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## CURIUM PROCESS DEVELOPMENT

II-I. SEPARATION OF AMERICIUM FROM CURIUM  
BY PRECIPITATION OF  $K_3AmO_2(CO_3)_2$

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Chemical Separations Processes  
for Plutonium and Uranium  
(TID-4500)

## CURIUM PROCESS DEVELOPMENT

### II-I. SEPARATION OF AMERICIUM FROM CURIUM BY PRECIPITATION OF $K_3AmO_2(CO_3)_2$

by

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### ABSTRACT

A chemical process was developed for the separation of  $^{243}\text{Am}$  from  $^{244}\text{Cm}$  for use in the production of kilogram quantities of  $^{244}\text{Cm}$ . In the process, americium is oxidized to  $\text{AmO}_2^+$  ion in concentrated potassium carbonate solution, and  $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$  is precipitated. A study of the variables affecting the separation is reported.

## FOREWORD

This report is one in a series that describes the development of separations processes for purifying  $^{244}\text{Cm}$  produced in Savannah River reactors. The series is being issued under the general title Curium Process Development. Following the general title, a roman numeral designates the subject area of the report, and an arabic numeral designates the series report number in that subject area. A subtitle describes the content of each report. Subject areas foreseen for this series are:

- I. General Process Description
- II. Chemical Processing Steps
- III. Analytical Chemistry Support

Reports issued in this series include:

- I. General Process Description by I. D. Eubanks and G. A. Burney (USAEC Report DP-1009).
- III-1. Analytical Techniques for Characterizing Solvent by R. Narvaez (USAEC Report DP-1010).
- III-2. Identification of Solvent Degradation Products by D. L. West and R. Narvaez (USAEC Report DP-1016).
- III-3. Analytical Control by E. K. Dukes (USAEC Report DP-1039).

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## INTRODUCTION

About 5.5 kilograms of  $^{244}\text{Cm}$  is being produced at Savannah River for evaluation as an isotopic heat source. In this program, curium is produced from  $^{239}\text{Pu}$  in two successive reactor irradiations. The  $^{244}\text{Cm}$  is separated from the targets of the second irradiation and purified; residual plutonium (predominantly  $^{242}\text{Pu}$ ) and  $^{243}\text{Am}$  are recovered and can be used for subsequent irradiations to produce additional  $^{244}\text{Cm}$ . A general description of the overall program has been given in previous reports.<sup>(1,2)</sup>

In the separations process planned for use at Savannah River, the irradiated targets are dissolved in nitric acid, and plutonium is recovered by a conventional solvent extraction process with dilute tributyl phosphate (TBP). The americium and curium are then recovered from the aqueous raffinate by batch extraction with 50% TBP in kerosene;<sup>(3)</sup> lanthanide fission products are extracted with the americium and curium. The lanthanides are subsequently rejected in a solvent extraction process in which americium and curium are extracted from lithium chloride solution into a mixture of tertiary amine hydrochlorides in diethylbenzene.<sup>(2,4)</sup>

Processing steps were required for use following the amine solvent extraction process to separate the americium from the curium and to isolate both in a form suitable for the preparation of purified  $\text{CmO}_2$  and  $\text{AmO}_2$ . On the basis of information reported in the literature<sup>(5-7)</sup> and preliminary laboratory tests, separation by carbonate precipitation was chosen for development. Americium is separated by oxidation to  $\text{AmO}_2^+$  ion in potassium carbonate solution followed by precipitation as the double carbonate. This report summarizes the laboratory development of the carbonate precipitation method. The work had the following principal objectives:

- Development of a suitable method for coupling the carbonate process with the amine solvent extraction process.
- Determination of optimum conditions for the carbonate precipitation.
- Determination of the effects on process performance of radiation-induced chemical reactions at high curium concentrations.
- Selection and demonstration of a method for recovering the curium from the filtrate solution containing potassium carbonate.
- Evaluation of the usefulness of the method for routine production operation.

## SUMMARY

A chemical process was developed for the separation of americium from curium by precipitation of  $K_3AmO_2(CO_3)_2$  from concentrated potassium carbonate solution. In addition, auxiliary processing steps were developed to couple the carbonate precipitation process to a preceding amine solvent extraction process, and to recover the separated americium and curium in a form suitable for the preparation of purified  $AmO_2$  and  $CmO_2$ . The sequence of process steps is summarized in Figure 1. All of the steps were tested on a scale of  $\sim 2$  g  $^{244}Cm$ , with concentrations of  $^{243}Am$  and  $^{244}Cm$  typical of those expected in a production process.

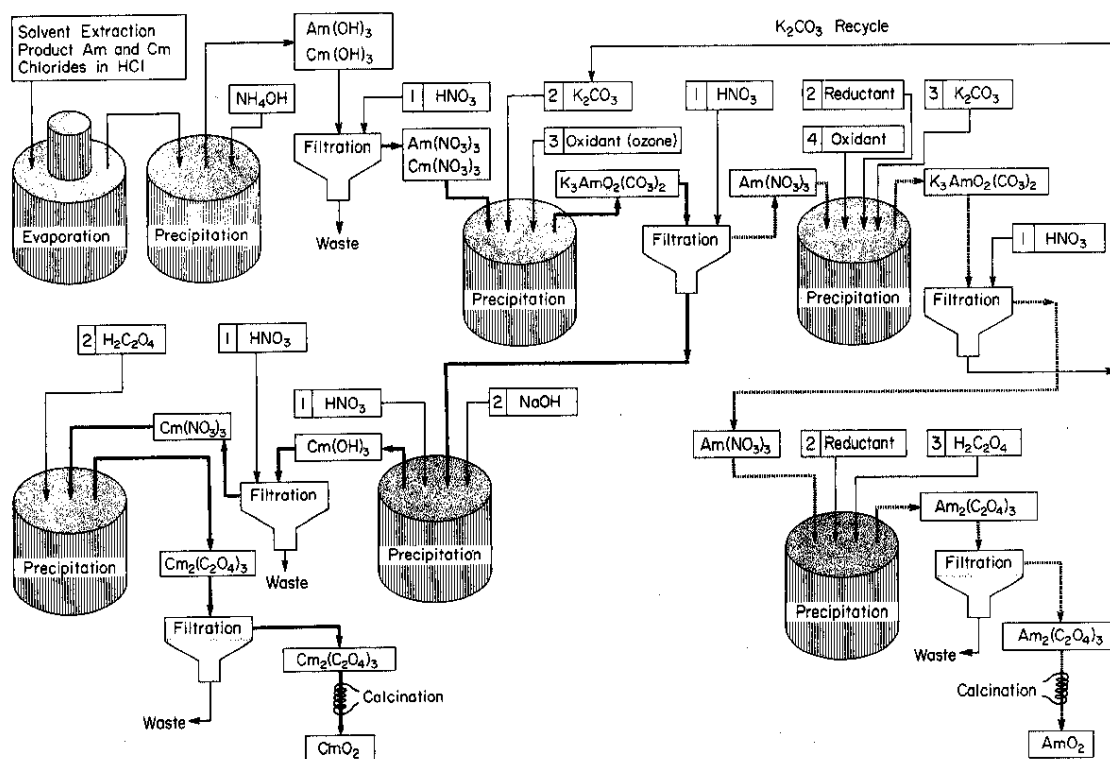


FIG. 1 SEPARATION OF AMERICIUM FROM CURIUM AND PREPARATION OF OXIDES



Two sequential cycles of carbonate precipitation were required to obtain adequate separation and recovery of americium and curium when the americium and curium were present in approximately equal quantity. After two cycles, each product contained less than 0.5 wt % of the other actinide.

Ozone was the most satisfactory oxidant tested for the oxidation of Am(III) to Am(V) in concentrated potassium carbonate solution. The complete oxidation and precipitation of the americium required from 1 to 2 hours at 60-80°C in 3.5M  $K_2CO_3$ . The precipitate, identified by analysis as  $K_3AmO_2(CO_3)_2 \cdot H_2O$ , was crystalline and was readily filtered.

The carbonate precipitation was coupled to the preceding amine solvent extraction process most effectively by precipitating americium and curium hydroxides from the solvent extraction product and redissolving the hydroxides to form feed for the carbonate process. Following the carbonate precipitation cycle, the curium was recovered from the carbonate filtrate by another hydroxide precipitation step.

The major losses of americium and curium in the overall process were due to incomplete separation of the actinides from each other; total losses were less than 0.5% of each actinide.

## EXPERIMENTAL

Laboratory tests were performed with solutions that contained  $^{243}Am$ ,  $^{244}Cm$ , and fission products in concentrations similar to those planned for use in the kilogram-scale processing of  $^{243}Am$  and  $^{244}Cm$ . About 2 grams each of curium and americium were used in each test.

Precipitation studies were done in small glass vessels; the precipitator was heated or cooled in a water bath maintained within  $\pm 3^\circ C$  of the stated temperature.

Am(III) was oxidized in potassium carbonate solution with potassium hypochlorite, potassium peroxydisulfate, or ozone. Potassium hypochlorite solution was prepared by bubbling chlorine into dilute potassium hydroxide solution; potassium peroxydisulfate solution was prepared from the reagent-grade chemical; and ozone was produced with an OREC\* Model 0306 generator at a concentration of approximately 3 vol % in oxygen. Potassium hypochlorite and potassium peroxydisulfate solutions were added to the solution of Am(III) and Cm(III) in potassium carbonate. The ozone-oxygen gas

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\* Ozone Research & Equipment Corp., Phoenix, Arizona.

mixture was passed through a calibrated flow meter and then through a solution of potassium carbonate at the same temperature as the precipitator to saturate the gas stream with water vapor before passage through the precipitator. The ozone content of the gas mixture from the generator was determined by absorbing the ozone from a measured volume of gas in potassium iodide solution and titrating the iodine produced with standard sodium thiosulfate.<sup>(8)</sup>

The curium content of the solutions was determined by alpha counting and alpha spectrometry. The americium content was determined by extraction and gamma counting<sup>(9)</sup> of the  $^{238}\text{Np}$  daughter of  $^{243}\text{Am}$  after a known period of in-growth.

The concentrated curium product was stored in tantalum tubes to maintain purity.

Special precautions were necessary to handle gram quantities of curium in concentrations of 1 to 100 grams per liter. These included diluting the hydrogen evolved from aqueous solution to maintain nonexplosive conditions, shielding to regulate neutron exposure, containment for the high levels of alpha activity, precautions to prevent loss of curium in aerosols formed by radiolysis, and care in handling and storage to maintain product purity.

## DISCUSSION

### PROCESS SELECTION

Precipitation, solvent extraction, and ion exchange methods were considered for the separation of americium from curium. The precipitation methods considered included:

- Oxidation of Am(III) to Am(V) in potassium carbonate and precipitation of  $\text{K}_3\text{AmO}_2(\text{CO}_3)_2$ .<sup>(5-7)</sup>
- Oxidation of Am(III) to Am(VI) in dilute acid solution and precipitation of curium(III) fluoride.<sup>(7)</sup>
- Oxidation of Am(III) to Am(VI) in dilute acid solution and precipitation of curium(III) oxalate.
- Oxidation of Am(III) to Am(VI) in dilute carbonate, bicarbonate, or hydroxide solution and precipitation of curium(III) hydroxide.<sup>(7)</sup>

All of these precipitation methods depend, for the separation of americium and curium, upon the oxidation of Am(III) to a higher oxidation state. The first method, the precipitation of  $K_3AmO_2(CO_3)_2$ , was chosen for further development as a production process. A number of considerations led to this choice, which is the only one of the procedures in which the americium, rather than the curium, is precipitated. Precipitation of the americium avoids the intense alpha radiolysis from a curium precipitate that would prevent complete oxidation of americium. Also, the feed for the  $K_3AmO_2(CO_3)_2$  method is a homogeneous solution of americium and curium; whereas the feed for those procedures carried out in dilute carbonate, bicarbonate, or hydroxide solutions is a slurry of americium and curium hydroxides. The oxidation and leaching of americium from such precipitates is difficult and inefficient. The methods that rely upon maintaining americium as soluble Am(VI) are inefficient in solutions containing high concentrations of curium as a result of reduction of Am(VI) by radiolysis products. The oxalate method is inefficient because oxalate ion reduces Am(VI). Finally, the fluoride method is objectionable because of the neutron radiation from  $(\alpha, n)$  reactions with fluoride ion.

A number of potential ion exchange and solvent extraction methods would depend on the considerable difference in distribution coefficients or extraction coefficients for  $AmO_2^{2+}$  and  $Cm^{3+}$ ; however, all the common ion exchange resins and organic extractants reduce  $AmO_2^{2+}$  to  $Am^{3+}$  rapidly in chloride, nitrate, sulfate, and carbonate solutions, and thus interfere with the americium-curium separation.

Separation of Am(III) from Cm(III) by chromatographic elution with 4M  $LiNO_3$  from anion exchange resin<sup>(10, 11)</sup> is reasonably satisfactory, but the absorption of large quantities of curium on anion exchange resin produces severe problems of column gassing and resin degradation. Chromatographic separation of americium and curium with a chelating organic acid from cation exchange resin is also possible, but the separation efficiency is low, and gassing and resin degradation would be troublesome in large-scale application.

## PROCESS DEVELOPMENT

### Coupling Step

In the planned chemical process, americium and curium are purified from lanthanide fission products by solvent extraction with an amine extractant from concentrated lithium chloride solution.<sup>(2)</sup> The product of the solvent extraction process contains ~1 g of curium and ~1 g of americium per liter, in 6M HCl. For compatibility with the subsequent precipitation of  $K_3AmO_2(CO_3)_2$ ,

the actinides must be concentrated fifty- to one hundredfold, and 99.9% of the hydrochloric acid must be removed.

Three alternative processes to obtain the desired composition were evaluated in the laboratory:

- Tenfold concentration by evaporation, precipitation of americium and curium hydroxides, and redissolution of the hydroxides in nitric acid to the required actinide and acid concentrations.
- Fiftyfold concentration by evaporation, and subsequent self-radiolysis to decompose hydrochloric acid.
- Fiftyfold concentration by evaporation, and subsequent electrolysis to decompose hydrochloric acid.

The first process was selected because it is the only method that provides a needed separation of the americium and curium from lithium chloride, an impurity from incomplete phase separation in the solvent extraction contactors. Separation from lithium chloride is necessary because of the relatively low solubilities of lithium carbonate and potassium chloride in the 3.5M  $K_2CO_3$  required in the separation of americium from curium. These salts would contaminate the  $K_3AmO_2(CO_3)_2$  precipitate and would accumulate to relatively high concentrations in the process because of the planned recycle of the  $K_2CO_3$  filtrate solution.

Evaporation and Precipitation of Cm-Am Hydroxides. The selected coupling process was demonstrated in laboratory tests both with simulated process solutions and with samples of americium-curium product solution obtained from laboratory-scale solvent extraction tests. The solutions were evaporated tenfold without significant foaming caused by the organic impurities, and americium and curium hydroxides were precipitated with either concentrated sodium hydroxide or ammonium hydroxide. Sodium hydroxide precipitant provides limited separation from amphoteric cations (e.g.,  $Al^{3+}$ ,  $Sn^{4+}$ ); ammonium hydroxide provides limited separation from cations that form soluble ammine complexes (e.g.,  $Ni^{2+}$ ,  $Ag^+$ ,  $Zn^{2+}$ ). Hydroxides precipitated with ammonium hydroxide filter more rapidly and are more dense than those precipitated with sodium hydroxide. Either precipitant quantitatively precipitates the americium and curium and effectively separates them from lithium. Typically, dilute solvent extraction product solution containing ~1 g Am/l and ~1 g Cm/l in ~0.1M LiCl and 6M HCl could be converted by this process to a solution containing ~50 g Am/l and ~50 g Cm/l, ~0.04M LiCl, ~0.2M HCl, and 0.25M  $HNO_3$ . This represents a concentration factor of 50, removal of >99.9% of the chloride, and a lithium separation factor of ~125.

Important considerations in the americium-curium hydroxide precipitation process were the relative bulk of the precipitate and the filtration times. These properties were affected by the choice of precipitant and by the amount of lithium chloride impurity present in the americium-curium solution. Tests were made with lanthanum as a stand-in for americium and curium to evaluate these effects and to specify the limit for lithium chloride in the feed solution for the hydroxide precipitation step. The tests, summarized in the following table, show the adverse effects of increased concentrations of lithium chloride and the superior filtration of hydroxides prepared with ammonium hydroxide. The feed solutions for these tests contained 10 g La/l, 6M HCl, and LiCl. The hydroxides were precipitated by adding 12M NH<sub>4</sub>OH to the feed solution (direct precipitation), or by adding the feed solution to 12M NH<sub>4</sub>OH or to 15M NaOH (reverse precipitation).<sup>\*</sup> The data indicate that ~1M LiCl in the feed to the hydroxide precipitation step is the maximum compatible with the planned processing times. This is equivalent to 0.1M LiCl in the solvent extraction product, or to 0.3% entrainment of 11M LiCl in the organic phase in the second amine solvent extraction cycle.

#### Precipitation of Lanthanum Hydroxide

30-minute precipitation periods, ~30°C

<u>LiCl in Feed, M</u>	<u>Relative Filtration Time</u>	<u>Relative Bulk</u>
<u>Direct Precipitation with NH<sub>4</sub>OH</u>		
0	1.0	1.00
1	1.0	1.00
4	5.0	1.44
4(a)	6.4	1.92
<u>Reverse Precipitation with NH<sub>4</sub>OH</u>		
1	1.1	1.10
<u>Reverse Precipitation with NaOH</u>		
0	14	1.15
4	31	1.54

(a) Feed contained 1M HCl

\* Scouting tests of the precipitation of hydroxides by the addition of sodium hydroxide to the feed solution resulted in prohibitively long filtration times.

Alpha Radiolysis. In other tests, the rate of depletion of hydrochloric acid in curium solutions by self-radiolysis was determined, and the practicability of using this method of acid depletion in the coupling step was evaluated. The rate of depletion of hydrochloric acid increased as expected with increasing concentration of curium in the solution. About 40 hours would be required to reduce the residual hydrochloric acid to the goal value of ~0.3M after about fiftyfold evaporation of the amine solvent extraction product solution (to ~50 g Cm/l in 6M HCl). Although the rate of depletion was compatible with the planned process time cycles, the need to separate lithium chloride in the coupling operation excluded this method from further consideration.

Electrolysis. After a sample of product solution from the amine solvent extraction was evaporated about fortyfold (to ~40 g Cm/l, 6M HCl), the hydrochloric acid was reduced to ~0.3M in 45 minutes by electrolysis in a small glass cell equipped with platinum electrodes. The cell was operated at ambient temperature, 1.8 to 2.0 volts DC, and a cathode current density of ~0.2 amp/cm<sup>2</sup>. Foaming in the electrolysis cell was acceptably low for efficient operation at large scale. However, as in the case of alpha radiolysis, the electrolytic method of hydrochloric acid depletion was rejected because of the need to separate the curium and americium from lithium.

#### Solubility of Am(III) and Cm(III) in Potassium Carbonate Solution

After the coupling step, the concentrated solution of americium and curium in nitric acid is added to potassium carbonate to prepare a solution suitable for the separation of americium from curium by precipitation of  $K_3AmO_2(CO_3)_2$ . For maximum separation efficiency and to minimize cross-contamination of the separated americium and curium, high concentrations of americium and curium are required in the potassium carbonate solution. To determine optimum process conditions, the solubilities of Am(III) and Cm(III) in potassium carbonate solutions were measured.

The solubility data, summarized in Figure 2, show that Am(III) and Cm(III) are appreciably soluble in strong potassium carbonate solution. The solubilities increase with increasing potassium carbonate concentration, presumably because of the formation of soluble carbonate complexes. The equilibrium solubilities are only slightly dependent upon temperature in the range studied.

Concentrations of ~15 g Am/l and ~15 g Cm/l in 3.5M  $K_2CO_3$  were chosen as optimum for the americium-curium separation.

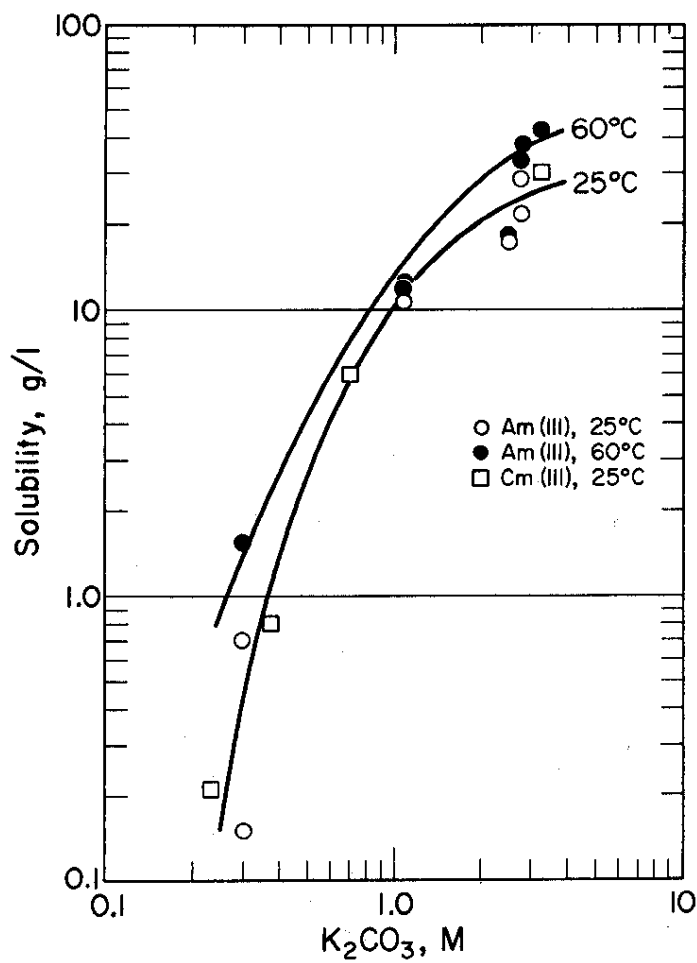


FIG. 2 SOLUBILITY OF Am(III) AND Cm(III) IN POTASSIUM CARBONATE SOLUTION

### Precipitation of $K_3AmO_2(CO_3)_2$

A solution of americium and curium of the composition desired for the precipitation of  $K_3AmO_2(CO_3)_2$  was prepared by adding slowly with mixing a solution containing 50 to 75 g/l each of americium and curium in  $\sim 0.25M$   $HNO_3$  to  $\sim 5M$   $K_2CO_3$  at  $65^\circ C$ . Heating to  $65^\circ C$  increased the rate of dissolution.

The  $Am(III)$  was oxidized to  $Am(V)$  with ozone, potassium peroxydisulfate, or potassium hypochlorite. When the reaction was carried out at 65 to  $80^\circ C$ ,  $AmO_2^+$  was formed slowly and precipitated as  $K_3AmO_2(CO_3)_2$  — a finely divided, tan-brown solid, which was readily filtered. Ozone is the most satisfactory oxidant for process use because it introduces no undesirable cationic impurities. In a typical oxidation test with 3 vol % ozone in oxygen from a commercial generator, 75 to 100 moles of ozone per mole of americium was required for complete oxidation when the gas mixture was passed at 3 l/min through 75 to 100 ml of solution at  $70^\circ C$ .

In tests with the other oxidants, potassium hypochlorite or potassium peroxydisulfate solution was added to the carbonate solution of americium and curium until the oxidant concentration reached  $\sim 0.1M$ . Then, the combined solutions were heated 1 to 2 hours at  $75^\circ C$ . Greater than 99% of the americium was precipitated when the americium concentration was  $> 5$  g/l. With these oxidants, some  $K_2S_2O_8$ ,  $K_2SO_4$ , or  $KCl$  may precipitate because of their limited solubility in concentrated potassium carbonate solution.

An additional advantage in the use of ozone is that a smaller volume of waste solution is produced. The relatively low solubilities of  $K_2S_2O_8$ ,  $K_2SO_4$ , and  $KCl$  in potassium carbonate solution require the use of larger volumes of solution to attain the desired concentrations of  $KOCl$  and  $K_2S_2O_8$ . For example, the volume of waste solution resulting from the separation of a given quantity of americium and curium using  $K_2S_2O_8$  as an oxidant is  $\sim 50\%$  greater than that resulting from the use of ozone.

When the feed contained equal quantities of americium and curium, a reprecipitation of  $K_3AmO_2(CO_3)_2$  was necessary to meet the goal limit of  $\leq 0.5$  wt % Cm in the separated americium. The americium salt from the first precipitation carried 3 to 5% of the curium, which could not be removed by exhaustive washing with carbonate solution. When the  $K_3AmO_2(CO_3)_2$  precipitate was dissolved in nitric acid and reprecipitated, the curium content was reduced to  $\sim 0.5$  wt %. In a repetitive production operation the  $K_2CO_3$  filtrate from the second precipitation cycle, containing several percent of the curium, can be conveniently recycled by using it as the precipitating solution for the subsequent first



cycle precipitation step. The curium remaining in the carbonate filtrate of the first cycle precipitation is sufficiently free of americium (<0.5 wt %) to be processed without additional purification.

Am(V) prepared by dissolving  $K_3AmO_2(CO_3)_2$  in nitric acid is not completely reduced to Am(III) for periods of several days. This transient stability could not be exploited to simplify the second precipitation cycle, however, because when a solution of Am(V) is added to concentrated potassium carbonate solution, the  $K_3AmO_2(CO_3)_2$  precipitate formed is extremely difficult to filter. Therefore, a reductant (such as hydroxylamine) is added to the acid solution of Am(V) to ensure complete reduction to Am(III) before the potassium carbonate solution is added in preparation for the reprecipitation.

Analysis of the americium compound precipitated from 3.5M  $K_2CO_3$  by ozone oxidation established its composition to be  $K_3AmO_2(CO_3)_2 \cdot H_2O$ . An air-dried sample was weighed, and then dissolved immediately (to limit radiolytic degradation) in an excess of standardized acid. Carbonate was determined by the quantity of standardized acid reacted. Americium was determined by the method described previously. Potassium was determined by atomic absorption spectroscopy, after separation of Am(III) by absorption on  $CaF_2$ .<sup>(12)</sup> Total oxygen was determined on a separate sample by inert gas fusion and gas chromatography in a Nitrox-6 Analyzer.\* Water content was calculated by difference and from the total oxygen content. Observed values were: 22.0 wt % K, 45.6 wt % Am, 22.5 wt %  $CO_3^{2-}$ , 28.0 wt % oxygen; theoretical values are: 22.1 wt % K, 46.0 wt % Am, 22.7 wt %  $CO_3^{2-}$ , 27.2 wt % oxygen.

The solubility of  $K_3AmO_2(CO_3)_2$  in 3.5M  $K_2CO_3$  is 10 to 40 mg Am/l. These values were obtained from numerous precipitation tests in which ozone was used to oxidize americium, and the precipitate was separated from the supernatant solution immediately after oxidation was complete. An attempt was made to measure equilibrium solubilities by equilibrating  $K_3AmO_2(CO_3)_2$  precipitate with solutions containing 0.1 to 5.5M  $K_2CO_3$  and 0.005M  $K_2S_2O_8$  for a period of 72 hours. The results were erratic; the indicated solubilities ranged between 15 and 50 mg Am/l and were not dependent upon the carbonate concentration. The data were probably influenced by partial reduction of Am(V) to Am(III).

\* Laboratory Equipment Corporation, St. Joseph, Michigan.

### Recovery of Curium from Potassium Carbonate Filtrate

After americium is separated from the curium by precipitation of  $K_3AmO_2(CO_3)_2$ , the Cm(III), which is strongly complexed in 3.5M  $K_2CO_3$ , must be separated from the filtrate. Five methods were tested for precipitating the curium from the filtrate; the method chosen for the process involves reaction of the carbonate solution with nitric acid and subsequent precipitation of curium(III) hydroxide from the  $KNO_3-HNO_3$  solution. This was the only method that gave both quantitative precipitation of curium and adequate separation from potassium ion. The other methods tested and the reasons they were rejected were:

- Reaction of the carbonate solution with nitric acid, followed by precipitation of curium(III) oxalate from the  $KNO_3-HNO_3$  solution. Potassium acid oxalate is carried with the curium(III) oxalate from the highly salted solution.
- Precipitation of curium(III) hydroxide directly from the carbonate filtrate with sodium hydroxide. Curium hydroxide could not be precipitated quantitatively when the carbonate filtrate was adjusted to 3M NaOH.
- Precipitation of curium(III) oxalate directly from the carbonate filtrate with oxalic acid. Carbonate complexing of curium(III) is so strong that curium oxalate is not precipitated when oxalate ion is added directly to the 3.5M  $K_2CO_3$  filtrate.
- Precipitation of curium(III) cupferrate, mandelate, or tricarballoylate by addition of the ammonium salts of these compounds to the carbonate filtrate. Curium was not precipitated from the carbonate filtrate with tricarballoylate or mandelate ions. When the carbonate solution was adjusted to 0.2M cupferron a voluminous precipitate containing >99.5% of the curium formed immediately. The solid was easily filtered and was decomposed to curium oxide at  $\sim 225^\circ C$ ; however, it was not adequately separated from potassium.

To prepare the  $CmO_2$  product, the curium hydroxide is dissolved in nitric acid, curium(III) oxalate is precipitated, and the oxalate is calcined in air at 600 to  $700^\circ C$ .

## ACKNOWLEDGMENTS

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