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Actinides and fission products extraction behavior in TBP/XAD7 chromatographic column

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A study for separation and sequential recovery of uranium and plutonium from nitric acid solutions by extraction chromatography using tributyl phosphate (TBP)/Amberlite XAD7 as stationary phase is presented. Distribution ratios of actinides, lanthanides and fission products were obtained. The column capacity was investigated and actinides retention conditions were established. Finally, U–Pu sequential separation was studied as well as the U and Pu recovery yields from nitric solutions containing Am/fission products were determined.

Introduction

The presence of small amount of mixed actinides and long lived heat generators fission products as ^{137}Cs and ^{90}Sr are the major problems for safety handling and disposal of high level nuclear wastes. To reduce the risk of environmental contamination and to simplify the final disposal of these residues, chemical research and process development for actinides recovery have been asked. In view of the complex chemical composition more and more selective and improved separation techniques are required.

At IPEN/CNEN-SP, R&D works on actinides partitioning in nuclear effluents have been done with simulated waste solutions.[1–3] Within separation techniques, extraction chromatographic separation[4–9] was elected, based on the known selective extraction of various organic solvents.

In this paper, the behavior and separation conditions of uranium, plutonium and americium from nitric solutions using TBP/XAD7 system are discussed.

Experimental

Reagents

Tributyl phosphate (TBP), 99% purity, Merck, was contacted with 0.5% sodium carbonate solution and distilled water to remove its degradation products.

Amberlite XAD7 resin, 35–65 mesh, supplied by Rohm and Haas Co., USA, washed with distilled water and methanol to remove preservative and residual monomers.

^{137}Cs, ^{106}Ru, ^{239}Pu and ^{241}Am tracer solutions in nitric medium were supplied by Radiochemical Centre, Amersham, England. ^{239}Pu solution was used without any valence state adjustment.

^{95}Zr, ^{85}Sr, ^{152}Eu, ^{141}Ce, ^{99}Mo and ^{131}I were supplied by Radiochemistry and Radioisotope Production Department of IPEN/CNEN-SP, BR.

Uranium nitrate solution was obtained by the dissolution of nuclear grade U_3O_8 prepared in Chemical Engineering Department of IPEN/CNEN-SP, BR.

Preparation of chromatographic material TBP/XAD7 resin

3 g of TBP diluted in methanol (1 : 1 v/v) is mixed with 3 g of XAD-7 resin slurried in methanol. The resulting slurry is gently stirred for 15 minutes. The methanol is then removed by evaporation at room temperature. The TBP sorbed resin is washed with distilled water and dried at room temperature. 46 wt.% TBP loaded resin is obtained.

Determination of distribution ratio

1 ml of nitric solution containing desired radioisotope was equilibrated with 0.40 g of 46 wt.% TBP/XAD7 by mechanical shaking for 15 minutes at room temperature (23–26 °C). The phases were separated and the distribution ratios were calculated from the following equation:

$$D = [C_0 - C)/C]\ (V/M)$$

where C_0 and C are the initial and final ion concentrations in the aqueous phase before and after equilibration, respectively, V is the aqueous phase volume (ml) and M is the weight of the dry TBP/XAD7 chromatographic material (g). The uranium concentration was determined by spectrophotometric method and ^{239}Pu and ^{241}Am were checked by measuring its characteristic alpha energies using surface barrier detector. All γ-emitter radioisotopes were controlled using NaI(Tl) scintillation detector.

Preparation of chromatographic column

Borosilicate glass chromatographic column with 4.6 mm inside diameter and 30 cm long was used. The column was filled with ca. 2 ml of 46 wt.% TBP/XAD7 (bed length = 18 cm) and then it was firstly rinsed with an excess of 0.1 mol/l HNO_3, followed by 1 mol/l HNO_3. Prior to introduction the sample, the column was pre-conditioned with 10 FCV of an appropriate nitric acid solution, depending on the acid concentration of the load

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solution. All column experiments were carried out at room temperature (23–26 °C). The flow rate was maintained at 0.2–0.3 ml · min^{-1} throughout.

Results and discussion

The effect of nitric acid on the actinides distribution ratio

The influence of HNO_3 concentration on the actinides retention in 46 wt.% TBP/XAD7 resin was verified by varying acid concentration in the range of 0.01 to 4 mol/l. Figure 1 shows that U(VI) and Pu(III, IV, VI) distribution

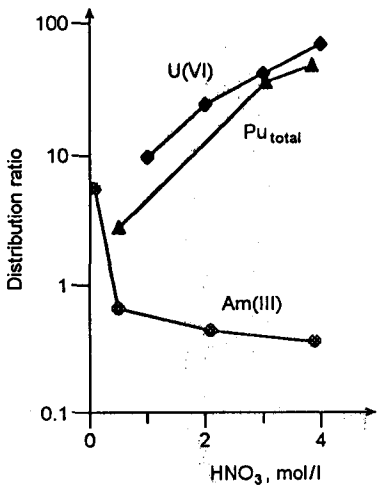

Fig. 1. Effect of HNO_3 concentration on U(VI), Pu(III, IV, VI) and Am(III) distribution ratios in TBP/XAD7 chromatographic material

ratios increase with increasing HNO_3 concentration, while the Am(III) shows lower extraction value at high nitric acid concentration. Solutions of 0.59 g/l U and tracer amounts of ^{239}Pu and ^{241}Am in nitric medium were used.

46 wt.% TBP/XAD7 column capacity

Breakthrough curves were obtained for the determination of 46 wt.% TBP/XAD7 column capacity, using uranyl nitrate solution, 0.59 g/l U with 2, 3 and 4 mol/l acid concentration, as shown in Fig. 2. The results are summarized in Table 1 where the breakthrough

Table 1. Uranium breakthrough capacity in HNO_3 medium

Column	HNO_3, mol/l	Flow rate, ml · min^{-1}	mg U/g 46 wt.% TBP/XAD7	
			1% BT	10% BT
1	2	0.2	5.0	8.1
2	2	0.3	5.1	8.2
3	3	0.2	12.1	15.6
4	4	0.3	14.7	21.2

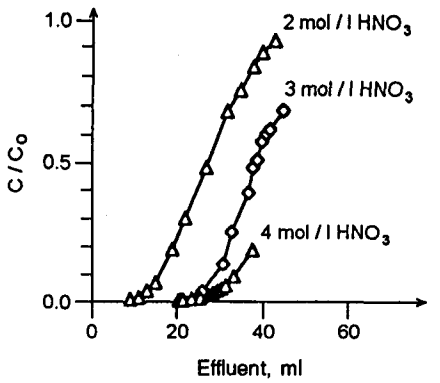

Fig. 2. Effect of HNO_3 concentration on uranium breakthrough capacity for the 46 wt.% TBP/XAD7 resin. Column bed: 0.98 g of 46 wt.% TBP/XAD7

capacity is done in milligram of uranium extracted per gram of 46 wt.% TBP/XAD7. The breakthrough capacity increases with increasing the HNO_3 concentration, nevertheless, the uranium extraction from diluted uranyl nitrate solution is not affected by lower flow rate variation (0.2 or 0.3 ml · min^{-1}).

Retention and elution behavior of uranium

In this experiment, 38 ml of $UO_2(NO_3)_2$ solution, 0.59 g/l U and 4 mol/l HNO_3, was passed through the 46 wt.% TBP/XAD7 resin. Uranium loaded column was washed with 9 ml of 4 mol/l HNO_3 and then, eluted with 13.5 ml of 0.01 mol/l HNO_3. 99% retention, 1% lost in column washing step and 100% recovery of sorbed uranium were obtained (Fig. 3). Using the same column, stability tests were carried out, by repeating full cycle (sorption, washing and elution operations) ten times. For each cycle, 4 ml of uranyl nitrate solution, 0.06 g/l U in 4 mol/l HNO_3, was passed through the column, washed

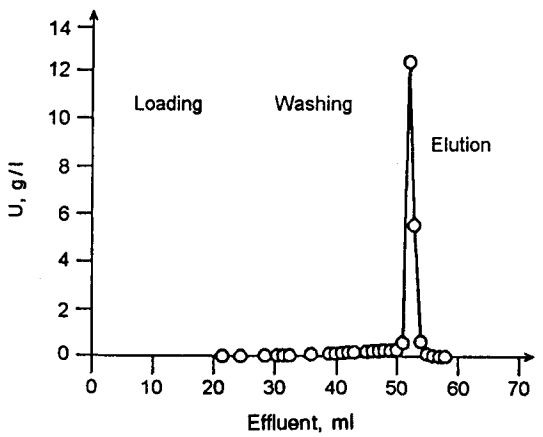

Fig. 3. Retention and elution behavior of U(VI). Column bed: 0.94 g of 46 wt.% TBP/XAD7; load solution 0.59 g/l U in 4 mol/l HNO_3; washing: 4 mol/l HNO_3, eluent: 0.01 mol/l HNO_3

Table 2. Stability studies of 46 wt.% TBP/XAD7 column

Cycles	U(VI) retention, %	U(VI) recovery, %
1	100	100
5	99	100
10	99	100

with 2 ml of 4 mol/l HNO_3 and sorbed uranium was eluted with 8 ml of 0.01 mol/l HNO_3 and finally the column was conditioned with 3 ml of 4 mol/l HNO_3. The results are shown in Table 2. Uranium retention and elution efficiency were the same after 10 cycles, presenting a good stability in nitric acid medium.

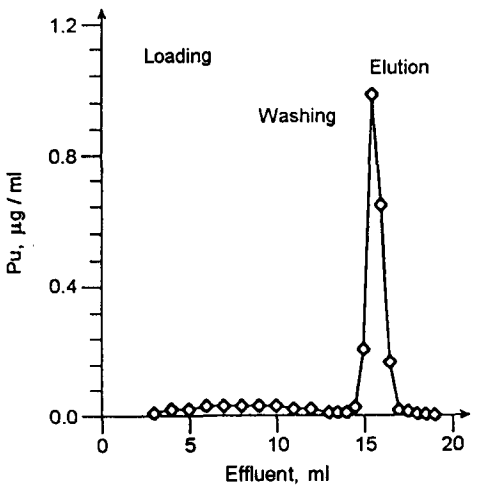

Fig. 4. Plutonium behavior in TBP/XAD7 column. Column bed: 0.90 g of 46 wt.% TBP/XAD7, load solution: tracer amounts of ^{239}Pu and ^{241}Am in 3 mol/l HNO_3, washing: 3 mol/l HNO_3, eluent: 0.01 mol/l hydroxylamine nitrate in 0.6 mol/l HNO_3

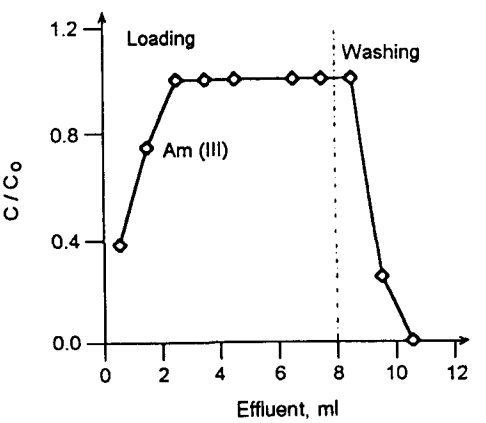

Fig. 5. Americium behavior in TBP/XAD7 column. Load solution: tracer amounts of ^{239}Pu and ^{241}Am in 3 mol/l HNO_3, washing: 3 mol/l HNO_3, column bed: 0.90 g of 46 wt.% TBP/XAD7

Retention and elution behavior of plutonium and americium

The efficiency of the 46 wt.% TBP/XAD7 resin to plutonium retention was determined using tracer amounts of ^{239}Pu and ^{241}Am in 3 mol/l HNO_3 as load solution. 8 ml of this solution was passed through the TBP/XAD7 resin. 88% Pu retention was achieved and 99% of sorbed plutonium was recovered using 0.01 mol/l hydroxylamine nitrate in 0.6 mol/l HNO_3 as eluent (Fig. 4). Am(III) showed lower retention and it was easily removed during the washing phase with 3 mol/l HNO_3 solution (Fig. 5).

Uranium–plutonium separation

Uranium as well as the plutonium are extracted by TBP/XAD7 resin and are separated by selective elution. Plutonium is firstly eluted based on redox reaction using

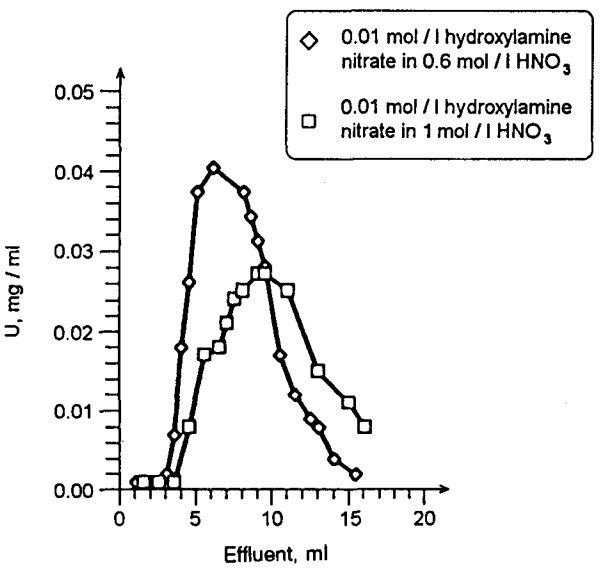

Fig. 6. Elution of U(VI) from of 46 wt.% TBP/XAD7 column

hydroxylamine nitrate as reductant agent and then uranium is recovered using diluted HNO_3. For U–Pu separation studies, uranium behavior during plutonium elution was verified. These experiments were carried out using a 0.01 mol/l hydroxylamine nitrate solution in 0.6 and 1 mol/l HNO_3 medium as eluent. The elution curves of Fig. 6 show that higher HNO_3 concentration lower is the uranium remotion from the column. This result suggests that U–Pu separation may be done with 0.01 mol/l hydroxylamine nitrate in 1 mol/l HNO_3.

Effect of HNO_3 on fission products distribution ratios

The influence of HNO_3 concentration on ^{95}Zr, ^{85}Sr, ^{106}Ru, ^{152}Eu, ^{141}Ce, ^{137}Cs, ^{99}Mo and ^{131}I fission products distribution ratios in 46 wt.% TBP/XAD7 resin were determined as shown in Fig. 7. ^{131}I shows higher

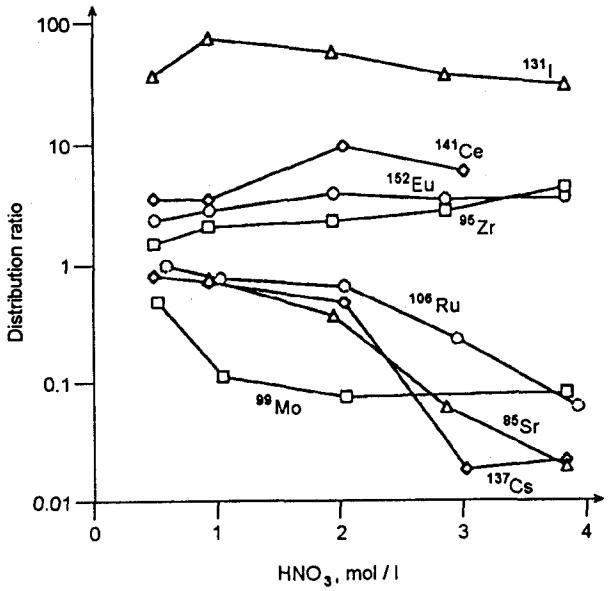

Fig. 7. Distribution ratios of ^{95}Zr, ^{85}Sr, ^{106}Ru, ^{152}Eu, ^{141}Ce, ^{137}Cs, ^{99}Mo and ^{131}I in 46 wt.% TBP/XAD7 resin; $2.4 \cdot 10^{-4}$ mol/l Zr, $2.1 \cdot 10^{-3}$ mol/l Sr, $2.2 \cdot 10^{-5}$ mol/l Ru, $1.2 \cdot 10^{-3}$ mol/l Ce(III) traced with respective γ-emitter radioisotope and tracer amounts of Eu, Mo, Cs and I nitrate solutions

distribution ratio followed by ^{141}Ce, ^{152}Eu and ^{95}Zr. At higher 3 mol/l HNO_3, the distribution ratios of ^{106}Ru, ^{99}Mo, ^{137}Cs and ^{85}Sr are low enough.

Fission products behavior in TBP/XAD7 column

The first experiment was carried out using $5.0 \cdot 10^{-4}$ mol/l Ce(III) traced with ^{141}Ce and tracer amounts of ^{152}Eu and ^{131}I in 4 mol/l HNO_3 as load solutions. Ca 0.90 g of TBP/XAD7 resin was used in each experiment. The curves of Fig. 8 show that only ^{131}I is retained on the column and is partially desorbed during washing step with 4 mol/l HNO_3 and during Pu and U elution phase with

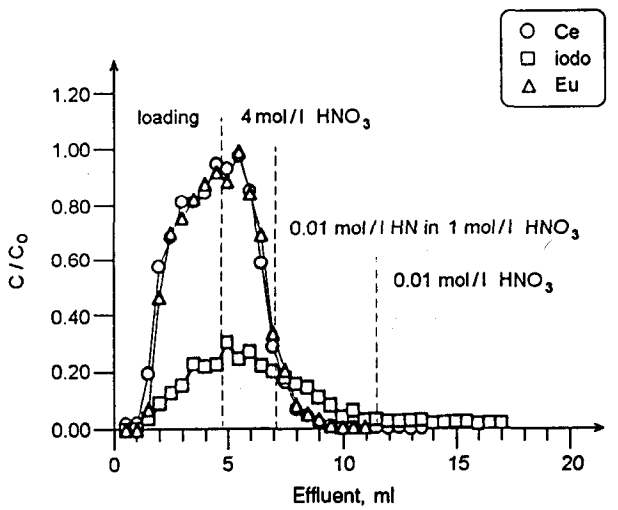

Fig. 8. I, Ce and Eu behavior in 46 wt.% TBP/XAD7 column (HN – hydroxylamine nitrate)

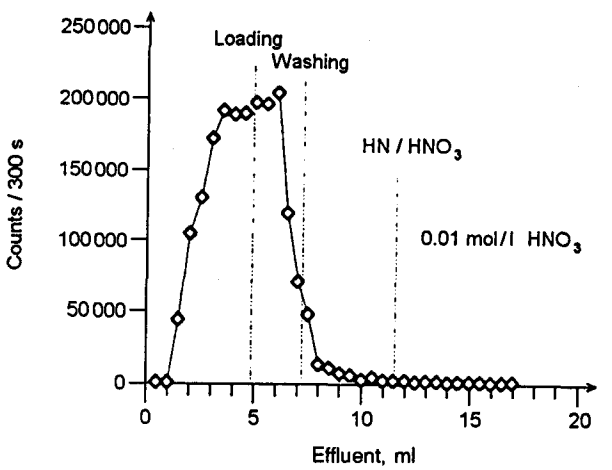

Fig. 9. Fission products behavior in 46 wt.% TBP/XAD7 column (HN – hydroxylamine nitrate)

0.01 mol/l hydroxylamine nitrate in 1 mol/l HNO_3 and 0.01 mol/l HNO_3, respectively.

The second experiment was performed using 4 mol/l nitric acid solution containing $5.2 \cdot 10^{-5}$ mol/l Zr, $2.3 \cdot 10^{-3}$ mol/l Sr, $5.0 \cdot 10^{-4}$ mol/l Ce(III) traced with respective γ-emitter radioisotope and ^{106}Ru, ^{152}Eu, ^{137}Cs, ^{99}Mo, ^{131}I tracers as load solution. The loaded column was washed with 4 mol/l HNO_3, 0.01 mol/l hydroxylamine nitrate in 1 mol/l HNO_3 and 0.01 mol/l HNO_3 (Fig. 9). The results showed that 84% of total γ-activity is desorbed during HNO_3 washing step, 5% during hydroxylamine nitrate in 1 mol/l HNO_3 elution and 1% during the 0.01 mol/l HNO_3 elution represented only by ^{131}I.

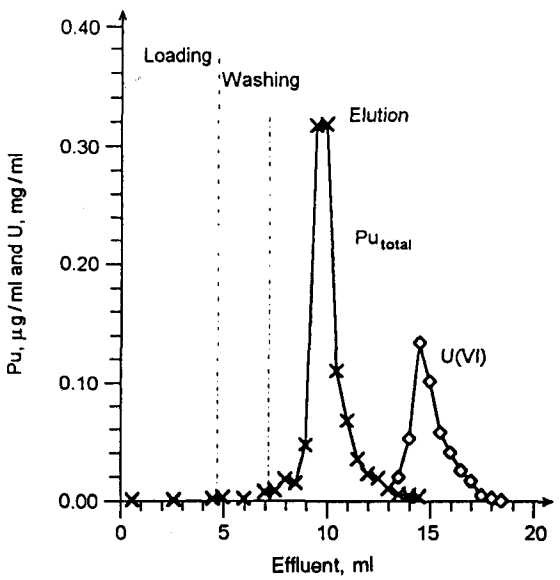

Fig. 10. Sequential separation of Pu(IV, VI) and U(VI) from 4 mol/l nitric acid containing Am(III) and fission products using a 46 wt.% TBP/XAD7 column

U and Pu separation from Am and fission products

This separation study was performed using 4 mol/l HNO_3 solution containing mixed uranium (0.06 g U/l), ^{239}Pu and ^{241}Am tracers and fission products (^{95}Zr, ^{85}Sr, ^{137}Cs, ^{106}Ru, ^{152}Eu, ^{141}Ce, ^{99}Mo and ^{131}I) as load solution. 4.5 ml this solution was passed through the column containing 0.90 g of 46 wt.% TBP/XAD7 resin. Lightly retained Am(III) was removed by washing the column with 2.5 ml of 4 mol/l HNO_3. U and Pu were separated from the loaded resin by selective elution. Pu was firstly eluted with 4.5 ml of 0.01 mol/l hydroxylamine nitrate in 1 mol/l HNO_3 and then the remained uranium was recovered with 7 ml of 0.01 mol/l HNO_3. An efficiency of 93% recovery for Pu with 2% U contamination and 98% U recovery with 7% Pu contamination were achieved. Figure 10 shows sequential separation curves of Pu and U.

Conclusions

TBP/XAD7 chromatographic material is efficient to U and Pu separation from Am and fission products and shows good stability in nitric acid medium. It is also efficient to U and Pu separation from solutions of lower concentrations.

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