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RFP-2206

RFP-2206
May 27, 1974

RECOVERY AND PURIFICATION OF AMERICIUM-241 FROM AN ALUMINUM-AMERICIUM OXIDE MIXTURE

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U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

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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 $4.00 Microfiche $1.45

Printed
May 27, 1974

RFP-2206
UC-4 CHEMISTRY
TID-4500-R60

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Chemistry Research and Development
CHEMICAL TECHNOLOGY

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

SUBJECT DESCRIPTORS
Aluminum
Americium
Dissolution
Purification
Recovery

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RECOVERY AND PURIFICATION OF AMERICIUM-241 FROM AN ALUMINUM-AMERICIUM OXIDE MIXTURE

Stephen G. Proctor

Abstract. A method for the separation and purification of americium from a mixture of aluminum and americium oxide has been developed. The precipitation procedure was designed to recover americium from gross amounts of aluminum by utilizing aluminum solubility in caustic solutions. Additional purification was obtained by successive fluoride and oxalate precipitations. The developed procedure has been used to recover and purify 57 g of americium from 204 g of aluminum-americium oxide.

INTRODUCTION

A simple recovery procedure has been devised to recover americium-241 from a composite of aluminum powder metal and americium oxide. Approximately 57 g of americium-241 have been recovered in purified oxide form from a 204-g, aluminum-americium oxide mixture. The basic recovery and purification scheme involved dissolving aluminum metal away from the americium oxide using sodium hydroxide, then purifying the recovered americium oxide by successive fluoride and oxalate precipitations. The caustic aluminum-dissolution step was selected based upon previous experience at Savannah River Laboratory[1] and Rocky Flats where plutonium-aluminum residues were processed for plutonium recovery.

SUMMARY

A composite mixture of aluminum metal and americium oxide was processed using a described procedure for recovery and purification of the americium. An americium recovery of 96.3% was realized from the processing. The AmO_2 product contained only 920 ppm of detectable impurities as determined by optical emission spectroscopy.

EXPERIMENTAL PROCEDURE

Aluminum Separation

A 2-liter solution of 5-M NaOH made 1-M in $NaNO_3$ was prepared for dissolving the Al-AmO_2 material. The solution was placed in a resin reaction kettle and Al-AmO_2 powder was slowly added. A total of 204.1 g of Al-AmO_2 mixture was added and the solution then allowed to cool. After cooling, the solution was filtered to remove the insoluble AmO_2. The AmO_2 was dried and weighed, and the filtrate from the dissolution was sampled for americium content. The dried AmO_2 (103.2 g) was dissolved in 1 liter of 10-M HNO_3 by heating the solution to 95 °C for 2 hours. After the dissolution was complete, acidity of the solution was adjusted to 0.1-M (H^+) by adding 8-M NH_4OH. Sufficient oxalic acid was added to precipitate the americium and leave the solution 0.1-M in oxalic acid. The resulting slurry was digested at 60 °C for 30 minutes followed by a 16-hour digestion period at 20 °C. The solution was then filtered to remove the insoluble americium oxalate ($Am_2[C_2O_4]_3$). The oxalate cake was washed with water and calcined at 600 °C for 6 hours to form AmO_2. The calcined AmO_2 was then weighed and sampled for americium content and impurity concentrations.

Rare Earth Separation

The aluminum-free AmO_2 (69.9 g) was divided into three, approximately equal batches in preparation for rare-earth separation. The three batches of AmO_2 were each dissolved in 200 ml of 10-M HNO_3 and processed identically. The acidity of each solution was reduced to 0.1-M (H^+) by adding 8-M NH_4OH. The solutions were then heated to 80 °C and made 0.25-M in ammonium persulfate ($[NH_4]_2S_2O_8$) and 0.002-M in argentic oxide (Ag_2O). After digesting the solutions at 80 °C for 45 minutes, the solutions were made 0.2-M HF and allowed to digest for five minutes before filtering. The insoluble rare-earth fluoride precipitate was washed with water, dried, and weighed. The three fluoride residues were combined and sampled for americium content. Americium in the resulting filtrate was then reduced to the trivalent state by adding ascorbic acid until the brown color of the hexavalent americyl ion disappeared.

The filtrate containing the americium was precipitated with oxalic acid using the method previously described. The three batches of americium oxalate were calcined to AmO_2 and composited. The resulting AmO_2 was redissolved in 500 ml of 8-M HNO_3 in preparation for the silver and lead removal. The silver and lead were precipitated by making the solution 0.1-M in NH_4Cl, thereby forming insoluble $PbCl_2$ and $AgCl$. The insoluble chloride precipitate was filtered from the solution, washed with water, and discarded. The americium in the resulting filtrate was again precipitated and the resulting $Am_2(C_2O_4)_3$ calcined to AmO_2. The purified AmO_2 was weighed and sampled for an impurity analysis and calorimetric americium assay.

DISCUSSION

Selective aluminum dissolution was successful because of the amphotericity of aluminum and the insolubility of AmO_2 in caustic solutions. The aluminum forms an aluminate complex, $Al(OH)^-_4$, in the dissolving reaction as shown by Equation 1.

$$Al + 4NaOH \rightarrow Al(OH)^-_4 + 4Na^+ \qquad (1)$$

The total reaction is shown in Equation 2.

$$Al + NaOH + 3H_2O \rightarrow Al(OH)^-_4 + Na^+ + \tfrac{3}{2}H_2\uparrow \qquad (2)$$

The evolution of hydrogen gas was suppressed by the addition of sodium nitrate, which reacts as shown in Equation 3.

$$NO^-_3 + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O \qquad (3)$$

This reaction prevents accumulation of a potentially hazardous hydrogen-oxygen mixture during the dissolution step.

The aluminum dissolution was vigorous but was controlled by limiting the addition of aluminum-americium oxide feed material. After the aluminum was dissolved, the insoluble AmO_2 was easily separated from the solution by filtration. The AmO_2 was then dissolved in nitric acid in preparation for precipitation of americium as americium oxalate. This precipitation further reduced the aluminum contamination in the americium product. The americium oxalate was then calcined to AmO_2, which was analyzed for impurities. Analysis showed the aluminum concentration was reduced from an initial concentration of 65.6 wt % to 0.02 wt %. Other impurities were mainly rare earths (7000 ppm) as shown in Table 1.

The rare-earth impurities were removed by fluoride precipitation;[2] however, americium was maintained in solution by being oxidized to the hexavalent state (Am VI). Trivalent americium will precipitate along with rare earths so complete oxidation of the americium was essential for a high recovery of americium. Oxidation was carried out in dilute nitric acid with ammonium

Table 1. Detectable Impurities in Americium Oxide After Aluminum Separation.

Element	Concentration (ppm)*
Al	200
Ca	150
Cu	100
Fe	300
Ce	5000
Nd	500
Tm	500
Y	1000
TOTAL	7750

---

*ppm – μg of impurity element per gram of AmO_2.

Table 2. Detectable Impurities in the Americium Oxide Product.

Element	Concentration (ppm)*
Al	20
Ca	500
Cr	50
Cu	100
Fe	100
Si	100
Tm	50
TOTAL	920

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*ppm – μg of impurities per gram of AmO_2.

persulfate by heating the solution to 80 °C for 45 minutes. Argentic oxide was added as a holding oxidant. The addition of fluoride ion (HF) caused the rare-earth fluorides to precipitate while the americium VI remained soluble. The rare-earth fluoride material was separated from the americium by filtration and checked for americium content.

The americium-bearing filtrate was again precipitated with oxalic acid and the resulting americium oxalate calcined to AmO_2. The AmO_2 product was analyzed for impurities as shown in Table 2. Results of rare-earth separation from americium showed the rare earths were reduced from 7000 ppm to 50 ppm (Tm) with a single precipitation. The AmO_2 product, calorimetrically assayed for americium content, had 0.875 g Am/g AmO_2.

Recovery of americium as pure AmO_2 totaled 96.3%, which was considered excellent. Most of the lost americium was in the rare-earth fluoride precipitate. The filtrate from the caustic dissolution contained 1.85×10^{-4} g Am/liter of solution; the oxalate filtrate contained 6.4×10^{-3} g Am/liter of solution. Both filtrates were subsequently discarded.

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