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DIFFUSION PROCESS

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URANIUM HEXAFLUORIDE PURIFICATION

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CLASSIFICATION CANCELLED

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For The Atomic Energy Commission

H. P. Carver
Chief, Classification Branch

AEC RESEARCH AND DEVELOPMENT REPORT

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CARBIDE AND CARBON CHEMICALS DIVISION
UNION CARBIDE AND CARBON CORPORATION
K-25 Plant
Oak Ridge, Tennessee

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A B S T R A C T

An experimental batch distillation column was used to purify uranium hexafluoride containing metal impurities of the order of 350 ppm. The degree of purification was determined by comparing the spectrographic analyses of the uranium hexafluoride distillate material with the original feed or not material. From approximately half of the distilled batches $87\% \pm 5\%$ of the impurities were removed. From the others the per cent of impurities removed was $70\% \pm 13\%$. The limits shown are the 95% confidence limits.

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INTRODUCTION

If the enriched uranium hexafluoride produced by the K-25 Plant should contain greater quantities of metallic impurity than are desirable, a preliminary purification operation would be necessary in order to utilize the vapor phase trichloroethylene reduction of uranium hexafluoride to uranium tetrafluoride (1,2). The present method for reducing enriched uranium hexafluoride to uranium tetrafluoride does reduce metallic impurity to an acceptable level, but several process operations and considerable handling of the material are necessary. Consequently, it was desired to develop a preliminary purification operation in order that the one-step vapor phase trichloroethylene reduction might be utilized.

Since the major contaminants to be removed by the purification operation are non-volatile metallic fluorides, which may be slightly soluble in liquid uranium hexafluoride, it was proposed that these impurities be removed by scrubbing the uranium hexafluoride vapors in a packed tower.

APPARATUS AND PROCEDURE

The purification still shown in figure 1 was constructed of nickel and monel with all joints welded so that little or no unaccountable metallic impurities were added during operation.

A 48 inch column was constructed of 1 inch O.D. by 1/8 inch wall nickel tubing and was packed with 1/8 inch nickel helices. A still pot 6 inches long was fabricated from 4 inch O.D. by 1/8 inch wall nickel tubing and was equipped with two sight windows which aided in following the progress of the distillation. Heat was supplied to the pot with nichrome resistance wire and was controlled with a voltage regulator. A nickel sampling tee, which was welded to the bottom of the pot, was used for taking liquid samples of the feed material.

The reflux condenser (methanol coolant) was 12 inches long and was fabricated from 1 inch O.D. by 1/16 inch wall nickel tubing. The condenser was enclosed in a copper coolant jacket 2 inches in diameter. The condenser was off-set about 4 inches from the top of the column so that the condensed uranium hexafluoride was returned to the column through a calibrated Fluorothene tube located directly below the condenser. A shut-off valve was placed between the calibrated tube and the column so that intermittent checks could be made of the column throughput rates and reflux ratio by closing the valve and noting the time required to fill the tube to a given volume. The uranium hexafluoride reflux was returned to a point about 10 inches from the top of the column where a sight window was located. All sight windows were machined from 3/16 inch Fluorothene sheet.

The distillate line was constructed of 3/8 inch nickel tubing and contained a 0.030 inch nickel orifice to measure the distillate withdrawal rate. The pressure drop across the orifice was measured by a 0.0 to 1.0 psi. DBM (differential pressure transmitter) and was indicated by a calibrated pressure indicator. A distillate sample line was also constructed of 3/8 inch nickel tubing and was tied into the distillate line. For two distillations a metal filter unit was installed between the distillate line and sample

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URANIUM HEXAFLUORIDE PURIFICATION STILL

tube. The filter unit consisted of a 1 inch disc of the metal filter clamped between two nickel flanges and sealed with Teflon gaskets. The distillate receiver consisted of a standard 5 pound Harshaw cylinder.

The distillate and pot sample tubes were machined from 3/4 inch Fluorothene rods. The outside dimensions of the tubes were 2-1/2 inches long by 1/2 inch in diameter and each tube was equipped with 1/2 inch plastic (Saran) flare nut for making connection to the sampling points.

In addition to Bourdon tube pressure gauges located at the pot and at the top of the column, a 0.0 to 1.0 psi DBM (differential pressure transmitter) was installed to measure the pressure drop across the column. The pressure drop was indicated on a calibrated pressure indicator. Temperatures of the column, the condenser and the pot were measured with iron-constantan thermocouples and were indicated by a continuous Micromax recorder.

Although the column and auxiliary lines were placed within a thermostatically controlled box, all lines were heated with nichrome resistance wire and were insulated with asbestos tape. The column was also heated with nichrome resistance wire and was insulated with 85% magnesia. The additional heat supply was controlled by several voltage regulators and was used only to bring the apparatus to operating temperature in a minimum period of time.

Before the column was placed in operation the number of theoretical plates was determined experimentally by distilling a known mixture of n-heptane and methylcyclohexane (3,4). The results indicated 16 theoretical plates.

The feed cylinder was placed in an inverted position inside a smaller heated box so that the still pot was gravity-fed with liquid uranium hexafluoride. Immediately after the column was charged, several liquid samples of the feed material were withdrawn from the bottom of the pot. In every case it was necessary to bleed-off the non-condensable gases (HF, F₂, phosphorous and chromium fluorides) present in the feed material through the reflux condenser before a steady reflux of uranium hexafluoride could be obtained. These gases were passed through a cold trap and chemical trap to recover the small quantity of uranium hexafluoride which was entrained during the bleed-off operation. The column was brought to equilibrium and operated at total reflux for several hours before uranium hexafluoride vapor was removed as distillate. The distillate flow rate was controlled by a needle valve located on the up-stream side of the orifice. The distillate vapor was collected in a cylinder maintained at a temperature of -80°C. Immediately after the distillate flow was started the first of a series of distillate vapor samples was taken. The number of distillate samples taken for each run varied from 4 to 8, depending on the operation time for each run. During a run the distillate flow rate, reflux ratio, temperatures, and pressures were periodically checked and recorded. Since the major contaminants in the feed material were non-volatile impurities, the column was essentially operated at constant temperature and pressure. Usually the run was terminated before all the uranium hexafluoride feed material was distilled from the pot; however, in some cases the run was allowed to proceed until the pot was completely dry. At the conclusion of each run the distillate flow rate was checked by weighing the tared distillate receiver.

Every precaution was taken to prevent the addition of extraneous impurities during sampling of the distillate vapors and feed material. The samples were taken in Fluorothene tubes fitted with Saran flare nuts so that no metal, other than nickel, came in contact with the sample material. When a distillate sample was taken, the sample line valve was opened slowly to prevent any disturbance of the column equilibrium. The samples were condensed in the tubes by cooling with liquid nitrogen. The tubes were immediately disconnected from the system and were sealed with a threaded Fluorothene flare plug. The samples were then prepared for spectrographic analysis by hydrolysis, using distilled water, and conversion of the resulting uranyl fluoride to uranous uranic oxide (U_3O_8). During the course of sample preparation and sample handling there was some opportunity for sample contamination even though every effort was made to minimize this possibility. The samples of the distillate and feed material were analyzed in the same manner (4) as samples of the enriched uranium hexafluoride taken from the K-25 Plant.

Twelve batch distillations were made from two cylinders of feed material. Large quantities of impurities found in samples from the first two runs indicated that the apparatus was not completely free of impurities. After the third distillation, the first feed cylinder, which contained excessive quantities of chromium and phosphorous fluorides, was empty. From the second feed cylinder the remaining nine batch distillations were made. Runs 5 through 11 were completed before the metal filter unit was installed between the distillate line and sample tube. The filter was installed for runs 12 and 13. Data from the nine runs, 5 through 13, are summarized in tables 1 and 2.

RESULTS AND DISCUSSION

Table I presents a summary of the operating conditions and the results of each batch distillation.

In table II are listed, with one exception, the various elements found in the distillate samples and the average amount of each element per run. Zinc, which was present in five of the fifty-two samples, was excluded from the gross total ppm. of impurities in making comparisons among the various samples because of the relative unreliability of the zinc analysis. The precision of the spectrographic analysis for zinc is only ± 25 ppm., while the analysis for each of the other elements in the distillate samples is reliable within ± 2.5 ppm. Thus, the inclusion of zinc in the summation of impurities would obscure the results of the more precise analyses.

Data from the nine runs and from the feed cylinder samples were used to make three kinds of comparisons: comparisons among samples from any given batch of distillate, among the nine distillation batches, and between the feed and distillate materials.

As was expected, an examination of the individual elements found among samples from any given run showed larger quantities of the more volatile fluorides such as chromium in the first sample withdrawn than in the last. There was no significant clean-up of magnesium or of silicon. Even though distilled water was used for hydrolyzing the samples in preparation for analysis, small quantities of magnesium and silicon were added in this manner.

TABLE I

SUMMARY OF URANIUM HEXAFLUORIDE DISTILLATION DATA

Run No.	Pot Temperature, °C.	Column Pressure, psig.	Column ΔP, psi.	Reflux Ratio	Vapor Velocity, ft./min.	Throughput, g./hr.	Distillate Flow Rate, g./hr.	*Average Gross Impurity, ppm.	Ave. Impurity and 95% Confidence Limits	Per Cent Removal of Impurities
5	68.1	12.7	0.20	108	12.2	1622	15	104	105 ± 33	70 ± 13
6	66.6	11.1	0.10	33	16.1	2150	65	71		
8	68.1	12.3	0.15	41	13.8	1846	45	97		
10	69.9	13.1	0.10	73	12.5	1674	23	166		
11	67.8	11.3	0.05	57	11.1	1480	26	86		
7	65.6	10.4	0.05	28	11.7	1555	56	42	45 ± 10	87 ± 5
9	66.0	11.4	0.10	34	10.6	1406	41	37		
12	66.7	10.6	0.05	25	9.9	1321	51	46		
13	69.2	12.8	0.25	35	11.4	1526	42	60		
(Uranium Hexafluoride Feed Material, 14 samples, for Runs 5 thru 13)								355	355 ± 128	

*Zinc not included. See discussion section of report

TABLE II

SUMMARY OF THE SPECTROGRAPHIC ANALYSES OF URANIUM HEXAFLUORIDE FEED AND DISTILLATE

Run No.	Average Impurity, ppm per element															Average Gross Impurity, PPM
	<u>Ag</u>	<u>Al</u>	<u>Be</u>	<u>Bi</u>	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Mn</u>	<u>Mo</u>	<u>Ni</u>	<u>Pb</u>	<u>Si</u>	<u>Sn</u>	
Feed Material	3.3	1	0	0	0.8	83	27	187	.2	0.5	1	26	19	3	2	355
5	7.0	1	0	0.1	6.1	3	47	5	6	0	0	6	2	21	0	104
6	3.3	1	0	0	2	0	17	7	6	0.4	0	30	3	2	0	71
8	18.2	2	0	0	0.1	0	41	12	4	0	0	6	3	11	0	97
10	34.8	2	0	0	2.5	4	36	46	3	1	0	21	8	7	1	166
11	14.7	4	0	0	0	4	14	26	5	0.9	0	6	2	9	0	86
7	2.9	0	0	0	0	0	10	4	6	0	0	1	10	8	0	42
9	1.4	0	0	0	0.7	1	5	7	4	0.5	0	8	2	7	0	37
12	1.9	2	0	0	0	2	10	15	4	0.3	0	8	1	2	0	46
13	18.5	4	0	0	0	4	8	9	3	0	0	4	6	3	0	60

In order to make comparisons among the various batches of distillate, the average gross impurities and the standard deviation for each run were computed from the total impurities found in samples from the run.

It was found that the distillate from the nine runs could not be considered as one homogeneous lot. Runs 7, 9, 12, and 13 constitute one lot of distillate which is significantly purer than that comprised by runs 5, 6, 8, 10, and 11. There is also significantly less variation among the sample purities (resulting in lower batch standard deviations) in the second group than in the first group of runs. As shown in table I, column 10, the two group means with their respective 95% confidence limits, expressed in ppm. impurities, are 45 ± 10 and 105 ± 33 .

The reason for this division of the distillate into two lots is unexplained. It cannot be attributed to the differences in operating conditions under which the runs were made. Since runs 12 and 13 are not significantly different from either run 7 or run 9, it cannot be concluded that use of a dust filter in the sample line increased the purity of the product.

As shown in table I, the column was operated at various reflux ratios and throughput rates. The expected increase in product purity at the higher reflux ratios was not shown by the data. It is concluded that the column was operated at reflux ratios and throughput rates above those which would tend to affect the purification efficiency of the still. This conclusion was also supported by the fact that preliminary one-plate vapor distillations of uranium hexafluoride at room temperatures show a fair clean-up of metallic impurities.

The degree of purification of uranium hexafluoride by distillation is determined by comparing the purity of the feed material with that of the distilled product. Expressed in ppm. impurities, the feed material mean with its 95% confidence limits is 355 ± 128 , table I, column 10. Comparison between the original material and the distillate from runs 7, 9, 12, and 13 indicates that $87\% \pm 5\%$ of the impurities were removed during these four distillations. During the other five runs $70\% \pm 13\%$ of the impurities were removed.

It was expected that a more complete removal of impurities would result from the distillations. Consideration, however, should be given to the fact that very small quantities of metallic impurities were present.

SUMMARY

The degree of purification of uranium hexafluoride by distillation was studied using an all nickel rectification column packed with 1/8 inch nickel helices. The column was operated at various reflux ratios and throughput rates. Distillate was removed from the column as uranium hexafluoride vapor. The degree of purification was determined by comparing the spectrographic analyses of the distillate material and original feed or pot material.

In determining the purity of the distillate, it was found that approximately half of the runs yielded product which was significantly purer than that resulting from the other runs. Although this difference is signifi-

cant at the 0.05 probability level, a survey of the operating conditions failed to reveal its cause. The per cent of impurities removed by the one group of runs was $87\% \pm 5\%$, while $70\% \pm 13\%$ was removed during the other runs.

The use of a metal filter in the distillate line did not significantly affect the purity of the product.

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1. Allen, A. L., Bernhardt, H. A., Maroney, W. L., Massey, B. J., Schaffner, J. G., and Wiggin, E. A., Continuous Method of Reducing Uranium Hexafluoride to Uranium Tetrafluoride by Means of Trichloroethylene, Carbide and Carbon Chemicals Division, K-25 Plant, May 17, 1948, (K-215).
2. Allen, A. L., Bernhardt, H. A., and Schaffner, J. G., Continuous Method of Reducing Uranium Hexafluoride to Uranium Tetrafluoride by Means of Trichloroethylene, Part II, Product Purity, Carbide and Carbon Chemicals Division, K-25 Plant, October 11, 1948, (K-280).
3. Perry, John H., editor, Chemical Engineers Handbook, 2nd ed., McGraw-Hill Book Company, Inc., 1941, p. 1337.
4. Scribner, B. F., A System of Methods for the Spectrochemical Analysis of Uranium - Base Materials, National Bureau of Standards, September 14, 1945 (A-2907).
5. Willingham, C. B., and Rossini, F. D., The Assembly, Testing and Operation of Laboratory Distilling Columns of High Efficiency, National Bureau of Standards, Washington D. C., December 31, 1945.

NOTEBOOK REFERENCE

Allen, A. L., K-25 Notebook Number HL-1572, p. 6-37, 90-99.

The experimental work was completed December 20, 1950.

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