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**THE EVAPORATION OF PLUTONIUM
FROM SMALL PIECES OF URANIUM
REACTOR FUEL**

By
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**North American Aviation, Inc.
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**THE EVAPORATION OF PLUTONIUM FROM
SMALL PIECES OF URANIUM REACTOR FUEL**

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DOWNEY, CALIFORNIA

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ABSTRACT

The rate of evaporation of plutonium from small pieces of uranium containing initially about 0.01 per cent plutonium has been measured at 1600° and 1680° C. The results show that the rate of evaporation follows the equations based on Raoult's Law. The evaporation of fission products was approximately as expected from their relative vapor pressures.

I. INTRODUCTION

The possibility of separating Pu from spent U fuels by direct evaporation at high temperatures has been the subject of some discussion.^{1, 2, 3, 4} In order to make any intelligent estimate of the feasibility of such a process, it is necessary to know the rates of the evaporation and the degree of completeness that can be attained in practice. The present study was made to determine the experimental rates for comparison with theoretical values using fuel that simulated actual reactor material.

In a previous study⁵ it was found that the rates of evaporation of tracer Pu agreed with values calculated on the assumption of ideal solution behavior at 1600° C and above. However, at large values of the fraction of Pu evaporated, the uncertainties in the experimental values were large, and some question has been raised as to whether or not the experimental rate fell markedly below the theoretical value beyond 90 per cent Pu removed.⁶ The present experiments were more accurate because of the higher concentrations of Pu. They show that the evaporation rate follows the theoretical values closely to at least 99 per cent Pu removed.

II. EXPERIMENTAL

The experimental method was essentially the same as that used in the tracer study;⁵ however, the techniques were complicated by the higher levels of Pu and fission product activities used.

A. Materials

The samples used in the study were pieces of an X-10 fuel slug obtained from Oak Ridge. The slug was cut into slices about 1/8-inch thick and then broken into pieces of about 3 grams. The irradiation history of the slug was unknown; however, it was known to have been discharged from the reactor in October, 1951. Plutonium analyses on several of the pieces gave the results shown in Table I. The average value of 94.5 $\mu\text{g Pu/g U}$ indicates that the slug received a total integrated flux of about $3.8 \text{ by } 10^{19}$ neutrons per cm^2 .

TABLE I
PLUTONIUM ANALYSES OF UNTREATED SAMPLES

<u>Micrograms Pu per Gram U</u>	
	95.4
	92
	95.5
	91.5
	93.2
	96.8
	97
	} different analyses on same sample
Average:	94.5

The radiation from 1 gram of sample at a distance of 1 centimeter was found to be about 1 roentgen per hour of gamma and about 100 times that level from beta. Because of these levels of activity it was necessary to handle the samples so that the hands were at least 6 inches away at all times.

B. Gloved Boxes

All the work with the sample and undiluted solutions made from the sample was performed in two "Berkeley" gloved boxes. One contained a vacuum line and all the apparatus necessary to handle the sample prior to, during and immediately after heating. The other box was equipped for Pu analysis of and dilution of the solutions made from the treated samples.

These boxes were sealed and lined with plastic so that no activity could leak out as dust or liquid in case of a spill. A negative pressure was maintained in them by connecting the exhaust of the boxes to the main exhaust system of the building through a CWS filter. Although the interior of the boxes became highly contaminated, periodic smears of the outsides showed no contamination. The gloved box system, though somewhat cumbersome in use, served as a positive control for the activity and contaminated articles, which might otherwise have been spread about the laboratory.

Figures 1 and 2 are photographs of the interiors of the boxes. The vacuum box was mounted on a movable dolly which housed a high vacuum pumping system and gauge. The analytical box was mounted on a dolly which also supported a scaler for the alpha counter.

C. Method

In a typical run a piece of active uranium in a closed container was delivered into the box, cleaned in nitric acid, dried with acetone and weighed. A layer of the surface of the sample was dissolved in nitric acid for a control. The remainder was dried with acetone and reweighed. The sample was then put in a CeS crucible which was placed on a tantalum plus zirconia stand and enveloped by a silica jacket with tantalum radiation shield liner. This assembly was lowered into a silica test tube which was then evacuated. A schematic diagram of this arrangement is shown in Fig. 3.

After the system had been evacuated overnight to a good vacuum, the crucible and contents were heated to temperature by induction heating. The induction heating system was a 6 kilowatt Ajax-Northrup converter and coil. The temperature was measured with a Leeds and Northrup optical pyrometer. To correct the readings of the pyrometer to true temperature an absorption correction was applied for the windows and prism through which the light passed and an emissivity correction for the surface of the uranium measured. The emissivity of the uranium surface was assumed to be the same as that measured in the tracer results,⁵ namely 0.82. The absorption by the window system was equivalent to an emissivity of 0.67. Therefore, the pyrometer readings were corrected by applying an over-all emissivity correction of 0.55. The temperatures thus calculated were probably within 30° of the true temperature.

When the heating period was completed, the system was allowed to cool and then disassembled. The CeS crucible, containing the residual uranium, was inverted in a carbon crucible and replaced in the vacuum system. The crucible was then reheated so that the uranium either melted out or at least pulled away from the CeS facilitating its removal. The uranium was cleaned in dilute acetic acid to remove any CeS and dissolved in nitric-hydrochloric acid. The tantalum radiation shield and silica parts were washed with hydrochloric acid and then etched with hydrofluoric acid; however, it was never

Fig. 1. Photograph of Interior of Vacuum-line Gloved Box, Showing Equipment Ready for Use

Fig. 2. Photograph of Gloved Box for Analyses, Showing Apparatus Used

Fig. 3. Schematic Diagram of Evaporation Cell

possible to recover all the activity that had distilled. Presumably some of it diffused into the fused silica during the heating.

The solutions made from the control, the uranium residue and the washings of the container were then transferred to the analytical gloved box. Analyses for plutonium were made on them by a lanthanum fluoride method with only one precipitation. A few milliliters of each of the solutions were transferred to clean volumetric flasks and removed from the gloved box for bench top fission product analyses. Because of the long cooling period of the fuel material the only fission products that could be determined by radio-chemical analysis were Ce, total rare earths, Sr, Cs, Ru and Te. The analyses were made by the methods suggested by Coryell and Sugarman.⁷

III. RESULTS AND DISCUSSION

A. Plutonium Data

The results of the plutonium evaporations are given in Table II. The first five columns give the experimental conditions and the next two give the observed distribution of the plutonium. The eighth column lists the measured per cent removal based upon the per cent plutonium left in the metal. The recovery of the distillate was not sufficiently quantitative to allow comparisons based on it.

The data are shown in Fig. 4 plotted as logarithm of fraction of plutonium left vs the parameter $\frac{a \cdot t}{w}$, i. e., the area of sample per unit weight multiplied by the time of heating. The dotted lines were calculated on the basis of Raoult's Law and ideal kinetic theory evaporation from the surface.⁸ The crosses are experimental points at 1680° C and the circles are those at 1600° C.

Figure 4 shows that the results at each temperature fall within a region of 25° spread. That is, the experimental data fall inside a band of width equivalent to 25° centered on the full lines of Fig. 4. Since the errors expected in the temperature determinations were at least 25°, the data may be said to agree within experimental error except for the point at the lowest per cent plutonium. The curves drawn through the averages of the experimental points lie at about 1585° and 1665° C rather than 1600° and 1680° as measured. This

TABLE II 14
PLUTONIUM EVAPORATION UNDER VARYING CONDITIONS

Corrected Temperature °C	Surface Area of Evaporation cm ²	Weight of Samples g	Time of Evaporation sec	$\frac{a}{w}$	% Pu Found		% Pu Evaporated	
					In Residue	In Sublimate	Measured	Calculated
1680	1.4	3.60	8400	3800	1.4	53	98.6	99
1680	2.3	3.30	2460	1700	9.1	36	90.9	89
1600	1.7	3.79	14,400	6500	3.4	-	96.6	97
1600	2.1	5.63	9900	3700	10	55	90	86
1600	1.1	2.74	1800	740	77	7	23	33

Fig. 4. Fraction of Pu Left in Sample as a Function $\frac{a t}{w}$

discrepancy is minor. In the ninth column of Table II are listed values of the per cent plutonium evaporated taken from the solid lines of Fig. 4.

The agreement, then, of the measured values with those calculated from Raoult's Law indicates that the rate of evaporation may justifiably be calculated as proposed in Ref. 8. It should be noted here that in the tracer study, determinations at 1500° C did not follow the expected curves. Therefore, for evaporations below 1600° C it is not possible to assume the Raoult's Law rate without further justification; however, the rate of evaporation below 1600° C is so low that such temperatures will probably not be of commercial interest.

B. Fission Product Data

The per cent fission products remaining in the residual uranium after the distillations are given in Table III. The results there are probably of qualitative significance only because of possible cross contamination of activities during analysis. In general, the results are as expected. The vapor pressures of some fission products are given in Table IV. From these vapor pressures one would expect that cesium would show the least residual percentage tellurium, strontium, cerium, then the rare earths, and all of these should be less than plutonium. In fact, the Te values are too large possibly because of analytical error or because the tellurium tends to form a compound with uranium. The cerium values should be smaller than the rare earths but are not. The ruthenium values are reasonable and, in fact, should probably all be 100 per cent.

IV. CONCLUSIONS

The rate of evaporation of plutonium from uranium has been found to follow the equation calculated from Raoult's Law. The present experiments show that the calculated equation is applicable to the distillation for as much as 99 per cent plutonium removed. The evaporation of the fission products was in general as expected.

TABLE III
FISSION PRODUCT EVAPORATION RESULTS

Temperature °C	a t w	% Activity Found in Residue						
		Pu	Ce	Rare Earths	Sr	Cs	Te	Ru
1680	3800	1.4	2	1	1	0.2	5	100
1680	1700	9.1	3	2	2	0.2	2	100
1600	6500	3.4	1	1	2	0.1	3	75
1600	3700	10	7	2	2	0.3	3	90
1600	740	77	7	4	4	0.2	7	95

TABLE IV
VAPOR PRESSURE OF SOME FISSION PRODUCT ELEMENTS AT 1680° C

Element	Vapor Pressure* Atm.
Cs	90
Te	60
Sr	4
Ba	1
Ce	3×10^{-3}
La	6×10^{-4}
Pr	3×10^{-4}
Pu†	1×10^{-4}
Y	2×10^{-5}
U	8×10^{-7}
Zr	2×10^{-7}
Ru	10^{-10}
Nb	10^{-11}

*Data extrapolated from data of Ref. 9.

†From Ref. 10.

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