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LABORATORY AND PILOT-PLANT STUDIES ON THE CONVERSION OF URANYL NITRATE HEXAHYDRATE TO UF_6 BY FLUIDIZED-BED PROCESSES

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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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LABORATORY AND PILOT-PLANT STUDIES ON THE CONVERSION OF URANYL NITRATE HEXAHYDRATE TO UF_6 BY FLUIDIZED-BED PROCESSES

E. L. Youngblood, I. J. Urza,* and G. I. Cathers**

ABSTRACT

This report describes laboratory and pilot-plant studies on the conversion of uranyl nitrate hexahydrate (UNH) to UF_6 and on purification of the UF_6. Experimental laboratory studies on the removal of residual nitrate from uranium trioxide (UO_3) calcine and the fluorination of technetium and subsequent sorption on MgF_2 were conducted to support the pilot-plant work. Two engineering-scale pilot plants utilizing fluidized-bed processes were constructed for equipment and process testing of the calcination of UNH to UO_3 and the direct fluorination of UO_3 to UF_6.

1. INTRODUCTION

Since 1970, the Exxon Nuclear Company, Inc. (ENC) has been engaged in design and licensing activities required to construct and operate the Nuclear Fuel Recovery and Recycling Center (NFRRC). The preliminary safety analysis report for the NFRRC (XN-FR-32) was docketed on June 16, 1976 (Docket 50-564). The NFRRC will use the Purex process followed by fluidized-bed conversion of the resulting uranyl nitrate hexahydrate (UNH) to uranium hexafluoride (UF_6). The main Purex process has been developed and successfully demonstrated through many years of plant operation; however, certain functions and innovative processes are unique to the NFRRC.

In the uranium calcination step, UNH is thermally denitrated in a fluidized-bed calciner using air as a fluidizing gas. The following

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endothermic reaction occurs:

$$UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow[\text{heat}]{280\text{-}400°C} UO_3 + NO + NO_2 + O_2 + 6H_2O \qquad \Delta H° = 140 \text{ kcal/g-mole}$$

In the uranium fluorination step, uranium trioxide (UO_3) is directly fluorinated with elemental fluorine in a fluidized bed using inert alumina. The following exothermic reaction occurs:

$$UO_3 + 3F_2 \rightarrow UF_6 + 3/2\ O_2 \qquad \Delta H° = -247 \text{ kcal/g-mole}$$

Oak Ridge National Laboratory, under AEC Contract No. AT-(40-1)-4708, has assisted ENC in the development of a process for converting UNH to UF_6. In compliance with Appendix C of the contract, the present report was written to provide a meaningful account of the overall technical aspects of the ENC Assistance Program. Proprietary information that would reveal the sponsor's proprietary equipment, process design, or operating conditions has been excluded.

ORNL assistance to ENC consisted of: (1) a literature survey on the removal of technetium, neptunium, and plutonium from UF_6 (Appendix A), (2) a laboratory study on the removal of residual nitrate from UO_3, (3) a laboratory study on the behavior of technetium in the uranium conversion process, (4) testing of pilot-plant-scale fluidized-bed calcination of UNH to UO_3, and (5) testing of pilot-plant-scale fluidized bed fluorination of UO_3.

2. OBJECTIVES OF THE RESEARCH AND DEVELOPMENT PROGRAM

Thermal denitration of UNH to UO_3 in a fluidized bed has been developed and demonstrated in long-term pilot-plant- and plant-scale operation. The potential problems have been identified, and the effects of process variables on product characteristics have been investigated. Consequently, process development was not the primary goal of the research and development program described here. The objectives of the uranium calcination development program were to:

1. Test the performance of ENC-designed uranium calcination equipment.
2. Produce fluidized-bed UO_3 product suitable for fluorination.
3. Verify operating and design parameters needed for start of detailed design.
4. Study the behavior of technetium and ruthenium and the removal of impurities (nitrate and water) by heat treatment of UO_3.
5. Develop operating procedures and gain experience with the process.

Since limited information has been reported in the open literature on direct fluorination of UO_3, basic operating and design parameters required definition. Potential problem areas included the formation of intermediate uranium fluoride compounds, fluidized-bed temperature control, and solids transfer. The general, overall objectives of the uranium fluorination development program were to:

1. Develop and demonstrate a pilot-plant-scale direct fluorination process.
2. Determine the range of acceptable operating conditions.
3. Test the performance of ENC-designed uranium fluorination equipment.
4. Study the fluorination of UO_3 produced by various calcination methods.
5. Study methods for increasing fluorine utilization.
6. Study the behavior of technetium in the system.

ENC designed and constructed the major pilot-plant equipment items, including the fluorination and calcination vessels. ORNL was responsible for the design and construction of supporting components. Some of the equipment provided by ORNL was available from previous experimental facilities and does not necessarily represent an ideal design.

3. LABORATORY STUDIES

Experimental laboratory studies on the removal of residual nitrate from UO_3 calcine and the fluorination and sorption of technetium on MgF_2 were conducted to support pilot-plant work and to explore areas not covered by the pilot-plant experimentation.

3.1 Removal of Residual Nitrate from UO_3

Laboratory studies were performed to investigate the treatment of UO_3 at high temperatures under nitrogen, air, and hydrogen atmospheres as a means of reducing the residual nitrate content. Following preliminary development work to determine suitable experimental and analytical methods, a series of tests was made to determine the effect of important variables on nitrate removal. These tests were made using UO_3 supplied by ENC and UO_3 produced in fluidized beds.

In each test, 10 g of UO_3 was placed on a porous support plate in a 1-in.-O.D. by 12-in.-long stainless steel reactor. The reactor was then placed vertically in a 1-in. tube furnace to heat gases and UO_3 to the desired temperature. The nitrate content of the UO_3 was determined by first leaching the nitrate from the UO_3 sample with distilled water and then analyzing the leachate with an ion-selective electrode.

3.1.1 Removal of residual nitrate from UO_3 supplied by ENC

The procedure used in each of these tests was to place a UO_3 sample (10 g in most cases) in the vertical reactor, heat it to the desired temperature as quickly as possible (usually in 15 to 25 min) without any gas flow, and then start the gas flow. When the test was terminated, the sample was quickly cooled, removed, and sampled for analysis.

Data from tests using a hydrogen-nitrogen atmosphere are given in Table 1. These data show that the nitrate removal rate is initially high but decreases with time. It is also evident that the nitrate removal rate increases with increasing temperature.

Table 1. Removal of residual nitrate from UO_3[a] using hydrogen-nitrogen

Run number	H_2 conc. (%)	Time (hr)	Temp. (°C)	Residual NO_3^- (%)	U_3O_8 (%)
36	18	0.5	400	0.31	0.41
35	18	1.0	400	0.16	2.81
39	18	1.5	400	0.22	5.25
48	18	1.5	425	0.13	10.4
41	18	1.5	450	0.065	52.5
47	18	1.5	475	0.013	48.3 (UO_2)
50	3.6	1.5	450	0.20, 0.21	0.15
51	7.2	1.5	450	0.29, 0.20	1.21
52	10.8	1.5	450	0.16, 0.15	9.54
53	14.4	1.5	450	0.14, 0.14	16.7

[a] 10 g of ENC-supplied UO_3 (initial NO_3^- content, 0.75%) was used in each run.

Data from runs using nitrogen, air, and oxygen as a carrier gas are given in Table 2. These runs were designed to study the effects of time and temperature on nitrate removal.

Table 2. Removal of residual nitrate from UO_3[a] using nitrogen, air, and oxygen

Run number	Time (hr)	Temp. (°C)	Residual NO_3^- (%)	U_3O_8 (%)
		Nitrogen tests		
37	1	500	0.20	0.14
40	2	500	0.24	0.06
43[b]	1	500	0.24	0.16
49[c]	1	500	0.21	0.10
45	3	525	0.10	0.16
46	3	550	0.061	11.8
38	1	575	0.072	10.4
42	2	575	0.040	29.1
44	3	575	0.010	76.2
		Air test		
54	1	575	0.11	0.22
		Oxygen test		
55	1	575	0.12	0.13

[a] 10 g of ENC-supplied UO_3 (initial NO_3^- content, 0.75%) was used in each test.

[b] Double the normal flow rate of 120 ml/min.

[c] Ground and sieved to -325 mesh.

3.1.2 Removal of residual nitrate from UO_3 produced in a fluidized bed

Uranium trioxide produced in the fluidized-bed pilot plant was used in nitrate removal tests using hydrogen-nitrogen and nitrogen as the carrier gas. The results are summarized in Table 3.

Table 3. Removal of residual nitrate from UO_3 produced in the fluidized-bed pilot plant

Run number	Conditions	NO_3^- conc. (%)	U_3O_8 (%)
	UO_3 produced from concentrated UNH (Run CU-3); initial NO_3^- content, 0.49%		
DN-67	3 hr at 525°C; 18% H_2/N_2	0.089	<0.13
DN-68	3 hr at 575°C; N_2	0.16	6.2

3.1.3 Conclusions

1. All of the work relative to removal of residual nitrate indicates that heat treatment and sparging of UO_3 with nitrogen, hydrogen, or air is an effective method of reducing the level of residual nitrate.
2. The residual nitrate content can be reduced to lower levels at a lower temperature with hydrogen. The use of hydrogen also promotes reduction of UO_3 to U_3O_8 and even UO_2, as indicated in Run 47, Table 1.
3. Additional studies will be required to completely define quantitative relationships between residual nitrate and the various parameters.

3.2 Fluorination and Sorption of Technetium on MgF_2

The use of MgF_2 to remove technetium from gas streams containing UF_6 has previously been studied on both a laboratory and a production scale by Golliher et al.[1] at the Paducah Gaseous Diffusion Plant. They found that the recovery efficiency for technetium was >99% with a superficial gas velocity of 0.27 fps (residence time of 9.3 sec).

In the studies carried out at ORNL, UO_3 containing ^{99}Tc was fluorinated, and the UF_6 and volatile technetium compounds produced were passed through a bed of MgF_2 to determine the feasibility of removing technetium by sorption on MgF_2. The procedure used in these studies can be described as follows.

A batch of UO_3-Tc_2O_7 calcine was prepared by adding ammonium pertechnetate (NH_4TcO_4) to UNH which was then thermally denitrated (350°C) in a 500-ml flask. Alumina was subsequently added to form a granular product. The technetium volatilized during the calcination process amounted to only 0.021%. The behavior of technetium was also studied in tests using spiked UO_3 produced in the fluidized-bed pilot plant.

A schematic of the equipment used in the fluorination-sorption tests is shown in Fig. 1. The fluorinator consisted of a 1-in.-OD nickel tube with a sieve plate at the bottom to support the bed. In each run, 100 g of UO_3-alumina was used to give a static bed depth of 4 in. Usually the bed was heated and held at 450°C with a nitrogen flow of less than 10 ml/min before starting the test. After the fluorine flow (the usual flow rate was 50 ml/min for fluorine and 100 ml/min for nitrogen) was started, the internal temperature in the bed increased to 500-525°C. The reaction zone was followed with a movable thermocouple located in the bed.

The off-gas from the fluorinator (a mixture of UF_6-N_2-O_2 and any excess fluorine) was routed through 1/4-in.-OD copper tubing to the sorption reactor either directly or after passage through the auxiliary

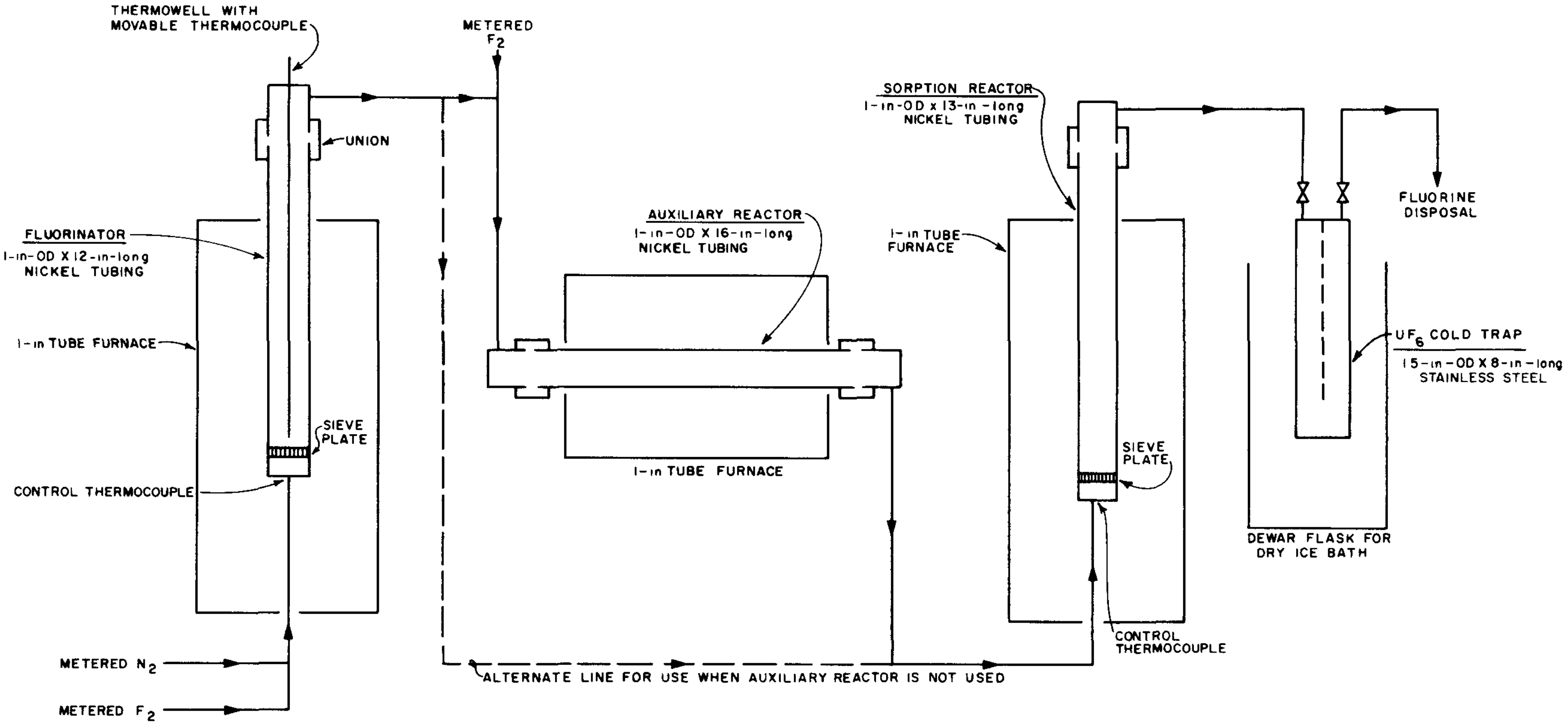

Fig. 1. Schematic diagram of equipment used in laboratory fluorination-sorption tests.

reactor. The auxiliary reactor was simply an empty 1-in.-diam nickel tube operated at 500°C to provide more opportunity for volatile Tc_2O_7, TcO_3F, or $TcOF_4$ to be converted to TcF_6 by reaction with excess fluorine at a high temperature.

The sorption reactor was a 1-in.-diam nickel tube mounted vertically with a sieve plate at the bottom to support the MgF_2 bed. The MgF_2 bed used in the sorption reactor always consisted of 7-g sections of -4 +12 mesh MgF_2 which had been dried several hours in an oven at 125°C. The original MgF_2 pellets, which were ∿1/4-in.-diam spheres, were obtained from the Paducah Gaseous Diffusion Plant. However, the pellets were crushed and screened to -4 +12 mesh since material of this size is more suitable for use in a 1-in.-OD sorption tube. Each 7-g section was about 1 in. deep. The different sections of the MgF_2 were kept separate by use of 32-mesh nickel screens which were held in place by friction.

The cold traps used for collecting UF_6 during the fluorination step and for collecting TcF_6 during the desorption step were made of stainless steel to avoid excessive corrosion when the material was removed from the trap by hydrolysis [usually with 1.5 $\underline{M}$ $Al(NO_3)_3$].

All analyses in this work were carried out using a radiochemical separation procedure, with perrhenate as carrier, and an end-window tube for beta proportional counting. Samples, which were always run in duplicate, generally showed a spread of <10%. Yields in the radiochemical separation were determined via weighing of the perrhenate carrier; these yields were then used to correct the counting of ^{99}Tc.

All technetium used in this work was obtained by dilution of a source solution containing 40.2 mg of ^{99}Tc per milliliter. This solution was analyzed directly by beta scintillation counting.

3.2.1 General description of the technetium fluorination runs

Thirteen fluorination-sorption runs (F1 through F13) were made in this study; the conditions are given in Table 4. F1 was a preliminary run made to determine whether the fluorination procedure was suitable; no sorption of technetium was attempted in it. The same fluorination conditions were used in all the runs, with the following exceptions: (1) a temperature of 300°C was used instead of 500°C in run F3, (2) a leak allowed air to enter the system and dilute the fluorine in run F5, (3) nitrogen diluent was not used in run F12, and (4) pilot-plant UO_3 was fluorinated in run F13 instead of laboratory-prepared UO_3.

The auxiliary reactor was used in runs F6 through F12. The minimum fluorine concentrations to the auxiliary reactor of 15% in runs F6 through F11 and 55% in F12 are based on 100% utilization in the fluorination reactor, along with appropriate assumptions about the flow rates of the UF_6 and oxygen generated by the reaction. In runs F2 through 10, the MgF_2 was conditioned with fluorine at a relatively high temperature (400 to 550°C) before operation. A lower temperature (100 to 125°C) was used for conditioning in runs F11 through 13. The temperature of the MgF_2 sorption bed was maintained at 100°C in each run. In runs F7 through F10, the technetium was desorbed from the MgF_2 bed into a cold trap after each run and the same bed was used in the subsequent run without opening the sorption reactor for sampling. The lines and vessels were washed out after

Table 4. Run conditions used for the technetium fluorination-sorption studies

Fluorinator feed	28.8 g of UO_3 + 71.2 g of 60-mesh alumina containing 13.7 mg of technetium (except 10.6 mg of technetium was used in run F13).
Fluorinator flow rate	4 hr with 50 ml/min F_2 plus 100 ml/min N_2 (except no N_2 was used in run F12).
Side-stream flow rate to auxiliary reactor	25 ml/min F_2 (50 ml/min in run F12).
Minimum F_2 concentration to auxiliary reactor in runs F6 through F11	15%
Minimum F_2 concentration to auxiliary reactor in run F12	55%
MgF_2 sorption reactor temperature	100°C

runs F5, F6, F11, F12, and F13 in an attempt to obtain an accurate material balance for the technetium.

Table 5 summarizes the objectives, conditions, and data for the 13 runs.

3.2.2 Results of technetium fluorination runs

Sorption of technetium on MgF_2. Determination of the efficiency of the MgF_2 for collecting technetium in the experiments is complicated by the poor technetium material balances for the runs. The total recovery of technetium for each run averaged only about 75% of the amount added before the run. Scatter in the analytical data could partially account for the poor material balances. Table 5 shows the amount of technetium collected on each section of the MgF_2 bed and the total amount collected

Table 5. General summary of technetium fluorination tests

Run Number	Objective	Number of 7-g MgF_2 sections	Auxiliary reactor and excess F_2	MgF_2 conditioning temp (°C)	Residence time in MgF_2 sorber (sec)	Tc sorbed in each section of MgF_2 (% of Tc input)						Total Tc collected on MgF_2 (% of Tc input)	Tc in UF_6 product (% of Tc input)
						1	2	3	4	5	6		
F1	To test fluorination procedure	None	No										
F2	Fluorination at 500°C, sorption	1	No	550	3.6	13						13	49.8
F3	Fluorination at 300°C, sorption	1	No	550	3.6	52						52	9.7
F4	Sorption on larger MgF_2 bed	3	No	550	10.7	7.9	17.6	25.8				51.3	13.3
F5	Larger MgF_2 bed long run due to leak	6	No	500	a	22.5	22.4	7.3	0.16	0.03	0.05	52.4	0.13
F6	First use of auxiliary reactor	5	Yes	500	15	40.1	0.2	0.02	0.02	0.01		40.4	22.4
F7	First MgF_2 recycle run	4	Yes	400	12.	Desorbed at 350°C						8^b	40.1
F8	Second MgF_2 recycle run	4	Yes	400	12	Desorbed at 350°C						8^b	40.8
F9	Third MgF_2 recycle run	4	Yes	400	12.	Desorbed at 500°C						22^b	30.4
F10	Fourth MgF_2 recycle run	4	Yes	400	12	Desorbed at 500°C						24^b	40.1
F11	Low-temp conditioning of MgF_2, no desorption	4	Yes	100	12	80.5	4.4	0.4	1.4			86.7	4.6
F12	Low-temp conditioning of MgF_2, no use of N_2	4	Yes	125	21.6	19.4	28.8	13.0	1.5			62.7	0.16
F13	Pilot-plant UO_3	4	No	125	14	60.1	9.1	0.3	0.004			69.5	0.01

[a] Not determined because of air leak

[b] The value listed is the amount recovered by desorption of all four sections of the MgF_2 trap

in terms of a percentage of the technetium initially added. The amount collected on the MgF_2 ranged from 13 to 87% of the input; however, based on the amount of technetium found in the UF_6 product downstream of the MgF_2 bed, removal of >99% of the technetium from the UF_6 was achieved in two runs (F12 and F13).

In terms of the amount of technetium in the UF_6 product, the runs made with MgF_2 conditioned at 100°C and 125°C appear to have given considerably better results than those using MgF_2 conditioned at 400 to 550°C.

The use of excess fluorine and the auxiliary reactor does not appear to improve the collection of technetium on the MgF_2. The UF_6 products from runs in which the auxiliary reactor was used with MgF_2 conditioned at a high temperature (runs F6 through F10) were found to have very high (22 to 41%) technetium contents. There was a significant amount of technetium in the UF_6 product in two runs (F6 and F11), even though some sections of the MgF_2 bed contained little technetium. As shown in Table 6, the highest concentration of technetium found in the MgF_2 during any of the runs was about 0.16%, which is considerably lower than the loading (0.44 to 0.77%) achieved at Paducah; however, this low value may be caused by our failure to fully load even the first section of MgF_2 with technetium.

The data from runs F2 and F3 and the amount of technetium collected on individual sections of MgF_2 during the other runs indicate that one 7-g section (residence time, 3 sec) is inadequate for removing the technetium and that at least three or four sections are needed under the test conditions used here.

Table 6. Technetium and uranium loadings on the MgF_2 beds

Run	Bed section	Percent of bed weight		
		^{99}Tc	U	
F2	One 7-g section	0.015	1.86	
F3	One 7-g section	0.102	1.46	
F4	First 7-g section	0.015	2.06	1.42[b]
F4	Second 7-g section	0.034	0.96	
F4	Third 7-g section	0.051	1.24	
F5	First 7-g section	0.044	2.33	1.58[b]
F5	Second 7-g section	0.044	1.45	
F5	Third 7-g section	0.014	1.16	
F5	Fourth 7-g section	<0.001	1.08	
F5	Fifth 7-g section	<0.001	1.33	
F5	Sixth 7-g section	<0.001	2.10	
F6	First 7-g section	0.078	0.37	0.52[b]
F6	Second 7-g section	<0.001	0.49	
F6	Third 7-g section	<0.001	0.53	
F6	Fourth 7-g section	<0.001	0.57	
F6	Fifth 7-g section	<0.001	0.63	
F10	First 7-g section[a]	<0.001	<0.001	<0.001[b]
F10	Second 7-g section	<0.001	<0.001	
F10	Third 7-g section	<0.001	<0.001	
F10	Fourth 7-g section	<0.001	<0.001	
F11	First 7-g section	0.16	0.37	2.63[b]
F11	Second 7-g section	0.009	3.49	
F11	Third 7-g section	<0.001	3.45	
F11	Fourth 7-g section	0.003	3.21	
F12	First 7-g section	0.038	1.19	1.86[b]
F12	Second 7-g section	0.056	1.77	
F12	Third 7-g section	0.025	2.19	
F12	Fourth 7-g section	0.003	2.32	
F13	First 7-g section	0.091	10.8	4.58[b]
F13	Second 7-g section	0.014	2.72	
F13	Third 7-g section	<0.001	2.33	
F13	Fourth 7-g section	<0.001	2.46	

[a] After desorption at 500°C.

[b] Average.

Technetium and uranium material balances. In several runs, the lines and equipment were washed out in an attempt to improve the technetium material balance. The location of technetium for the runs in which the equipment was washed is shown in Table 7. The amount of technetium found by washing the fluorinator, auxiliary reactor, sorption reactor, and lines ranged from 3.9% in run F13, which used pilot-plant UO_3, to 29.8% in run F5, during which a leak developed in the system. The average technetium material balance for runs in which the equipment was washed out after the run was 81% of the input, as compared with 63% for runs made without the washing operation.

Except for run F3, where low-temperature fluorination (300°C) was used, the maximum amounts of technetium and uranium remaining in the fluorinator bed residue were 1.4% and 0.9%, respectively, of the initial input. Such results indicate that almost complete volatilization of technetium and uranium was achieved.

4. DESCRIPTION OF PILOT-PLANT FACILITY

The pilot-plant calcination and fluorination systems were located in the east cells in Bldg. 3503 at Oak Ridge National Laboratory. These cells were used to provide confinement for the slightly radioactive materials used (depleted uranium and ^{99}Tc tracer) and for fluorine in the event leakage occurred. Shielding was not required for the low level of radioactivity associated with the experiments.

Table 7. Location of technetium in runs where equipment and lines were washed

	Amount of technetium (% of input) in run:				
	F5	F6	F11	F12	F13
MgF_2 trap					
First section	22.5	40.1	80.5	19.4	60.1
Second section	22.4	0.2	4.4	28.4	9.1
Third section	7.3	0.02	0.4	13.0	0.3
Fourth section	0.16	0.02	1.4	1.5	0.004
Fifth section	0.03	0.01	Not used	Not used	Not used
Sixth section	0.05	Not used	Not used	Not used	Not used
MgF_2 trap, subtotal	52.4	40.4	86.7	62.3	69.5
UF_6 product	0.1	22.4	4.6	0.2	0.01
Alumina residue in fluorinator	1.4	0.1	0.9	0.2	0.6
Fluorination vessel	3.8	3.4	9.0[a]	7.9	3.0
Lines and auxiliary reactor	22.2	0.8		3.1	0.1[b]
Sorption reactor	3.8	13.4		2.4	0.8
Total Tc material balance	83.7	80.5	101.2	76.1	74.0

[a] Estimated as one-fifth of the amount found after five runs (runs 7, 8, 9, 10, 11).

[b] Auxiliary reactor was not used.

4.1 General Layout of Equipment

The major pieces of denitration equipment including the calciner, UNH feed system, off-gas treatment system, and product vessel were installed in a cell 6 ft wide x 14 ft long x 30 ft high. The instrumentation and control panelboard for the denitration system was located on the second level just outside the cell.

The main fluorination equipment was installed in two adjacent cells, each of which was 6 ft x 6 ft x 30 ft high. The panelboard for the fluorination system was mounted just outside the cells on the second level. The fluorine metering station was located outside of the building on the east side.

Access to the denitration cell and the cell containing the fluorinator was made through air locks. Laboratory coats, shoe covers, rubber gloves, and gas masks (where needed) were worn inside the cell and were removed before leaving the air lock. Alpha survey meters were stationed at the entrance to each cell to be used to check for contamination.

4.2 Cell Ventilation System

Cell ventilation was provided by a 20-hp fan with a capacity of about 8000 cfm. The normal air flow through each cell was maintained at about 2000 cfm in order to provide a minimum velocity of 150 fpm through the doors and openings into the cells. Air entering the cell passed through fiberglass roughing filters. Air leaving the cell passed through a fire barrier, prefilters, and HEPA filters before being exhausted to the atmosphere above the roof of the building.

4.3 Building Services

The building services used in the pilot-plant facility are described below. Steam at 125 psig and 15 psig was used for heating the UNH tank and lines, to preheat the denitration system off-gas, and to provide hot water for the fluorination system. Plant air at 90 psig was used as the fluidizing gas, purge gas, and filter blowback for both the denitration and fluorination systems. Demineralized water was used for UNH makeup, flushing the feed nozzle, cooling the fluorinator, and equipment cleanup. The off-gas lines from both the fluorination and denitration systems were attached to the plant off-gas system which operated at a negative pressure of ∿3 in. Hg. Contaminated liquid waste or condensate from the denitration system and cleaning solutions were discharged to the ORNL radioactive waste system through drains located in the cells. Solid radioactive waste was packaged and sent to the burial ground for disposal.

5. URANIUM CALCINATION PILOT PLANT

5.1 Description of Process

Dilute uranyl nitrate solution can be concentrated to uranyl nitrate hexahydrate (bp ∿120°C) without decomposition. Upon cooling, this material crystallizes to a solid (sp gr = 2.8) at 60°C.

Uranyl nitrate hexahydrate can be thermally denitrated to UO_3 according to the following endothermic reaction:

$$UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow{\text{heat}} UO_3 + NO + NO_2 + O_2 + 6H_2O \ .$$

Decomposition of UNH begins at ∿180°C, but the reaction is not driven to completion until the temperature is raised to about 300°C.[2] Uranium trioxide is a chemically stable, mildly hygroscopic solid with a crystal density of 7.3 g/cc and a bulk density of 3.8 to 4.3 g/cc.

Investigators at various facilities have conducted extensive fluidized-bed UNH denitration programs at pilot plant as well as plant scale. Of particular interest is the work done by Mallinckrodt,[3,4] in which a fluidized-bed denitration system was operated successfully with uranyl nitrate feed concentrations as high as 1400 g of uranium per liter and at production rates greater than 350 $lb/hr\text{-}ft^2$ (based on the cross-sectional area of the vessel). The development work at Mallinckrodt included over 160 experimental runs, some as long as 100 hr. From this work, a plant-size fluidized-bed denitrator was designed to produce 3890 lb of UO_3 per hour. The unit was successfully operated on an experimental basis for two years (3200 hr of operation), during which over 9 million pounds of UO_3 was produced. However, the process was abandoned because the product was insufficiently reactive for the hydrofluorination conversion process.

5.1.1 Description of pilot-plant process

Uranyl nitrate hexahydrate was prepared in two feed tanks. When concentrated UNH was used, the feed tanks were heated to maintain the UNH above its freezing point.

The UNH was pumped into the calciner through an atomizing feed nozzle. Preheated air was passed through a distributor plate near the bottom of the vessel to fluidize the bed of UO_3 particles. Uranyl nitrate solution was converted to solid UO_3 and gases by thermal decomposition in the fluidized bed. Trace quantities of technetium and ruthenium compounds were also converted to solid oxides in the denitration process. The formation and volatilization of RuO_4 provide some decontamination of UO_3 product.

The bed inventory was held constant by allowing product to continuously overflow by gravity to a product vessel.

Off-gas from the calcination process was passed through sintered-metal filters located in the upper section of the vessel. These filters were cleaned sequentially with a pulse of air to loosen UO_3 dust and allow it to fall back into the bed. The process off-gas was then cooled in a condenser where most of the NO_2 released in the denitration process was recovered as a nitric acid and collected in the condensate tank. Uncondensed vapors were passed successively through a de-entrainer, a preheater, and a HEPA filter, and then vented to the plant hot off-gas system. A block flow diagram of the system is shown in Fig. 2.

5.2 Description of Equipment

ENC provided the calcination vessel, off-gas filters, spray nozzle, and heaters for the uranium calcination system. ORNL provided the UNH feed system, vessel off-gas system, and other auxiliary equipment.

5.2.1 Calcination vessel

The calcination vessel was designed to test geometric parameters important to the design of the NFRRC plant-scale unit. Careful consideration was given to the size and capacity of the calciner in order to reduce uncertainties involved in scale-up.

ORNL DWG 77-749

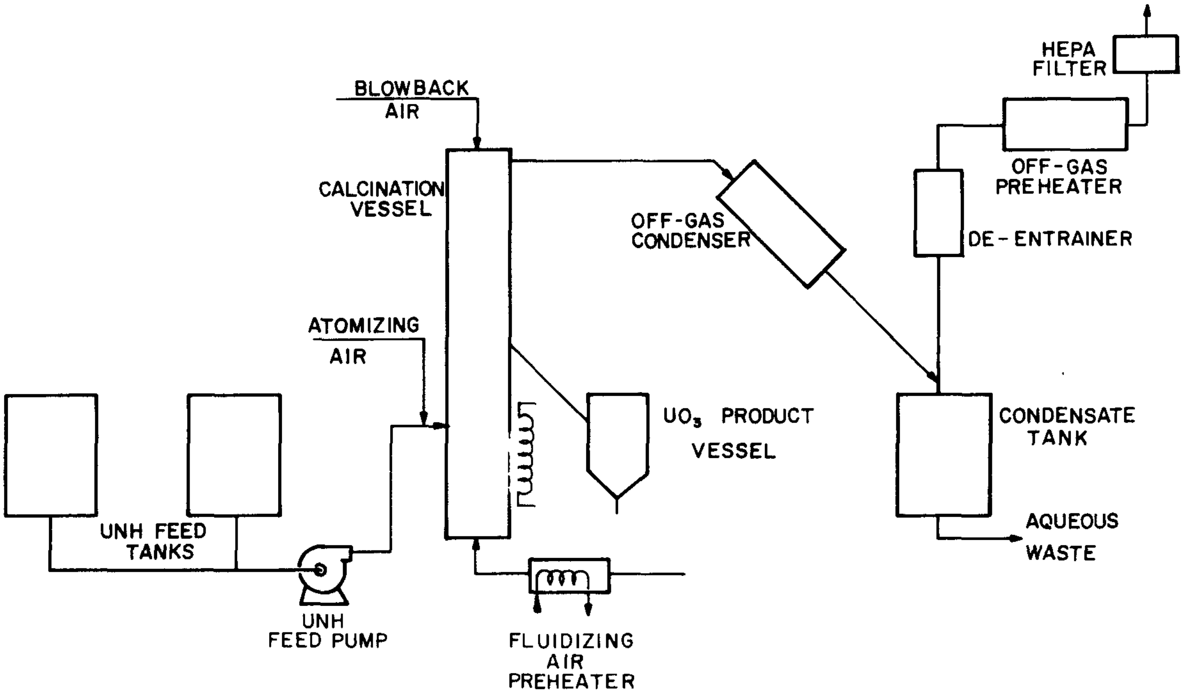

Fig. 2. Block flow diagram of the uranium calcination pilot plant.

The UNH calciner was constructed of 304 L stainless steel and consisted of four sections: the plenum, the fluidized bed, the expanded filter section, and the filter housing. The plenum contained the fluidizing air inlet, a bed drainage outlet, and a fluidizing air distributor plate. The fluidized-bed section contained the feed nozzle, product take-off line, bed charging line, internal and external thermocouples, and pressure taps. The expanded filter section contained sintered-metal filters. The filter housing supported the filters and contained the off-gas vent line. The vessel was externally heated.

5.2.2 Filter and blowback system

Sintered-metal filters in the calciner filter section were used to remove UO_3 dust from the process off-gas. These filters were sequentially blown back with a short pulse of air to return any UO_3 dust collected on the outer surfaces back to the bed. The air pulse was directed into the top of each filter by solenoid-actuated nozzles. Venturi nozzles were used to increase the cleaning action.

5.2.3 UNH feed system

The UNH feed system included two tanks (23-1/2 in. ID x 37 in. high) with a volume of 60 gal each. The vessels were jacketed for 15-psig steam and contained steam coils for 125-psig steam. The tanks were constructed of 300 series stainless steel.

A tri-piston positive displacement metering pump* was used to feed the UNH. The liquid end assemblies were constructed of 300 series stainless steel with Teflon packing.

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*Obtained from the Milton Roy Co., Philadelphia, Pa.

5.2.4 Off-gas system

A shell-and-tube (water-cooled) heat exchanger with a heat transfer area of 23.5 ft^2 was used to condense process off-gas vapors. A 260-liter-capacity stainless steel tank was used to collect condensate from the off-gas condenser. Uncondensed vapors were passed through a stainless steel wire-mesh de-entrainer, a shell-and-tube (steam-heated) preheater, and a HEPA filter.

5.2.5 Process instrumentation

The principal process instrumentation included:

1. thermocouples (with temperature recorders) to monitor the temperature at various locations in the UNH feed system, calcination and product vessels, and an off-gas treatment system;
2. a flow controller (with recorder) to measure the rate at which the fluidizing air flowed to the calciner, and indicating rotameters to measure the flow rate to the air atomizing nozzle and to pressure probes;
3. set-point temperature controllers to control the fluid-bed temperature; and
4. differential-pressure transmitters (with recorders) to monitor the UNH feed tank levels and the pressure drop across the distributor plate, the fluidized bed, and the sintered-metal filters.

5.3 Operating Procedures

Concentrated UNH feed was made up to the desired concentration by boiling dilute UNH in the feed tanks. UNH was also prepared by dissolving product UO_3 with concentrated nitric acid. The vapors (mostly water) were condensed and collected in the condensate tank. UNH has a freezing point of ~65°C and a boiling point of 120°C; therefore, the UNH temperature in the feed system must be maintained within these limits. Before each run, UO_3 was charged to the calcination vessel for "seed" material if the bed from the previous run had been removed.

The calciner instruments, purgers, filter blowback, fluidizing air, and atomizing air were placed in operation before the start of each run. Then the calciner heaters were turned on. The calciner vessel walls, product overflow line, and UO_3 product vessel walls were allowed to reach at least 100°C, and the temperature of the fluidized bed was increased to the operating temperature. Water was then pumped to the feed nozzle at about 70% of the proposed UNH feed rate. After the system had been allowed to reach thermal equilibrium, the feed was switched to UNH. Granular UO_3 product overflowed to a product vessel where the weight was monitored with a load cell.

Fluidized-bed samples of UO_3 were taken periodically during each run. Upon completion of the experimental run, the UNH feed lines, pump, and feed nozzle were flushed with water to avoid plugging of lines. The heaters were turned off, and the flow of fluidizing air was reduced. Usually the bed was removed and internal surfaces were inspected for caking and deposits around the nozzle.

5.4 Description of Calcination Runs

Fifteen calcination runs were made to test the equipment performance and to provide UO_3 for fluorination. A wide range of operating conditions was investigated: run durations from a few hours to a maximum of 16 hr, UNH feed concentrations from 500 to 1200 g of uranium per liter, feed rates from 150 to 415 ml/min, superficial fluidizing velocities below the feed nozzle of 1.0 to 1.3 fps, and bed temperatures of 250 to 350°C. The behavior of technetium and ruthenium was studied during one of the runs, and the removal of residual nitrate and water was tested by heat-treating UO_3. Typical experimental operating conditions are given in Table 8.

Table 8. Typical operating conditions for calcination pilot plant

Nominal bed temperature	300°C
UNH feed	
Feed rate	150 ml/min
Uranium concentration	900 g U/liter
NO_3/U ratio	2.0
Sp gr at 85°C	2.14
Superficial fluidizing velocity	1.0 fps
Off-gas filter blowback	
Pressure	50 psig
Pulse duration	0.5 sec
Cycle	5 min/filter
Blowback volume/filter volume	1.3
Atomizing air/UNH feed ratio	150

5.5 Discussion of Results

The experimental work can be broken down into two phases. During the first (or "shakedown") phase, numerous problems were identified over a period which amounted to about half of the experimental effort. The data on product properties obtained during this phase were not highly significant because the system had not achieved steady-state operation. In the second phase, the operational problems had essentially been resolved. These problems, which were initially related to caking of UO_3 on the overflow line and instrument purges due to condensation of water vapor on cold surfaces, were resolved by heating the surfaces where plugging occurred.

Dilute UNH and low feed rates were used during the first few runs; subsequently, the UNH feed lines were heat-traced so that concentrated UNH feed could be used. Shortly thereafter it became apparent that the off-gas filters were not functioning properly. A progressive increase in pressure drop across the filters was observed during most of the early runs, especially at higher production rates. Excessive pressure drop was apparently due to an accumulation of fines on filter surfaces.

A review of the filter section design revealed that, at high production rates, the capacity of the filters was questionable. It was also evident that UO_3 caking on the filter section walls had occurred even though the filter section was allowed to reach 100°C before the UNH feed was started. Therefore, the filter section was enlarged, the blowback system was modified, and Calrod heaters were added to heat the filter housing walls. Following these modifications, the filter system functioned properly (i.e., fines were released from the filters and returned to the bed by a pulse of air, and a low pressure drop across the filters was maintained). During the shakedown period, process instabilities were experienced, fines were not being returned to the fluidized bed on a regular basis, and a high rate of particle growth was observed in the fluidized bed. (In order for the particle size distribution in the bed to reach steady state, fines must be returned periodically to act as a nucleus for "new" particles.) A decrease in the wall-to-bed heat transfer with increasing average particle diameter was also noted. This was also observed in the Mallinckrodt work (Fig. 3), where the heat transfer coefficient decreased significantly with an average particle diameter greater than 0.009 in.

A total of 74 hr of satisfactory operation was demonstrated during the second phase of the experimental work. Throughout this period, the average particle size remained well within the range that provides good heat transfer characteristics.

5.5.1 Behavior of technetium and ruthenium

Several tests were conducted to study the behavior of trace quantities of impurities that will be present in the uranium calcination process. The UO_3 product from these tests was also used in fluorination studies.

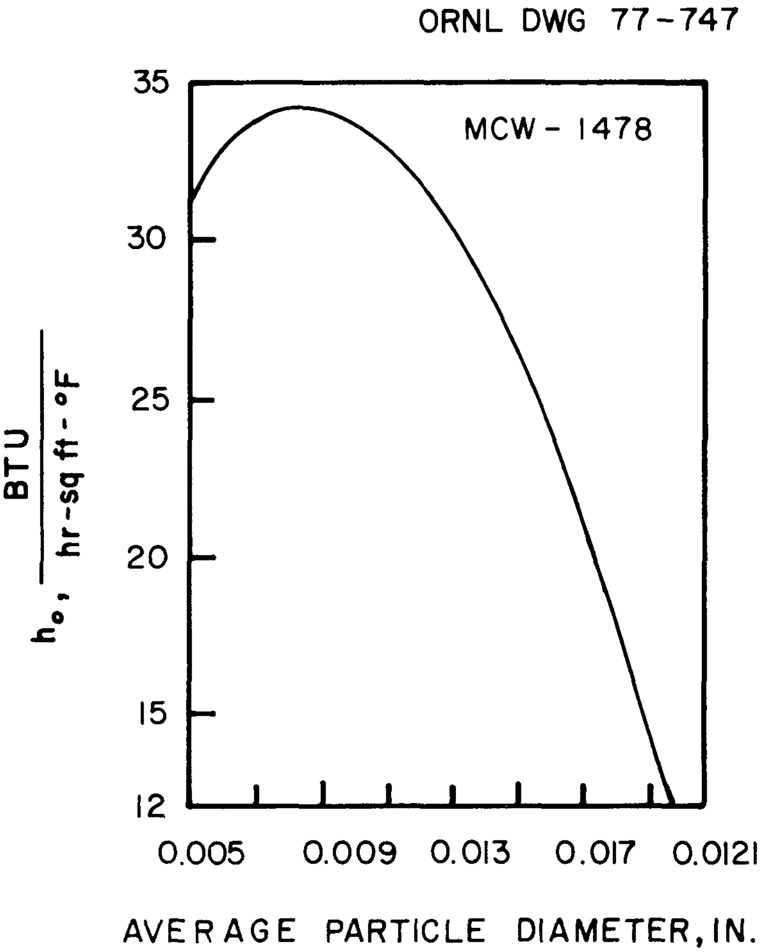

Fig. 3. Effect of average particle diameter on the heat transfer coefficient, h_o.

The UNH feed was spiked with ^{99}Tc (as ammonium pertechnetate) and nonradioactive ruthenium (as ruthenium nitrate), and then denitrated under normal run conditions. As expected, most of the technetium was found in the UO_3 product as technetium oxide. Over half of the ruthenium (RuO_4) was volatilized and found in the condensate from the off-gas.

5.5.2 Removal of residual nitrate and H_2O

Typical UO_3 produced in the fluidized bed contains about 0.5 wt % nitrate and 0.2% water. The levels of these impurities can be significantly reduced by additional heating of the UO_3. Several batches of UO_3 were treated at 500°C or 600°C in the fluidized-bed calciner to determine optimum conditions for removing these impurities. Results indicated that the residual nitrate and water contents of UO_3 produced in the fluidized bed could be reduced to acceptable levels.

6. URANIUM FLUORINATION PILOT PLANT

Five batch and ten continuous fluorination runs were made to study the direct fluorination of UO_3 with elemental fluoride in a fluidized bed. The effects of temperature, UO_3 concentration, fluorine concentration in the fluidizing gas, and variables related to fluid-bed dynamics were investigated to determine a suitable range of operation. A wide range of operating conditions was tested to identify any instabilities associated with the process or deficiencies in equipment design. Fluorination tests were made with UO_3 from two sources — UO_3 produced in the fluidized-bed calcination pilot plant and UO_3 supplied by ENC.

Several runs were made to study the fluorination of technetium and its subsequent sorption on MgF_2.

6.1 Description of Process

The process developed and used at most ERDA facilities for converting UO_3 to UF_6 involves three steps: (1) reduction of UO_3 to UO_2 with hydrogen, (2) conversion of UO_2 to UF_4 with HF, and (3) fluorination of UF_4 with elemental fluorine.

Development work has been done on the direct fluorination of uranium oxide (UO_2 and U_3O_8) to UF_6 with fluorine at the Argonne National Laboratory[5,6] and the Oak Ridge Gaseous Diffusion Plant.[7] Experimental studies on the direct fluorination of U_3O_8 in a fluidized bed have also been reported by Russian investigators.[8] Laboratory studies on the kinetics of the fluorination of UO_2, U_3O_8, and UO_3 were reported by Iwasaki.[9] Direct fluorination of UO_3 in a fluidized bed was proposed by the General Electric Company for use in their reprocessing plant at Morris, Illinois; however, very little of this technology is available. Goodyear Atomic Corporation uses a flame tower to fluorinate U_3O_8 in their uranium conversion facility.[10]

6.1.1 Description of pilot-plant process

The granular UO_3 product from the UNH calciner was metered into a bed of alumina (Al_2O_3) contained in the fluidized-bed fluorinator. Fluorine in the fluidizing gas converts UO_3 solids to UF_6 gas. The trace quantities of fission products in UO_3 and corrosion products also react to form solid and/or volatile fluorides. Although the alumina is relatively inert, some nonvolatile AlF_3 is formed in this bed material. The fluorination of UO_3

is highly exothermic; therefore, some means of cooling must be provided to control the bed temperature.

Off-gas from the fluidized bed was routed through sintered-metal filters to remove virtually all solids; it was then cooled to about 100°C and passed through three static beds of NaF to collect UF_6 by chemical sorption. The remaining off-gas (primarily air, oxygen, and fluorine) was sent through static beds of activated alumina and soda lime for removal of unreacted fluorine.

Activated alumina reacts with fluorine to produce AlF_3. The disposal capacity is about 1.4 moles of fluorine per mole of activated alumina.[11] Soda lime reacts with fluorine to form CaF_2 and NaF-HF with a capacity of about 1.0 mole of fluorine per mole of reagent.[11]

During runs when the behavior of technetium was being tested, the product gases were passed through a static bed of MgF_2 pellets to collect TcF_6 prior to UF_6 collection on NaF.

A block flow diagram of the fluorination system is shown in Fig. 4.

6.2 Description of Equipment

The fluorination vessel, off-gas filters, and UO_3 feeder were provided by ENC. ORNL provided the fluorine metering system, UF_6 collection system, off-gas treatment system, and process instrumentation.

6.2.1 Fluorinator

The basic requirements of the fluidized-bed fluorinator are: (1) to provide a high rate of heat and mass transfer between the solid and fluid, ORNL DWG 77-748

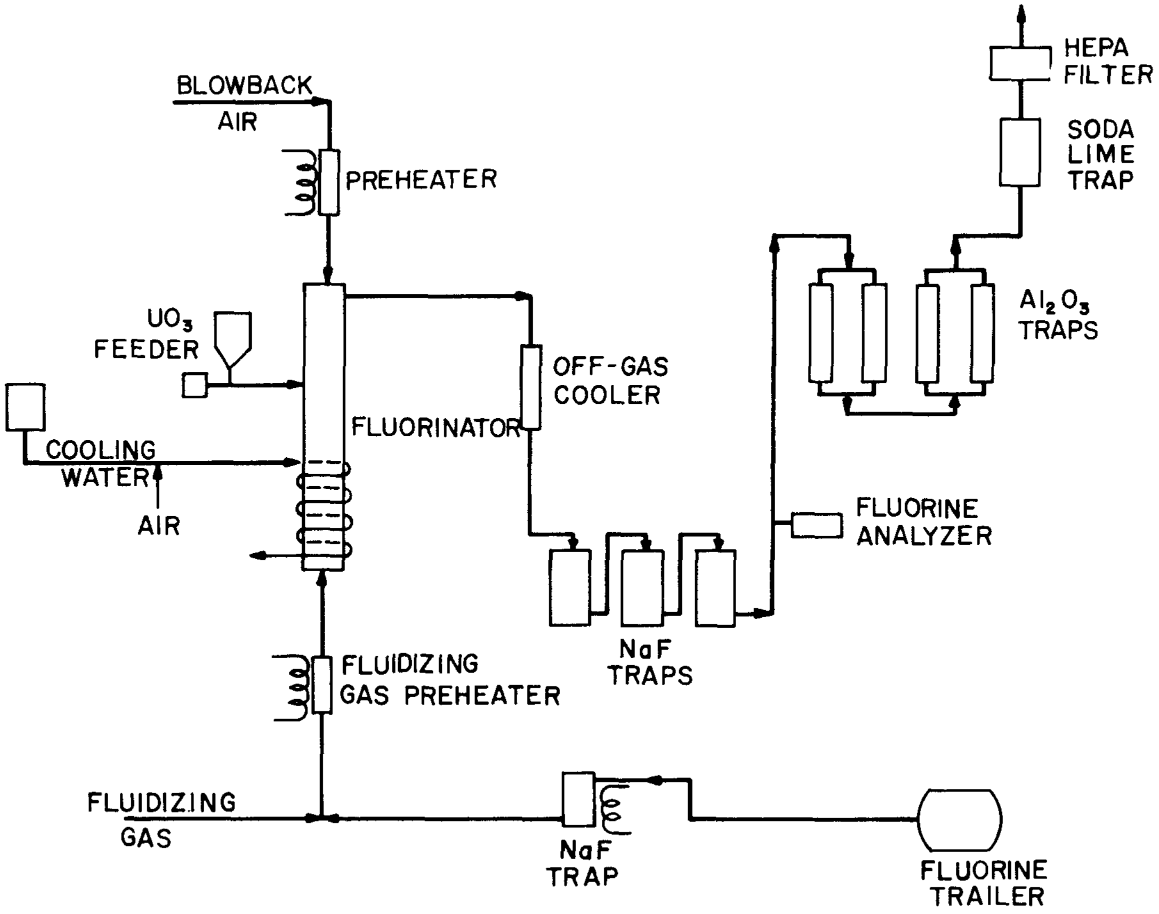

Fig. 4. Block flow diagram of the fluorination pilot plant.

(2) to provide complete mixing of the feed and bed solids, and (3) to ensure criticality control through appropriate geometric design. The vessel design incorporated features that added flexibility to the mode of operation.

The fluorination vessel consisted of two sections: the fluidized-bed section and an expanded filter section. The fluidized-bed section contained the fluidizing gas inlet, a bed drainage outlet, a bed charging and feed inlet, a bed solids sampler, and the distribution plate. Uranium trioxide was metered to the fluorinator with a solids screw feeder. Cooling coils were attached to the outer vessel wall. The expanded filter section contained sintered metal filters and an off-gas line.

The vessel was heated with electrical heaters.

6.2.2 NaF traps

Three 10-in.-OD by 48-in.-long NaF traps were used to remove UF_6 from the fluorinator off-gas. The vessels and support plates were constructed of Monel and Inconel. The vessels were designed for operation at a pressure of 15 psig and a temperature of 200°C. A 10-in.-diam blind flange was used to charge and remove solid absorbent. Each trap contained about 50 kg of NaF pellets. Calrod heaters on the outer vessel surface were used to heat the traps.

6.2.3 Fluorine metering system

Gaseous fluorine was obtained in 650-std ft^3 steel tank trailers at about 55 psig. The composition of the gas, as received, was typically 90 to 95% fluorine, 5% HF, and 1 to 2% nitrogen-oxygen. The HF was removed by passing the gas through a trap containing about 10 kg of 1/8-in.

NaF pellets. Flow control and pressure control valves were used to meter the fluorine. Monel was used as the material of construction in most cases.

6.2.4 Filter and blowback system

The design of the filter and blowback system was basically the same as that used in the calcination system, except that material in contact with fluorine was constructed of Monel.

6.2.5 Fluorine disposal system

Activated alumina traps. Unreacted fluorine was passed through four static-bed disposal traps (two in series) containing activated alumina. The traps (4 in. ID x 60 in. long) and support plates were constructed of Monel and were designed for operation at a pressure of 15 psig and a temperature of 500°C. A 4-in.-diam blind flange at the top of each trap was used to charge and remove solid disposal agents. Each trap contained about 10 kg of Al_2O_3.

Soda lime trap. The activated alumina traps were backed up by a 6-in.-ID by 48-in.-long static-bed soda lime trap constructed of 304 stainless steel. Access to the trap was through a 6-in.-diam blind flange on top of the trap.

6.2.6 Process instrumentation

The fluorination system contained the following process instrumentation:

1. Thermocouples with temperature recorders to monitor the temperature at various locations in the fluorine metering system, fluorination vessel, and off-gas treatment system.

2. Flow controllers with recorders and indicating rotameters to measure fluidizing gas flow to the fluorinator, and indicating rotameters to measure gas flow to purges on pressure probes.
3. Differential-pressure transmitters with recorders were placed across the distributor plate, fluidized bed, and the sintered-metal filters.
4. A Du Pont 400 photometric analyzer to continuously monitor fluorine in the off-gas.

6.3 Operating Procedure

The fluorination system was conditioned with fluorine before each run. If necessary, Al_2O_3 and UO_3 were charged to the fluorinator to make up the desired bed composition. Before each run, the fluorinator instruments, purges, filter blowback, and fluidizing air were placed in operation. Electrical heaters were turned on to bring the fluidizing gas preheater, fluorinator, and NaF traps to the desired temperature. A tempered-water heat exchanger was used to control the off-gas temperature at about 100°C. When the vessels had reached the desired temperature, fluorine from the supply trailer was passed through a NaF trap (for HF removal) and metered through flow control valves. The fluidizing gas and fluorine mixture was preheated and introduced to the fluorinator below the distributor plate.

The UO_3 feeder was started at a rate equivalent to the UO_3 reaction rate. Unreacted fluorine in the off-gas was monitored continuously downstream of the NaF traps. When necessary, the fluorinator was cooled by injecting water into external cooling coils purged with air. The inventory of the fluidized bed was monitored by the pressure differential across the bed.

6.4 Fluorination Runs and Results

6.4.1 Results of batch runs

The first five runs were short, batch-type experiments used to shake down and test the system. In these runs, UO_3 and inert Al_2O_3 were charged to the bed. After the fluorinator had been heated to the desired temperature, fluorine was admitted to the fluorinator as part of the fluidizing gas. Initially, low concentrations of reactants (UO_3-F_2) were used until the behavior of the reaction and the fluidized-bed temperature control were established.

The following conclusions were drawn from the batch runs:

1. The reaction of UO_3 with F_2 was initiated readily at bed temperatures greater than 400°C.
2. Utilization of fluorine decreased with decreasing UO_3 concentration in the bed.
3. The reaction rate is highly dependent on temperature.
4. Post-run examination revealed no evidence of sintering of the bed diluent (Al_2O_3).
5. Substantial cooling was required to control the bed temperature at normal fluorination rates.

6.4.2 Results of continuous runs

A screw feeder was used to meter UO_3 to the fluorinator. Since the feed rate was usually equal to the fluorination rate, a constant UO_3

inventory was maintained in the bed. The UO_3 feeder was accurate and reliable.

Steady-state conditions were achieved rapidly; thus various temperatures and fluorine concentrations could be tested in each run. Several runs were made to determine the effects of bed depth and fluidizing velocity.

A fluorination run using UO_3 supplied by ENC was made to study various aspects of the fluorination procedure and to gain experience in handling the material. The material was fluorinated without difficulty. The most significant difference in the fluorination of this material vs the fluidized-bed product was that it appeared to be slightly more reactive.

Sintering of Al_2O_3. Russian investigators studied various factors that would be expected to affect the stability of direct fluorination of U_3O_8 in an inert, fluidized bed of Al_2O_3. They found that sintering occurred with a high concentration of reagents. The boundary of stable operation was determined experimentally as a function of fluorine concentration, U_3O_8 concentration, and specific surface area. Sintering was reportedly due to a high heat load near Al_2O_3 particles, which caused overheating and subsequent fluorination of Al_2O_3 to AlF_3. The AlF_3 then acted as a cementing agent to form agglomerates.

A series of tests was made in the fluorination pilot plant to define the boundaries of stable operation by progressively increasing the production rate. The results of these tests established a region of operating conditions in which the fluidized bed was thermally stable and sintering of Al_2O_3 did not occur.

6.4.3 Runs with technetium-spiked UO_3

Two continuous uranium fluorination runs were made to determine the behavior of technetium in the pilot-plant fluorination system. Fluidized-bed-produced UO_3 containing 300 µg of technetium per gram of UO_3 was fluorinated and then separated from UF_6 by passing the volatile fluorination products through a static bed of MgF_2.

During the first run, about 95% of the technetium contained in UO_3 was leached from the first 14 in. of the MgF_2 trap with dilute nitric acid. A negligible amount was detected on the remaining 18 in. of the trap. Only a trace was accounted for downstream of the MgF_2 trap or between the fluorinator and the MgF_2 trap. The second run was made under similar conditions to verify results of the first run and to obtain an overall technetium material balance for both runs.

During the second run, about 75% of the technetium that was contained in UO_3 was recovered from the MgF_2. The technetium concentration was at the top of the bed where first contact was made with the fluorinator off-gas. The overall technetium material balance for these tests was 84%.

Proper conditioning of MgF_2 for removal of impurities (mostly water) proved to be important in reducing the uranium loading of the MgF_2.

7. REFERENCES

1. W. R. Golliher et al., Separation of Technetium-99 from Uranium Hexafluoride, TID-18290 (1960).

2. W. L. Marshall et al., "The Uranyl Nitrate-Water System Above 60°C," J. Am. Chem. Soc. 73, 1867 (1951).

3. S. Simecek and W. T. Trask, The Integrated Fluid-Bed System, MCW-1478, Malinckrodt Chemical Works, Weldon Spring, Mo. (1963).

4. S. N. Robinson and J. E. Todd, Plant Scale Fluid-Bed Denitrator, MCW-1509, Malinckrodt Chemical Works, Weldon Spring, Mo. (1966).

5. R. L. Jarry et al., The Fluid-Bed Fluorination of U_3O_8, ANL-6763, Argonne National Laboratory (October 1963).

6. L. J. Anastasia et al., The Fluorination of UO_2-PuO_2 in a 2-in. Diameter Fluid-Bed Reactor, ANL-7372, Argonne National Laboratory (December 1967).

7. D. C. Brater et al., "Preparation of Uranium Hexafluoride," Prog. Nucl. Energy, Ser. 3, 2 (1958).

8. O. G. Lebedev et al., Investigation of the Stability of the Fluorination Process of Uranous-Uranic Oxide in a Fluidized Bed, IAE-2328, Moscow (1973); translated May 1975, ORNL-tr-2938.

9. M. Iwasaki, "Kinetic Studies of the Fluorination of Uranium Oxides by Fluorine," J. Inorg. Nucl. Chem. 26, 1853-1861 (1964).

10. J. G. Crawford, Fluorination of Enriched Uranium Oxides, GAT-P-43, Goodyear Atomic Corporation, Piketon, Ohio (June 24, 1968).

11. J. D. Navratil, Disposal of Fluorine, RFP-1200, Rocky Flats Div., Golden, Colorado (Aug. 29, 1968).

8. APPENDIX A: LITERATURE SURVEY ON THE REMOVAL OF TECHNETIUM, NEPTUNIUM, AND PLUTONIUM FROM URANIUM HEXAFLUORIDE

8.1 Introduction

The material presented in this literature survey pertains particularly to the behavior of technetium and neptunium as volatile fluorides in the fluoride volatility method for reprocessing nuclear fuels. It includes, however, for comparison, some references to other volatile fluorides such as those of uranium and plutonium and to volatile fission product fluorides. This survey was conducted for ENC with the emphasis directed toward their proposed fuel reprocessing flowsheet, which includes conversion of uranium to the hexafluoride. The uranium hexafluoride must conform to certain specifications as recycle feed to the gaseous-diffusion uranium enrichment facilities, and meeting the specifications for technetium and neptunium (and also plutonium) represents one of the main criteria in a final choice of processing procedures. It is hoped that this literature survey will help in making the proper choice of the process flowsheet.

Most of the literature surveyed was found in Nuclear Science Abstracts (NSA) or as references in papers abstracted in NSA. The material generally falls into one of the following categories: (1) progress reports, (2) patents, (3) reviews presented at meetings or in journal articles, and (4) topical reports and topical journal articles. Considerable duplication or repetition of data material or of ideas being developed is found in the first three categories. This is particularly true of progress reports covering process development work conducted at various nuclear energy laboratories. There is justification in believing that more definite information is obtainable from review articles, patents, and topical reports or journal articles.

The referenced material is listed roughly in chronological order. The numbers (see Sect. 8.4) assigned to the references are used when discussing the material.

8.2 Discussion

8.2.1 General chemistry of technetium, neptunium, and plutonium

The hexafluorides of technetium, neptunium, and plutonium are generally considered to be the important volatile compounds encountered in fluoride volatility processing. Technetium hexafluoride has a much higher volatility than TcO_3F (ref. 36). $TcOF_4$ is also a known compound (ref. 1a), although it may not have a high volatility. However, as stated in ref. 3, the volatile compound of technetium encountered in fluoride processing has not been identified. Formation of TcO_3F and TcF_6 appears to be possible at moderate fluorination temperatures (near 150°C), whereas at higher temperatures the electronegativity of F_2 would probably favor only the formation of TcF_6.

Neptunium hexafluoride is the volatile compound of neptunium found in fluoride volatility processing; PuF_6 and UF_6 form, together with NpF_6, a homologous series of compounds with closely related physical properties but with markedly different stabilities (refs. 1a, 1b, 34). The volatility of the oxyfluorides of these actinide elements does not need to be considered (refs. 23, 30). The behavior of solid fluoride complexes of the three hexafluorides is discussed in ref. 18.

8.2.2 Stability of NpF_6 and PuF_6 in UF_6 mixtures, and solubility of PuF_4 reduction products

Neptunium hexafluoride and PuF_6 exhibit widely different stabilities in liquid UF_6 mixtures. Plutonium hexafluoride is easily reduced to PuF_4 by the metal container wall, as described in ref. 13. The solubility of PuF_4 in UF_6 is reported to be $\leq$ 5 ppb. Plutonium hexafluoride per se, in the solid form, has quasi-stability at room temperature due to slow autoreduction kinetics.

8.2.3 Chemical reduction of the hexafluorides of uranium, neptunium, and plutonium

The hexafluorides of uranium, neptunium, and plutonium are not stable to chemical reductants. For example, UF_6 can be chemically reduced by SO_2, CO, or hydrogen at temperatures above ambient. The reduction of NpF_6 with bromine (refs. 9, 11, 14, 18) has been investigated to a considerable extent. Plutonium hexafluoride is reducible with BrF_3 (ref. 10) or with CO_2 (ref. 24). Mention has already been made of the metal wall reduction effect (ref. 13).

8.2.4 Reduction of NpF_6 and PuF_6 in gaseous UF_6 with solid CoF_2 sorbent bed

A commercially attractive method for removing neptunium and plutonium from UF_6 involves passage of the gases through a CoF_2 bed (refs. 31, 35, 37, 38). This treatment reduces the volatile NpF_6 or PuF_6 impurity to a nonvolatile form. It is necessary, however (ref. 38), to use a 10-μ metal filter with the CoF_2 bed to prevent transfer of particulate neptunium and plutonium material out of the bed with the UF_6.

In ref. 38, the optimum temperature of operation is stated to be 300 to 440°F. In the case of plutonium, at least, this is a sufficiently high temperature to cause autoreduction of PuF_6 (ref. 1c). The PuF_4

thus produced would be entrained in the UF_6 gas. Presumably, this PuF_4 would be at least partially removed by the CoF_2 bed.

8.2.5 Use of fluoride sorption beds for trapping volatile fluorides - trapping of technetium with MgF_2

The use of various fluorides as media for sorbing fission product fluorides and actinide hexafluorides has been investigated extensively. One of the most commercially attractive processes uses MgF_2 pellets to remove technetium (probably TcF_6, possibly TcO_3F) and neptunium as NpF_6 from gaseous UF_6 (refs. 1, 3, 6, 8, 14, 37). Some work (ref. 14) that has been reported gives a negative view of this process, but this should be discounted in view of the reported use of MgF_2 on a large scale in the governmental UF_6 diffusion-enrichment facility (ref. 1). There is, however, uncertainty about the chemistry involved in the sorption of volatile technetium species on MgF_2, and about the effects of the proposed operating conditions on technetium removal.

Two other relevant references for work with the MgF_2 process are those specifying the preparation of the MgF_2 pellets (ref. 16) and the procedure used to dry the pellets so as to minimize UF_6 pickup (ref. 2).

8.2.6 Trapping NpF_6 with MgF_2

The basic patent (Golliher) covering the trapping of technetium on MgF_2 also makes the claim of NpF_6 sorption on MgF_2 (ref. 3) (see also refs. 14, 18, 26, 28, and 29). The chemistry involved in this process is not understood. A large amount of work has been reported on the interaction of NpF_5 complex with the release of fluorine (refs. 10, 12, 15, 17, 19, 20, 21, 26, 27, 28, and 33). This reduction is possibly related to the thermodynamic instability of NpF_6 (less stable than UF_6, much more stable than PuF_6), and to the possibility of a sodium fluoride--actinide fluoride complex (ref. 5). The same type of autoreduction possibly occurs with NpF_6 sorption on MgF_2, but this has not been studied.

8.2.7 Removal of technetium and neptunium from MgF_2 sorption beds

The recovery of technetium and neptunium from MgF_2 sorption beds is feasible using aqueous or aqueous nitric acid washing (ref. 3). Desorption of the technetium by subjecting the bed to fluorine has also been described (ref. 1); however, this method has the disadvantage of requiring a temperature of 1000°F. It can be surmised that the desorption of neptunium from MgF_2 with fluorine would be equally if not more difficult than removal by aqueous methods.

8.2.8 Trapping PuF_6 with fluoride sorbent beds

There was early recognition that PuF_6 was easily and nearly irreversibly sorbed on NaF (refs. 7, 9, 11, 12, 17, and 22). Study of the process showed that a PuF_4-NaF complex was formed (ref. 22), and that the NaF could be dissolved away from the PuF_4 with anhydrous HF. Plutonium hexafluoride sorbed on LiF forms a weaker complex, with the result that fluorination can be used to regenerate and desorb the PuF_6 (refs. 8, 15, and 25).

8.3 Conclusions Regarding Areas of Interest Pertinent to Development of the ENC Process Flowsheet

1. There is uncertainty about the chemistry involved in the sorption of technetium on MgF_2. There is also uncertainty about whether this process step would be affected by the fluorination conditions prevalent in the ENC flowsheet. It would appear desirable, therefore, to do some work in the following areas:

   (a) Determine whether the material sorbed on MgF_2 is TcF_6 or TcO_3F.

   (b) Determine whether a definite chemical complex is formed with MgF_2, and how the equilibrium partial pressure of the sorbed species varies with temperature if such a complex is formed.

   (c) Determine whether technetium undergoes a valence change in MgF_2 sorption. (The fact that fluorine is required for desorption indicates that this is true.)

   (d) Study the volatile compounds of technetium formed under the conditions of temperature and fluorine concentration to be used in the ENC flowsheet. This study would be initiated with technetium oxide, in the absence of uranium.

2. Regeneration of the MgF_2 by fluorine treatment appears feasible for technetium but is less suitable for neptunium. The question arises as to how the sorptive capacity of the bed for technetium changes with an increasing buildup of neptunium. This is, in part, related to the mechanism appearing in item (1). Some work should be done at high neptunium loadings on MgF_2 to determine how such loadings affect technetium sorption.

3. From what is known about the difficulty of desorbing plutonium from alkali or alkaline-earth fluoride beds with fluorine, one is perhaps justified in questioning whether desorption of plutonium or neptunium from $CoF_2(CoF_3)$ beds as a regeneration method is feasible. The patents specify 700 and 900°C, respectively, for neptunium

and plutonium (refs. 31 and 35). Although CoF_2 or CoF_3 is less likely to form a chemical complex than, for example, NaF or MgF_2, a solid solution is at least possible, and this would hinder regeneration and revolatilization of the neptunium and plutonium hexafluorides. At the very least, the sorptive condition (reactivity and surface area) of the CoF_2 bed could be affected. Hence more definitive data on this subject would be desirable prior to inclusion of this step in the ENC flowsheet.

4. More information should probably be obtained on the optimum conditions for the various fluoride beds used in the ENC process. This pertains particularly to methods of bed preparation and their regeneration (as in item 3 above), particularly with regard to sorptive capacity, sorptive kinetics, mechanical stability of pellets, and the effects of regeneration.

8.4 References for Appendix A

1. W. R. Golliher, R. A. LeDoux, S. Bernstein, and V. A. Smith, "Separation of Technetium-99 from Uranium Hexafluoride," published in Industrial Cooperation Information Bulletin (July 23, 1974); also issued as TID-18290 (1960).

This article contains a description of how to use MgF_2 to trap technetium in a UF_6 gas stream and how the technetium is recovered either by gas fluorination or by extraction with water. The efficiency of recovery is dependent on residence time. At a superficial velocity of 0.59 fps (residence time = 2.63 sec), the recovery was initially 83%, decreasing rapidly to 40%. At a velocity of 0.27 fps (residence time = 9.26 sec), the retention was 99% until a loading of 0.77% had been obtained.

1a. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, New York, 1962, 1966, 1972.

This is an excellent reference text on inorganic chemistry.

1b. J. J. Katz and G. T. Seaborg, Chemistry of the Actinide Elements, Wiley, New York, 1957.

This is a reference text for uranium and other actinide elements.

1c. L. E. Trevorrow, R. K. Stenenberg, and W. A. Shenn, "The Thermal Decomposition of Plutonium Hexafluoride," J. Phys. Chem. 65, 398 (1961).

2. S. Katz, Reduction of Uranium Hexafluoride Retention on Beds of Magnesium Fluoride Used for Removal of Technetium Hexafluoride, ORNL-3544 (Jan. 17, 1964).

The deposition of uranium on MgF_2 was shown to be minimized by heating, fluorination, and hydrofluorination pretreatment of the MgF_2 pellets used in the technetium process. Formation of a UF_6-MgF_2 complex probably does not occur.

3. W. R. Golliher, "Process for Separation and Recovery of Volatile Fluoride Impurities from Uranium Hexafluoride Containing the Same," U.S. Patent 3,165,375 (Jan. 12, 1965).

The process described employs MgF_2 to remove the impurities of technetium, neptunium, molybdenum, and vanadium from gaseous or liquid UF_6, preferably in the temperature range 200 to 250°F, to remove up to 99% of the contained technetium and greater than

90% of the contained Np. Recovery of the sorbed technetium and neptunium by water or dilute nitric acid is also described.

4. B. Moncelon, J. Lucas, and T. Kikindai, "Etude chimique et cinetique de la reaction entre l'anhydride sulfureux et l'hexafluorure d'uranium," Compt. Rend. <u>261</u>, 1855-58 (Aug. 18, 1965).

   Sulfur dioxide reduces gaseous UF_6 to form SO_2F_2 and a lower fluoride of uranium, depending on the conditions of temperature and pressure. The reaction was studied for different SO_2/UF_6 ratios over the temperature range 60 to 380°C.

5. <u>Investigations in the System Alkali Fluoride-Lanthanide/Actinide Fluoride</u> (German), KFK-431 (July 1966).

   An extensive investigation was made of the solid-state phase relationships of LiF, NaF, KF, and RbF with various lanthanide and actinide fluorides, including the tetrafluorides of neptunium and plutonium.

6. <u>Reprocessing of Irradiated Fuels</u>, EURAEC-1832 (1966).

   This report contains data from process development, including work on the behavior of TeF_6 and NpF_6 on NaF and MgF_2.

7. "Volatility Processing," pp. 79-95 in <u>Semiannual Report Chemical Engineering Division, Argonne National Laboratory, July-Dec. 1966</u>, ANL-7325.

   Miscellaneous information is presented on the sorption of PuF_6 and associated fission product fluorides on NaF beds, in the temperature range 45 to 500°C.

8. Chemical Technology Division Annual Progress Report, Oak Ridge National Laboratory, May 31, 1967, ORNL-4145, pp. 58-94.

   Information on many aspects of fluoride volatility processing is presented, including a LiF sorption-desorption system for PuF_6 and a MgF_2 sorption-desorption system for NpF_6.

9. "Volatility and Fluidization Processes," pp. 21-37 in Chemical Engineering Division Research Highlights, Argonne National Laboratory, May 1966-April 1967, ANL-7350.

   Miscellaneous information is presented on the sorption of PuF_6 on NaF and on the reduction of NpF_6 with bromine.

10. "Fluoride Volatility Processes," pp. 71-74 in Reactor Development Program Progress Report, ANL-7329 (April 1967).

    Work is reported on the reduction of PuF_6 with BrF_3, the removal of RuF_5 from PuF_6 by gas sorption on alkaline-earth fluorides, and the interaction of NpF_6 with NaF.

11. Chemical Engineering Division Semiannual Report, Argonne National Laboratory, Jan.-June 1967, ANL-7375, pp. 64-66.

    Some work is reported on the sorption of PuF_6 on NaF and plutonium recovery by refluorination. The reaction of NpF_6 with bromine was also studied.

12. Chemical Engineering Division Semiannual Report, Argonne National Laboratory, ANL-7425, pp. 43-70.

    This report contains some data on the interaction of PuF_6 and NpF_6 with NaF.

13. Paducah Plant Laboratory Progress Report, July-December 1967, KY-L-437.

This report contains interesting data on the stability of NpF_6-UF_6 liquid mixtures in well-conditioned nickel equipment. Plutonium hexafluoride in PuF_6-UF_6 mixtures, on the other hand, is unstable with the solubility of PuF_4 in UF_6 being $\leq$ 5 ppb.

14. J. J. Barghusen, "Volatility Processes," Reactor Fuel-Reprocess. 10, 309-13 (1967).

Data are presented on the behavior of TcF_6, MoF_6, and NpF_6 on NaF and MgF_2 sorption beds. Some of the information is contradictory to other published work. The reduction of NpF_6 to NpF_4 with bromine is reported.

15. Reactor Development Program Progress Report, Argonne National Laboratory, March 1968, ANL-7438, pp. 107-11.

Work is reported on the interaction of PuF_6 with LiF and on the interaction of NpF_6 with NaF. The latter is discussed in reference to measurement of the equilibrium constant and its significance with respect to thermodynamic considerations.

16. E. W. Richardson and L. E. McNeese, "Process for Making Porous Sodium Fluoride Pellets," U.S. Patent 3,372,004 (Mar. 5, 1968).

This patent describes a method for obtaining porous and stable NaF pellets by using powder as a wet agglomerate, followed by drying and sintering at an elevated temperature.

17. Annual Progress Report, Chemical Technology Division, Oak Ridge National Laboratory, May 31, 1968, ORNL-4272, pp. 68-71.

Information is presented on the sorption of fission product fluorides and neptunium and plutonium hexafluorides on various solid sorbent fluoride beds.

18. L. E. Trevorrow, Process Chemistry of Neptunium Hexafluoride, CONF-680610 (June 1968), pp. 140-60.

This review report covers, in considerable detail, the chemistry of NpF_6 in fluoride volatility processing. The sorption of NpF_6 on MgF_2 is not viewed favorably.

19. Chemical Engineering Division Research Highlights, Argonne National Laboratory, December 1968, ANL-7550, pp. 27-28.

Work is reported on the equilibrium of the reaction between NpF_6 and NaF.

20. S. Katz and G. I. Cathers, "A Gas Sorption-Desorption Method for Separating the Hexafluorides of Neptunium and Uranium," Nucl. Appl. 5, 206-10 (1968).

Neptunium hexafluoride was sorbed more effectively by NaF at 200°C than by the fluorides of lithium, magnesium, and calcium at 100 to 400°C. Neptunium is separated from uranium by sorption of the hexafluorides on NaF, reduction of the neptunium of the NpF_6-NaF complex, desorption of the UF_6, refluorination, and desorption of the NpF_6.

21. L. E. Trevorrow, T. J. Gerding, and M. J. Steindler, "The Reaction of Neptunium Hexafluoride with Sodium Fluorides," Inorg. Chem. 7, 2226-29 (1968).

The sorption of NpF_6 on NaF at 250 to 400°C was found to involve autoreduction, that is, the release of free fluorine and the formation of a NpF_5-NaF complex. The equilibrium of this reaction was measured.

22. M. J. Steindler and A. A. Jonke, "Plutonium Tetrafluoride Preparation and Separation by Sorption on Sodium Fluoride," U.S. Patent 3,423,140 (Jan. 21, 1969).

Plutonium is separated from uranium and fission products present in an irradiated fuel element by fluorinating the element in a fluidized bed and passing the volatile hexafluorides thus formed through a settled bed of NaF. The NaF with the plutonium, uranium, and fission products sorbed thereon is heated to 400°C and flushed with fluorine to remove the uranium and volatile fission product fluorides. The NaF is alternately washed with liquid anhydrous hydrogen fluoride and liquid bromine pentafluoride, which dissolves the NaF and leaves a purified precipitate of PuF_4.

23. Recent Preparative Chemistry at Harwell, CONF-690426 (April 1969), pp. 152-68.

The preparation and properties of neptunium and uranium oxyfluorides are reported on in a general study.

24. G. Manevy, "Selective Reduction of PuF_6," U.S. Patent 3,450,509 (June 17, 1969).

For selectively reducing PuF_6 present in a mixture containing PuF_6, UF_6, and fission products, the mixture of hexafluorides is mixed with a proportion of CO_2 greater than that stoichiometrically necessary and maintained at about 350°C at a pressure of between 0.5 and 3 bars for a time sufficient for complete reduction of PuF_6. The process may be carried out in either a batch or a continuous mode (by flowing the mixture through a vertical reaction vessel).

25. J. G. Reha, L. E. Trevorrow, and M. J. Steindler, "Separation of Ruthenium and Plutonium by a Lithium Fluoride Sorption Technique," U.S. Patent 3,458,291 (July 29, 1969).

    Ruthenium fluoride is separated from PuF_6 by flowing a mixture of the fluorides and fluorine gas through a bed of LiF particles maintained at $\sim$ 400°C. The ruthenium fluoride forms a stable complex with the LiF. The plutonium is not sorbed under these conditions.

26. <u>Study of Volatility Processing Methods, Semiannual Report (No. 5), Fontenay-aux-Roses, December 1968</u>, ANL-trans-751 (June 1969).

    In process development work, the kinetics of fluorination of NpF_4 was studied along with tests relative to the retention of NpF_6 on NaF and MgF_2.

27. S. Katz and G. I. Cathers, "Method of Separating Neptunium and Uranium Values," U.S. Patent 3,451,790 (June 24, 1969).

    A method of separating neptunium values from a mixture containing NpF_6 and UF_6 consists of contacting the mixture with NaF at a temperature of 100 to 250°C (thereby sorbing these hexafluorides on the NaF), converting the neptunium to a state in which it is more strongly sorbed than UF_6, and selectively desorbing the UF_6 by heating the NaF to a temperature of 250 to 350°C.

28. G. Matcheret, Contribution a l'etude de la formation de l'hexafluorure de neptunium et de son comportement avec certains fluorures metalliques, CEA-R-4051 (November 1970).

This work, which is a thesis, provides an excellent overall review of the literature on the formation of NpF_6 and the interaction with metal fluorides. It also contains new experimental work in these two areas, particularly emphasizing the chemistry of the NpF_6 interaction with NaF, MgF_2, and BaF_2.

29. G. Matcheret, "Etude de l'adsorption de l'hexafluorure d'uranium sur le fluorure de magnesium et de l'hexafluorure de neptunium sur les fluorures de magnesium et de baryium," Radiochem. Radioanal. Lett. 3, 287-94 (1970).

The interaction of UF_6 with MgF_2 is characteristic of a physical monolayer adsorption behavior. Analogous to UF_6, the adsorption of NpF_6 involves, in addition, a chemical autoreduction with probable formation of NpF_5 and the release of free fluorine. The sorption of NpF_6 on BaF_2 is comparable to that on NaF.

30. K. W. Bagnall, D. Brown, and J. F. Easy, Protactinium(V) and Neptunium(V) Oxyfluorides, BNBW-FBK-71-17, pp. 91-96 (October 1971).

Some of the chemistry of neptunium oxyfluorides is included in this general study.

31. W. R. Golliher, R. L. Harris, and R. A. LeDoux, "Separation of Neptunium from Uranium Hexafluoride Containing the Same," U.S. Patent 3,615,267 (Oct. 26, 1971).

This invention relates to a method for selectively removing neptunium values from a gaseous mixture containing NpF_6 and UF_6 by passing the mixture through a bed of pelletized cobaltous fluoride at a temperature in the range 220 to 440°F to effect removal of neptunium. The operation to remove neptunium appears quite similar to the plutonium removal method (U.S. Patent 3,708,568). A load factor of > 3.3% is said to be feasible with a superficial gas velocity of up to 1 fps.

32. O. Hartmenshenn and J. C. Barral, "New Methods for Reducing Uranium Hexafluoride," Compt. Rend., Ser. C, 272, 2139-40 (1971).

Information is presented on reducing UF_6 with uv radiation, and with the chemical reductants of H_2, CO, and SO_2.

33. M. Vanka, Neptunium Fluoride and the Behavior of Neptunium During Fluoride Regeneration of Nuclear Fuel, UJV-2736-Ch (1971).

This report compares the reactivity of NpF_6 with UF_6 and PuF_6, and discusses methods of separating neptunium from other actinides. Sorption of NpF_6 on NaF and the selective reduction of NpF_6 and PuF_6 are described.

34. W. W. Schulz and G. E. Benedict, Neptunium-237 Production and Recovery, TID-25955 (1972).

This report summarizes much of the available data on the behavior of neptunium in fluoride volatility processes, including work at the Argonne and Oak Ridge National Laboratories.

35. W. R. Golliher, R. L. Harris, and R. A. LeDoux, Jr., "Removal of Plutonium Hexafluoride from Plutonium Hexafluoride-Uranium Hexafluoride Mixtures," U.S. Patent 3,708,568 (Jan. 2, 1973).

This invention relates to a method for selectively removing plutonium values from a mixture containing PuF_6 and UF_6 by passing the mixture through a bed of pelletized CoF_2 at a temperature in the range 134 to 1000°F to effect removal of plutonium. More specifically, the best temperature range is 200 to 400°F, with the superficial gas velocity being 0.25 to 1 fps to give a residence time of 1 to 10 sec. Decontamination factors of 10^5 are obtained under these conditions.

36. J. P. Roux and M. Valladon, Principal Physical Properties of Fluorides and Oxyfluorides of Fission Products, CEA-R-4424 (February 1973).

The physical properties of TcF_6, TcF_5, TcO_3F, and $TcOF_4$ are included in this general report.

37. "Removal of Neptunium, Plutonium, and Technetium from Uranium Hexafluoride," in Industrial Cooperation Technology Information Bulletin, Union Carbide Corp. Nuclear Division (July 23, 1974).

This is a compilation of four patents and two articles on work performed mainly at the diffusion facility at Paducah, Kentucky, on UF_6 purification with CoF_2 and MgF_2. The contents are described elsewhere under separate headings.

38. R. L. Harris, "Transuranic Trapping Facility," in Industrial Cooperation Technology Information Bulletin (July 23, 1974).

This article covers, in some detail, the use of CoF_2 to remove neptunium and plutonium alpha contaminants from gaseous UF_6. The preparation and drying of CoF_2 pellets are described. The recommended operating temperature range for both neptunium and plutonium is 300 to 440°F, with the neptunium loading factors being > 3 and $\sim 10\%$, respectively, at 300 and 440°F. Higher loading factors can be obtained for plutonium. A proposed Paducah trap (5 ft high x 20 in. in diameter) will have a superficial velocity of 1 fps, or a residence time of about 5.0 sec. The CoF_2 trap should be used in conjunction with a 10-μ filter downstream to prevent particulate transfer of NpF_4 and PuF_4.

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