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IMPURITY REMOVAL BY FLUORINATION OF PLUTONIUM DIOXIDE BETWEEN 28 AND 300°C

James D. Navratil
Ralph O. Wing

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401
U.S. ATOMIC ENERGY COMMISSION
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CONTENTS

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James D. Navratil and Ralph O. Wing

Abstract. Fluorination of plutonium dioxide between 28 and 300°C has been investigated in a static-bed fluoride volatility system at Rocky Flats.

Boron, chromium, molybdenum, silicon, tantalum, and titanium impurities were significantly removed from the plutonium dioxide after fluorinating at 300°C for 15 minutes. Less than 1% of the plutonium was volatilized during these fluorinations, and approximately 99% of the plutonium dioxide was converted to plutonium tetrafluoride. All effective impurity removal, for the system investigated, was accomplished in the initial 15 minutes of reaction. Conversion of plutonium dioxide to plutonium tetrafluoride was essentially complete within the same period of time.

INTRODUCTION

A plutonium recovery and purification process utilizing the volatile property of the hexafluoride to recover and purify plutonium from various waste streams is being evaluated. Impure plutonium dioxide, generated in the production of pure plutonium metal, is a major part of this waste material. The impurities range from a few thousand parts per million to several percent.

The process includes the following reactions:

$$PuO_{2(s)} + 2F_{2(g)} \rightarrow PuF_{4(s)} + O_{2(g)} \quad (1)$$

$$PuF_{4(s)} + F_{2(g)} \rightarrow PuF_{6(g)} \quad (2)$$

$$\text{Net} \quad PuO_{2(s)} + 3F_{2(g)} \rightarrow PuF_{6(g)} + O_{2(g)} \quad (3)$$

Reaction (2) does not occur at an appreciable rate below 300°C, and at all temperatures of process interest, it is the rate limiting step. Reaction (2) is slightly endothermic and requires an excess of fluorine gas for practical completion.

Reaction (1) is of interest in this report. It is an exothermic reaction, giving rise to a rapid thermal excursion, or heat spike, when the gas contacts the solid.

The purposes of these experiments were: (a) to determine if low temperature volatile impurities could be removed by fluorination from plutonium dioxide before plutonium hexafluoride is produced, (b) to determine how much plutonium would be lost during low temperature fluorination, and (c) to determine the amount of plutonium dioxide converted to the tetrafluoride. The effect of fluorination on the mean crystallite size and the specific surface area of the original oxide was also investigated.

SUMMARY AND CONCLUSIONS

Fluorination of plutonium dioxide between 28 and 300°C has been investigated in a static-bed, fluoride volatility system. The volatile impurities which were partially removed when plutonium oxide was fluorinated at 300°C were B, Cr, Mo, Si, Ta, and Ti. Complete removal of these elements was not achieved. The removal of these impurities increased with temperature. The remaining detectable elements which did not volatilize were: Al, Be, Ca, Cd, Cu, Fe, Ga, Mg, Mn, Ni, Pb, Sn, and Zn.

The average plutonium loss under 300°C was less than 1%. Maximum loss of about 4% occurred on fluorination at 300°C for 4 hours. The conversion of plutonium dioxide to plutonium tetrafluoride was approximately 93% complete at 28°C and approximately 99% complete at 300°C within 15 minutes of fluorination. Dilution of fluorine with argon lowered the plutonium dioxide conversion yield. The percent of conversion would probably be higher in a fluid-bed system where better gas-solid contact would be achieved.

The mean crystallite size of the solid plutonium phase increased as the temperature of fluorination increased. The specific surface area of the solid plutonium phase decreased from 3.3- to 0.4-m^2/g as the fluorination temperature increased.

EXPERIMENTAL

EQUIPMENT – The experiments were conducted in a static-bed reactor fluoride volatility system. The main components of the system are shown in Figure 1. The system has been described in detail elsewhere (1).

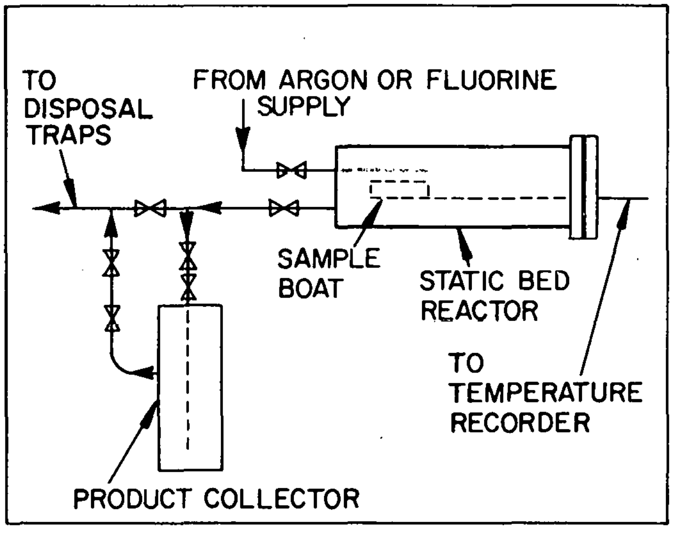
The nickel static-bed reactor is 13-in.-long by 1¾ i.d., and is heated with a horizontal tube furnace. Three thermocouples are positioned under the front, middle and rear of the sample boat. The nickel sample boat (1½ in. by 2 in. by ¼ in.) rests on the thermocouple well. One 8 in. by ¾ in. product collector, immersed in a liquid argon-filled Dewar flask, was used to desublime the volatile materials.

MATERIALS USED – Two types of feed material were used during this investigation. The first oxide feed material was typical of the burned plutonium metal at Rocky Flats. Before this feed was used, it was screened to minus 325 mesh. The entire batch was then blended and sampled. The second feed material was plutonium dioxide mixed with about 5% plutonium tetrafluoride. This material was ground in a mortar and pestle, blended, and sampled.

The fluorine was supplied from 4½ pound cylinders. Hydrogen fluoride present as an impurity in the fluorine was removed by passing the fluorine through a heated (100°C) sodium fluoride trap. Gaseous argon for purging purposes was obtained from a liquid argon storage tank.

PROCEDURE – Eight grams of plutonium feed material were placed in a tared sample boat for each experiment. The depth of the feed was approximately one-eighth inch. The boat and feed were weighed and placed in the reactor. An empty collection vessel was evacuated, tared, and placed in the system. The reactor and the collection vessel were leak-checked. After the desired temperature was reached in the reactor, and after the collector was cooled with liquid argon, gaseous argon was purged through the system at 400 cc per minute to remove moisture. Fluorine was introduced at 400 cc per minute after a 5-minute argon purge. At the completion of the fluorination time, the argon purge was again introduced and continued for 10 minutes. Argon flow was stopped, the furnace heat supply was turned off, and the valve between the reactor and the down-stream system was closed. The rest of the system was evacuated for 5 minutes. The collector was sealed, removed from the system, warmed to room temperature and weighed. The collector was then placed back in the static-bed system and vapor pressure measurements were taken on the contents. Finally, the sample boat was removed from the reactor and weighed. The contents were sampled for various analyses. A new sample of plutonium dioxide feed was used for each of the temperature runs.

Figure 1. Main components of the static-bed fluoride volatility system.



SAMPLING PROCEDURE – The plutonium tetrafluoride was ground in a mortar and pestle, blended, and sampled for the following analyses: percent plutonium by volumetric ceric sulfate titration, percent plutonium dioxide by x-ray diffraction, percent fluoride by neutron counting, mean crystallite size by x-ray diffraction, specific surface area by BET adsorption technique, and trace metal impurities by emission spectroscopy. The starting material was treated in the same manner, and the same analyses, except for the fluoride analysis, were performed.

In three experiments, samples were taken of the gases collected in the collection vessel. The gas sample was transferred from the collection vessel to a 10-cm potassium bromide gas cell. An absorption curve of the gases was then recorded using a Perkin-Elmer 521 infrared spectrophotometer.

RESULTS AND DISCUSSION

IMPURITY RESULTS – Table I lists the boiling or sublimation (2,3) points of some fluorides that are volatile below 300°C. The compounds listed will

Table I. Boiling or sublimation temperatures of various fluorides.

Compound	Temperature (°C)
CF_4	-128
BF_3	-100
SiF_4	- 95
C_2F_4	- 76
SF_6	- 64
SF_4	- 40
GeF_4	- 36
Si_2F_6	- 19
WF_6	17
MoF_6	35
UF_6	56
Te_2F_{10}	60
MoF_5	227
TaF_5	229
WF_5	237
TiF_4	284
CrF_4	300

Table II. Emission spectroscopy impurity results of first feed material (PuO_2) before and after fluorination.

Material was fluorinated for 15 and 30 minutes at various temperatures.
Results are in parts per million of plutonium.
Asterisk denotes no significant change in results as compared to the unfluorinated feed.

Initial Fluorination Temperature (°C)		28	55	100	151	200	250	300
Maximum Temperature (°C)		190	209	244	287	334	395	420
Element Analyzed	Unfluorinated Feed	Fluorinated Feed						
Aluminum	296	*	*	*	*	*	*	*
Beryllium	0.08	*	*	*	*	*	*	*
Boron	6	<1	<1	2	2	<1	<1	<1
Calcium	42	*	*	*	*	*	*	*
Cadmium	<10	*	*	*	*	*	*	*
Chromium	58	*	15	21	*	22	20	22
Copper	112	*	*	*	*	*	*	*
Iron	861	*	*	*	*	*	*	*
Potassium	4	1	*	*	*	*	1	<1
Magnesium	175	*	*	*	*	*	*	*
Manganese	17	*	*	*	*	*	*	*
Molybdenum	10	2	1	3	*	3	2	<1
Nickel	136	575	304	*	*	*	*	*
Lead	36	*	*	*	*	*	*	*
Silicon	176	39	25	25	37	41	37	17
Tin	10	*	*	*	*	*	*	*
Tantalum	1328	*	*	*	*	*	*	*
Titanium	13	<1	1	1	1	1	1	1
Zinc	65	*	*	*	*	*	*	*

be produced from fluorination of plutonium dioxide generated at Rocky Flats.

The emission spectroscopy results presented in Tables II and III represent the detectable metal impurities found in both feed materials. Analyses for twelve additional elements showed them to be below detectable limits.

Table II presents the impurities of the first feed material before and after fluorination for 15- and 30-minute periods. The impurity results of the unfluorinated feed material are an average of the results from four separate determinations. The fluorinated feed material impurity results are from a single determination. Asterisks denote no significant change in the results as compared to the unfluorinated feed. A significant change is one in which the analyses show a change by a factor of approximately three or greater, e.g., 100 ppm to <33 ppm. The choice of factor was determined by the precision of the analytical method. The maximum temperature that the sample experienced was the reactor temperature plus any heat-spike.

The data of Table II show decontamination of boron, chromium, molybdenum, silicon, and titanium as would be expected from the data in Table I. The reduction of potassium concentration is unexpected and unexplained. The increase in nickel indicates contamination from the furnace walls.

Impurity results in Table III compare the second feed material (plutonium dioxide with 5 w/o plutonium tetrafluoride) before and after fluorination. The results of the unfluorinated feed material are an average of four determinations. For the remainder of the table, each datum is the result of a single determination.

Decontamination of chromium, molybdenum, silicon, and titanium again is in accord with the data presented in Table I. Each tantalum result is an average of two emission spectroscopy analyses and one wet chemistry analysis. The results agree with the reported volatility of tantalum fluorides.

Significant quantities of chromium, molybdenum, and silicon are removed below 200°C. Tantalum and titanium fluoride volatilization seems to require temperatures between 200 and 300°C. Complete volatilization of these elements was not observed

Table III. Emission spectroscopy impurity results of second feed material ($PuO_2 + 5$ w/o PuF_4) before and after fluorination at various temperature and time intervals.

Results in parts per million of plutonium.

Asterisk denotes no significant change in results as compared to unfluorinated feed results.

Fluorination Temperature (°C)		98	100	200	300	300
Maximum Temperature (°C)		228	220	318	409	395
Fluorination Time (minutes)		15	240	15	15	240
Element Analyzed	Unfluorinated Feed					
Aluminum	168	*	*	*	*	*
Beryllium	0.09	*	*	*	*	*
Calcium	138	*	*	*	*	*
Cadmium	10	*	*	*	*	*
Chromium	57	18	21	16	15	19
Copper	95	*	*	*	*	*
Iron	705	*	*	*	*	*
Gallium	3600	*	*	*	*	*
Potassium	2	*	*	*	*	*
Magnesium	268	*	*	*	*	*
Manganese	18	*	*	*	*	*
Molybdenum	10	*	*	3	3	3
Nickel	244	*	*	*	*	*
Lead	31	*	*	*	*	*
Silicon	119	22	40	30	13	*
Tin	8	*	*	*	*	*
Tantalum	1303	*	*	*	287	157
Titanium	18	*	*	*	5	5
Zinc	65	*	*	*	*	*

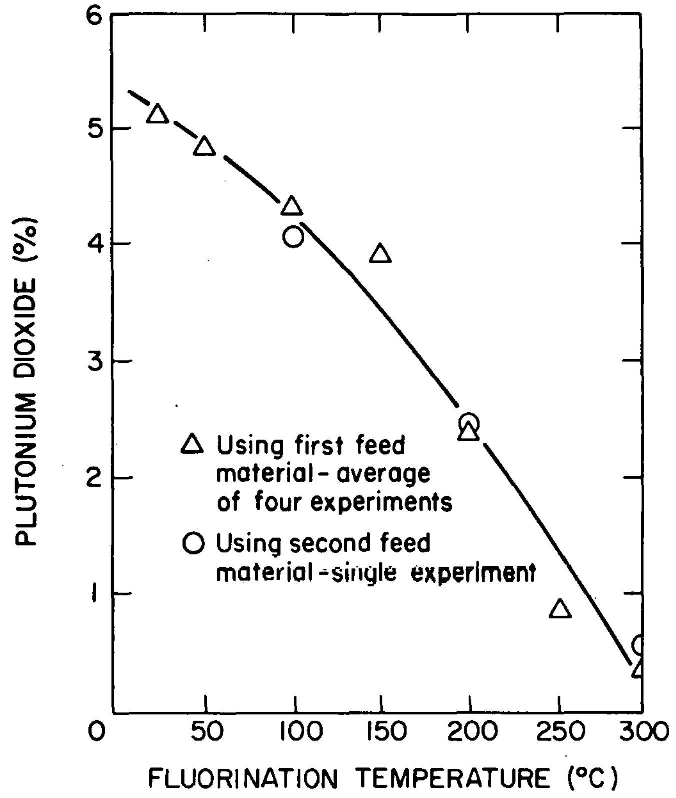


Figure 2. The effect of fluorination temperature on the concentration of plutonium dioxide remaining in residue.

even at 300°C. The remaining fourteen elements do not appear to volatilize below 300°C.

Fluorination times in excess of 15 minutes, as indicated in Table III, have little effect on the volatilization of impurities. After the heat spike is completed, which takes approximately 15 minutes, additional fluorination time appears unnecessary.

The percent plutonium dioxide remaining in the sample after fluorination at several temperatures is shown in Figure 2. Figure 3 shows the percent of plutonium tetrafluoride in the same fluorinated samples. The fluorination times were 15, 30, and 240 minutes. Fluorination times greater than 15 minutes did not increase the conversion of plutonium dioxide to the tetrafluoride. Figure 2 shows that approximately 95% of the oxide was converted at 28°C. Greater than 99% conversion was achieved at 300°C.

Figure 3 indicates that approximately 92% conversion at 28°C and 97% conversion at 300°C is obtained.

The percent plutonium tetrafluoride was calculated from the equation,

$$(\%\ \mathrm{Pu}) - (\%\ \mathrm{PuO_2})\ (0.88) + \%\mathrm{F} = \%\ \mathrm{PuF_4}.$$

PLUTONIUM LOSS DURING LOW-TEMPERATURE FLUORINATIONS – The plutonium loss for the experiments is presented in Table IV. The percent plutonium loss was calculated using the following equation:

$$\frac{(\text{Feed Wt})\ (\%\ \text{Pu in Feed}) - (\text{Residue Wt})\ (\%\ \text{Pu in Residue})}{(\text{Feed Wt})\ (\%\ \text{Pu in Feed})} \times 100$$

equals % Pu loss.

The percent plutonium loss as shown in Table IV might be due to spillage of feed material or residue, a weighing error, or an analytical error as well as plutonium hexafluoride volatilization. The weight gain in the collectors is caused by several volatile impurities. Analytical gas sample results taken from these collectors are shown in Table V.

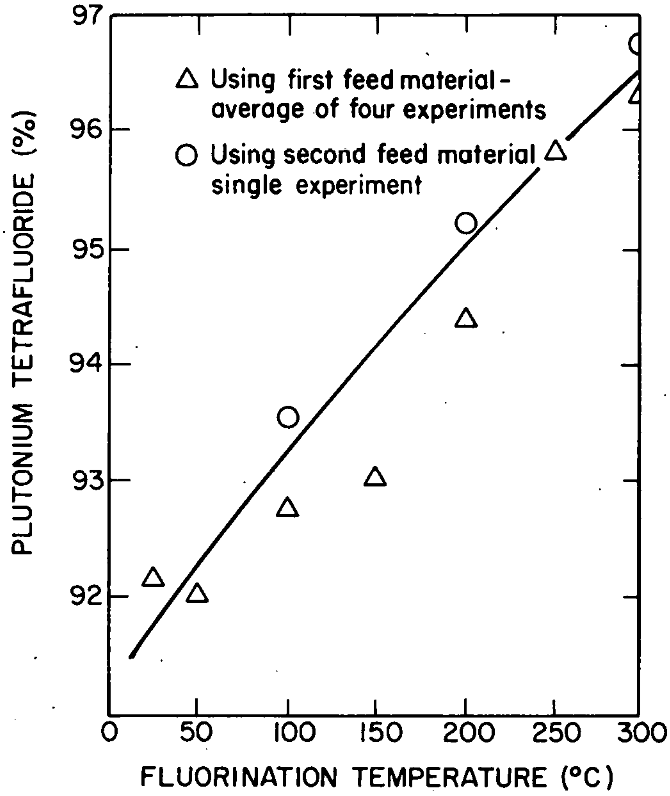


Figure 3. The effect of fluorination temperature on the formation of plutonium fluoride in feed.

Table IV. Plutonium loss during low-temperature fluorinations.

The data shown are an average of two experiments.

Fluorination Temperature (°C)	Heat Spike (°C)	Fluorination Time (minutes)	Average Weight Gain in Collectors (g)	Plutonium Loss (%)
28	164	15	0.11	1.2
28	159	30	0.12[b]	0.1
55	156	15	0.14	3.0
54	152	30	0.12	0.0
99	137	15	0.15	0.2
100	144	30	0.10	1.0
100[b]	110	240	0.09	-
150	138	15	0.10[a]	0.9
152	134	30	0.10	1.3
200	125	15	0.07	0.7
200	136	30	0.12[a]	1.6
250	130	15	0.11	1.4
250	120	30	0.10	4.2
300	115	15	0.08	0.6
300	123	30	0.10	1.3
300[b]	95	240	0.56	4.4

[a] Gas sample taken after completion of experiment.
[b] Result of one experiment.

Table V. Gas sample results.

Temperature (°C)	Major Gases Detected	Minor Gases Detected
28	CF_4, $CClF_3$, CO_2	PuF_6, HF
150	CF_4, $CClF_3$, CO_2	PuF_6, HF
200	CF_4, $CClF_3$, CO_2	PuF_6, HF

The indicated 4.2% plutonium loss at 250°C is not plausible. A plutonium loss of this magnitude should be reflected by a significant weight gain in the collectors. In addition, calculations involving equilibrium constant data (4) show that the maximum plutonium loss should be approximately 2.5%. From previous work, it is known that the system was not at equilibrium under these reaction conditions.

The fluorination time appears to have little effect on plutonium volatilization below 300°C. A 4-hour run at 300°C apparently caused a 4.4% plutonium loss. The average plutonium loss below 300°C is less than 1%. In general, the weight gain in the collectors substantiates the average percent loss figure.

PROPERTIES OF FEED MATERIAL BEFORE AND AFTER FLUORINATION – The second feed material was analyzed before and after fluorination for mean crystallite size and specific surface area. Results are shown in Table VI. The unfluorinated feed data are averages of four analyses and each fluorinated feed result represents one analysis. Table VI outlines the changes in the feed at different fluorination times and temperatures. The mean crystallite size for the fluorinated material are for the plutonium dioxide present in the residue. The mean crystallite size of the plutonium tetrafluoride in the residue could not be accurately measured by x-ray diffraction. The specific surface area is that of the entire material, both plutonium dioxide and tetrafluoride.

The mean crystallite size of the solid plutonium phase appears to increase with fluorination time and temperature. The mean crystallite size increases could be the result of increased temperature alone (5).

The results of Table VI indicate a decreasing specific surface area with fluorination time and temperature. The specific surface area decrease has also been reported as a function of temperature (5).

Table VI. Properties of solid plutonium phase before and after fluorination.

Fluorination Temperature (°C)	Heat Spike (°C)	Fluorination Time (minutes)	Mean Crystallite Size (microns)	Specific Surface Area (m^2/g)
0[a]	0[a]	0[a]	0.04[a]	3.3[a]
98	130	15	0.08	0.6
100	110	240	0.06	0.6
200	118	15	0.07	0.5
300	109	15	0.08	0.5
300	95	240	0.16	0.4

[a] Unfluorinated feed.

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