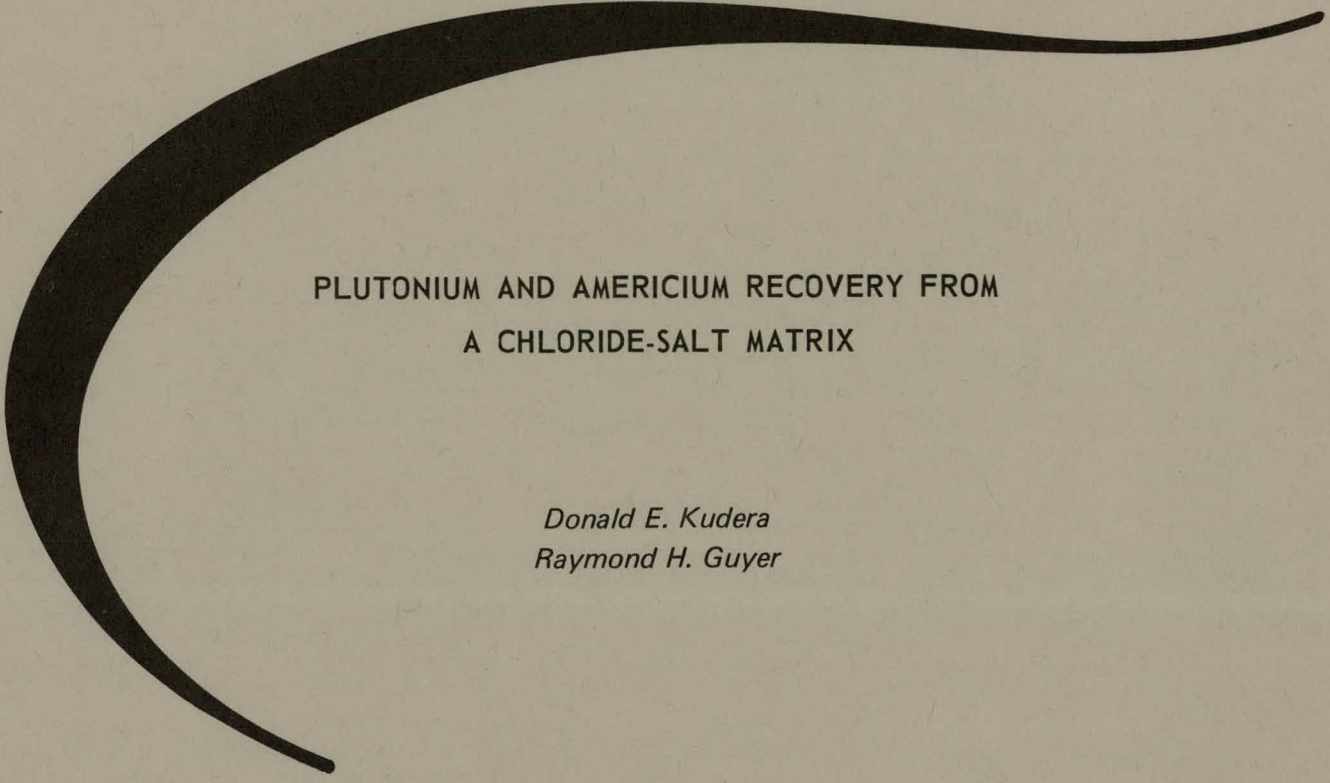


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RFP-1642  
June 4, 1971

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PLUTONIUM AND AMERICIUM RECOVERY FROM  
A CHLORIDE-SALT MATRIX

*Donald E. Kudera  
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Printed in the United States of America  
Available from the  
National Technical Information Service  
U. S. Department of Commerce  
Springfield, Virginia 22151  
Price: Printed Copy \$3.00; Microfiche \$0.65

June 4, 1971  
Publication Date

RFP-1642  
UC-4 - CHEMISTRY  
TID-4500 - 56th Ed.

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**Prepared under Contract AT(29-1)-1106  
for the  
Albuquerque Operations Office  
U. S. Atomic Energy Commission**



## CONTENTS

Abstract . . . . .	1
Summary . . . . .	1
Introduction. . . . .	1
Experimental . . . . .	2
Feed Preparation . . . . .	2
Ion Exchange . . . . .	2
Product Purification. . . . .	3
Results . . . . .	3
Production Results . . . . .	3
Discussion . . . . .	3
Dissolution . . . . .	3
Cation Exchange Adsorption . . . . .	3
Cation Exchange Wash and Elution . . . . .	3
Flow Rates . . . . .	4
Processing of the Americium Effluent . . . . .	4
Future Improvements . . . . .	4
References . . . . .	4

## PLUTONIUM AND AMERICIUM RECOVERY FROM A CHLORIDE-SALT MATRIX

*Donald E. Kudera and Raymond H. Guyer*

**Abstract.** A cation-anion exchange process has been developed for the recovery of americium and plutonium from alkaline, chloride-salt residues. The residues are generated by a molten-salt process used for the extraction of americium from plutonium metal. The salts are dissolved in dilute nitric acid and the chloride is separated from the plutonium and americium by cation exchange. The americium is separated from the plutonium by anion exchange. Kilogram amounts of chloride salts were successfully processed by this cation-anion procedure.

### SUMMARY

A recovery process for separating plutonium and americium from chloride salts has been developed. The chloride residues were generated by a molten salt process used for extracting americium from molten plutonium metal. The objective was to develop a method of separation that could be used routinely on a kilogram scale.

The method developed consisted of loading the plutonium and americium onto cation exchange resin while the chloride anion remained in the effluent solution and was subsequently discarded. The actinides were eluted from the cation resin with nitric acid. The plutonium was loaded onto anion exchange resin while the americium remained in the anion column effluent.

The americium solution was further purified by a thiocyanate anion-cation exchange process. The plutonium was eluted from the anion exchange resin and further purified by peroxide precipitation. Process rates are discussed and suggestions for possible process improvements are also mentioned.

### INTRODUCTION

The americium-241 level in plutonium metal can be reduced by a molten salt extraction process.<sup>1</sup> The process consists of extracting americium from molten plutonium metal into a molten salt phase. The salt

system is composed of 54.5 wt% potassium chloride, 43.0 wt% sodium chloride, and 2.5 wt% magnesium chloride. The extraction is carried out with 2500 grams of plutonium metal, and 2500 grams of combined salt. Approximately 68 wt% of the americium and ~0.6 wt% of the plutonium are extracted into the salt phase with each salt contact. Calculations indicate that each kilogram of salt will contain ~0.7 gram of americium and ~6 grams of plutonium. A process was required to recover the plutonium and americium from the salt system.

Consideration was given to several different methods for processing these salts:

The first method consisted of dissolving the salts in 0.35 *M* nitric acid and separating the plutonium, americium, and chloride by a thiocyanate cation-anion exchange process.<sup>2</sup>

The second method consisted of dissolving the salts in 7 *M* nitric acid so that the plutonium would be in the hexanitrate form for adsorption onto anion exchange resin.<sup>3</sup> The chloride and americium ions would not adsorb on the resin and would separate from the plutonium. The americium would then have to be separated from the chloride by some other procedure.

The third method consisted of dissolving the plutonium-americium contaminated chloride salts in water or caustic. The plutonium and americium could be precipitated as hydroxides by making the solution basic.<sup>3</sup> The chloride-free hydroxide precipitate could be dissolved in nitric acid and the americium separated from the plutonium by anion exchange.

None of the three processes were used because of anticipated corrosion problems, radiation exposure problems, and material through-put limitations.

A fourth process utilizing cation-anion exchange was developed which minimized the processing difficulties mentioned above. The plutonium-americium contaminated chloride salts were dissolved in 0.35 *M* nitric acid. The plutonium and americium were loaded onto cation exchange resin and the chloride was washed



through the resin with 0.35 M nitric acid. The plutonium and americium were eluted with 7 M nitric acid and the plutonium was loaded onto anion exchange resin. The plutonium was eluted with 0.35 M nitric acid and purified by peroxide precipitation.<sup>4</sup> The americium was not adsorbed on the anion resin and remained in the effluent solution. The americium containing effluent was further purified by the thiocyanate cation-anion exchange procedure.<sup>2</sup> Kilogram amounts of chloride salts were successfully processed by this cation-anion method.

## EXPERIMENTAL

### Feed Preparation

Any water soluble chloride salts that are generated by an electrorefining procedure<sup>5</sup> or by a molten salt procedure<sup>1</sup> can be processed by this separation scheme. Figure 1 is a flow diagram of the recovery process.

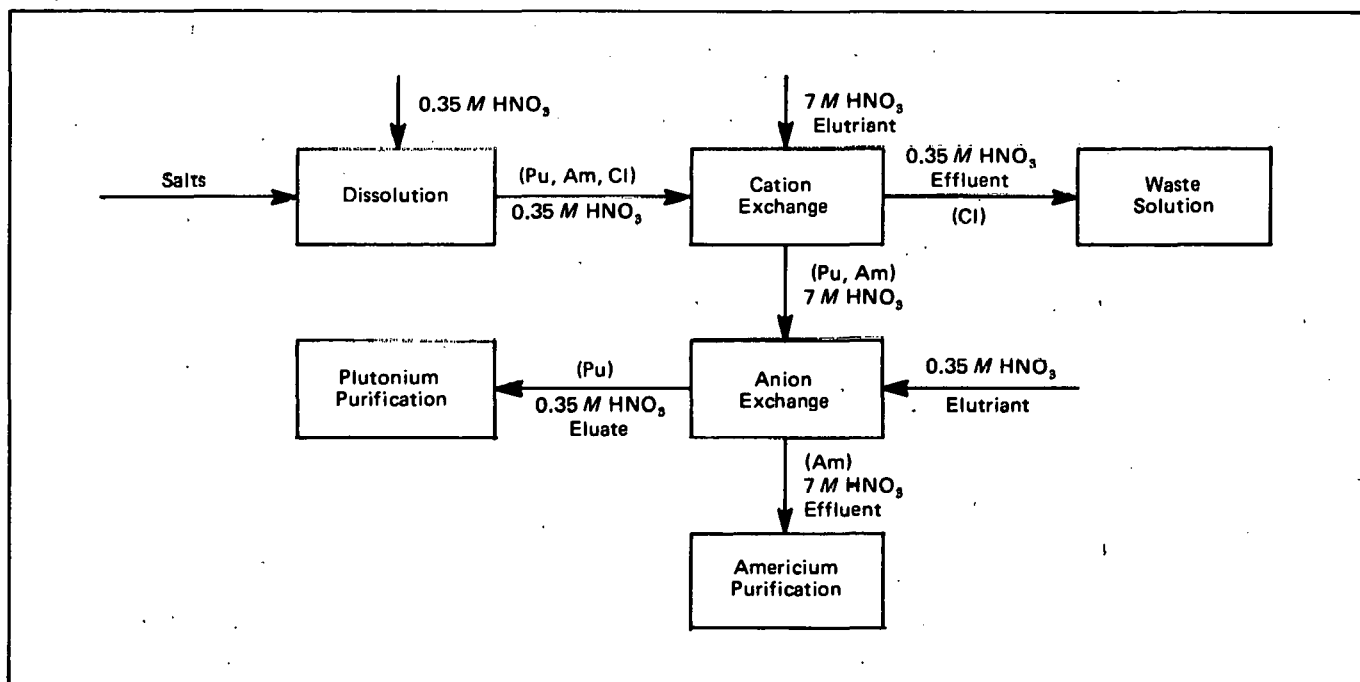
The chloride residues are received in half-gallon, wide mouth plastic containers that have been wrapped in lead foil. The salt is removed from the container and dissolved in 0.35 M nitric acid to a concentration of

1 kilogram of salt in 4 liters of acid. This feed solution contains approximately 1.5 grams of plutonium, 0.17 grams of americium, and 135 grams of chloride per liter. The Pu(IV) and Pu(VI) are reduced to Pu(III) with 1.5 grams of ascorbic acid per liter of feed solution. The solution is diluted with 0.35 M nitric acid to a chloride concentration of 25 grams per liter.

### Ion Exchange

The feed solution is passed through two 6-inch (15.2 cm) by 30-inch (76.2 cm) ion columns in series containing 50-to 100-mesh Dowex® 50-X8 cation resin. The flow is in an upward direction at a rate of 60 liters per hour. Most of the chloride remains in the column effluent. The residual traces of chloride are washed from the column with 0.35 M nitric acid. The plutonium content of the cation effluent is approximately  $4 \times 10^{-3}$  grams per liter. The plutonium and americium are eluted in an upward direction from the cation column with 7 M nitric acid at a rate of 10 liters per hour. This eluate is used as feed solution for an anion column. The plutonium is loaded in an upward direction onto two 6-inch (15.2 cm) by 30-inch (76.2 cm) ion columns in series containing Dowex 1® -X4 (50 to 100 mesh) anion resin.

Figure 1. Plutonium-Amercium Recovery from Chloride Salts.



## Product Purification

The concentration of the americium in the anion column effluent solution is approximately 0.1 gram per liter. The americium is purified by a thiocyanate cation-anion exchange process. The plutonium is eluted from the anion resin with 0.35 *M* nitric acid at a flow rate of 10 liters per hour and at a concentration of 10 grams per liter. Further purification is accomplished using peroxide precipitation.

## RESULTS

Table I shows the average processing rates that were attained for a 30-day processing period. During this period, 150 kilograms of salt were processed.

Table I. Average Process Rates.

	Flow Rate l/hr	Grams of Pu/hr	Grams of Am/hr	Grams of Cl/hr
Cation Feed	60	18.0	1.8	1,500
Cation Effluent	60	0.24	0.0024	1,450
Anion Effluent	10	0.05	1.0	50
Anion Eluate	10	100.0	not analyzed	not analyzed

The average plutonium loss to the cation effluent was 1.3 wt% as calculated from the data in Table I. The cation column system separated an average of 97% of the chloride, which was considered adequate for this process step.

## Production Results

This separation process was used on a routine basis for approximately 80 days. During this time, ~1000 kg salts were processed at a maximum rate of ~14 kg of salt per day.

## DISCUSSION

### Dissolution

The decision to dissolve the chloride salts in hot 0.35 *M* nitric acid was based upon plutonium polymerization data discussed by Cleveland.<sup>6</sup> No evidence of polymerization was observed using hot 0.35 *M* nitric acid for the dissolution of these salts.

A small insoluble residue remained after dissolution and was identified as mainly plutonium dioxide. No significant amount of chloride was found in the oxide residue. The residue was dissolved in 12 *M* nitric acid and 0.1 *M* hydrofluoric acid. The plutonium and americium content of the residue was analyzed at less than 1% of the original amounts of plutonium and americium in the salt matrix. The plutonium was recovered by standard nitric acid anion exchange methods. The small amount of americium was discarded.

### Cation Exchange Adsorption

A reducing agent, ascorbic acid, was added to the dissolved salts to reduce any Pu(VI) formed during the dissolution step to Pu(III) or Pu(IV). This improved cation adsorption which is more favorable for Pu<sup>3+</sup> or Pu<sup>4+</sup> than for PuO<sub>2</sub><sup>2+</sup>.

Another important process parameter was the dilution of the chloride feed solution with 0.35 *M* nitric acid. Incomplete loading of the plutonium and americium onto the cation resin was experienced from high chloride feed solutions. Previous work<sup>7</sup> suggested the formation of a plutonium chloride anion complex. Experimental work demonstrated that the distribution coefficient of both plutonium and americium increased as the chloride concentration decreased. A chloride concentration of less than 35 grams per liter gave satisfactory distribution coefficients.

Since a dilution of the chloride concentration was necessary, a study was made to determine the difference between dilution with water and dilution with 0.35 *M* nitric acid. When the dilution was made with water, the plutonium concentration of the cation effluent was approximately 0.02 gram per liter. However, when the dilution was made with 0.35 *M* nitric acid, the plutonium concentration of the cation effluent was approximately 0.004 gram per liter. The undesirable results from the water dilution were probably the result of polymer formation.<sup>6</sup>

### Cation Exchange Wash and Elution

The chloride was easily removed from the cation column with two column volumes of wash. Although decontamination from other impurities was not investigated, it is reasonable to assume that sodium, potassium, and magnesium decontamination could be improved by increasing the volume of wash.

The elution of the plutonium and americium from the cation resin with 7 M nitric acid was only ~50 grams per hour. An attempt was made to increase the elution rate of the two actinides by using 12 M nitric acid. No apparent increase in the elution rate was observed. Further studies to improve the elution rate<sup>9</sup> are proposed using reducing agents such as hydrazine and ferrous sulfamate.

### Flow Rates

The flow rates used were typical for large anion column work. An increase in some of these flow rates would be beneficial to the through-put of the process provided the recovery efficiency is not adversely affected. Therefore, studies to optimize the flow rates of the process are recommended.

### Processing of the Americium Effluent

The anion column effluent containing the americium had very few common elemental impurities as shown in Table II. The results were obtained by optical emission spectrography, except for the plutonium and americium which were determined by radiometric methods.

Table II. Average Anion Effluent Impurities.

Element	Concentration g/l
Al	0.1
Ca	0.02
Cr	0.2
Fe	1.0
K	2.0
Mg	0.2
Na	1.0
Ni	0.02
Pb	0.02
Sn	0.02
Pu	0.005
Am	0.1

No difficulties were experienced with the separation of americium from the anion effluent column impurities using the thiocyanate cation-anion exchange process.<sup>2</sup> A significant decrease in the sodium and potassium concentration is anticipated by increasing the volume of cation exchange wash.

### Future Improvements

The plutonium and americium in the chloride salts can be pyrochemically reduced into a concentrated metallic (black) phase.<sup>8</sup> A plutonium free chloride (white) phase would be produced which could be discarded. The weight and volume of material to process would be substantially reduced.

A more expedient process than ion exchange might be the dissolution of the chloride salts in water or caustic followed by a precipitation of the plutonium and americium as hydroxides.<sup>3</sup> The present difficulty with this proposed procedure is the slow filtration of the gelatinous hydroxide precipitate. If this filtration difficulty could be overcome, the hydroxide separation procedure would require less processing time than the cation-anion exchange process.

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