Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Pu-Am from the Leachant of a Deposit in an Acid Digestion Solution by Calcium Oxalate Coprecipitation

J. Akatsu[a]; Y. Kobayashi[a]; H. Matsuzuru[b]; S. Dojiri[b]; N. Moriyama[b]
[a] DIVISION OF CHEMISTRY, JAPAN ATOMIC ENERGY RESEARCH INSTITUTE, JAPAN [b] DIVISION OF ENVIRONMENTAL SAFETY RESEARCH, JAPAN ATOMIC ENERGY RESEARCH INSTITUTE, JAPAN

To cite this Article Akatsu, J. , Kobayashi, Y. , Matsuzuru, H. , Dojiri, S. and Moriyama, N.(1983) 'Separation of Pu-Am from the Leachant of a Deposit in an Acid Digestion Solution by Calcium Oxalate Coprecipitation', Separation Science and Technology, 18: 2, 177 — 186

To link to this Article: DOI: 10.1080/01496398308055667

URL: http://dx.doi.org/10.1080/01496398308055667

SEPARATION SCIENCE AND TECHNOLOGY, 18(2), pp. 177–186, 1983

Separation of Pu-Am from the Leachant of a Deposit in an Acid Digestion Solution by Calcium Oxalate Coprecipitation

J. AKATSU and Y. KOBAYASHI
DIVISION OF CHEMISTRY

H. MATSUZURU, S. DOJIRI, AND N. MORIYAMA
DIVISION OF ENVIRONMENTAL SAFETY RESEARCH

JAPAN ATOMIC ENERGY RESEARCH INSTITUTE
TOKAI-MURA IBARAKI-KEN, JAPAN

Abstract

Pu and Am were recovered from the deposit in a synthetic acid digestion solution. After being leached out from the deposit with water, they were separated from the resultant solution by Ca-oxalate coprecipitation. The alpha radioactivity in the solution was reduced from about 4 mCi/L to 0.1 μCi/L by the technique. The precipitate obtained was dissolved in 7 *M* nitric acid solution, from which Pu-Am were separated by the use of anion and cation exchange resin columns, respectively. The coprecipitation technique was also utilized for the concentration of Am in the effluent of the anion column prior to its separation by a cation column. The overall recovery efficiencies of Pu and Am were about 80 and 85%, respectively.

INTRODUCTION

Combustible waste contaminated with Pu is on the increase at the Japan Atomic Energy Research Institute (JAERI). From now on, a larger quantity of it will of necessity be generated due to the increasing use of fissile material. It is extremely urgent to minimize the waste arising from Pu handling processes (*1*). More effort must be paid to convert it into a less troublesome waste (*2*).

0149-6395/83/1802-0177$3.50/0

Several techniques concerning waste disposal have been proposed and developed in order to reduce its volume and to convert it into an inorganic waste. These include several types of incineration (*3–6*) and acid digestion (*7–11*). There are many studies for their feasibility and for Pu recovery from incinerator ash (*12–16*). Among them, the acid digestion technique is considered to be excellent for enclosing the accumulating Pu-Am and HCl, one of the decomposition products of chloroprene and polyvinyl chloride, in shredded waste. The technique has been chosen and studied on a laboratory scale at JAERI (*17*). The combustible waste is digested in a system of concentrated H_2SO_4 and H_2O_2. During the process, most of Pu-Am in the waste is accumulated as a deposit together with many metal sulfates.

In the present work attention is paid to the recovery of Pu-Am from the deposit in a digestion solution. Its precipitation behavior with Ca-oxalate is studied in the leaching solution of the deposit.

EXPERIMENTAL

Materials and Description

Pu and Am, used as tracers, were purified by anion and cation exchange resin columns, respectively. The cross-contamination of them was less than 1/200 by α-ray spectrometry. Pu(III), Pu(IV), and Am(III) were dissolved and stocked in 0.1 *M* H_2SO_4 solutions, individually, after a HNO_3 solution containing each of them was gently evaporated. As described in a previous paper (*18*), the decontamination effect of a treated solution was verified by measuring its α radioactivity. The effect is reported by the evaluating decontamination factor, D.F. The factor was defined as

$$\text{D.F.} = I_i/I_f$$

where I_i and I_f represent the intensities of α activity in the initial and final states of the solution, respectively.

To prepare an acid digestion solution, 5.0 g of stainless steel chips, SUS-304, were dissolved in a dilute H_2SO_4 solution. The solution obtained was mixed with a HNO_3 solution containing 1070 mg of Pu(IV). The resultant solution was poured into 0.3 L of concentrated H_2SO_4 in a digester. The amounts of Pu and Am were estimated from the total α activity (Pu + Am) and the activity ratio (Pu/Am). Pu, in a solid residue after leaching, was assayed by measuring the γ-rays from ^{239}Pu (360–470 KeV). Then the amount of it in the sample was determined by comparing with the data obtained from the calibrating sources as described in a previous paper (*19*).

RESULTS AND DISCUSSION

Leaching of Pu-Am

Most metals and their oxides are considered to be converted into their sulfates in hot concentrated H_2SO_4 solution containing H_2O_2. The sulfates will precipitate in the solution since it is a poor solvent for most inorganic salts. It was expected that most of the Pu-Am could be recovered from the sulfate (*8*).

About 1 kg of nonradioactive shredded waste was fed batchwise into the synthetic acid digestion solution. The digestion was carried out at about 250°C by adding 35% H_2O_2 solution continually (*17*). At the end of the run the digestion solution was allowed to stand at about 250°C until water vapor ceased to condense in the cooling system. The solution was removed to a beaker together with the deposit. While still rather hot, the solution was separated from the deposit by decantation. Water was added to the deposit, heated to 95–105°C, and separated by decantation as shown in the flow sheet in Fig. 1. Fresh water was added again and mixed. This solution was also separated by decantation. The two solutions were mixed. The solution obtained and the residual solid were named Solution I and Deposit I. Deposit I was washed with 1 *M* HNO_3 solution by filtration. This solid and solution were named Deposit II and Solution II. Deposit II was dried under infrared rays.

The amounts of Pu-Am in Solutions I and II and the concentrated H_2SO_4 solution were determined as shown in Table 1. Most of the actinide elements were concentrated in the deposit and were leached out in the aqueous solutions. About 95% of the amounts of Pu and Am found are contained in Solution I.

Ca-Oxalate as Scavenger

The scavenging effect of Ca-oxalate has been studied for Am(III) in H_2SO_4 solution. Two techniques for precipitation in H_2SO_4 solution are shown in Table 2. In the first experiment, a Ca(II) solution is added to a

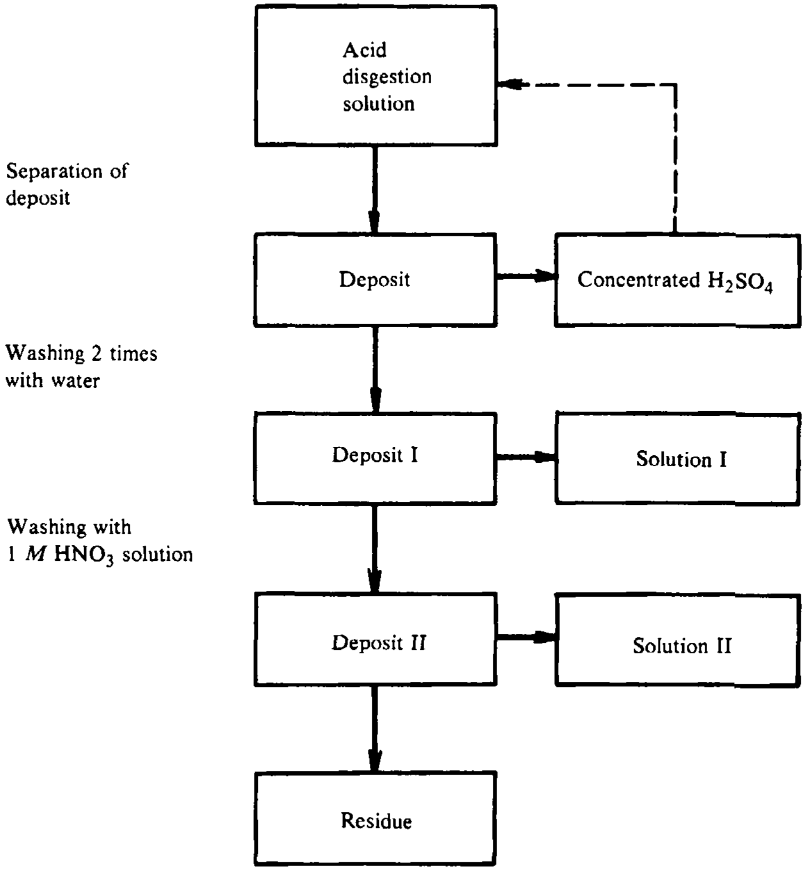

Fig. 1. Flow sheet for the recovery of Pu-Am from the deposit in acid digestion solution.

H_2SO_4 solution containing 0.2 M $K_2C_2O_4$. Ca-oxalate gradually precipitates in the solution. In this case, most Am(III) remains in the supernatant. In the second experiment, a few drops of 1.5 M $K_2C_2O_4$ solution are added and mixed after a Ca(II) solution is added to a H_2SO_4 solution containing 0.2 M $K_2C_2O_4$. Fine Ca-oxalate precipitates immediately in the solution under heterogeneous nucleation. The supernatant is sufficiently decontaminated for the technique to play an important role in the present work.

The sedimentation of Ca-oxalate in HNO_3 solution is very slow. The solution must be allowed to stand for several hours in order to get a large D.F. value, as seen in Fig. 2. However, the oxalate made in H_2SO_4 solution

TABLE 1. Pu-Am Obtained by Washing the Deposit in a Synthetic Acid Digestion Solution

Synthetic acid digestion solution: Concentrated H_2SO_4: 0.3 L
SUS-304 component parts (as metal): 5g
Pu: 1070 ± 30 mg
α activity: 69 ± 2 mCi
α activity ratio: 21.4 (Pu/Am)

Solution	Volume (L)	α Activity		Found weight	
		Pu/Am	Pu + Am (mCi)	Pu (mg) (yield %)	Am (μg) (yield %)
Concentrated H_2SO_4	0.3	18.5	0.93 ± 0.02	14.4 ± 0.3	13.9 ± 0.3
Solution I	0.15	21.9	58 ± 2	904 ± 31 (94.8)	739 ± 25 (94.3)
Solution II	0.1	20.4	2.26 ± 0.02	35.1 ± 0.3 (3.7)	30.8 ± 0.3 (4.0)
Dried residue: 8.2 g				^{239}Pu: 7.8 ± 0.3 mg	

precipitates rapidly, and most of it settles down within 5 min. About 30 min seem to be enough time for it to settle.

When the carrier is prepared fresh in a H_2SO_4 solution, the scavenging effect depends on the concentrations of $K_2C_2O_4$ and H_2SO_4. The coprecipitation of Am(III) with it and the dependence of $K_2C_2O_4$ concentration is shown in Fig. 3(A). Effective scavenging will be carried out in a solution of 0.1–0.2 *M* $K_2C_2O_4$. The influence of H_2SO_4 concentration for the scavenging of Pu(III), Pu(IV), and Am(III) is presented in Fig. 3(B). They are removed satisfactorily by the carrier in a solution of less than 1 *M* H_2SO_4,

TABLE 2
Scavenging Effect of Ca-oxalate for Am(III) Generated in H_2SO_4 Solution by Two Techniques

No.	Solution	Added solution	D.F. value
1	H_2SO_4:0.8 *M* $K_2C_2O_4$: 0.2 *M* Am: 2×10^{-6} *M*	2 *M* Ca(II) (0.1 L/L)	2.2 ± 0.1
2	Same as above	2 *M* Ca(II) (0.1 L/L) 1.5 *M* $K_2C_2O_4$ (2–3 drops)[a]	835 ± 97

[a] fine Ca-oxalate precipitates immediately by using drops of the solution

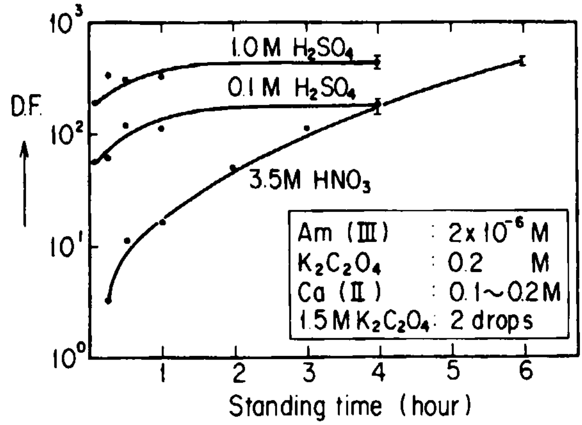

FIG. 2. Scavenging effect of Ca-oxalate for Am(III) in the dependence on sedimentation of the precipitate generated in solution.

but only slightly in a solution of more than 1 *M*. In a solution of more than 2 *M*, calcium sulfate predominates. The precipitate is not efficient for scavenging Am(III), as shown in Fig. 3(B).

Recovery of Pu-Am

On the basis of the results described above, a proposed flow sheet for Pu-Am recovery is presented in Fig. 4. Decontamination is carried out under dual successive processes. The solution and precipitate obtained in the first are named Supernatant I and Precipitate I. Supernatant II and Precipitate II are obtained in the second. When a considerable amount of Pu is contained in the starting solution, Pu-oxalate will precipitate itelf in the first and be obtained in Precipitate I. Pu and Am will be recovered from the mixture of Precipitates I and II.

The actinide elements were recovered from the leachants described in Table 1. The results obtained are shown in Table 3. The hydrogen-ion concentrations in Solutions I and II are about 7 and 1 *M*, respectively. They are too high for decontaminating. Solution I was diluted 10 times with water. A Solution I aliquot was diluted 5 times. Solution II was diluted twice with water. These solutions were decontaminated according to the procedures in Fig. 4. The H_2SO_4 solution diluted from Solution I was reduced from about 4 mCi/L to 0.1 μCi/L in α activity. The mixture solution of HNO_3 and H_2SO_4

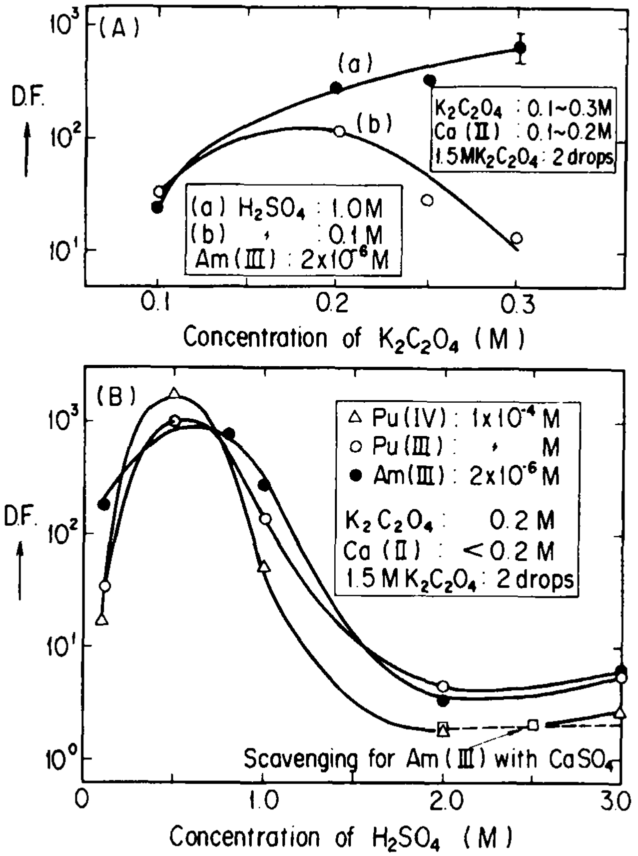

FIG. 3. Scavenging effects of Ca-oxalate for Am(III), Pu(III), Pu(IV) in the (A) dependency on $K_2C_2O_4$ concentration and (B) dependency on H_2SO_4 concentration.

diluted from Solution II was reduced from about 6 mCi/L to 4 μCi/L in α activity by a single coprecipitation.

The mixture of Precipitate I and II was dissolved at about 100°C in 7 *M* HNO_3 solution. The resultant solution was filtrated and poured onto an anion exchange resin column (Dowex 1-X4, 50-100 mesh) in order to separate the Pu(IV). In the meantime, the effluent from the anion column (7 *M* HNO_3 solution) was diluted twice with water for Am recovery. Then Am(III) was scavenged with Ca-oxalate generated in the HNO_3 solution, as described in Fig. 2. The precipitate obtained was dissolved at room temperature by adding a 7 *M* HNO_3 solution equal in volume to the

TABLE 3
Results Obtained in the Demonstration Experiment

Initial solution		Solition I, H^+ acidity: 7 *M*		Solution II, H“ acidity: 1 *M*
Starting solution	Dilution with water (times)	$(\times 5)^a$	$(\times 10)$	$(\times 2)$
Decontaminated solution	Supernatant I (α, μCi/L)	2009 ± 60	5.4 ± 0.9	3.8 ± 0.9
	Supernatant II (α, μCi/L)	404 ± 8	0.12 ± 0.04	
		Pu		Am
Recovered Pu and Am	Weight (mg)	855 ± 97		0.77 ± 0.07
	Yield (%)	91		100

[a] Aliquot experiment.

slurrylike precipitate. The resultant solution was diluted 10 times with water and poured onto a cation column (Dowex 50W-X8, 50-100 mesh) for the separation of Am(III). By these techniques 855 mg Pu and 770 μg Am were recovered from the starting solutions which contained 940 mg of Pu and 770 μg Am.

CONCLUSION

Pu and Am were recovered from the deposit in an acid digestion solution. After being leached out from the deposit with water, they were separated from the resultant solution by Ca-oxalate coprecipitation. Although Ca-oxalate formation is slow in H_2SO_4 solution, it is promoted by adding a nearly saturated solution of potassium oxalate dropwise to the solution. A fine precipitate can be obtained by this technique. The improved carrier precipitates rapidly in the solution. It is effective for the removal of Pu-Am in a solution of less than 1 *M* H_2SO_4. The carrier separated from the mother solution was dissolved for the succeeding process. Although pure Ca-oxalate dissolves easily at a room temperature in 7 *M* HNO_3 solution, dissolution of it in the leachant was difficult because of a mixture of some metal oxalates such as Ni-oxalate. It was heated to about 100°C in 7 *M* HNO_3 solution, but it could not be dissolved completely. Filtration of the solution was needed for separation of Pu-Am.

The overall recovery yields of Pu and Am were about 80 and 85%, respectively. Dual coprecipitations should not be needed in this work,

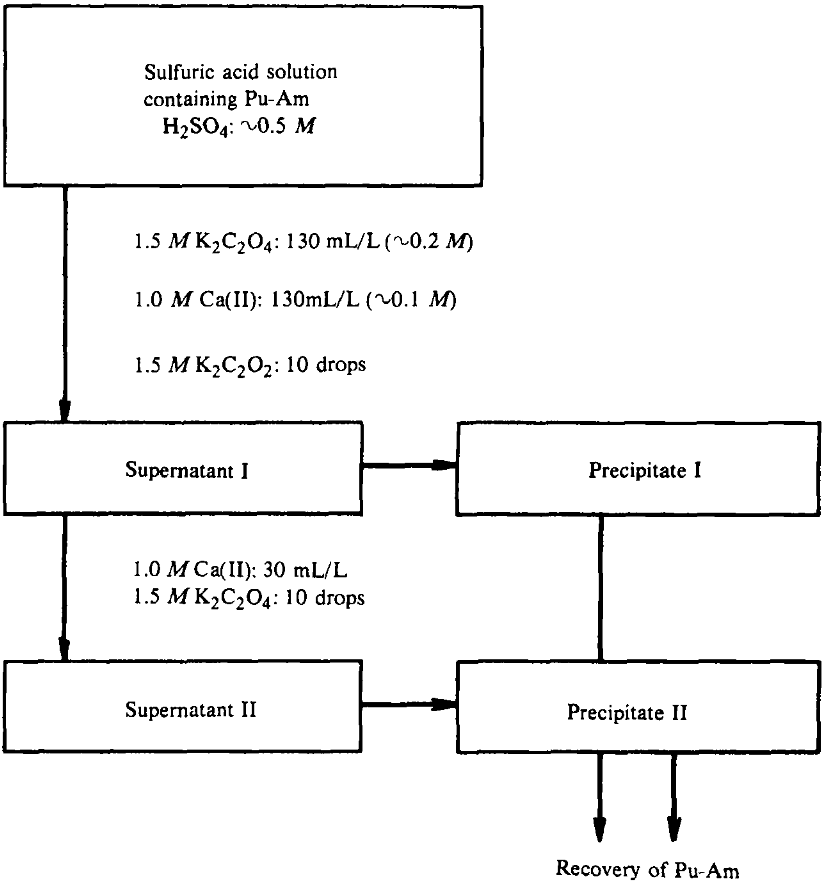

FIG. 4. Flow sheet for the recovery of Pu-Am from dilute sulfuric acid solution.

although Pu-oxalate will precipitate in the first step in the case of a solution containing a considerable amount of Pu. Further decontamination is carried out in the second step. Thus the separation technique can also be applied to the treatment of a solution containing macroamount of Pu. The hydrogen-ion concentration of the leachant, Solution I, was relatively high. The solution was diluted 10 times with water prior to scavenging of Pu-Am. The deposit in the digestion solution was separated by decantation. It should be filtered in order to make the succeeding process easy, since the digestion solution is concentrated H_2SO_4.

In order to verify the recovery efficiency of Pu-Am, a synthetic acid digestion solution was prepared by adding a HNO_3 solution containing Pu(IV) and Am(III) to a concentrated H_2SO_4 solution. However, many forms of actinide elements, such as their oxides, will be contained in actual combustible wastes. It will be necessary to ascertain in future work whether they are converted to a water-soluble deposit in a digestion system of concentrated H_2SO_4 and H_2O_2.

REFERENCES

1. W. B. Bremner and K. C. Macleod, *EUR-6629,* 1979.
2. H. A. Taylor, J. M. Leblanc, P. Pottier, and M. N. Elliot, in *Management of Alpha-Contaminated Waste* (International Symposium Held in Vienna, 1980), International Atomic Energy Agency, Vienna, 1981, p. 31.
3. L. C. Borduin and A. L. Taboas, *LA-UR-80-692,* 1980.
4. R. Simon, H. Wieczorek, G. Brambilla, and J. R. Grover, in *Radioactive Waste Management and Disposal* (Conference held in Luxembourg, 1980) (R. Simon and S. Orlowski, eds.), Harwood, New York, 1980, p. 92.
5. B. Longstaff, P. W. Cains, M. N. Elliot, and R. F. Taylor, *EUR-7339,* 1981.
6. M. N. Elliot, B. Longstaff, and P. W. Cains, *Eur. Appl. Res. Rep.—Nucl. Sci. Technol. Sect.,* *2*(2), 365 (1980).
7. R. E. Lerch, *HEDL-TME 75-5,* 1975.
8. C. R. Cooley and R. E. Lerch, *HEDL-TME 75-41,* 1975.
9. R. E. Lerch and C. R. Allen, *HEDL-TME 78-73,* 1978.
10. A. G. Blasewitz, C. R. Allen, R. E. Lerch, P. C. Ely, and G. L. Richardson, *HEDL-SA-1967,* 1980.
11. C. R. Allen, *HEDL-SA-2239-FP,* 1980.
12. J. D. Navratil and G. H. Thompson, *Nucl. Technol., 43*(2), 136 (1979).
13. E. L. Christensen, *LA-UR 80-1168,* 1980.
14. T. C. Johnson, *RFP 2520,* 1976.
15. J. D. Navratil, *RFP 2774,* 1978.
16. J. Miner, *RFP-2803,* 1978; *RFP-2870,* 1979.
17. Y. Kobayashi, H. Matsuzuru, J. Akatsu, and N. Moriyama, *J. Nucl. Sci. Technol., 17*(11), 865 (1980).
18. J. Akatsu, *Sep. Sci. Technol., 17,* 1433 (1982).
19. J. Akatsu, *Nucl. Mater. Manage. 10*(40), 22 (1981).