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PLUTONIUM TRIFLUORIDE; PREPARATION BY REACTION WITH FREON-12, AND BOMB REDUCTION TO METAL

BY

R. C. SMITH AND W. E. ROAKE

TECHNICAL SECTION
ENGINEERING DEPARTMENT

SEPTEMBER 15, 1953

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PLUTONIUM TRIFLUORIDE; PREPARATION BY REACTION WITH FREON-12, AND BOMB REDUCTION TO METAL

By

R. C. Smith and W. E. Roake

Metallurgy Unit
Applied Research Sub-Section

September 15, 1953

HANFORD ATOMIC PRODUCTS OPERATION
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PLUTONIUM TRIFLUORIDE; PREPARATION BY REACTION WITH FREON-12, AND BOMB REDUCTION TO METAL

INTRODUCTION

Plutonium metal is produced in the Hanford 234-5 Building by reducing plutonium tetrafluoride with calcium metal in a hermetically sealed bomb. Plutonium tetrafluoride is prepared by treating plutonium oxide with hydrogen fluoride gas at elevated temperatures according to the following reaction:

$$PuO_2 + 4HF \longrightarrow PuF_4 + 2H_2O$$

Since hydrogen fluoride is generally contaminated with hydrogen which reduces plutonium tetrafluoride to plutonium trifluoride, the fluorination reaction is always carried out in the presence of oxygen. Therefore, the Task II (hydrofluorination) equipment in the 234-5 Building exists in an environment of hydrogen fluoride, oxygen, and water vapor. This system is known to be exceedingly corrosive with respect to most materials of construction. It is estimated that a cost of approximately $500,000 a year is incurred as a direct result of the gross corrosion of equipment and hoods by the hydrogen fluoride, oxygen, water vapor system.

OBJECTIVES

The purpose of this investigation was to find and to determine the conditions of use of an alternate fluorinating agent for plutonium oxide with emphasis on reduction of corrosion of equipment caused by the use of hydrogen fluoride. Further, it was within the scope of this work to demonstrate that the plutonium fluoride produced by use of the alternate fluorinating agent could be reduced to plutonium metal with high yield by static bomb reduction with calcium.

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SUMMARY

Several Freons[1] have been examined with respect to their relative usefulness as replacements for hydrogen fluoride in the preparation of plutonium fluoride.

Among those tested, Freon-12 (dichlorodifluoromethane) was found to be the most satisfactory. The optimum conditions for the preparation of plutonium trifluoride from plutonium oxalate by freonation[2] with Freon-12 are embodied in the following steps. (1) Dry the aqueous slurry of plutonium(IV) oxalate in a stream of dry air at 125 to 150 C for as long as necessary to remove all unbound water. (2) Convert the plutonium(IV) oxalate to plutonium(IV) oxide in a stream of dry air at a temperature of 275 to 300 C, the cake temperature not exceeding 400 C. (3) React the oxide with Freon-12 under oxygen-free conditions at 400 C until converted. Cool to below 100 C before exposure to oxygen.

Plutonium trifluoride has been found to be capable of reduction to the metal with high yields using conventional stationary bomb techniques. Calcium is used as the plutonium trifluoride reductant, and 0.6 to 1.0 moles each of calcium and iodine per mole of plutonium are added to the reaction mixture as an internal "booster". Metal button yields of about 95 to 97 per cent have been consistently obtained using these bomb conditions on a 20 gram scale.

The corrosion resistance of a variety of metals of construction was investigated under actual freonation conditions. Haynes 25, Inconel, or Hastelloy A, B, or C appear to be quite suitable for equipment fabrication as they are attacked at the very slow rate of approximately 0.0002 to 0.0006 inches per month.

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(1) Freon is a trade term designating a class of aliphatic chlorofluoro compounds.

(2) Freonation is a term invented to include all reactions, including fluorination, between a Freon and another substance.

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DISCUSSION

A. Preparation of Metal Fluorides

The use of Freons for the conversion of metal oxides to their respective fluorides is not novel to this investigation. Several such instances have been reported in the literature. (3, 4, 5)

The compounds examined for possible value as fluorinating agents for plutonium compounds included: Freon-12 (dichlorodifluoromethane), Freon-13 (chlorotrifluoromethane), Freon-21 (dichlorofluoromethane), Freon-22 (chlorodifluoromethane), Freon-113 (trichlorotrifluorethane), Freon-114 (dichlorotetrafluoroethane), carbon tetrafluoride and ammonium bifluoride.

1. Cerium and Uranium Fluorides

Cerium and uranium were selected as non-hazardous substitutes for plutonium during the initial work in which the several Freons and other compounds were investigated as fluorinating agents. Cerium is thermodynamically more like plutonium than is uranium; therefore, the greater part of the preliminary investigations were made with cerium. In each case the cerium or uranium oxide was treated with the fluorinating compound by placing the oxide in a furnace tube and subjecting it to the particular fluorinating agent at elevated temperatures. The resultant products were evaluated as to the time and temperature required to obtain a complete reaction, the purity of the fluoride produced, and the physical and chemical properties of the fluoride. It was desirable that the fluoride be a free-flowing powder adaptable to remote mechanical handling.

---

(3) Webb, A. D., and Young, H. A., A Study of the Reactions between Tungsten Dioxide and Difluoridichloromethane, AECD-2315.

(4) Booth, Krasny-Ergen, and Heath, J. Am. Chem. Soc. 68, 1969-70 (1946).

(5) Kraus, C. A., CC-1717, July 29, 1944.

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Table I lists the various compounds examined and gives the general conditions and results of the tests. Freon-12 was observed to be the best fluorinating agent among those tested. By each criterion it was as good or better than the best results obtained using the other fluorinating agents.

2. Plutonium Trifluoride

Plutonium trifluoride is prepared by the reaction of plutonium dioxide with Freon-12 at a temperature of 400 C according to the theoretical equation:

$$2PuO_2 + 3CCl_2F_2 \longrightarrow 2PuF_3 + CO_2 + 2COCl_2 + Cl_2$$

As is common in reactions involving organic compounds, the reaction does not exactly follow the theoretical equation. Other reaction products which have been identified in small quantities include fluorophosgene, fluorine, and carbon monoxide. Early in the course of halogenation of the metal oxide a substantial amount of plutonium trichloride appears which is later converted to trifluoride. This is shown in Figure 1. No volatile plutonium compounds have been observed.

The conditions of preparation of plutonium oxide exhibit a profound effect on the rate of subsequent freonation. The oxidation of plutonium(IV) oxalate to plutonium(IV) oxide is sufficiently exothermic that cake temperatures between 125 and 250 C greater than the ambient furnace temperature have been observed during experimental runs. The results of several experiments have demonstrated that freonation of plutonium(IV) oxide with Freon-12 occurred readily only when the plutonium(IV) oxide had been prepared from plutonium(IV) oxalate at a cake temperature not exceeding 400 C.

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TABLE I

REACTIONS OF METAL OXIDES WITH FREONS

Fluorinating Agent	Material Fluorinated	Temperature °C	Fluoride Obtained	Average % Conversion	Appearance	Remarks
Freon-12	UO_3	400°	mixture	--	badly caked	Sensitive to water vapor. Organic polymers formed.
	CeO_2	400°	CeF_3	98	white powder	Free flowing product
Freon-13	CeO_2	600-700	CeF_3	92	white powder	CeF_3 obtained but much more vigorous treatment necessary
Freon-21	CeO_2	500	mixture	--	yellow	Extensive pyrolysis of Freon
Freon-22	CeO_2	325	CeF_3	--	grey	Organic polymer formed above 375 C Carbon deposited above 375 C
Freon-113	CeO_2	700	CeF_3	75	white powder	
Freon-114	UO_3	700	mixtures	50	green to black caked	This Freon was also tried with Pu without encouraging results.
NH_4FHF	CeO_2	500	CeF_3	--	dark grey badly caked	Experiments made with mixtures of solids and no attempt to flow gaseous product over the cerium
CF_4	CeO_2	750-800	CeF_3	59	grey powder	23 hours required(1) for 66% conversion

(1) Work of W. B. Tolley, HW-27773.

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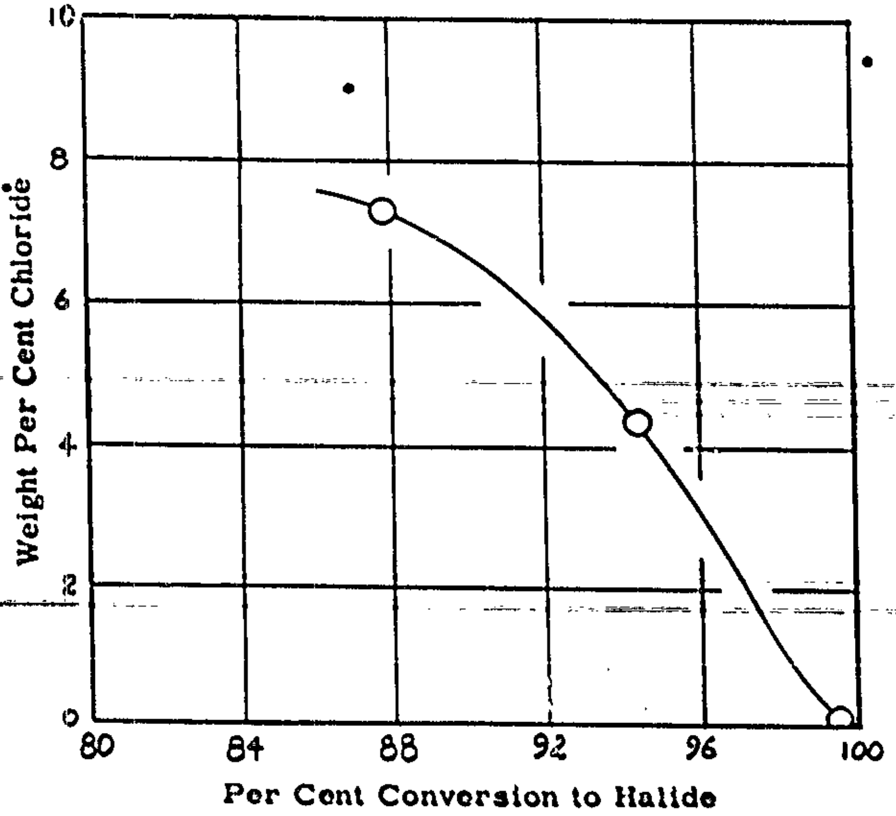

CHLORIDE FORMATION AND CONVERSION DURING FREONATION OF PLUTONIUM OXIDE

FIGURE 1

[redacted]

The optimum conditions for the preparation of plutonium trifluoride on a fifty gram scale are contained in the following steps:

(1) Precipitate plutonium(IV) oxalate from a plutonium(IV) nitrate solution. Wash precipitate and decant slurry.

(2) Transfer slurry to platinum or nickel reaction boat to a slurry depth of approximately one half inch. Dry three hours in a stream of air (approximately 1/2 lineal foot per minute) at a temperature of 125 to 150 C.

(3) Increase temperature to 275 or 300 C for one hour to convert the dried plutonium(IV) oxalate to plutonium(IV) oxide. During this step do not allow cake temperature to exceed 400 C in order to prevent formation of a poorly reactive oxide.

(4) Shift from air to an oxygen free Freon-12 atmosphere and raise temperature to 400 C. Freon-12 flow rate should be about 1/3 lineal foot per minute. Two hours exposure under these conditions are considered sufficient for complete conversion to plutonium trifluoride.

(5) Cool plutonium trifluoride to less than 100 C before exposing to air or oxygen to prevent oxidation. Plutonium trifluoride stored for several months at room temperature has shown no oxidation.

Plutonium trifluoride produced in this manner is a dark blue or lavender powder which is free-flowing and easily poured.

Several attempts were made to prepare plutonium trifluoride by reaction of plutonium oxide with Freon-114 (dichlorotetrafluoroethane). The reaction proceeds at 750 C and produces a badly caked plutonium trifluoride. A side reaction produces halogenated ethylene which is polymerized on the walls of the reaction vessel to produce a polymer not unlike Teflon. The process was not considered satisfactory.

B. Reduction of the Fluorides

Several investigators have reported poor results in the reduction of plutonium trifluoride with calcium by the stationary bomb method. However, no rigorous investigation of the reduction methods has been reported, and it was, therefore, within the scope of this work to give this problem a critical examination. The criteria for a successful bomb reduction require that a pure, dense, coherent piece of metal be obtained which is easily separated from the resultant slag, and that the reduction produces a nearly theoretical yield.

The reduction reaction for the production of plutonium from the trifluoride is:

$$2PuF_3 + 3Ca \longrightarrow 2Pu + 3CaF_2$$

The considerations important in the adaptation of plutonium trifluoride to bomb reduction include the melting points of the products of reaction, external heat input and heat loss to surroundings, and the physical characteristics of the reactants. To evaluate these considerations, cerium trifluoride prepared by freonation with Freon-12 was used as a "stand-in" for plutonium.

1. Cerium trifluoride

a. Slag Melting Point

The successful application of the bomb reduction technique depends on efficient use of the heat generated during the reaction. To allow the formation of a single coherent button of metal following a trifluoride reduction, the slag material must remain molten long enough for all of the more dense metal to settle to the bottom of the reduction crucible and coagulate into a single button. In a small sized reduction bomb of 20 grams batch size or less, the heat losses to the surroundings are relatively great.

Consequently, it is more difficult to maintain the calcium fluoride molten long enough for the metal to settle properly to the bottom of the crucible and form a button. In most cases a "booster" charge of calcium and iodine is added to the reduction charge which assists the formation of a coherent button in two ways. First, the reaction between calcium and iodine is highly exothermic and the heat thus released tends to keep the slag molten. Second, the calcium iodide lowers the melting point of the resulting slag, allowing it to remain molten for a longer time. W. B. Tolley has partially worked out the calcium fluoride-calcium iodide phase diagram which indicates an eutectic at 82.5 mole per cent calcium iodide with a melting point of 660 C. As the per cent calcium iodide decreases from that of the eutectic composition, the melting point of the mixture rises rapidly and at 60 mole per cent calcium iodide the melting point is 900 C. It is evident then that a great reduction of the slag melting point could be accomplished if the calcium iodide content of the slag were increased sufficiently. Iodine, however, is known to cause mechanical difficulties in Hanford bomb reduction equipment and large amounts are, therefore, to be avoided. Two series of experiments were devised to determine whether or not significant improvement in metal yields could be obtained by adding calcium iodide to the reaction charge. This would accomplish a lowering of the slag melting point without introducing excessive amounts of iodine. In the first series of experiments the total heat input into the reaction, including the external heat applied and the heats of reaction from the charge and "booster", was held as constant as possible and the slag composition was varied by the addition of calcium iodide. Table II gives the results of these experiments and indicates that the lowering of the melting points of the slag by the addition of calcium iodide does not produce better metal yields.

[redacted]

TABLE II
EFFECT OF CALCIUM IODIDE ADDITION ON REDUCTION YIELD*

Charge Composition Ratio: One mole CeF_3; 33% excess Ca; one mole Ca plus one mole I_2 as booster; CaI_2

Moles Added CaI_2	Mole Per Cent CaF_2 in slag	Per Cent Yield of Ce
0.0	60	98.3
0.5	50	98.3
1.25	40	93.8

* "Booster" is held constant.

In the second series of experiments the slag composition was held constant and the heat input into the reaction was varied by changing the relative amounts of calcium iodide and "booster". Results shown in Tables II and III indicate that the addition of small amounts of calcium iodide was of doubtful value and large additions were found to be detrimental.

TABLE III
VARIATION OF REDUCTION YIELD AS A FUNCTION OF ADDED THERMAL "BOOSTER"*

Charge Composition Ratio: One mole CeF_3 plus 33% excess Ca; CaI_2 and booster.

Distribution of Additives, Mole Per Cent		Per Cent Yield of Ce
Booster CaI_2	CaI_2	
100	0	80.2
75	25	76.9
50	50	57.1
25	75	37.6

* Slag composition held constant at 40 mole per cent CaF_2.

[redacted]

A third series of experiments was then carried out to determine the relative amount of calcium and iodine "booster" necessary to give optimum metal yields. The results of these experiments are shown in Table IV. One mole of "booster" for each mole of cerium has been found to give the best metal yields.

TABLE IV
VARIATION OF REDUCTION YIELD AS A FUNCTION OF BOOSTER: METAL FLUORIDE RATIO

Charge Composition: CeF_3 plus 33% excess calcium.

$\frac{\text{Moles } (Ca + I_2)}{\text{Moles } CeF_3}$	Slag Composition mole % CaF_2	Per Cent Yield* of Ce
1.5	50	93.4
1.0	60	97.1
0.6	70	88.2
0.4	79	68.1

* Each number is an average of three or more reductions.

b. External Heat Input and Heat Loss to Surroundings

Inasmuch as the effect of reducing the slag melting point, obtained by adding calcium iodide to the reaction mixture, appears to be insignificant when compared to the effect of heat loss to the surroundings, experiments were undertaken to decrease this heat loss by increasing the rate of external heating. The external heat was supplied by means of a 10 kw induction generator. The variables tested were the rate of heating of the bomb to firing temperature and time of continued application of external heat after bomb firing. Pre-firing heating rates were varied through a range providing firing times between 1.75 and 12 minutes. No trend in the metal yield was observed. It was found, however, that a better metal yield was obtained when the external heating was continued at the same rate for three-fourths to one minute after bomb firing. Table V indicates that an average of approximately 6% better yields was obtained when the heating was continued for one minute after the firing of the reaction charge.

TABLE V
EFFECT OF POST FIRING HEATING ON BOMB REDUCTION OF CeF_3

Charge Composition: CeF_3 plus 33% excess Ca; booster.

Slag Composition Mole % CaF_2	Post Firing Heating for One Minute	Per Cent Yield of Cerium
50	yes	98.0
50	yes	96.3
50	no	90.2
50	no	93.7
60	yes	98.3
60	yes	96.5
60	yes	96.5

c. The Physical Characteristics of the Reactants.

The general physical makeup of the reaction mixture offers some variables worthy of consideration. The location of the "booster" charge with respect to the reduction charge was varied to find the most advantageous position. Experiments were carried out with the entire "booster" charge below the reduction charge, above the reduction charge, splitting the booster and placing half below and half above, and mixing the booster and reduction charge homogenously. The last method was finally adopted as standard preparation although no significant difference was detected with any charge-"booster" arrangement.

Ground calcium is susceptible to surface oxidation and a large amount of surface oxide was found detrimental. The calcium was, therefore, kept in an inert atmosphere at all times and was added last to the reaction mixture after which the bomb was immediately closed, evacuated, filled with an inert atmosphere, and sealed.

An excess of calcium above the stoichiometric amount necessary for reduction was always added to the reduction charge. A very short series of experiments was carried out to determine the optimum calcium excess. Table VI gives the results of these experiments. Thirty-three per cent excess calcium was found to give the best results with cerium trifluoride reductions on the 20 gram scale.

TABLE VI
EFFECT OF VARIATION OF CALCIUM EXCESS ON PLUTONIUM TRIFLUORIDE REDUCTION YIELD

Slag Composition Per Cent CaF_2	Per Cent Calcium Excess	Per Cent Yield of Plutonium
70	33	97.1
60	15	83.7
60	7	84.1
60	7	65.6
70	7	64.8

2. The Reduction of Plutonium Trifluoride

Utilizing the information obtained with the cerium reduction experiments, several reductions of plutonium trifluoride prepared by freonation with Freon-12 were carried out. Plutonium trifluoride was found to be easily reduced to metal with good yield. Table VII shows the results of the plutonium trifluoride reductions. Optimum conditions for a 20 gram scale reduction of plutonium trifluoride require a 30% excess calcium, a "booster" of from 0.6 to 1.0 mole each of calcium and iodine per mole of plutonium, and post firing heating for at least one minute after the reaction has taken place. Yields of 95 to 97% are obtained, the buttons are well-formed and easily separated from the slag.

TABLE VII
BOMB REDUCTION OF PLUTONIUM TRIFLUORIDE

Charge Composition; PuF_3 plus 30% excess calcium, ($Ca + I_2$) booster.

Moles Booster per Mole PuF_3	Per Cent Yield of Plutonium Metal	
1	97.0	
0.64	94.4	95.6 average
0.64	96.8	
0.5	92.7	94.0 average
0.5	93.5	
0.5	95.8	
0.4	92.1	---
0.4	78.1*	

* Possibly MgO mixed with slag.

C. Corrosion and the Use of Freon-12

Freons have long been noted for their inertness and lack of corrosive properties at room temperatures.(6) Their reactivities, of course, increase as temperatures are elevated. A variety of metals and alloys which are commonly used for fabrication of equipment were tested for corrosion resistance to Freon-12 at and above the temperatures required for the freonation reaction. The results are shown in Table VIII.

The products of the freonation reaction include gaseous compounds known to be corrosive toward metals, particularly in the presence of water vapor. In order to provide a meaningful test the more satisfactory metals of those indicated in Table VIII were tested under actual freonation conditions. The results of one freonation cycle are listed in Table IX.

---

(6) Thompson, R. J., Refrigerating Engineering, November, 1942.

TABLE VIII
CORROSION OF VARIOUS METALS BY FREON-12

Metal	Temperature (°C)	Corrosion Rate[a] (inches/month)
Copper	400	0.0042
Brass	400	0.002
Nickel	400	0.00015
Hastelloy A	500	0.0031
Hastelloy B	400	0.00019
Hastelloy C	500	0.0018
Hastelloy D	500	0.0016
Inconel	400	0.000053
Aluminum-2S	500	0.0019
Stainless Steel-Type 304	500	0.004
Haynes 25	500	0.0017
Platinum	500	Undetectable

(a) Each test was run for forty-eight hours, and the data extrapolated to one month.

TABLE IX
THE CORROSION OF VARIOUS METALS BY FREON-12 DURING A SIMULATED PROCESS CYCLE[a]

Metal	Corrosion Rate[b] (inches/month)
Platinum	0.000066
Inconel	0.00056
Nickel	0.00031
Haynes 25	0.00024
Hastelloy A	0.00062
Hastelloy B	0.00063
Hastelloy C	0.00014
Hastelloy D	0.0019
Aluminum-2S	0.0024

(a) Moist cerium oxide was placed upstream of the metal sample in the furnace tube. Water saturated Freon-12 was passed through the tube during a simulated process cycle which consisted of drying for one hour at 125 C, oxidizing for three hours at 300 C, and freonating for four hours at 450 C.

(b) The corrosion data obtained through one-eight hour cycle was extrapolated to one month's operation.

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It might be argued that one cycle does not provide an adequate test due to the lack of alternate exposure to reaction products and steam. However, the conditions of this test are considered to be more stringent than those encountered in continued cycling due to the presence, in the test, of steam during the freonation reaction which was carried out at a higher temperature than that necessary for freonation of plutonium(IV) oxide.

It can be seen from Table IX that the corrosion rates for all metals tested under actual freonation conditions are quite low with the exception of Hastelloy D and aluminum-2S. Inconel, Haynes 25, and the remaining Hastelloy alloys are probably the best materials for equipment fabrication. An extended corrosion study is, of course, necessary before a final choice of the best material can be made.

R. C. Smith
R. C. Smith

Wm. E. Roake
W. E. Roake

RCS:WER:lj

ABSTRACT

The results of this study show Freon-12 (dichlorodifluoromethane) to be an excellent gaseous reactant for converting plutonium oxalates and the "low temperature" form of plutonium(IV) oxide to plutonium(III) fluoride by reaction at 400 C. Plutonium(III) fluoride produced in this manner is easily reduced with good yield to a well-formed metal button by the stationary bomb technique using calcium as a reductant. The optimum conditions for reduction on a twenty-gram scale are a 30 per cent excess calcium, between 0.6 and 1.0 mole each of calcium and iodine per mole of plutonium (as a thermal booster), and post firing heating for at least one minute after the reaction has taken place. Yields of 95 to 97 per cent are obtained.

The chemical inertness of Freon-12 at ordinary temperatures is well known. Preliminary corrosion studies indicate the corrosion of Inconel, Haynes 25, and Hastelloys A, B, and C by Freon-12 and the products of the reaction, which produces plutonium(III) fluoride, to proceed at rates less than 10^{-3} inches per month at the temperature required for the reaction.

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