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LABORATORY INVESTIGATIONS IN SUPPORT OF
FLUID BED FLUORIDE VOLATILITY PROCESSES

*PART III. SEPARATION OF GASEOUS MIXTURES OF
URANIUM HEXAFLUORIDE AND PLUTONIUM
HEXAFLUORIDE BY THERMAL
DECOMPOSITION*

by

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LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID BED FLUORIDE VOLATILITY PROCESSES

Part III. Separation of Gaseous Mixtures of Uranium Hexafluoride and Plutonium Hexafluoride by Thermal Decomposition

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L. Trevorrow, J. Fischer, and J. Riha

I. SUMMARY

Experiments have been carried out to determine the extent and rate of separation of mixtures of uranium hexafluoride and plutonium hexafluoride by selective thermal decomposition. Gaseous mixtures of uranium hexafluoride, plutonium hexafluoride, and helium were circulated for varying lengths of time through nickel vessels packed with nickel wool at temperatures of 150, 200, and 300 C. The initial ratios of uranium hexafluoride to plutonium hexafluoride in the mixtures were of the order of 10 to 1. The gas phase was analyzed for uranium and plutonium before and after circulation. The amounts of uranium and plutonium in the solid compounds deposited in the vessels were also determined. Passage of the mixtures through the hot vessels resulted in the removal of 99.5 to 99.9 percent of the plutonium. The solid product remaining in the vessels was plutonium tetrafluoride containing 0.09 to 1.3 percent uranium. The separation of plutonium hexafluoride from uranium hexafluoride by selective thermal decomposition is applicable to fluid bed fluoride volatility processes for the recovery of fissile material from reactor fuels.

II. INTRODUCTION

Fluid bed fluoride volatility processes⁽¹⁾ are being developed at Argonne National Laboratory for the recovery of both uranium and plutonium from low-enrichment oxide fuels of the type used in power reactors. These fuels are typified by high-density uranium dioxide pellets clad in Zircaloy or stainless steel.

In a conceptual fluid bed fluoride volatility process, the cladding is removed and the fuels are converted to fluoride compounds by a series of gas-solid reactions at elevated temperatures. The reactions are carried out by immersing the fuel elements in a bed of granulated, recrystallized

alumina. The alumina granules are fluidized by reactant gases. The term fluidization is used to describe the operation of suspending a multitude of fine solid particles in a vertical rising column of gas.⁽²⁾ This operation efficiently removes the heat evolved in the reactions of the gases with the solid fuel elements. A chlorinating gas, chlorine or hydrogen chloride, is first blown through the bed to convert the metal jackets to volatile metal chlorides which pass out of the bed in the stream of off-gases. The exposed, oxide fuel pellets remaining in the bed are oxidized with air at about 450 C, and the resultant uranosoic oxide and plutonium dioxide are then reacted with fluorine gas at 500 C to convert the oxides to the volatile compounds uranium hexafluoride and plutonium hexafluoride. Most of the fission products remain as nonvolatile fluorides in the alumina bed and are discarded with the alumina as a solid waste. The plutonium hexafluoride and uranium hexafluoride in the off-gases are condensed to solids in refrigerated traps. The hexafluorides are then melted and fed into a simple distillation column for separation from the volatile fission product fluorides. It has been suggested that, after decontamination, the mixture of uranium and plutonium hexafluorides could be separated by fractional distillation or by selective thermal decomposition. Uranium hexafluoride is very stable compared with plutonium hexafluoride, which decomposes to plutonium tetrafluoride and fluorine.^(3,4,5) In process application of selective thermal decomposition the mixture of hexafluorides would be passed through a nickel vessel heated to a temperature at which plutonium hexafluoride decomposes rapidly and at which uranium hexafluoride is stable.

The process of separation by selective thermal decomposition has been studied. Experiments have been carried out in which gaseous mixtures of uranium hexafluoride and plutonium hexafluoride were circulated through heated nickel vessels. The rate of thermal decomposition of plutonium hexafluoride increases with the ratio of surface to volume.^(4,5) Therefore, in order to increase the rates of separation, the ratio of internal surface area to volume was increased by packing the vessels with nickel wool.

The chemical reaction of interest was the thermal decomposition of plutonium hexafluoride. The reaction of either plutonium hexafluoride or uranium hexafluoride with nickel metal would have been undesirable. Reaction of the hexafluorides with nickel metal was prevented by thoroughly treating the interior of the vessels and the nickel wool packings with fluorine gas to cover the metal surfaces with a film of nickel fluoride. The rate of thermal decomposition of plutonium hexafluoride is increased by the presence of the decomposition product, plutonium tetrafluoride.^(4,5,6) An initial coating of plutonium tetrafluoride was therefore deposited on the inner surfaces and packing of the vessels to serve as an additional factor to increase the rate of separation and to prevent reaction between nickel metal and either uranium or plutonium hexafluorides.

In the separation experiments, the gas mixtures were sampled and analyzed for plutonium and uranium before and after circulation through the heated vessels. A different vessel was used in each circulation, and in some cases the solids deposited in the vessel were also analyzed for uranium and plutonium.

The objectives of the work were to determine the extent of depletion of plutonium from the vapor phase and the purity of the uranium hexafluoride obtained, to gain some information on the rate of the process, although this was not designed to be a precise kinetic study, and to determine the purity of the plutonium tetrafluoride deposited in the thermal decomposition vessel. This work was carried out on the laboratory scale. The information obtained in the realization of the above objectives is to be used in design of equipment to carry out the separation on a pilot-plant scale.

III. EXPERIMENTAL DETAILS

Materials

Fluorine gas, assayed to be 99.5 percent pure, was obtained commercially. Before use, it was passed through sodium fluoride pellets at 100 C to remove a small amount of hydrogen fluoride.

Uranium hexafluoride was prepared by the fluorination of uranium tetrafluoride.

Plutonium hexafluoride was prepared by the fluorination of either plutonium dioxide or plutonium tetrafluoride.⁽⁵⁾

The helium used in the experiments was dried by passing it through a bed of type 4A Linde molecular sieves.

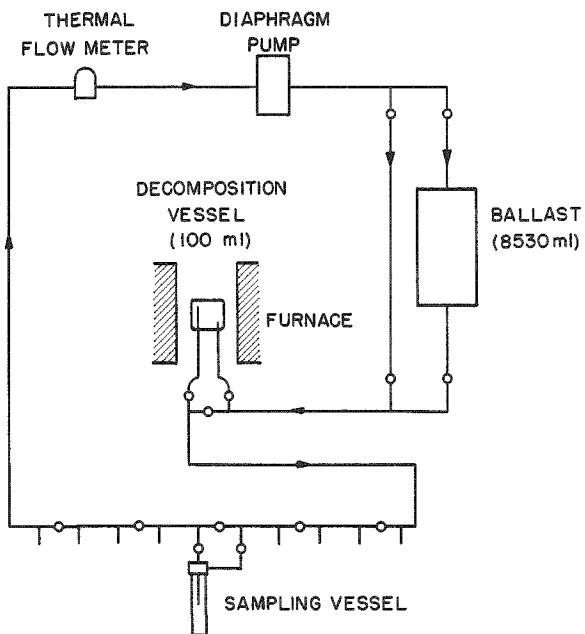
Apparatus

A schematic diagram of the apparatus used in the separation experiments is shown in Fig. 1. The apparatus was constructed from tubing and diaphragm valves of nickel and Monel, and was contained in a glove box.⁽⁷⁾

A pump* with a Monel diaphragm was used to circulate gases through the apparatus. Both mechanical pumps and an oil diffusion pump were used for evacuation of the apparatus. The pumps were protected from fluorides and fluorine by traps filled with activated alumina as well as a series of traps cooled with dry ice and liquid nitrogen.

*Lapp Pulsafeeder No. CPS-1, Lapp Insulator Co., Inc., LeRoy, New York.

Figure 1
SYSTEM USED IN SEPARATION
OF PuF_6 AND UF_6



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creased the interior surface area. It was not possible to measure directly the surface area of the plutonium tetrafluoride deposit in the thermal decomposition vessels. However, the specific surface area of a sample of loose crystallites and powder of plutonium tetrafluoride produced by the thermal decomposition of plutonium hexafluoride was $0.02 \text{ m}^2/\text{g}$ as determined by a Perkin-Elmer Soprtometer. It is expected, however, that the specific surface area of the film of plutonium tetrafluoride on the walls and packing of the thermal decomposition vessels was less than that of the sample of crystallites and powder. The specific surface area of plutonium tetrafluoride can vary greatly depending on its method of preparation.

The thermal decomposition vessels were heated in a tubular furnace, and temperatures were measured by a Chromel-Alumel thermocouple in $\frac{1}{4}$ -in.-diameter wells which extended down into the center of the vessels.

Each vessel was exposed to fluorine and plutonium hexafluoride prior to use in the separation experiments as follows: (1) Fluorine gas at 1 atm pressure was circulated through the vessel at 300 C for 6 hr. (2) Plutonium hexafluoride vapor was then circulated through the vessel at 250 C so that several grams of plutonium tetrafluoride were deposited as a coating on the walls and packing of each vessel. The quantity of plutonium tetrafluoride deposited in this initial treatment of the vessel was determined by weighing.

The cylindrical nickel decomposition vessels were 2 in. in diameter and 2 in. long. They were packed with 25 to 28 g of nickel wool to increase their internal geometric surface area to the order of $1.5 \times 10^2 \text{ sq cm}$.

The surface area of the walls of the vessel was calculated from the geometry of the vessel. The surface area of the nickel wool was calculated from the total weight and the surface area per unit weight which had been determined by micrometer measurements on weighed samples chosen at random from the supply of wool. It is clear that this procedure yields a geometric surface area since the roughness factor of the metal surfaces is unknown.

The deposition of solid plutonium tetrafluoride probably in-

Procedure

The gas mixtures were prepared by adding the constituent gases at room temperature to a ballast tank of 8530 ml volume. The tank was filled with plutonium hexafluoride to a pressure of 10 ± 2.5 mm. Uranium hexafluoride was added to make the combined pressures of hexafluorides 100 ± 2.5 mm. Helium was then added to make the total pressure of the system 760 ± 10 mm. The gases remained overnight in the ballast tank and were then circulated through the system at room temperature, bypassing the reaction vessel, for a total of about ten complete cycles. This preliminary circulation served to mix the gases and to recondition portions of the line which had to be dismantled and reassembled between experiments owing to space limitations in the glove box. Experimentation with reactive fluorides is best carried out after conditioning, with fluorine or with the reactive fluoride itself, any portion of the vacuum line which has been exposed to the atmosphere. Probably some plutonium hexafluoride, which is a very reactive compound, was consumed in this reconditioning process.

The probable consumption of a small amount of plutonium hexafluoride during the reconditioning and the limitations of the pressure measurements in filling the ballast tank with plutonium hexafluoride were the causes of variation in quantities and ratios of uranium to plutonium in the starting mixtures. However, the initial ratios of uranium to plutonium in the gas mixtures were not determined by the partial pressures of the constituents initially added to the ballast tank. Rather, the initial ratios were determined by sampling the gas mixture after the preliminary circulation and by analyzing this sample for uranium and plutonium. It has been demonstrated that in conditioned equipment plutonium hexafluoride can be transferred with high efficiency by vacuum distillation or by carrier gases such as fluorine or helium.⁽⁵⁾ Therefore, it was deemed unnecessary to design the separation experiments to obtain data for calculations of material balances.

After the preliminary circulation and the initial sampling for analysis of uranium and plutonium, the mixture was circulated through a closed loop which included the heated nickel vessel (of 100 ml volume), the ballast tank (of 8530 ml volume), and associated lines (of 670 ml volume). Thus, at any given instant during circulation, only a small fraction of the mixture was in the heated nickel vessel.

The pressure gages which were included in the system during the circulation were accurate to ± 10 mm. These gages indicated that the total pressures in the system remained constant during the separation experiments.

An experiment was carried out to determine the effect of circulation through nickel and Monel equipment at room temperature on the composition of a uranium hexafluoride-plutonium hexafluoride mixture. The

mixture of vapors was circulated through the system, bypassing the decomposition vessel, sampled periodically, and analyzed for plutonium and uranium. The results are summarized in Table 1. The percentage of plutonium hexafluoride in the gas mixture did not vary regularly with the number of times the gas was cycled through the apparatus. If the percentage of plutonium hexafluoride is treated as a constant, i.e., the average, with an associated standard deviation, the result is 3.60 ± 0.19 percent plutonium hexafluoride. The deviation from the average can then be assumed to be due to errors associated with the sampling and hydrolysis procedures, and to errors of analysis. The error associated with the plutonium analysis is two percent of the determined value, and the error associated with the uranium analysis is five percent of the determined value. From these estimates of analytical error and the average determined values of uranium hexafluoride and plutonium hexafluoride, the standard deviation associated with the average percentage of plutonium hexafluoride was calculated to be ± 0.2 percent plutonium hexafluoride. Thus, the standard deviation calculated from estimated analytical errors alone is essentially equal to the observed total standard deviation of ± 0.19 percent plutonium hexafluoride. It is apparent, however, from the data in Table 1 that there are errors in the sampling and hydrolysis procedures also. Samples 4 and 5 are duplicates taken under similar conditions, but the percentage of plutonium hexafluoride in these two samples differs by an amount much greater than that expected for analytical error alone. The results of the experiment are sufficient to show, however, that plutonium hexafluoride is not separated from mixture with uranium hexafluoride by circulation through nickel and Monel equipment at room temperature, and therefore that any separation accomplished in later experiments was the result of circulating mixtures through the heated vessel.

Table 1

RESULTS OF PERIODIC ANALYSIS OF A UF_6 - PuF_6
MIXTURE DURING CIRCULATION THROUGH
NICKEL AND MONEL EQUIPMENT AT
ROOM TEMPERATURE

Sample No.	Number of Cycles ^a	Percentage of PuF_6 in Mixture
1	3.9	3.65
2	11.4	4.02
3	21.3	3.33
4	28.8	3.04
5	28.8	3.97

^aA cycle is the passage of the total volume of mixture past a given point in the system. The number of cycles was calculated from the flow rate and the time of flow.

Although an error of five percent of the determined value was expected in the uranium analysis and the data in Table 1 indicate that there was an additional error associated probably with the sampling or hydrolysis procedures, the accuracy was considered to be adequate for the separation study, since the subject of interest was the ratio of uranium to plutonium covering a range of several orders of magnitude.

In an experiment at 150 C the gas mixture was sampled for analysis throughout the course of the circulation. In all other experiments the gas phase was sampled only initially and finally after a given period of circulation through the vessel. All gas circulations were carried out at a flow rate of 800 ml/min.

In the experiment carried out at 150 C, the gas mixture was sampled by stopping the gas circulation, closing the valves leading to the thermal decomposition vessel and ballast tank, and expanding the gas in the remainder of the lines into the sampling vessel, which contained a frozen, aqueous mixture of aluminum nitrate and nitric acid cooled in liquid nitrogen. In all other experiments gas was sampled by momentarily stopping the gas circulation, closing the valves leading to the thermal decomposition vessel and ballast tank, and then using the diaphragm pump to circulate the gas in the remainder of the lines repeatedly through the sampling vessel containing the frozen, aqueous mixture of aluminum nitrate and nitric acid cooled in liquid nitrogen. In both procedures the sample of hexafluorides was condensed onto the frozen, aqueous mixture, which was melted subsequently to hydrolyze the hexafluorides. The resulting aqueous solutions were analyzed for plutonium by radioactive-counting techniques, and they were analyzed for uranium by a colorimetric procedure with dibenzoylmethane. Thus, the weights of uranium and plutonium in each gas sample were obtained.

After several experiments, the thermal decomposition vessel was cut into pieces which were then immersed in solutions of aluminum nitrate in nitric acid. The nickel wool packing was completely dissolved, and the pieces of the vessel were thoroughly etched by the solution. The solid uranium and plutonium compounds deposited in the vessel were completely dissolved. The resulting solution was analyzed for plutonium by a radioactive-counting procedure, and for uranium by a fluorophotometric procedure. Thus, the total weights of uranium and plutonium in the solids deposited in the thermal decomposition vessel were obtained.

IV. RESULTS AND DISCUSSION

Table 2 summarizes the experimental details and shows the analyses of the gas mixtures and the solids deposited. The procedures for sampling the gas mixture yielded samples of varying size. The data used to interpret the experiments, therefore, are not the quantities of uranium

or plutonium in a sample, but the ratios of uranium to plutonium. The analyses of the solids deposited in the thermal decomposition vessel showed that only a very small fraction of the uranium deposited during an experiment. Approximately 15 g of uranium hexafluoride (~10 g uranium) were used in making up the mixture for a typical experiment. The largest quantity of uranium found in the thermal decomposition vessel after a circulation was 0.0055 g. It is assumed, therefore, that the concentration of uranium hexafluoride remained constant in any experiment. Thus, the change of the ratio of uranium to plutonium during a given circulation time reflects the change of the plutonium hexafluoride concentration only, and the change of the ratio with time is an indication of the rate of removal of plutonium hexafluoride from the gas phase.

Table 2

SEPARATION OF GASEOUS MIXTURES OF URANIUM HEXAFLUORIDE AND PLUTONIUM HEXAFLUORIDE BY THERMAL DECOMPOSITION

Mixtures of UF_6 (~90 mm), PuF_6 (~10 mm), and He (~660 mm), were circulated through nickel vessels packed with nickel wool.

Volume of each packed vessel: 100 ml
Volume of total system: 9300 ml

Temp Decomp Vessel (C)	Total Internal Geometric Surface ($\text{cm}^2 \times 10^{-3}$)	Wt PuF_4 Initially in Vessel (g)	Circulation ^a Time (hr)	Analysis of Gas Sample			Percentage ^b of Initial Pu Removed from Gas	Analysis of Solids Deposited from Gas Mixture		
				Wt U (mg)	Wt Pu (mg)	Ratio (U/Pu)		Wt U (g)	Wt Pu ^c (g)	Percent U of Solid ^d
150	1.6	3.891	0	34.9	3.3	10.6	6	0.00092	0.37	0.25
			1-1/4	45.1	3.96	11.4				
			5	37.6	2.22	16.9				
			10	30.6	0.76	40.0				
200	1.5	4.225	0	763	62.1	12.3	70.0	0.00092	0.37	0.25
			1-1/3	438	10.7	40.9				
200	1.4	4.483	0	474	14.8	32.0	99.4	0.0055	0.42	1.3
			2-2/3	405	0.085	4.8×10^3				
200	1.4	4.117	0	429	28.3	15.2	99.4	0.0044	0.66	0.67
			4	411	0.164	2.51×10^3				
200	1.6	4.456	0	504	39.5	12.8	99.9	0.0081	0.60	1.3
			10	472	0.0243	1.94×10^4				
300	1.6	3.810	0	477	48.3	9.90	99.7	0.00098	1.08	0.091
			1-1/3	397	0.114	3.48×10^3				
300	1.6	4.218	0	456	26.4	17.3	99.7	0.00172	0.65	0.26
			2-2/3	474	0.0772	6.17×10^3				
300	1.6	4.644	0	445	37.4	11.9	99.5	0.0030	0.84	0.36
			4	406	0.147	2.76×10^3				
300	1.5	5.370	0	511	38.6	13.2	99.6	0.0081	0.60	1.3
			10	472	0.13	3.63×10^3				

^aOne hour of circulation time is equivalent to 0.66 min of residence time of the entire sample in the decomposition vessel.

^bPercentage Pu removed from gas = $\frac{(\text{Pu}/\text{U})_{\text{initial}} - (\text{Pu}/\text{U})_{\text{final}}}{(\text{Pu}/\text{U})_{\text{initial}}} \times 100$

^cThis does not include the quantity of plutonium deposited as tetrafluoride in the vessel prior to each experiment.

^dPercentage U of Solid = $\frac{(\text{Wt U in solid}) \times 100}{(\text{Wt U in solid}) + (\text{Wt Pu deposited from mixture})}$

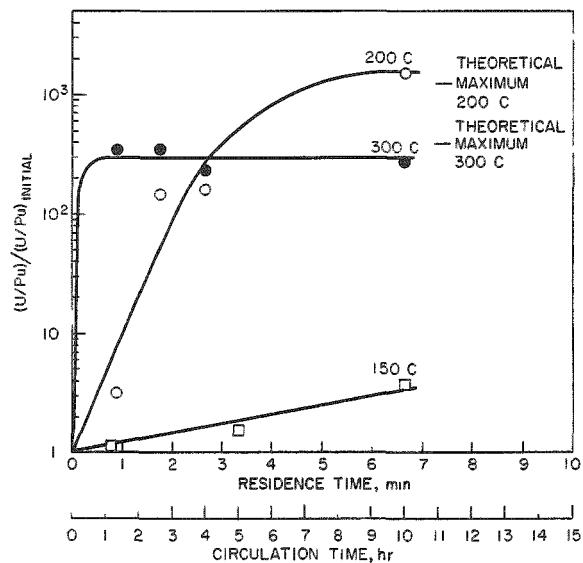
Since the circulation path in these experiments was a closed loop, the average residence time of the total mixture in the decomposition vessel is dependent only on the total circulation time and the ratio of the

volume of the decomposition vessel (100 ml) to the total volume of the system (9300 ml):

$$\begin{aligned} \text{Residence time of total sample in vessel} &= \frac{\text{vessel volume}}{\text{total volume}} \times (\text{circulation time}) \\ &= 1.1 \times 10^{-2} \quad \times (\text{circulation time}) \end{aligned}$$

In Fig. 2, the ratios $(U/Pu)/(U/Pu)_{\text{initial}}$ are plotted as a function of the circulation and residence times. A tangent to any of the curves in Fig. 2 gives an indication of the rate of separation obtained by thermal decomposition. Even though data were not obtained on the kinetic portion of the curve at 300 C, the gas analysis obtained for the shortest circulation time provides a lower limit for the rate, and indicates that it is relatively fast at this temperature. The rate of separation at 150 C is probably too slow for process application.

Figure 2
CHANGE OF URANIUM-TO-
PLUTONIUM RATIO OF
 $\text{UF}_6\text{-PuF}_6$ MIXTURE



obtained experimentally and the theoretical maximum ratios. The maximum ratio of uranium to plutonium increases as the temperature of the vessel decreases. This is expected since the equilibrium constant, $(\text{PuF}_6)/(\text{F}_2)$, for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) = \text{PuF}_6(\text{g})$ increases as temperature increases. A higher percentage of the plutonium was removed from the gas mixture at 200 C than at 300 C, and an even higher percentage should be removed at 150 C, but the circulation was not continued long enough to obtain the maximum ratio of uranium to plutonium at 150 C. The extent of the separation decreases as temperature increases, but the rate of separation increases as temperature increases.

Since the change in the ratio of uranium to plutonium in the gas stream is caused by the thermal decomposition of plutonium hexafluoride, a theoretical limit for the ratio of uranium to plutonium in a gas mixture can be calculated from the initial ratio and the equilibrium constant⁽³⁾ for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) = \text{PuF}_6(\text{g})$ at the temperature of the decomposition vessel. The theoretical maximum ratio is

$$\frac{(U/Pu)}{(U/Pu)_{\text{initial}}} = \frac{K + 1}{K} .$$

Figure 2 also shows the comparison between the maximum ratios

Both the experimental and theoretical information show that the circulation of mixtures of uranium hexafluoride and plutonium hexafluoride through hot vessels at 200 to 300 C can remove 99.5 to 99.9 percent of the plutonium initially present. The percentages of plutonium removed from the gas listed in Table 2 are based on the analyses of the gas phase:

$$\% \text{ of initial Pu removed} = \frac{(\text{Pu}/\text{U})_{\text{initial}} - (\text{Pu}/\text{U})_{\text{final}}}{(\text{Pu}/\text{U})_{\text{initial}}} \times 100 \quad .$$

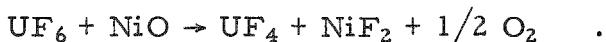
The percentage of initial plutonium retained in the thermal decomposition vessel was not obtained since the initial total quantities of plutonium in the gas phase were not determined precisely. The solid plutonium tetrafluoride which deposited in the thermal decomposition vessels was observed to be an adherent coating on the walls and packing of the vessel. The nickel wool may have played the role of a filter to some extent in retaining any finely divided plutonium tetrafluoride in the thermal decomposition vessel. In practice it might be best to include a filter immediately downstream from the thermal decomposition vessel to retain any finely divided solid plutonium tetrafluoride.

It is anticipated that in process practice the plutonium tetrafluoride would be recovered from the thermal decomposition vessel as a granular or powdered product. The tetrafluoride obtained in the separations experiments was a very thin film of solid spread over a large surface area. It has been observed, however, that when higher surface loadings are obtained, for example, when 25 to 50 g of plutonium tetrafluoride are deposited in decomposition vessels which are not packed with nickel wool, that the plutonium tetrafluoride is a deposit of crystallites which are rather easily shaken loose from the walls of the vessel. Plutonium tetrafluoride would be deposited with high surface loadings in a process vessel, and the vessel would be vibrated periodically to loosen the crystallites and a portion of the plutonium tetrafluoride drained off as product.

For the experiment at 300 C, the percentage of uranium in the plutonium tetrafluoride varied from 0.091 to 1.3. The significance of the concentration of uranium in the plutonium tetrafluoride depends on how the plutonium compound is to be used. For example, the presence of a small percentage of uranium in the plutonium tetrafluoride should be unobjectionable if it is used to prepare fuel for a mixed oxide reactor. A mixed oxide fuel which has received a good deal of attention is a mixture of plutonium oxide and uranium oxide with a 1 to 5 ratio of plutonium to uranium, the uranium being either natural or depleted.⁽⁹⁾

Various mechanisms have been considered to explain the deposition of small amounts of uranium in the vessel. One possible mechanism is chemisorption of uranium hexafluoride on plutonium tetrafluoride. Another

possible mechanism is the corrosive attack of uranium hexafluoride on the packing, walls, or weldments of the vessels in spite of pretreatment. Thermal decomposition of uranium hexafluoride is an implausible mechanism to explain the presence of uranium in the solids. Calculations of gaseous equilibria by Brewer *et al.*, (10) showed that at 300 C the extent of thermal dissociation of uranium hexafluoride is negligible. Values for thermodynamic properties of uranium fluorides have been critically reviewed more recently by Rand and Kubaschewski. (11) Recommended values from this work together with others recently published (12,13) have been used to calculate the extent of dissociation of uranium hexafluoride by several hypothetical mechanisms. These calculations also show that uranium hexafluoride is essentially undissociated at 300 C. It has been shown (14) that uranium hexafluoride will react with welded nickel vessels to release oxygen. This is probably a reaction of uranium hexafluoride with small amounts of nickel oxide which are invariably formed in the construction of nickel vessels by the usual Heliarc welding process. The reaction is presumed to be:



This could very well be the reaction responsible for the deposition of small amounts of uranium in the thermal decomposition vessel.

The results listed in Table 2 indicate that the percentage of uranium in the solids increases with the residence time of the gas in the vessel. Therefore, to minimize the concentration of uranium in the plutonium tetrafluoride in process application, the residence time of the gas in the thermal decomposition vessel must be kept to the minimum necessary to decompose the plutonium hexafluoride.

Assuming that the purity of the uranium and plutonium compounds obtained are adequate for desired applications, the technique of separation of uranium hexafluoride-plutonium hexafluoride mixtures by thermal decomposition offers the advantages of high rates, small holdup for a process stream, and simplicity of equipment compared to that necessary for other separation techniques.

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