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Studies on the Adsorption of Americium on Alumina from Aqueous Nitric Acid-Oxalic Acid Solutions

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Abstract

This paper reports a study on the adsorption of Am(III) on alumina from oxalic acid-nitric acid solutions. Distribution coefficients for Am(III) on alumina at different oxalic acid-nitric acid concentrations have been determined and optimum conditions for loading and elution of Am from alumina columns have been established. Separation of Am from Pu and the effects of other ions, such as U(VI) and Fe(III), have also been studied. Am and Pu recoveries better than 99.5% were obtained.

INTRODUCTION

Plutonium containing a high percentage of plutonium-241 is one of the sources of americium, the americium content increasing with time. When plutonium containing significant amounts of americium is precipitated as oxalate, the aqueous supernatant contains substantial amounts of americium in addition to some plutonium. One of the methods reported for the recovery of small amounts of trivalent actinides from oxalate solutions is by cation exchange (*1*, *2*). This paper describes a new and simple method for recovering americium from oxalate solutions containing both plutonium and americium. We have studied the sorption of plutonium on alumina from oxalate medium (*3*). The present investigation is concerned with the adsorption of trace quantities of americium along with plutonium on

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alumina from oxalic acid–nitric acid solutions and the subsequent elution of americium and plutonium sequentially.

EXPERIMENTAL

Materials

Americium and plutonium used in the experiments were purified by standard methods reported in the literature. The radiochemical purity was ascertained by α-spectrometry. The oxidation state of plutonium was adjusted as Pu(IV) by heating with $NaNO_2$ and was checked by TTA extraction.

Chromatographic grade Al_2O_3 (B.D.H. supplied) was used. A glass column having a diameter of 0.5 cm and a capacity of 15 mL was filled with 8 g of alumina and used in the column experiments.

All other reagents used were of A.R. grade.

Batch and Column Experiments

Batch experiments were carried in which 0.2 to 0.3 g of alumina were equilibrated for 2 h with 5 mL of the aqueous phase containing the specified amounts of oxalic acid, nitric acid, and americium. The distribution coefficient D was obtained by the equation

$$D = \frac{[\mathrm{Am}]_R/\mathrm{g\ of\ alumina}}{[\mathrm{Am}]_A/\mathrm{mL\ of\ aqueous\ phase}}$$

expressed as

$$D = \frac{\mathrm{Counts\ g^{-1}}}{\mathrm{Counts\ mL^{-1}}}$$

where $[\mathrm{Am}]_R$ and $[\mathrm{Am}]_A$ represent the concentrations of americium in the alumina and aqueous phases, respectively. The initial and equilibrium concentrations of americium were assayed by a NaI(Tl) detector. Americium concentration in the alumina phase was obtained by difference. The distribution coefficients were determined in duplicate experiments.

In column experiments, prior to loading americium or a mixture of americium–plutonium on the alumina column, it was preconditioned with oxalic acid–nitric acid solution having the same composition as that of the loading solution. In one column run, about 25 mL of a mixture containing americium (2.0–7.0 μg/L) or a mixture of americium (7 μg/L), plutonium (30 mg/L), oxalic acid (0.1 *N*) and nitric acid (0.5 *M*) was introduced into the column at a constant flow rate with a column residence time of 10–12 min and washed with 0.1 *M* nitric acid until the oxalate concentration in washings was less than 0.002 *M* (3 to 4 column volumes). Americium was first eluted with 0.5 *M* HNO_3, followed by the elution of plutonium using 3 *M* HNO_3.

The eluted solutions were quantitatively collected and subjected to radiochemical assay for plutonium and americium content. Radiochemical purity of the eluted nuclides was confirmed by α-spectrometry.

RESULTS AND DISCUSSION

Distribution Coefficients

The distribution of Am(III) on alumina in the presence of different concentrations of oxalic acid and nitric acid was studied and the results are summarized in Table 1. It can be seen that the distribution coefficient decreases with increasing nitric acid concentration and with increasing oxalic acid concentration. An increase of equilibrium temperature results in a decrease of the distribution coefficient. The highest distribution coefficient for americium has been observed from solutions containing 0.2 *M* oxalic acid and 0.3 *M* nitric acid at room temperature. The separation factors for

TABLE 1
Effect of Oxalic Acid–Nitric Acid Concentrations on the Distribution Coefficient of Am(III) at 25°C[a]

Concentration of HNO_3 (*M*)	*D* at different concentrations of oxalic acid (*M*)			
	0.05	0.10	0.20	0.45
0.3	10.1	22.0 (10.0)	41.9 (32.5)	32.5
0.5	10.4	22.1 (26.8)	29.1 (26.7)	33.7
1	3.9	7.2 (2.5)	11.4 (7.3)	11.1
2	1.0	2.7	2.5 (0.4)	2.3
3	0.4	2.4	1.8	0.5

[a] The numbers in parentheses represent values of *D* at 40°C.

Am and Pu at different oxalic acid–nitric acid concentrations are summarized in Table 2. The separation factor is the highest in 0.3–0.5 *M* HNO_3 containing 0.05 *M* oxalic acid. Though the separation factors may be higher at lower concentrations of oxalic acid and nitric acid, they were not used in these studies, since the solutions resulting from oxalate precipitation are about 0.1 to 0.2 *M* in oxalic acid and 1 to 2 *M* in nitric acid. They have to be diluted considerably before applying this method for the recovery of plutonium and americium.

Column Experiments

Table 3 summarizes the results of experiments on the loading of Am(III) from solutions containing oxalic and nitric acids. Loading was done in the presence of 0.05 *M* and 0.1 *M* oxalic acid while varying the nitric acid concentration from 0.33 to 3.0 *M*, keeping in view the conditions of oxalate precipitation. These data indicate that Am recoveries better than 99.5% can be achieved when the nitric acid concentration in the feed is 0.35–0.5 *M*. It has been observed that loading from solutions containing 1 *M* and higher concentrations of nitric acid result in poor recovery of americium.

Separation of Americium from Plutonium

Column separations of americium from plutonium were performed using synthetic mixtures containing varying amounts of Am and Pu in solutions containing 0.5 *M* nitric acid and 0.1 *M* oxalic acid. The results of the separation are summarized in Table 4. It can be seen that more than 98% of americium can be recovered by eluting with 0.5 *M* nitric acid. The eluted americium was found to be radiochemically pure as confirmed by α-

TABLE 2
Separation Factor $\alpha = D_{(Pu)}{}^a / D_{(Am)}$

	Separation factor at different oxalic acid concentrations (*M*)			
HNO_3 (*M*)	0.05	0.10	0.20	0.45
0.3	15.98	7.48	2.17	2.10
0.5	15.67	7.40	2.80	2.40
1.0	9.20	7.24	3.57	3.20
2.0	8.0	4.10	5.53	5.34
3.0	7.56	3.08	3.70	12.02

[a] $D_{(Pu)}$ values taken from our Ref. 3 data.

TABLE 3
Recovery of Americium Loaded on Alumina Column[a]

Feed composition			
HNO_3 (*M*)	Oxalic acid (*M*)	Am (in 25 mL) (μg)	Am obtained in elution (μg)
0.35	0.10	0.041	0.041
	0.05	0.041	0.041
0.50	0.10	0.046	0.046
	0.05	0.046	0.046
1.00	0.10	0.041	0.035
2.00	0.10	0.046	0.026
3.00	0.10	0.041	0.020

[a] Eluting solution: 3 *M* HNO_3. Column characteristics: length 15 cm, diameter 0.5 cm, volume 8 mL. Washing solution: 0.1 *M* HNO_3. Flow rate: 10–12 min per column volume.

spectrometry. When plutonium was subsequently eluted with 3 *M* HNO_3, the first few fractions were found to contain the remaining 4 to 5% of americium. Plutonium recovery was found to be of the order of 99.5%. Figure 1 shows a typical elution curve for sequential elution of Am and Pu.

The effect of U(VI) and Fe(III) on the loading of Am(III) or a mixture of Am(III) and Pu(IV) was studied, and the results (Table 5) show that they have no effect on Am and Pu recoveries. Both U(VI) and Fe(III) can be washed off quantitatively prior to elution of Am and Pu from the column.

A proposed flow sheet for the recovery of americium and plutonium from the oxalic acid–nitric acid waste solution is shown in Fig. 2. By using this procedure, 5 L of oxalate waste containing 0.2 mg of americium and 515

TABLE 4
Sequential Elution of Am and Pu from an Alumina Column[a]

Am taken (μg)	Pu taken (mg)	Am obtained[b] in elution with 0.5 *M* HNO_3 (μg)	Pu obtained in elution with 3 *M* HNO_3 (mg)
0.180	0.215	0.175	0.210
0.045	0.134	0.044	0.133

[a] Feed composition: HNO_3 = 0.5 *M*, oxalic acid = 0.1 *M*. Eluting solution: 5 column volumes of 0.5 *M* HNO_3 followed by 5 column volumes of 3 *M* HNO_3.

[b] The remaining 3–5% Am is associated with the Pu fraction.

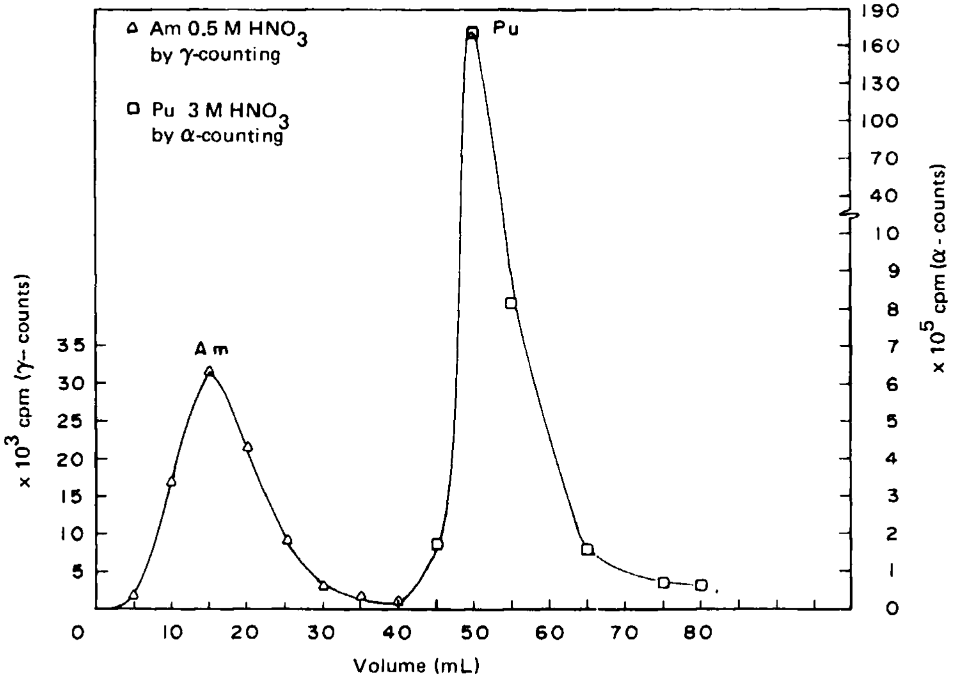

FIG. 1. Sequential elution.

TABLE 5
Effect of U(IV) and Fe(III) on Am and Pu Recoveries[a]

Amounts of various constituents in 25 mL of loading solution, HNO_3 = 0.5 *M*, $H_2C_2O_4$ = 0.1*M*	Amounts in 60 mL of effluents during loading with 0.5 *M* HNO_3 and washing with 0.1 *M* HNO_3	Amounts in 40 mL of eluate or eluting solution
Am = 0.058 μg	NL	0.056 μg (0.5 *M* eluent)
Pu = 0.75 mg	0.002 mg	0.748 mg (3 *M* eluent)
U(VI) = 21.3 mg	20.9 mg	
Fe(III) = 17.8 mg	17.8 mg	

[a] Column characteristics: Weight of Al_2O_3 = 8 g, length 15 cm, diameter 0.5 cm, flow rate during loading, washing, and elution = 10–12 min/column volume.

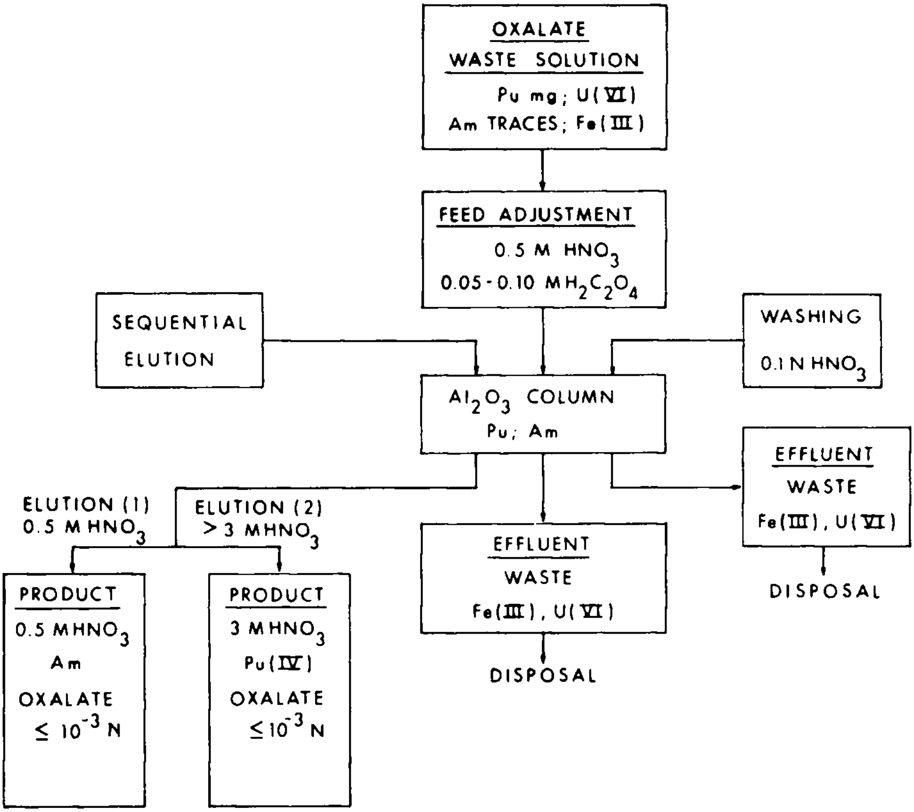

FIG. 2. Proposed flow sheet for the recovery of Am and Pu from oxalate waste solutions.

mg of plutonium was processed. It was found that the extent of recovery of these elements was 99.5%.

Americium and plutonium in the eluates can be concentrated by the conventional method of hydroxide precipitation followed by dissolution in nitric acid. Alternatively, the dilute plutonium solution can be recycled to the plutonium processing operations because of the very low oxalate concentration (<0.001 *N*) in the eluate.

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REFERENCES

1. D. O. Campbell and S. R. Burton, U.S. Patent 4,025,602/A/(1977); *INIS Atom Index, 9*, 374–409 (1978).
2. D. E. Ferguson, Oak Ridge National Laboratory, *ORNL-5050*, 6–11, 30–51 (1975).
3. M. Subba Rao, A. M. Gaikwad, V. K. Rao, and P. R. Natarajan, *Radiochem. Radioanal. Lett.*, *56*(5), 281–290 (1982).

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