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 lantanide 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 successfuly 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 uCi/ml (160 µg/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/XYLOL. The samples for quantitative determination were prepared by eletroplating according to WENZEL and HERZ (9). The alpha energy measurement was made by a

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surface barrier detector associated with a ORTEC multichannel analyser. 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 Al_2O_3 - 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 ± 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 ± 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: $1,5 \times 10^{-8}$M ^{239}Pu; alpha activity = 230,000 ± 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.

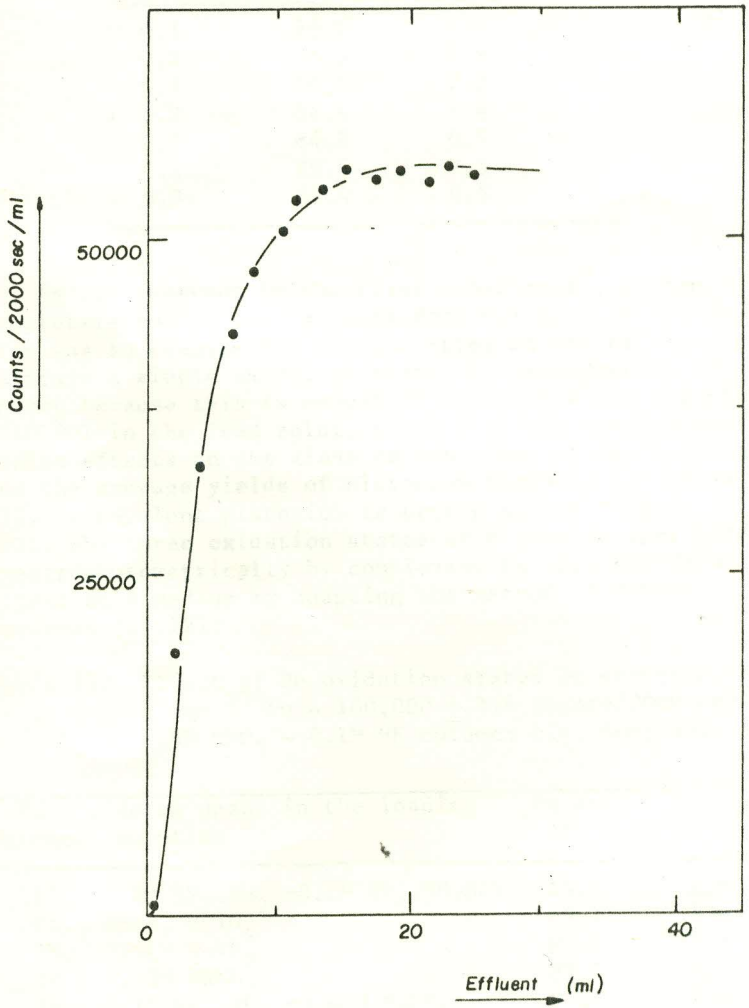

Figure 1. Breakthrough curve of Pu onto Al_2O_3 column; feed: 25 ml ^{239}Pu–0.8M HNO_3; ^{239}Pu activity = 55,000 ± 235 counts/2000 sec/ml; column = 1 ml Al_2O_3; flow rate = 0.8 ml/min/cm².