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RECOVERY OF URANIUM HEXAFLUORIDE FROM FEED PLANT VENT GASES

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OAK RIDGE GASEOUS DIFFUSION PLANT

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A B S T R A C T

Pilot-plant studies of the use of a fluidized bed of uranium tetrafluoride to scrub small amounts of uranium hexafluoride from feed plant vent gas streams are described. No operating problems were encountered, and greater than 90% recovery of the uranium hexafluoride was obtained with bed temperatures of 150 to 500°F. At higher temperatures, however, a loss in recovery efficiency was noted. Gases containing up to 11.5% uranium hexafluoride, 17.0% fluorine, and 10.5% hydrogen fluoride were handled without difficulty; studies were not made at higher concentrations.

RECOVERY OF URANIUM HEXAFLUORIDE FROM FEED PLANT VENT GASES

In the existing cascade feed preparation facilities, the gaseous uranium hexafluoride product is collected in refrigerated cold traps by condensation as a solid, and any noncondensable gases, primarily nitrogen and oxygen, are vented to the atmosphere. At Paducah, the final trap in the system is operated at a pressure of 7 to 10 psia. and minus 55°F.; under these conditions, the uranium hexafluoride concentrations in the vent gases range from 400 to 1,000 ppm.

Since exploratory laboratory tests at Paducah[1] had indicated that a fluidized bed of uranium tetrafluoride could be employed to strip the uranium hexafluoride from vent gases, the Technical Division was requested in October, 1956, to investigate the feasibility of applying this method to the Paducah feed plant. Although the loss of uranium was small at that time, operating procedure changes were contemplated which would increase greatly the amount of noncondensables vented from the feed plant and thus result in a significant loss of uranium. The following report summarizes the experimental studies which were made in a single-stage fluid-bed reactor operated with a continuous feed and withdrawal of solids.

SUMMARY

The pilot-plant tests verified the results of the earlier Paducah laboratory studies in which essentially complete recovery of uranium hexafluoride was obtained when dilute uranium hexafluoride was passed through a fluid bed of uranium tetrafluoride. Although the powder bed depth in the pilot-plant reactor was only 24 inches, the stripping efficiency was greater than 90%, with an operating temperature of 400°F., inlet uranium hexafluoride concentrations from 0.1 to 11.5% (the maximum tested), and a uranium tetrafluoride feed rate of about 65 pounds per hour per cubic foot of bed. Inlet concentrations as low as the 400 ppm. expected in the plant could not be obtained with the pilot-plant equipment, but the observed outlet concentrations, less than 0.01%, showed that the percentage recovery would be at least 75% under these conditions. No operating difficulties, such as uncontrollably high temperatures or bed caking, were observed with fluorine or hydrogen fluoride concentrations up to 17 and 10.5%, respectively.

Studies of the effects of processing conditions showed that superficial gas velocities of 0.2 to 0.5 foot per second, calculated at the inlet gas pressure and powder bed temperature, could be employed successfully. It was also found that good absorption was possible with temperatures ranging from 150 to 500°F., but it appeared that the stripping efficiency was lower when bed temperatures of 550 and 600°F. were employed.

Following the exploratory pilot-plant tests during which 110 hours of trouble-free operation was accumulated, a run lasting 106-1/2 hours was made. During this period, variations in fluorine and uranium hexafluoride flows and concentrations, more severe than those expected in plant operation, were simulated. The test was made without interruption except for scheduled shutdowns. The over-all uranium hexafluoride recovery efficiency for the run was about 93%.

Based on the pilot-plant experience, design criteria were submitted to Paducah and a plant facility was subsequently installed in July, 1958(3). Operation of the unit has been satisfactory.

PROCESS TECHNOLOGY

Uranium hexafluoride reacts with uranium tetrafluoride to form intermediate compounds, U_4F_{17}, U_2F_9, and UF_5, which increase in volatility with the proportion of uranium hexafluoride to uranium tetrafluoride. The same compounds can also be formed by the reaction of fluorine with uranium tetrafluoride. The equilibrium pressures of uranium hexafluoride above these compounds at 400°F. are 6.45×10^{-3}, 2.4×10^{-2}, and 97.5 mm. mercury, respectively(2). At 500°F., these values for U_4F_{17} and U_2F_9 increase to 2.29×10^{-1} and 1.1 mm. mercury. Since 100 ppm. uranium hexafluoride in the gas stream at 1 atmosphere pressure is equivalent to a vapor pressure of 7.6×10^{-2} mm. mercury, formation of either U_2F_9 or U_4F_{17} with satisfactory recovery of the uranium hexafluoride is theoretically possible.

The recovery process involves contacting uranium tetrafluoride powder with a vent stream to remove uranium hexafluoride which is normally present in very low concentrations, about 400 ppm. The fluidized bed reactor was selected for this application because the high heat and mass transfer coefficients in this type equipment allow good temperature control and the gas-solids contact is excellent.

EQUIPMENT DESCRIPTION

The pilot-plant unit, figure 1, consisted of a uranium tetrafluoride hopper and screw feeder assembly, a single-stage fluid-bed reactor, a gas metering manifold, and a combination product hopper, gas filter, and screw conveyor. Both the feed and product hoppers had a capacity of about 2 cubic feet and were equipped with standard screw feeders which were driven by variable speed drives. The feed hopper was fitted with a cyclone to facilitate pneumatic loading of the uranium tetrafluoride. The reactor was fabricated from 6-inch, Schedule 40, Monel pipe, and the fluidizing gas was introduced through a multiple orifice gas distribution plate. Uranium tetrafluoride was charged at a point 6 inches above the plate, and the powder and gas were discharged together through an overflow line located 24 inches above

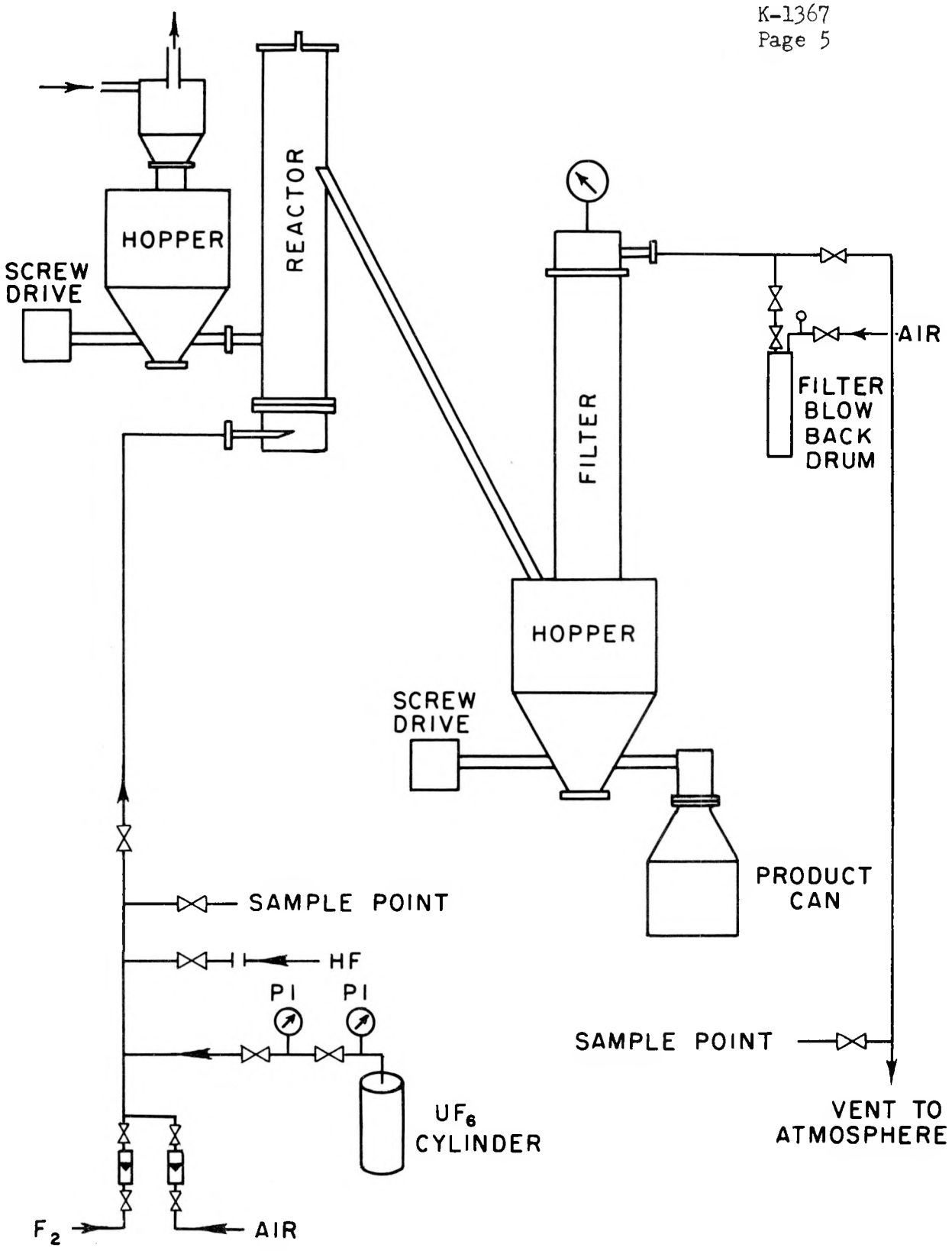

Figure 1
UF_6 RECOVERY PILOT PLANT

the plate. After run 15, a tripod of 1/2-inch diameter Monel rod with the apex about 8 inches from the top of the powder bed was added to the reactor in an attempt to improve the fluidization.

Heat was supplied to the reactor by beaded Nichrome resistance wire and was controlled automatically to maintain the desired wall temperature. Reactor wall and powder bed temperatures were measured at several points. The feed gas manifold was equipped to meter and control the flows of fluorine, hydrogen fluoride, and air. The uranium hexafluoride flow was adjusted by varying the pressure upstream of a manually set needle valve, and the concentration was determined by analyses of gas samples. Sample taps were provided in both the inlet and outlet gas lines.

DATA AND DISCUSSION

The experimental studies were made with uranium tetrafluoride prepared from ground Hanford continuous-calciner oxide in one of the Paducah fluid-bed reduction, screw hydrofluorination lines. The average composition of this powder was 92.0% uranium tetrafluoride, 3.5% uranyl fluoride, and 4.5% uranium dioxide. Tests made at various temperatures, inlet fluorine, hydrogen fluoride, and uranium hexafluoride concentrations, and fluidizing velocities are summarized in table I and described in detail below. All the runs were made with a uranium tetrafluoride feed rate of 65 pounds per hour per cubic foot of bed (the lowest possible with the available feeder).

After about 12 hours of shakedown operation, runs 3 through 9 and 12 through 15 were made to determine the effect of bed temperature on the uranium hexafluoride recovery efficiency. The tests were made with superficial gas velocities of 0.21 to 0.37 foot per second and inlet fluorine concentrations of about 3.5%. It can be noted that the outlet uranium hexafluoride concentrations are essentially the same with temperatures of 150 to 500°F., but are marginally higher at 550°F. and significantly higher at 600°F.

Runs 10, 11, 16 through 20, and 24, made with different concentrations of uranium hexafluoride in the inlet gas, produced interesting results. In run 24, the uranium hexafluoride flow was increased for three periods of 25 minutes each, and gas samples were taken 10 minutes after the change of conditions. The flows were held constant in the remaining tests. Although the percentage uranium hexafluoride recovered was good in all cases, the outlet concentrations appeared to be dependent on the inlet concentration, and in view of the large excesses of uranium tetrafluoride employed, it appears probable that either minor channeling was occurring or that the gas was passing up through the bed in the form of large bubbles. The use of deeper powder beds would minimize these effects. Following run 15, a tripod of metal rods was placed in the powder bed in an attempt to improve the fluidization and decrease the outlet concentrations, but no significant improvement was observed.

TABLE I

ABSORPTION OF URANIUM HEXAFLUORIDE BY URANIUM TETRAFLUORIDE
SUMMARY OF PILOT-PLANT RUNS

Run Number	Bed Temperature, °F.	Gas Velocity, ft./sec.	Inlet Gas		Outlet Gas		UF_6 Stripped, %	F_2 Stripped, %	Operating Time, hours
			UF_6, mol %	F_2, mol %	UF_6, mol %	F_2, mol %			
1	425	0.30	0.47	3.6	0.09	1.2	81	67	4.3
2	415	0.30	1.44	3.1	<0.01	1.9	>99	39	7.8
3	410	0.30	1.36	3.3	0.03	1.6	98	51	6.0
4	390	0.30	0.92	2.7	<0.01	2.0	>99	26	2.0
5	335	0.27	0.57	3.1	0.04	2.2	93	29	5.5
6	315	0.27	0.52	3.1	0.03	2.1	94	32	3.0
7	260	0.25	0.77	3.6	0.04	2.7	95	35	3.0
8	210	0.23	0.78	3.3	0.03	2.9	96	12	3.0
9	155	0.21	0.75	3.3	0.03	2.8	96	15	3.0
10	150	0.21	1.53	3.9	0.05	2.8	97	28	1.5
11	225	0.24	2.74	3.0	0.06	2.6	98	13	2.5
12	455	0.31	0.90	3.5	0.02	2.2	98	37	4.1
13	505	0.33	0.52	3.4	0.03	2.1	95	38	1.0
14	550	0.35	0.55	3.1	0.06	1.6	89	48	1.0
15	600	0.37	0.71	4.2	0.11	1.5	84	64	2.5
16	410	0.31	1.20	3.5	0.06	1.6	95	54	2.5
17	410	0.31	0.55	3.5	0.05	1.6	91	54	2.5
18	410	0.31	0.35	3.5	0.01	1.6	97	54	1.0
19	410	0.31	0.19	3.5	<0.01	1.6	>95	54	1.5

TABLE I (Cont'd.)

ABSORPTION OF URANIUM HEXAFLUORIDE BY URANIUM TETRAFLUORIDE
SUMMARY OF PILOT-PLANT RUNS

Run Number	Bed Temperature, °F.	Gas Velocity, ft./sec.	Inlet Gas		Outlet Gas		UF_6 Stripped, %	F_2 Stripped, %	Operating Time, hours
			UF_6, mol %	F_2, mol %	UF_6, mol %	F_2, mol %			
20	410	0.31	0.09	3.5	<0.01	1.6	>89	54	2.0
21a	380	0.30	0.36	3.1	0.03	1.7	92	45	6.4
21b	380	0.30	0.75	9.2[a]	0.08	7.7	90	16	
21c	380	0.30	0.55	8.6[a]	0.02	5.1	97	41	
21d	380	0.30	0.47	8.3[a]	0.02	5.0	96	40	
22	385	0.29	0.40	3.2	0.01	2.4	98	25	5.3
23	385	0.31	0.45	17.1	0.01	14.7	98	14	2.5
24a	400	0.29	0.38	3.4	0.02	2.8	95	18	5.9
24b	400	0.29	1.40[b]	3.4	0.03	2.8	98	18	
24c	400	0.29	2.64[b]	3.4	0.04	2.8	99	18	
24d	400	0.29	4.50[b]	3.4	0.06	2.8	99	18	
25	400	0.29	0.24	3.1	0.02	2.9	92	65	2.5
26	400	0.15	0.30	3.5	0.01	2.1	97	40	5.0
27	400	0.07	0.33	4.7	0.01	1.5	97	68	6.0
28	400	0.52	0.40	3.7	<0.01	1.9	>97	49	2.5
29	400	0.50	0.17	3.6	0.01	2.7	94	25	5.2
30	390	0.78	0.18	2.6	0.03	1.4	83	46	3.0
31	400	0.37	0.27	3.0	0.01	2.3	96	23	6.2

a - Ten-minute surge of fluorine.
b - Twenty-five minute surge of uranium hexafluoride.

In runs 21 and 23, the fluorine concentration in the inlet gas was increased to a maximum of 17% without affecting the uranium hexafluoride recovery efficiency. It is of interest that no tendency for a rapid, uncontrollable reaction was noted with the high fluorine concentration. Some of the fluorine apparently reacted with the uranium tetrafluoride, however, and a decrease in the absorptive capacity of the powder bed would be expected.

The effect of superficial gas velocity was determined in runs 25 through 30, which were made with velocities ranging from 0.1 to 0.8 foot per second. No operating difficulties were encountered at 0.2 foot per second and higher, but at 0.1 foot per second, the feed screw overloaded. Inspection of the reactor showed no caking, and when operation was resumed with the 0.1 foot per second velocity, a 3-hour run was made without difficulty. It is felt, however, that this was a borderline condition, and accordingly, the minimum fluidizing velocity is recommended as 0.2 foot per second. The highest velocity tested, 0.8 foot per second, resulted in a decrease in recovery to 83%, thus indicating that the gas contact time was too low or that short circuiting of the gas was occurring.

To conclude the experimental program, test 31 was made in which it was shown that satisfactory operation of the unit was possible with as high as 10.5 mol percent hydrogen fluoride in the inlet gas.

Following the 110 hours of operation accumulated during the above tests, the unit was operated for an additional 106-1/2 hours under conditions at least as rigorous as those expected in plant service. During the run, summarized in table II, the average bed temperature was maintained at 400°F., the average uranium tetrafluoride feed rate was 36 pounds per hour per cubic foot of bed, the average uranium hexafluoride feed rate was 0.88 pound per hour, and the superficial gas velocity was approximately 0.3 foot per second. The over-all uranium tetrafluoride to uranium hexafluoride ratio was 15.3 to 1, and the on-stream efficiency for the run was 93%. All downtime was scheduled.

In order to simulate more closely the conditions expected in actual operation, the inlet uranium hexafluoride and fluorine concentrations were varied according to the following schedule:

First Hour:	The uranium hexafluoride flow was increased for 15 minutes. The flows were then returned to normal for 45 minutes.
Second Hour:	The fluorine flow was increased for 30 minutes. The flows were returned to normal for 30 minutes.
Third Hour:	The uranium hexafluoride and fluorine flows were increased for 15 minutes. The flows were then returned to normal for the remaining 45 minutes.

TABLE II

ABSORPTION OF URANIUM HEXAFLUORIDE BY URANIUM TETRAFLUORIDE
SUMMARY OF 106-1/2 HOUR RUN

Run Number	Inlet Gas		Outlet Gas		UF_6 Stripped, %	F_2 Stripped, %
	UF_6, mol %	F_2, mol %	UF_6, mol %	F_2, mol %		
	Normal UF_6 and F_2 Flows					
1	0.04	3.2	0.03	1.6	25	50
2	0.15	5.2	< 0.01	3.6	> 93	31
3	0.20	3.4	0.01	2.3	95	32
4	0.18	3.4	0.01	2.3	94	32
5	0.28	3.5	0.02	2.8	93	20
6	0.39	4.4	0.05	2.6	87	41
7	0.19	2.4	0.01	1.8	95	25
8	0.16	2.8	< 0.01	1.6	> 94	43
9	0.41	3.1	0.06	2.4	85	23
10	0.31	3.1	< 0.01	2.3	> 97	26
11	0.19	3.3	< 0.01	2.6	> 95	21
12	0.05	2.1	0.01	1.9	80	10
13	0.11	3.2	0.02	2.5	82	22
14	< 0.01	3.3	< 0.01	2.4		27
15	0.07	3.9	0.06	3.8	14	3
16	0.14	4.6	0.06	3.8	57	17
17	0.02	3.9	< 0.01	1.6	> 50	59
18	0.29	3.4	0.06	2.8	79	18
19	0.31	3.2	< 0.01	2.7	> 97	16
20	0.02	3.9	0.02	2.8	0	28
21	< 0.01	3.1	< 0.01	2.5		19
22	< 0.01	3.5	< 0.01	2.4		31
23	< 0.01	4.4	< 0.01	2.1		52
24	0.31	3.4	0.04	1.7	87	50
25	0.47	2.7	0.08	2.6	83	4

TABLE II (Cont'd.)

ABSORPTION OF URANIUM HEXAFLUORIDE BY URANIUM TETRAFLUORIDE
SUMMARY OF 106-1/2 HOUR RUN

Run Number	Inlet Gas		Outlet Gas		UF_6 Stripped, %	F_2, Stripped, %
	UF_6, mol %	F_2, mol %	UF_6, mol %	F_2, mol %		
26	0.36	3.2	<0.01	2.5	>97	22
27	0.12	3.3	0.11	2.2	8	33
28	0.15	3.9	0.04	3.2	73	18
			High UF_6, Normal F_2 Flows			
1	1.48	2.2	<0.01	2.0	>99	10
2	1.37	3.7	0.20	3.6	85	3
3	2.06	3.0	0.11	2.7	95	10
4	0.56	3.1	0.18	2.7	68	13
5	10.10	2.6	0.03	2.6	100	0
6	1.80	4.5	0.09	3.1	95	31
7	8.69	3.6	0.01	1.7	100	53
8	0.84	2.9	0.06	1.6	93	45
9	1.50	3.1	0.03	2.9	98	6
10	2.50	3.8	0.06	3.6	98	5
11	1.30	3.2	0.05	3.0	96	6
12	0.68	3.8	<0.01	3.2	>98	16
13	1.50	3.2	0.04	1.6	97	50
14	1.20	3.4	0.04	2.7	97	20
15	7.10	4.2	0.21	3.0	97	29
16	1.30	3.9	0.04	2.5	97	36
17	5.40	3.1	0.03	2.1	99	32
18	1.30	4.3	0.03	3.1	98	28
19	11.20	4.2	0.15	3.6	99	14
20	0.70	5.0	0.02	2.6	97	48
21	1.30	4.4	0.01	2.8	99	36
22	1.10	4.2	0.08	3.4	93	19

TABLE II (Cont'd.)

ABSORPTION OF URANIUM HEXAFLUORIDE BY URANIUM TETRAFLUORIDE
SUMMARY OF 106-1/2 HOUR RUN

Run Number	Inlet Gas		Outlet Gas		UF_6 Stripped, %	F_2 Stripped, %
	UF_6, mol %	F_2, mol %	UF_6, mol %	F_2, mol %		
23	1.20	3.5	0.07	2.3	94	34
24	1.20	3.5	0.08	2.3	93	34
			Normal UF_6, High F_2 Flows			
1	0.14	12.2	0.01	6.7	93	45
2	1.08		0.06	9.0	94	
3	0.48	14.5	<0.01	13.3	>98	8
4	0.33	12.7	<0.01	11.5	>97	9
5	0.18	12.9	0.01	11.4	94	12
6	0.12	13.5	0.08	12.5	33	7
7	0.51	14.4	0.06	13.1	88	9
8	1.15	13.0	0.02	10.6	98	19
9	0.63	11.3	0.06	9.2	91	19
10	3.15	10.8	0.03	10.6	99	2
11	0.45	10.5	0.02	9.1	95	13
12	0.63	12.0	0.03	8.1	95	48
13	0.09	13.3	0.13	11.9	0	11
14	0.15	12.6	0.24	11.0	0	12
15	0.38	12.0	0.03	9.8	92	18
16	1.98	12.8	0.15	12.5	92	2
17	0.73	5.0	0.02	2.6	96	48
18	1.12	16.0	0.09	18.7	92	0
			High UF_6, High F_2 Flows			
1	3.40	11.7	<0.01	7.9	100	33
2	1.54	6.4	0.18	3.4	88	47
3	1.25	8.5	<0.01	8.0	>99	6
4	6.30	12.2	0.09	12.9	99	0

TABLE II (Cont'd.)

ABSORPTION OF URANIUM HEXAFLUORIDE BY URANIUM TETRAFLUORIDE
SUMMARY OF 106-1/2 HOUR RUN

Run Number	Inlet Gas		Outlet Gas		UF_6 Stripped, %	F_2 Stripped, %
	UF_6, mol %	F_2, mol %	UF_6, mol %	F_2, mol %		
5	5.45	12.0	<0.01	11.4	100	5
6	0.51	14.4	0.06	13.1	88	9
7	1.30	16.1	0.07	14.5	95	10
8	1.21	10.0	0.01	8.1	99	19
9	1.15	12.0	0.02	10.6	98	12
10	6.03	14.7	0.21	15.6	97	0
11	0.63	11.3	0.06	9.2	91	19
12	0.73	10.7	0.08	8.7	89	19
13	0.56	17.8	0.06	14.7	89	17
14	15.65	12.0	0.06	11.1	100	8
15	10.10	7.4	0.06	3.9	99	47
16	4.67	6.7	0.51	3.1	89	54
17	3.15	10.8	0.03	10.0	99	7
18	9.00	15.3	0.38	9.5	96	38
19	11.25	12.1	0.26	11.3	98	7
20	2.92	13.1	0.12	10.5	96	20
21	3.03	18.3	0.03	11.0	99	40
22	1.98	12.8	0.15	12.5	92	2
23	6.18	12.7	0.04	10.7	99	16
24	3.11	14.1	0.03	9.4	99	33
25	1.12	16.0	0.09	8.7	92	46
26	1.15	9.9	0.10	9.3	91	6

Fourth Hour: The unit was operated with the standard flows for the entire 60 minutes.

The inlet gas concentrations employed are shown in table I. The above schedule was repeated throughout the duration of the run.

No caking of the powder was encountered during the run, and the bed temperatures remained essentially constant during the surges of fluorine and/or uranium hexafluoride. Although the over-all uranium hexafluoride recovery was good, some variability in stripping efficiencies was noted under similar operating conditions. A possible explanation for this inconsistency is that the average solids feed rate was only about one-half that noted in the earlier tests, although the feeder setting was the same. This was probably due to bridging of the powder in the hopper which would result in a surging rather than a steady low feed rate. Short circuiting of the gas through the relatively shallow bed could also be responsible for some of the high outlet analyses.

The pilot-plant studies indicate that operation of a fluid-bed absorption system should be essentially trouble-free. Good uranium hexafluoride recovery was possible over a wide range of inlet gas compositions and processing conditions, and there appeared to be no tendency toward overheating of the powder bed.

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