

Recovery of Plutonium Traces from Nitric Acid-Fluorhydric Acid Solutions by Sorption onto Alumina

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Sorption of plutonium traces onto alumina from uranyl nitrate solutions has been investigated. Several methods have been previously proposed for the recovery of plutonium traces from reprocessing solutions. Those methods include ion exchange (1,2), solvent extraction (3,4) and, extraction chromatography (5,6).

Several hydrous oxides, such as those of aluminum, silicon and, iron have been used to extract traces ions. Nevertheless, the sorption mechanism is not definitively established. Those oxides probably exhibit some ion exchange capacity among their properties and they can act as anionic or cationic exchangers and sometimes both. The separation of plutonium traces in the presence of HF by sorption onto an alumina column is based on its chemical similarities with thorium and lanthanide elements reported by Abrão (7). In this case only thorium and rare earths are sorbed onto alumina from nitric acid-fluoride solutions while uranium remains in the effluent.

The redox methods are well known for the purification and concentration of plutonium from the Purex process solutions. This paper deals with three different oxidation states of plutonium Pu(III), Pu(IV), and Pu(VI) in HNO_3 -HF systems. The chromatographic column method using alumina has been applied successfully to the separation of plutonium when uranyl nitrate solution containing 0.1-0.3M HF was percolated through the column.

EXPERIMENTAL

All ^{239}Pu solutions used during the runs were prepared from a standard solution (Amersham/Searle), of 1 $\mu\text{Ci/ml}$ (160 $\mu\text{g/ml}$) specific activity. The uranium solutions were obtained by dissolution of nuclear grade uranium oxides. One ml of Al_2O_3 chromatographic grade was conditioned according BROCKMANN (8) with 0.8M HNO_3 in glass columns 0.6cm in diameter and 20cm long. The experiments were followed by alpha spectrometry after the plutonium was extracted with 0.5M TTA/XLLOL. The samples for quantitative determination were prepared by eletroplating according to WENZEL and HERZ (9). The alpha energy measurement was made by a

surface barrier detector associated with a ORTEC multichannel analyzer. The plutonium oxidation states were determined by a photometric method using ARSENAZO III. The determinations were carried out with a double beam PERKIN-ELMER spectrophotometer using quartz microcells.

The first experiments were carried out to understand the performance of plutonium in an $\text{Al}_2\text{O}_3 - \text{HNO}_3$ medium. This was done by percolation of 25 ml of ^{239}Pu solution in 0.8M HNO_3 with alpha activity of $55,000 \pm 235$ (counts/2000 sec/ml), through a glass chromatographic column (i.d. 6mm) containing 1 ml of Al_2O_3 .

All runs were made with 0.8M HNO_3 solutions with a Pu alpha activity of $10,000 \pm 316$ (counts/2000 sec/ml) and, HF concentration ranging from 0.1 to 0.3M.

The feed solution for the Al_2O_3 column has the following composition: $1.5 \times 10^{-8}\text{M}$ ^{239}Pu ; alpha activity = $230,000 \pm 480$ (counts/2000/sec/20ml); 0.8M HNO_3 ; 0.1 - 0.3M HF; uranyl nitrate 47.6 g U/l; 0.005M FeSO_4 and 0.04M NaNO_2 . Pu(IV) was obtained in this solution by previous reduction of total plutonium to Pu(III) with Fe(II) followed by oxidation with nitrite. No interference of uranium was observed in the process. To avoid the interference of ^{234}Th (a uranium daughter) on the measurements of plutonium, it was previously removed by percolating the solution into another alumina column before the addition of ^{239}Pu .

RESULTS AND DISCUSSION

The results (Table I) show that only 1% of the plutonium is retained by the alumina from 0.8M nitric acid and therefore plutonium must likely be complexed to be sorbed. Figure 1 shows a typical plutonium breakthrough curve from 0.8M nitric acid.

Table I. Plutonium Retention from 0.08M HNO_3 onto Al_2O_3

Exp.	^{239}Pu retained (%)
1	1.8
2	1.0
3	0.8
4	0.9
5	1.1

Table II shows that the plutonium sorption onto Al_2O_3 is around 87% and it was demonstrated that with the aid of fluoride ions the recovery of plutonium traces from waste solutions was possible.

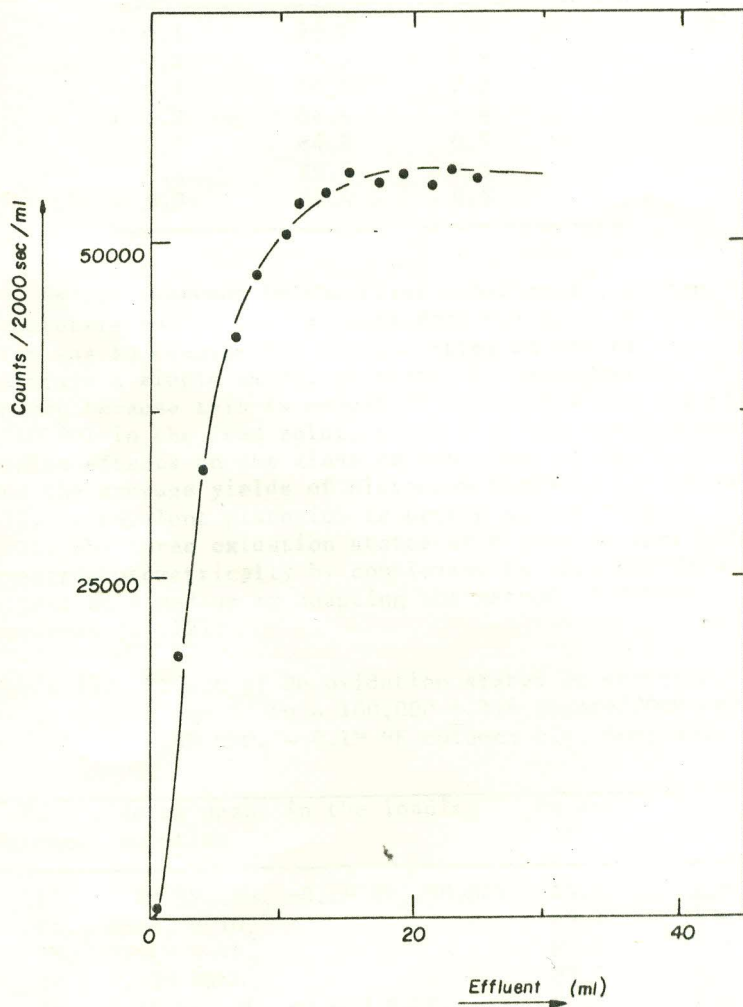


Figure 1. Breakthrough curve of Pu onto Al_2O_3 column; feed: 25 ml ^{239}Pu -0.8M HNO_3 ; ^{239}Pu activity = $55,000 \pm 235$ counts/2000 sec/ml; column = 1 ml Al_2O_3 ; flow rate = 0.8 ml/min/cm 2 .

Table II. Effect of HF on Pu Retention on Al_2O_3

HF (M)	^{239}Pu ret. (%)	D.F. (^{239}Pu)
0.1	85.7	7.0
0.1	85.5	6.9
0.1	86.1	7.2
0.2	84.4	6.4
0.2	84.8	6.5
0.3	89.6	9.5
0.3	89.4	9.5

As was observed in the first experiments, plutonium was not completely sorbed onto alumina from 0.1 to 0.3M HF. So the next step was to examine the possibilities of adding redox agents to maintain a single oxidation state. A concentration of 0.1M HF was chosen because this is enough HF to complex all the plutonium ($\text{Pu} \sim 10^{-8}\text{M}$) in the feed solution and will not cause significant corrosion effects on the glass column. Some of the redox agents used and the average yields of plutonium recovery are given in Table III. Tetravalent plutonium is better sorbed than Pu (III) or Pu (VI). The three oxidation states of plutonium were determined spectrophotometrically by complexing Pu with ARSENAZO III (10) in nitric acid medium by adapting the method of NEMODRUCK and collaborators (11,12).

Table III. Effect of Pu oxidation states on sorption. Feed solution: $^{239}\text{Pu} \sim 100,000 + 316$ counts/2000 sec/10 ml;
0.8M $\text{HNO}_3 \sim 0.1\text{M}$ HF column: i.d. 6mm; vol. 1 ml Al_2O_3 .

Pu Valence	Redox agent in the loading solution	Pu ret. (%)	D.F. (^{239}Pu)
III	0.2M $\text{NH}_2\text{NH}_2 - 0.2\text{M}$ $\text{NH}_2\text{OH.HCl}$	65.0	2.8
VI	conc. HClO_4	69.7	3.6
IV	0.01M NaNO_2	87.2	7.8
IV	0.03M NaNO_2	89.0	9.0
IV	0.1M $\text{NH}_2\text{NH}_2 - 0.01\text{M}$ NaNO_2	90.9	11.0
IV	0.002M $\text{Fe}(\text{NO}_3)_3 - 0.1\text{M}$ $\text{NH}_2\text{OH.HCl} - 0.02\text{M}$ NaNO_2	92.3	13.0
IV	0.005M $\text{FeSO}_4 - 0.04\text{M}$ NaNO_2	97.8	47.2

A set of laboratory experiments proved that the most effective and consistent method to elute plutonium from the alumina was by reducing plutonium to trivalent state in nitric acid. The collected data (Table IV) present good results when 3M $\text{HNO}_3 - 0.005\text{M}$ FeSO_4 solution was used as elutrient. Ap-

proximately 95% of the plutonium was recovered at room temperature (25°C). To determine if the temperature could improve the plutonium desorption, the elution was done with the same elutrient at 25 and 50°C. Figure 2, shows these curves and, at 50°C, the elution presents a sharper peak while the curve at 25°C exhibits some tail.

Table IV. Plutonium elution from Al_2O_3 column at 25°C.

Elutrient		Pu eluted (%)
(M) HNO_3		
1		62.9
2		65.3
3		78.9
4		70.6
5		22.6
6		15.7
(M) HNO_3 - (M) $FeSO_4$		
1	0.005	80.8
2	0.005	81.3
3	0.005	94.7

To demonstrate the validity of this procedure for the recovery of trace amount of plutonium from dilute solutions, 30 liters of solution with a specific activity of ^{239}Pu 135 ± 12 (counts/2000/sec/ml) was percolated through a small column containing 10 ml of Al_2O_3 . About 97% of plutonium were sorbed onto the alumina.

The experiments have shown that trace sorption of Pu(IV) onto Al_2O_3 is almost complete from 0.8M HNO_3 - 0.1M HF. The stabilization of Pu(IV) state was obtained by prior reduction to Pu(III) and reoxidation to Pu(IV) using Fe(II) and nitrite.

The Al_2O_3 column loaded with plutonium was satisfactorily washed with an 0.1M HNO_3 - 0.05M HF solution for the removal of the last traces of uranium and other elements not sorbed. The effluents contained less than 0.01% of plutonium. Washing the column with an 0.8M HNO_3 - 0.05M HF solution resulted in 0.1% of plutonium activity in the effluent. This indicates that the column should be washed with more dilute nitric acid. The effectiveness of elution with HNO_3 plus a reducing agent at room temperature and 50°C was confirmed in both cases. As Pu(IV) is more sorbed onto alumina than the other plutonium oxidation states, it was reduced to Pu(III) to improve the elution. On the other hand HNO_3 is the most convenient medium for further uses of plutonium, so for that reason nitric acid (1-6M) was selected as elutrient. Pure 3M HNO_3 at room temperature eluted 79% of plutonium. A 3M HNO_3 - 0.005M $FeSO_4$ solution was chosen as eluting agent and, the elution yield

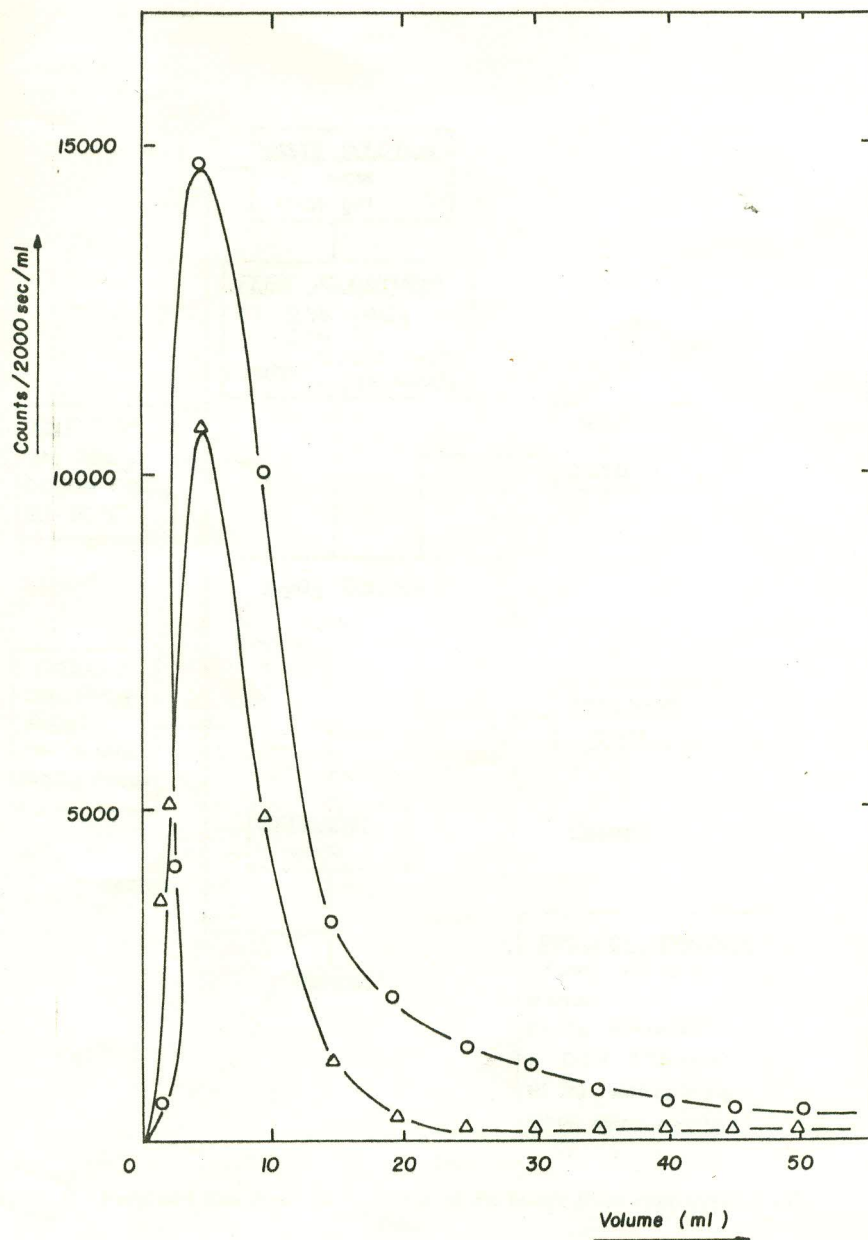


Figure 2. Elution curve of ^{239}Pu from Al_2O_3 column; $\text{Al}_2\text{O}_3 = 1$ ml; flow rate = 1.4 ml/min/cm 2 , surface barrier detector; (○) 3M HNO_3 - 0.005M Fe^{2+} , temperature $\sim 25^\circ\text{C}$; (△) 3M HNO_3 - 0.005M Fe^{2+} , temperature $\sim 50^\circ\text{C}$.

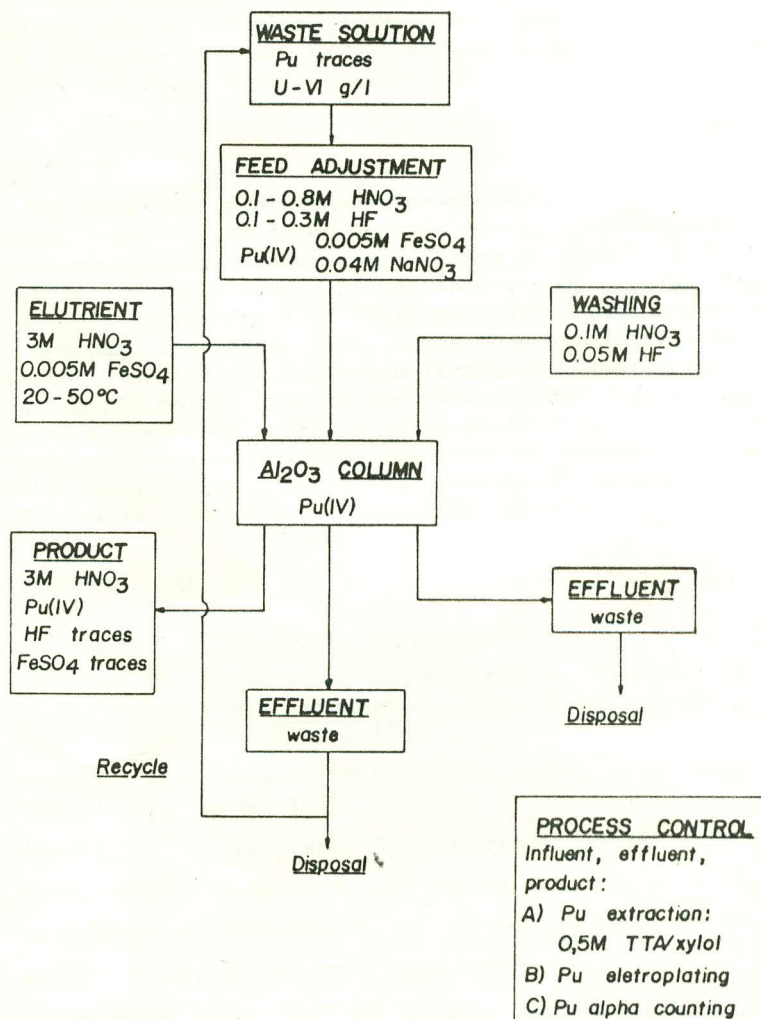


Figure 3. Proposed flowsheet for recovery of Pu traces from reprocessing solutions

being improved to about 95%. Also the temperature has some influence in the elution.

The descontamination of plutonium traces from macroquantities of uranyl nitrate by sorption of Pu(IV) onto an Al_2O_3 column was easily and successfully accomplished. Percolation of a 0.8M $\text{UO}_2(\text{NO}_3)_2$ solution, 0.8M in HNO_3 and 0.3M in HF traced with plutonium-239, the Pu was sorbed while uranium passed through the Al_2O_3 column.

CONCLUSION

The successful experiments for the retention of plutonium onto alumina from HNO_3 -HF solution gave enough confidence to recommend the proposed method to separate traces of plutonium from waste solutions in the presence of macroamounts of uranium (VI). Of course, only macroamounts of thorium, uranium (IV) and rare earths are serious interfering ions, since they precipitate with HF. The behavior expected for neptunium in the same system should be similar to plutonium, thorium and rare earths. The retention of neptunium from HNO_3 - HF solutions is in progress. The sorption yield for Pu was around 95%. The sorption mechanism is not well established. Figure 3 shows the proposed flowsheet for recovery of Pu traces from reprocessing waste solutions.

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