Uranium and Plutonium Recovery by Tributylphosphate Solvation and Trioctylamine Ion association Mechanisms

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Abstract:

In this work a flowsheet has been put for the recovery of uranium and plutonium from 2.5M nitric acid solutions using 17.5% tributyl phosphate (TBP) and 2.5% trioctylamine (TOA) in kerosene diluent . The fission products (resulting from irradiated of uranium samples in nuclear research reactor) were removed from the desired actinides U & Pu .The organic phase TBP/TOA/Kerosene, containing both actinides U&Pu were stripped using 0.1 M HNO_3.

Trioctylamine (2.5 volume ratio) in mesitylene , has been used in conditions appropriate for the recovery of Pu . From the experiments done using mixer- settler , the concentration of uranium in the organic phase in such conditions was very low ,not exceeding parts of a million .

Key words : Uranium, plutonium , tributylphosphate , trioctylamine , actinide

Introduction:

Organic solutions of high molecular weight amines such as Tricapryl amine(TCA) or Tri-n-Octylamine (TOA) or tridodecylamine, have been used as Liquid – Liquid extractant for mineral acids , organic acids and metal ions from aqueous solution . In addition the Liquid – Liquid extraction techniques are widely used for the processing of irradiated reactor fuels using the high molecular weight amines as extracting agents [1-5] .

Keder et al[6] reported that long chain tertiary amine salts are soluble in a variety organic solvents such as kerosene, xylene, mesitylene which are immiscible with aqueous solutions .

This property of long chain tertiary amines permits extraction of metallic anions from acids solutions .

Trilaurylamine (TLA) has been suggested for the recovery of plutonium from nitric acid solutions. [7]. The extraction mechanism is most likely to be of the following ion – association type [8]:-

1- The organic solvent containing the amine can extract an aqueous acid to from an amine salt in the organic phase:

$(R_3N)_{org} + H^+_{aq.} + A^-_{aq} \longleftrightarrow (R_3NH^+A^-)_{org}.$

Where:

R_3N = is a high molecular weight amine.

A= Anion of a simple acid

2- An amine salt in the organic phase can undergo anion exchange with an ion in the aqueous phase:

$(R_3NH^+A^-)_{org} + B^-_{aq.} \longrightarrow (R_3NH^+B^-)_{org} + A^-_{aq}.$

Where :

$B^-_{aq.}$ = is an anionic complex in the aqueous phase.

Large plants have been built for the reprocessing of the irradiated fuel based on the use of Tri-n-butyl phosphate (TBP) in an inert diluents as extracting agent [9,10]. The separation by solvation mechanism of uranium

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and plutonium from fission products is as the following [11] :

$$UO_2^{2+} + 2NO_3^- + 2TBP \longrightarrow UO_2(NO_3)_2.2TBP$$

$$Pu^{4+} + 4NO_3^- + 2TBP \longrightarrow Pu(NO_3)_4.2TBP$$

The aim of this study are :

1- Studing the extraction of uranium and plutonium and their separation from fission products by using a mixture of tertiary amine (Tri-octylamine) and (Tributyphosphate) .

2- Investigating the behavior of the major fission products with the trioctylamine as an extracting agent and to study the effect of nitric acid , and ligand concentration on the extraction process.

3- Studing the behavior of plutonium with tri-octylamine as a extracting agent in an effort for leaving the uranium in the aqueous layer , i.e study the conditions for separation of plutonium from uranium.

4-Finally is using the optimum conditions in a mixer-settler run.

Materials and Methods:

Mterials:

The following reagent grade (analar) materials were used in this work:

1- Uranium oxide (U_3O_8).
2- Uranyl nitrate hexahydrate $UO_2(NO_3)_2.6H_2O$.
3- Plutonium nitrate tracer.
4- Tri-n-Butyl phosphate.
5- Tri-n-Octyl amine.
6- Treated kerosene.
7- Mesitylene.
8- Nanonal-1
9- Magnesium nitrate hexahydrate $Mg(NO_3)_2.6H_2O$
10- Aluminum nitrate $Al(NO_3)_3.9H_2O$.
11- Nitric acid.
12- The following tracers provided from Amersham England. ^{103}Ru, ^{137}Cs , ^{95}Zr, ^{144}Ce , ^{152}Eu.

Methods:

Preparation of irradiated uranium sample:

About 1 gram of U_3O_8 sample was irradiated for 72 hours in the research reactor-Twaitha-Baghdad netron flux 0.5*10n/cm3.sec and then dissolved in nitric acid after a cooling time of about 3 months , part of it was used for the mixer – settler run.

Test tube extraction experiments :

Extraction of uranium and plutonium by different volume ratio of TBP/TOA .

To accomplish this, the following procedure was followed:

1- Preparation of the feed solution (35g U/l in 3M HNO_3).

2- Preparation of the organic solutions which consisted of different ratios of TBP & TOA in kerosene .

3- After equilibration of the organic solutions with the desired nitric acid molarity , 5ml of feed solution was mixed with equal volume of the organic solution. Time of mixing was set to be 20 minutes after which phase disengagements was done by centrifugation for 2 minutes.

4- Sample from the organic and the aqueous layers were taken for analysis.

5- The above experiments were repeated using plutonium (trace level) instead of uranium as feed solution.

Investigation the behavior of some fission products by the above TBP/TOA/kerosene/HNO_3 Systems.

The fission products ^{144}Ce , ^{95}Zr , ^{95}Nb , ^{137}Cs and ^{103}Ru were investigated in different ratios of TBP and TOA in kerosene the procedure is as that given in section 2-3.

Effect of uranium on the extraction of some fission products by 17.5%TBP & 2.5%TOA.

To the 35 gu/l in 3M nitric acid solution the fission products ^{144}Ce , ^{95}Zr , ^{95}Nb , ^{137}Cs and ^{103}Ru were added as tracers . The procedure in section 2-3 was repeated using 17.5% TBP and 2.5% TOA in kerosene as the extractant.

Effect of nitric acid concentrations on the extraction of uranium and plutonium by TOA .

To accomplish this , uranium solutions of 35 gu/l were prepared in different nitric acid concentrations (0.5-8M HNO_3). 2.5% TOA was used as extractant , following the procedure described previously .

Another set of experiments were done for the extraction of plutonium (trace level) from different nitric acid concentrations (0.5-8M HNO_3).

Extraction of uranium using (2.5-10%) TOA/kerosene /HNO_3 system.

Different organic solutions of (2.5-10%) TOA in kerosene were equilibrated with an excess of 2.5M nitric acid solution. In a different centrifuge tubes , (5) ml of 35 gu/l solution was added to each of the organic solutions and then shaken for 20 minutes in a mechanical shaker. After the tubes being centrifuged for 2 minutes , samples from organic and aqueous layers were taken for analysis.

Extraction of plutonium by different volume ratios of TOA/kerosene /HNO_3 system.

The procedure mentioned in section 2-7 was repeated for the extraction of plutonium by using different volume ratios of TOA (1-20%). Samples were taken for analysis.

During doing the above experiments i.e sections 2-3 to 2-8 , the formation of a third layer have been noticed in many cases .To get rid of this layer , nananol-1 was added to the organic solution until the third layer disappeared (50-100 microlitre usually is enough) .For this reason a suggestion was made to use mesitylene in stead of kerosene as a diluents during the mixer-settler run due to the technical complication associated with large scale work.

Effect of using mesitylene as diluents instead of kerosene for the extraction system.

In this part of the work a comparison was made for the results obtained using mesitylene as diluents with those obtained by using kerosene. Thus the optimum condition for the extraction of uranium and plutonium by using mixer-settler were set from the previous test tubes experiments.

Mixer settler experiments :

Extraction of uranium by 2.5% TOA +17.5% TBP/mesitylene/HNO_3 system using mixer settler

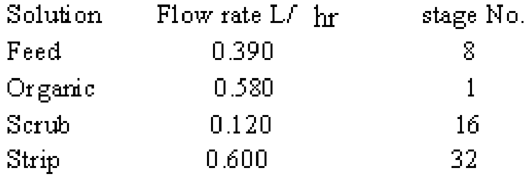
1- For this experiment , the feed solution was prepared , containing 35 gu/l uranium , 7.04 g/l magnesium and 6.94 g/l aluminum . To this solution tracers of the following fission products where added ^{144}Ce , ^{95}Zr , ^{95}Nb , ^{137}Cs and ^{103}Ru with addition of carriers in concentrations equivalent to that predicted by origin programme [21].

2- The organic solution was prepared from 2.5%TOA +17.5%TBP in mesitylene as diluent.

3- The scrubbing solution 3M HNO_3.

4- The stripping solution 0.1M HNO_3.

The conditions under which this experiments was carried out are as follows



Solution	Flow rate L/ hr	stage No.
Feed	0.390	8
Organic	0.580	1
Scrub	0.120	16
Strip	0.600	32

After each hour from the beginning of this experiment, samples were taken from the points , aqueous waste , organic waste , organic product and aqueous product.

At the end of the experimental (after 4 hours from the starting time) samples of organic and aqueous layers were taken from each stage for analysis.

Use of 2.5% TOA/mesitylene /HNO_3 in mixer settler run

The product from the above run was 17 gu/l in 0.5M HNO_3 , this was used in a second mixer settler run with flow rate of 0.364 L/hr at stage 8. The organic was 2.5% TOA in mesitylene was fed in stage 1 and the scrub was 0.5M of nitric acid in stage 16.

Samples were taken from the outlet points of the battery every hour for analysis. At the end of the run, samples from aqueous and organic layers of each stage were analyzed.

Analysis

Uranium analysis:

Aliquots of the aqueous phase were analyzed spectrophotometrically appling dibenzoylmethane method . This method is based on the selective extraction of uranium as tetrapropyl ammonium –uranyl nitrate complex and color developing with dibenzoyl methane. The obserbance was measured at 415 nm . For ppm uranium concentration florometry method of analysis was carried out. Fission products activity were measured using 724.23 , 765.83 , 497.14 , 662 , 87.1 Kev γ – energies , for ^{95}Zr , ^{95}Nb , ^{103}Ru , ^{137}Cs and ^{155}Eu respectively , with the aid of Ge Li detector of 97 cm3 active volume and 4096-multi channel analyzer , camac ADC type 9060 linked with HP-computer (Princeton-Gamma Tech , Germany).

Plutonium was analyzed using α-spectrometer using ZnS detector linked to the above computer.

Results and Discussion:

The results of the distribution ratio of uranium and plutonium by different volume ratios of TBP/TOA are given in Fig I(a,b) , from which one can observe a decrease in distribution ratios of uranium with a decrease of TBP percentage in the 20% volume ratio of TBP+TOA on the contrary an increasing in distribution ratio of Pu is observed as TBP percentage is decreased . Cerium is not effected by the change in the volume ratios of the extractant , Ruthenium seems to be less extracted in none amine system . As Zirconium is less extracted in amine system , Niobium is not that much affected in different volume ratios of the extractant.

A further investigation of the behavior of the fission products studied in presence of uranium was shown in (table 1) from which no appreciable differences in distribution were obtained.

In Fig 2 , the distribution ratios of U (VI) and Pu(IV)from nitric acid concentrations of 0.5 to 8M are presented. For the case of uranium ,the distribution ratios increases with the increase with

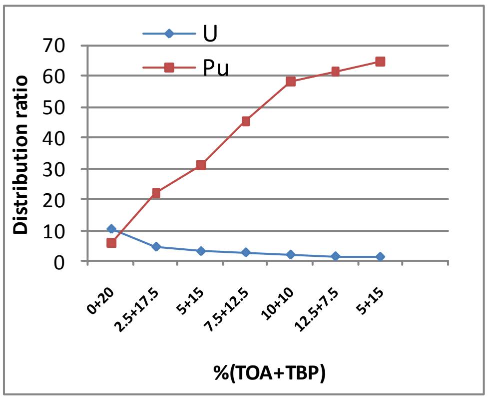


Fig-1a:effect of using different volume ratios of TBP&TOA on the recovery of uranium & plutonium

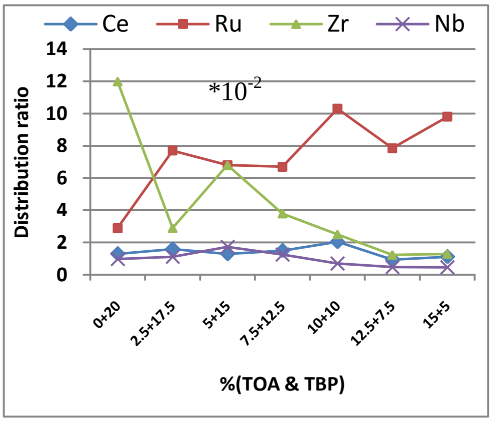


Fig-1b:effect of using different volume ratios of TBP&TOA on the extraction of some fission products

Table-1: Distribution ratios of some fission products in the presence and absence of uranium

isotope	With 35 gu/l in 3M HNO3	Without u
Ce	N.D*	$1.6*10^{-2}$
Ru	$2.6*10^{-2}$	$7.7*10^{-2}$
0Cs	N.D	N.D
Zr	$3.8*10^{-2}$	$2.9*10^{-2}$
Nb	$1.3*10^{-2}$	$1.1*10^{-2}$

N.D * =not detected by instrument used

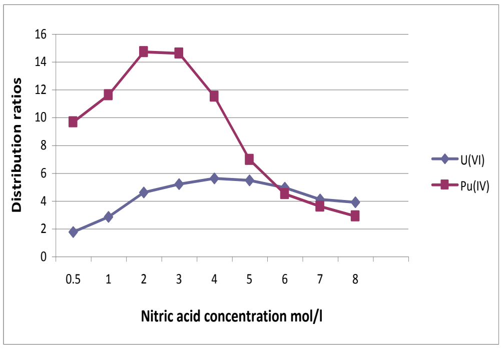


Fig 2 : Distribution Ratios of U(VI) and Pu(IV) from nitric acid with 2.5% Tri-n-Octylamine in kerosene

The increase in morality with maximum values in the range of 3-5M nitric acid solutions. For the case of Pu(IV) as maximum distribution ratios obtained between 2-3M nitric acid. On the other hand, the distribution ratio of Pu is considerably high at lower acidities (0.5M) .To investigate the behavior of U and Pu as the volume percent of TOA increases. In fig III an increase in the distribution ratios of Pu, follows the increase in volume percent of the extractant thus using 1%volume ratio of TOA will give 3.08 distribution ratios for Pu, increasing the percentage of TOA to 2.5 give a distribution ratio of 14.67. Thus a remarkable increase in distribution ratio.

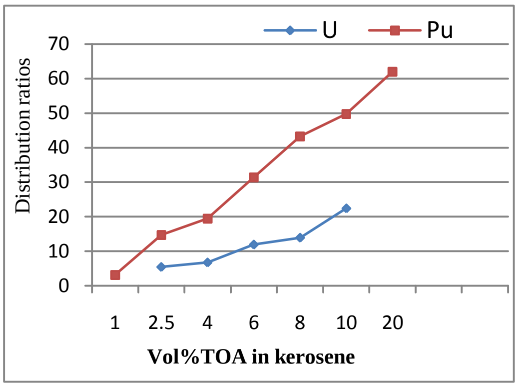


Fig 3: Distribution ratios for U and Pu from 2.5M HNO3 and as a function of amine concentration

The same thing is true for the uranium. Since our aim is to leave uranium in the aqueous phase at 2.5% vol.percent of TOA only $5.4*10^{-2}$ distribution ratio is obtained for U over 14.67 for Pu.

In table 2 a comparison is given by using mesitylene as diluents instead of kerosene , changing the diluents from kerosene to mesitylenen enhance the distribution ratios of both U and Pu by extractant (17.5% TBP & 2.5% TOA). This is most likely attributed to the formation of 3rd phase in the case of kerosene which results in some loss of both U and Pu. Also a comparison is between the previous two systems and 20% TBP . The distribution ratio for U in 17.5% TBP and 2.5%TOA mesitylene tend to be close to that of 20%TBP kerosene while fo Pu the amine system is far much better than the TBP system . Also a comparison is given for the behavior of the fission products (Ce , Ru , Zr, Nb) in such systems ,where no appreciable difference was observed.

Table-2: Distribution Ratio for U , Pu and some fission products in two different diluents

Isotope	Distribution Ratios 20% TBP in kerosene	Distribution Ratios 17.5% TBP+2.5% TOA in kerosene	Distribution Ratios 17.5% TBP+2.5% TOA in meistylene
U	10.24	4.33	9.89
Pu	5.6	22.11	28.77
Ce	$6.3*10^{-3}$	N.D*	$6.68*10^{-3}$
Ru	$9.26*10^{-3}$	$2.59*10^{-2}$	$3.30*10^{-2}$
Cs	N.D	N.D	N.D
Zr	$5.1*10^{-2}$	$3.8*10^{-2}$	$7.78*10^{-2}$
Nb	$1.18*10^{-2}$	$1.3*10^{-2}$	$1.19*10^{-2}$

For the same purpose as above , a comparison is carried out in (table 3) for the 2.5% TOA system in kerosene and mesitylene which shows a better distribution ratios of Pu in mesitylene than that in kerosene. Also the stripping of Pu was found to be easier.

In (table 4), the decontamination factors for uranium from the fission products are given. A high decontamination factor is obtained over 10^5 for many of the fission products present in the irradiated uranium, values of of decontamination factor of 10^5 was obtained for Zn/Nb , while lower values were obtained for Ru and Ce , 311 and 327 respectively.

Table-3: Effect of diluents on the extraction of Pu(IV) by 2.5% TOA from 0.5M HNO3 and Stripping by 0.01M HNO3

Diluent	D.R. for extraction section	D.R. for stripping section
Kerosene	9.3	0.0013
Mesitylene	25.75	0.0022

D.R.= Distribution ratio.

Table-4: Decontamination factors of U from fission products in the mixer settler extraction scrubbing battery.

F.P	Eu	Ce	Ru	Cs	Zr	Nb
D.F	V.H*	327	311	V.H	23000	39000

V.H*= very high decontamination factors obtained

In (table 5) are given the uranium concentration lost in the waste streams i.e. aqueous waste and organic waste . ppm scale level are obtained in all cases.

Table-5: uranium concentration in the aqueous and organic raffinate obtained from 17.5%TBP +2.5%TOA mixer settler run.

Time/ hr	AW/ ppm	CW/ ppm
1	<1	18
2	<1	2.5
3	<1	9.8
4	<1	49.5

In (table 6) and (Fig 4), the results of the second mixer settler run experiment are shown. The aim of the experiment was set so that uranium is left in the aqueous phase. Any uranium that is extracted to the amine phase is a contaminate to the system.

Table- 6: The concentration of uranium in both aqueous and organic outlets of mixer settler batteries

Time/ hr	AW/ ppm	CW/ ppm
1	<1	18
2	<1	2.5
3	<1	9.8
4	<1	49.5

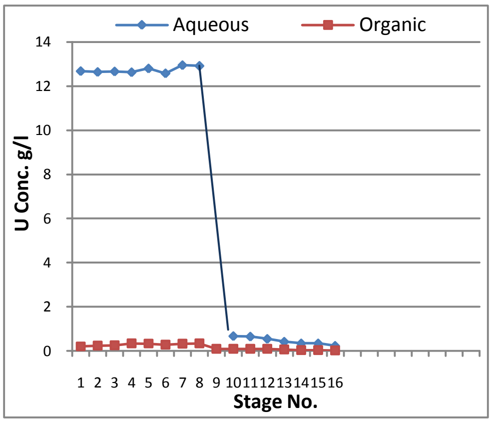


Fig 4 : Uranium concentration in the 16 stages of the mixer settler extraction battery using 2.5% TOA system

Table 6 , shows the concentration of uranium extracted to the amine phase during the hours of the experiment , ppm level was obtained.

Also almost all of uranium feed to the battery is rejected to the aqueous raffinate as waste.

Fig 4 shows the concentrations of uranium in the 16 stages of the battery in the organic and aqueous phases. In the first 8 extraction stages, the concentrations of uranium in organic phase is in ppm scale and gradual decrease in uranium concentration as the organic phase moves away for feed stream. While scrubbing of the organic phase is beneficial and the organic phase results in even less loaded with uranium i.e. from stages 9 to 16 . For the aqueous phase almost all the uranium is remaining in the first stages of the battery in the aqueous later. Also increasing in uranium concentration is observed as aqueous stream moves toward the aqueous raffinate tank.

Fig 5 shows the final run of mixer settler which represents the optimum condition flow sheet .

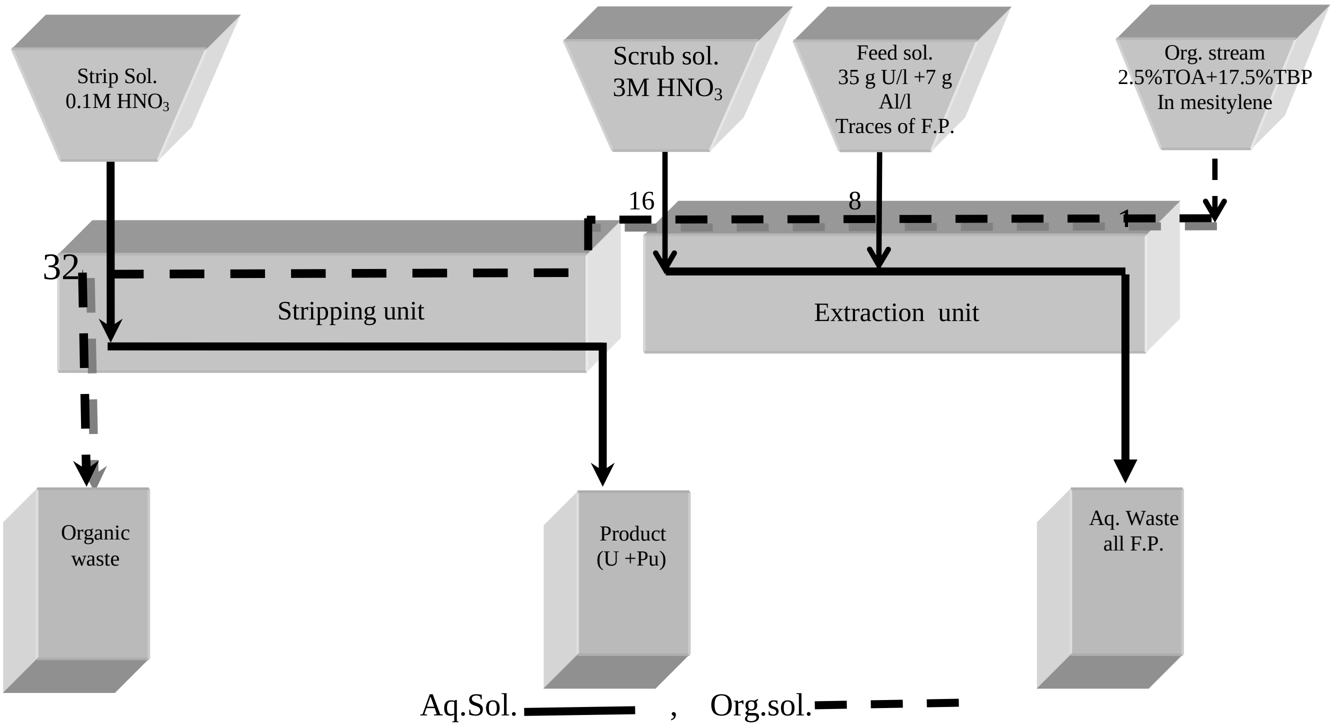


Fig- 5 : Final flow sheet of extraction Uranium and Plutonium from fission products

Conclusion:

A flowsheet using 2.5%TOA and 17.5% TBP in mesitylene diluents, has been successfully applied for the coextraction of U and Pu and their separation from fission products. Stripping of both U and Pu was carried out using dilute nitric acid solution.

Another flowsheet using 2.5 TOA% in mesitylene has been put for the extractions of Pu and its separation from U using one mixer-settler.

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استرداد اليورانيوم والبلوتونيوم بميكانيكية التمذوب بال (TBP) والايون المرافق بال (TOA)

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الخلاصة:

في هذا البحث ، تم وضع منهج تدفق عمليات للاسترداد المشترك لليورانيوم والبلوتونيوم من محيط 2.5M حامض النتريك باستخدام 17.5% ثالث بيوبيل الفوسفات و 2.5% ثالث أوكتيل أمين في الكيروسين. تم فصل نواتج الانشطار (الناتجة من تشعيع نماذج اليورانيوم في مفاعل الأبحاث النووية) من عناصر الأكتينات (Pu&U) ، ثم أعيد استرداد ما تحمله الطبقة العضوية "TBP/TOA/Kerosene" من عناصر الأكتينات بواسطة عمليات الانتزاع stripping باستخدام محلول مخفف من حامض النتريك. تم أستخدام ثالث أوكتيل أمين (بمقدار 2.5 نسبة حجميه) في مخفف المستلين لاسترداد البلوتونيوم في المرحلة التالية باستخدام أجهزة الخلط والفصل ، وفي هذه الظروف وجد أن اليورانيوم المستخلص بواسطة 2.5 % ثالث أوكتيل أمين قليل جدا في هذه الظروف وبمستوى أجزاء من المليون