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Union Carbide and Carbon Corporation

K-25 Laboratory Division

SEPARATION OF RUTHENIUM FROM URANIUM HEXAFLUORIDE

R. A. Gustison, S. S. Kirsliis, T. S. McMillan, H. A. Bernhardt

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A B S T R A C T

In the uranyl ammonium phosphate process for recovery of uranium from Hanford waste, ruthenium 106 is an undesirable radioactive contaminant in the phosphate precipitate. Ruthenium forms a very reactive volatile fluoride which is carried along with the uranium hexafluoride when uranyl ammonium phosphate is fluorinated. It was found that passing the uranium hexafluoride through a distillation column effectively reduces the ruthenium activity in uranium hexafluoride to an acceptable level. It was shown that the decontaminating effect of the distillation operation was due largely to the scrubbing of ascending gases by refluxing liquid uranium hexafluoride. To a lesser extent, absorption of ruthenium on the column packing and the distillation action contributed to the decontamination.

SEPARATION OF RUTHENIUM FROM URANIUM HEXAFLUORIDE

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INTRODUCTION

Nature of the Problem

When uranium is recovered from aged Hanford waste solutions by a single uranyl ammonium phosphate precipitation the precipitate retains considerable β activity, approximately 60% of which is due to ruthenium 106. The removal of the remaining ruthenium activity is difficult by wet chemical methods and results in radioactive waste liquors to be stored. The fluorination of singly precipitated uranyl ammonium phosphate produces uranium hexafluoride free of all β -emitters except ruthenium, which forms a volatile pentafluoride. In this work a method was sought by which the ruthenium activity in uranium hexafluoride could be reduced to an acceptable level.

Properties of Ruthenium Pentafluoride

Ruthenium pentafluoride is a green solid at room temperature, melting at 106°C., and boiling at 313°C.¹ It is an extremely reactive compound, corroding most metals rapidly at room temperature. Its reactivity with oxidizable substances is in general greater than that of uranium hexafluoride. The solubility of ruthenium pentafluoride in uranium hexafluoride was found to be 20.8 mole percent at 65°C., very close to the ideal solubility of 23.5 mole percent.² This indicates an activity coefficient of 1.10.

Exploratory Experiments

A number of exploratory experiments were conducted to determine whether the lower volatility and greater reactivity of ruthenium pentafluoride might be used to separate it from uranium hexafluoride. Some experiments were also made to determine the chemical and physical form of ruthenium after a solution of ruthenium pentafluoride in uranium hexafluoride had been allowed to stand in a nickel cell for several days at room temperature. These tests are described in detail in the Appendices.

¹Bernhardt, H. A., R. L. Farrar, Jr., and S. S. Kirsliis, "The Preparation and Properties of Ruthenium Pentafluoride", Carbide and Carbon Chemicals Division, K-25 Plant, K-294, November 1, 1948.

²Letter from E. J. Barber, R. H. Capps, and R. L. Farrar, Jr., to S. S. Kirsliis, dated June 2, 1949, KLI-247.

Tests on the reduction of ruthenium activity in uranyl ammonium phosphate by conversion to uranium hexafluoride are described in Appendix A. It was found that the ruthenium activity in the uranium hexafluoride was only one-tenth of that in the phosphate.

Tests on the absorption of ruthenium from uranium hexafluoride solution on the walls of a nickel container are described in Appendix B. It was found that the concentration of ruthenium in solution decreased to approximately one-tenth of its original value on standing in a nickel cell for several days at room temperature. The rate of absorption was greater at higher temperatures. Large differences in activity were found between duplicate samples of either the vapor or the solution, so that accurate absorption rates were not obtained. This source of difficulty is explained below.

The sampling problem was encountered again in some tests on the separation of radioactive ruthenium from uranium hexafluoride by simple sublimation and evaporation, described in Appendix C. Successive uranium hexafluoride vapor samples contained progressively less ruthenium activity. The vapor samples usually contained less ruthenium activity than the solid or liquid phase.

The reason for the sampling difficulties became evident in the filtration and viewing-cell tests described in Appendix D. Examination of a solution of ruthenium pentafluoride in uranium hexafluoride in a cell with Fluorothene windows showed that the solution had a light yellow color and contained a large amount of suspended dust particles most of which settled out on standing. It is impossible to avoid some nickel fluoride and uranium tetrafluoride dust when uranium hexafluoride is stored in nickel containers. When the dust was filtered from the solution through Fluorothene frits and counted, it was found that at least half of the ruthenium activity in the solution was contained in the dust particles. Either the ruthenium pentafluoride was reduced by the nickel wall to a solid ruthenium compound which came out on the filter or was strongly absorbed as the pentafluoride on the dust particles. In either case, a large part of the ruthenium activity was associated with the dust particles which were unevenly distributed in the solution. The variability of vapor samples indicates that the dust may be entrained in the uranium hexafluoride gas during vapor sampling.

Selection of the Distillation Method of Ruthenium Removal

The exploratory studies summarized in the previous section indicated that ruthenium pentafluoride might be separated from uranium hexafluoride by taking advantage of the lower volatility and greater reactivity of the ruthenium compound. The consideration of various methods for taking advantage of these separative properties led to the selection of a distillation

FIRST RUTHENIUM REACTOR

FIGURE 1

method. In this method all of the separative properties mentioned above are advantageously brought into play. The distillation action would tend to concentrate ruthenium pentafluoride in the still pot. A nickel packing of large surface area would provide opportunity for chemical and physical sorption on nickel or nickel fluoride. If the ruthenium were converted to a solid form by chemical reduction or by adsorption on dust particles, the refluxing uranium hexafluoride would tend to scrub the ascending gas and return solid particles to the pot. The distillation method combined distillation action, adsorption action and scrubbing action and was therefore chosen as the most promising method for the separation of ruthenium from uranium hexafluoride.

In order to test the distillation method, three types of mixtures of radioactive ruthenium and uranium hexafluoride were used. The first was a mixture of uranium hexafluoride, radioactive ruthenium 106 pentafluoride and 0.1% normal ruthenium pentafluoride. The normal ruthenium pentafluoride was added to minimize the effect of absorption of ruthenium activity on the column walls and packing, to allow the testing of the scrubbing and distillation actions of the column. The second mixture was prepared by the fluorination of singly precipitated uranyl ammonium phosphate from aged Hanford waste solution. The activity in the uranium hexafluoride obtained was due largely to ruthenium 106. This mixture was prepared and distilled to test on a small scale the complete proposed method for decontamination of uranyl ammonium phosphate. The third mixture contained only uranium hexafluoride and ruthenium 106 pentafluoride. This mixture was similar to the second mixture except that a higher level of ruthenium activity was used in order to facilitate counting of samples.

EXPERIMENTAL

Preparation of the Charge

Synthetic Mixture of Ruthenium 106 Pentafluoride-Normal Ruthenium Pentafluoride and Uranium Hexafluoride. A batch of uranium hexafluoride containing both normal and radioactive ruthenium pentafluoride was prepared using the apparatus shown in figure 1. Into the side-arm of the reactor shown in figure 1 was placed 3 millicuries of ruthenium 106 trichloride solution and 2.5 grams of normal ruthenium metal. To reduce the ruthenium 106 to the metal, the solution was dried and hydrogen was passed through the side-arm at 800°C. for 8 hours. The side-arm was heated by means of an electrical sleeve heater to which voltage was applied through a Variac. The side-arm was allowed to cool to room temperature and the body of the reactor was cooled in a dry ice-trichloroethylene mixture. Five kilograms of uranium hexafluoride was charged into the cooled reactor. The side-arm was heated to 300°C. by means of the sleeve heater and fluorine was passed over the ruthenium metal for 8 hours, maintaining the body of the reactor

at dry ice temperature. By this procedure, the ruthenium pentafluoride was largely condensed on solid uranium hexafluoride, minimizing reaction of ruthenium pentafluoride with the nickel walls. The entire reactor was then heated to 70°C. in an oven to melt the uranium hexafluoride, and the reactor was agitated vigorously to mix the components. If none of the ruthenium were lost to the walls, the mixture should have contained 0.1% normal ruthenium pentafluoride and an activity of 2000 disintegrations per min. per mg. of uranium. After standing in the reactor for 5 days, approximately 450 grams of this synthetic mixture was transferred as liquid into a Harshaw cell (a nickel clad container with a capacity of 2.5 kg. of uranium hexafluoride). During the transfer, the mixture flowing in the copper line connecting the reactor with the Harshaw cell was sampled intermittently into a Fluorothene sampling tube. The sample was hydrolyzed and counted for β activity.

The counting procedure used generally in this work was as follows: A counting sample of the hydrolyzed solution was prepared by pipetting 1/2 cc. of the solution into a small nickel hemispherical counting dish and evaporating the solution slowly to dryness. A piece of Scotch tape was pasted over the dish and the sample was counted on an Instrument Development Laboratory β counter, Model 164, using an end window Geiger tube at approximately 20% geometry. A normal uranium β standard was counted with each sample. Counting results were expressed on an arbitrary relative basis by using the formula:

$$\beta \text{ counts/min./mg. U} = \frac{\beta \text{ counts/min. for sample}}{\text{mg. U in sample}} \times \frac{3000}{\beta \text{ counts/min. for standard}}$$

Using this formula, with the arbitrary constant 3000, the calculated counts could be converted approximately to absolute disintegrations per min. per mg. uranium by multiplying by a factor of 30. The factor 30 is the ratio of the absolute β activity of normal uranium (1500 disintegrations per min. per mg. uranium) to the observed β activity of normal uranium calculated using the formula given above (48 to 49 β counts per min. per mg. uranium).

The activity of the sample obtained directly from the ruthenium fluorination reactor was 51 β counts per min. per mg. uranium. This value multiplied by the factor 30 is to be compared with the value of 2000 β disintegrations per min. per mg. uranium calculated from the amount of ruthenium 106 added to the reactor. The counting sample was taken from the reactor 5 days after fluorination.

Another charge of the mixture was transferred from the fluorination reactor to a second Harshaw cell on the same day. Several samples of this material were hydrolyzed and counted after standing in the Harshaw cell for 16 days. The β counts per min. per mg. uranium varied from 3 to 11, averaging 7.4.

These results indicate that ruthenium activity in uranium hexafluoride is decreased markedly on standing in a nickel container. This effect is described in more detail in Appendix B.

The normal ruthenium was introduced into the mixture of uranium hexafluoride with radioactive ruthenium for the purpose of reducing losses of radioactive ruthenium to metal walls by adsorption or reaction. It was thought that normal ruthenium would "condition" the walls so that relatively less active material would be taken up. It was found, however, that the solution reacted rapidly with metal surfaces. When the liquid was passed through copper, phosphor bronze or brass apparatus, a highly radioactive black deposit remained on the metal surface. The reactivity of the solution caused sticking of brass Kerotest valves with Fluorothene seats. Because of this difficulty, Kerotest valves in the apparatus were replaced with Crane HAP valves (phosphor bronze sylphon, Fluorothene seat), modified in such a way that the seat could be loosened in case of sticking by means of a bolt soldered to the top of the sylphon.

The extreme reactivity of the solution resulted in an heterogeneous distribution of radioactivity between solution, dust and walls. For this reason, representative sampling of the solution was impossible and counting results were questionable.

Uranium Hexafluoride Made from Uranyl Ammonium Phosphate from Hanford Waste. Uranium hexafluoride containing ruthenium activity was prepared from uranyl ammonium phosphate from Hanford waste solution using the apparatus shown in figure 2. A batch of uranyl ammonium phosphate slurry, prepared by a single precipitation of Hanford waste solution, was obtained from the X-10 pilot plant³. Approximately one kilogram of uranyl ammonium phosphate was filtered out of the slurry and placed in a nickel boat in a nickel fluorination tube, which was a 30 in. length of 4 in. nickel pipe. The reactor was placed in a 5 in. tube furnace and attached to the system shown in figure 2. To remove water, a stream of nitrogen was passed over the salt at 200°C. for 4 hours. To remove ammonia and to convert the resulting uranyl hydrogen phosphate to uranyl pyrophosphate, nitrogen was passed through the reactor at 700°C. until no ammonia was detected in the exit gas. The uranyl salt was reduced to uranous pyrophosphate by treatment with a stream of hydrogen at 650°C. for 8 hours. The latter compound was converted to uranium tetrafluoride by passing a stream of hydrogen fluoride through the reactor for 16 hours at 600°C. Finally the tetrafluoride was converted to uranium hexafluoride by

³Korsmeyer, R. B., R. C. Olson, H. W. Saylor, J. L. Waters, and W. J. Wilcox, Jr., "Hanford Waste Uranium Recovery, Review of Pilot Plant Results and Process Design", Carbide and Carbon Chemicals Division, K-25 Plant, K-510, September 23, 1949.

UAP FLUORINATION REACTOR AND MANIFOLD

FIGURE 2

fluorination at 450°C. for 4 hours. The uranium hexafluoride thus produced was condensed out of the fluorine stream in a nickel cold trap immersed in a dry ice-trichloroethylene bath. When the fluorination was complete, the fluorine was evacuated from the cold trap at dry ice temperature. When the cold trap was warmed to room temperature, a pressure of approximately 100 psig. was developed. When the cold trap was cooled to -78°C. again, the high pressure was only slightly diminished. The non-condensable gas was evacuated at -78°C. into a chemical trap and the cold trap was again warmed to room temperature. The pressure build-up was only slightly less than before. The non-condensibles were evacuated at room temperature. When the valve to the pump was closed, the pressure rose above atmospheric. After several evacuations at room temperature, the pressure rose to only 5 psia., approximately twice the pressure of uranium hexafluoride at room temperature. The material was then transferred, vapor phase, into the still where it was warmed to 70°C. A pressure of approximately 100 psig. was again observed. After several evacuations of the column the pressure dropped to approximately 18 psig.

A sample of the high pressure gas was taken and analyzed chemically. The results are given in table I.

TABLE I
CHEMICAL ANALYSIS OF NON-CONDENSIBLE GAS

<u>Component</u>	<u>Mole %</u>
F ₂	90.6
UF ₆	0.3
PF ₅	1.4
SiF ₄	9.3

According to these data, the non-condensable gas was composed largely of fluorine and silicon tetrafluoride. The presence of the latter component was traced back to some glass present in the original uranyl ammonium phosphate obtained from X-10. The presence of fluorine is more difficult to explain. It has been previously noted in the plant that when uranium hexafluoride is condensed out of a stream of fluorine gas, anomalous pressure increases sometimes occur on warming the cold trap to room temperature.

No direct liquid samples of the uranium hexafluoride were taken from the cold trap for counting. The average of five pot samples taken after transfer into the still was 4.8 β counts per min. per mg. uranium.

Synthetic Mixture of Ruthenium 106 Pentafluoride and Uranium Hexafluoride.

A batch of uranium hexafluoride containing ruthenium 106 but no normal ruthenium was prepared using the reactor shown in figure 3. A solution containing 6 millicuries of ruthenium 106 trichloride was placed in the side-arm of the reactor and carefully evaporated to dryness without spattering. The reactor body was cooled to dry ice temperature. One kilogram of uranium hexafluoride was transferred into the reactor to coat its walls. Without previous reduction to the metal, the ruthenium 106 trichloride was fluorinated for six hours at 600°C., heating the side-arm with a sleeve heater. The side-arm was allowed to cool to room temperature and the reactor was evacuated. Three kilograms of uranium hexafluoride was transferred into the reactor. The reactor was heated to 70°C. and agitated vigorously to mix the components.

Two liquid samples were taken directly from the reaction vessel into Fluorothene tubes. The samples were hydrolyzed and counted. Their activities were 20.4 and 18.5 β counts per min. per mg. uranium, respectively. No anomalous high pressure was noted on warming the cold trap to room temperature. It was noted that copper lines and brass fittings through which the solution passed were highly radioactive.

Distillation

Distillation Column. The distillation column was designed to operate above the triple point, 64.1°C. and 1172 mm. Hg⁴, so that solid uranium hexafluoride would not plug the column. In previous work on the distillation of uranium hexafluoride⁵, the condenser temperature was maintained slightly above 64.1°C. by the use of a boiling methanol condenser. The alcohol which vaporized was condensed by a water condenser and returned to the still condenser. A similar scheme was used in this work. A diagram of the still and condenser system is shown in figure 4. In order to avoid local chilling and plugging, the still was enclosed in a thermostated box heated slightly above the triple point, as shown in figure 5.

⁴Crist, R. H., and B. Weinstock, "The Vapor Pressure of Uranium Hexafluoride", SAM Laboratories, A-571, February 9, 1942.

⁵Priest, H. F., and F. Kerze, "Construction and Operation of a Distillation Column for Hex", SAM Laboratories, A-248, September 10, 1942.

SECOND RUTHENIUM REACTOR

FIGURE 3

Tw ----- Thermocouple well.

FIGURE 4

CHEMISTRY DEPARTMENT LABORATORY DIVISION	
UF ₆ STILL	
K-25 PLANT CARBIDE & CARBON CHEMICALS CORP	
DRWN <i>B. Hammer</i>	APPV'D <i>RG</i>
DATE: SEP. 27, 1949	DWG NO: LD-B988

FIGURE 5

CHEMISTRY DEPARTMENT LABORATORY DIVISION	
CONSTANT TEMPERATURE BOX FOR UF ₆ STILL	
K-25 PLANT CARBIDE & CARBON CHEMICALS CORP	
DRWN <u>B. Hammer</u>	APPV'D <u>RAE</u>
DATE: SEP. 28, 1949	DWG NO: LD-A936

The still pot was made of a 5 in. length of 2 1/2 in. nickel tubing. It was connected to the column by a welded seal. The pot connections included a 3/8 in. feed line, a 1/4 in. sampling line, a 1/4 in. thermowell and a 1/4 in. pressure gauge lead. The pot capacity was approximately one kilogram of uranium hexafluoride. The pot was heated by a 250 watt heater controlled by a Variac.

The column consisted of a 5 ft. length of 1/2 in. nickel tubing. The lower portion was welded directly to the pot and a one inch perforated section admitted the uranium hexafluoride vapor. The packing consisted of 1/4 in. #28 B & S nickel helices cleaned with dilute hydrochloric acid, water, alcohol and acetone. The total packed length was about 58 in.

The condenser was welded to the top of the column. It was a 1/2 in. diameter nickel tube 16 in. long enclosed in a 3 in. diameter copper jacket 16 in. long. In the design of this condenser, it was important to have sufficient alcohol cross-section to permit steady boiling without bumping. The vaporized alcohol passed to a 10 in. water cooled condenser located outside the box and was returned through a burette section where the rate of methanol condensation was measured. In this way, it was possible to approximate the uranium hexafluoride reflux rate from a ratio of the latent heats of uranium hexafluoride and methanol. A convenient expression of this ratio⁴ is as follows:

$$630 \times \text{ml. methanol/min.} = \text{gm. UF}_6/\text{hr.}$$

The column was lagged with standard magnesite pipe lagging. Six three-junction thermopiles were spaced along the column as shown in figure 4. The box was heated by two 600 watt cone heaters. One cone operated as a constant heater, voltage being controlled by a Variac. The other heater operated as an intermittent heater controlled by a mercury thermoregulator and an Emil Greiner relay. A small centrifugal blower was placed by each heater to circulate the air in the box.

Procedure. The uranium hexafluoride to be distilled was transferred as liquid into the still pot through the charging line. The box was heated to 67 or 68°C. When the uranium hexafluoride was completely liquefied as shown by the temperature and pressures in the column, the pot heater was turned on. Uranium hexafluoride was allowed to reflux at a rate of approximately 400 gm. per hour. While a light fraction, probably hydrogen fluoride, was accumulating in the condenser the reflux rate was low; also the temperatures and pressures were high. The light fraction was slowly bled off and absorbed in the soda-lime trap. When equilibrium was reached, the temperatures and pressures in the column remained constant at total reflux. The top valve on the condenser was carefully cracked and a 5 to 10 gram distillate sample of uranium hexafluoride was collected in a Fluorothene tube maintained at dry ice

temperature outside the box. The sampling was usually completed in 1/2 to 1 hour at a reflux ratio of 10 to 1 or 20 to 1. The reflux rate was checked by closing the lower stopcock on the burette section below the water condenser and observing the rate of methanol condensation. From this rate and the total weight of uranium hexafluoride sampled, the reflux ratio during sampling was calculated. The uranium hexafluoride samples were then hydrolyzed and counting samples were prepared from the solution. A liquid pot sample was taken by attaching a Fluorothene sampling tube to the pot sampling line, opening the pot sampling valve, and allowing liquid uranium hexafluoride to flow into the Fluorothene tube. The sample in the Fluorothene tube was frozen with dry ice, detached from the still and hydrolyzed. Counting samples were prepared from the hydrolyzed solution.

The hydrolysis of uranium hexafluoride in a Fluorothene sampling tube was accomplished by adding several milliliters of water through the open end and stirring until all of the uranium hexafluoride dissolved. The reaction with water was slow due to the formation of a pasty layer of uranyl fluoride between the water and uranium hexafluoride.

RESULTS AND DISCUSSION

Synthetic Mixture of Ruthenium 106 Pentafluoride, Normal Ruthenium Pentafluoride and Normal Uranium Hexafluoride. Three separate batches of this material were distilled, evacuating the still between batches. The distillation results are summarized in table II.

The data in table II show that distillate samples invariably contained less β activity than the pot samples. In no case was a β activity greater than 0.9 counts per min. per mg. of uranium observed in the distillate. It is therefore evident that the passage of uranium hexafluoride containing ruthenium activity through a distillation column packed with nickel helices effectively removes the activity.

Although the decontamination effected by this procedure is satisfactory from a practical standpoint there are many features of the data in table II which are difficult to explain in detail. It may be observed that there is no correlation between reflux ratio, through-put and clean-up factor. It is therefore indicated that the principal decontaminating action of the still was not due to the distillation. Explanations based on chemical absorption of ruthenium pentafluoride on the nickel column packing or on a scrubbing action in the still whereby ruthenium-containing dust is washed back to the pot by refluxing uranium hexafluoride serve better to account for the results.

TABLE II
DISTILLATION RESULTS

	Sample Number	P _T *	P _B **	T _B ***	Reflux, gm. UF ₆ /hr.	Reflux Ratio	Thru-Put, gm. UF ₆ /hr.	Distillate Sample, β counts/ min./mg. U	Pot Sample, β counts/ min./mg. U	Decontamin- ation Factor
Batch I	1	9.9	10.4	67.7	38	1.4	27.9	0.9	55.6	62
	2	10.1	10.7	68.2	38	26	1.5	0.7	15	21
	3	10.4	11.0	68.6	76	13	5.8	0.7	4.6	6.6
	4	10.1	10.8	68.4	65	8.8	7.2	0.8	13.3	16.6
	5	9.8	10.6	68.1	63	2.2	28.8	0.8	5.7	7.1
	6	9.7	9.9	67.0	13	1.0	12.7	0.5	10.5	21
Batch II	1	10.8	11.3	70.3	386	20	19.3	0.3	3.1	10.3
	2	10.8	11.3	70.8	363	16	22.7	0.6	----	----
	3	11.0	11.5	72.6	380	81	4.7	0.7	19.8	28
Batch III	1	10.4	11.2	69.3	316	27	11.6	0.6	3.7	6
	2	10.2	11.0	69.2	264	41	6.45	0.2	3.7	21
	3	10.0	11.0	69.6	328	40	8.15	0.4	3.6	9.2
Average								0.6	12.6	21

*P_T = Pressure in psig. at top of column.

**P_B = Pressure in psig. in the pot.

***T_B = Pot Temperature in °C.

The difficulty of representative sampling of the still pot is shown by the wide scatter of activities of successive pot samples in table II. It is shown in appendices B and D that a large part of the total activity of the mixture was contained in suspended dust particles which were not uniformly distributed through the mixture. The activity of a given sample would therefore depend in large measure on the amount of this dust which was carried into the sample. In table II, it is noted that there is a general downward trend of activities of successive samples of both distillate and pot, with some exceptions. This effect is undoubtedly due to the gradual adsorption of activity by the walls and by the column packing during the distillation. The magnitude of the counting variations was outside the range of counting errors. Since a standard β source was counted with each sample, the relative counting results were presumed to be accurate within 10% on the 95% confidence level. In a test of the self-absorption effect of samples covering the uranium concentration range encountered in the experimental work, the accuracy of counting was incidentally checked. Aliquots of a solution of hydrolyzed uranium hexafluoride containing ruthenium 106 activity were evaporated in counting dishes and counted. The first sample was prepared with 0.10 cc. of the solution, the second with 0.20 cc. etc.

TABLE III
SELF-ABSORPTION OF RUTHENIUM SAMPLES CONTAINING URANIUM

<u>cc. of</u> <u>Radioactive Solution</u>	<u>Activity,</u> <u>β counts/min./mg. U</u>
0.1	7.2
0.2	8.1
0.3	7.9
0.4	7.9
0.5	8.4

From table III, it may be seen that self-absorption corrections were not required for the sample sizes used in this work. Also, the variation of a given activity from the average was less than 10%. In view of the order of magnitude of variations observed from other effects, the errors due to counting may be neglected.

The variation of the clean-up factors in table II is due to the large differences in pot activities. The operation of the still is therefore better described in terms of the low activities observed in the distillate samples. The activity of the distillate was invariably reduced below 1 β count per min. per mg. uranium by the distillation operation, while the average pot activity was 13 β counts per min. per mg. uranium.

Uranium Hexafluoride Made from Uranyl Ammonium Phosphate from Hanford Waste. The gradual build-up of non-condensable gas pressure during distillation made it impossible to achieve reflux equilibrium during distillation of this material since the condenser was filled with non-condensable gas. Repeated withdrawals of non-condensibles did not rectify this difficulty. It was possible, however, to withdraw uranium hexafluoride together with the non-condensable gas. Samples were taken in this way and counted. The results for successive samples of a single run are given in table IV.

TABLE IV

DISTILLATION OF HANFORD MATERIAL

Pot Samples, β counts/min./mg. U	Distillate Samples, β counts/min./mg. U
2.85	3.3
3.3	2.2
4.5	3.7
5.0	5.3
8.0	---
Average 4.8	3.6

It is seen from table IV that there was little if any reduction of ruthenium activity in the distillate when the distillation was carried out without reflux of the uranium hexafluoride. This confirms the previous hypothesis that the main decontaminating action of the distillation operation was due to scrubbing of radioactive dust out of the ascending uranium hexafluoride by the descending refluxing liquid.

The level of ruthenium activity in the still pot was so low that a significant lowering of activity by distillation was difficult to observe. A large part of the original activity in the uranyl ammonium phosphate slurry remained behind in the fluorination reactor, as described in Appendix A.

Synthetic Mixture of Ruthenium 106 Pentafluoride and Normal Uranium Hexafluoride. A summary of the results obtained on distillation of a single batch of this material is given in table V, the data in each horizontal line representing one sampling period.

In these results, again, there was no correlation between reflux ratio, through-put, and clean-up factor. The decrease in activity of both pot and distillate samples indicated that the ruthenium was being absorbed by the walls and column packing.

CONCLUSIONS

It was found that ruthenium 106 contamination could be effectively removed from uranium hexafluoride by passing the mixture through a distillation column packed with nickel helices. The distillation data indicated that the decontamination was effected by absorption on nickel walls and packing and by the scrubbing action of the still rather than by actual distillation action.

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LABORATORY REFERENCES

Notebook number 996 issued to R. A. Gustison, pages 41-89.
Notebook number 1091 issued to T. S. McMillan, pages 67-76.

APPENDIX A

REDUCTION OF RUTHENIUM ACTIVITY BY FLUORINATION

It was found that fluorination of the uranyl ammonium phosphate precipitate obtained from Hanford waste resulted in uranium hexafluoride containing much less activity than the material before fluorination. The results of several typical fluorinations are given in table VI.

TABLE VI

DECONTAMINATION OF UAP BY FLUORINATION

UAP, β counts/min. mg. U	UF ₆ , β counts/min./mg. U	Decontamination Factor of Fluorination
620	146	4
1325	100	13
748	63	12
944	50	19
1904	129	15

The practical objective for the decontamination work was the reduction of β activity to a level of 10 β counts per mg. uranium. Therefore, fluorination alone was not sufficient to reduce the activity to an acceptable level.

APPENDIX B

REDUCTION OF RUTHENIUM ACTIVITY BY REACTION WITH METAL SURFACES

It had been observed qualitatively in early work that when uranium hexafluoride containing ruthenium 106 contamination was allowed to stand in a nickel container, gas samples withdrawn contained progressively less activity. Also, when the mixture was passed through nickel or copper lines, the metal was found to be highly radioactive. It was therefore thought desirable to study the removal of activity by metal walls in more detail.

A sample of uranium hexafluoride containing ruthenium 106 was transferred simultaneously into three nickel cans and allowed to stand at room temperature for five days. The hexafluoride from the first of these cans was withdrawn and hydrolyzed. The can was then dissolved in nitric acid. The ratio of total counts associated with the uranium to total counts in the can was found to be 3.81×10^{-3} . The uranium hexafluoride from the second of these cans was withdrawn at 250°C ., and the ratio, determined as before, was found to be 1.07×10^{-3} . The uranium hexafluoride from the third can was withdrawn at 250°C . Half an atmosphere of fluorine was introduced into the can for 30 minutes and the gas was evacuated through the cold trap containing the uranium hexafluoride previously withdrawn. The ratio, determined as before, was found to be 0.467. These results indicate chemical absorption of ruthenium activity on nickel walls, and also that a large part of the ruthenium activity is removed from nickel walls by fluorination.

To substantiate this conclusion, the sign of the temperature coefficient of the reaction was determined. A sample of radioactive uranium hexafluoride was transferred simultaneously into two nickel cans. One can was kept at room temperature for 24 hours while the other was kept at 60°C . for 24 hours. The ratio determined as above for the can at room temperature was 0.121. The ratio for the can at 60°C . was 0.062. The positive temperature coefficient indicates chemical absorption thus confirming the results of the first experiment.

In order to test the practicability of decontamination by allowing uranium hexafluoride to remain in a nickel container a quantity of radioactive uranium hexafluoride was transferred into a nickel cell 10 in. long and 2 in. in diameter and allowed to stand for 14 days. During this time vapor samples were taken to follow the decontamination. These results are tabulated in table VII.

TABLE VII
RUTHENIUM ABSORPTION ON NICKEL WALLS

Sample	Sampling Time	β counts/min./mg. U
1	One day after preparation	880
2	Seven days after preparation	329
3	Nine days after preparation	55
4	Thirteen days after preparation, after liquefaction	48
5	Fourteen days after preparation, one day after liquefaction	31
6	UF ₆ remaining in trap	27

These results apply only to the particular geometry of the container used. Results with other types of containers would be different since the absorption rate is probably controlled by the distance ruthenium must diffuse in order to strike a metal surface. Therefore extrapolation of these results to production scale is difficult.

APPENDIX C

REDUCTION OF RUTHENIUM ACTIVITY BY VAPORIZATION

Early in the work on ruthenium removal it was observed that vapor samples taken from either liquid or solid uranium hexafluoride were not representative. A more detailed study was made of this phenomenon.

A quantity of uranium hexafluoride containing ruthenium activity was transferred into a nickel cell and heated to 70°C. to liquefy the material. Three vapor samples were flashed off allowing 30 min. between withdrawals to equilibrate the system. The samples counted 48, 8 and 3.7 β counts per min. per mg. uranium. The high result obtained on the first sample may be explained by entrainment of radioactive dust during vaporization.

Throughout the study of ruthenium removal, data were taken regarding decontamination by sublimation. A summary of these results is given in table VIII below:

TABLE VIII
DECONTAMINATION BY SUBLIMATION

<u>Solid,</u> <u>β counts/min./mg. U</u>	<u>Vapor,</u> <u>β counts/min./mg. U</u>	<u>Clean-up</u> <u>Factor</u>
15.7	4.4	3.6
4246	290	14.6
94	42.1	2.2
15.7	5.4	2.9
94	8.3	11.3

From these results, it is seen that some decontamination can be effected by either evaporation or sublimation. These experiments were not refined and it is possible that the ruthenium activity carried over was in the form of radioactive dust.

APPENDIX D

REDUCTION OF RUTHENIUM ACTIVITY BY FILTRATION

The variation in activity of vapor and liquid samples of uranium hexafluoride containing ruthenium activity suggested that the ruthenium was in a solid form distributed unevenly throughout the mixture. A study was conducted to investigate this possibility.

For this work, 800 grams of the mixture containing uranium hexafluoride, 0.1% normal ruthenium pentafluoride and radioactive ruthenium 106 pentafluoride was used. Seven liquid samples were transferred from the Harshaw cell into transparent Fluorothene sample tubes. The samples were not homogeneous and their color varied from light yellow to muddy brown. As mentioned in the body of the report, the activity varied from 3.1 to 11.1, averaging 7.4 β counts per min. per mg. uranium.

To determine whether the variation in color and activity of the sample was due to suspended dust particles, a series of filtration experiments were performed. A Fluorothene sampling tube was prepared with a Fluorothene frit sealed into the central portion, as shown in figure 6. The mixture in the Harshaw cell was allowed to flow as liquid into the sampling tube. The part of the sample which flowed through the frit was filtered while the portion above the frit was unfiltered. The material in both portions of the sampling tube was hydrolyzed and counted. The results of a number of tests are shown in table IX.

TABLE IX

FILTRATION OF RUTHENIUM ACTIVITY

<u>Treatment</u>	<u>β counts/min./mg. U</u>
Unfiltered	2.55
Unfiltered	2.56
Unfiltered	2.48
Unfiltered	2.49
Filtered	1.96
Filtered	1.86
Filtered	1.84
Filtered	2.91

FRIT TUBE

FIGURE 6

It is seen from table IX that the β count of filtered material was usually lower than that of unfiltered material. Unfortunately the activity level of the unfiltered material used in these tests was so low that very definitive results could not be obtained. Also, a source of error which was difficult to control was the possibility that some UX_1 and UX_2 was carried into the sample. The amount of UX_2 in equilibrium with uranium would give an activity of approximately 40 β counts per min. per mg. U, calculated on the arbitrary relative basis described previously. It was assumed in all of the work described here that no UX_1 nor UX_2 was carried out of the Harshaw cell, so that correction for UX_2 build-up was made only for the time between sampling and counting. Due to the low activities used in this experiment it was not possible to identify the β radiation by absorption curves.

To carry out more definitive tests on the physical nature of ruthenium in the mixture, the viewing cell shown in figure 7 was constructed. All of the material remaining in the Harshaw cell was transferred as liquid into the viewing cell. The liquid was turbid. Some of the suspended solid settled to the bottom of the viewing cell and the remainder formed a scum on the surface of the liquid. The solution was light yellow in color. The liquid was transferred back into the Harshaw cell through a Fluorothene tube containing a Fluorothene frit, using nitrogen pressure to force the liquid through the frit. A black, strongly radioactive solid was deposited on the frit. This material contained an activity of 12800 β counts per min. per mg. of material, corresponding to approximately half the total activity in the liquid passed through the frit. Analysis of the black solid by the X-10 Spectrographic Laboratory indicated that it was largely nickel. In a second similar filtration experiment the black solid contained 26,800 β counts per min. per mg. of material.

The viewing cell was filled with material from the original fluorination reactor, using nitrogen pressure to force it through two Fluorothene frits in series. The second frit was colored black as well as the first. The filtered liquid was perfectly clear and light yellow in color. Two determinations of the activity of the filtered liquid gave 0.73 and 0.82 β counts per min. per mg. of uranium. The material on the Fluorothene frits was highly radioactive, giving readings with a survey meter similar to those of the previous filtered solids.

It was found that the solution containing only ruthenium 106 pentafluoride and uranium hexafluoride was similar to that also containing normal ruthenium pentafluoride. Black solid particles were visible in a liquid sample. The particles settled toward the bottom of a sampling tube before the sample solidified. The bottom half of the sample had an activity of 50 β counts per min. per mg. uranium while the upper half counted only 18 β counts per min. per mg. uranium. A second sample was turbid but no individual particles were visible. The liquid was filtered through a Fluorothene frit. The activity of the material before filtration was 7.5 β counts per min. per mg. uranium while the β count of the filtered material was 0.6 per min. per mg. uranium.

VIEWING CELL

FIGURE 7

These tests show definitely that a large part of the ruthenium activity in the uranium hexafluoride mixtures exists in a solid form, either absorbed on nickel fluoride or as a solid ruthenium compound. These results explain the difficulty in obtaining representative samples of the mixtures and also the action of the distillation column as a scrubbing tower.

APPENDIX E

EXAMINATION OF THE DISTILLATION COLUMN

At the completion of the distillation experiments, the column was taken out of the box and the magnesite lagging removed. The γ activity of the pot and column was measured with a survey meter. The column was then cut into four 15 in. lengths and the packing poured into large glass test tubes. The test tubes were counted for γ activity in a high pressure ionization chamber. A ruthenium tetroxide distillation was made on the material in each test tube. Chemically detectable amounts of ruthenium were recovered only from the bottom portion of the column. The β activity of this material was determined.

The survey meter readings of the pot and column were less than 2 milliroentgens per hour except for a 6 in. length of the column two thirds of the distance up the column, which gave a reading of 20 milliroentgens per hour.

When the pot was cut off the column, it was noted that a large quantity of black dust had collected in the perforated section where the pot joined the column. The nickel helices in the bottom section of the column were coated with a layer of black ruthenium oxide. The helices in the three upper portions of the column were not visibly affected by exposure to the corrosive fluorides. The results of the γ activity measurements in the high pressure ionization chamber are given in table X.

TABLE X

DISTRIBUTION OF γ ACTIVITY ON DISTILLATION COLUMN

<u>Sample</u>	<u>Shield</u>	<u>γ Reading</u>
1 Top	Lead	0.51
2	Lead	1.20
3	Lead	0.95
4 Bottom	Lead	0.40
1	Brass	0.77
2	Brass	1.70
3	Brass	1.40
4	Brass	0.60

These results correspond roughly to the survey meter readings, indicating a concentration of activity about two-thirds of the distance up the column.

Only the bottom section (4) of the column contained sufficient ruthenium to allow chemical separation from the nickel by means of a ruthenium tetroxide distillation. The upper portions contained more ruthenium activity but not sufficient ruthenium to detect chemically. The bottom section had an activity of 4110 β counts per min. per mg. ruthenium.

A number of inferences may be drawn from the results of the examination of the distillation column. First, it is evident that a large amount of ruthenium activity was chemically absorbed by the column packing. Second, the presence of the black dust in the bottom section substantiates the conclusion that the still was acting as a scrubbing tower. Third, the distribution of activity in the column is an indication that the nickel helices became "conditioned" to ruthenium pentafluoride. The mixture first passed through the column contained 0.1% normal ruthenium pentafluoride. From the black coating on the helices in the bottom section of the column, it is apparent that most of the ruthenium was absorbed at this point. The later charges contained only radioactive ruthenium, and this material deposited further up the column. It is thus indicated that the bottom portion was "conditioned" by the first charge so that the ruthenium pentafluoride in later charges traveled further up the column before it was absorbed.