on maximum stripping of uranium from loaded TOA was studied from 10°C to 60°C while the other optimum previous factors were kept constant. It was observed from Table (IX) that maximum stripped uranium was performed at 25°C.

Table IX. Effect of temperature on the stripping process

Temperature (°C)	U Stripping (%)
10	79
25	92
40	81
60	70

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

Mc Cabe-Thiele diagram is a composite plot of the distribution isotherm and the operating line. The diagram can be used to approximate the number of theoretical stages required for the given process. In this study, 10 g of loaded organic (TOA) and 10g of 10M HCl (stripping reagent) were contacted for 5 minutes at the previously determined optimum stripping conditions till equilibrium was attained.

The phases were allowed to separate (after 3 minutes). A measured portion of the aqueous phase was taken for analysis. Fresh loaded TOA was added to the separating funnel containing the remainder of the aqueous phase, in amount to give the same phase ratio as the originally used. The phases were again contacted until equilibrium was attained and this process was carried out until saturation of the aqueous phase with U was reached. The obtained results Illustrated in Figure (4) showed that two stages were found sufficient for the stripping of U from the loaded organic phase at a phase ratio of 1:1.

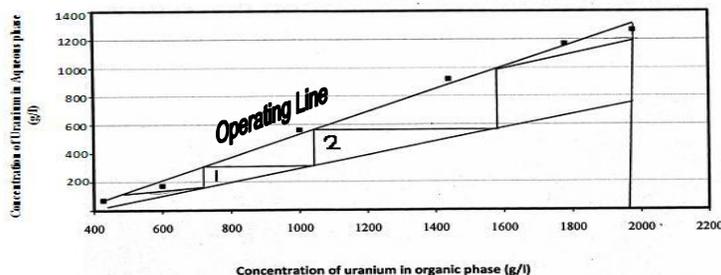


Fig.4. Mc Cabe Thiele diagram for stripping process

Precipitation of uranium from the strip solution

The strip solution containing uranium from the loaded TOA was precipitated using hydrogen peroxide [6] as an efficient selective precipitating agent to produce uranyl peroxide. The dried uranyl peroxide was subjected to XRD as a confirmation analysis tool.

X-ray Diffraction for Uranyl Peroxide

The X-Ray diffraction pattern shows that it has the same pattern lines as that of ASTM card No. 10-0309 specified for uranyl peroxide.

Proposed Flow Sheet

In the light of the obtained results for the recovery of uranium a flow sheet was elucidated to sum up the obtained results as shown in Figure (5).

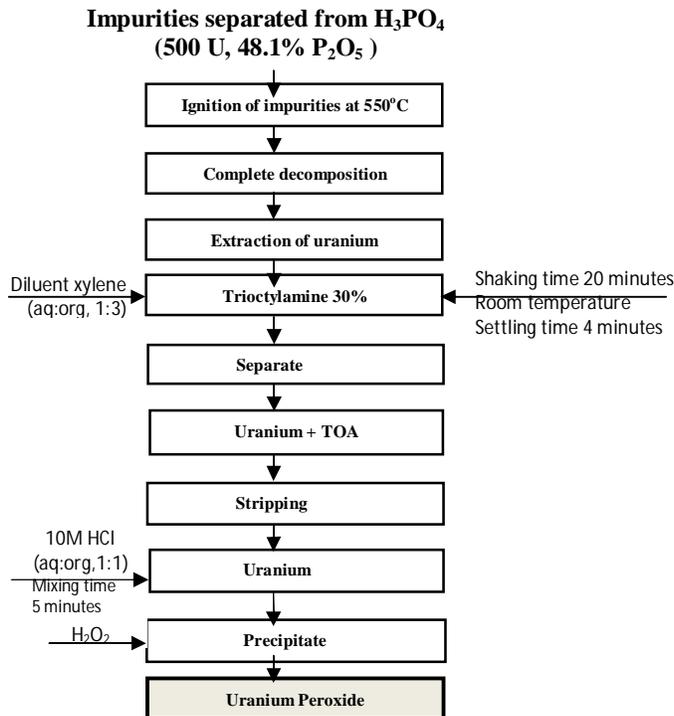


Figure (5): Flow Sheet for recovery of uranium from hydrophilic residue of phosphoric acid

Conclusions

The present work is a quick, accurate, economic method for the extraction and precipitation of uranium as uranyl peroxide from hydrophilic solvent extraction residue of the food grade phosphoric acid, using methyl isobutyl ketone and ethanol. It is clear that the used solvents are available and industrially produced in Egypt. Finally, on the light of the obtained results a technological flow sheet is elucidated.

Acknowledgment

The authors declare that they have no conflicts of interest in this research.

REFERENCES

- 1) EL-BAYAA, A.A., N.A. BADAWEY, A.M. GAMAL, I.H. ZIDAN, A.R. MOWAFY, 2011. Purification of Wet Process Phosphoric Acid by Decreasing Fe and U using White Silica. *J. Hazardous Materials*, **190** (1-3): 324.
- 2) GUPTA, R., V.M. PANDEV, S.R. PRANESH, A.B. CHAKRAVARTY, 2003. Study of an Improved Technique for Precipitation of Uranium from Eluted Solution, *Hydrometal.*, **71**,(3-4): 429.
- 3) SINGH, H., S.L. MISHRA, R.VIJAYALAKSHMI, 2004. Uranium Recovery from Phosphoric Acid by Solvent Extraction using Synergistic Mixture of Dinonyl Phenyl Phosphoric Acid, *Hydrometal*, **73** (1-2), 63.
- 4) .NAZARI, K., M.G. MARAGHEH, A.J. RAD, 2004. Studies on Extraction of Uranium from Phosphoric Acid using PN-1200 Extractant”; *Hydrometal.*, **71** (3-4), 371.
- 5) VESELSKY, J.C., P.C. KIRL and N.SEZINGER, 1974. “The Determination of U, Np and Pu in Urine by Sequential Extraction with Alamine-336 from Hydrochloric Acid Medium “*J. of Radioanal and Nucl. Chem.*, **21**(1), 97.
- 6) Hardwick, T.J., 1984. Method of precipitating uranium by hydrogen peroxide. US patent 442811A.