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Separation of Pu–Am from an Aqueous Waste by Successive Oxalate and Lead Oxalate Precipitations

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Abstract

Decontamination of an aqueous waste of Pu and Am was carried out stepwise by making an oxalate and then a lead oxalate precipitate. The alpha radioactivity was reduced from 6.8 mCi/L to 10 μCi/L by these techniques. The precipitates obtained were dissolved in 7 *M* nitric acid solution, from which Pu and 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 prior to its separation by the cation column. The overall recovery yields were about 90% for both Pu and Am.

INTRODUCTION

Waste solutions containing Pu and Am are of necessity generated at the plutonium handling laboratory in the Japan Atomic Energy Research Institute (JAERI). They pose a long-time hazard to man since most nuclides of the actinides are α-radioactive and of long-term half-life. The hazard is not reduced even if the waste, as it is, is safety kept for a long time. The waste should be converted to a solid waste after the actinides have been removed.

Many investigations concerning the recovery of actinides have been reported: solvent extraction (*1–3*), adsorption column (*4–7*), and precipitation (*8–11*). Much effort has been paid, particularly to Pu recovery, to minimize the process loss (*12–15*) and to have accurate accountancy. However, there are still some problems to be solved when one of these methods is applied to the disposal of the waste. The waste should be well decontaminated, and it is desirable to bring the bulk of the actinides to a small volume of solution or precipitate for their separation. It is also necessary that any wastes containing macro- and microamounts of the actinides be decontaminated in a given process. The method selected treats the waste within the limited space of a glove box. Decontamination is carried out by the use of simple equipment.

A precipitation technique is presented in the present work. Pu and Am oxalate precipitates are formed in order to remove their bulk from the waste. For further decontamination, the Pb(II) ion, which forms a dense precipitate, is used as a scavenger. Pu and Am are separated from the precipitates obtained by the decontamination technique.

EXPERIMENTAL

Materials

Pu and Am used as tracer were purified by anion and cation exchange resin columns, respectively. Their mutual contamination was less than 1/200 by α-ray spectrometry. Pu(IV) was eluted from the anion column with a 0.5 *M* HNO_3 solution and stocked in a 5 *M* HNO_3 solution. Pu(III) was eluted with a 0.5 *M* HNO_3 solution containing 0.03 *M* hydroxylamine. Pu(VI) was prepared by heating Pu(IV) in 0.5 *M* HNO_3 solution for several hours with an infrared heater. The oxidation states of Pu(III), Pu(IV), and Pu(VI) were checked by observing the spectrophotometric absorption bands at 560–600, 665, and 820 nm, respectively. Am(III) was stocked in a 0.5 *M* HNO_3 solution after the eluting solution (5 *M* HNO_3) was nearly evaporated.

The decontamination effect of a treated solution was verified by measuring the α-activity in it after the solution was allowed to stand for several minutes. Aliquots of the solution (0.02 mL) were mounted on two to five stainless steel disks (23 mm diameter). The α-activities were measured by a 2π-gas-flow counter. The Decontamination factor (D.F.) was defined as I_i/I_f, where I_i and I_f represent the intensities of α-activity in the initial and final states of a treated solution, respectively.

The aqueous waste solutions of the purification and analytical process of Pu were used as samples of the actual waste. Most of the solutions were of HNO_3. Their acid concentrations were about 1 *M* when they were mixed. They contained Pu, Am, and sizable amounts of many ions such as Fe(III), Cr(III), Ni(II), PO_4^{3-}, and SO_4^{2-}. The amounts of Pu and Am were estimated from the total α-activity, Pu + Am, and the activity ratio Pu/Am. their factors were conventionally given by measuring the α-activity of $^{239(240)}Pu$ and ^{241}Am and the ratio $^{239(240)}Pu/^{241}Am$.

Pu in a solid residue was assayed by measuring the γ-radiation from ^{239}Pu. The activity in the 360–470 keV region was accumulated for 400 s by the use of a NaI(T1) scintillation detector (76 mm diameter × 76 mm thickness). In the meantime, the γ-activities from 20, 40, 60, and 80 mg of Pu (NBS-949d) were measured in the same geometry with the sample for 400 s. The amount of Pu in the sample was determined by comparison with data obtained from the calibrating sources (*16*).

RESULTS AND DISCUSSION

Lead Oxalate as Scavenger

Pb(II) oxalate precipitates immediately in a dilute HNO_3 solution containing oxalic acid when a Pb(II) solution is added. The behavior of Pu and Am with Pb(II) oxalate have been studied as shown in Fig. 1. The ordinate represents the decontamination factor (D.F.) while the abscissa represents the concentration of HNO_3 in a solution containing 0.2 *M* oxalic acid. Pu(IV) is largely eliminated from a dilute HNO_3 solution. A D.F. value of $>10^2$ can be obtained even from a HNO_3 solution of fairly high concentra-

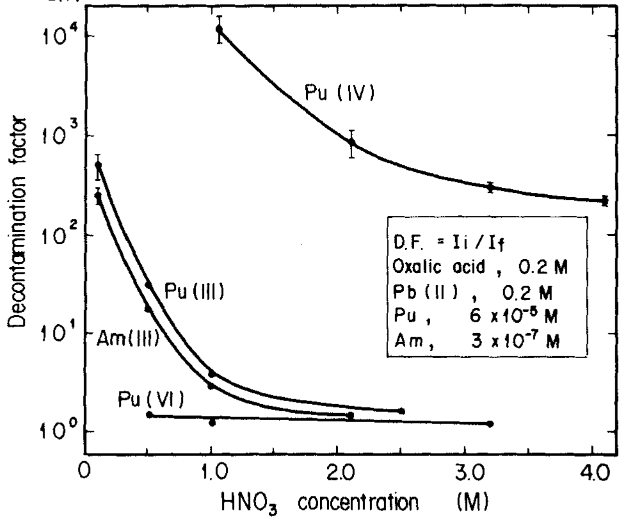


FIG. 1. Behavior of Pu(IV), Pu(VI), Pu(III), and Am(III) with Pb oxalate generated in HNO_3 solution.

tion (<4 *M*). Pu(III) and Am(III) are eliminated from about 0.1 *M* acid solution. Pu(VI) is never removed with the scavenger unless the oxidation state is reduced. From the obtained results, a D.F. value of $>10^2$ can be expected in the decontamination of a solution containing Pu(III), Pu(IV), and Am(III) when the acidity is adjusted to about 0.1 *M* by neutralization with an alkaline reagent such as NaOH (or by dilution with water).

The influence of the oxalic acid and $NaNO_3$ concentrations have also been studied (Fig. 2). The scavenging effects of Pb(II) oxalate for Pu(III) and Am(III) are substantially independent of oxalic acid concentration (0.1–0.3 *M*) in 0.1 *M* HNO_3 solution, as seen in Fig. 2(A). The effects are dependent on $NaNO_3$ concentration in 0.1 *M* HNO_3–0.2 *M* oxalic acid solution, as seen in Fig. 2(B), although the influence is rather small in a solution of <2 *M* $NaNO_3$.

In order to decontaminate a solution containing Pu(VI) by the technique, the oxidation state must be reduced to a lower state, Pu(IV) or Pu(III). H_2O_2 has been selected as the reducing reagent in this work since it does not cause trouble in disposing of the solution. Decontamination of the solution contain-

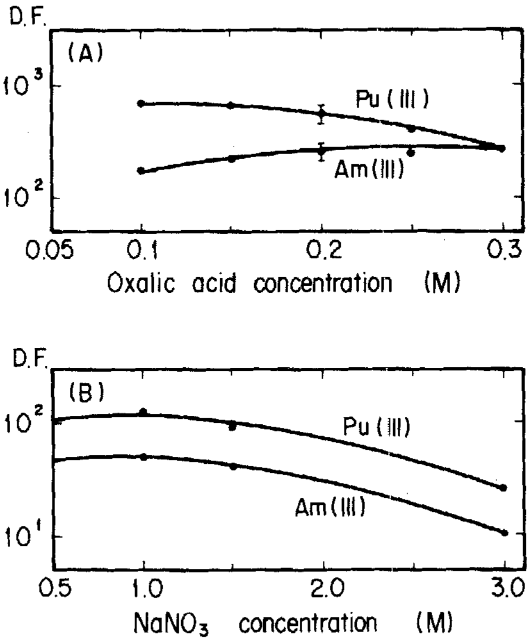
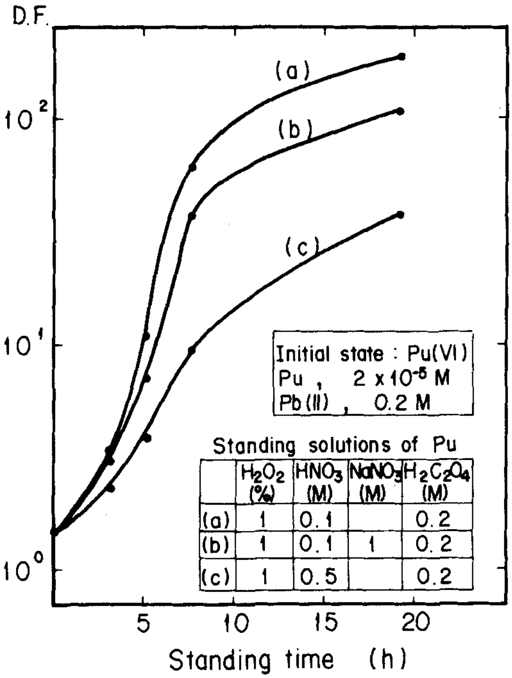


FIG. 2. Behavior of Pu(III) and Am(III) with Pb oxalate generated in (A) oxalic acid–0.1 *M* HNO_3 solution and (B) $NaNO_3$–0.1 *M* HNO_3 solution.

ing Pu(VI) is improved by the addition of H_2O_2 as seen in Fig. 3, although overnight standing at room temperature (~25°C) is necessary. The photometrical absorption band at 820 nm is instantly extinguished by the addition of H_2O_2 to the solution, and the spectrum of Pu(IV) appears gradually in the standing solution.

Decontamination of the Waste

A flow steet for the decontamination of the waste is proposed in Fig. 4. The acidity of the waste is adjusted to about 0.1 *M* (pH ~ 1) with NaOH after oxalic acid and 30% H_2O_2 water have been added (0.2 *M* and 1% solution, respectively). Supernatant I is separated from Precipitate I by decantation. Next, 1 *M* $Pb(NO_3)$ solution is added dropwise to Supernatant I (~1 mL/L of the treated solution) and mixed thoroughly. Supernatant II is again separated from Precipitate II by decantation.



	H_2O_2 (%)	HNO_3 (M)	$NaNO_3$ (M)	$H_2C_2O_4$ (M)
(a)	1	0.1		0.2
(b)	1	0.1	1	0.2
(c)	1	0.5		0.2

FIG. 3. Scavening effect of Pb oxalate for Pu in oxidation states reduced by the addition of H_2O_2 to Pu(VI) solutions.

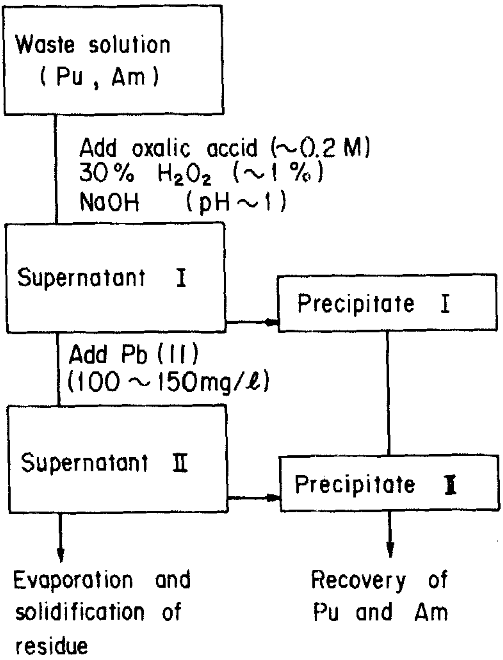


FIG. 4. Flow sheet for the disposal of waste solutions containing Pu and Am.

As a demonstration, 30 L of actual waste were decontaminated by the technique. The wastes were contained in 5-L polyethylene bottles. Each sample differed in acidity and Pu content. Three liters of each, as one batch, were poured into a treatment vessel. Before and after the decontamination, each aliquot of the batch, 0.5 mL, was separated for analysis. The results obtained are shown in Table 1. The decontamination of Supernatant I is not enough, but the activity in Supernatant II is reduced to about 10 μCi/L. The value of the α-activity ratio, 14.3, means that Pu is the main residual actinide. The solution was evaporated under infrared light. The residue was solidified with anhydrous gypsum (*17*).

Separation of Pu and Am

Pu and Am are concentrated in Precipitate I and II as a slurry when the wastes are decontaminated according to the flow sheet of Fig. 4. After dissolution of the precipitates, the actinides are separated from the resultant solution with ion exchange resins.

TABLE 1

		Waste solution	
Starting solution	Volume (l)	30	Estimated values* Pu, 1.89 g Am, 25.6mg
	HNO_3 (M)	~1	
	α activity (mCi/l)	6.80 ± 0.09	
	α ratio (Pu/Am)	1.32	
		Supernatant I	Supernatant II
Decontaminated solution	$[H^+]$ (M)	~0.1	
	$H_2C_2O_4$ (M)	~0.2	
	H_2O_2 (%)	~1	
	Pb(II) (mg/l)		100~150
	α activity (mCi/l)	~4	$(1.03 \pm 0.04) \times 10^{-2}$
	α ratio (Pu/Am)	1.4	14.3
	D.F.		660
		Pu	Am
Recovered Pu and Am	Weight	1.78±0.07 g	22.8±0.5 mg
	Yield (%)	94	89
Pu in undissolved precipitate**		~0.18 g	

* Estimated from total α activity and α ratio (Pu/Am)
** Determined by measuring the γ ray from Pu-239

In order to separate Pu, the slurrys obtained by decontamination of the actual waste were mixed and dissolved by adding an equal volume of concentrated HNO_3 solution. Pb(II) oxalate dissolves easily in the solution [the solubilities of it and $Pb(NO_3)_2$ are shown in Fig. 5]. The solution obtained was poured onto an anion exchange resin column (Dowex 1 × 4, 50–100 mesh). The Pu in the column was washed with 7 *M* HNO_3 solution and then eluted with a 0.5 *M* HNO_3 solution containing 0.03 *M* hydroxylamine.

Am was contained in the effluent (~7 *M* HNO_3 solution) from the anion column. It was separated with a cation exchange resin after being brought to small scale by lead oxalate coprecipitation. The solution was diluted 3 times with water. Oxalic acid was added to make ~0.2 *M* solution. The acidity was reduced to about 0.1 *M* (pH ~ 1) with NaOH. Then the Pb(II) solution was added dropwise and mixed thoroughly. The generated precipitate was separated by decantation. The obtained slurry was made alkaline to dissolve the precipitate. After the solution was acidified again, it was poured onto a

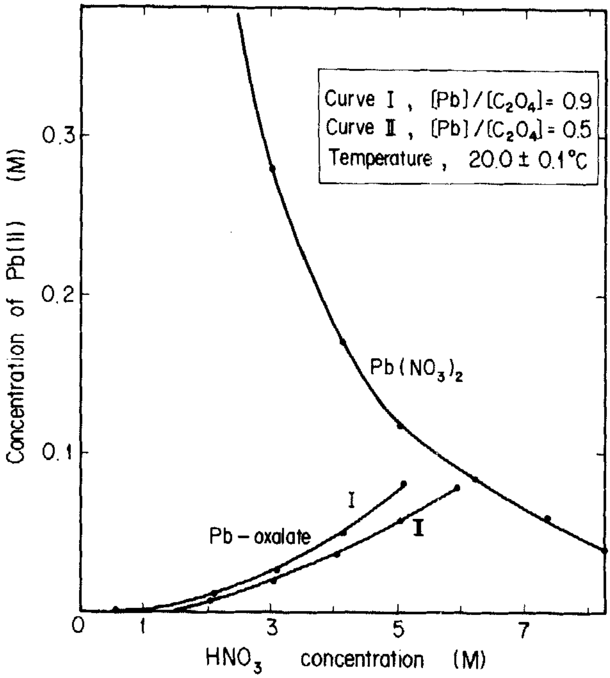


FIG. 5. Solubility of $Pb(NO_3)_2$ and Pb oxalate in HNO_3 solution at 20C.

cation exchange resin column (Dowex 50W × 8, 50–100 mesh). The Am in the column was washed with 0.05 *M* HNO_3 solution, 0.03 *M* oxalic acid solution, and eluted with 5 *M* HNO_3 solution (*17*).

Overall recovery yields of Pu and Am are about 90%. When Precipitates I and II were dissolved in 7 *M* HNO_3 solution, some solid remained in the solution. After being separated, washed with fresh 7 *M* HNO_3 solution, and dried under an infrared heater, the residue (~12 g) was assayed for Pu by measuring the γ-rays from ^{239}Pu. From the results obtained (Table 1), the unrecovered Am and Pu are considered to be fixed in the residue.

CONCLUSIONS

An aqueous waste containing Pu and Am were decontaminated by a two-step process. First, their oxalates were created for their removal. A lead oxalate precipitate was also created for further elimination. The α-activity was reduced from 6.8 mCi/L to 10 μCi/L by these scavenging techniques.

The oxalates of Pu and Am are dense and relatively favorable precipitates for filtration. They precipitate in acid solution, leaving many other metal ions in solution. For these reasons they are often utilized for the treatment of actinides in solution chemistry. Lead oxalate precipitates together with trace amounts of the actinides in conditions similar to those for the formation of Pu and Am oxalates (*18*). Thus the aqueous waste can be decontaminated by the two-step processes without selecting solutions containing macro- and microamounts of the actinides. Lead oxalate is also dense (*d* 5.28), so that it may be a convenient scavenger for the decontamination of a large volume of aqueous solution.

The precipitates obtained by decontamination were dissolved in 7 *M* HNO_3 solution for Pu recovery; lead oxalate dissolves instantly in such a solution. This is very useful in the recovery process. On the other hand, lead oxalate was dissolved in an alkaline solution for Am recovery. It dissolved immediately in the solution. When the solution was acidified again, no precipitates formed. The technique is also advantageous for the separation of Am.

The actinides were recovered from the aqueous waste in about 90% yields. Although the purity of the products was not checked, removal of Pb(II) from them will be necessary when operating on a larger scale (*19, 20*). Most of the unrecovered actinides might be removed with insoluble material in 7 *M* HNO_3 solution. The amount of ^{239}Pu in the insoluble material was determined by γ-ray measurement. The insoluble material is considered to be impurities such as Ca and Si from the alkaline reagent used, since about 1 kg of the reagent was added for the neutralization of HNO_3 in the waste. The Ca(II) ion forms its oxalate precipitate. When a considerable amount of sulfuric ion is contained in the aqueous waste, the Ca(II), and the scavenging ion, Pb(II) may precipitate partially as $CaSO_4$ and $PbSO_4$. Their dissolution is also difficult in 7 *M* HNO_3 solution. The insoluble solid reduces the recovery yields of the actinides. This is an unfavorable aspect of the precipitation technique.

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