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Uranium recovery from concentrated phosphoric acid by using a synergistic organophosphorous solvent

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ABSTRACT

Extraction of U(VI) from concentrated Egyptian phosphoric acid with synergistic mixture of di-nonyl phenyl phosphoric acid (DNPPA) and di-butyl butyl phosphonate (DBBP), was investigated. The distribution of U(VI) was studied at different concentrations of DNPPA, DBBP, phosphoric acid and other parameters. The data on the effect of temperature on the extraction showed that the enthalpy change is -11.5 KJ/mol. Uranium extracted by DNPPA-DBBP is further subjected to a second cycle of extraction and scrubbing impurities. The uranium is finally converted to a high purity UO_3 product using precipitation with hydrogen peroxide and heat treatment at 375°C

KEYWORDS

Extraction;
Uranium (VI);
Phosphoric acid;
Stripping.

INTRODUCTION

World rock phosphates ores estimated to produce considerable amount of phosphoric acid for the use of the fertilizer industry. During the process of phosphoric acid production, 75% to 90% of uranium was present in the sedimentary rock extracted with phosphoric acid. Hence the acid product containing uranium up to 300 mg/L becomes a potential source of uranium. The extraction of uranium from H_3PO_4 has two main advantages: produce uranium as by product and to prevent the pollution of soil by the radionuclide present in wet process phosphoric acid[4,9,16].

At current global rate of consumption, phosphatic uranium can meet the global demand for 440 years as against a life of 86 years for known uranium resources[14]. The separation of uranium from phosphoric acid may be carried out using different separation techniques like ion-exchange[12], membrane separation[8] and precipitation[10,18] have been investigated. Synergistic mixtures of D2EHPA and TOPO, D2EHPA and DBBP, DOPPA and TOPO or DNPPA and TPP have been reported as a suitable for extraction of uranium from acidic mediums[2,3,6,7,13].

In the present work applied and kinetics study for the entrained solvent separation for DNPPA+ DBBP/ WPA system has been described. The activation energy, enthalpy of activation and entropy of activation for uranium extraction from concentrated Egyptian phosphoric with DNPPA+ DBBP has been studied.

EXPERIMENTAL

Solvent

DNPPA was synthesised by the following procedure[15]. A mixture of di- and mono-esters of nonyl phenyl phosphoric acid was obtained by reacting p-nonyl phenol with phosphorus oxy-chloride in the presence of pyridine in mole ratio of 2:1:2. The reaction mixture was hydrolysed with excess of 6 M HCl at 80°C for 12 h. The di-and mono-esters were separated by extraction from benzene solution with 70% methanol. The unreacted nonyl phenol and neutral compounds were separated by loading the benzene layer with neodymium Nd, and precipitating the Nd diester salt in excess acetone. Di-ester was obtained by dissolving the salt in benzene and stripping the Nd with oxalic acid. The concentrations of mono- and di-esters were determined by potentiometric titration with alkali in ethanol medium. The di-(2-ethylhexyl) phosphoric acid (D2EHPA) used were obtained from indigenous sources while commercially available di-butyl butyl phosphonate (DBBP) and tri- butyl phosphate (TBP) of 95 % purity were used for the work. The kerosene used was from MISR-Petroleum Ltd. Company, Egypt and had as main properties: specific gravity 0.8; flash point 70°C; initial boiling point 200°C; final boiling point 250°C; aromatics < 1%.

Phosphoric acid

The Egyptian phosphoric acid used in this study is 44% P_2O_5. Its average chemical composition is shown in TABLE 1. Before the extraction process, the acid was cooled down to a temperature of 30°C, filtrated for removal of suspended solid particles, treated with activated carbon for removal of soluble organic matter, which is very important factor for the success of uranium recovery and finally oxidized with hydrogen peroxide till EMF > 450 mV.

Analytical procedures

Uranium was all the time analyzed in the different working aqueous phases by the ArsenazoIII method[19]. Absorbance of the formed uranium ArsenazoIII complex was measured at 650 nm against proper standard solutions. For this purpose, a Lambada3 UV/VIS spectrophotometer (Perkin-Elmer, USA) was used.

The extraction and stripping experiments were carried out by equilibrating aqueous and organic phases (25 ml each) in 100 ml separating funnels, it is very important to note that no third phase or any precipitation was observed during the extraction process and uranium were analyzed in the aqueous phase and the content in the organic phase was calculated by difference. From latter values, the distribution coefficients D_u were properly determined where,

$$\mathrm{Du} = \frac{\begin{array}{c}\textbf{concentration of}\\ \textbf{uranium in organic phase}\end{array}}{\begin{array}{c}\textbf{concentration of}\\ \textbf{uranium in aqueous sphase}\end{array}} \times \frac{\begin{array}{c}\textbf{volume of}\\ \textbf{aqueous phase}\end{array}}{\begin{array}{c}\textbf{volume of}\\ \textbf{organic phase}\end{array}} \quad (1)$$

RESULTS AND DISCUSSION

Effect of DNPPA concentration on uranium extraction

The effect of DNPPA concentration on selective uranium extraction efficiency from WPPA was studied, a series of extraction experiments was performed using DNPPA/Kerosene in various concentrations (0.1 to 0.8M). In these experiments, the other extraction conditions were fixed at a V_{org}/V_{aq} ratio of 1/1 and using 5 min. shaking time at room temperature. From the obtained results shown in figure 1, it is clearly obvious that the uranium distribution coefficient increase with increasing initial DNPPA concentration.

Effect of DBBP concentration on uranium extraction at constant DNPPA

The synergistic effect of DBBP concentration on the extraction percent of uranium from WPPA, 9.2 M, has been investigated. A set of experiments were performed by shaking the treated phosphoric acid with DBBP having concentration ranging from (0.1 to 0.5 M) at constant DNPPA concentration (0.6 M) and in V_{org}/V_{aq} ratio equal 1.0 for 5.0 min at room temperature (25°C). The obtained results shown in figure 2, indicates that the uranium distribution coefficient increase with increase DBBP concentration up to 0.3 M followed by slight increase at higher DBBP concentration.

From these results, it is clear that DBBP has a good synergistic effect on the extraction of uranium from commercial Concentration phosphoric acid. A plot of log D_u vs. log [DBBP] at constant DNPPA concentration of 0.6 M is presented graphically in figure 3, shows a slope of ~1, which indicates that 1 mole uranium in organic phase is associated with 1 mole of DBBP.

TABLE 1 : Chemical composition of phosphoric acid produced by Abu-Zaabal Co, Egypt

Constituent	%	Constituent	mg/L
P_2O_5	44.00	Mn	673.3
SO_4^{-2}	6.10	Zn	358.9
Fe	2.50	U	62.0
Ca	0.26	Pb	53.9
Mg	0.17	Ni	7.8

TABLE 2 : Effect of aqueous / organic phase ratio on uranium distribution ratio from Egyptian concentrated phosphoric acid, 9.2 M, by 0.6 M DNPPA + 0.3 M DBBP in kerosene

aq/org phase ratio	U concentration, ppm		D ratio
	aq	Org	
1:1	12	50	4.16
2:1	17	45	5.29
3:1	29	33	3.41
4:1	37	25	2.7

Effect of DNPPA concentration on uranium extraction at constant DBBP

To study the effect of DNPPA concentration on the extraction of uranium from 9.2 M WPPA at constant 0.3 M DBBP concentration, Equal volumes (25 mL) of DNPPA and 0.5 M DBBP/kerosene and 9.2 M phosphoric acid were mixed together. The extraction was carried out by mixing the equilibrated DNPPA and DBBP/kerosene solutions with the aqueous phases mentioned previously at $V_{org}/V_{aq} = 1$, DBBP = 0.3M and T = 25 °C. The results represented in figure 4 shows that the uranium distribution coefficient (D_u) increases with increasing the DNPPA concentration. The plot of log D_u vs. log [DNPPA] M is shown in figure 5 and indicates a linear relationship with slope ~ 1.This contrasts with the results on DNPPA-TBP system where second-order dependence has been observed[5].

Effect of aqueous / Organic phase ratio

The effect of the V_{aq}/V_{org} phase ratio on uranium extraction from WPPA, 9.2 M, was investigated at aq / org phase ratio varying from 1.0 to 4.0. All experiments were performed using DNPPA & DBBP mixture, 0.6M & 0.3 M respectively, in kerosene for a mixing time of 5.0 minute T =25°C. From the obtained results shown in TABLE 2, it is clear that by increasing V_{aq}/V_{org} phase ratio the uranium extraction ratio was decreased. Subsequently, a relative decrease in the distribution ratio is expected and deviation in the distribution ratio is noticed.

Effect of shaking time

To study the effect of the shaking time on uranium extraction efficiency from WPPA, 9.2 M, by 0.6 M DNPPA + 0.3 M DBBP /kerosene,a series of extraction experiments was performed using different shaking times ranging from 1 up to 8 min. In these experiments, the other extraction conditions were fixed at a $V_{aq} / V_{org} = 2$, T = 25°C for various time intervals. Figure 6 shows the variation of uranium distribution coefficient (D_u) against time. It is clear that 5 minute is the minimum time to reach the equilibrium.

Effect of phosphoric acid concentration

The extraction of uranium from WPPA in the range of (4.06, 5.79, 6.90 and 9.23 M) by 0.6 M DNPPA + 0.3M DBBP/kerosene at an organic to aqueous phase ratio ($V_{org}/ V_{aq} = 1/2$), and at 25°C was examined. From the obtained data plotted in figure 7, it can be shown that uranium distribution coefficient (D_u) decrease with increasing the concentration of phosphoric acid. By using the log-log plot of D_u and phosphoric acid concentration as shown in figure 8, the linear relationship with slope of ~ -3 indicates that 3 moles of acid are liberated for extraction of 1 mole of uranium. Based on the above results, plausible extraction equilibrium is postulated as:

$$UO_2^{+2} + (HX)_3 + DBBP \rightarrow UO_2X_3.DBBP + 3H^+ \qquad (2)$$

where $(HX)_3$ is DNPPA.

Stability test of the extracting

In two parallel experiments, aliquots of 0.6 M DNPPA + 0.3M DBBP/kerosene were mixed with 9.2 M WPPA at room temperature and at 70°C, respectively for 15 days. Samples of the organic phase were withdrawn at intervals and uranium extraction test was carried out. No detectable change in uranium distribution coefficient (D_u) was found during this period indicating good stability of the solvent towards strong acid and temperature.

Effect of temperature on uranium extraction

The extraction of uranium from WPPA, 9.2 M, at different temperature was investigated. The extraction

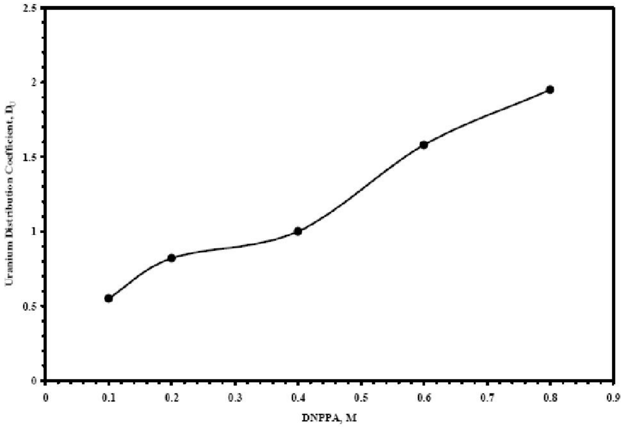

Figure 1 : Variation of uranium distribution coefficient (D_u) against DNPPA concentration, H_3PO_4 = 9.2M, V_{org}/V_{aq} = 1, T = 25°C

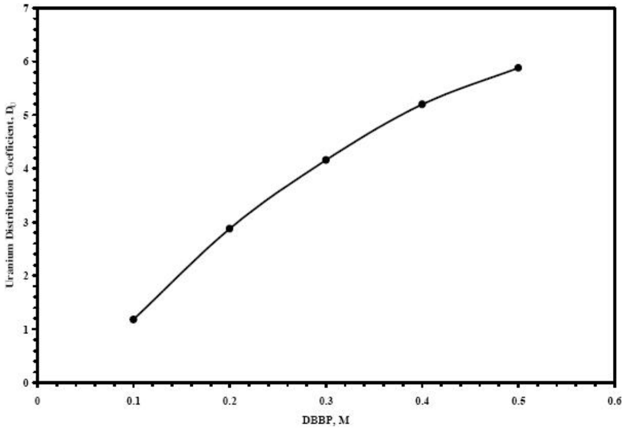

Figure 2 : Effect of DBBP concentration on uranium distribution coefficient (D_u) at constant DNPPA, H_3PO_4 = 9.2M, V_{org}/V_{aq} = 1, DNPPA= 0.6 M, T = 25°C

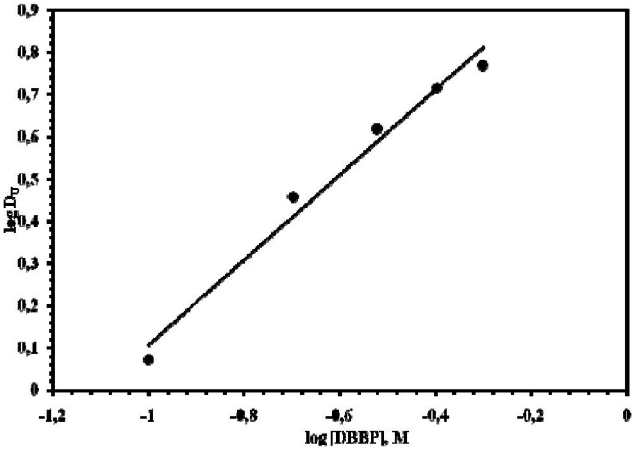

Figure 3 : The plot of uranium distribution coefficient (D_u) Vs log [DBBP] M, at constant DNPPA, H_3PO_4 = 9.2M, V_{org}/V_{aq} = 1, DNPPA = 0.6 M, T = 25°C

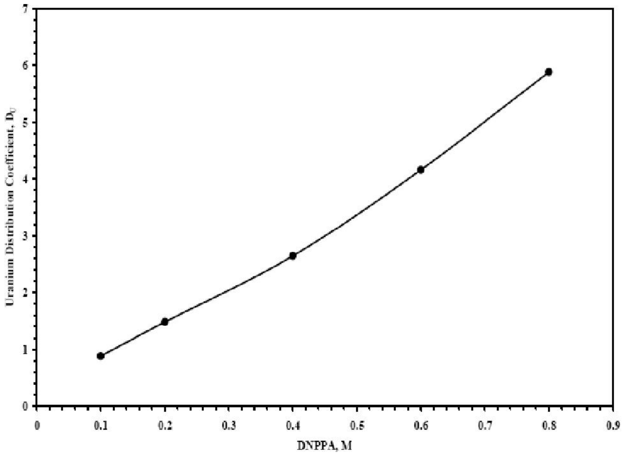

Figure 4 : Variation of uranium distribution coefficient (D_u) against DNPPA concentration at constant DBBP, H_3PO_4 = 9.2M, V_{org}/V_{aq} = 1, DBBP = 0.3 M, T = 25°C

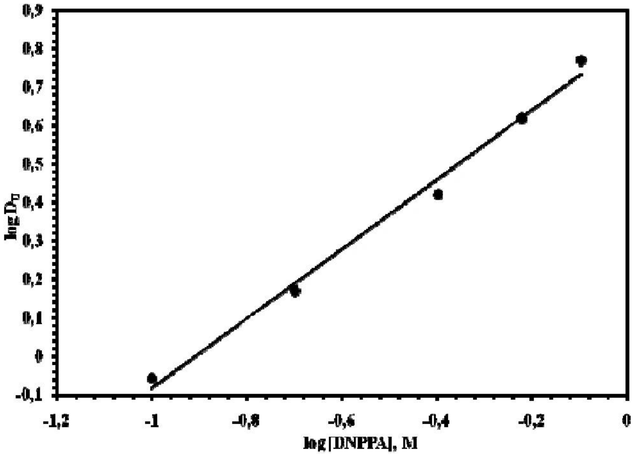

Figure 5 : The plot of uranium distribution coefficient (D_u) Vs log [DNPPA] M, at constant DBBP, H_3PO_4 = 9.2M, V_{org}/V_{aq} = 1, DBBP = 0.3 M, T = 25°C

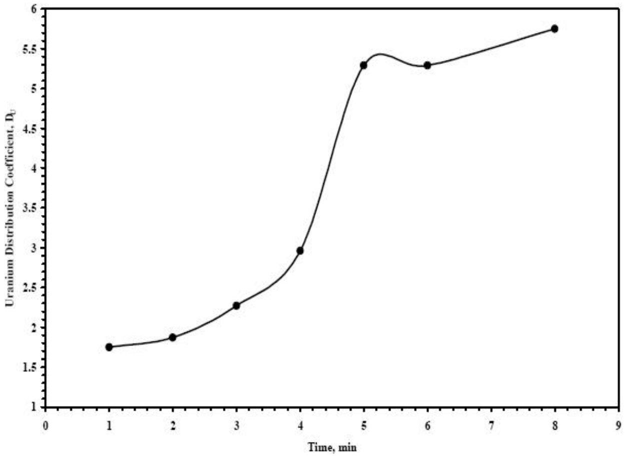

Figure 6 : Variation of uranium distribution coefficient (D_u) against time, H_3PO_4 = 9.2M, V_{org}/V_{aq} = 1/2, DNPPA = 0.6 M, DBBP = 0.3M, T = 25°C

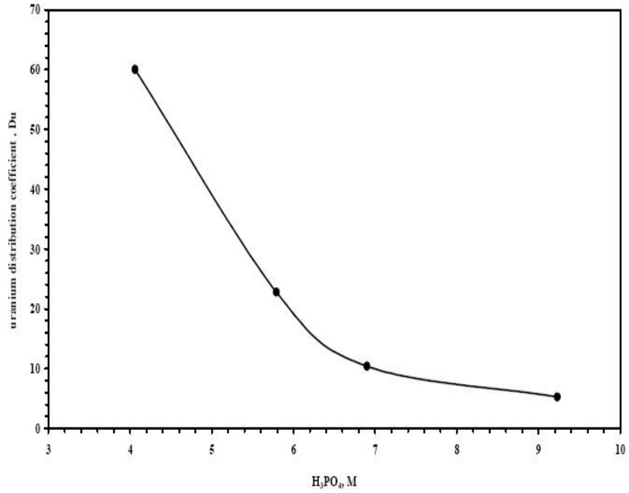

Figure 7 : Variation of uranium distribution coefficient (D_u) against H_3PO_4 concentration, $V_{org}/V_{aq} = 1/2$, DNPPA = 0.6 M, DBBP = 0.3 M, time = 5 min, T= 25°C

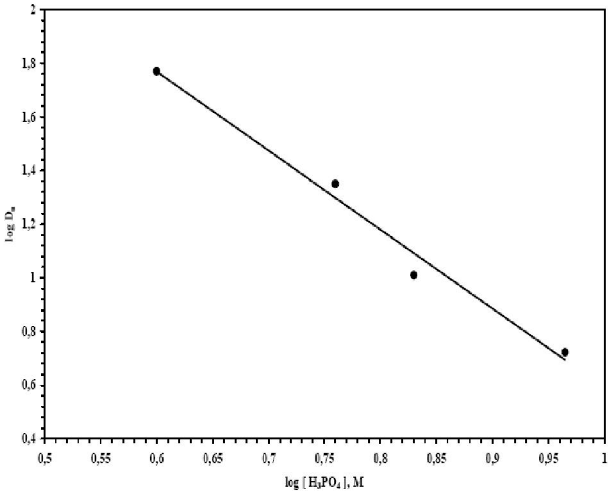

Figure 8 : Effect of phosphoric acid concentration on uranium distribution coefficient, $V_{org}/V_{aq} = 1/2$, DNPPA = 0.6 M, DBBP = 0.3 M, time = 5 min, T = 25C

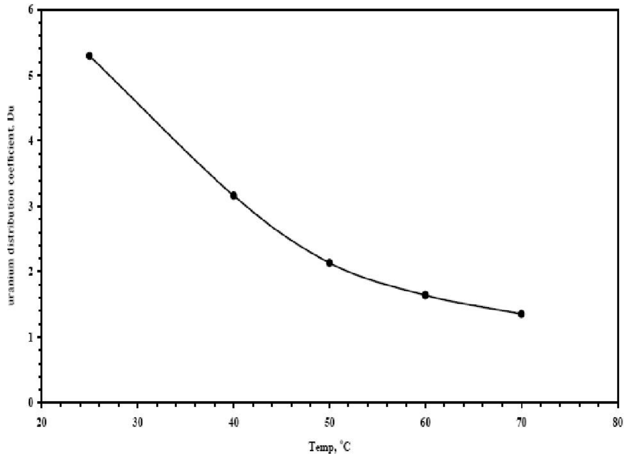

Figure 9 : Variation of uranium distribution coefficient (D_u) against temperature, $V_{org}/V_{aq} = 1/2$, DNPPA = 0.6 M, DBBP = 0.3 M, time = 5 min

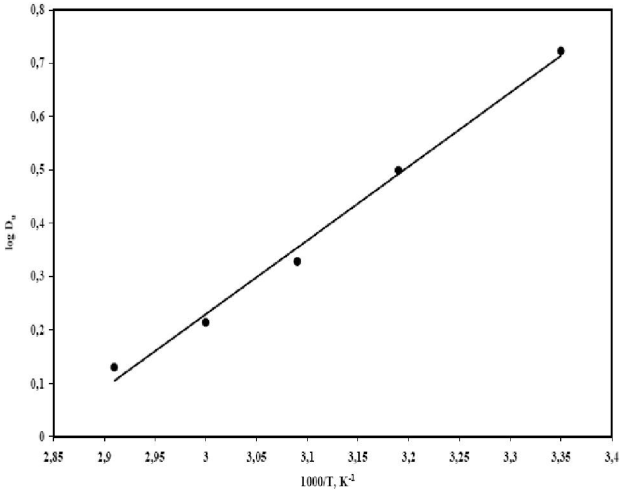

Figure 10 : log D_u as a function of 1000/T, $V_{org}/V_{aq} = 1/2$, DNPPA = 0.6 M, DBBP = 0.3 M, time = 5 min

experiments were carried out by contacting phosphoric acid with a 0.6 M DNPPA + 0.3M DBBP/kerosene for 5 minutes while the V_{org}/V_{aq} phase ratio was fixed 1/2 but the temperature was varied.

The results are presented in figure 9 as a relation between temperature and uranium distribution coefficient (D_u). From the obtained data, it can be noticed that D_u is decreased by increasing the temperature which demonstrates the exothermic nature of the extraction process. Therefore the applied temperature was room temperature 25°C. The effect of temperature on the distribution coefficient can be quantified by making use of the Vant Hoff equation, which relates the chemical equilibrium constant with temperature:

$$d \ln K/dT = \Delta H/R.T^2 \qquad (3)$$

By integration,

$$\ln K = (-\Delta H/R)(1/T) + c \qquad (4)$$

where c is constant. And since the distribution ratio D is related by definition to the equilibrium constant K the previous equation can be written as:

$$\ln D = (-\Delta H/R)(1/T) \qquad (5)$$

The plot of log D_u against 1/T yields a straight line equation with slope (x) = -ΔH°/2.303 R. Figure 10 shows that extraction uranium by 0.6 M DNPPA + 0.3M DBBP/kerosene from Egyptian wet process phosphoric acid decrease with temperature. An enthalpy change of -11.5 kJ/mol was determined by using eq. 5

in the given range of temperature, which indicates that the extraction is an exothermic process.

Stripping of uranium from extract

Uranium stripping from the loaded extract using raffinate is generally the most economic technique in the industry. There are many other efficient stripping reagents such as ammonium carbonate, ammonium hydrogen fluoride and a HF-H_2SO_4 mixture. Hydrazine carbonate has also been recently reported as an effective stripping agent[17]; this has the advantage that no additional cations are introduced into the process. Reductive stripping with concentrated phosphoric acid can also be used[11], and is adopted for the present work since the resulting strip solution, concentrated in uranium, can form the feed for a second cycle of solvent extraction directed at obtaining a pure uranium product.

Uranium is stripped from loaded organic with pure phosphoric acid containing 10 g/l Fe^{+2} to reduce the less stripped uranium form (VI) to the more stripped uranium form (IV). The different parameters that affected in uranium stripping process were investigated.

The preferred stripping results were found to be pure phosphoric acid concentration: 8-10 M; temperature: 60-70°C; contact time: 4 min; org / aq phase ratio is equal 20 and five stages were sufficient for stripping about 98.4 % of total uranium in loaded organic[5]. The loaded organic containing 382 mg/l U_3O_8 yielded a product solution containing 7.09 g/l U_3O_8.

Uranium recovery from strip solution

The obtained strip solution was found to contain uranium in a concentrated form, which, however, is not suitable for direct precipitation due to the presence of high level of impurities. The strip solution can be processed in a second cycle of extraction-stripping with an additional scrubbing step by sulfuric acid to obtain a high purity uranium cake. The high selectivity is an important factor in the selection of the solvent for the second cycle taken in consideration the co-extracted rare earths, iron and phosphates. The extractant used in the second cycle was 1.5 M D2EHPA+ 0.2 M TPP, as per earlier reports[5].

From the loaded organic phase, uranium was stripped with 1 M ammonium carbonate solution. The strip liquor was filtered to remove traces of iron precipitate. The uranium tri-carbonate solution contained excess ammonium carbonate and pH was found to be 8.3.

Uranium precipitation was carried out using H_2O_2. To bring down the pH of the solution, an addition of sulphuric acid to the solution with a slight excess of H_2O_2 was added after the solution had been filtered to remove the traces of iron hydroxide precipitate. The neutralization was carried out with sulphuric acid. In a pH range of 3-4, the uranium precipitation was complete (< 99%). Uranium peroxide hydrate ($UO_4.H_2O$) was filtered, washed, dried and calcined at 375°C to obtain UO_3 powder with high purity.

ABBREVIATIONS

DNPPA	:	Di nonyl phenyl phosphoric acid
K	:	Equilibrium constant
DBBP	:	Di-butyl butyl phosphonate
ΔH^o	:	Standard enthalpy (kJ/mol)
D2EHPA	:	Di (2-ethylhexyl) phosphoric acid
V	:	Volume
TOPO	:	Tri-octyl phosphine oxide
X	:	Slope
TBP	:	Tri-butyl phosphate
ΔH	:	Enthalpy (KJ/mol)
WPPA	:	Wet process phosphoric acid
D_u	:	Distribution coefficient
Aq	:	Aqueous phase
E	:	Extraction efficiency
Org	:	Organic phase
EMF	:	Electromotoive force
DOPPA	:	Di octyl phenyl phosphoric acid
T	:	Absolute temperature (K)
R	:	Universal gas constant (8.314 J K^{-1} mol^{-1})
[ ]	:	Concentration of species in brackets M
V_{Org}/V_{Aq}	:	Volume ratio between organic phase and aqueous phase

CONCLUSION

The synergistic extractant DNPPA + DBBP in kerosene as a diluent can be used for recovery of uranium from concentrated Egyptian phosphoric acid. The solvent is stable and an organic phase composed of 0.6M

DNPPA and 0.3 M DBBP in kerosene as a diluent at room temperature for 5 minutes is optimal for simultaneous extraction of uranium. An extraction mechanism for uranium has been postulated based on the results of slope analysis. High-purity uranium is recovered from the strip solution by a second cycle of extraction with D2EHPA-TPP mixture where in scrubbing step has been incorporated and stripping is performed by an alkaline solution. From the resulting alkaline uranium solution, a precipitation process yields high purity uranium peroxide which is filtered, washed, dried and calcined at 375°C.

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