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CURIUM PROCESS DEVELOPMENT

III-3. ANALYTICAL CONTROL

by

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ABSTRACT

Established methods were modified and new methods were developed to provide analytical control for demonstration of the process to separate and purify curium from lanthanides and americium. Included are methods for determining americium, amine, californium, curium, lanthanum, lithium, and nitrate.

FOREWORD

This report is one in a series that describes the development of separations processes for purifying ^{244}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).

CONTENTS

INTRODUCTION

Irradiation of ^{239}Pu for production of 4.5 kg of ^{244}Cm at Savannah River started in May 1964.(1) The curium will be processed and ready for delivery as CmO_2 in 1967. Irradiated target elements will be dissolved, and the residual plutonium will be recovered by solvent extraction in a production facility of the Savannah River Plant. In this initial phase of the process, aluminum and some of the fission products will be separated from americium, curium, and rare earths by batch extraction with 50% tri-n-butyl phosphate (TBP).(2) This crude mixture of americium and curium will then be processed in a special facility at the Savannah River Laboratory (SRL). The americium and curium will be separated from rare earths by a modification of the amine extraction process developed at Oak Ridge National Laboratory.(3) In finishing steps, the curium will be separated from the americium by precipitation as the carbonate, and then will be converted to the oxide. (The curium process is described in the Appendix.)

During the past two years, tests have been made in miniature mixer-settlers at SRL to demonstrate the feasibility of the extraction process for the production of pure curium from the crude mixture. Analytical support for the laboratory tests required many different analyses for radioactive and nonradioactive constituents. This report describes methods that were developed or adapted for studies of the separation of americium and curium from rare earths by amine extraction and separation of americium from curium by carbonate precipitation.

SUMMARY

Demonstrations of the amine extraction and carbonate precipitation processes for separation and purification of americium and curium required accurate determinations of americium and curium, and close control of the concentration of acid in the amine extractant. In addition, methods were required for determination of aluminum, amine, lanthanum, lithium, nitrate, californium, and rare earths.

Successful analytical methods established for process control include potentiometric titrations for acid and amine, complexometric titrations for aluminum and rare earths, a mass spectrometric method for lanthanum, a flame photometric analysis for lithium, a neutron counting method for californium, a spectrometric method for nitrate, and three independent methods for americium. Curium-244 was determined in all solutions by direct alpha counting.

DISCUSSION

CONSTITUENTS CONTROLLED

Constituents that were controlled to ensure that the process operated efficiently are listed in Table I.

TABLE I

ANALYSES FOR PROCESS CONTROL

Constituent	Method
Acid	Potentiometric Titration
Amine	Potentiometric Titration
Aluminum	Complexometric Titration
Americium	Mass Spectrometry and 2 Radiochemistry Methods
Californium	Spontaneous Fission Counting
Curium	Alpha Counting
Gamma Energy	400 Channel Analyzer
Lanthanum	Mass Spectrometry
Lithium	Flame Photometry
Nitrate	Ultraviolet Spectrometry
Rare Earths	Complexometric Titration

EXCESS ACIDITY OF AMINES AND AMINE CONCENTRATION

The extractant used in all cycles of the process is a 30 vol % (~0.6M) solution of tertiary amine in diethylbenzene. The amine is a mixture of tri-n-octylamine and tri-n-decylamine that is relatively free from primary and secondary amines. The extractant is used as the amine nitrate in the conversion cycle and the amine hydrochloride in the lanthanide removal cycles. Analyses are needed to verify that the amine (0.6M) and excess acid (0.02-0.05M) concentrations are within the specified limits. If less than the stoichiometric amount of acid is used to convert the amine to the salt, the amine extracts acid from the aqueous phase, resulting in hydrolysis and possible precipitation of the actinides and lanthanides. If greater than the recommended small excess of acid is present in the solvent, extraction of actinides is decreased causing excessive losses to the aqueous waste.

The concentrations of excess acid and amine are determined by potentiometric titration.(4) Two milliliters of the sample (amine nitrate or amine hydrochloride) are added to a beaker containing 50 ml of ethyl alcohol that has been adjusted to pH 5.0 ±0.1. Then, the solution is titrated back to pH 5.0 with standardized 0.1N sodium hydroxide from a 1-ml microburet, and the excess acid is calculated. If the pH increases above 5.0 when the amine salt is added to the ethyl alcohol, the amine has insufficient acid. To determine this acid deficiency the solution is titrated to pH 5.0 with 0.1N HCl. After the solution has been titrated to pH 5.0 to determine excess acid or acid deficiency, the amine concentration is determined by continuing the titration to pH 10.5 with 0.1N NaOH from a 25-ml buret. An aliquot of the adjusted alcohol solution is titrated from pH 5.0 to 10.5 to determine the blank correction.

The relative standard deviation for a single determination is about 2% for excess acid and amine concentration.

ALUMINUM AND TOTAL RARE EARTHS

Aluminum concentration is controlled in the feed solution to ensure good extraction of the actinides and lanthanides, and the concentration of total rare earths is controlled to prevent precipitation of the rare earth chlorides in the second cycle.

Aluminum and total rare earths are determined chelometrically with ethylenediaminetetraacetic acid (EDTA).(5,6) The total of the rare earth and aluminum concentrations is determined by complexing both species with EDTA, and then backtitrating the excess EDTA with standard lanthanum solution. The rare earth concentration is determined by titrating directly with EDTA using sulfosalicylic acid to mask aluminum; the aluminum concentration is obtained by difference. Arsenazo solution is the indicator in both titrations.

Organic samples are ignited to destroy organic matter. The ignited residue is dissolved in hydrochloric acid and analyzed by the regular procedure. The relative standard deviation is 2 to 3% for both the rare earth determination and the total aluminum plus rare earth determination in either aqueous or organic solutions.

AMERICIUM

Three different methods are used to determine ^{243}Am in samples where the alpha activity of ^{244}Cm is as much as 1000 times the ^{243}Am alpha activity. The mass spectrometric–isotope dilution method is the most precise (rel std dev: 1%) of the three methods.

When less precise results are acceptable (2-3%), ^{243}Am is determined either by alpha counting and pulse height analysis after the ^{244}Cm and lanthanides are separated with calcium fluoride or by counting the ^{239}Np daughter of ^{243}Am after a separation step.

Isotopic Dilution Method

A known amount of ^{241}Am is added to the ^{243}Am-^{244}Cm sample, the sample is purified by liquid-liquid extraction, and the mass ratio of ^{241}Am to ^{243}Am is determined with a surface emission mass spectrometer.(7) The relative standard deviation for a single determination is 1% (n = 7).

Calcium Fluoride Method

Americium and any plutonium present are oxidized to the (VI) state by a silver(I)-catalyzed persulfate treatment or by a silver(I)-catalyzed perxenate treatment.(8,9) The solution is then passed through a column of solid calcium fluoride to remove Cm^{3+} and other trivalent actinide and lanthanide elements as insoluble fluorides. Am(VI) and Pu(VI) pass through the column. The plutonium is removed by anion exchange, and the americium in the anion exchange effluent is determined by alpha counting and pulse height analysis. Electrodeposited mounts are used to ensure good resolution.(10) A known amount of ^{241}Am may be added prior to the separation step to determine the yield, if the ^{241}Am initially in the sample is low. The relative standard deviation was 1.9% (n = 6) using ^{241}Am for the yield correction.

The calcium fluoride column used in the separation consisted of a small glass column (10-mm ID) that contained a 1/4 to 5/16-inch layer of preoxidized calcium fluoride. The calcium fluoride is placed on a layer of treated glass beads to prevent plugging of the glass frit.

^{239}Np Activity Method

The concentration of ^{243}Am is determined by separating and counting ^{239}Np, the product of the alpha decay of ^{243}Am(11). Neptunium is extracted into 2-thenoyltrifluoroacetone, and the extract is counted in a 5 x 5-inch NaI(Tl) well crystal connected to a 256 channel pulse height analyzer. The neptunium is corrected to equilibrium, and ^{243}Am is calculated from a predetermined relationship between neptunium counts and ^{243}Am (mg). The relative standard deviation for a single determination is 3.3%.

CALIFORNIUM - 252

Californium-252 is determined by counting total spontaneous fission neutrons and using a correction for neutrons from the spontaneous fission of ^{244}Cm.(12)

CURIUM

Curium is determined in process samples by counting the alpha activity in a known aliquot. No correction is needed for the small amount of americium present. For aqueous samples, mounts are prepared by evaporating a sample aliquot, and the alpha activity was determined with a proportional counter.

Accurate results are not obtained when standard techniques are used to prepare organic samples for alpha counting. Low results are obtained when tertiary amine–diethylbenzene was evaporated directly or diluted in diethylbenzene before evaporation. The low results are attributed in the first instance to the amount of residue on mounts. In the second instance, the difference in solubilities of the aqueous solution in tertiary amine and in diethylbenzene may cause the dissolved aqueous to separate to form a minute second phase. Higher results are obtained by diluting the tertiary amine in 30% TBP—"Ultrasene."* This is expected because the solubilities of the aqueous solution in tertiary amine and in TBP are similar.

On the basis of the results in Table II, dilution in nitric acid was adopted for determinations of alpha activity in tertiary amine–diethylbenzene. The activity is extracted into 1.0M HNO_3 and diluted in one operation. Alpha mounts are prepared by the standard method used for aqueous samples.

TABLE II

DETERMINATION OF CURIUM IN TERTIARY AMINE-DIETHYLBENZENE

Sample Treatment	Activity, dis/(min)(ml)
Diluted in diethylbenzene	1.1×10^6
Direct mount of 0.6M tertiary amine–diethylbenzene	1.1×10^6(a)
Diluted in 30% TBP-"Ultrasene"	1.3×10^6
Diluted and stripped with 1M HNO_3	1.4×10^6

(a) Evaporation required several hours.

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* Trademark of Atlantic Refining Co., Philadelphia, Pa.

GAMMA ENERGIES

Decontamination factors are required for each of the radionuclides ^{144}Ce, ^{154}Eu, ^{106}Ru, ^{95}Zr, and ^{95}Nb during process demonstrations. Generally these fission products are determined by direct gamma pulse height analysis.

Fission products that cannot be detected by direct counting, especially in the second cycle, are determined by selective chemical extractions of the individual radionuclides; the separated fission product is verified by gamma pulse height analysis. Small amounts of ^{95}Zr are determined by the thenoyltrifluoroacetone method,(13) and small amounts of ^{144}Ce are determined with bis-2-ethylhexyl)-phosphoric acid extractions.(14)

Pulse height measurements are made with a Radiation Counter Laboratories 256-channel analyzer or a Technical Measurement Corporation 400-channel analyzer in conjunction with 3- and 5-inch sodium iodide crystals (Table III). Results are calculated from measurements of known gamma energies. Published energy values of these radionuclides are ^{144}Cr-^{144}Pr (0.134, 0.694, 2.18 Mev), ^{154}Eu (0.998, 1.130, 1.40, 1.723 Mev), ^{106}Ru-^{106}Rh (0.513, 1.13 Mev), and ^{95}Zr-^{95}Nb (0.724, 0.757 Mev).(15)

TABLE III

GAMMA ENERGY ANALYSIS

Process Stream	Emitter				
	^{144}Ce	^{154}Eu	^{239}Np	^{103,106}Ru	^{95}Zr-^{95}Nb
1st Cycle					
Feed	-	-	-	0.5 Mev 5" crystal	0.75, 0.76 Mev 5" crystal
Product	-	-	-	0.5 Mev 5" crystal	0.75, 0.76 Mev 5" crystal
2nd Cycle					
Feed	134 kev 3" crystal	1.28 Mev 5" crystal	-	0.5 Mev 5" crystal	0.75, 0.76 Mev 5" crystal
Product	134 kev 3" crystal	1.28 Mev 5" crystal	-	Chem. sepn. 0.5 Mev 5" crystal	Chem. sepn. 0.75, 0.76 Mev 5" crystal
Waste	-	-	0.22, 0.29 Mev 5" crystal	Chem. sepn. 0.5 Mev 5" crystal	Chem. sepn. 0.75, 0.76 Mev 5" crystal
3rd Cycle					
Feed	134 kev 3" crystal	-	-	Chem. sepn. 0.5 Mev 5" crystal	-
Product	Chem. sepn. 134 kev 3" crystal	-	-	Chem. sepn. 0.5 Mev 5" crystal	-

LANTHANUM

The importance of controlling the rare earth concentration was discussed in an earlier section. Since lanthanum is present in amounts greater than the fission product lanthanides in the solution used in these studies, a separate determination is required. Lanthanum (0.2-0.4M) carrier was added during the double sulfate precipitation that was used to separate americium and curium from aluminum.

Lanthanum was determined by isotopic dilution-mass spectrometry with lanthanum, enriched to 2.14% ^{138}La, as the standard.(16) The relative standard deviation is approximately 1%.

LITHIUM

Lithium nitrate is used as a scrub solution in the conversion cycle to remove fission products, and lithium chloride is used for salting and scrubbing in the lanthanide removal cycles. Decontamination from fission products and extraction of americium and curium depend greatly on the concentration of lithium; therefore, precise analyses are required. An automated flame photometric method was developed that gives the required precision.(17) Samples are passed through a calcium fluoride column prior to the analyses to remove most of the trivalent lanthanide and actinide elements so that the flame photometer can be operated in a ventilated hood without spread of alpha activity. The relative standard deviation for a single analysis is ~1%.

NITRATE

Small amounts of nitrate (10^{-2}M) adversely affect the separation of americium and curium from lanthanides in the lanthanide removal cycles. A sensitive method for determination of nitrate was needed to determine if the conversion cycle achieved good decontamination from nitrate. Most available methods lacked the sensitivity needed for determining 10^{-3} to 10^{-4}M NO_3^-. An ultraviolet spectrometric method with the required sensitivity was available(18); however, curium present in samples must be removed since it also absorbs ultraviolet radiation. Samples are passed through a calcium fluoride column to remove curium and any other ions that might interfere, and the absorbance of the column effluent is measured at 210 mμ.(19) The estimated relative standard deviation is ±10% for 10^{-3} to 10^{-4}M NO_3^-.

APPENDIX

THE CURIUM PROCESS

The process for separation of ^{243}Am and ^{244}Cm from rare earths consists of three similar solvent extraction cycles. The first cycle converts from a nitrate system to a chloride system, and the second cycle separates ^{243}Am and ^{244}Cm from rare earths and californium. A third cycle, identical with the second cycle, provides additional decontamination from fission products.

Conditions for the first cycle (conversion cycle) are designed to recover 99.9% of the trivalent actinides and lanthanides in a nitrate-free ($<0.01M$ NO_3^-) solution of hydrochloric acid (Figure A-1). Trivalent actinides and lanthanides are extracted from an $Al(NO_3)_3$ solution into tertiary amine—HNO_3—diethylbenzene. Good extraction is ensured by controlling the concentrations of Al^{3+}, H^+, and amine. The extract is scrubbed with $LiNO_3$ to remove some of the ^{95}Zr-^{95}Nb and the monovalent and divalent fission products. The actinides and lanthanides are then separated from nitrate by re-extraction into hydrochloric acid. Finally, the hydrochloric acid solution is scrubbed with tertiary amine—HCl—diethylbenzene to remove any residual NO_3^-, Zr, Nb, and Ru.

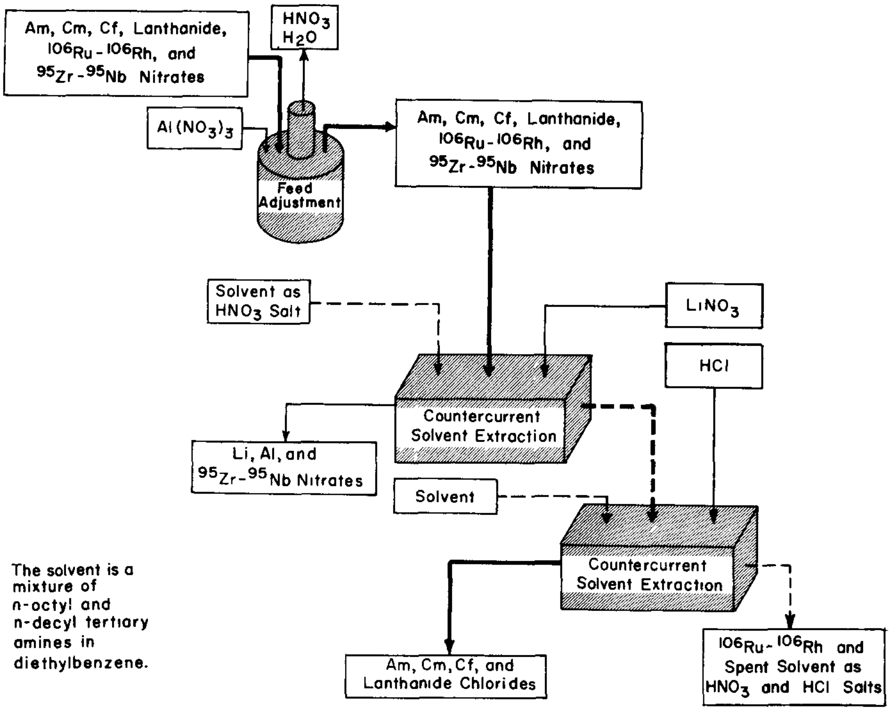

FIG. A-1 NITRATE - TO - CHLORIDE CONVERSION

Conditions for the first extraction of the second cycle are designed to obtain yields of at least 99.9% of all transplutonium actinides with decontamination factors greater than 10^4 for removal of the rare earths (Figure A-2). The conditions for the second extraction are designed to provide adequate separation from all fission products that are extracted with americium and curium in the first extraction. The product solution from the first cycle is adjusted with lithium chloride and fed to the second cycle. Americium and curium are extracted into tertiary amine—HCl—diethylbenzene, and the rare earths and residual fission products remain in the aqueous stream. The organic extract is scrubbed with lithium chloride solution to further decontaminate from rare earths. Americium and curium are re-extracted into hydrochloric acid solution, and this solution is scrubbed with tertiary amine—diethylbenzene. Americium and curium are scrubbed in the product stream which is then adjusted for the third cycle. The second cycle can be used to separate californium from americium and curium. If lithium chloride is used instead of hydrochloric acid in the strip solution, californium stays with the fission products in the organic waste.

The third cycle is identical with the second cycle and is necessary to give additional decontamination from cerium.

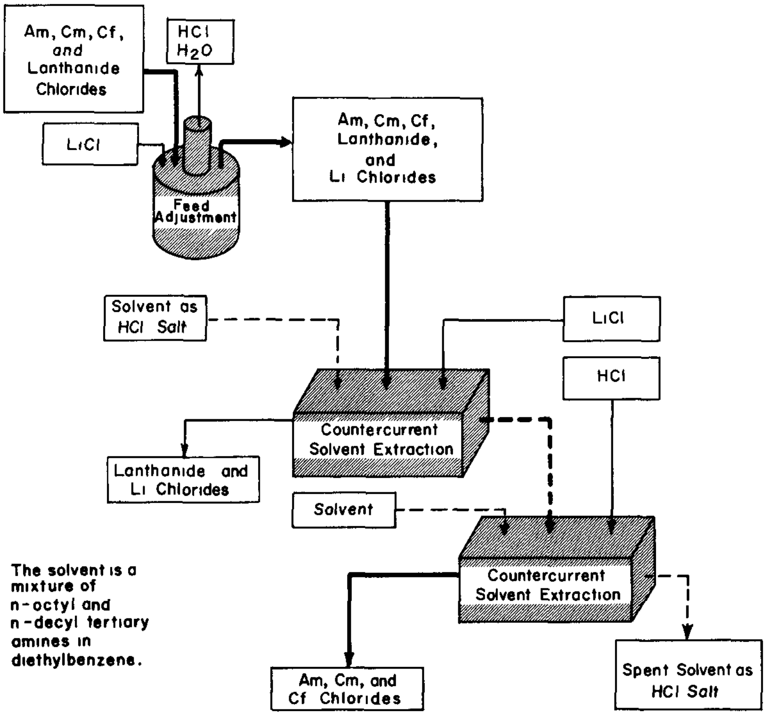

FIG. A-2 LANTHANIDE REMOVAL

The finishing operation (Figure A-3) is designed to yield AmO_2 containing less than 0.5 wt % Cm, and CmO_2 containing less than 0.5 wt % Am. Americium and curium chlorides from the third extraction cycle are concentrated, and americium and curium are precipitated as hydroxides to remove lithium. The precipitate is dissolved to yield a solution containing 50 g/l each of americium and curium in 0.25M HCl. After a valence adjustment, potassium carbonate is added to precipitate Am(V). The curium in the supernate then contains less than 0.5 wt % Am. Curium is precipitated as the hydroxide to remove potassium; the hydroxide is dissolved, precipitated as the oxalate, and calcined to CmO_2.

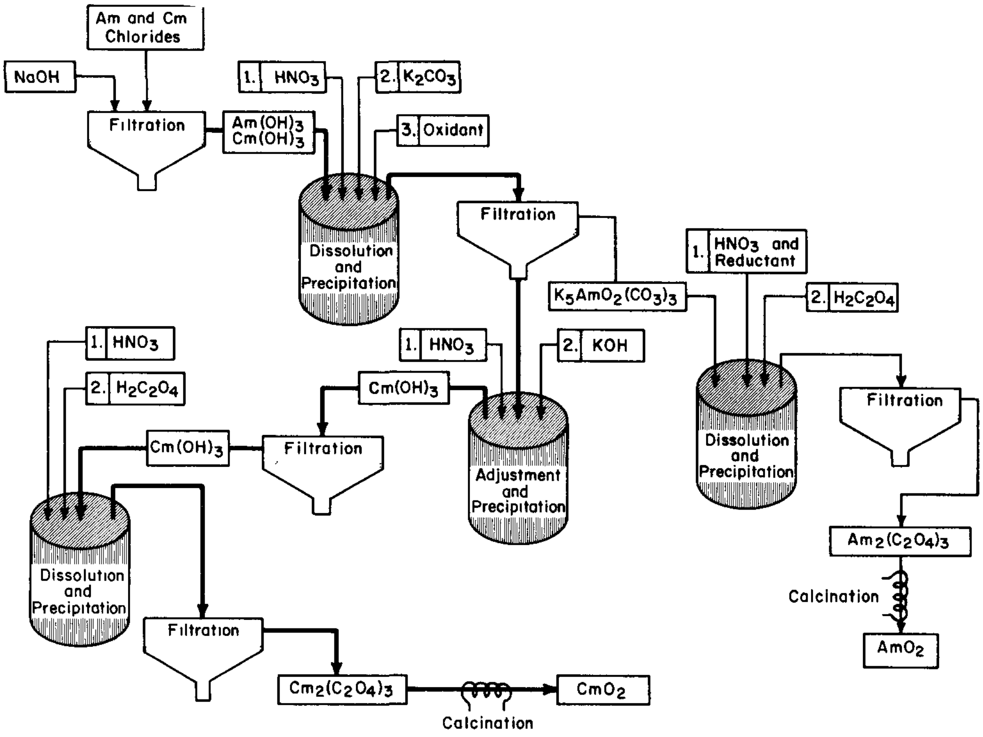

FIG. A-3 REMOVAL OF AMERICIUM AND PREPARATION OF OXIDES

After the carbonate precipitation, the americium precipitate contains 3-5 wt % Cm. A second carbonate precipitation is required to produce americium containing less than 0.5 wt % Cm. The final carbonate precipitate is dissolved and precipitated as hydroxide to remove potassium. The hydroxide is dissolved, precipitated as oxalate, and calcined to AmO_2.

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