

Study on the Separation of MAs from HLLW and Their Extraction Behavior Using New Extractants of Amido Podand

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ABSTRACT:

The extraction of three kinds of amido podands, N,N,N',N'-tetrabutyl-3-oxapentanediamide (TBDGA), N,N,N',N'-tetra-isobutyl-3-oxapentanediamide (TiBDGA) and N,N,N',N'-tetra-butyl-3,6-dioxa-octanediamide (TBDODA) on U(VI), Pu(IV), Am(III), Eu(III) and other metal ions is studied in nitric acid solutions. 40% octanol-kerosene is chosen as diluent to eliminate third phase and emulsion. TBDGA and TiBDGA show extraction selectivity to An(III) and Ln(III) much higher than to U(VI) and Pu(IV). Fe, Ru and Mo is poorly extracted by the three kinds of amid podands in 2~3 mol/L HNO₃ solutions. Aiming to eliminate interface crud when using simulated HLLW solution in the system of 0.2 mol/L TBDGA/Octanol+kerosene, acetohydroxyamic acid was adapted. Distribution ratio of zirconium was decreased when adding acetohydroxyamic acid in aqueous solution, and interface crud disappeared as mixing extractant with HLLW. The counter-current extraction test is carried out in a set of miniature mixer-settler, with 0.2 mol/L TBDGA/ 40% octanol-kerosene as extractant to separate U(VI), Pu(IV), Am(III) and Eu(III) from simulated high level liquid waste (HLLW) solution. In battery A, lanthanides and actinides are coextracted into organic phase with the recovery of 99.98% for U(VI), >99.99% for Pu(IV), and >99.99% for Am(III) and Eu(III) respectively. In battery R1, 99.99% U, 86.2% Pu and a part of Am or Eu are stripped into aqueous phase by 0.2 mol/L acetohydroxyamic acid (AHA) in 0.01 mol/L HNO₃ solution. In battery R2, Am, Eu and remained Pu are completely back-extracted by 0.2 mol/L AHA. This separation process contains no salt reagent, and it is not necessary to dilute HLLW feed.

Key Words : Amido Podand, Extraction, HLLW, Separation,
Pu(IV),U(VI),Am(III),Eu(III)

1. INTRODUCTION

Actinides(MA) and some long-live fission products(LLFP) in spent fuel constitute long and potential threaten to mankind because of their high radioactivity and high toxicity. Minor actinides and almost all of fission products are still in high level liquid waste (HLLW), even though after recovering almost uranium and plutonium through reprocessing of spent fuel. So the treatment and disposal of HLLW is one of the key issues that has great influence on sustainable development of nuclear energy. Nuclear power will be developed greatly in near future, it will reach 36GWe/y by the year of 2020, and more than 10000 tones spent fuel will be discharged every year by the time. As state policy, China will realize enclosed recycle of nuclear fuel and does its best to decrease the toxicity of radioactive waste. Two significant R&D projects have already been launched in China aiming at declining radioactivity of radwaste and making full use of uranium resources. One of them is Accelerator Driven System(ADS) organized by China Academy of Sciences(CAS), the other is China Experimental Fast Reactor under construction in CIAE. According the long term programming of these projects, China will have some ability of transmutation MA and LLFP in several decades.

Partitioning of minor actinides and long lived fission product from high level liquid waste(HLLW) solution is of great importance for safely disposal of nuclear waste. Several flowsheets such as TRPO1), TRUEX2), DIDPA3) and DIAMEX4) have been suggested for this purpose.

These flowsheets, however show relatively low distribution ratio for An(III) in the extraction sequence of An(III),An(IV) and An(VI). TRPO and DIDPA extract poorly Am(III) in 2~3mol/L HNO₃. On the other hand, because of containing sulphur or phosphor the extractants used in TRPO, TRUEX and DIDPA flowsheets cannot be incinerated completely.

Recovery of An(III) must be considered seriously owe to its high radioactivity and toxicity. As for the selection of extractant, CHON principle should be complied to decrease secondary waste amount.

Cuillerdier et al.⁵) reported that some manlonamides, $[R_1R_2NC(O)]_2CHR_4$ have good extractive ability for An(III) and Ln(III), if R_4 is oxyalkyl. H. Stephan⁶) and Yang YuSheng⁷) also reported that another kind of diamide: $[R_1R_2NC(O)]_2R_3$, can extract a great many metal ions in +2, +3, +4 or +6 states in low acidity and in the co-existence of big anion such as picrate, if R_3 is $-(-CH_2OCH_2-)n-$. When R_3 is oxyalkyl, this kind of compound is also called amido podand⁶). In recent years, Y. Sasaki⁷) studied the extraction behaviour of lanthanides and actinides using N,N'-dimethyl-N,N'-dihe-xyl-3-oxapentanediamide with nitro- benzene as diluent in low acidity.

2. EXPERIMENTAL

Reagent

N,N,N',N'-tetrabutyl-3-oxa-pentanediamide (TBDGA), N,N,N',N'-tetraisobutyl-3-oxa-pentanediamide (TiBDGA) and N,N,N',N'-tetrabutyl-3,6-dioxaoctanediamide (TBDOODA) were synthesized in Sichuan University which was checked by I.R., M.S. and NMR, their

purity exceeded 98%.

AHA: acetohydroxyamic acid was synthesized in our laboratory and its purity was more than 98%. Other used chemicals were analytical grade reagents.

²³³U, ²³⁹Pu, ²⁴¹Am, ¹⁵²⁻¹⁵⁴Eu and ⁹⁰Sr were used as radioactive tracer. ²³³U and ²³⁹Pu were purified by anion exchange to remove their daughter or impurity. ²⁴¹Am, ¹⁵²⁻¹⁵⁴Eu and ⁹⁰Sr was supplied by Isotope Department of CIAE, and their purity is more than 99.9% respectively. ⁹⁹Tc solution was prepared by dissolving NH₄TcO₄ (Cambridge Laboratory of U.S.A.) in nitric acid without further purification. Other non-radioactive substances were of analytical grade.

Procedure

In extraction test, 2ml aqueous solution and then radioactive tracer were added into a test-tube. Same volume of organic phase which had been precontacted with corresponding blank aqueous solution 3 times, was added into the tube. Then it was agitated vigorously for 5min at 25±1°C. After centrifugation, aliquots of each phase were sampled for analysis.

Analysis

For measuring distribution ratio(D) of nuclides, 1.0mL of sample was taken into a measuring bottle. α and β emitters were measured by LS6000 liquid scintillometer (Beckmann Corp., ^{90}Sr was analysed 1 month later after sampling) and γ -radioactivity was measured by NaI(Tl) scintillation counter. Mo, Cs, Zr, Ru and Fe were determined with spectrophotometry. In counter-current extraction test with HLLW solution, samples of organic and aqueous phase from each stage were taken after reaching balance state. γ -spectrometer was used to measure ^{241}Am and $^{152-154}\text{Eu}$, α -spectrometer was used to measure ^{239}Pu and ^{233}U .

3.RESULT AND DISCUSSION

3.1 Extraction of U, Np, Pu, Am, Tc, Sr

The order of distribution ratio of actinides and lanthanides is: $\text{Ln(III)} \geq \text{An(III)} > \text{An(IV)} > \text{An(VI)} > \text{An(V)}$, the extraction order of three kinds of amido podand is: $\text{TBDGA} > \text{TiBDGA} > \text{TBDOODA}$. The extraction order is: $\text{TBDGA} \sim \text{TiBDGA} > \text{TBDOODA}$ for the extraction of TcO_4^- , and $\text{TiBDGA} > \text{TBDGA} > \text{TBDOODA}$ for the extraction of Sr.

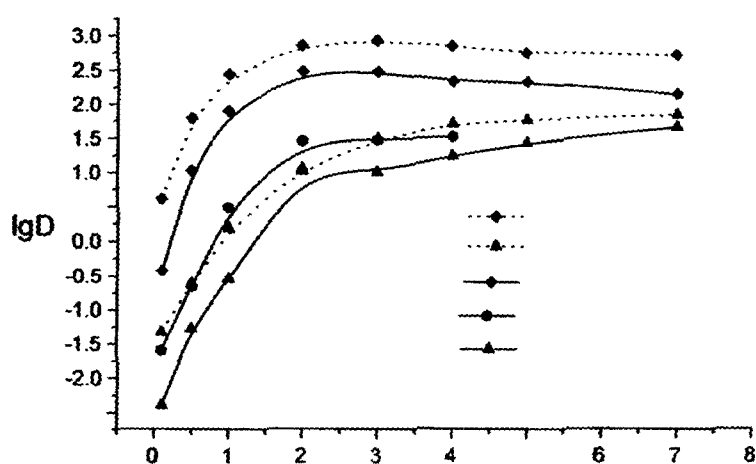


Fig.1 Extraction distribution ratio of Eu and Am

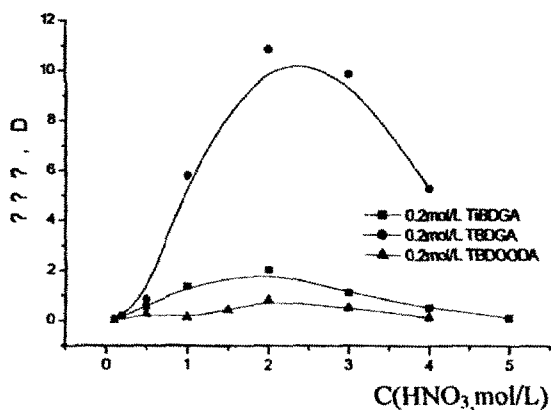


Fig. 2 Distribution ratio of Np(VI) and Pu(VI)

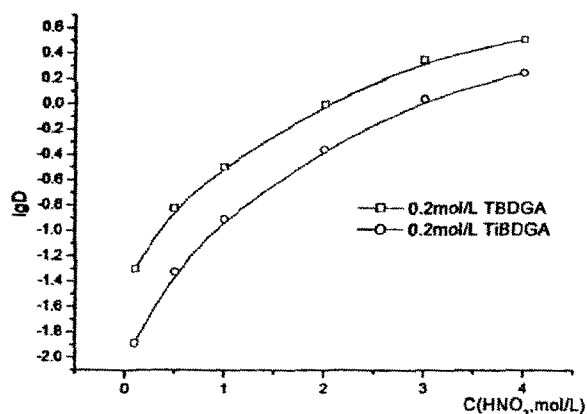


Fig. 3 Distribution ratio of Np(V)

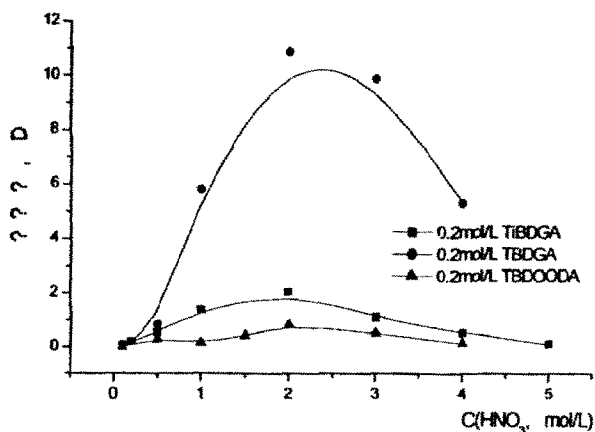


Fig. 4 Distribution ratio of Sr

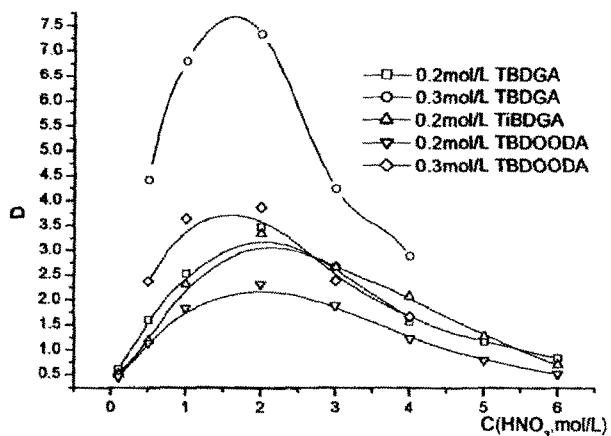
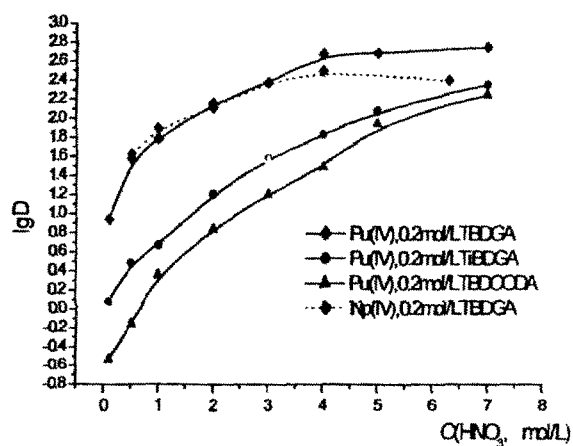


Fig. 6 Distribution ratio of Tc

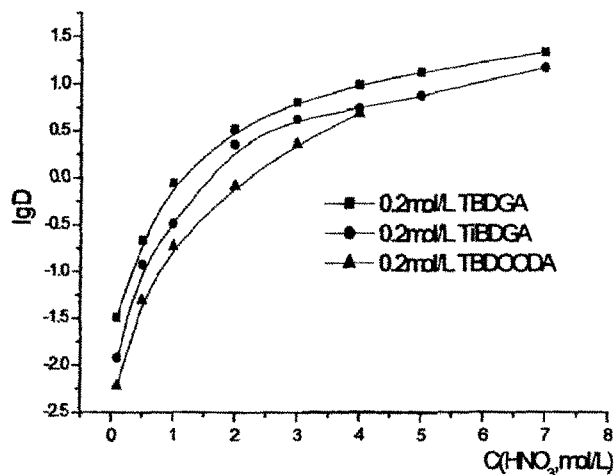


Fig. 7 Distribution ratio of U(VI)

TBDOODA can not be used to recovery actinides and lanthanides from HLLW, because of its lower distribution ratio for U(VI), neither can be TiBDGA/octanol+kerosene, due to the third phase forming easily when it mixed with simulated HLLW. Only TBDGA is suitable for the purpose, when 40% octanol+kerosene is used as diluent.

3.2 Study on extraction mechanism

Taking the extraction of Am and Eu for example, the results a lot of experiments show that the extraction of metal ions by amido podand belongs to neutral complex extraction, which can be written as: $M^{n+} + nNO_3^- + iS_{(O)} \Leftrightarrow M(NO_3)_n iS_{(O)}$

The numbers of extractant molecule in the extracted complexes (i) are given in the above table 1.

extractant	TBDGA	TiBDGA	TBDOODA
Am(III), Eu(III)	3	3	2.5
Np(V)	2	2	—
Np(IV) Pu(IV)	1	1	1
U(VI), Np(VI), Pu(VI)	1.5	1.5	1
Sr(II)	3	3	2.5
TcO ₄ ⁻	0.5mol/LHNO ₃	2	1
	2.0mol/L HNO ₃	1.5	1
	4.0mol/L HNO ₃	1	1
	HNO ₃	1	—

This conclusion was identified indirectly by measuring the electro-conductivity of organic phase loaded with metal ion (Table 2).

Table 2. Values of α , Λ and η of TBDGA loaded with Nd(III)

c(Nd ³⁺)/(mol/L)	$\Lambda/(s \cdot cm^2)$	$\Lambda_m/(s \cdot cm^2 \cdot mol^{-1})$	$\eta/(cp_a \cdot s)$	$\alpha/\%$
5×10^{-3}	8.5	1.7	2.7	7.6
8×10^{-3}	9.0	1.1	2.9	5.3
10^{-2}	13	1.3	3.2	6.9
2×10^{-2}	14.4	0.7	3.2	3.7
5×10^{-2}	25.7	0.5	3.6	1.8

note: c(TBDGA)=0.2mol/L.

3.3 EXAFS study of complex molecular Eu-TBOPDA

Taking the complex compound of Eu with TBDGA for example, its EXAFS (Extended X-ray Absorption Fine Structure) spectrum was investigated. The experimental result shows that around Eu atom there are 11 oxygen atoms which are

arranged into two layers according to their distance to Eu. There are 8–9 oxygen atoms in the first layer for TBDGA and TiBDGA, their average distance to Eu is 0.240nm, there are 3 oxygen atoms in the second layer, the average distance is 0.257nm.

3.4 Extraction of Other Metal Ions

Alkali metals such as Na⁺ and Cs⁺ are not extracted by amido podands. But Sr(II) is extracted by amido podands as shown in Fig.4. It is known from this figure that distribution curve of Sr(II) has a maximum value at about 2mol/L HNO₃. TiBDGA has the greatest distribution ratio among three extractants and TBDOODA is the least (its maximum is less than one). The extraction ability of amido podands on Sr(II) decreases as follows: TiBDGA > TBDGA > TBDOODA. This sequence is different from that observed in extracting actinides and lanthanides as previously stated. This phenomenon can not be explained at present. Distribution ratio of Sr(II) extracted by TBDGA is about one in 3.0mol/L HNO₃, so strontium can be partially coextracted into organic phase with actinides when using TBDGA as extraction system. Sr(II) can be extracted directly from ~2mol/L HNO₃ by TiBDGA is one of important success in separation field, and will be studied further next step.

As indicated in Table 3, Zr is well extracted by amido podands. There is a maximum distribution ratio for TcO₄⁻ about at 2.0mol/LHNO₃ medium, and its value is above 3. Technetium may also be extracted into the organic phase with actinides. Diluent or concentrated nitric acid can be used to backextract technetium. Fe Ru and Mo are poorly extracted by TBDGA or TiBDGA.

Table 3: Distribution ratio of other metal ions in HNO₃ medium, 20 °C
Note: a, 0.2mol/L TiBDGA; b, 0.02mol/L TBDGA; c, 0.2mol/L TBDGA.

C/HNO ₃ , mol/L	0.1	0.5	1.0	2.0	3.0	4.0	6.0
D/Fe(III) ^a	0.099	0.035	0.016	0.012	0.0081	—	
D/Zr(IV) ^b	0.621	1.53	29.1	81.2	152	213	
D/Ruc	—	—	0.26	0.27	0.20	0.19	
D/Tc(VII) ^c	0.609	1.601	2.536	3.485	2.671	1.579	0.535
D/Moc	0.151	0.192	0.264	0.783	1.24	—	

3.5 Observation of Emulsion Formation

As stated above, using octanol with kerosene as diluent, third phase can be eliminated basically. But when the three kinds of extractants are contacted with fresh simulated HLLW, a little third phase or emulsion are found. The tendency of forming third phase is TBDOODA > TiBOPDA > TBOPDA. A little emulsion is found for TBOPDA system. In order to eliminate emulsion completely without adding complexant, the simulated HLLW has been placed for 1 year. Under these circumstances, the concentration of Zr in feed becomes very low because of precipitation, and emulsion automatically completely disappears for TBOPDA system. So the HLLW used here was prepared 1 year before operation.

3.6 Elimination of interface crud

If TBDGA/octanol+OK is contacted with newly simulated HLLW, it is very easy to form surface crud. After keeping the simulated HLLW for one year, the phenomenon disappears.

The research of eliminating the crude formed in the extraction of simulated HLLW with amido podand (TBDGA) was conducted by adding hydroxamic acid to the simulated HLLW. The results of solvent extraction show that the distribution ratio of Zr (IV) decreased remarkably with rising concentration of AHA in the simulated HLLW, the distribution ratio of Pu (IV) is still high enough under experimental conditions, so the recovery of Pu should not be affected in the processing of HLLW by amido podand. The results of stripping experiments show that the Zr (IV) in organic phase can be stripped effectively to aqueous phase by one stage stripping, the Pu (IV) in organic phase can be stripped effectively to aqueous phase by 3 stage cross current stripping. The effect of adding AHA to the stripping solution on the accumulative stripping percentage of ²⁴¹Am (III) is neglectable. The stripping of ²⁴¹Am (III) can be restrained by raising the concentration of nitric acid in the stripping solution.

Table 4. Distribution ratio of Zr in SHLLW at different concentration of AHA (phase ratio 1 : 1, t=28°C)

AHA con.(mol/L)	0.10	0.20	0.30	0.40
D	0.962	0.619	0.243	0.172

3.7 Test of Counter-current Extraction

As stated previously, 0.2mol/L TBDGA/ 40%Octanol-kerosene is chosen counter-current extraction in a set of mixer-settler. The chemical flowsheet for recovering actinides and lanthanides from HLLW is shown in Fig.11. The set of miniature mixer-settler comprise three batteries: battery A (16 stages), battery R1(7 stages) and battery R2(7 stages). The volume of mix chamber of each battery is 3mL, and the settler chamber is 5mL. The mixing time of two phase is about one minute when the flow rate is 3mL/min in totally.

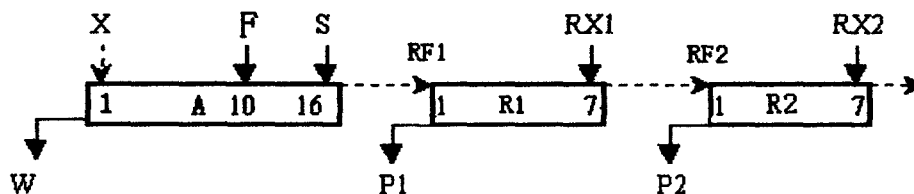


Fig.11 The flowsheet diagram of the separation experiment with a set of miniature mixsettler using 0.2mol/L TBDGA as extractant.

F---HLLW, + 0.15mol/L AHA

X---0.2mol/L TBDGA/40%octanol-kerosene,

S---2.0mol/LHNO₃,

RX1---0.01mol/L HNO₃+0.2mol/L AHA

RX2---0.2mol/L AHA

F:X:S=1:1.5:0.5

RF1:RX1=1:1

RF2:RX2=1:1

F=1.0mL/min

X=RF1=RF2=1.5mL/min

S=0.5mL/min

The composition of feed is given in table 5. In battery A, U(VI), Pu(IV), Am(III) and Eu(III) are coextracted into organic phase quantitatively. In battery R1 the salt-free complexant acetohydroxyamic acid(AHA) is added into stripping stream(RX1) to back-extract Pu(IV), then total U(VI) and most part of Pu(IV) are separated with Am(III) and Eu(III) from organic flow. The AHA can be decomposed completely by concentrated nitric acid, which make it easy to decompose it in next steps. Low acid is necessary in battery R1 to strip Pu(IV) and to decrease the acidity in organic effluent. In R2 Am(III) and Eu(III) are stripped into aqueous solution completely by pure 0.2mol/L AHA. The results are listed in table 6, and the concentration profile of these species in three batteries is shown in figure 12.

Table 5. Composition of simulated HLLW:g/l

M	amount	M	amount	M	amount
Rb	0.075	Sr	0.186	Y	0.099
Zr	0.43	Mo	0.731	Tc	0.181

Ru	0.464	Rh	0.127	Pd	0.267
Ag	0.019	Cd	0.016	Sn	0.015
Te	0.103	I	0.052	Sb	0.005
Cs	0.544	Ba	0.309	La	0.264
Ce	0.533	Pr	0.244	Nd	0.826
Pm	0.028	Sm	0.164	Eu	0.023
Gd	0.016	Na	3.00	Fe	0.501
Cr	0.101	Ni	0.102		

$\text{HNO}_3=3.0\text{mol/l}$

$\text{PO}_4^{3-}=0.05\text{mol/l}$

Note: Added Mo is the sum of Tc and Mo. Zr initially is 0.771 mol/L, after daysr its concentration becomes low.

Table 6: The recovery and stripping rate of the 4 nuclides in 3 batteries

	A contactor				R1 contactor				R1 contactor		
	U	Pu	Am	Eu	U	Pu	Am	Eu	Pu	Am	Eu
Recovery, %	99.98	>99.99	>99.99	>99.99							
Stipping, %					>99.99	86.2	7.69	0.19	13.40	91.79	98.14

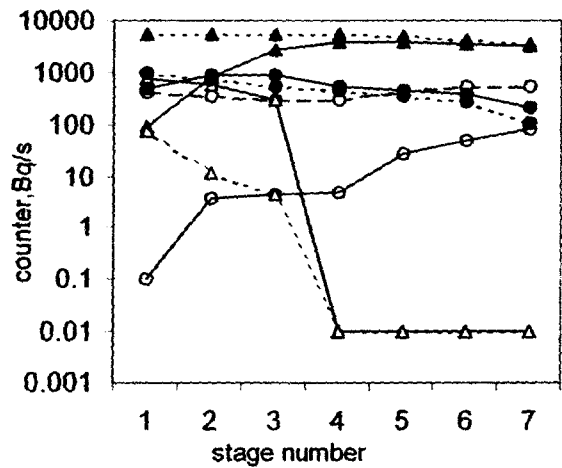
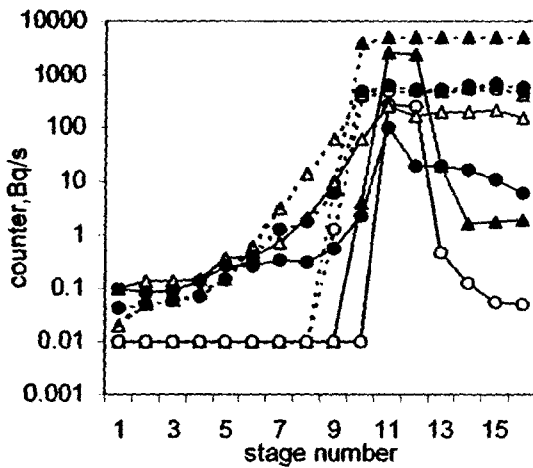
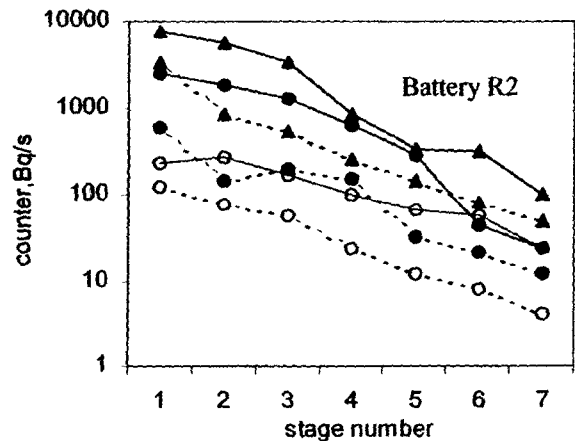


Fig.12. Concentration Profile of U(VI), Pu(IV), Am(III) and Eu(III) in battery A, R1 and R2 respectively.

— organic phase, - - aqueous phase.

▲ - Am, ○ - Eu, △ - U(VI), ● - Pu(IV)



4. SUMMARY:

In general speaking, the extraction ability of three amido podands is

TBDGA>TiBDGA>TBDOODA, the sequence of distribution ratio of actinides in different state is as follows: Am(III) >Pu(IV)>U(VI).

The extraction of Amido Podand of metal ions is belong to neutral complex system.

EXAFS experimental result shows that around Eu atom there are 11 oxygen atoms which are arranged into two layers. There are 8—9 oxygen atoms in the first layer for TBDGA, their average distance to Eu is 0.240nm, there are 3 oxygen atoms in the second layer, the average distance is 0.257nm.

Sr(II) can be well extracted by TiBOPDA in 2~3mol/L HNO₃ solution. But for TBDGA and TBDOODA, its distribution ratio is relatively low.

Fe, Ru and Mo shown low distribution ratio in TBDGA system, whereas Tc and Sr may be partially extracted into organic phase.

TBDOODA can not be used practically, because of its relatively low D value for U(VI) and being apt to forming third phase.

By using octanol and kerosene as diluent, third phase can be eliminated effectively. Slightly third phase is also formed when TiBDGA and TBDOODA/octanol- kerosene is mixed with HLLW. But for TBDGA system interface crud can be completely eliminated by placing SHLW for a year to form Zr precipitation or adding AHA in feed solution. It can be concluded that TBDGA is the most best for recovering actinides and lanthanides from HLLW among three kinds of extratants.

The investigated separation process for HLLW is totally salt-free. Extractant and complexant can be decomposed completely in following procedures.

Very high recovery is obtained for U(VI), Pu(VI), Am(III), and Eu(III) from HLLW solution, and then all of these species are grouped basically.

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