J.RADIOANAL.NUCL.CHEM.,LETTERS 165 (4) 209-217 (1992)

PLUTONIUM REMOVAL BY ION EXCHANGE CHROMATOGRAPHY

B.F. Araujo, H.T. Matsuda, E.I. Carvalho, I.C. Araujo

Comissão Nacional de Energia Nuclear - SP,
Instituto de Pesquisas Energèticas e Nucleares,
Caixa Postal 11049 - Pinheiros,
05499 - São Paulo, Brazil

Received 30 March 1992
Accepted 10 April 1992

A study of Pu recovery at trace level from U solutions by ion exchange technique is presented. Plutonium retention >99.5% onto strong anionic resin, AG-X8, from nitric acid solutions and a 92% recovery using 0.4M HNO_3 at 60 °C as eluent, were obtained. Uranium interference in Pu sorption from mixed U/Pu nitrate solutions with low U/Pu ratio (~25) was not verified. However, for high U/Pu ratio solutions (~10000), uranium interference in Pu retention on the resin, decreases to 59%. Selecting the loading conditions and using AG-X4 resin, 99% Pu retention was achieved. The Pu product is still contaminated with U and another purification cycle is recomended. A scheme for U/Pu first cycle separation is proposed.

INTRODUCTION

In spent nuclear fuel chemical treatment, the main process is the Purex Process. Several investigators have outlined some modifications to increase the ef-

Elsevier Sequoia S. A., Lausanne
Akadémiai Kiadó, Budapest

ficiency of the process[1-4]. Meanwhile, promising applications of ion exchange techniques have also been reported[5-8], mainly on the Pu purification step or Pu recovery from nitric acid streams generated from Purex Process operations. The strong anionic resin was found to be more efficient due to the great affinity of tetravalent plutonium nitrate complexes for the anion exchanger.

Recent works[9,10] show the use of anionic resin and extraction chromatography columns to remove final traces of Pu from high activity waste, aiming at safety of waste disposal.

The goal of this study is Pu removal at trace level from uranyl nitrate solutions coming from Purex Process where U/Pu ratio is near 10000.

EXPERIMENTAL

Materials

- AG-1X8, AG-1X4, 50 to 100 mesh, gel type anion exchange resin, chloride form from BIO-RAD Laboratories.
- Feed solutions for Pu loading tests were prepared by mixing appropriate aliquots of stock plutonium nitrate solutions (19.38 g l^{-1}) in 7M nitric acid giving 20 mg l^{-1}, 80 mg l^{-1} and 150 mg l^{-1} concentrations. A redox valency was performed to ensure that all Pu is in the tetravalent state, before ion exchange separation is done.
- Feed solutions for U/Pu separation experiments were prepared by mixing appropriate aliquots of stock plutonium nitrate solutions and stock uranyl nitrate so-

lution (300 g l^{-1}) in 7M nitric acid, giving mixed solutions containing near 200 g U l^{-1} - 20 mg Pu l^{-1} and 2 g U l^{-1} - 80 mg Pu/l^{-1} to have U/Pu ratios of 10000 and 25 respectively.

- Chromatographic columns were made from 7 mm or 4 mm inside diameter borosilicate glass, 30 cm long and filled with selected anionic resin.

Procedure

Based on the results of past investigators, some recommended conditions such as 7M acidity of the feed solution onto a strong anionic resin with 8 or 4% cross-linking and about 0.45M dilute mineral acid as eluent had been considered.

The resin in chloride form as received, was conditioned in 7M nitric acid, by washing twice with distilled water, twice with 0.1M HNO_3, twice with 1M HNO_3, twice with 4M HNO_3 and finally with 7M HNO_3 until chloride reaction is absent in the effluent.

The column was filled with a known volume of resin, washed with 7M nitric acid and then plutonium nitrate or mixed uranyl and plutonium nitrate solutions in 7M nitric acid were passed through the column. The column was washed with 7M HNO_3 to remove the weakly sorbed U from the plutonium-loaded resin. Finally, the Pu was eluted with 0.4M HNO_3. The flow-through of the column was adjusted in each phase of the column operation.

Analysis

Plutonium was checked radiochemically by measuring the 5.15 MeV α-energy using a surface-barrier detector[11]. Uranium was determined by X-ray fluorescence[12]

in the range of 2 to 300 g l^{-1} and spectrophotometry using DBM as chromogenic agent for low uranium concentration solutions[13].

RESULTS AND DISCUSSION

Plutonium separation

The efficiency of the anion exchange resin for Pu separation was determined first in the absence of U. This was accomplished using a 7 mm inside diameter chromatographic column filled with 3 ml AG-1X8 resin conditioned in 7M nitric acid. 100 ml of 7M HNO_3 plutonium nitrate solution, 244 mg l^{-1}, was passed through the column. Then the column was washed with 15 ml 7M HNO_3 and the loaded Pu was displaced with excess 0.4M HNO_3. Flow-through of the column was 1 ml min^{-1} in the loading and washing operations and 0.6 ml min^{-1} in the elution phase. From Fig. 1 it is easy to see the breakthrough point at 30 ml corresponding to 3.25 mg Pu/ml resin. The elution curve (Fig. 2) shows that 0.4M HNO_3 does not remove total loaded Pu. Only 75% of adsorbed Pu was reached using 30 ml of eluent at 30 ^{o}C. On the other hand, a minimum concentration of Pu was found in the wash solution.

On the basis of these results, other experiments with decreasing Pu concentration in the feed solution were carried out. These were made by passing 50 ml of 7M HNO_3 plutonium nitrate solution 150 mg l^{-1}, 100 ml of 80 mg l^{-1} and 100 ml of 20 mg l^{-1}. An efficiency of >99.5% for Pu removal was obtained.

Uranium(VI) behavior was also verified in the same experimental conditions. Tests were done with 7M HNO_3 uranyl nitrate solutions, 2.2 g l^{-1}. Uranium(VI) is

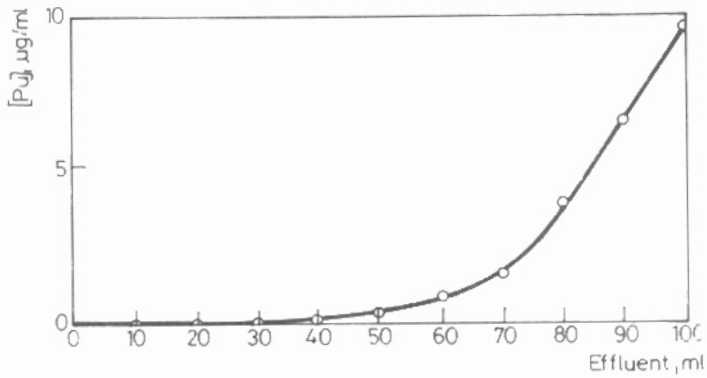

Fig. 1. Plutonium break-through curve. Feed solution: V = 100 ml, [Pu] = 244 µg l^{-1}, [H] = 7M. Resin: AG-1x8, NO_3^-

weakly adsorbed on the column (≈5%) and removed by washing with 7M nitric acid.

Uranium-plutonium separation

Uranium-plutonium separation studies were firstly carried out using a 7M nitric acid mixed plutonium and uranyl nitrate solutions containing 79.8 mg Pu l^{-1} and 2.2 g U l^{-1} giving U/Pu = 25 w/w as feed solution. 100 ml of this solution was passed through the column according to the experimental conditions of former experiments.

Uranium interference in Pu sorption was not observed. An efficiency of 99.5% Pu removal was obtained. To avoid further U contamination in the Pu eluate, an excess of washing solution was used to remove as much as possible of the adsorbed U. Nevertheless, U was detected in the recovered Pu solution, showing that an additional purification must be realized.

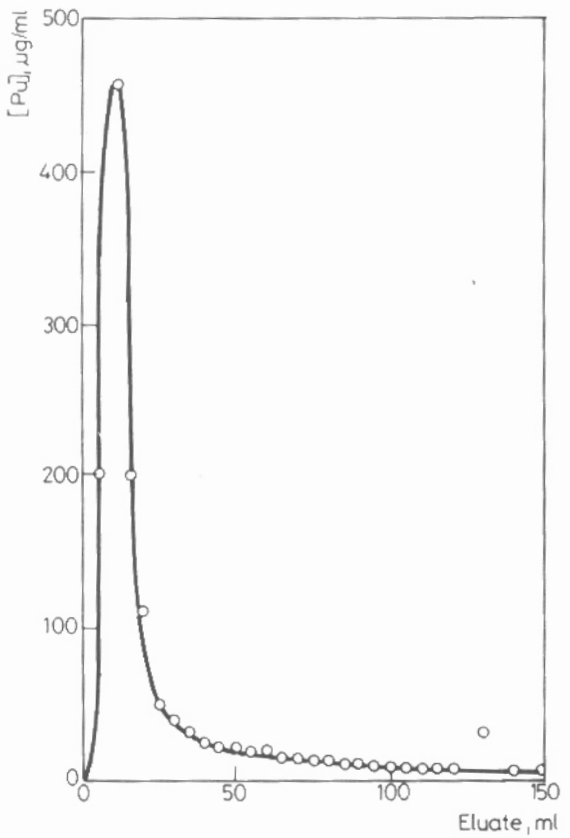

Fig. 2. Plutonium elution curve. Eluent: 0.4M HNO_3

A second set of experiments was done with a mixed plutonium and uranyl nitrate solution 7M nitric acid, containing 20 to 25 mg Pu l^{-1} and 190 to 220 g U l^{-1}, in such a way as to maintain a U/Pu ratio of 10000. The preliminary tests showed U interference in Pu adsorption, decreasing the efficiency to 59%.

The effect of percent cross-linking, flow rate, temperature and HNO_3 concentration in loading operation and inside diameter of the chromatographic column on the efficiency of Pu separation was investigated to

TABLE 1

Plutonium sorption from mixed plutonium-uranium nitrate solutions, U/Pu ≈ 10000 w/w

Experimental conditions					Plutonium retention
Column Øi, mm	Anionic resin	HNO_3, M	Flow rate, ml min^{-1}	Temperature, °C	%
7	AG-1X8	7	1.0	30	59.2
7	AG-1X8	7	0.5	30	78.5
7	AG-1X8	7	0.2	30	93.1
7	AG-1X4	7	0.2	30	98.2
4	AG-1X4	7	0.2	30	99.5
4	AG-1X4	7	0.3	30	99.6
4	AG-1X4	7	0.5	30	99.3
4	AG-1X4	8	0.3	30	99.4
4	AG-1X4	9	0.3	30	99.5
4	AG-1X4	10	0.3	30	99.4
4	AG-1X4	7	0.3	60	99.6

determine the optimum values for these parameters. Experimental conditions are shown in Table 1.

Best results were obtained using a 4 mm diameter column filled with AG-1X4 anionic resin and a 0.2 to 0.3 ml min^{-1} flow-through for loading operation. In these conditions, the efficiency of Pu separation was 99%. No significant differences were observed on varying the temperature and HNO_3 concentration of the feed solution. However, the effect of the temperature has been noted on the elution rate of Pu, reaching 92% efficiency at 60 °C.

It is known that addition of complexing agent as HF increases the elution rate of Pu. But in this study only dilute HNO_3 was selected because the recovered Pu must be subjected to purification cycle.

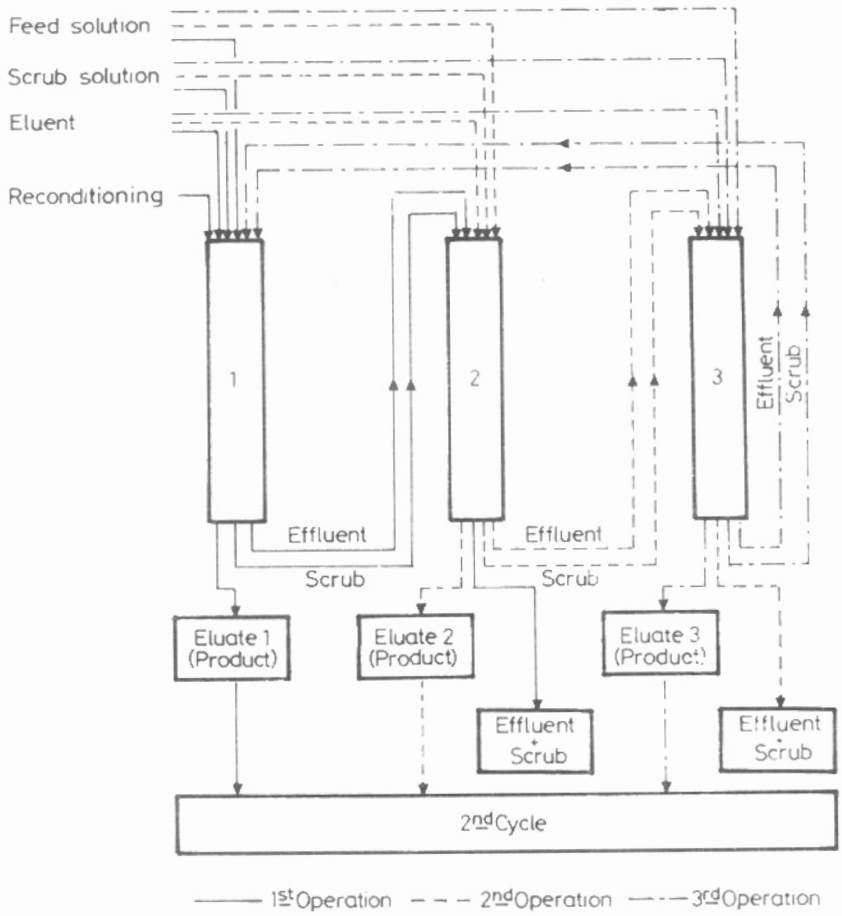

Fig. 3. Uranium-plutonium separation diagram

CONCLUSION

This study indicated that Pu can be separated from uranyl nitrate solution with an initial U/Pu ratio of nearly 10000, using strong anionic resin AG-1X4 type. One cycle is not enough to have uranium-free plutonium nitrate product. Based on the results, a scheme using three chromatographic columns for first cycle separation is proposed (Fig. 3).

REFERENCES

1. E.R. Irish, W.H. Reas, In: Reprocessing of irradiated fuels: Symposium held in Brussels, Belgium, May 20-25 (1954). Oak Ridge, Tenn., USAEC, s.d. V. 1, p. 83-106. (TID-7534).

2. J.D. Navratil, R.G. Leebl, RFP-2675 (1978).

3. H. Schimieder, H. Henrich, K. Ebert, Proc. European Nuclear Conference 86, Geneva, June 1-6, Vol. 4 (1986) 101.

4. H.J. Bleyl, D. Ertel, H. Goldacker, G. Petrich, J. Römer, H. Schimieder, Kerntechnik, 55 (1990) 21.

5. G. Valentini, N. Mostin, G. Stroo, L. Galer, L. Taglioni, EUR 2840f (1968).

6. E.J. Wheelwright, HW-75309 (1962).

7. R.E. Brooksbank, W.T. McDufee, ORNL-3566 (1964).

8. V.P. Caracciolo, DP-624 (1961).

9. A.C. Muscatello, J.D. Navratil, RFP-3936 (1986).

10. A.C. Muscatello, J.D. Navratil, J. Radioanal. Nucl. Chem., Lett., 128 (1988) 463.

11. M. Yamaura, M.A. Gonçalves, H.T. Matsuda, B.F. Araujo, Publ. IPEN, 318 (1990).

12. V.H. Cohen, H.T. Matsuda, B.F. Araujo, J.A. Araujo, In: Proc. X. Annual Symposium ACIESP, São Paulo, Brazil, November 6-8, Vol. 1 (1986) 209.

13. I.C. Araujo, H.T. Matsuda, B.F. Araujo, J.A. Araujo, In: Proc. XXVI. Congresso Brasileiro de Química held in Fortaleza, Brazil, October 7-11 (1985).