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REMOVAL OF IMPURITIES FROM
UF₆ URANIUM HEXAFLUORIDE
BY SELECTIVE SORPTION TECHNIQUES

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REMOVAL OF IMPURITIES FROM URANIUM HEXAFLUORIDE BY SELECTIVE SORPTION TECHNIQUES

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Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

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A B S T R A C T

Results of Oak Ridge Gaseous Diffusion Plant investigations of the effec-
tiveness of various solid sorbents in removing volatile impurities from
uranium hexafluoride are described, and the future program is discussed.
Purification of uranium hexafluoride produced from power reactor returns
by passing the fluorinator outlet gases through solid sorbents, such as
sodium fluoride, magnesium fluoride, calcium fluoride, etc., appears
promising. High concentrations of columbium pentafluoride and ruthenium
pentafluoride were reduced to less than 1 ppm. using either sodium
fluoride or magnesium fluoride. Removal of small quantities of titanium
tetrafluoride also seems possible. Work with other impurities is planned.

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REMOVAL OF IMPURITIES FROM URANIUM HEXAFLUORIDE
BY SELECTIVE SORPTION TECHNIQUES

A program is under way at the Oak Ridge Gaseous Diffusion Plant to develop methods for removing volatile impurities from uranium hexafluoride. Successful development of purification techniques could allow the U. S. Atomic Energy Commission to relax the rigorous specifications for uranium materials returned for cascade use and could result in large overall reprocessing cost savings. The present emphasis has been on use of solid sorbents which can collect the relatively small amounts of impurities while allowing the uranium hexafluoride gas to pass through. Such sorbent systems could be economically placed in uranium hexafluoride feed lines to the plant and also in uranium hexafluoride production systems employed for the reprocessing of scrap material. As a spinoff, information in this area could be very useful for the fluoride volatility reactor fuel reprocessing methods presently being investigated by the AEC Division of Reactor Development and Technology. The following report summarizes the results of the work completed to date and describes the future program.

SUMMARY

The studies were initiated with a series of screening tests to evaluate the sorptive capabilities of calcium, aluminum, magnesium, lithium, nickel, sodium, copper, strontium, barium, and bismuth fluorides. Urano-uranic oxide was "spiked" with one of the elements, arsenic, columbium, chromium, molybdenum, ruthenium, antimony, tantalum, titanium, vanadium, tungsten, and zirconium, by mixing with a solution or fine suspension of the impurity and then evaporating to dryness. The impure oxide was then exposed to fluorine in a muffle furnace, and the product gas was passed through a shallow bed of the sorbent.

The data indicated that seven of the eleven impurities are sorbed to a reasonable extent by one or more of the solid fluorides. Only small amounts of antimony and tungsten were sorbed. Most of the zirconium was not volatilized from the furnace, and it appeared that the tantalum, after volatilization, deposited in the equipment before reaching the sorber.

Following the screening tests, simulated process studies were made with the two types of reactors which would probably be used for fluorination of any returned materials. These were (a) a 4-inch diameter flame reactor, and (b) a 6-inch diameter fluid-bed reactor. Sorbents studied included pelleted sodium fluoride, magnesium fluoride, calcium fluoride, and aluminum fluoride.

Uranium trioxide was "spiked" with 100 ppm. of each of the desired impurities and was either fluorinated directly or converted to uranium tetrafluoride and then processed. "Spiking" was accomplished by adding a solution or suspension of the impurity to a stock batch of uranium

trioxide and agitating in a sigma blade dough mixer. The amount of impurity was sufficient to give a concentration of 10,000 ppm. After dehydration and grinding, this stock material was then dry-blended with sufficient uranium trioxide to give the desired impurity level.

The system used for the studies consisted of the fluorinator, an outlet gas filter, sorbent traps, and a desublimer to collect the uranium hexafluoride. Test runs were usually for a period of 20 to 30 hours to allow time for the required sampling and to furnish data on sorber capacity.

In most of the tests, definitive data on sorber performance were not obtained because the impurity did not reach the sorbent, apparently because of deposition in the outlet gas filter or lines. Materials with which this phenomenon was encountered included arsenic, antimony, columbium, tantalum, titanium, vanadium, and zirconium. Molybdenum and tungsten volatilized as expected, but little sorption was noted on sodium fluoride, magnesium fluoride, and calcium fluoride at 250°F. and on sodium fluoride at 750°F. Uranium hexafluoride samples taken after the sorbent traps showed quantities of chromium, cadmium, and ruthenium, but only ruthenium was found in the final product cold trap. This apparent discrepancy in results could indicate that the cold trapping conditions were not adequate to collect the chromium and cadmium compounds or possibly that the materials deposited on the cold trap walls. It is also possible that contamination was an error introduced during sampling or analysis.

In a fluid-bed test using a fluorination temperature of 950°F. and a magnesium fluoride diluent, essentially all the tantalum, titanium, and zirconium remained in the bed. Columbium apparently volatilized but then deposited in the outlet gas filter. Unexpectedly, only a small amount of the molybdenum was found in the outlet gas, indicating sorption either on the magnesium fluoride diluent or on the unreacted uranium tetrafluoride left in the bed. In contrast to the experience with the flame fluorinator, vanadium was volatilized; it was then removed by the sorbents. As expected, tungsten concentrations in the outlet gas were high, and no sorption was noted.

Since these tests indicated that most of the impurity introduced did not even reach the sorber, it might appear that application of sorption was redundant in the overall effort to achieve uranium hexafluoride purification. It should, however, be realized that these tests were relatively short term and therefore did not offer proof that, with longer operation characteristic of production system, the impurities would not break through. Additionally, other equipment might be used for the fluorination with a possible change in results. Thus, uranium hexafluoride containing substantial amounts of impurities could be received for diffusion plant feed.

Accordingly, the experimental approach was altered. A volatile fluoride of the desired impurity was vaporized into a stream of gaseous uranium hexafluoride, and the mixture was immediately passed through sorbent traps. It was found that the concentration of columbium pentafluoride in a uranium hexafluoride stream could be reduced from several hundred

parts per million to less than 1 ppm. by passing the gas through either
a 750°F. sodium fluoride trap or a 250°F. magnesium fluoride trap. The
sorptive capacities of both materials appeared high, but a low melting
compound formed with sodium fluoride and eventually plugged the trap.
Hot, 650°F., sodium fluoride pellets also effectively sorbed ruthenium
pentafluoride. Results were not so definitive, however, with titanium
tetrafluoride. The data could indicate that magnesium fluoride and
sodium fluoride sorb this fluoride but that their capacity is relatively
low when the initial concentration of the impurity is 50 to several
hundred parts per million. It also appeared that the sorption rate was
slow; thus, a long gas residence time would be required. With only a
few parts per million of the impurity in the starting material, however,
a fair capacity of these sorbents for titanium might be expected. In
fact, effectiveness of magnesium fluoride in reducing the titanium con-
centration from about 3 ppm. to less than 1 ppm. has been shown by
recovery operations at the Oak Ridge Gaseous Diffusion Plant, but the
total quantity of impurity involved was not known; therefore, trap
capacity could not be determined.

The experimental work is discussed in some detail in the following report,
and the future program is described.

EXPERIMENTAL STUDIES

Sorbent Screening Tests

The sorptive capabilities of nine metal fluoride powders were determined
by a series of bench-scale studies. In these tests, urano-uranic oxide
was "spiked" with 400 ppm. of one of the elements, arsenic, columbium,
chromium, molybdenum, ruthenium, antimony, tantalum, titanium, vanadium,
tungsten, and zirconium, by mixing with a solution or fine suspension of
the impurity and then evaporating to dryness. Compounds used included
V_2O_5, MoO_3, $SbCl_3$, As_2O_3, $Zr(OH)_4$, $RuCl_3$, TiO_2, $Cr(NO_3)_3$, Ta_2O_5, $TiO(NO_3)_2$,
KH_2AsO_4, WO_3, and Cb_2O_5. The impure oxide was then fluorinated batchwise
in a small muffle furnace, and the product gas was passed through a
shallow sorbent bed which was held at about 300°F. The uranium hexa-
fluoride was condensed in series-connected cold traps held at dry ice
temperature. Sorbent, fluorination residue (ash), and trapped uranium
hexafluoride were analyzed spectrographically.

Results of the tests are shown in table I. The ratings for the various
sorbents are based on the following criteria:

    Excellent: Greater than 75% of the impurity sorbed
    Good: 35 to 75% of the impurity sorbed
    Fair: 15 to 34% of the impurity sorbed
    Poor: Less than 15% of the impurity sorbed

An additional requirement for an Excellent rating was that the ratio of
the impurity to the uranium hexafluoride in the sorbent was at least ten
times the ratio in the feed gas stream. These required concentration

factors were greater than 5 for the Good rating and greater than 1 for
the Fair classification. If the total quantity of impurity found in the
sorbent and in the uranium hexafluoride was too small to show that an
adequate amount had reached the sorbent, the results were called
Indeterminate.

TABLE I

EFFECTIVENESS OF VARIOUS SORBENTS IN
REMOVING IMPURITIES FROM URANIUM HEXAFLUORIDE

Sorbent	As	Cb	Cr	Mo	Ru	Sb	Ta	Ti	V	W	Zr	Uranium Concentration In Exposed Sorbent, %	Initial Sorbent Surface Area, sq.m./g.
CuF_2	G	G	P	P	*	P	*	E	G	P	*	11.0	20
SrF_2	P	G	E	F	F	P	*	G	E	F	P	0.1	8
MgF_2	*	E	F	E	*	P	*	E	E	P	G	4.5	65
CaF_2	*	P	F	E	P	P	*	E	E	G	G	3.8	77
NiF_2	P	G	P	E	*	*	*	E	E	P	P	0.6	87
NaF	G	G	P	F	G	*	*	G	G	F	*	19.3	2
AlF_3	E	G	F	E	G	*	*	E	F	P	E	3.0	31
BaF_2	P	E	G	F	F	*	*	E	P	P	F	-	-
BiF_3	P	*	E	E	*	P	*	E	E	*	P	-	-
LiF	*	*	P	*	P	P	*	P	*	*	P	-	-

Legend: E - Excellent
         G - Good
         F - Fair
         P - Poor
         * - Indeterminate

The data indicate that nine of the eleven impurities are removed with
relative effectiveness by one or more sorbents. All tests gave indeter-
minate results for tantalum, and only a small amount of antimony was
sorbed. The tantalum compound probably deposited on the system walls,
although it is possible, but less likely, that it passed through the
cold trap. Similar difficulties were encountered in some of the tests
with ruthenium, antimony, and to a lesser extent, columbium and arsenic.

The uranium contents of some of the sorbents are higher than would be
expected for operation at the 300°F. temperature level. Possibly, small

amounts of water were present in the sorbents, and the uranium holdup
was caused by hydrolysis.

It should be noted that, for a sorbent material which forms a compound
with uranium hexafluoride at lower temperatures, such as sodium fluoride,
an Excellent rating was impossible at 300°F. because of the high uranium
content of the sorbent. As will be shown later, sodium fluoride is an
effective sorbent for some impurities when higher trapping temperatures,
650 to 750°F., are used. It must also be pointed out that higher tem-
peratures might also change the affinity of some sorbents for the impuri-
ties. It is obvious therefore that, to be comprehensive, a screening
study should be made at several temperature levels. The small-scale
program was, however, discontinued because it would have been necessary
to construct a much more refined experimental system to allow more
definitive results, and considerable analytical cost would also have
been involved in a multifactor small-scale program. Thus, it was felt
that more practical and significant results could be attained by use of
equipment more closely allied to that which would be employed on a pro-
duction scale.

Simulated Process Studies

Following the screening tests, simulated process studies were made in a
4-inch diameter flame reactor and in a 6-inch diameter fluid bed. Tests
were made in both types of reactors because the operating temperatures
are considerably different, and some effects on impurity removal might
be expected.

A flow sheet of the pilot-plant system is shown as figure 1. The impure
uranium compound was fluorinated in one of the reactors, and the outlet
gases passed successively through a sintered Monel filter and 3-inch
diameter, 3-foot deep pellet beds to dry ice-cooled cold traps. Two to
four different sorbents were evaluated in each run. Gas samples were
taken immediately before and after the sorbers and, in some cases, were
withdrawn between the reactor and the filter. Solid residues collected
below the reactor and in the filter were also analyzed. Because of the
large number of samples required and the difficult analytical procedure
for some of the materials, the time required to evaluate each test was
about one month.

The following procedure was used for the experimental runs. Uranium
trioxide was "spiked" with 100 ppm. of each of the desired impurities
and was either fluorinated directly or converted to uranium tetrafluoride
and then processed. "Spiking" was accomplished by adding a solution or
a suspension of the impurity to a stock batch of uranium trioxide and
agitating for about 1 hour in a sigma blade dough mixer. The amount of
impurity added was sufficient to give a concentration of 10,000 ppm.
After dehydration and grinding, this stock material was then dry-blended
with enough pure uranium trioxide to give an overall impurity concentra-
tion of 100 ppm. Analyses of final blends of oxides showed uniform dis-
tribution of the impurity. To simplify the analytical task, the con-
taminants were divided into groups. Group A included antimony, arsenic,
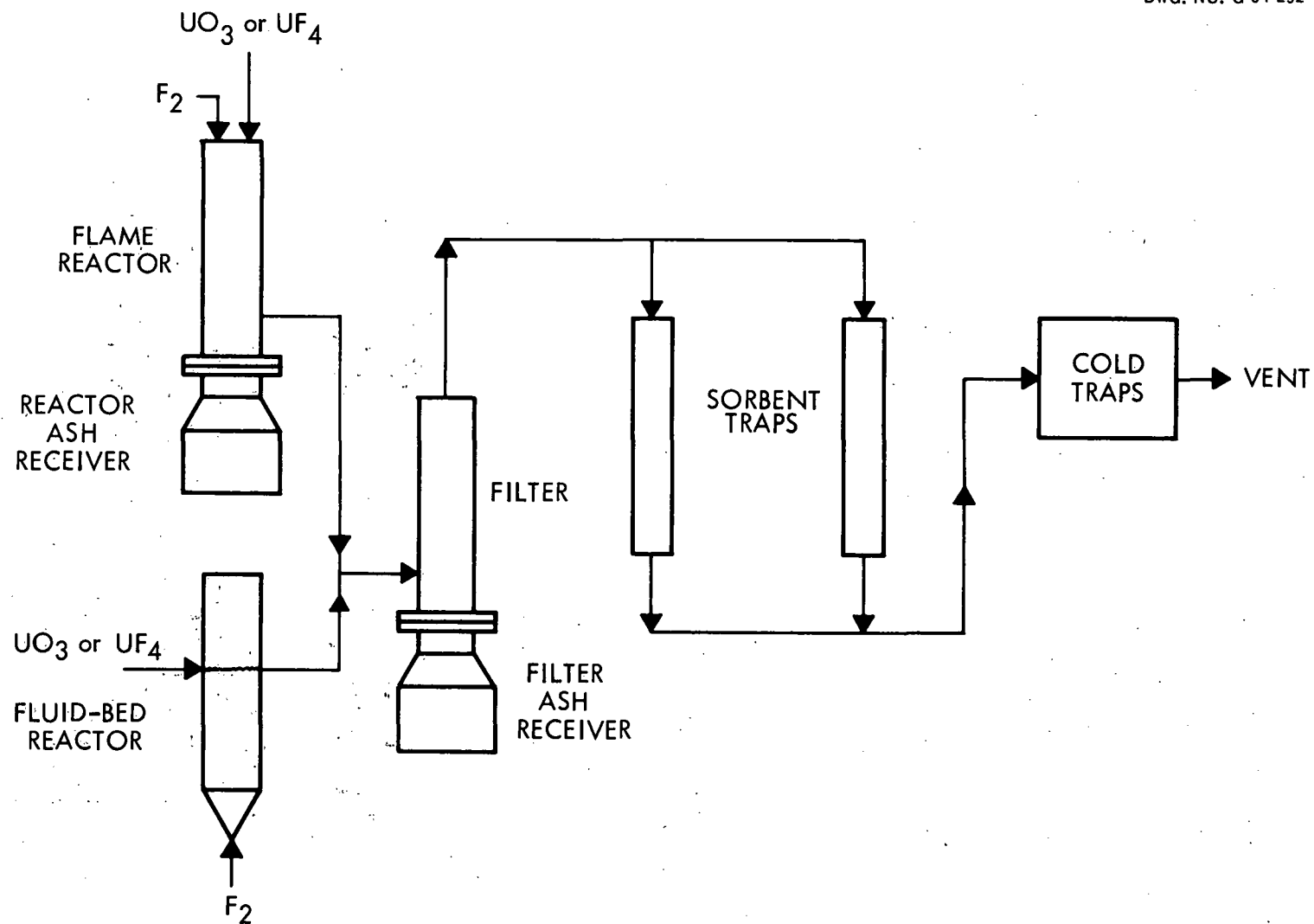
Figure 1

PILOT PLANT FLUORINATION SYSTEMS

cadmium, chromium, and ruthenium. Group B elements were titanium, tantalum, tungsten, columbium, molybdenum, vanadium, and zirconium.

The pellets described below were used for all of the sorption tests:

Sodium Fluoride. Prepared by heating commercially available 1/8-inch by 1/8-inch sodium bifluoride pellets to 1000°F. for 5 hours. The pellet surface area is less than 1 sq.m./g.

Magnesium Fluoride. Pellets produced at the Paducah Gaseous Diffusion Plant by tumbling moistened magnesium fluoride powder. These particles are 3/16 to 5/16 inch in diameter and have a surface area of about 44 sq.m./g.

Calcium Fluoride. Prepared by the reaction of dilute fluorine with Drierite. The surface area of the resulting material is about 200 sq.m./g.

Aluminum Fluoride. Formed by fluorinating activated alumina pellets. The pellet surface area is about 46 sq.m./g.

Results of the simulated process tests are summarized in tables II through VIII. As can be seen from the typical run described below, results of the tests were inconsistent for some of the impurities. In 26 hours of running time, runs A-7, A-8, and A-9, tables II, III, V, and VII, involving flame reactor fluorination of uranium trioxide containing group A impurities and using calcium fluoride and magnesium fluoride sorbents at 250°F., sample analyses were very erratic. Concentrations of chromium, cadmium, and ruthenium in the sorber inlet gas streams ranged from less than 3 ppm. to 300 ppm., less than 1 ppm. to 5 ppm., and less than 1 ppm. to 10 ppm., respectively.

Values for the same impurities in the sorber outlet samples ranged from less than 3 ppm. to 200 ppm., less than 1 ppm. to 5 ppm., and less than 1 ppm. to 10 ppm. Frequently, the sorber outlet concentrations were higher than those for the inlet. In no case did the sample analyses indicate that the impurities were leaving the reactor consistently or that the sorbents were effectively decreasing the concentrations. The other two impurities, arsenic and antimony, were not detected in any of the fifty-nine samples analyzed. A liquid sample from a cylinder which contained 500 pounds of uranium hexafluoride collected after the sorbers showed only ruthenium present with a concentration of 12 ppm.

Performance of the reactor was very good during this 26-hour series of tests; as indicated in table II, about 2% of the feed powder was collected in the ash receivers. Spectrographic analyses of the reactor and filter ash showed that 30, 58, 47, 46, and 41% of the amounts of arsenic, cadmium, chromium, ruthenium, and antimony, respectively, fed to the tower were present in the ash. In most cases of this material, at least 95% of the impurities found was in the filter ash; the remaining 5% was in the tower ash. This distribution suggests difficulty either in fluorinating the impurity or in sorption of the impurity by the fine ash in the cooler filter zone. Thus, in processing impure

TABLE II

REACTOR PERFORMANCE
SIMULATED PROCESS TESTS

Run Number	Length of Run, hr.	Feed Material	Feed Rate, lb./hr.	Ash Rate, Percent of Feed	
				Tower	Filter
A-7	4.3	UO_3	36	5.2	1.0
A-8	10.5	UO_3	29	0.3	1.0
A-9	11.0	UO_3	22	0.9	0.6
B-1	5.8	UO_3	27	1.3	Trace
B-2	5.8	UO_3	28	2.5	0.5
B-3	4.1	UO_3	28		
C-1	7.5	UO_3	27	4.4	0.1
D-1	5.1	UF_4	41	1.4	0.1
D-2	8.0	UF_4	50	5.3	0.6
D-3	9.3	UF_4	49	4.6	Trace
I-2*	12.3	80% UF_4-20% MgF_2	25		
I-3*	12.4	80% UF_4-20% MgF_2	34		

* Fluid-bed runs, bed temperature = 950°F.

TABLE III

ANALYSES OF FEED POWDERS AND FLUORINATION ASH
SIMULATED PROCESS TESTS

Material	Run Number	Impurity Concentration, ppm.				
		As	Cd	Cr	Ru	Sb
UO_3	A-7	30	150	100	85	100
UO_3	A-8, A-9	142	100	100	51	49
Tower Ash	A-7	< 100	400	< 100	< 100	< 100
Filter Ash	A-7	> 1,000	1,500	1,600	600	1,200
Tower Ash	A-8	135	1,240	210	25	460
Filter Ash	A-8	4,300	7,600	6,000	3,400	2,200
Tower Ash	A-9	< 100	600	< 20	< 20	250
Filter Ash	A-9	14,400	13,200	25,000	9,000	10,000

TABLE IV

ANALYSES OF FEED POWDERS AND FLUORINATION ASH
SIMULATED PROCESS TESTS

Material	Run Number	Impurity Concentration, ppm.						
		Cb	Mo	Ta	Ti	V	W	Zr
UO_3	B-1, B-2, B-3, C-1	50	95	40	65	125	55	30
UF_4	D-1, D-2, D-3, I-2, I-3	80	50	105	50	55	70	60
Tower Ash	B-1	< 10	30	< 10	15	50	300	200
Filter Ash	B-1	500	60	300	300	500	60	100
Tower Ash	B-2	100	NF	50	50	20	NF	500
Filter Ash	B-2	2,000	150	100	3,000	2,000	NF	1,000
Tower Ash	C-1	100	50	100	45	3	4	50
Filter Ash	C-1	100	50	100	100	100	60	500
Tower Ash	D-1	20	6	60	8	6	2	10
Filter Ash	D-1	2,500	50	10	100	5	30	50
Tower Ash	D-2	20	4	40	6	4	2	5
Filter Ash	D-2	1,500	50	15	300	10	10	50
Tower Ash	D-3	25	3	30	8	3	3	5
Filter Ash	D-3	50	100	5	200	200	2	200
Ash*	I-2	35	200	900	250	30	250	300
Ash*	I-3	300	180	400	200	50	5	60

* In a fluid bed, the ash, or overflow solids, and bed material will have the same composition.

TABLE V

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent		Impurity Concentration, ppm.				
			Material	Temperature, °F.	As	Cd	Cr	Ru	Sb
A-7	Sorber Inlet	0.5			< 10	< 1	5	< 1	< 3
		2.2			< 10	1	5	3	< 3
		3.2			< 10	2	5	7	< 3
		3.8			< 10	1	5	6	< 3
		4.2			< 10	< 1	< 3	7	< 3
A-7	No. 1 Sorber Outlet	0.5	CaF$_2$	250	< 10	5	5	7	< 3
		2.2			< 10	2	5	2	< 3
		3.2			< 10	2	5	6	< 3
		3.8			< 10	2	5	4	< 3
		4.2			< 10	< 1	5	·10	< 3
A-7	No. 2 Sorber Outlet	0.5	MgF$_2$	250	< 10	< 1	5	< 1	< 3
		2.2			< 10	1	5	< 1	< 3
		3.2			< 10	1	5	3	< 3
		3.8			< 10	2	5	5	< 3
		4.2			< 10	1	< 3	< 1	< 3

TABLE V (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temperature, °F.	Impurity Concentration, ppm. As	Cd	Cr	Ru	Sb
A-8	Sorber Inlet	2.25			< 10	1	5	< 1	< 3
		5.25			< 10	2	10	< 1	< 3
		7.25			< 10	1	11	< 1	< 3
		10.00			< 10	< 1	6	< 1	< 3
A-8	No. 1 Sorber Outlet	2.25	CaF_2	250	< 10	1	6	< 1	< 3
		5.25			< 10	1	300	< 1	< 3
		7.25			< 10	2	10	< 1	< 3
		10.00			< 10	2	10	< 1	< 3
A-8	No. 2 Sorber Outlet	2.25	MgF_2	250	< 10	< 1	45	1	< 3
		5.25			< 10	1	10	< 1	< 3
		7.25			< 10	1	6	< 1	< 3
		10.00			< 10	1	120	< 1	< 3
A-9	Sorber Inlet	1.5			< 10	1	10	1	< 3
		3.3			< 10	< 1	250	< 1	< 3
		5.0			< 10	< 1	10	< 1	< 3
		9.9			< 10	5	5	< 1	< 3

TABLE V (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temperature, °F.	Impurity Concentration, ppm.				
					As	Cd	Cr	Ru	Sb
A-9	No. 1 Sorber Outlet	1.5	CaF$_2$	250	< 10	1	5	< 1	< 3
		3.3			< 10	1	200	< 1	< 3
		5.0			< 10	< 1	5	< 1	< 3
		9.9			< 10	< 1	10	< 1	< 3
A-9	No. 2 Sorber Outlet	1.5	MgF$_2$	250	< 10	5	5	< 1	< 3
		3.3			< 10	2	10	< 1	< 3
		5.0			< 10	< 1	5	< 1	< 3
		9.9			< 10	1	10	< 1	< 3

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TABLE VI

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
B-1	Sorber Inlet	0.2			< 0.2	100	< 1	1	< 0.2	200	1
		5.3			< 0.2	50	< 1	0.5	< 0.2	50	1
B-1	No. 1 Sorber Outlet	0.2	NaF	250	< 0.2	100	< 1	0.5	< 0.2	100	1
		3.9			< 0.2	100	< 1	0.5	< 0.2	150	10
B-1	No. 2 Sorber Outlet	0.2	MgF$_2$	250	< 0.2	100	< 1	1	< 0.2	150	10
		5.3			< 0.2	100	< 1	0.5	< 0.2	100	1
B-2	Sorber Inlet	2.2			< 0.5	100	< 1	< 0.4	< 0.2	80	2
		3.1			< 0.3	100	< 1	< 0.2	< 0.2	60	6
		4.1			3	50	< 1	< 0.4	20	70	5
B-2	No. 1 Sorber Outlet	1.5	NaF	250	30	100	< 1	0.6	< 0.2	100	5
		4.1			< 0.3	100	< 1	0.4	< 0.2	60	5
B-2	No. 2 Sorber Outlet	3.1	MgF$_2$	250	1.2	80	< 1	< 0.4	10	40	2

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
B-3	Sorber Inlet	0.9			< 0.3	100	< 1	< 0.2	< 0.2	200	6
		1.9			< 0.3	90	< 1	< 0.2	0.3	70	10
		2.9			< 0.3	120	< 1	< 0.2	< 0.2	400	8
		3.9			< 0.3	120	< 1	< 0.2	0.5	80	6
B-3	No. 1 Sorber Outlet	0.9	NaF	250	< 0.3	50	< 1	< 0.2	< 0.2	200	4
		1.9			< 0.3	150	< 1	< 0.2	0.3	100	5
		2.9			< 0.3	100	< 1	< 0.2	< 0.2	80	4
		3.9			< 0.3	110	< 1	< 0.2	0.3	70	6
B-3	No. 2 Sorber Outlet	0.9	MgF_2	250	< 0.3	40	< 1	< 0.2	< 0.2	160	6
		1.9			< 0.3	15	< 1	< 0.2	< 0.2	6	6
		2.9			< 0.3	8	< 1	< 0.2	0.3	1	6
		3.9			200	120	< 1	6	< 0.2	20	NF
C-1	Sorber Inlet	0.5			< 0.3	100	< 1	5	< 0.2	120	5
		1.4			< 1	60	< 1	< 0.2	< 0.2	200	1
		2.9			< 1	30	< 1	< 0.2	< 0.2	400	2

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
C-1	Sorber Inlet	4.3			< 1	4	< 1	25	< 0.2	NF	NF
		5.8			< 0.3	20	< 1	< 0.2	< 0.2	25	NF
		6.9			< 1	80	< 1	< 0.2	< 0.2	60	1
C-1	No. 1 Sorber Outlet	0.5	CaF_2-MgF_2	750	< 1	8	< 1	< 0.2	< 0.2	5	NF
		1.4			< 1	60	1	< 0.2	0.5	130	NF
		2.9			< 0.3	100	< 1	< 0.2	< 0.2	70	NF
		4.3			100	5	10	6	< 0.2	50	5
		5.8			10	100	< 1	< 0.2	< 0.2	15	NF
		6.9			< 1	60	< 1	1.5	< 0.2	200	5
C-1	No. 2 Sorber Outlet	0.5	NaF	750	< 10	100	< 1	0.8	10	70	NF
		1.4			2	20	< 1	< 0.2	5	150	1
		2.9			1.5	100	< 1	< 0.2	< 0.2	200	2
		4.3			< 1	60	< 1	10	< 0.2	> 500	5
		5.8			< 0.3	60	< 1	< 0.2	3	25	NF
		6.9			60	60	1	< 0.2	< 0.2	80	2

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
D-1	Sorber Inlet	0.3			15	> 200	< 2	< 1	50	200	2
		1.9			3.5	30	< 2	< 1	< 0.2	150	2
		3.4			3	65	< 2	< 1	50	50	2
		4.9			80	65	< 2	< 1	< 1	200	15
D-1	No. 1 Sorber Outlet	0.3	NaF	250	8	30	< 2	< 1	< 0.2	150	2
		1.9			11	30	< 2	2.0	< 0.2	180	2
		3.4			2	50	< 2	4	45	100	10
		4.9			2	50	< 2	4	45	100	5
D-1	No. 2 Sorber Outlet	0.3	MgF_2-CaF_2	250	2	60	< 2	< 1	45	200	5
		1.9			2	25	< 2	< 1	15	200	4
		3.4			2	20	< 2	< 1	< 0.2	15	2
		4.9			60	30	< 2	< 1	< 1	100	5
D-2	Sorber Inlet	0.6			4.0	40	< 1	0.5	< 0.2	140	10
		7.6			< 0.3	40	< 1	0.8	< 0.2	100	2

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
D-2	No. 1 Sorber Outlet	0.6	NaF	250	2.0	40	< 1	0.6	0.6	80	2
		3.3			1.5	20	< 1	0.5	5	60	10
		6.9			50	10	< 1	0.4	5	30	1
D-2	No. 2 Sorber Outlet	5.8	MgF_2-CaF_2	250	15	20	< 1	0.5	7		30	10
D-3	Tower Outlet	3.0			1.8	15	< 1	0.2	12	600	4
		5.1			12.0	20	5	0.8	15	200	2
		8.5			1.0	20	< 1	0.4	15	300	4
D-3	Sorber Inlet	1.1			4.5	20	< 1	0.3	20	60	2
		3.1			5.0	20	< 1	0.4	19	40	4
		5.1			2.0	20	< 1	0.8	20	60	4
		7.6			5.0	30	< 1	0.4	20	7	2
		9.0			2.5	20	< 1	0.3	9	30	2
D-3	No. 1 Sorber Outlet	1.1	NaF	250	8.0	20	< 1	< 0.2	20	25	2
		3.1			8.0	20	< 1	< 0.2	18	60	4

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
D-3	No. 1 Sorber Outlet	5.1			2.0	40	< 1	0.6	18	70	6
		7.6			7.0	20	< 1	< 0.2	16	80	2
		9.0			1.5	20	< 1	0.5	14	80	4
D-3	No. 2 Sorber Outlet	3.1	MgF$_2$-CaF$_2$	250	1.5	20	< 1	< 0.2	< 0.2	14	2
		5.1			1.5	11	< 1	< 0.2	< 0.2	10	5
		7.6			< 0.3	20	< 1	< 0.2	2	20	2
I-2	Reactor Outlet	2.0			2	2	< 1	< 0.2	6	150	1
		3.0			15	10	< 1	2.0	50	400	2
		5.0			20	4	< 1	0.8	4	> 500	2
		7.0			2	4	< 1	0.4	2	250	2
		8.0			5	2	< 1	0.8	15	200	1
		11.0			2	2	< 1	0.4	10	8,000	2
I-2	Sorber Inlet	2.0			15	10	< 1	0.3	50	400	2
		3.0			< 0.3	< 0.2	< 1	0.5	0.2	> 500	2
		5.0			< 0.3	10	< 1	0.5	10	300	2

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
I-2	Sorber Inlet	8.0			4.5	5	< 2	4	7.5	5,000	1
I-2	No. 1 Sorber Outlet	2.0	NaF-MgF$_2$	250	< 0.3	4	< 1	0.4	0.2	250	2
		3.0			< 0.3	4	< 1	0.4	< 0.2	300	2
		5.0			< 0.3	0.8	< 1	0.4	< 0.2	> 1,000	2
		8.0			12	12	< 8	25	20	9,000	20
		11.0			0.8	1	< 1	0.4	< 0.2	550	2
I-2	No. 2 Sorber Outlet	2.0	CaF$_2$-AlF$_3$	250	< 0.3	2	< 1	0.8	< 0.2	> 500	2
		3.0			< 0.3	2	< 1	0.8	< 0.2	400	1
		5.0			< 0.3	2	< 1	0.5	< 0.2	350	1
		8.0			< 0.3	2	< 1	0.6	< 0.2	> 1,000	2
		11.0			< 0.3	0.6	< 1	2.5	< 0.2	1,800	2
I-3	Reactor Outlet	1.7			6	20	< 1	1	24	400	2
		4.0			2.5	2	4	1	10	800	2
		5.0			20	6	< 1	1	2	200	2
		7.5			3.5	2	< 1	1	10	160	1
		11.9			2.5	6	< 1	1	10	1,000	4

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
I-3	Sorber Inlet	2.5			< 0.3	10	< 1	0.2	< 0.2	3	1
		3.5			1.5	20	< 1	1	6	400	2
		4.7			0.8	10	< 1	1	2	100	2
		5.7			20	20	< 1	1	20	100	1
		7.0			< 0.3	10	< 1	0.6	20	150	1
		8.0			50	20	< 1	1	20	100	1
		11.9			0.8	2	< 1	1	2	1,000	1
I-3	No. 1 Sorber Outlet	2.5	$NaF-MgF_2$	250	2	20	< 1	1	10	20	1
		3.5			4	15	< 1	1	14	150	2
		4.7			0.3	4	< 1	1	0.8	150	1
		5.7			0.3	1	< 1	0.2	2	70	10
		7.0			0.3	2	< 1	1	1	250	1
		8.0			0.3	2	< 1	1	1	150	1
		11.9			< 0.3	4	2	3	< 0.2	1,200	1
I-3	No. 2 Sorber Outlet	2.5	CaF_2-AlF_3	250	< 0.3	0.5	< 1	0.6	0.3	100	10
		3.6			< 0.3	0.5	< 1	1	1	150	4

TABLE VI (Contd.)

ANALYSES OF GAS SAMPLES
SIMULATED PROCESS TESTS

Run Number	Sample	Onstream Time, hr.	Sorbent Material	Temp., °F.	Impurity Concentration, ppm.						
					Cb	Mo	Ta	Ti	V	W	Zr
I-3	No. 2 Sorber Outlet	4.7			0.3	2	< 1	1.5	0.5	450	2
		5.7			< 0.3	3	2	3	< 0.2	800	1
		7.0			0.3	1	< 1	0.7	0.3	10	1
		8.0			0.3	1	< 1	0.3	0.3	150	2
		11.9			5.5	6	< 1	0.6	20	300	4

TABLE VII

SORBENT ANALYSES
SIMULATED PROCESS TESTS

Sorbent	Bed Segment, in.	Impurity Concentration, ppm.				
		As	Cd	Cr	Ru	Sb
		Runs A-7, A-8, A-9				
CaF_2	0 - 6	< 100	< 100	840	140	< 20
	6 - 13	< 100	< 100	150	< 20	< 20
	13 - 18	< 100	< 100	< 20	< 20	< 20
	18 - 24	< 100	< 100	< 20	< 20	< 20
	24 - 30	< 100	< 100	< 20	< 20	< 20
MgF_2	0 - 6	< 100	< 100	760	< 20	< 20
	6 - 12	< 100	< 100	560	< 20	< 20
	12 - 18	< 100	< 100	340	< 20	< 20
	18 - 24	< 100	< 100	300	< 20	< 20
	24 - 30	< 100	< 100	130	< 20	< 20
	30 - 36	< 100	< 100	100	< 20	< 20

TABLE VIII

SORBENT ANALYSES
SIMULATED PROCESS TESTS

Sorbent	Bed Segment, in.	Impurity Concentration, ppm.						
		Cb	Mo	Ta	Ti	V	W	Zr
		Runs B-1, B-2, B-3						
MgF_2	0 - 6	10	100	NF	10	100	200	30
	6 - 12	15	25	NF	20	90	200	20
	12 - 18	10	25	NF	20	60	300	10
	18 - 24	15	30	NF	15	50	300	30
	24 - 30	30	30	NF	10	25	230	30
	30 - 36	30	45	NF	15	20	250	30
NaF	0 - 6	10	40	NF	2	100	30	NF
	6 - 12	10	25	NF	3	100	70	5
	12 - 18	10	30	NF	2	100	30	10
	18 - 24	10	30	NF	2	90	30	10
	24 - 30	5	25	NF	2	75	200	5
	30 - 36	10	30	NF	2	90	350	10
		Run C-1						
NaF	0 - 6	3	5	2	5	800	5	NF
	6 - 12	10	5	3	2	40	3	5
	12 - 18	11	5	NF	15	4	2	NF
	18 - 24	9	5	10	40	4	6	NF
	24 - 30	8	5	7	13	4	5	NF
	30 - 36	4	5	3	1	3	4	10
CaF_2	0 - 6	70	10	NF	10	500	5	5
	6 - 12	50	10	3	10	100	5	5
	12 - 18	50	10	3	10	100	5	5
MgF_2	18 - 24	8	10	6	10	14	6	NF
	24 - 30	11	5	2	30	55	4	10

TABLE VIII (Contd.)

SORBENT ANALYSES
SIMULATED PROCESS TESTS

Sorbent	Bed Segment, in.	Impurity Concentration, ppm.						
		Cb	Mo	Ta	Ti	V	W	Zr
MgF_2	30 - 36	10	5	NF	15	30	4	10

Runs D-1, D-2, D-3

Sorbent	Bed Segment, in.	Cb	Mo	Ta	Ti	V	W	Zr
MgF_2	0 - 7	< 0.3	20	NF	< 0.2	200	4	2
CaF_2	7 - 12	< 0.3	20	NF	< 0.2	200	2	2
CaF_2	12 - 18	< 0.3	20	NF	6	200	5	2
CaF_2	18 - 24	< 0.3	40	NF	8	200	10	2
CaF_2	24 - 30	< 0.3	40	NF	8	200	15	2
CaF_2	30 - 36	< 0.3	40	NF	8	200	10	2
NaF	0 - 6	< 0.3	6	NF	< 0.2	200	1	2
	6 - 12	< 0.3	30	NF	0.5	950	50	100
	12 - 18	< 0.3	20	NF	0.5	850	50	10
	18 - 24	< 0.3	30	NF	0.5	950	50	10
	24 - 30	< 0.3	10	NF	0.5	100	20	2
	30 - 36	< 0.3	10	NF	0.5	100	10	4

Runs I-1, I-2

Sorbent	Bed Segment, in.	Cb	Mo	Ta	Ti	V	W	Zr
MgF_2	0 - 6	180	650	NF	30	300	800	10
MgF_2	6 - 12	160	500	NF	10	250	700	5
MgF_2	12 - 18	100	350	NF	40	150	800	10
MgF_2	18 - 24	10	30	NF	20	10	800	10
NaF	24 - 30	2	15	NF	15	5	400	10
NaF	30 - 36	10	10	NF	15	10	200	10
AlF_3	0 - 6	10	70	NF	30	10	200	10
AlF_3	6 - 12	5	40	NF	10	5	100	10
AlF_3	12 - 18	40	200	NF	35	50	300	15

TABLE VIII (Contd.)

SORBENT ANALYSES
SIMULATED PROCESS TESTS

Sorbent	Bed Sorbent, in.	Impurity Concentration, ppm.						
		Cb	Mo	Ta	Ti	V	W	Zr
CaF$_2$	18 - 24	160	600	NF	20	250	900	10
CaF$_2$	24 - 30	30	150	NF	35	50	300	10
CaF$_2$	30 - 36	2	40	NF	50	5	700	10

returns containing the above impurities, some significant purification should be achievable immediately by the ash collection part of the fluorination system.

After approximately 860 pounds of uranium hexafluoride had been passed through each sorber (runs A-7, A-8, and A-9) at an average rate of 33 pounds of uranium hexafluoride per hour, the pellet beds were separated into 6-inch long segments, and each part was analyzed spectrographically. The analytical results showed that ruthenium, at a concentration of 140 ppm., was present only in the top (inlet) section of the calcium fluoride trap and not at all in the magnesium fluoride. Chromium was present in concentrations of 840 and 150 ppm. in the two top segments of the calcium fluoride and was present throughout the magnesium fluoride, ranging in concentration from 760 ppm. at the top to 100 ppm. at the bottom of the bed. The other elements, cadmium, arsenic, and antimony, were not detected.

It is difficult to interpret some of the data from the test. Obviously, a large percentage of the impurities was not converted to a volatile fluoride; moreover, a substantial amount of the impurities fed could not be accounted for by sample results. Product uranium hexafluoride samples taken after the sorbent traps showed detectable and quite variable quantities of chromium, cadmium, and ruthenium, but only ruthenium was found in the final product cold trap, possibly indicating that the fluorides or oxyfluorides of chromium and cadmium formed are more volatile than expected and were not condensed in the dry ice-cooled trap. Sampling problems are also a possible explanation. It appeared quite definite that no arsenic or antimony was leaving the reactor system; thus, sorption would be expected to be an effective method of removing these impurities from the fluorination product of impure returns.

In additional flame fluorination runs with both uranium trioxide and uranium tetrafluoride "spiked" with group B materials (runs B-1, B-2, B-3; C-1; and D-1, D-2, D-3), tables II, IV, and VIII, most of each impurity was converted to a volatile form, based on analyses of the unreacted ash. The columbium, tantalum, titanium, and vanadium, however, apparently deposited in the tower outlet system and did not reach the sorbent traps in detectable quantities. Also, only small amounts of zirconium, about 5 ppm., were observed at the trap inlet. Molybdenum and tungsten inlet concentrations were as high as expected, but little sorption was noted on sodium fluoride, magnesium fluoride, and calcium fluoride at 250°F. and on sodium fluoride at 750°F.

In fluid-bed tests, runs I-2 and I-3, tables II, IV, VI, and VIII, uranium tetrafluoride containing about 70 ppm. each of the group B elements was premixed with 20% ground magnesium fluoride bomb slag and was fed into a fluidized bed of the same type magnesium fluoride. The bed temperature was held at 950°F., the fluidizing velocity was 0.7 foot per second, and the inlet fluorine concentration was 30%. The outlet gases were passed through two sorbent traps, each of which contained 18-inch deep beds of two different sorbents. Sodium fluoride and magnesium fluoride pellets were in one trap, while the other had calcium

fluoride and aluminum fluoride.

Columbium concentrations of 2 to 20 ppm. were noted in samples taken between the reactor and the filter, but essentially none of this material remained in the gas after passing through the filtering system.

The molybdenum content of the reactor outlet uranium hexafluoride was about 4 ppm., and no sorptive effect was noted with any of the trapping materials. This low value of molybdenum in the fluorination product was unexpected and might be explained by the fact that either the magnesium fluoride diluent or the small amount of unreacted uranium tetrafluoride remaining in the bed is an effective molybdenum sorbent at 950°F.

The vanadium concentration at the reactor outlet ranged from 2 to 50 ppm. and averaged about 15 ppm. Most of this impurity apparently reached the sorbent traps where it was reduced to less than 1 ppm.

Tungsten concentrations were up to 1,200 ppm. in the reactor outlet gas, indicating that the system was still contaminated from earlier runs made to study the fluid-bed fluorination of tungsten powder. No effective trapping was noted with any of the four sorbents.

With respect to the remaining impurities, none of the tantalum and very little of the titanium and zirconium appeared in the off-gas; titanium and zirconium concentrations were 0.2 to 3.0 ppm. and 1 to 10 ppm., respectively, at all the gas sampling points. The fact that no significant amounts of any of these three materials left the bed is not surprising, since magnesium fluoride could have been an effective sorbent.

Studies with "Spiked" Uranium Hexafluoride

In view of the inconclusive results of the simulated process tests, it was decided to introduce the impurity to the uranium hexafluoride stream directly before the sorbent traps, thus minimizing the possibility of deposition in the lines. A nitrogen stream containing the impurity as a volatile fluoride is injected into a stream of gaseous uranium hexafluoride and fluorine, and the mixture is passed through the sorbent. Sorption efficiency is based on the impurity content of condensed samples taken before and after the trap. To date, the effectiveness of magnesium and sodium fluorides in removing columbium pentafluoride, ruthenium pentafluoride, and titanium tetrafluoride has been evaluated.

Sorption of Columbium Pentafluoride by Sodium Fluoride. Two sorption studies, table IX, were made with sodium fluoride pellets. In test 1, the system was operated for 23.7 hours with uranium hexafluoride, fluorine, and columbium pentafluoride rates of 21, 1.5, and 0.0232 pound per hour, respectively, a trap temperature of 750°F., and a trap charge of 13 pounds of sodium fluoride pellets. A total of 498 pounds of uranium hexafluoride containing 0.55 pound of columbium pentafluoride was passed through the trap. Analyses of samples of the condensables showed average values of 410 ppm. of columbium in the trap inlet and 0.5 ppm. in the outlet. Flow rates for the second run were 17.4, 1.5, and 0.0082 pound per hour,

TABLE IX

SORPTION OF COLUMBIUM PENTAFLUORIDE BY
750°F. SODIUM FLUORIDE PELLETS

Run Number	Onstream Time, hr.	UF$_6$ Rate, lb./hr.	Inlet Columbium, ppm.	Outlet Columbium, ppm.	Sorbent Analyses		Uranium, %
					Bed Segment, in.	Columbium	
Sorbent: 36-Inch Deep Bed of Sodium Fluoride Pellets (13 Pounds)							
1	1.1	21.0	130	0.3	0 - 2	11.7%	0.01
	3.1	21.0	865	0.4	2 - 4	8.3%	0.08
	21.1	21.0	315	0.7	24 - 30	35 ppm.	0.04
	23.1	21.0	505	0.7			
	26.9	21.0	230	0.4			
Sorbent: 36-Inch Deep Bed of Sodium Fluoride Pellets (13 Pounds)							
2	2.4	17.4	300	0.5	0 - 2	14.5%	0.01
	5.4	17.4	390	1.5	2 - 4	8.3%	0.05
	37.7	17.4	260	0.9	24 - 30	275 ppm.	0.01
	41.7	17.4	430	2.0			

respectively, and the trap charge and temperature were the same as for run 1. The test was terminated after 42 hours when the sorber plugged. A total of 731 pounds of uranium hexafluoride containing 0.34 pound of columbium pentafluoride was fed. Average inlet and outlet columbium concentrations were 345 and 1.2 ppm., respectively.

Inspection of the trap revealed that a solid cake had formed in the first 2 inches of the bed. Analyses showed that this portion of the bed contained 14.5% columbium. As can be seen from the data in table IX, the columbium content of the sorbent near the trap outlet was only 35 ppm. in one case and 275 ppm. in the other. Based on a large number of analyses of sodium fluoride beds in uranium hexafluoride service, the sorbent should contain about 0.05% uranium.

It was apparent that sodium fluoride is a very good sorbent for columbium pentafluoride. The 1/8-inch pellets used in the tests would probably be quite satisfactory for recovery operations involving impurity concentrations considerably less than 300 ppm. For the higher concentrations, use of larger or diluted pellets at the trap inlet might be desirable.

Sorption of Columbium Pentafluoride by Magnesium Fluoride. Results of the two sorption tests made with magnesium fluoride are shown in table X. In the first test, the system was operated for 84 hours with a uranium hexafluoride rate of 19.2 pounds per hour, a fluorine rate of 1.5 pounds per hour, a columbium pentafluoride rate of 0.015 pound per hour, a trap temperature of 250°F., and a charge of 8.4 pounds of magnesium fluoride pellets. A total of 1,613 pounds of uranium hexafluoride containing 1.25 pounds of columbium pentafluoride was fed. The average inlet concentration was 294 ppm. of columbium. Outlet columbium concentrations ranged from 0.4 to 1.5 ppm. and averaged 0.8 ppm. No trend of concentration with time of operation was noted. Examination of the pellets showed no evidence of caking. Analyses showed a pellet uranium content of 0.2% and a surprisingly high columbium content of 2.4% at the outlet of the trap.

In an attempt to determine the sorbent capacity in a reasonable operating time, a second test was made under nearly similar conditions but with a trap charge of only 2.9 pounds of pellets. The uranium hexafluoride feed rate was 20 pounds per hour, and the inlet columbium concentration averaged about 500 ppm. As can be seen from the outlet concentrations, breakthrough occurred some time after 12.5 hours and before 18.5 hours. The outlet gas columbium concentrations during the first 12.5 hours averaged slightly higher than the 1 ppm. noted in the earlier test, possibly because of insufficient contact time or short circuiting of gas through the shallow bed. It is interesting that, after breakthrough, the bed continued to sorb more than one-half the columbium pentafluoride for the remainder of the 59-hour run. Columbium concentrations in the pellets were comparable to those for the first run.

Sorption of Ruthenium Pentafluoride by Sodium Fluoride. In a single test, table XI, a gas mixture with target rates of 21 pounds of uranium hexafluoride per hour, 1.5 pounds of fluorine per hour, 0.013 pound of

TABLE X

SORPTION OF COLUMBIUM PENTAFLUORIDE BY
250°F. MAGNESIUM FLUORIDE PELLETS

Run Number	Onstream Time, hr.	UF$_6$ Rate, lb./hr.	Inlet Columbium, ppm.	Outlet Columbium, ppm.	Sorbent Analyses		
					Bed Segment, in.	Columbium, %	Uranium, %
Sorbent: 36-Inch Deep Bed of Magnesium Fluoride Pellets (8.4 Pounds)							
3	0.6	19.2	305	0.4	0 - 2	8.4	0.26
	5.7	19.2	280	0.5	2 - 8	6.4	0.14
	41.7	19.2	440	1.0	18 - 24	4.0	0.03
	77.7	19.2	240	0.5	30 - 36	2.4	0.23
	83.7	19.2	205	1.5			
Sorbent: 12-Inch Deep Bed of Magnesium Fluoride Pellets (2.9 Pounds)							
4	0.5	20.0	210	2.0	0 - 2.4	6.2	0.04
	6.5	20.0	420	2.4	2.4 - 5.0	6.2	0.04
	12.5	20.0	14	0.4	5.0 - 7.2	5.5	0.03
	18.5	20.0	580	315	7.2 - 10.3	4.9	0.04
	24.8	20.0	560	166	10.3 - 12.0	4.6	0.04
	30.8	20.0	800	150			
	52.8	20.0	560	230			
	58.8	20.0	500	230			

TABLE XI

SORPTION OF RUTHENIUM PENTAFLUORIDE BY
650°F. SODIUM FLUORIDE PELLETS

Run Number	Onstream Time, hr.	UF_6 Rate, lb./hr.	Inlet Ruthenium, ppm.	Outlet Ruthenium, ppm.
Sorbent:	36-Inch Deep Bed of Sodium Fluoride Pellets (9.9 Pounds)			
5	0.5	21.0	190	< 2
	6.4	21.0	250	< 2
	17.7	21.0	220	< 2
	19.7	21.0	210	< 2
	21.2	21.0	420	< 2
	25.7	21.0	310	70
	29.7	21.0	220	35
	37.7	21.0	200	55
	49.7	21.0	240	130

ruthenium pentafluoride per hour, and 0.23 std.cfm. of nitrogen was passed through a charge of 9.9 pounds of sodium fluoride pellets held at 650°F. Based on weights, a total of 1,044 pounds of uranium hexafluoride containing 366 grams of ruthenium pentafluoride was fed.

Analyses of samples of the condensables showed an average of 250 ppm. of ruthenium in the trap inlet gas. Excellent removal of the impurity was achieved during the first 21 hours of the run; trap outlet gas samples contained less than 2 ppm. ruthenium. The sample taken after 26 hours contained 70 ppm. ruthenium, thus showing that breakthrough occurred some time after 21 hours and before 26 hours.

Reliable ruthenium contents of solid sorbent samples were not obtained because of sampling problems. A volatile ruthenium compound formed when the sorbent was exposed to air, and much of the material was lost.

Sorption of Titanium Tetrafluoride by Magnesium Fluoride and Sodium Fluoride. Three tests were made to determine the effectiveness of 250°F. magnesium fluoride in sorbing titanium tetrafluoride, table XII. A single test was also made with 650°F. sodium fluoride, table XIII. Uranium hexafluoride feed rates were about 20 pounds per hour, and the inlet titanium concentrations ranged from a nominal 50 to several hundred parts per million.

In the magnesium fluoride runs, there was little apparent sorption except possibly during the first several hours of the run. In the first run, number 6, no reduction in the titanium concentration was noted in any of the sample pairs, but in runs 7 and 8, the initial sample pairs indicated reductions from about 50 to 10 ppm. No further sorption was observed during the remainder of the runs. Titanium contents of the magnesium fluoride pellets were much higher than would be predicted by the gas analyses, thus indicating some sampling or analytical problems.

In the hot sodium fluoride run, run 9, the initial sample pair taken after 1.9 hours of operation showed a decrease from 590 to 15 ppm. of titanium. Outlet concentrations for the remainder of the 50.9-hour run averaged slightly above 100 ppm. and, in all cases, indicated that about one-half the titanium was being sorbed. Concentrations of titanium in the sodium fluoride pellets were on the order predicted by the gas analyses.

TABLE XII

SORPTION OF TITANIUM TETRAFLUORIDE BY
250°F. MAGNESIUM FLUORIDE PELLETS

Run Number	Onstream Time, hr.	UF$_6$ Rate, lb./hr.	Inlet Titanium, ppm.	Outlet Titanium, ppm.	Sorbent Analyses Bed Segment, in.	Titanium, %	Uranium, %
Sorbent: 12-Inch Deep Bed of Magnesium Fluoride Pellets (2.9 Pounds)							
6	2.4	20.0	38	59	0 - 2.2	0.93	0.15
	3.4	20.0	50	62	2.2 - 4.9	0.95	0.34
	6.7	20.0	67	101	4.9 - 6.9	1.02	0.28
	8.1	20.0	51	37	6.9 - 9.3	1.24	0.67
	9.1	20.0	73	54	9.3 - 12.0	1.57	1.17
	10.1	20.0	70	33			
Sorbent: 36-Inch Deep Bed of Magnesium Fluoride Pellets (7.8 Pounds)							
7	2.5	22.7	44	11	0 - 4.7	7.6	0.17
	6.8	22.7	37	67	4.7 - 11.7	5.5	0.15
	8.8	22.7	106	58	11.7 - 17.5	4.4	0.10
	12.8	22.7	80	121	17.5 - 22.6	3.5	0.38
	15.9	22.7	98	79	22.6 - 27.7	3.7	0.54
	18.1	22.7	46	30	27.7 - 36.0	3.3	0.63

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TABLE XII (Contd.)

SORPTION OF TITANIUM TETRAFLUORIDE BY
250°F. MAGNESIUM FLUORIDE PELLETS

Run Number	Onstream Time, hr.	UF$_6$ Rate, lb./hr.	Inlet Titanium, ppm.	Outlet Titanium, ppm.	Sorbent Analyses		
					Bed Segment, in.	Titanium, %	Uranium, %
8	0.5	20.5	76	10	0 – 7.0	1.7	2.3
	6.0	20.5	12	10	7.0 – 14.3	1.6	2.6
	12.0	20.5	76	23	14.3 – 19.9	1.6	2.9
	18.0	20.5	420	240	19.9 – 24.3	1.4	2.9
	20.0	20.5	580	17	24.3 – 30.6	1.4	3.1
	23.0	20.5	10	295	30.6 – 36.0	1.9	2.9
	26.0	20.5	199	330			
	30.0	20.5	136	28			
	34.0	20.5	13	159			
	38.0	20.5	271	277			
	42.0	20.5	160	123			

Sorbent: 36-Inch Deep Bed of Magnesium Fluoride Pellets (7.9 Pounds)

TABLE XIII

SORPTION OF TITANIUM TETRAFLUORIDE BY
650°F. SODIUM FLUORIDE PELLETS

Run Number	Onstream Time, hr.	UF$_6$ Rate, lb./hr.	Inlet Titanium, ppm.	Outlet Titanium, ppm.	Sorbent Analyses		
					Bed Segment, in.	Titanium, %	Uranium, %
	Sorbent:	36-Inch Deep Bed of Sodium Fluoride Pellets (9.8 Pounds)					
9	1.9	19.9	590	15	0 - 6.0	1.05	0.002
	3.9	19.9	370	141	6.0 - 11.9	1.46	0.003
	9.9	19.9	535	127	11.9 - 16.1	2.89	0.003
	15.9	19.9	320	167	16.1 - 20.5	1.91	0.004
	21.9	19.9	172	97	20.5 - 26.6	0.94	
	24.9	19.9	360	150	26.6 - 36.0	0.46	
	34.9	19.9	213	126			
	50.9	19.9	248	68			

DISCUSSION

For the intended application of selective sorption, it is obvious that a simulated process test is the desirable evaluation method. It is very important that actual processing conditions be duplicated as nearly as possible because the volatility of the impurity will be dependent on the compound formed. For example, in some cases, oxyfluorides, instead of fluorides, might result. Of course, the fluorinated product might also be dependent on the chemical form of the impurity in the oxide. Investigation of this latter factor is not felt practicable in view of the numerous possible ways of contaminating uranium returns; however, it must be kept in mind that each returned lot might present different problems.

The results of the tests in the flame and fluid-bed reactors were inconclusive with respect to the capabilities of the various sorbents. The data do, however, point out that some impurities are converted to volatile fluorides which deposit in the fluorinator outlet lines or filter before reaching the sorber. With continued operation under such conditions, the system might become saturated with these impurities, and eventually, carryover into the uranium hexafluoride product might occur. Since the impurities appeared to be sorbed very easily, probably several of the metal fluorides tested would be effective strippers.

It should be pointed out that the results of the simulated process tests are contradictory in some aspects to those obtained in the screening tests. For example, titanium and columbium were apparently volatilized in the small-scale tests and reached the sorbent. Also, the sorbents seemed more effective in the screening tests than in the larger scale tests. Several attempts have been made recently to confirm the screening results with titanium; however, as in the simulated process tests, this impurity could not be detected in the uranium hexafluoride produced by fluorinating impure uranium trioxide in a static bed. The reason for the discrepancy is not clear at this time.

In the tests in which specific compounds of the undesirable elements were mixed directly with the uranium hexafluoride, sorption of columbium pentafluoride and ruthenium pentafluoride was apparently quite effective. Removal of titanium tetrafluoride was incomplete under the conditions tested; however, there is evidence from routine reprocessing of slightly contaminated material in the Oak Ridge Gaseous Diffusion Plant recovery facilities that uranium hexafluoride meeting the 1 ppm. titanium specification can be produced if a magnesium fluoride trap is installed in the fluorinator outlet gas line. The titanium level in the starting material was estimated to be on the order of 2 to 3 ppm. Based on the experimental studies, sodium fluoride would be expected to be a better sorbent than magnesium fluoride. In view of the probable low level of this impurity in uranium returns, the quantities of titanium removed by both sorbents may be adequate.

It is planned to continue the sorption studies to investigate stripping of antimony and tantalum fluorides. Some additional work will also be

done with titanium and ruthenium. It appears especially important with titanium to obtain sorption data for very low concentrations of the impurity. Use of solid sorbents other than magnesium fluoride and sodium fluoride will also be initiated if these two materials prove unsatisfactory in any case.

As the information in the body of the report shows, encouraging results have been obtained in the tests with "spiked" uranium hexafluoride. In order to extend the sorption data further and to provide important new information, it would be necessary to operate fluorination recovery facilities on returns high in impurities; e.g., columbium and titanium. With such feed materials, it should be possible to determine the distribution of impurities in both the uranium recovery and product purification systems.

Information on sorption of other impurities expected in spent nuclear fuels, such as neptunium, should become available from studies currently under way at the National Laboratories. It has already been demonstrated by recovery operations in the Paducah feed plant that technetium is sorbed by magnesium fluoride. Additional data on impurities will probably be obtained in the studies being made jointly by the National Laboratories and the Oak Ridge Gaseous Diffusion Plant on the fluoride volatility methods of reprocessing spent power reactor fuels.