AEC RESEARCH AND DEVELOPMENT REPORT

DEVELOPMENT OF A PLANT-SCALE RESIN CALCINATION SYSTEM FOR PREPARING TRANSPLUTONIUM OXIDES OR OXYSULFATES

R. F. BRADLEY
G. A. BURNEY

Savannah River Laboratory
Aiken, South Carolina

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

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DP-1307

Chemistry
(TID-4500, UC-4)

DEVELOPMENT OF A PLANT-SCALE RESIN CALCINATION
SYSTEM FOR PREPARING TRANSPLUTONIUM OXIDES AND OXYSULFATES

by

R. F. Bradley
G. A. Burney

Approved by

A. S. Jennings, Research Manager
Separations Engineering Division

and

J. A. Porter, Research Manager
Separations Chemistry Division

September 1972

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ABSTRACT

A plant-scale system was developed to prepare ~100 mg batches of californium-252, or other transplutonium isotopes, as the oxysulfate or oxide without directly handling small quantities of liquid or solid. The californium is sorbed on ~50 cm³ of cation exchange resin in a platinum column, the resin is burned away, and the column is heated to form oxysulfate at 800°C or oxide at 1250°C. The platinum column is then sealed and shipped to the user, who can dissolve and remove the product by passing nitric acid through the column. Process operating conditions and equipment requirements were first defined by tests with stainless steel columns using dysprosium as a stand-in for the transplutonium isotopes. Calcination tests were then conducted to demonstrate the process in platinum columns with terbium, californium-252, curium-242, and curium-244.

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INTRODUCTION

Several grams of ^{252}Cf are being produced at Savannah River for evaluation as neutron sources. The ^{252}Cf is produced by irradiation of targets containing the higher isotopes of plutonium, americium, and curium. In addition to californium, the byproducts berkelium, einsteinium, and fermium may be present in recoverable quantities. A general description of the overall program has been given in previous reports¹⁻³ and is shown in Figure 1.

*These steps discussed in this report

FIGURE 1. Recovery and Purification of ^{252}Cf

In the separations process planned for use at Savannah River, the irradiated targets are dissolved in nitric acid, and plutonium is separated by a conventional solvent extraction process with dilute tributylphosphate (TBP). This feed is then divided into batches for ion exchange processing. After a feed preparation step, californium, americium, and curium are partially separated from each other and from lanthanide fission products by pressurized displacement development chromatography on cation exchange resin with diethylenetriaminepentaacetic acid (DTPA). The californium is separated from DTPA solution by conventional cation exchange, and californium is eluted from this column with nitric acid. The nitric acid concentration is then reduced, and the solution is fed to a second pressurized cation exchange column where the californium is further purified by elution development chromatography using alphahydroxyisobutyrate (AHIB).

Processing steps were required for use following the elution development chromatography to separate the californium from the large volume of AHIB and to isolate it in a form suitable for shipping and subsequent dissolution in nitric acid. The method chosen was sorption of ~ 100 mg of ^{252}Cf from the AHIB solution on cation resin contained in a 50-cm^3 platinum column; the resin is then burned in the column to yield californium oxysulfate or oxide. The column is then sealed and sent to the user who removes the californium from the column with nitric acid.

The work reported here had the following principal objectives:

- Demonstrate conditions for quantitative sorption of californium from AHIB solution on a small volume of cation exchange resin.
- Determine optimum conditions for safe burning of the cation exchange resin to yield a californium product soluble in nitric acid and low in cationic impurities.
- Demonstrate that the californium oxysulfate or oxide produced by calcination can be quantitatively removed from the column.

Although these studies were carried out principally for the purpose of developing a plant-scale process for ^{252}Cf recovery, the equipment and techniques developed are also applicable to the other transplutonium isotopes. The same equipment and techniques will be used to recover byproducts berkelium, einsteinium, and fermium.

SUMMARY

A plant-scale resin calcination system was developed to prepare ~100 mg of californium oxysulfate or oxide without directly handling small quantities of liquids or solids. The californium is sorbed on a small volume of cation resin in a platinum column, the resin is burned, and the column is heated to form either oxysulfate at 800°C or oxide at 1250°C. The platinum column is then sealed and shipped to the user, who can dissolve and remove the californium by passing nitric acid through the column. The steps involved in this process are shown in Figure 2.

FIGURE 2. Recovery of ^{252}Cf by Resin Calcination

Process operating conditions and equipment requirements were first defined by tests with stainless steel columns using dysprosium as a stand-in for the transplutonium isotopes. Calcination tests were then conducted to demonstrate the process in platinum columns with terbium, californium-252, curium-242, and curium-244.

All phases of the process were demonstrated, including column loading, resin calcination, and product removal. Techniques were also demonstrated for recovery of product lost from a column due to a leaking or ruptured frit.

DISCUSSION

PREVIOUS STUDIES

The oxides of californium⁴ and berkelium⁵ have been prepared by heating single beads of cation exchange resin at 1200 to 1250°C. Two-gram samples of "Dowex"* 50W-X8, 50- to 100-mesh resin saturated with neodymium (as a stand-in for Cf and Cm) were calcined by Hale⁶ in open platinum containers with air and oxygen to yield Nd₂O₂SO₄ at 600-1000°C and Nd₂O₃ at 1200°C and above.

Oak Ridge National Laboratory has developed several new encapsulation techniques for fabrication of sources containing up to 5 mg of ²⁵²Cf.^{7,8} One of these techniques involves the use of resin calcination.⁸ The primary container consists of a 3/8-inch-OD by 1-inch-long platinum-plated column filled with ion exchange resin. The ²⁵²Cf is loaded onto the resin, and then the resin is calcined at 650°C for 3 hours in a low air flow. The capsule is then sealed and welded into a secondary container for shipping.

EXPERIMENTAL APPROACH

Differential thermal analyses were carried out in flowing air with small samples of resin. These tests were conducted to determine the ignition behavior of small quantities of various resins, including unirradiated resin, resin irradiated in water and then washed, and damp irradiated resin.

Due to the high cost of platinum and the limited availability of ²⁵²Cf, process development was carried out by first making resin calcination tests using stainless steel equipment with dysprosium as a nonradioactive stand-in for ²⁵²Cf at temperatures up to 800°C. These tests defined the calcination conditions, equipment requirements, process control, yields, and process operating behavior. Microscopic examination of the calcined product gave evidence of the particle size distribution, but stainless steel corrosion products prevented exact determination of product purity. Corrosion of the stainless steel also precluded calcination at temperatures in excess of 800°C.

A total of twelve calcination tests were made in stainless steel columns. Two of the tests were in 5-cm³ columns, and the remainder were in plant-scale 50-cm³ columns.

*Registered trademark of Dow Chemical Co.

After determining operating conditions and process behavior with the stainless steel columns, calcination tests were conducted in platinum columns that contained ion exchange resin loaded with small (<1 mg) quantities of ^{252}Cf and with plant-scale quantities (~ 100 mg) of ^{244}Cm , ^{242}Cm , and terbium as stand-ins for ^{252}Cf . These tests further confirmed operating conditions and product yield and purity. Five calcination tests were made in the platinum columns. Two of the tests were made with <1 mg of ^{252}Cf in 5-cm³ columns, two tests were made with Tb and ^{244}Cm as stand-ins for ^{252}Cf in plant-scale 50-cm³ columns, and a final test was made with ~ 100 mg of a mixture of ^{242}Cm and ^{244}Cm in a 50-cm³ column that simulated both the mass and the nuclear energy (~ 2.5 watts) expected for a full-scale ^{252}Cf calcination.

Tests in the stainless steel and platinum columns demonstrated all phases of the process, including column loading, resin calcination, and product removal. Tests were also conducted to determine methods of recovering any product that might be lost from the column due to a defective frit which might leak or rupture.

RESIN LOADING AND COLUMN PREPARATION

In plant-scale processing, 100 mg of ^{252}Cf will be loaded onto ~ 50 ml of "Dowex" 50W-X8, 50 to 100-mesh resin from several liters of 0.4M AHIB solution adjusted to 0.25M HNO_3 . The size of the column is fixed mainly by the column loading step. The diameter is ~ 1 inch for adequate loading rate, and the length is ~ 5 inches to ensure all the product will be retained by the resin. The stainless steel columns used for the cold tests were of the same dimensions as those for the hot test; they differed only in that six thermocouples were attached externally to better define resin burning behavior in the hot test (Figure 3).

For two tests, each with ~ 1 mg of ^{252}Cf , platinum columns of 3/8-inch diameter and ~ 5 -inch length containing ~ 4.5 ml of "Dowex" 50W-X8 resin were used. Two 3/8-inch-diameter stainless steel columns were also tested. The resin was contained between two H-porosity platinum frits. All interior portions of the columns were platinum or platinum-rhodium to prevent contamination of the product with cationic corrosion products. The columns were designed for at least 100 psig at 600°C.

Each column was loaded with resin from a water slurry to within $\sim 1/4$ inch of the top frit to prevent channels or voids in the resin. The resin temperature did not exceed 100°C during welding of the second platinum frit to retain the resin. After the resin was sealed in place between the frits, the column was flow tested with water and air. The columns gave a water flow of 50 ml/min at <10 psig and an air flow of 1 liter/minute at <5 psig.

FIGURE 3. Resin Calcination Equipment

PRODUCT LOADING

The Cf-AHIB fraction from elution development chromatography is adjusted to 0.25M HNO_3 to decrease the ligand concentration, so that californium is effectively sorbed by the cation resin. At lower concentrations, sorption is less effective because of complexing of the metal ion by AHIB, and at higher concentrations of acid, sorption is less effective because of competition for the resin sites by hydrogen ion. In all tests, either the feed was produced by elution development chromatography with AHIB, or a synthetic feed was prepared using 0.4M AHIB at pH 3.4.

The column was loaded by: 1) direct pumping of the adjusted AHIB solution to the column, or 2) displacement of the AHIB solution from the feed tank with three tank volumes of dilute nitric acid; the latter method is planned for plant operation. The flow to the column was 50 to 100 ml/min, and loss to the absorption effluent was always $<0.1\%$. Analyses were obtained on "flowing stream" samples of the effluent and also on a sample of the total effluent. In the plant system, the effluent will be passed through a monitoring loop equipped with high- and low-range BF_3 detectors to detect californium breakthrough.

After sorption, the loaded resin was washed with ~ 0.5 liter of water to remove most of the nitric acid and AHIB. Then the resin was air-dried for ~ 30 minutes by applying vacuum at the column outlet.

TESTS WITH STAINLESS STEEL COLUMNS

Resin calcination tests were made in stainless steel columns to define calcination conditions, equipment requirements, process control, yields, and process operating characteristics. Microscopic examination of the calcined product defined particle size distribution, but corrosion products of stainless steel prevented determination of product purity.

Resin columns were loaded with ~ 0.4 mmol of dysprosium (equivalent to 100 mg of ^{252}Cf) from an AHIB solution as described previously. Two tests were made without dysprosium loading; however, only $\sim 1\%$ of the resin exchange sites are required to contain all of the dysprosium, so that in all tests the resin was essentially all in the H^+ form. Each column was washed and air dried, and the resin calcined in flowing air by heating the column in the apparatus shown in Figure 4. The off-gas equipment and additional inlet tubing were added for the later tests.

FIGURE 4. Apparatus for Calcination of Resin in Stainless Steel Columns

Each column was heated from ~25 to 400°C in 1 hour, from 400 to 800°C in 3 hours, and then cooled and opened to examine the product, determine that all resin had burned, and examine the general condition of the column. In several tests the calcined product was leached out with nitric acid before the column was opened. The tests are summarized in Table I.

Resin calcination tests in the stainless steel columns established the following:

- The resin was completely burned in 3 hours or less at an air flow rate of 1 liter/minute through the 50-cm³ columns.
- The ignition and burning of the resin did not result in unacceptably high temperatures at the air flow rates investigated (up to 2.25 liters/minute).
- Most of the product was in the form of spherical particles of approximately the same size as the original resin beads. There was no significant loss of product fines through the G-porosity outlet frit.
- The product formed at 800°C was mainly oxysulfate and was easily dissolved in dilute nitric acid.
- Elimination of channels in the resin by filling and compacting resin to within ~1/4 inch of the top frit ensured efficient and predictable resin burning rates.
- Pressure and temperature surges and a decrease in air flow at ignition provided convenient means of determining that ignition had occurred.
- The principal gaseous combustion products were SO₂ and CO₂ (<1% H₂, CH₄, or CO).
- All portions of the system must be heated to >400°C to prevent condensation of organic pyrolysis products.
- The off-gas should be passed through a condenser and one or more filters to remove moisture and organic tars. Filters should be changed periodically due to the accumulation of tar.

TABLE I

Resin Calcination In Stainless Steel Columns

Test	Column Volume, cm ³	Air Velocity, cm/sec	Off-Gas System	Notes
1	5	16.7	-	No stand-in.
2	50	4.9 ^a	-	No stand-in.
3	50	4.9	Filter	Oxysulfate product. Analysis for Dy in all downstream portions of system.
4	5	12.5	Filter	Channel; ~1/2 burned; no ignition.
5	50	4.9	Filter, Condenser	Microscopic exam of product; gas samples.
6	50	4.9	Filter, Condenser H ₂ SO ₄ Absorber, Drierite Column	Dysprosium leached from column; gas samples.
7	50	4.9	Filter, Coiled Condenser	Dysprosium leached from column; gas samples.
8	50	4.9	Filter, Coiled Condenser	Dysprosium leached from column; gas samples.
9	50	7.3	Filter, Coiled Condenser	Microscopic exam of product; gas samples.
10	50	11.0	Filter, Coiled Condenser	Microscopic exam of product; 675°C at ~10 min after 450°C ignition.
11	50	4.9	Filter, Coiled Condenser	106 ft of 3/8 in. tubing added to inlet; microscopic exam of product.
12	50	11.0	Filter, Coiled Condenser	106 ft of 3/8 in. tubing added to inlet; system shut down after ignition and restarted at lower air flow rate; microscopic exam of product.

a. Corresponds to one liter per minute flow in the 50-cm³ columns.

Thermal Behavior

Thermocouples located on the column, in the off-gas stream and in the furnace cavity gave detailed information on the thermal behavior of the system during calcination. Before the calcinations, differential thermal analyses were conducted with a few milligrams of resin in flowing air to ensure that there would be no unusual exotherms. These tests were carried out on several samples of resin including unirradiated resin, irradiated resin, and irradiated-washed resin. Resin ignition temperature varied from 290 to 425°C; the variation was basically a function of the particular batch of resin that was used for the test. No significant correlation was found between irradiation of the resin and ignition temperature. Tests with small samples of the resin used in the stainless steel columns established that this resin should ignite at ~450°C and that the ignition would be preceded by an endothermic pyrolysis reaction (Figure 5). Ignition always occurred between approximately 400 and 470°C in the stainless steel column tests with this resin. In most tests, a large quantity of organic mist and fog was produced by the endothermic pyrolysis (or decomposition reaction) before ignition (~300 to 400°C).

FIGURE 5. Differential Thermal Analysis of Resin Used in Stainless Steel Columns

The temperature profiles for all tests (except Test 4) were essentially the same. The profiles for Tests 1 and 2 are shown in Figures 6 and 7 as typical examples.

Due to heat losses from the ends of the furnace, initially the center of the column was always at the highest temperature, and ignition occurred in this area. The column inlet was always at a lower temperature than the outlet due to the cooling effect of the inlet air. The heat evolved at ignition increased the temperature of the system rapidly until a new "steady-state" condition was reached at a much higher column temperature. The rate of heat removal from the column (primarily radiant heat transfer) once again equaled the rate of heat generation at the elevated temperature. This transient period lasted approximately 5 to 10 minutes, and the column temperature usually leveled off 100 to 200°C higher than before ignition.

FIGURE 6. Resin Calcination in 5-cm³ Column (Test 1)

FIGURE 7. Resin Calcination in 50-cm³ Column (Test 2)

Increased system temperature can lead to increased system pressure, especially if the volume of tubing on the system inlet is small. The abrupt increase in pressure at ignition is shown in Figure 8 for Test 2. The air flow rate decreased at ignition. In all tests, the pressure drop necessary to maintain air flow across the column increased with temperature.

FIGURE 8. Pressure Increase During Calcination

The ignition process is self-regulating. When the system pressure approaches the upstream pressure on the metering valve, air flow decreases due to the decrease in the pressure driving force across the valve. The decrease in the air flow rate immediately decreases the rate of oxidation in the system, and the system pressure never exceeds the upstream pressure.

Oxygen was rapidly depleted in the region of ignition, and as the inlet section was heated to the ignition temperature, the reaction moved toward the column inlet. As oxidation in the inlet section approached completion, the reaction moved back downstream. After all of the resin had been burned, the column temperature became less than or equal to the outside furnace temperature. These various stages are well illustrated in the temperature profiles for Tests 1 and 2 (Figures 6 and 7).

Test 4 was the only exception to the general ignition behavior. For this test, no ignition was observed and column temperatures never exceeded furnace temperatures. Thermocouples located on the column outlet also gave significantly lower temperatures than those on the column inlet. At the end of the normal 3-hour calcination period, the column was opened for examination; only $\sim 1/2$ of the resin had burned. This behavior is attributed to the formation of a channel, due to insufficient packing of the resin in the column. Most of the air bypassed through the channel, and combustion took place only at the interface between the channel and the resin, rather than throughout the resin as in the case of normal plug flow behavior. The cooling of the outlet thermocouple indicates that it was located adjacent to the channel (the thermocouples were located in different positions radially around the column). After this test, all columns were compacted completely to within $1/4$ inch of the upper frit, and all flows were in the same direction to maintain a well-packed bed. Normal ignition behavior and complete resin calcination within 3 hours of ignition were observed for all other tests.

Approximately 100 ft of $3/8$ -inch-OD tubing was added to the column inlet to measure temperature and pressure surges under conditions more closely simulating plant conditions. These tests were run at air flow rates of 1 and 2.25 liters/minute, respectively. Results of these tests and previous tests with ~ 6 ft of tubing on the column inlet are compared in Figure 9. Comparisons of Curve A with C and Curve B with D show that the additional tubing on the column inlet decreases, but does not completely eliminate, the pressure pulse at ignition by acting as a damping reservoir. Comparisons of Curve A with B and Curve C with D also show that the column over-temperature relative to the furnace is proportional to the air flow and is not affected by the length of inlet tubing. The rate of temperature increase at ignition (an index of the oxidation rate) was also greater at higher air flow rates (Figure 10).

In Test 12, as soon as the column temperature leveled out after ignition, the system was shut down by turning off both heat and air flow and cooling to room temperature. The system was then restarted at an air flow of 1 liter/minute and run in the normal manner. The resin reignited; however, the temperature surge was smaller than that obtained in the initial ignition. The second ignition occurred at $\sim 300^{\circ}\text{C}$ (vs. 450°C for the first ignition), and the maximum column temperature exceeded the furnace temperature at $\sim 400^{\circ}\text{C}$. Three hours after the second ignition the system was again shut down and the column opened for examination. Approximately 99% of the resin had been burned, demonstrating the calcination can be interrupted and restarted without problems.

FIGURE 9. Effects of Air Flow and Volume on Resin Calcination

FIGURE 10. Rate of Temperature Increase at Ignition

A summary of the effect of air flow rate on thermal behavior is given in Table II. At the higher air velocities, the maximum column temperatures at ignition are somewhat higher, and the column temperature increase due to ignition is greater (except in the smaller 5-cm³ column used in Test 1). The burning period decreased as the air flow rate was increased.

TABLE II

Thermal Tests in Stainless Steel Columns

Test	Air Velocity, cm/sec	Max. Column Temp. at Ignition, °C	Column Temp. Increase due to Ignition, ^a °C	Burning Period, ^b minutes
2	4.9	410	150	75
3	4.9	430	130	67
5	4.9	460	70	106
6	4.9	405	150	136
7	4.9	440	160	96
8	4.9	435	120	106
11	4.9	445	150	122
2-11 Avg	4.9	432	133	101
9	7.3	440	170	96
10	11.0	470	150	83
12	11.0	450	200	^c
1 ^d	16.7	460	70	60

^a. Difference between the maximum column temperature at ignition and after the temperature has leveled out (5-10 minutes after ignition).

^b. Difference between ignition and point at which the maximum column temperature is no longer greater than the furnace temperature.

^c. Test 12 was interrupted after ignition.

^d. Test 1 was in a 5-cm³ column. The other tests in this table were in 50-cm³ columns.

Product Form

The presence of stainless steel corrosion products prevented accurate determination of product purity in these tests; however, the particle size and form of the product were determined, and product losses were estimated. In all tests, the columns were cut open, and the product was weighed and examined to verify that all of the resin had burned.

The product from Test 3 was determined to be oxysulfate from its infrared absorption spectrum. Neutron activation analysis indicated that <0.01% of the feed dysprosium was in all downstream portions of the system.

Microscopic examination of the product from these tests indicated that most particles were approximately the same size and shape as the original resin beads, but some spalled at the edges (Figure 11). Almost all of the product was 10 to 100 μ m in diameter. The product was easily dissolved in dilute nitric acid.

FIGURE 11. Product Form

Off-Gases

During calcination all of the resin material is evolved as vapors or gases (except for a small amount of sulfur which combines with the metal to form oxysulfate). Moisture is evolved from the system first at $\sim 100^{\circ}\text{C}$. This water is condensed and collected. At 300 to 400°C , organic vapors are evolved from the endothermic pyrolysis reaction. These organic vapors condense on surfaces which are below $\sim 400^{\circ}\text{C}$. Therefore all portions of the column that will be subsequently contacted with nitric acid in the product removal step must be maintained above 400°C during calcination so no organic material will deposit. A portion of these organic vapors form a fine spray or mist that is difficult to collect. An H_2SO_4 absorber followed by a "Drierite" column was added to the off-gas system for removal of this mist in Test 6; however, the small removal of mist obtained in this equipment did not justify its inclusion in subsequent tests. Downstream filters must be changed periodically because they collect these organic materials.

The principal products of combustion were SO_2 , CO_2 , and H_2O . Off-gas samples were taken in Tests 7 and 8 and analyzed for non-condensable gases on an SO_2 -free basis. At ignition, the O_2 concentration decreases and the CO_2 concentration increases (Figure 12). A gas sample was taken immediately after ignition in Test 8. At this point, the O_2 concentration of the off-gas stream was almost negligible. The concentrations of potentially flammable H_2 , CH_4 , and CO in the off-gases were less than 1% in all of the samples (Table III).

Approximately 10 to 20 cm^3 of condensate (mainly H_2O) were collected during each test. Most of the water, which was in the system initially or was produced by combustion, was collected in the condensate collection vessel. The downstream filters collected much of the organic tars. The remainder of the material evolving from the column passed out of the system in the air stream.

In the plant installation, the downstream submicron filter would prevent loss of californium product in abnormal circumstances, such as fines passing through the downstream column frit or in the case of accidental rupture of the downstream column frit. The probability of significant quantities of product escaping the column by either of these mechanisms is very low.

*Registered trademark of W. A. Hammond Drierite Company, Xenia, Ohio.

TABLE III

Off-Gas Composition from Test 8

Time, minutes	Column Temperature, °C	Off-Gas Composition, mol %					
		O ₂	CO ₂	CO	H ₂	CH ₄	N ₂
60	425	19.4	0.4	<1	0.1	0.1	79
67	550	1.5	12.1	<1	0.69	0.96	83.6
84	625	8.2	11.0	<1	0.08	0.015	79.8
110	650	11.7	8.0	<1	0.03	0.008	79.3
128	650	14.9	5.2	<1	0.04	0.009	78.8
150	650	16.7	3.0	<1	0.018	0.007	79.0
178	625	20.4	0.2	<1	0.017	0.006	78.4
213	660	20.5	0.07	<1	0.017	0.007	78.5

FIGURE 12. Off-Gas Composition in Test 8 (SO₂-Free Basis)

TESTS WITH PLATINUM COLUMNS

Several tests were made with platinum columns to establish that the cationic impurities in the calcined product were no greater than in the feed to the ion exchange sorption. These tests further confirmed the operating conditions and resin ignition properties, which had been defined initially in stainless steel columns. These tests also showed that there was no significant change in pressure drop across the H-porosity platinum frits after heating to 1250°C for as long as 16 hours. These tests are summarized in Table IV.

TABLE IV
Resin Calcination in Platinum Columns

Test	Column Volume, cm ³	Loading	Calcination °C	hr	P _{max} , psig	Notes
1	4.5	~400 µg ²⁵² Cf	1250	8	10	Leached by 4 to 8M HNO ₃
2	4.5	~800 µg ²⁵² Cf	800	3	8	Leached by 0.1M HNO ₃
3	45	~65 mg Tb	800	3	15	Tar in exit line <400°C
4	45	~100 mg ²⁴⁴ Cm	800	4	9	Leached by 0.25M HNO ₃ ; good oxalate precipitate; brown solid in exit line after calcination
5	45	~18 mg ²⁴² Cm ~82 mg ²⁴⁴ Cm	800	3	10	Leached by 0.25M HNO ₃ ; good oxalate precipitate; trace of brown solid in exit line after calcination

Californium

²⁵²Cf was loaded on ~4.5 cm³ of resin (~0.1 prototype scale) because of the small quantity of californium available. Two tests were made: Test 1 with ~0.4 mg of ²⁵²Cf; Test 2 with ~0.8 mg. About 1 liter of 0.4M AHIB adjusted to 0.25M HNO₃ was loaded on the resin for each test. For all tests described, the resin bed was washed with water after sorption and then air dried by vacuum aspiration.

The column in Test 1 was maintained at 1250°C for 8 hours to produce californium oxide. The column in Test 2 was heated to 800°C, as described for the stainless steel column tests, and was held at 800°C for 3 hours to produce californium oxysulfate.

The oxide in Test 1 did not dissolve completely with 0.1, 0.5, or 1M HNO₃; 4M followed by 8M HNO₃ was used for complete dissolution. A total of 80 ml of acid was used. Because such a small quantity of californium was processed, the cationic impurities in the feed for the test were eight times the total californium, and this may have caused more difficult dissolution. The oxysulfate in Test 2 was dissolved completely from the column with ~47 ml of 0.1M HNO₃; ~95% of the oxysulfate was in the first 10 ml.

The dilute nitric acid solution from the oxysulfate dissolution (~800 µg ²⁵²Cf) was precipitated as californium oxalate; >90% of the californium precipitated. Precipitation is normal at this concentration when no carrier is used. Filtration was satisfactory. The strong nitric acid product from dissolution of the oxide (~400 µg ²⁵²Cf) was processed through chemical separations to yield feed for medical source preparation by electrodeposition.

Terbium Stand-In

Terbium was used as a stand-in for californium in Test 3 because its elution position in elution development chromatography with AHIB is quite similar to that of californium. Nonradioactive cation impurities commonly occur when processing californium; 65 mg of terbium were added to the feed for a full-scale elution development chromatography test using 0.4M AHIB at pH 3.6. Flow rates, temperature, and all conditions for the plant were duplicated, except terbium was substituted for californium. The terbium was collected in ~6 liters; this fraction was adjusted to 0.24M HNO₃, and the terbium was loaded quantitatively on the ~45-ml bed of "Dowex" 50W-X8, 50- to 100-mesh resin at a flow of ~50 ml/min. The bed was washed with water after sorption, dried for 30 minutes, and ignited using the same temperature conditions as Test 2. Air flow was 1 liter/minute. Ignition temperature and pressure behavior were similar to tests with stainless steel columns.

Pyrolysis tar collected in the exit line from the system because this line was not maintained above 400°C during calcination. The tar interfered with the dissolution of the terbium oxysulfate; the product contained appreciable soluble and insoluble organic compounds. The terbium product contained ~25 wt % cationic impurities, mostly zinc and sulfur (oxysulfate) with minor amounts of iron, nickel, chromium, silicon, aluminum, and lead. No platinum was detected. Precipitation of terbium oxalate was not attempted

because of the tar. This test confirmed that all parts of the system which contact the dissolved product must be kept above 400°C during calcination.

Curium

There were two tests made with curium as a stand-in for ^{252}Cf . Test 4 was made with ~100 mg of ^{244}Cm , and Test 5 was made with a mixture of ~18 mg of ^{242}Cm and ~82 mg of ^{244}Cm . In Test 5, the mixture of curium isotopes simulated both the mass and the nuclear energy (~2.5 watts) expected for ^{252}Cf . In Test 4, ~100 mg of ^{244}Cm was loaded quantitatively from AHIB onto the resin by displacement with dilute nitric acid. Calcination conditions were similar to Test 3 except the column and contents were held at 800°C for 4 hours. The resin ignited at <400°C. Less than 0.01% of the curium was found in the exit lines, trap, and submicron off-gas filter after the calcination. More than 98% of the curium was removed from the column with 200 ml of 0.25M HNO_3 ; the exit line was heated to ~400°C during calcination, and no tar was seen in the product solution. More than 99% of the curium was precipitated from the dilute nitric acid solution when it was adjusted to 0.3M $\text{H}_2\text{C}_2\text{O}_4$. The total cationic impurities were <25 wt % of the curium in the solution from the column and <10 wt % in the solution from the dissolved curium oxalate. No platinum was detected.

A small amount of a finely divided orange-brown solid, which was only slightly soluble in strong nitric acid, was found in the exit frit and line after the ignition. The solid contained very little curium. Spark source mass spectrometry showed mainly iron and oxygen with smaller amounts of nickel, calcium, copper, aluminum, and silicon and traces of platinum, lead, cadmium, tin, chromium, and rhodium in the solid.

In Test 5, the mixture of curium isotopes was sorbed quantitatively from AHIB solution onto the resin by displacement with dilute nitric acid; pressure drop across the resin bed did not increase during the ~6 hours of loading. A thermocouple against the column near the top of the resin showed an equilibrium temperature of ~37°C after loading was complete and most of the liquid was removed. Temperature measurements indicated that most of the curium was sorbed on ~10 ml of resin. Storage of the column for ~3 days before calcination did not affect the pressure drop during calcination at air flow of 1 liter/minute.

The resin was calcined as in previous tests, except that the resin ignited at ~300°C (Figure 13) rather than 400 to 450°C. The lower ignition temperature probably results from variation in batches of resin, although an effect attributable to resin degradation and higher resin temperature because of the curium load cannot

FIGURE 13. Calcination of ^{242}Cm - ^{244}Cm in Resin

be precluded. Less than 0.01% of the curium was found in the exit lines, trap, and submicron off-gas filters.

After calcination for ~3 hours at 800°C, 98% of the curium was dissolved from the column with ~300 ml of 0.25M HNO_3 and precipitated with oxalic acid. Total cationic impurities were <15 wt % of the curium; however, the original feed was a simulated solution prepared from reagent chemicals. No platinum was detected. The column was opened after dissolution of the curium and found to contain only a barely visible insoluble brown deposit near the exit. This deposit, which was also seen in some of the previous tests with platinum columns, was free of product.

PRODUCT REMOVAL AND PURITY

After calcination, the oxysulfate product is dissolved and rinsed from the column with 200 to 300 ml of 0.25M HNO_3 (or ~4M for oxide product). Although not necessary, removal is more effective if the acid is heated.

Filling the volume between the frits with dilute acid for effective dissolution of californium oxysulfate is best accomplished by vacuum transfer of the acid upflow into the column. Filling the column three or four times with dilute acid and allowing each fill to remain in the column ~15 minutes removes

>99% of the californium. Because a small amount of solid was noted between the frits and in the gas exit line after some calcinations, the vacuum should be attached to the exit end of the system, the dilute acid should be added, and the dissolved product should be removed through the inlet end. This permits retention of insoluble solids by the column frits, and the californium nitrate solution will be free of solids. These solids are free of product and are quite insoluble in dilute nitric acid.

No attempt was made to determine purity of products from calcination in stainless steel columns because of the considerable corrosion. The product purity was determined for all tests made in platinum columns, and these data are shown in Table V. In general, there were no cationic impurities added during loading and calcination of the resin column; however, there was not appreciable separation attained from cationic impurities present in the feed. The total quantity of impurities is essentially dependent on the volumes of process solution and the previous process steps. The relatively high weight percent of impurities in the californium products (Tests 1 and 2) is due to the small quantity of californium used in these tests.

Based on these tests the weight percent impurities in a ~100 mg batch of product is expected to be ~25%, which is well below the 400 wt % limit acceptable for most applications.

TABLE V

Product Purity

Test	Product	Impurity in Product, wt %	Impurities	
			Major	Minor
1	0.4 mg ^{252}Cf	~800	Fe, Zn, Ca, S, Na	Ni, Cr, Si, Ba, Pb
2	0.8 mg ^{252}Cf	~600	Fe, Zn, Ca, S, Na	Ni, Cr, Si, Ba, Pb
3	~65 mg Tb	~25	Zn, S	Fe, Ni, Cr, Si, Al, Pb
4	~100 mg ^{244}Cm	~25	Pb, Fe, S	Zn, Ca, Si
5	~18 mg ^{242}Cm	<15 ^a	Pb, Fe, Si	Zn, Ca
	~82 mg ^{244}Cm			

a. Feed was a simulated solution prepared from reagent chemicals except spikes of curium isotopes.

RECOVERY OF PRODUCT LOSSES

Loss of californium to the effluent from sorption on cation exchange resin from AHIB solution and loss during ignition of the resin to yield californium oxysulfate were very low in all tests. High losses in the sorption effluent could occur if acid adjustment was omitted or if excess acid was added to the feed. Such losses could be recovered by readjustment of the acid concentration and recycling the solution through the cation resin bed. Because the plant system is designed so that the effluent passes through a low range BF_3 detector, losses resulting from improper feed adjustment would be detected immediately.

The experimental tests demonstrated that product loss from the column during ignition is not significant. Two cases of product loss which could result if the platinum frit failed were investigated to determine a method for recovery. The first case assumed oxysulfate in the exit part of the system along with the water and tar collected in the trap and on the submicron filter, simulating a frit failure after most of the resin had been burned. Oxysulfate was added to the mixture that was leached out of the off-gas system with 6M nitric acid; the resulting solution was heated to boiling, diluted with water to 0.25M nitric acid, and fed to the bed of cation exchange resin. The product was sorbed quantitatively on the resin.

The second case assumed partially charred or ignited resin getting into the exit system, simulating a frit failure in the early stages of ignition. Such material was prepared by heating resin containing product to $\sim 400^\circ\text{C}$. It was not possible to leach or elute the product completely from this residue with strong nitric acid. The product was recovered by heating the residue in air at $\sim 800^\circ\text{C}$ to yield the oxysulfate and then dissolving the oxysulfate in 0.25M nitric acid.

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