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TITLE SEPARATION OF PLUTONIUM AND AMERICIUM BY LOW-TEMPERATURE FLUORINATION

AUTHOR(S) T. R. Mills and L. W. Reese
Nuclear Materials Technology Division
Los Alamos National Laboratory

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SEPARATION OF PLUTONIUM AND AMERICIUM BY LOW-TEMPERATURE FLUORINATION

T. R. Mills and L. W. Reese,
Los Alamos National Laboratory
Box 1663, MS E510
Los Alamos, NM 87545

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ABSTRACT

We have demonstrated separation of Pu and in-grown Am using the gaseous reagent dioxygen difluoride. Aged PuF_4 was fluorinated at room temperature to generate PuF_6 gas, which was trapped separately and reduced to PuF_4. The reaction product contained very little Am. Unreacted solid had elevated concentrations of Am that were consistent with a material balance. Use of a gaseous reagent and product enabled remote handling during reaction and purification. This result demonstrated a simple and minimal waste alternative that may have application to a number of actinide purification problems.

INTRODUCTION

Americium is generated in plutonium by ^{241}Pu decay ($t_{1/2}$ = 14.4 yr) to ^{241}Am ($t_{1/2}$ = 432.7 yr). Concentrations of the nuclides as a function of time (in years) are given by:

$$[^{241}Pu] = [^{241}Pu]^{\circ} \; e^{-0.0481\,t} \qquad (1)$$

$$[^{241}Am] = [^{241}Am]^{\circ} \; e^{-0.0016\,t} + [^{241}Pu]^{\circ} \frac{0.0481}{0.0481 - 0.0016} \left(e^{-0.0016\,t} - e^{-0.0481\,t}\right) \qquad (2)$$

Plutonium hexafluoride (PuF_6) is a volatile, somewhat stable compound while americium fluorides are non-volatile. (Present information indicates AmF_6 does not exist, is extremely reactive, or has very little stability.) Accordingly, complete fluorination of a Pu sample containing Am should enable a gas-solid separation of the two elements.

The highly reactive fluorinating agent dioxygen difluoride (O_2F_2) can produce PuF_6 from PuF_4 at ambient temperature [1]. O_2F_2 is generated at cryogenic temperatures, but it is thermally unstable at room temperature, producing reactive F atoms and O_2. The F atoms are available to "oxidize" PuF_4 to PuF_6; however, F-atoms also quickly recombine to produce F_2, which does not react with PuF_4 at ambient temperature. Overall competing reactions are:

$$O_2F_2 \rightarrow F_2 + O_2 \quad (3)$$

$$PuF_4 + O_2F_2 \rightarrow PuF_6 + O_2 \quad (4)$$

The experimental approach is to vaporize O_2F_2 and transport it rapidly to a reactor bed containing a Pu solid. Gaseous PuF_6 will be produced and Am will remain in the solid.

EXPERIMENTAL DETAILS

The entire experimental apparatus was housed in gloveboxes for contamination control. All gas and solid-containing components of the experimental system were constructed of aluminum, 304 stainless steel, or monel and were made helium-leak tight and passivated with F_2 and O_2F_2. The reactor holding the solid to be reacted had multiple layers of fine-mesh stainless steel screen to support the solid and porous nickel filters to retard migration of solids in the gas exit stream. The experimental system included various traps, Metal Bellows™ pumps, an optical cell, and a vacuum system. Gas pumped from the system passed through chemical traps containing soda lime and alumina to react with fluorine. Pressures were measured using 0-1000 torr MKS™ Baratrons, and temperatures were measured using copper-constantan and chromel-alumel thermocouples.

A relatively pure, several year-old batch of PuF_4 was identified and sampled for actinide analysis. The PuF_4 solid powder was ground in a pestle to uniformity (20 mesh) and put into the reactor. O_2F_2 was produced from O_2 and F_2 in other apparatus using thermal generation of F-atoms [2, 3] and was cryogenically condensed into a trap preceding the reactor. The O_2F_2 trap was warmed slowly to volatilize O_2F_2 that flowed to the bottom of and through the reactor bed under its own vapor pressure. Gas exiting the reactor flowed successively through an IR cell, a refrigerated trap (-80°C), and a bellows pump into a trap cooled by liquid nitrogen. (PuF_6 was retained in the refrigerated trap, while O_2 and F_2 from O_2F_2 decomposition were condensed in the LN_2 trap.)

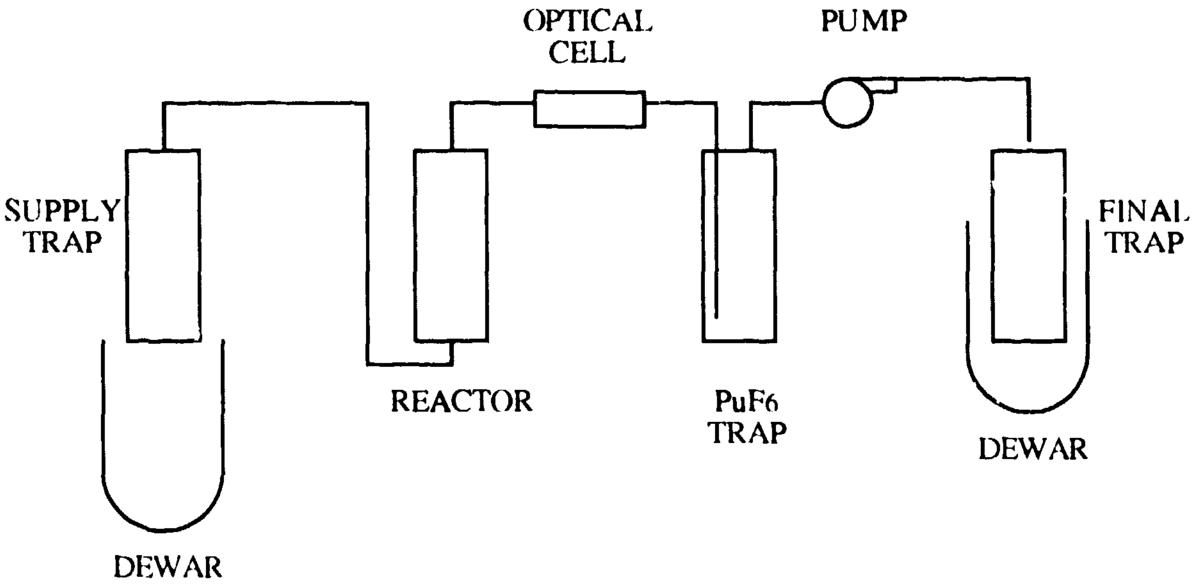

Figure 1. Schematic flow diagram of PuF_4 fluorination apparatus.

Following an experimental run, PuF_6 was transferred cryogenically into a removable trap for weighing. PuF_6 was then reduced to PuF_4 by reacting with CH_4 (5% in N_2) in a reduction volume. PuF_4 product, typically from several runs, was weighed and sampled for analyses.

A small amount of unreacted solid residue from the reactor was fluorinated with O_2F_2 in a smaller reactor to demonstrate further Pu/Am separation. Experimental apparatus and procedures were similar to those for the larger batch.

RESULTS

70% of the initial PuF_4 in the reactor was reacted in several runs, reduced to PuF_4, and analyzed. The reaction of O_2F_2 with PuF_4 began at a supply trap temperature of 110°C, corresponding to a O_2F_2 vapor pressure of ~10 torr. The temperature (and thus pressure) of O_2F_2 in the supply trap was held nearly constant by continual height adjustment of a LN_2 dewar below the trap. Thermocouples extending into the bed measured small temperature rises (5-20°C) at the onset of reaction, but temperatures returned shortly to ambient and remained so during the reaction period. When the O_2F_2 supply was exhausted, the reactor pressure dropped, and the run was terminated.

A Nicolet 20SX FTIR spectrometer was used to measure PuF_6 in reactor exit gas during the reaction period. The R-branch of the v_3 vibration at 622 cm^{-1} was used to identify and quantify PuF_6. The IR absorbance was calibrated with pure PuF_6 from the product trap. Absorbance was linear with PuF_6 pressure up to 6 torr.

Very small amounts of CF_4 were observed at the onset of reaction during some runs, but shortly PuF_6 was the only species observed by FTIR. Initial PuF_6 observation coincided with the bed temperature rise. Relatively constant PuF_6 concentrations were observed at constant O_2F_2 pressure. The PuF_6 partial pressure ran as high as 25% of the total pressure.

Using gravimetric PuF_6 product measurements, production of PuF_6 ranged from 0.24 to 1.59 g PuF_6/g O_2F_2. From Rxn (4), total O_2F_2 utilization would produce 5.04 g/g. Fluorine utilization efficiencies as high as 31% (1.58 g/g) were repeatable at the same reaction pressure. Efficiencies were highest at 15-20 torr total pressure.

Reduction of PuF_6 with diluted CH_4 initially proceeded rapidly but mildly, with a 2-3 °C temperature rise in the gas within 5 minutes. Because no provision was made for gas stirring, reductions were allowed to continue overnight. Gaseous reaction products were analyzed by FTIR in the optical cell. The reaction of CH_4 to CF_4 was not complete, as all CH_xF_y (x+y = 4) species were identified. Best results were obtained when the stoichiometric ratio of PuF_6:CH_4 was 3:1, to gave CHF_3 as primary reaction product.

$$CH_4 \quad + \quad 3PuF_6 \quad \rightarrow \quad 3PuF_4 \quad + \quad CHF_3 \quad + \quad 3HF \qquad (5)$$

The initial charge of PuF_4 was salmon-colored with a bulk density of about 4 g/cm^3 after grinding. PuF_4 removed from the reduction vessel was a very fine solid of a creamy yellow color, uniformly covering the floor of the vessel. Some PuF_4 was retained in the PuF_6 weighing trap due to decomposition of PuF_6. This solid was a loose solid, somewhat pink on the surface, but the bulk was a gray-green color. The bulk density of all product PuF_4 was quite low, ranging from 0.3 to 0.7 g/cm^3. The amounts of PuF_4 recovered from PuF_6 reduction was in stoichiometric agreement (within 5%) with the weighed amounts of PuF_6 in the trap. Residual PuF_4 from the reactor had a bulk density of 0.9 g/cm^3.

The initial PuF_4 sample had 0.734% ^{241}Pu (isotopic fraction) and 3025 ppm Am (µg Am/g Pu). Assuming the PuF_4 was initially pure, the sample was 1.05% ^{241}Pu initially and was 7.25 years old; this age agrees with other information. Am grows into this Pu at an approximate rate of 1 ppm/day. Significant time periods elapsed between conduct of experiments and analyses, thus it was necessary to correct Am results back to the date of experiments using Pu and Am measurements and Eqns (1) and (2). Am analyses presented are those corrected to such date.

Sequentially, samples of PuF_4 product (reduced from PuF_6) contained 25, 20, 160, 80, 60, and 300 ppm Am. The unreacted solid contained 8285 ppm Am at the end of the series of experiments.

A fraction of the remaining solids from the reactor bed was placed in a smaller reactor for further reaction. In a single experiment, 73% of the sample was volatilized, with PuF_6 generation confirmed by FTIR. During the run, production of PuF_6 ceased before all O_2F_2 had been volatilized. The reactor was opened after the reaction, and most of the remaining solid was on the reactor walls or at the exit filter. The solids put into the reactor had 8490 ppm Am; the remaining solid had 31760 ppm Am. The amount of PuF_6 collected was in good agreement with the amount of PuF_4 reacted.

DISCUSSION AND SUMMARY

The amount of PuF_4 remaining in the large reactor was 30% of the charge. However, the amount of PuF_6 weighed product, as well as PuF_4 product after reduction, accounted for only about 60% of the initial solid. Some PuF_6 may have been reacted with the chemical traps, but this is believed to be a quite small amount. Some PuF_4 may not have been removed from the reactor, or other PuF_4 may have been deposited elsewhere in the apparatus due to PuF_6 decomposition. Assuming all Am from the initial material was retained in the reactor and that no other PuF_4 is in the reactor, one expects 3025*100/30 = 10083 ppm Am in remaining solid. If all Am was retained but 10% of initial solid remains in the reactor, one expects 3025*100/40 = 7563 ppm Am. The observed value was 8285 ppm, and product analyses show little Am. Cleanup and dismantling of apparatus will help identify the location of remaining material. Among questions to be answered is whether any solids passed through or by exit filters.

Lack of total reaction in the smaller reactor was due to migration of the PuF_4 powder to reactor walls and the exit filter, resulting in poorer contact of O_2F_2 with the solid. Expected Am content for the solid, assuming total retention of Am, was 8490*100/27= 31444 ppm. The observed result was 31760 ppm, which supports the assumption within experimental error. While the PuF_6 from this last experiment has not yet been analyzed, this result indicates an efficient separation of Pu from Am.

The reaction of O_2F_2 with PuF_4 progressed efficiently and under very mild experimental conditions. The Am concentration in reaction product PuF_4 was reduced from that in the solid by a factor of 10-100. The rise in Am concentration of solid residue was consistent with retention of Am and a material balance. The reaction, separation, and reduction do not require "hands-on" treatment, which reduces potential for personnel radiation exposure. The direct waste products are gases that could be potentially reused (O_2, F_2), are easily neutralized (HF), or are non-hazardous (N_2, O_2, CHF_3). The reduction of PuF_6 can also be attained thermally, which avoids use of a reagent and a reduction in wastes. This result demonstrates a simple and efficient separation method that may have application to other actinide separations.

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