

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section A

PREPARATION OF AMERICIUM DIOXIDE BY THERMAL
DECOMPOSITION OF AMERICIUM OXALATE IN AIR

R. D. Baybarz

DATE ISSUED
DEC 20 1960

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

One hundred seventy-five grams of americium in a hydrochloric acid solution varying from 1 to 7 N was converted to americium dioxide. Americium oxalate was precipitated from 0.1 N HCl with 100% excess oxalic acid and was converted to the dioxide by calcination at 800°C in air. The solubility losses in the oxalate precipitation filtrate averaged approximately 7 mg per liter of solution, with a total loss of 0.09%.

CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	4
2.0 FLOWSHEET	4
3.0 SOLUBILITY LOSSES	5
4.0 PROCESS EQUIPMENT	5
5.0 RADIATION MEASUREMENTS	5
6.0 MATERIAL BALANCE	5

1.0 INTRODUCTION

A process is described by which americium in HCl solution was converted to AmO_2 . During the past several years americium has been stored at ORNL in the research pool as a hydrochloric acid solution. Several polyethylene bottles had disintegrated due to the radiation effects of the high alpha solution. The material was stored for such a length of time that the outer containers were badly corroded from evolved HCl. The explosion hazard from continuous hydrogen and oxygen production by the decomposition of water and the necessity of analysis prior to each withdrawal of material indicated the desirability of converting the americium chloride solution to a stable, safe form, such as a dry compound. It was decided that AmO_2 would be the best material to handle, and a process was set up to convert the 175 g of americium in 12 liters (25 bottles) of chloride solution to AmO_2 .

2.0 FLOWSHEET

The process used to convert the americium chloride solution to the dioxide consisted of introducing approximately 30 g of americium in 2 liters of solution into the precipitating vessel and neutralizing the acid (1 to 7 N) with a volume of 14 N NH_4OH to yield approximately 0.1 N free acid (Fig. 1). A saturated oxalic acid solution was added slowly to the neutralized solution, and large crystals of americium oxalate were allowed to grow. Upon completion of precipitation, 100% excess of oxalic acid was added and the slurry was agitated 1 hr prior to filtration. The digested americium oxalate was filtered on a medium-porosity glass frit and washed with approximately 10 vol of water. The americium oxalate cake, which is a dusty rose color, was partially dried by drawing air through it and was then transferred to a platinum boat for calcination.

The precipitate was dried in a furnace at 150°C for 1 hr and then the americium oxalate was decomposed at 350°C . The oxalate starts to decompose to the black dioxide at 300°C . In order to ensure conversion, the cake was held at 350°C for 1 hr before final firing at 800°C . The oxide was held at 800°C for 0.5 hr and then cooled to room temperature. The resultant oxide was a dense, fine-grained, black powder with a bulk density of approximately 3 g/cc. The oxide was transferred to tared bottles, weighed, sampled, and stored in lead shields.

Seven runs were made to convert the 175 g of americium in chloride solution to the dioxide. The amounts in the runs ranged from 9 to 35 g of americium. All the material on hand was converted to the oxide except 500 mg of solid americium trifluoride and the wash solutions of the process equipment. The process equipment was rinsed with nitric acid and the americium in the combined solutions was precipitated by sodium hydroxide. The americium hydroxide was filtered and dissolved in hydrochloric acid. The recovered americium solution contains 2.48 g in 500 ml of 5 N HCl.

UNCLASSIFIED
ORNL-LR-DWG. 53320

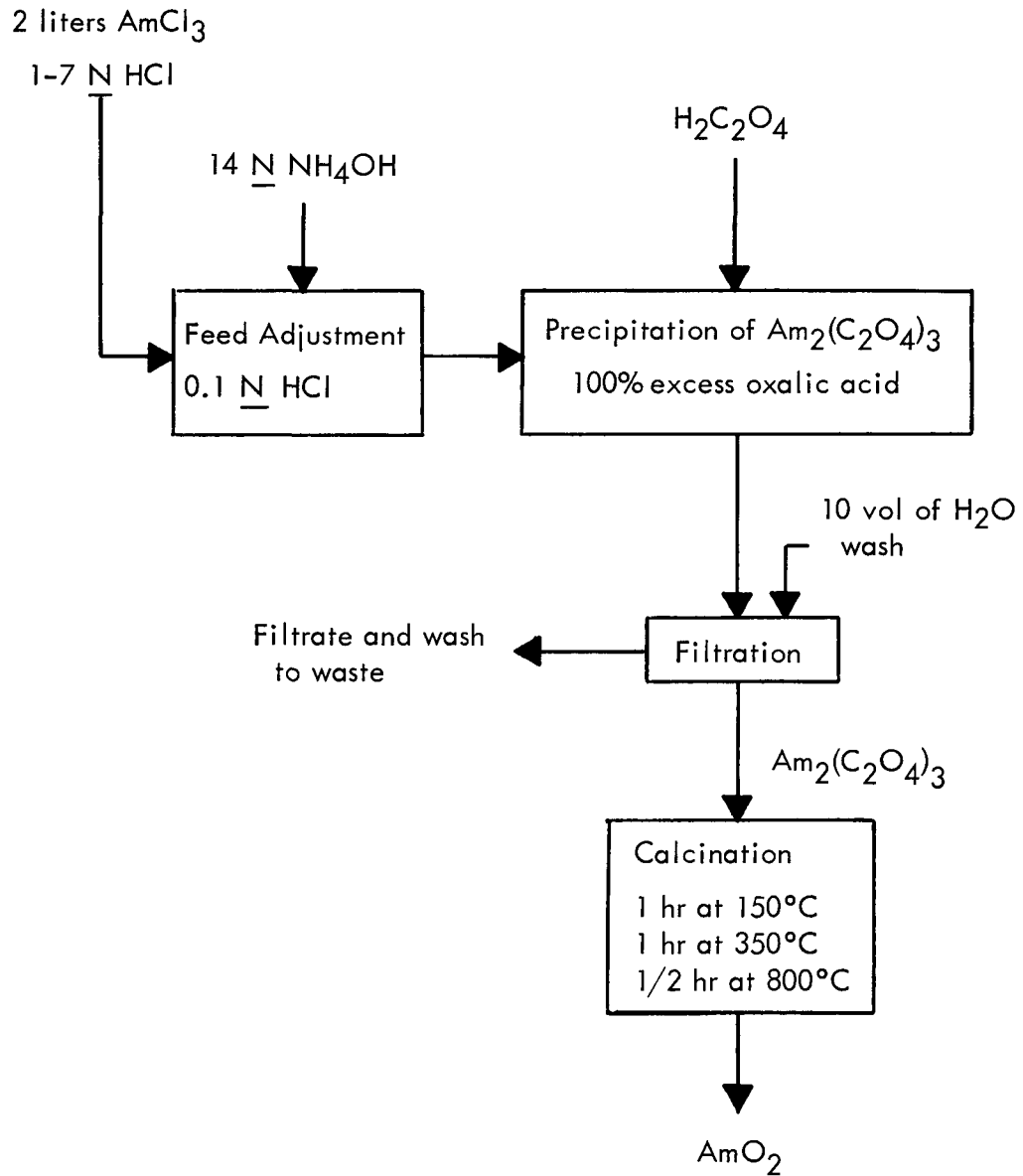


Fig. 1. Flowsheet for conversion of AmCl₃ solutions to AmO₂.

3.0 SOLUBILITY LOSSES

The solubility of americium is a function of the acidity of the solution. The lowest solubility loss, 1 mg per liter of solution, was at a pH of 4 when thermal hydrolysis of urea was used to neutralize the excess acid. Urea was used in only one process run, as the solubility losses averaged ~ 7 mg/liter when the solution was adjusted with ammonium hydroxide to ~ 0.1 N free acid. During one run the acid was 0.21 N and the solubility loss was 110 mg/liter. The americium in the filtrate was recovered by loading the americium on Dowex A-1 chelating resin and eluting with 2 N HCl. The total americium losses in the oxalate filtrates were 0.09% or a total of 0.17 g.

4.0 PROCESS EQUIPMENT

Three glove boxes were connected in series to process the Am^{241} . The first stainless steel box was used as storage for the packaged AmCl_3 solutions. The second and third boxes were covered with 1/4 in. of lead and were equipped with x-ray glass and lead oxide impregnated Neoprene gloves. The gloves had a lead equivalent of 50 mils. The second box was used to unpack the solutions and assay the solutions. The third box was used to precipitate, filter, calcine, and package the AmO_2 . The precipitation and filtration equipment used was modified glassware, and a platinum boat was used for calcination.

5.0 RADIATION MEASUREMENTS

Radiation measurements were made during the process. A 30-g batch of AmO_2 in a glass bottle read approximately 12 r/hr with a "cutie pie." The lead-impregnated Neoprene gloves decreased the radiation to ~ 150 mr/hr, and at the x-ray window the radiation was 0.7 mr/hr. The radiation through the 1/4-in. lead shield was < 0.2 mr/hr. The 60-keV γ ray from the Am^{241} requires light shielding for any quantity greater than ~ 100 mg.

6.0 MATERIAL BALANCE

Rocky Flats inventory	184.69 g	
Corrected for 457.7-yr $T_{1/2}$		179.85 g
ORNL Assay prior to processing		175.73 g
Material on hand		
AmO_2	170.16 g	
AmF_3	0.52 g	
AmCl_3 solution	2.48 g	
Americium waste solution discarded	0.17 g	
Total accounted for		173.33 g
Difference between initial and final assay (this is within the recognized analytical deviations of $\pm 3\%$)		2.40 g
Material lost in packaging (determined by difference)		4.12 g

Batches 1-6 were material received from Rocky Flats for the research pool. Batch 7 was an americium solution that has been purified from a highly contaminated shipment of waste solution from Los Alamos and stored at ORNL.

A discrepancy between the inventory value received from Rocky Flats and the assay taken before the processing indicated a 7% error. Part of the discrepancy is due to a difference in the half-lives used to determine the americium content of the solutions; Rocky Flats used a half life of 470 years where we used a half life of 457.7 years. This amounts to an error of 2.62% or 4.84 g of Am²⁴¹. The remaining discrepancy between the Rocky Flats assay and the inventory prior to processing was the loss of material from the polyethylene bottle into the shipping containers and the storage box environment. Some of the paint cans were badly corroded by the HCl fumes from the ruptured bottles. Also, solution was found in the open Lucite containers. The lids to all the containers were loose to prevent pressure buildup and possible explosion of the hydrogen and oxygen in the paint can, and loss of solution from the package is very likely. Recovery of material from the vermiculite, the lead shield, and the paint cans was not deemed practical, and the americium contained in these was not recovered. Some of the paint cans containing the vermiculite read as high as 500 mr/hr at 6 in. with a "cutie pie," and it is definite that americium was present in this material. This material was sealed in polyethylene bags and cast in concrete inside stainless steel drums. The drums were then buried in a cast concrete block to prevent escape of americium to the environment.

The recovered AmO₂ is stored in seven bottles, the product of each run in a separate container (Table 6.1). Five of the seven batches are pure AmO₂. The last two batches were contaminated with lanthanum, and the americium assays are 44.8 and 18.9%, respectively.

Method of Analysis. Radiometric analysis was used to determine the Am²⁴¹ content. This was done by alpha counting for assay analysis with gamma counting of the 60-kev Am²⁴¹ to check the alpha. The AmO₂ assay was taken as the theoretical 88.3%, as assays varied $\pm 5\%$ on triplicate samples. On batches A-6 and A-7, an average of four analyses was taken as the assay.

Table 6.1 Americium Products

Batch No.	Net Wt of Oxide, g	Americium	
		Assay, %	Net Wt, g
A-1	19.85	88.3	17.53
A-2	31.71	88.3	28.00
A-3	30.64	88.3	27.06
A-4	33.80	88.3	29.85
A-5	37.91	88.3	33.47
A-6	55.88	44.8	25.03
A-7	48.81	18.9	9.22
Totals	258.60		170.16

ORNL-3003
UC-10 - Chemistry-Separation Processes
for Plutonium and Uranium
TID-4500 (15th ed.)

INTERNAL DISTRIBUTION

- | | |
|--|--|
| 1. C. E. Center | 53. W. K. Eister |
| 2. Biology Library | 54. F. R. Bruce |
| 3. Health Physics Library | 55. D. E. Ferguson |
| 4-5. Central Research Library | 56. M. E. Whatley |
| 6. Reactor Experimental
Engineering Library | 57. H. E. Goeller |
| 7-26. Laboratory Records Department | 58. C. W. Hancher |
| 27. Laboratory Records, ORNL R.C. | 59. R. A. Charpie |
| 28. A. M. Weinberg | 60. J. A. Lane |
| 29. L. B. Emler (K-25) | 61. M. J. Skinner |
| 30. J. P. Murray (Y-12) | 62. R. E. Blanco |
| 31. J. A. Swartout | 63. G. E. Boyd |
| 32. E. H. Taylor | 64. W. E. Unger |
| 33. J. L. Fowler | 65. R. S. Cockreham |
| 34. E. D. Shipley | 66. A. T. Gresky |
| 35-36. F. L. Culler | 67. E. D. Arnold |
| 37. M. L. Nelson | 68. C. E. Guthrie |
| 38. W. H. Jordan | 69. J. W. Ullmann |
| 39. C. P. Keim | 70. K. B. Brown |
| 40. J. H. Frye, Jr. | 71. R. D. Baybarz |
| 41. S. C. Lind | 72. J. C. Bresee |
| 42. A. H. Snell | 73. P. M. Reyling |
| 43. A. Hollaender | 74. R. G. Wymer |
| 44. K. Z. Morgan | 75. J. W. Youngblood |
| 45. M. T. Kelley | 76. D. L. Katz (consultant) |
| 46. T. A. Lincoln | 77. I. Perlman (consultant) |
| 47. R. S. Livingston | 78. C. E. Larson (consultant) |
| 48. A. S. Householder | 79. H. Worthington (consultant) |
| 49. C. S. Harrill | 80. J. H. Rushton (consultant) |
| 50. C. E. Winters | 81. T. H. Pigford (consultant) |
| 51. H. E. Seagren | 82. ORNL - Y-12 Technical Library,
Document Reference Section |
| 52. D. Phillips | |

EXTERNAL DISTRIBUTION

83. Division of Research and Development, AEC, ORO
84-597. Given distribution as shown in TID-4500 (15th ed.) under Chemistry-Separation Processes for Plutonium and Uranium (75 copies - OTS)