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TITLE SEPARATION OF PLUTONIUM AND AMERICIUM
BY LOW-TEMPERATURE FLUORINATION

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SEPARATION OF PLUTONIUM AND AMERICIUM BY LOW-TEMPERATURE FLUORINATION

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ABSTRACT

We have demonstrated separation of Pu and in-grown Am using the gaseous reagent dioxygen difluoride. Aged PuF₄ was fluorinated at room temperature to generate PuF₆ gas, which was trapped separately and reduced to PuF₄. 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 ²⁴¹Pu decay ($t_{1/2} = 14.4$ yr) to ²⁴¹Am ($t_{1/2} = 432.7$ yr). Concentrations of the nuclides as a function of time (in years) are given by:

$$[^{241}\text{Pu}] = [^{241}\text{Pu}]^0 e^{-0.0481 t} \quad (1)$$

$$[^{241}\text{Am}] = [^{241}\text{Am}]^0 e^{-0.0016 t} + [^{241}\text{Pu}]^0 \frac{0.0481}{0.0481 - 0.0016} (e^{-0.0016 t} - e^{-0.0481 t}) \quad (2)$$

Plutonium hexafluoride (PuF₆) is a volatile, somewhat stable compound while americium fluorides are non-volatile. (Present information indicates AmF₆ 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 (O₂F₂) can produce PuF₆ from PuF₄ at ambient temperature [1]. O₂F₂ is generated at cryogenic temperatures, but it is thermally unstable at room temperature, producing reactive F atoms and O₂. The F atoms

are available to "oxidize" PuF₄ to PuF₆; however, F-atoms also quickly recombine to produce F₂, which does not react with PuF₄ at ambient temperature. Overall competing reactions are:



The experimental approach is to vaporize O₂F₂ and transport it rapidly to a reactor bed containing a Pu solid. Gaseous PuF₆ 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 F₂ and O₂F₂. 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 PuF₄ was identified and sampled for actinide analysis. The PuF₄ solid powder was ground in a pestle to uniformity (20 mesh) and put into the reactor. O₂F₂ was produced from O₂ and F₂ in other apparatus using thermal generation of F-atoms [2, 3] and was cryogenically condensed into a trap preceding the reactor. The O₂F₂ trap was warmed slowly to volatilize O₂F₂ 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. (PuF₆ was retained in the refrigerated trap, while O₂ and F₂ from O₂F₂ decomposition were condensed in the LN₂ trap.)

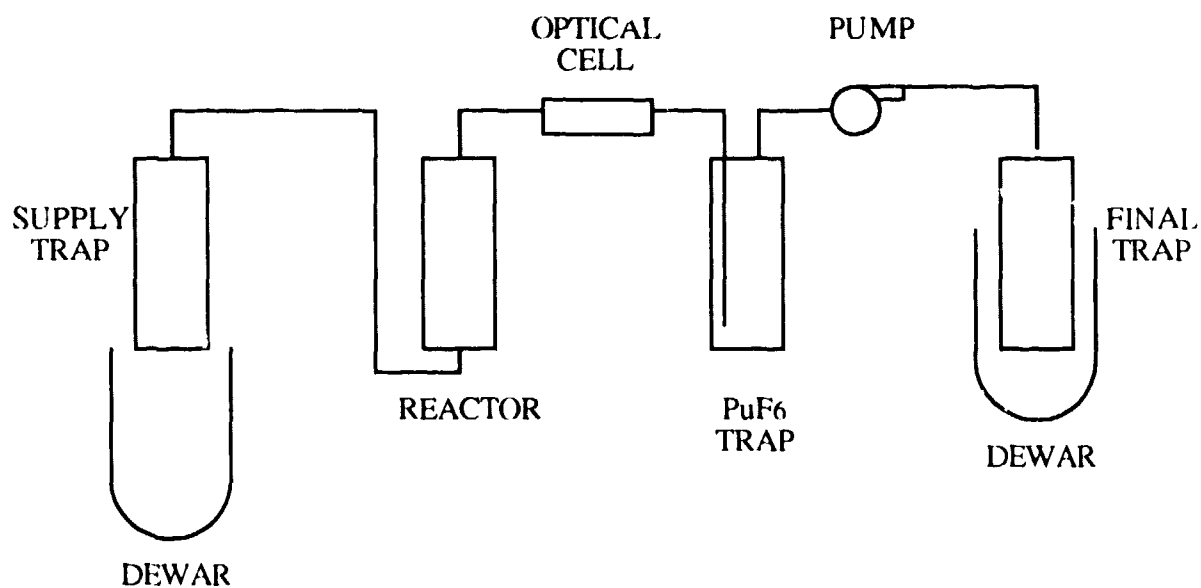


Figure 1. Schematic flow diagram of PuF₄ fluorination apparatus.

Following an experimental run, PuF₆ was transferred cryogenically into a removable trap for weighing. PuF₆ was then reduced to PuF₄ by reacting with CH₄ (5% in N₂) in a reduction volume. PuF₄ product, typically from several runs, was weighed and sampled for analyses.

A small amount of unreacted solid residue from the reactor was fluorinated with O₂F₂ in a smaller reactor to demonstrate further Pu/Am separation. Experimental apparatus and procedures were similar to those for the larger batch.

RESULTS

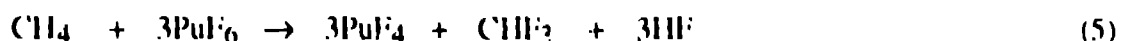
70% of the initial PuF₄ in the reactor was reacted in several runs, reduced to PuF₄, and analyzed. The reaction of O₂F₂ with PuF₄ began at a supply trap temperature of -110°C, corresponding to a O₂F₂ vapor pressure of ~10 torr. The temperature (and thus pressure) of O₂F₂ in the supply trap was held nearly constant by continual height adjustment of a LN₂ 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 O₂F₂ supply was exhausted, the reactor pressure dropped, and the run was terminated.

A Nicolet 20SX FTIR spectrometer was used to measure PuF₆ in reactor exit gas during the reaction period. The R-branch of the ν₃ vibration at 622 cm⁻¹ was used to identify and quantify PuF₆. The IR absorbance was calibrated with pure PuF₆ from the product trap. Absorbance was linear with PuF₆ pressure up to 6 torr.

Very small amounts of CF₄ were observed at the onset of reaction during some runs, but shortly PuF₆ was the only species observed by FTIR. Initial PuF₆ observation coincided with the bed temperature rise. Relatively constant PuF₆ concentrations were observed at constant O₂F₂ pressure. The PuF₆ partial pressure ran as high as 25% of the total pressure.

Using gravimetric PuF₆ product measurements, production of PuF₆ ranged from 0.24 to 1.59 g PuF₆/g O₂F₂. From Rxn (4), total O₂F₂ 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 PuF₆ with diluted CH₄ 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 CH₄ to CF₄ was not complete, as all CH_xF_y (x+y = 4) species were identified. Best results were obtained when the stoichiometric ratio of PuF₆:CH₄ was 3:1, to give CHF₃ as primary reaction product.



The initial charge of PuF₆ was salmon-colored with a bulk density of about 4 g/cm³ after grinding. PuF₄ removed from the reduction vessel was a very fine solid of a creamy yellow color, uniformly covering the floor of the vessel. Some PuF₄ was retained in the PuF₆ weighing trap due to decomposition of PuF₆. 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 PuF₄ was quite low, ranging from 0.3 to 0.7 g/cm³. The amounts of PuF₄ recovered from PuF₆ reduction was in stoichiometric agreement (within 5%) with the weighed amounts of PuF₆ in the trap. Residual PuF₄ from the reactor had a bulk density of 0.9 g/cm³.

The initial PuF₄ sample had 0.734% ²⁴¹Pu (isotopic fraction) and 3025 ppm Am (μg Am/g Pu). Assuming the PuF₄ was initially pure, the sample was 1.05% ²⁴¹Pu 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 PuF₄ product (reduced from PuF₆) 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 PuF₆ generation confirmed by FTIR. During the run, production of PuF₆ ceased before all O₂F₂ 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 PuF₆ collected was in good agreement with the amount of PuF₄ reacted.

DISCUSSION AND SUMMARY

The amount of PuF₄ remaining in the large reactor was 30% of the charge. However, the amount of PuF₆ weighed product, as well as PuF₄ product after reduction, accounted for only about 60% of the initial solid. Some PuF₆ may have been reacted with the chemical traps, but this is believed to be a quite small amount. Some PuF₄ may not have been removed from the reactor, or other PuF₄ may have been deposited elsewhere in the apparatus due to PuF₆ decomposition. Assuming all Am from the initial material was retained in the reactor and that no other PuF₄ is in the reactor, one expects $3025 \times 100/30 = 10083$ ppm Am in remaining solid. If all Am was retained but 10% of initial solid remains in the reactor, one

expects $3025 \times 100/40 = 7563$ 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 PuF₄ powder to reactor walls and the exit filter, resulting in poorer contact of O₂F₂ with the solid. Expected Am content for the solid, assuming total retention of Am, was $8490 \times 100/27 = 31444$ ppm. The observed result was 31760 ppm, which supports the assumption within experimental error. While the PuF₆ from this last experiment has not yet been analyzed, this result indicates an efficient separation of Pu from Am.

The reaction of O₂F₂ with PuF₄ progressed efficiently and under very mild experimental conditions. The Am concentration in reaction product PuF₄ 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 (O₂, F₂), are easily neutralized (HF), or are non-hazardous (N₂, O₂, CHF₃). The reduction of PuF₆ 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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