PR. 304

K-1775

REMOVAL OF IMPURITIES FROM URANIUM HEXAFLUORIDE
BY SELECTIVE SORPTION TECHNIQUES:
THIRD PROGRESS SUMMARY REPORT

M. J. Stephenson
J. H. Pashley

UNION
CARBIDE

OAK RIDGE GASEOUS DIFFUSION PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT Contract W-7405 eng 26*

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$4.00; Microfiche \$0.95

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Date of Issue: August 29, 1973

Report Number: K-1775

Subject Category: UC-10, Chemical
Separations Processes
for Plutonium and
Uranium

REMOVAL OF IMPURITIES FROM URANIUM HEXAFLUORIDE
BY SELECTIVE SORPTION TECHNIQUES:
THIRD PROGRESS SUMMARY REPORT

M. J. Stephenson

J. H. Pashley

Materials and Systems Development Department
Gaseous Diffusion Development Division

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

Prepared for the U. S. Atomic Energy Commission
Under U. S. Government Contract W-7405 eng 26

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

24

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

A B S T R A C T

The U. S. Atomic Energy Commission has placed limits on the types and amounts of various impurities permitted in uranium hexafluoride fed to its various gaseous diffusion complexes. To aid in providing industry with the required technology to meet these specifications, an experimental program is being conducted at the Oak Ridge Gaseous Diffusion Plant to evaluate the effectiveness of various solid sorbent materials for selectively removing certain volatile impurities from uranium hexafluoride. The basic testing procedure involves preparing a uranium hexafluoride feed containing some trace quantity of volatile impurity and subsequently passing this feed through a fixed bed of the test sorbent maintained at a selected temperature, and then obtaining representative samples of the contaminated uranium hexafluoride stream entering and leaving the sorption trap at various time intervals during the course of the run. Sorption tests using uranium hexafluoride-impurity fluoride gas mixtures have demonstrated the feasibility of using the selective sorption technique for the effective and economic purification of uranium. Recent tests, described in this report, showed that at 250°F aluminum fluoride, cryolite, sodium fluosilicate, lithium fluoride, and nickel fluoride selectively sorb niobium pentafluoride and titanium tetrafluoride, as well as magnesium fluoride had in earlier tests, and that the 1 ppm specification limit for niobium can be met using one or more of these new sorbents. It was also found that at 180° to 250°F, cryolite and sodium fluosilicate selectively sorb ruthenium fluoride significantly better than sodium fluoride had at 650°F and that the 1 ppm specification limit for ruthenium can also be achieved. Tests showed that the physical structure of the sorbent pellet plays a decisive role in determining the sorption qualities of a particular material, and consequently, the methods of pellet preparation, drying, sintering, and pretreatment are critical to the analysis and evaluation of new sorbent materials.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

TABLE OF CONTENTS

	<u>PAGE</u>
INTRODUCTION	11
SUMMARY	12
EXPERIMENTAL	13
Equipment	13
Testing Procedure	16
SOLID SORBENT PREPARATION	16
Magnesium Fluoride and Sodium Fluoride Pellets	17
Pellet Preparation by Extrusion	17
Pellet Preparation by Compaction	21
SELECTION OF SORBENT MATERIALS	21
IMPURITY PREPARATION	23
TEST RESULTS	23
Sorption of Niobium Pentafluoride	24
Sorption of Ruthenium Pentafluoride	30
Sorption of Titanium Tetrafluoride	34
CONCLUSIONS	39
APPENDIX - PRESENT SPECIFICATIONS FOR URANIUM HEXAFLUORIDE DELIVERED TO THE UNITED STATES ATOMIC ENERGY COMMISSION	41

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
I	Drying Test Summary	18
II	Sorption of Niobium Pentafluoride by 250°F Aluminum Fluoride	25
III	Sorption of Niobium Pentafluoride by 250°F Aluminum Fluoride	27
IV	Sorption of Niobium Pentafluoride by 250°F Cryolite	28
V	Sorption of Niobium Pentafluoride by 250°F Sodium Fluosilicate	29
VI	Sorption of Ruthenium Pentafluoride by 250°F Cryolite . . .	31
VII	Sorption of Ruthenium Pentafluoride by 180°F Cryolite . . .	32
VIII	Extended Sorption of Ruthenium Pentafluoride by 180°F Cryolite	33
IX	Sorption of Ruthenium Pentafluoride by 180°F Sodium Fluosilicate	35
X	Extended Sorption of Ruthenium Pentafluoride by 180°F Sodium Fluosilicate	36
XI	Bed Analyses After First Titanium Tetrafluoride Sorption Test on 250°F Magnesium Fluoride	38
XII	Bed Analyses After Second Titanium Tetrafluoride Sorption Test on 250°F Magnesium Fluoride	38
XIII	Specifications for Uranium Hexafluoride Delivered to the AEC	42

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1	Uranium Hexafluoride Impurity Trapping System	14
2	Trapping System Sorbent Traps	15
3	Cryolite Pellets Formed by Extrusion	20
4	Cryolite Pellets Formed by Compaction	22

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

REMOVAL OF IMPURITIES FROM URANIUM HEXAFLUORIDE
BY SELECTIVE SORPTION TECHNIQUES:
THIRD PROGRESS SUMMARY REPORT

Efficient operation of the gaseous diffusion complex depends in part on requiring that the uranium hexafluoride feed material have sufficiently high chemical purity. With toll enrichment and other contractual arrangements for uranium ownership and processing services, specifications for uranium hexafluoride delivered to the Atomic Energy Commission for enrichment were revamped*. These chemical and physical specifications have been published in the Federal Register; current values are also listed in the appendix of this report. Of immediate concern here are the 1 ppm restrictions for the metallic impurities niobium, tantalum, antimony, ruthenium, and titanium, all of which form volatile fluoride compounds.

The Oak Ridge Gaseous Diffusion Plant is engaged in an effort to develop efficient, low-cost processes for removing these impurities and others from uranium hexafluoride. With the development of effective purification techniques, the Commission can be assured that specifications for diffusion plant feed stock material can be met by companies engaged in feed preparation, scrap recovery, spent fuel treatment, and other uranium processing operations.

For removing trace quantities of impurities, the economics and simplicity of a fixed-bed solid sorption trap make the sorption process generally preferable over other separation schemes, such as distillation. Relatively small and inexpensive sorbent traps, for example, could be conveniently placed at the uranium hexafluoride product collection point in various processing installations. Current project emphasis is therefore placed upon finding effective solid sorbents capable of selectively removing volatile metallic impurity fluorides from a uranium hexafluoride gas stream without, at the same time, trapping significant quantities of the uranium.

The previous results of the program are detailed in two earlier progress reports†. The first report includes results of both qualitative scoping studies designed to screen various sorbents and flame reactor and fluid

* Arnold, E. D., Barton, J. C., Keller, E. L., Levin, R. W., and Voss, F. S., *Uranium Hexafluoride Specification Studies*, U.S.A.E.C., Division of Technical Information Services, July 12, 1967 (ORO-656).

† Brater, D. C., Kaufman, H. L., Pashley, J. H., and Smiley, S. H., *Removal of Impurities from Uranium Hexafluoride by Selective Sorption Techniques*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, June 6, 1966 (K-1666); and Stephenson, M. J., Merriman, J. R., and Kaufman, H. L., *Removal of Impurities from Uranium Hexafluoride by Selective Sorption Techniques: Progress Report for 1966*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, July 17, 1967 (K-1713).

bed fluorination-sorption studies with uranium oxide contaminated with trace quantities of the test impurities. Direct contamination of the uranium hexafluoride feed was employed later in the program. The second report includes a summary of nineteen sorption tests, with detailed results for the last nine of these runs. The tests were conducted using various combinations of impurity fluorides and the sorbents sodium fluoride and magnesium fluoride. The results of the tests indicated that magnesium fluoride pellets at 250°F could selectively remove significant quantities of niobium pentafluoride, tantalum pentafluoride, antimony pentafluoride, and titanium tetrafluoride and that sodium fluoride at 650°F was an effective ruthenium fluoride sorbent.

Current experimental work has been directed toward the same type of flow testing as discussed in the first two reports, but in addition, considerable emphasis has also been directed toward finding new, improved sorbent materials. Realizing the importance of the pellet structure upon the performance and loading potential of the various solid sorbents, methods of forming the powder into pellets and subsequent heat treatment processes have recently been investigated as an integral part of the project. In the sections which follow, both the pellet preparation work and the impurity removal tests conducted since the last report are discussed.

SUMMARY

Fundamental data on the reaction kinetics and loading capacity of particular impurity fluorides and uranium hexafluoride on various test solid sorbents have been obtained from engineering-scale flow tests. In these tests, a uranium hexafluoride feed containing some trace quantity of volatile impurity is prepared and subsequently passed through a sorption trap containing the test sorbent. Each sorption run involves obtaining representative samples of the contaminated uranium hexafluoride stream entering and leaving the sorption trap at various time intervals during the course of the test. Pellet loading data are obtained at the completion of each test by chemical analysis of the sorbent bed.

Sodium fluoride and magnesium fluoride were available in pellet form. Most of the new materials to be examined, however, were not available as pellets, and a program was initiated at the ORGDP to investigate various methods of pellet preparation. A commercial extruder and an automatic high-speed tablet compressing machine were used in the program to produce pellets from a number of powders. Drying and sintering is an important step in pellet production since this procedure largely determines the physical structure of the porous media and thereby contributes significantly to the observed sorption behavior of the final sorbent material.

Experimental conditions and test results for all sorption tests conducted since the last report are presented in detail in this report. From the flow tests, it can be concluded that, at 250°F, a sorbent bed of aluminum

fluoride, cryolite, or sodium fluosilicate can reduce the concentration of niobium in uranium hexafluoride from more than 50 ppm to less than 1 ppm. Scoping studies indicate that barium fluoride and nickel fluoride can also sorb significant quantities of niobium without retaining appreciable amounts of uranium. Sorption studies with ruthenium pentafluoride show that at 180 to 250°F both cryolite and sodium fluosilicate sorb ruthenium significantly better than either sodium fluoride at 650°F or magnesium fluoride at 250°F. Furthermore, the 1 ppm ruthenium specification can be achieved using either of these two new materials. Work with titanium tetrafluoride shows that lithium fluoride, calcium fluoride, aluminum fluoride, sodium fluosilicate, cryolite, and nickel fluoride, all at 250°F, sorb impressive quantities of titanium and, in general, perform at least as well as magnesium fluoride at 250°F and sodium fluoride at 650°F.

EXPERIMENTAL

Engineering-scale sorption flow tests are used to evaluate proposed materials as suitable solid sorbents. These tests provide fundamental data on the rate of loading and the loading capacity of particular impurity fluorides and uranium hexafluoride on the various sorbents. Such information is essential to the design of plant-size sorption systems. This section presents a description of the equipment and testing procedure.

Equipment

A schematic flow diagram of the engineering-scale impurity sorption system is given in figure 1. Basically, a uranium hexafluoride feed containing a trace quantity of volatile impurity is prepared and subsequently passed through a sorption trap containing the test sorbent. Uranium hexafluoride is fed from a steam-heated storage cylinder. The flow is metered by maintaining a given forepressure and pressure drop across an orifice. The volatile impurity, stored either as a liquid or solid fluoride, is similarly fed as a vapor from a feed cylinder contained within a temperature-controlled electrically heated oven. A small nitrogen entrainment flow is diverted into the impurity feed cylinder to transport the impurity and inject it into the uranium hexafluoride feed line upstream from the sorber. The amount of volatile impurity fed is controlled by the feed cylinder temperature and entrainment flow rate. The contaminated uranium hexafluoride is then directed through a fixed bed of the test sorbent material. The trapping station used in these studies consists of two sorbent beds, shown in figure 2. Each trap is constructed from a 4-foot section of 3-inch-diameter Monel pipe and is contained within a common electrically heated oven. The traps are charged and emptied from the top. Sample taps are provided on the inlet and outlet lines of the system. The feed material, after passing through the sorbent trap, is valved into a series of cold traps. Since these traps are maintained around minus 30°F, condensables are desublimed and the off-gas, consisting primarily of nitrogen or a mixture of nitrogen and fluorine, is vented.

Figure 1

URANIUM HEXAFLUORIDE IMPURITY TRAPPING SYSTEM

Figure 2

TRAPPING SYSTEM SORBENT TRAPS

Testing Procedure

Upon charging the sorbent trap with pellets, pretreating with fluorine, and placing the impurity feed cylinder in the feed oven, the various sections of the apparatus are raised to the desired operating temperature, and the gas flows established. The sorbent trap is commonly charged to a height of 3 to 4 feet with about 10 to 15 pounds of pellets. Small perforated metal cups containing gram quantities of experimental materials for scoping studies are sometimes placed upstream from the sorption bed. The uranium hexafluoride flow rate is typically maintained between 10 and 20 lb/hr and a nitrogen diluent flow of around 0.2 scfm is usually set up. The superficial velocity through the sorbent bed is near 0.1 ft/sec. An impurity entrainment flow rate of 500 sccm is common.

Once the test is initiated, samples of condensables entering and leaving the sorber are withdrawn periodically, generally every 1 to 5 hours during operation. Typically, five minutes are required to remove a 40- to 50-gram sample and from 20 to 30 samples are usually taken during the course of a test. After completion of a run, the equipment is cooled and purged with nitrogen for several hours to remove any residual uranium hexafluoride or fluorine. Incremental samples of the bed are removed from the trap and individually analyzed to establish the impurity and uranium loading profile in the sorbent bed.

SOLID SORBENT PREPARATION

The physical structure of the sorbent pellet plays a very important role in determining the sorption characteristics of a particular material. Attention is too easily directed entirely toward the material from which the pellets were fabricated, giving little consideration to the various methods of forming and heat treating by which pellets can be prepared. The importance of the pellet structure of sodium fluoride in the sorption of uranium hexafluoride has been defined*, and generalization of the theory to the current impurity sorption systems can be made. A description of several methods of pellet forming and heat treating is given in this section, with an account of current pellet work at the ORGDP. This information provides general guidelines only; normal variations in the physical makeup of the starting powders and pellets necessitate slight modifications of the preparation procedure to suit particular batches.

* McNeese, L. E., *An Experimental Study of Sorption of Uranium Hexafluoride by Sodium Fluoride Pellets and a Mathematical Analysis of Diffusion with Simultaneous Reaction*, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, November 1963 (ORNL-3494); and Stephenson, M. J., *A Design Model for the Dynamic Adsorption of Uranium Hexafluoride on Fixed Beds of Sodium Fluoride*, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, December 1968 (K-L-6195-2).

Magnesium Fluoride and Sodium Fluoride Pellets

Magnesium fluoride and sodium fluoride were the primary sorbent materials of the previously reported tests*. The sodium fluoride pellets were obtained by heating commercially available sodium bifluoride pellets in a nitrogen atmosphere for 5 hours at 1000°F. As was shown*, the preparation temperature had a considerable effect upon the resulting physical structure of the sodium fluoride pellet.

The bifluoride pellets, as purchased from the Harshaw Chemical Company† were compaction formed in the shape of 1/8-inch by 1/8-inch right circular cylinders. After treatment, these pellets typically had a surface area of 0.8 to 1.8 sq m/g and a void fraction between 0.35 and 0.50. The nominal bulk density of the pellets is 65 lb/cu ft.

Magnesium fluoride pellets used in earlier studies were obtained from the Paducah Gaseous Diffusion Plant. These spheroidal pellets, formed by tumbling moistened magnesium fluoride powder, were 3/16 to 5/16 inch in diameter. Prior to using the as-received material, the pellets were heat treated and fluorinated to remove residual water. Tests were conducted to investigate the effect of drying temperature, time, and atmosphere upon the magnesium fluoride pellet structure. The results are given in table I. Drying at 750°F for 4 to 6 hours in a nitrogen-fluorine atmosphere or at 400°F for 16 hours in a vacuum produced a very dry, but highly sintered, less reactive pellet. On the other hand, drying at 250°F for 16 to 18 hours in nitrogen or in vacuum resulted in a very porous, reactive pellet, but left an undesirable amount of residual water in the pellet. Since uranium hexafluoride will react with available water, residual moisture should be kept well below 1% in order to minimize uranium retention during use. Drying temperatures of 400 to 500°F in nitrogen were most commonly used in magnesium fluoride pellet preparation at the ORGDP, and resulting pellet surface areas ranged from 50 to 70 sq m/g, with a nominal bulk density of 56 lb/cu ft.

Pellet Preparation by Extrusion

The strict dependence of the sorption characteristics upon the pellet structure and the unavailability of commercial pellets of potential sorbent materials necessitated a program at the ORGDP to investigate methods of pellet preparation. A commercial pilot plant extruder, manufactured by the Bonnot Company, Kent, Ohio, was obtained for use in the impurity project. The machine operates on a screw feed principle, forcing the powder or powder mixture through a die. Depending upon the starting powder mix, the size and number of holes in the die, and the speed of the feed screw, the extruder can produce pellets of almost any desired

* K-1713, loc. cit.

† Technical Grade No. NA-0101T-1/8, Harshaw Chemical Company, Cleveland, Ohio.

TABLE I

MAGNESIUM FLUORIDE PELLET DRYING TEST SUMMARY*

Drying Temperature, °F	Drying Atmosphere	Drying Time, hr	Pellet Density, g/cc	Surface Area, sq m/g	Water Content, %
750	N ₂ + F ₂	4	3.11	29.67	0.11
750	N ₂ + F ₂	6	3.19	26.44	0.55
550	N ₂ + F ₂	4	3.14	51.20	0.05
400	N ₂	16	2.94	72.39	0.11
400	Vacuum	16	3.09	35.89	0.75
300	Vacuum	16	2.99	92.89	0.38
250	Vacuum	16	2.99	91.56	1.25
250	N ₂ + F ₂	5	3.12	101.0	0.90
250	N ₂	18	2.96	86.44	2.83

* The pellets used for this test were produced at the Paducah Gaseous Diffusion plant by tumbling moistened magnesium fluoride powder. The nominal pellet diameter was 3/16 to 5/16 inch.

size and consistency. A binder and a lubricant must be mixed with the starting powder for the direct forming process. For the work here, stearic acid $[\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}]$ was employed as the lubricant and water as the binding agent. The physical properties of the final product are dependent upon the relative amounts of stearic acid and water in the starting powder. The feed powder mixture typically contains 1.0 to 2.0 weight percent stearic acid and 10 to 12 weight percent water. If too little stearic acid is used, the surfaces of the extruded pellets will be rough. On the other hand, excessive amounts of lubricants are difficult to remove. Too little water will result in the production of extremely delicate pellets that crumble to the touch or disintegrate upon falling into the collection pan. If excessive water is used, the pellets will melt upon being formed.

Before the pellets can be used, the stearic acid and water must be removed and the pellets sintered. Most of the water is evaporated from the pellets as they are allowed to dry; the pellets become firm but crumble easily. The final drying and sintering is usually achieved by placing the pellets under an inert atmosphere in a high temperature muffle maintained at 800 to 1200°F for 3 to 5 hours, again depending upon the particular material. Next, the pellets are exposed to elemental fluorine for final drying at around 250°F for several hours. The sintering temperature and time is important not only in reducing the residual water content of the pellet but also in establishing a durable pellet structure. Soft pellets are more reactive but are relatively difficult to handle without falling apart and powder excessively when used, resulting in larger sorbent trap pressure losses. But on the other hand, the very dense or highly sintered pellet should, for the most part, be avoided because of its low reactivity and low loading capability.

An alternative procedure was developed at ORGDP to produce a unique, two layered sorbent pellet with a tough outer crust and soft, more reactive interior. The new method involves exposing the air dried pellets directly to elemental fluorine at 300 to 500°F for 4 to 8 hours. The fluorine reacts exothermically with the water diffusing from the interior of the pellet to the surface, resulting in localized surface sintering. The concentration of fluorine is maintained as high as possible without allowing the muffle temperature to rise. Only the periphery of the pellets appear to appreciably sinter. With only limited data available for actual comparison, the new method apparently produces pellets that have higher surface areas and void fractions than those produced via the conventional route. Preliminary data also show that, at least for niobium pentafluoride reacting with cryolite, the new method also produces pellets that load significantly more impurity and at a faster rate.

Materials that have been successfully formed by extrusion are: sodium fluoride, barium fluoride, nickel fluoride, cryolite (Na_3AlF_6), sodium fluozirconate (Na_2ZrF_6), potassium fluozirconate (K_2ZrF_6), and sodium fluosilicate (Na_2SiF_6). A photograph of cryolite extruded through a 3/16-inch-diameter die is shown in figure 3. The pellets can be cut or broken to any length after they are formed. Thin, short pellets are

Figure 3

CRYOLITE PELLETS FORMED BY EXTRUSION

generally preferable over larger ones because of the availability of more exterior surface for loading.

Pellet Preparation by Compaction

An automatic high-speed tablet-compressing machine manufactured by the J. F. Stokes Corporation, Philadelphia, Pennsylvania, was obtained to investigate compaction as a means of producing pellets. The machine is of the rotary type with 15 sets of punches and dies located at stations around the head. The punches are guided up and down by fixed cam tracks which control the proper sequence of filling, compressing, and ejecting the pellets. The powder is gravity fed from a feed hopper through a feed frame into the dies. Adjustments can be made to control the amount of material per pellet, the force of compaction, and the rate of pellet production, which ranges from 190 to 350 pellets per minute. By changing the size of the dies and punches, pellets of various diameters can be produced. The smallest die size for this particular unit is 5/16 inch; the largest, 3/4 inch.

Use of a binding agent is not necessary in the preparation of pellets by compaction, but a lubricant is usually recommended. Figure 4 presents a photograph of cryolite formed into cylindrical pellets 5/16 inch in diameter and approximately 5/16 inch in height. Because a binder is not used, drying is not required after formation; however, fluorination at 200 to 250°F is necessary to remove the lubricant and residual water. Sintering is not necessary after formation because the density of the finished pellet can be established within limits by the die fill and compaction pressure.

SELECTION OF SORBENT MATERIALS

Scoping tests are performed to screen trial sorbents before engineering-scale flow tests are considered. These simple flow tests involve exposing gram quantities of various test materials to contaminated uranium hexafluoride. Further testing of a proposed sorbent depends primarily upon the relative capability of the sample material to selectively sorb significant quantities of the particular impurity fluoride during the preliminary exposure. Based on current selection guidelines, "good" sorbents are those materials that load generally better than 1 to 2 weight percent impurity at saturation and, at the same time, retain less than 1.0 weight percent uranium.

Selection of new sorbent materials also involves several economic factors. Potential sorbents which are inexpensive and commercially available in bulk quantities are given primary consideration because the cost of the material will have to be balanced against its performance. Use of rare or expensive material is undesirable unless other sorbents are not available. The price of nickel fluoride powder, a promising sorbent, is near \$40 per pound, generally affecting its overall utility. On the other

Figure 4

CRYOLITE PELLETS FORMED BY COMPACTION

hand, cryolite and sodium fluosilicate sell for less than \$1.00 per pound and are attractive, economically, for use in applications where hundreds of pounds of material will be needed. A sorbent which loads twice as much impurity as another sorbent will obviously be preferred over the other to perform a given separation, all other things being equal, because proportionally less sorbent will be required and less waste material will be generated. On the other hand, uranium retained on the sorbent material after use will have to be accounted for. Naturally, from an economic point of view, sorbent materials that possess a low uranium loading capability are more desirable. Some sorbents, such as sodium fluoride, have to be maintained at elevated temperatures in order to minimize uranium sorption. With high temperature sorbents, heating and cooling requirements could represent a substantial fraction of the total equipment and operating cost of an impurities sorption facility. Sorbents that are efficient at lower temperatures therefore rank above higher temperature sorbents.

IMPURITY PREPARATION

The fluoride impurities used in the sorption tests were prepared locally by direct fluorination of the base metal or oxide of the base metal. The batchwise fluorination process was carried out in a 4-inch-diameter, 4-foot-long, nickel muffle furnace, using undiluted commercial-grade fluorine. Fluorination temperatures were different for the preparation of the various fluoride impurities but were generally below 1000°F. Fluorine was supplied to the reactor at a rate between 0.1 and 0.5 lb/hr. The resulting volatile fluorides were swept from the reactor system and trapped by desublimation.

TEST RESULTS

Experimental conditions and test results for all sorption tests conducted since the last report* are presented in the following sections. Magnesium fluoride and sodium fluoride pellets were the prime sorbents used in the earlier tests, and some additional work using magnesium fluoride is reported here, although project emphasis has been directed toward the use of new sorbent materials. Discussion is given comparing the relative effectiveness of the new sorbent materials with that of magnesium and sodium fluorides. During this report period, tests were not conducted using the impurities tantalum pentafluoride and antimony pentafluoride because it is believed that, based on prior test results, they generally exhibit similar sorption characteristics to niobium pentafluoride.

* K-1713, loc. cit.

In general, material balance data are not included in this report, although there are some exceptions. Material balances were used in the course of the work to identify sampling and analytical anomalies, but the accuracy of feed quantity integrations is not sufficient to be of use in computing the high removal efficiencies present in these absorption tests. The primary interest is the removal of an impurity to below a given specification level, and this can be measured directly.

Sorption of Niobium Pentafluoride

Much success has been achieved in removing niobium pentafluoride from uranium hexafluoride using either magnesium fluoride at 250°F or sodium fluoride at 650°F. In previous tests, the average niobium loading on a magnesium fluoride pellet bed was as high as 5.5%*, with uranium loading generally around 1.0%. In several tests, magnesium fluoride beds operated at 250°F effectively stripped over 99% of the niobium mixed with the uranium hexafluoride feed. Average niobium loading on a sodium fluoride pellet bed was as high as 7%, with the top section of the bed containing as much as 14% niobium. Although sodium fluoride pellet beds operated at 650 to 750°F were found to strip large quantities of niobium without retaining significant quantities of uranium, caking of the pellet bed appeared to be a problem.

In the search for sorbent materials other than magnesium and sodium fluorides, scoping tests were conducted along with a number of the regular sorption runs†. Gram samples of various test pellets were placed in separate perforated containers upstream from the regular sorbent beds. From these tests, aluminum fluoride, cryolite, and sodium fluosilicate appeared to be particularly promising sorbents for niobium pentafluoride, and consequently, fixed bed tests were conducted with these materials to complete their evaluation. The results of these tests are presented below.

For the first of these runs, the sorbent trap was charged to a height of 3 feet with 12.1 pounds of aluminum fluoride pellets. The pellets were prepared by batch-pan fluorination of aluminum oxide spheres and had a surface area of 18.8 sq m/g. The sorption test lasted 81.1 hours, with a uranium hexafluoride feed rate of 23.0 lb/hr, a fluorine rate of 1.5 lb/hr, and a nitrogen diluent flow of 0.20 scfm. A total of 1,885 pounds of uranium hexafluoride containing approximately 0.67 pound of niobium pentafluoride was fed to the sorber. Analyses of condensables entering and leaving the sorber are presented in table II. The niobium concentration in the sorber feed averaged 262 ppm. As can be seen, the pellets reduced the concentration of niobium to less than 0.5 ppm for the first 11.1 hours of operation, after which breakthrough occurred. The outlet stream analyses indicated an average 42 ppm niobium in the uranium hexafluoride for the remaining 70 hours of the test.

* All percentages are reported on a weight basis..

† K-1713, loc. cit.

TABLE II

SORPTION OF NIOBIUM PENTAFLUORIDE BY 250°F ALUMINUM FLUORIDE

On-Stream Time, hr	Niobium Concentration, ppm		Sorbent Analysis		
	Inlet	Outlet	Bed Segment, inches	Niobium, %	Uranium, %
1.0	50	< 0.2	Inlet 6	1.14	0.66
6.0	209	< 0.5	Second 6	0.70	0.93
11.0	320	< 0.8	Third 6	0.64	1.28
16.0	236	41	Fourth 6	0.93	1.33
21.5	240	41	Fifth 6	1.50	0.39
26.0	267	54	Bottom 6	0.86	0.60
31.0	220	97			
36.0	232	35			
41.0	503	85			
46.0	315	41			
51.0	243	18			
56.0	258	26			
61.0	232	18			
71.0	319	8			
81.0	224	98			

After completion of the test, the aluminum fluoride bed was sectioned and analyzed. The results of the analyses are also given in table II. As the pellets were removed from the trap, excessive surface degradation was evident from the amount of fines present. The bed was found to contain 0.96% niobium and 0.95% uranium.

The results of a second 80-hour sorption test with niobium pentafluoride and aluminum fluoride were in general agreement with those obtained from the first test. For the second test, the sorbent trap was charged to a nominal height of 3 feet with 11.0 pounds of pellets. These pellets, prepared in the same manner as those used previously, had a surface area of 6.11 sq m/g. Chemical analysis of this batch of pellets indicated a fluoride content of 31.3%, as compared to 67.9% theoretical if all the aluminum oxide had been converted to aluminum fluoride. The sorber was operated for 82.0 hours with a uranium hexafluoride feed rate of 23.5 lb/hr, fluorine rate of 1.5 lb/hr, and a nitrogen flow of 0.23 scfm. A total of 1,927 pounds of uranium hexafluoride, containing an estimated 1.62 pounds of niobium pentafluoride, was fed through the sorber. Analyses of condensables entering and leaving the sorber are presented in table III. Niobium concentration in the uranium feed averaged 613 ppm. The feed leaving the sorber averaged 3.2 ppm niobium for the initial 22 hours of operation after which breakthrough occurred. Following breakthrough, the feed was found to contain an average 303 ppm, or less than half of that fed, for the remaining 60 hours of the test. After completion of the flow test, the aluminum fluoride bed was removed from the trap in sections and analyzed. The results of the chemical analyses are presented in table III. The bed was found to contain 1.90% niobium and 3.07% uranium.

In another evaluation of new sorbent materials for niobium removal, a 50-hour test was completed using a sorbent bed of cryolite (Na_3AlF_6)* pellets maintained at 250°F. The trap was charged to a height of 3.8 feet with 15.0 pounds of pellets. The pellets were formed at the ORGDP by extrusion, and after drying, sintering, and pretreatment in fluorine, were found to have a surface area of 1.49 sq m/g and a porosity of 0.345. A uranium hexafluoride feed rate of 23.5 lb/hr and a nitrogen diluent flow of 0.21 scfm was used. Results of analyses of the condensables entering and leaving the sorber are presented in table IV. The average impurity concentration in the feed stream was 76 ppm niobium. The amount of niobium in the sorber outlet was initially high, possibly due to passage of a slug of material into the sampling system caused by the initially high inlet concentration or some other experimental artifacts. For the last 25 hours of the run, however, the niobium concentration in the inlet, averaging 48 ppm, was reduced to less than 0.2 ppm upon passing through the trap. Trap breakthrough was not reached.

* Anderson, L. W., and Stephenson, M. J., "Separation of Titanium Fluoride and Niobium Fluoride from Gaseous Uranium Hexafluoride Containing Same", U. S. Patent 3,625,661 (December 7, 1971).

TABLE III

SORPTION OF NIOBIUM PENTAFLUORIDE BY 250°F ALUMINUM FLUORIDE

On-Stream Time, hr	Niobium Concentration, ppm		Sorbent Analysis		
	Inlet	Outlet	Bed Segment, inches	Niobium, %	Uranium, %
1.0	210	0.5	Inlet 6	1.82	2.66
7.0	220	5.0	Second 6	1.27	1.10
12.0	127	1.0	Third 6	2.07	3.03
17.0	479	2.5	Fourth 6	2.04	3.80
22.0	335	9.0	Fifth 6	2.02	3.63
27.0	660	169	Bottom 6	2.02	3.68
32.0	760	128			
37.0	905	287			
42.0	755	320			
47.0	715	266			
52.0	720	258			
62.0	824	335			
72.0	688	320			
82.0	788	471			

TABLE IV
SORPTION OF NIOBIUM PENTAFLUORIDE BY 250°F CRYOLITE

On-Stream Time, hr	Niobium Concentration, ppm		Sorbent Analysis		
	Inlet	Outlet	Bed Segment, inches	Niobium, %	Uranium, %
1.0	363	54	Inlet 6	1.638	0.039
5.0	96	*	Second 6	1.361	0.039
10.0	75	12	Third 6	0.963	0.023
15.0	139	24	Fourth 6	0.480	0.19
20.0	82	24	Fifth 6	0.197	0.14
25.0	44	0.3	Sixth 6	0.062	0.15
30.0	83	0.2	Seventh 6	< 0.010	0.14
35.0	41	< 0.2	Bottom 6	< 0.010	0.15
40.0	53	< 0.2			
45.0	43	< 0.2			
50.0	26	< 0.2			

* Sufficient sample was not taken for analysis.

At the completion of the run, the cryolite bed and the sample pellets were removed from the trap and analyzed. The results are presented in table IV. The cryolite bed exhibited a good loading profile for both niobium and uranium. Very little niobium was found in the lower two sections of the pellet bed indicating that the low outlet concentrations observed in the latter half of the run accurately reflect the sorbent's capability. Uranium loading on the cryolite was very low, being less than 0.2%.

The final niobium pentafluoride sorption test was conducted with sodium fluosilicate (Na_2SiF_6). The pellets, as formed at ORGDP by extrusion, had a final surface area of 0.384 sq m/g and porosity of 0.326. The sorbent trap was charged to a height of 3 feet with 10.7 pounds of pellets and heated to 250°F. The run lasted for 26 hours and a uranium hexafluoride feed rate of 9.1 lb/hr and nitrogen diluent flow of 0.16 scfm were maintained. Test results are presented in table V. The average niobium concentration in the feed stream was 329 ppm while the trap effluent averaged about 0.5 ppm for the duration of the test. Analysis of the sorbent bed indicated that the main sorption zone had not penetrated the last two sections of the trap. Uranium loading on the sodium fluosilicate pellets was significantly higher than expected, possibly due to incomplete drying during pellet fabrication. Uranium loadings generally less than 1% were observed in earlier exposures.

TABLE V

SORPTION OF NIOBIUM PENTAFLUORIDE BY 250°F SODIUM FLUOSILICATE

On-Stream Time, hr	Niobium Concentration, ppm		Sorbent Analysis		
	Inlet	Outlet	Bed Segment, inches	Niobium, %	Uranium, %
1.0	370	0.5	Inlet 6	2.23	1.33
2.0	50	0.2	Second 6	1.53	1.19
6.0	980	2.5	Third 6	0.75	1.83
11.0	290	0.2	Fourth 6	0.12	2.28
16.0	330	0.2	Fifth 6	0.10	2.18
21.0	80	0.2	Bottom 6	0.10	1.48
26.0	310	0.2			

Other sorbent materials that have been identified through scoping studies as potentially good niobium sorbents include nickel and barium fluoride, although additional tests have not been made with these compounds. Sample pellets of nickel fluoride, for example, loaded 1.24% niobium and 0.985% uranium and barium fluoride loaded 0.77% niobium and only 0.058% uranium.

Sorption of Ruthenium Pentafluoride

Only limited success was achieved in removing ruthenium pentafluoride from uranium hexafluoride during the earlier sorption work with magnesium and sodium fluoride. No work on the sorption of volatile ruthenium compounds other than the pentafluoride has been done. In summary, sodium fluoride pellets at 650°F appeared promising for stripping ruthenium and performed markedly better than magnesium fluoride at 250°F. In one test* using a 3-foot-deep bed of sodium fluoride at 650°F, with a uranium hexafluoride feed rate of 21.0 lb/hr and inlet ruthenium concentration of 251 ppm, the sorber outlet ruthenium concentration remained less than 2 ppm for the first 21 hours of operation. Analyses of the sorbent bed showed average ruthenium content of 1.79% and uranium value of 0.65%.

The results of recent tests presented below indicate that both cryolite and sodium fluosilicate at 180 to 250°F are very effective ruthenium pentafluoride sorbents. Three tests were completed with cryolite and two tests with sodium fluosilicate. Both new sorbents appear to remove ruthenium significantly better than either sodium or magnesium fluoride.

For the first ruthenium test, the sorbent trap was charged to a height of 3 feet with 11.0 pounds of cryolite pellets†. The sorbent bed was heated to 250°F and a uranium hexafluoride feed rate of 8.6 lb/hr and nitrogen diluent flow of 0.16 scfm were established. Analyses of samples taken during the course of the 30-hour test showed that the uranium feed contained an average 93 ppm ruthenium and was reduced to 1 ppm or less upon passing through the cryolite bed. Test results are presented in table VI. The main concentration of ruthenium on the sorbent bed was found to be confined to the top two segments of the bed, indicating that the sorption front had penetrated about half the length of the trap at termination of the run. Uranium loading on the cryolite pellets averaged only 0.24%.

* K-1666, loc. cit.

† As typical of the cryolite pellets prepared at ORGDP during this campaign, the pellet surface area varied between 1.5 and 1.8 sq m/g and void fraction between 0.34 and 0.37.

TABLE VI
SORPTION OF RUTHENIUM PENTAFLUORIDE BY 250°F CRYOLITE

On-Stream Time, hr	Ruthenium Concentration, ppm		Sorbent Analysis		
	Inlet	Outlet	Bed Segment, inches	Ruthenium, %	Uranium, %
2.0	25	< 1	Inlet 7	0.22	0.74
4.0	105	< 1	Second 7	0.11	0.13
6.0	115	1	Third 7	27 ppm	0.16
8.0	93	1	Fourth 7	10 ppm	0.05
10.0	145	< 1	Bottom 7	10 ppm	0.11
15.0	140	< 1			
20.0	84	< 1			
25.0	70	< 1			
30.0	50	< 1			

The second ruthenium test with cryolite was very similar to the first one except that the sorption temperature was lowered from 250 to 180°F. This test was also conducted with a three-foot deep sorbent bed. The uranium hexafluoride feed rate was 9.0 lb/hr and nitrogen flow was 0.16 scfm. The test results are given in table VII. The uranium feed contained an average 87 ppm ruthenium while the trap effluent held less than 1 ppm for the duration of the test. The ruthenium and uranium loading profiles on the sorbent bed were found to be similar to those observed from the previous test. The inlet bed segment, however, reportedly contained 7.51% ruthenium. Since this value represents over two times the actual amount of ruthenium fed during the entire test, it has to be discounted. Unfortunately, the bed samples were discarded before another determination could be made.

The third test with ruthenium pentafluoride impurity and cryolite sorbent was an extended one, lasting 80 hours. For this test, the trap was again charged to a height of three feet and, as before, maintained at 180°F. Uranium hexafluoride was fed to the sorber at a rate of 9.4 lb/hr and contained an average 174 ppm impurity. A nitrogen diluent flow was not used for this test. Test results are given in table VIII. Except for

TABLE VII

SORPTION OF RUTHENIUM PENTAFLUORIDE BY 180°F CRYOLITE

On-Stream Time, hr	Ruthenium Concentration, ppm		Bed Segment, inches	Sorbent Analysis	
	Inlet	Outlet		Ruthenium, %	Uranium, %
2.0	127	< 1	Inlet 6	7.51*	0.02
4.0	60	< 1	Second 6	0.22	35 ppm
6.0	95	< 1	Third 6	17 ppm	0.17
8.0	61	< 1	Fourth 6	7 ppm	0.16
10.0	59	< 1	Fifth 6	7 ppm	0.14
15.0	75	< 1	Sixth 6	6 ppm	0.15
20.0	59	< 1			
25.0	125	< 1			
30.0	117	< 1			

For explanation, see text.

TABLE VIII

EXTENDED SORPTION OF RUTHENIUM PENTAFLUORIDE BY 180°F CRYOLITE

On-Stream Time, hr	Ruthenium Concentration, ppm		Bed Segment, inches	Sorbent Analysis	
	Inlet	Outlet		Ruthenium, %	Uranium, %
1.0	120	< 1	Inlet 6	3.69	0.23
5.0	183	7	Second 6	3.06	0.16
10.0	241	1	Third 6	1.54	0.12
15.0	131	< 1	Fourth 6	0.49	851 ppm
20.0	219	*	Fifth 6	0.12	239 ppm
25.0	204	< 1	Sixth 6	105 ppm	300 ppm
30.0	187	< 1			
35.0	188	< 1			
40.0	173	5			
45.0	161	4			
50.0	126	3			
60.0	182	< 1			
70.0	161	< 1			
80.0	156	1			

* This sample was not taken.

the fifth-hour sample, the trap effluent contained 1 ppm or less ruthenium for the first 35 hours of operation. Bed analyses showed heavy ruthenium loadings on the first three segments of the bed. Based on the ruthenium loading profile, specifically, the 105 ppm ruthenium value for the bottom bed segment, the sorption front appears to have penetrated the last segment of the bed, in agreement with the observed breakthrough based on outlet gas analyses. As before, the uranium loading on the cryolite bed was very low, this time averaging about 0.1%.

The last two tests with ruthenium were conducted with pellet beds of sodium fluosilicate at 180°F and were nearly alike, except the second one lasted for 78 hours while the first test was only 35 hours long. Both traps were loaded to a depth of 3 feet with approximately 10.9 pounds of pellets. The pellets had a surface area of 0.38 sq m/g and void fraction of 0.28. The uranium hexafluoride feed rate was maintained at 9.0 lb/hr for both runs. Test results are presented in tables IX and X. The ruthenium concentration was maintained at 18 ppm in the uranium feed for the first test and 62 ppm for the second. After passing through the sodium fluosilicate trap, the uranium contained less than 1 ppm ruthenium. Breakthrough was not reached during the 35-hour test with the lower impurity feed content, but did occur during the second test, after about 40 hours of operation. Bed analyses showed good ruthenium loading in both cases. The sodium fluosilicate pellets retained significantly more uranium than the cryolite beds did during earlier ruthenium runs.

Scoping studies indicate that nickel, calcium, lithium, and aluminum fluorides offer potential as possible ruthenium sorbents, each loading over 1% ruthenium during at least one test at 250°F.

Sorption of Titanium Tetrafluoride

A relatively large amount of sorption work has been performed with titanium tetrafluoride. In previous work, eight sorption runs were completed using magnesium fluoride pellets as the sorbent material and two runs using sodium fluoride pellets. Gas phase transport problems inherent with titanium tetrafluoride were frequently encountered, and the results of a number of these tests had to be discounted due to apparent problems with impurity feed, analytical discrepancies, and/or sorber sample line contamination. Improved impurity feed and sampling systems have since replaced the old ones and it is believed that future handling problems with difficult materials such as titanium will be reduced.

In earlier work with titanium moderate success was achieved using 650°F sodium fluoride pellets as a sorbent for titanium tetrafluoride. In a 50-hour test using a 3-foot bed of pellets and a uranium hexafluoride feed rate of 19.9 lb/hr, with the titanium concentration in the feed averaging 317 ppm, the outlet titanium concentration was 15 ppm after 1.9 hours of operation and 141 ppm after 3.9 hours. At the end of the run, the sodium fluoride pellets were found to contain an average of 2%

TABLE IX

SORPTION OF RUTHENIUM PENTAFLUORIDE BY 180°F SODIUM FLUOSILICATE

On-Stream Time, hr	Ruthenium Concentration, ppm		Sorbent Analysis		
	Inlet	Outlet	Bed Segment, inches	Ruthenium, %	Uranium, %
2.0	44	< 1	Inlet 6	0.75	2.10
4.0	27	< 1	Second 6	0.11	2.93
6.0	10	< 1	Third 6	22 ppm	2.35
8.0	10	< 1	Fourth 6	19 ppm	2.36
10.0	18	< 1	Fifth 6	17 ppm	2.21
15.0	26	< 1	Bottom 6	14 ppm	1.92
20.0	16	< 1			
25.0	15	< 1			
30.5	7	< 1			
35.0	14	< 1			

TABLE X

EXTENDED SORPTION OF RUTHENIUM PENTAFLUORIDE BY 180°F SODIUM FLUOSILICATE

On-Stream Time hr	Ruthenium Concentration, ppm		Bed Segment, inches	Sorbent Analysis	
	Inlet	Outlet		Ruthenium, %	Uranium, %
1.0	75	< 1	Inlet 6	0.99	1.28
3.0	105	< 1	Second 6	0.56	1.50
8.0	50	< 1	Third 6	0.58	1.20
13.0	45	< 1	Fourth 6	0.27	0.93
18.0	56	< 1	Fifth 6	506 ppm	1.02
23.0	67	1	Bottom 6	259 ppm	0.85
28.0	74	1.5			
33.0	50	1.5			
36.0	35	1			
41.0	45	2			
48.0	62	4			
58.0	95	1			
68.0	36	2			
78.0	80	< 1			

titanium and 30 ppm uranium*. The sorption of titanium tetrafluoride on magnesium fluoride at 250°F was found to generally compare with sorption on sodium fluoride at 650°F. Average titanium loadings on magnesium fluoride pellets were found to be around 1 to 4% at saturation. It was found that magnesium fluoride could be used effectively to reduce the titanium level of slightly contaminated material, containing less than 10 ppm, to below the current 1 ppm titanium specification†.

In this work, two more runs with titanium are presented which utilized beds of magnesium fluoride pellets. In-line sampling difficulties were encountered, and as a net result, only bed loading experimental data are given for these runs. The results of scoping tests are very encouraging and, in general, indicate that several other materials offer potential as titanium sorbents.

For the first test with titanium, the sorber was charged to a height of 3 feet with 8.25 pounds of magnesium fluoride pellets. The pellets had a surface area of 54.2 sq m/g and a porosity of 0.57. The sorber was operated for 50.0 hours at 250°F with a uranium hexafluoride feed rate of 31.1 lb/hr, a fluorine rate of 1.5 lb/hr, and a nitrogen flow of 0.23 scfm. A total of 1,565 pounds of uranium hexafluoride containing an estimated 22 ppm titanium was fed to the sorber. After completion of the tests, the magnesium fluoride bed was sectioned and analyzed. The results of the chemical analyses are presented in table XI. The second test using magnesium fluoride pellets was similar to the first. The sorbent trap was again charged to a height of 3 feet with 8.25 pounds of magnesium fluoride pellets. These pellets had a surface area of 57.7 sq m/g and a porosity of 0.58. The trap was operated at 250°F for 53.3 hours with a uranium hexafluoride feed rate of 23.0 lb/hr and a nitrogen rate of 0.23 scfm; no fluorine was used. A total of 1,230 pounds of uranium hexafluoride was passed through the bed during the run. Comparison of the initial and final feed cylinder weights indicated that nearly 0.1 pound of titanium tetrafluoride was actually fed. The average titanium concentration in the feed was estimated to be about 40 ppm for this run. The analyses of the magnesium fluoride pellet bed are given in table XII.

The second run differs from the first in that a lower mass flow was maintained through the trap and the titanium concentration in the uranium feed was higher. Elemental fluorine was also present in the uranium feed of the first test but was not used during the second. Although sufficient information is not available here, the presence of fluorine is generally believed to have no significant effect on the operation of a magnesium fluoride trap. Comparing bed profiles, the results of the second test generally agree with those of the first test. The sharp titanium loading gradient within the top three sections of pellets, being 0.81, 0.20, and 0.06% for the first test and 1.03, 0.44, and 0.14 for the second, suggests that the sorption zone was located in the upper half of the pellet bed at the termination of each run. The uniformly lower, yet

* K-1666, loc. cit.

† K-1713, loc. cit.

TABLE XI

BED ANALYSES AFTER FIRST TITANIUM TETRAFLUORIDE SORPTION TEST
ON 250°F MAGNESIUM FLUORIDE

Bed Segment, inches	Sorbent Analysis	
	Titanium, %	Uranium, %
Top 6	0.81	3.05
Second 6	0.20	3.79
Third 6	0.06	4.08
Fourth 6	0.02	2.82
Fifth 6	0.02	4.15
Bottom 6	0.07	4.30

TABLE XII

BED ANALYSES AFTER SECOND TITANIUM TETRAFLUORIDE SORPTION TEST
ON 250°F MAGNESIUM FLUORIDE

Bed Segment, inches	Sorbent Analysis	
	Titanium, %	Uranium, %
Top 6	1.03	2.22
Second 6	0.44	3.27
Third 6	0.14	3.71
Fourth 6	118 ppm	3.88
Fifth 6	43 ppm	3.68
Bottom 6	62 ppm	3.77

significant distribution of titanium in the bottom sections of each bed hints that at 250°F the equilibrium dissociation pressure of the titanium tetrafluoride-magnesium fluoride complex is appreciable and, therefore, would account for a significant concentration of titanium in the uranium leaving the sorption zone. In such cases, lower sorbent temperatures, say 180° to 200°F for magnesium fluoride sorption of titanium, are recommended to make the sorbent more effective for low concentration work and increase the effective trap life of the bed.

Scoping studies performed in conjunction with regular studies identified several other materials as possible titanium sorbents. Among these are cryolite, sodium fluosilicate, and the fluorides of nickel, barium, lithium, and aluminum. Pellet analyses of test pellets in one run showed that cryolite sorbed 1.12% titanium and 0.31% uranium, and sodium fluosilicate, 1.15% titanium and 0.41% uranium. During this same test, the top section of magnesium fluoride pellets contained 1.03% titanium and 2.22% uranium. In another test with a lower titanium feed concentration, nickel fluoride pellets loaded 0.65% titanium and 0.63% uranium, and barium fluoride pellets, 0.14% titanium and 260 ppm uranium. In a third test, sample pellets of lithium fluoride loaded 1.48% titanium and 0.36% uranium, and aluminum fluoride pellets, 0.70% titanium and 2.30% uranium.

CONCLUSIONS

Sorption tests using uranium hexafluoride-impurity fluoride gas mixtures have demonstrated the feasibility of using the selection sorption technique for the effective and economic purification of uranium. Magnesium and sodium fluorides were the primary sorbents used in the initial stages of the project. Based on test data, the series combination of a magnesium fluoride trap at 250°F with a sodium fluoride trap at 650°F was first proposed to reduce concentrations of niobium, tantalum, titanium, antimony, and ruthenium present in uranium hexafluoride feed to below the current 1 ppm cascade specification. Tests were continued, however, with new materials to identify alternative sorbents that might perform even better or more economically than either magnesium or sodium fluoride.

From recent tests, aluminum fluoride, cryolite, and sodium fluosilicate, all at 250°F, appear to selectively sorb niobium pentafluoride at least as well as magnesium fluoride. Tests showed that the 1 ppm niobium cascade specification can be met by processing off-specification uranium hexafluoride through pellet beds of any of these other materials. Sorption studies at 180° to 250°F with ruthenium pentafluoride show that cryolite and sodium fluosilicate can selectively sorb ruthenium better than sodium fluoride at 650°F and that the 1 ppm ruthenium cascade specification can also be achieved. Tests with titanium tetrafluoride have not been so definitive. Feeding and sampling problems plaguing the impurity test loop during the titanium tests have been essentially eliminated, and future runs are expected to yield more complete data. Based on available evidence, however, lower sorption temperatures, say 180° to

200°F, might make magnesium fluoride a more effective titanium sorbent. Scoping studies have shown that cryolite, sodium fluosilicate, aluminum fluoride, and nickel fluoride can selectively load titanium as well as any other sorbent tested so far, but additional tests will have to be performed to determine whether or not these materials can be used to achieve the 1 ppm titanium specification.

Sorption studies have shown that the physical structure of the sorbent pellet plays a decisive role in determining the sorption qualities of a particular material, and consequently, the methods of pellet preparation, drying, sintering, and pretreatment are critical to the analysis and evaluation of new sorbent materials. Extrusion and compaction are two methods of effective and efficient pellet preparation investigated at the ORGDP which allow for a variety of pellets exhibiting a wide range of sizes, shapes, and consistencies. The tumble-formed pellets produced in a rotating disc pelletizer at the Paducah Gaseous Diffusion Plant are also very acceptable for sorption work. Strict drying procedures are necessary after pellet formation because pellets containing more than 1% residual water can pick up excessive uranium hexafluoride during impurity sorption. Severely sintered or dense pellets are undesirable from an impurity loading standpoint, however, because of the lack of pellet void volume for diffusion and for holding the impurity-sorbent complex. Soft pellets should be avoided because they tend to crumble and powder excessively with handling and use.

Future work in the impurities program includes additional scoping and fixed bed sorption tests. Efforts will be concentrated on finding suitable sorbents for other volatile impurity metallic fluorides of interest, such as various fluorides of chromium, molybdenum, and tungsten. Work is also planned with actual off-specification uranium feed material. Overall, batch traps operated in a series arrangement appear to be best suited for removing volatile fluoride impurities from uranium hexafluoride and therefore tests are not planned with alternative trapping systems such as fluid bed and moving bed sorbers.

APPENDIX .

PRESENT SPECIFICATIONS FOR URANIUM HEXAFLUORIDE DELIVERED
TO THE UNITED STATES ATOMIC ENERGY COMMISSION

The latest (effective July 1, 1967) AEC specifications for uranium hexafluoride are listed in table XIII. This table appeared as table IV on page 16584 of the *Federal Register*, Vol. 31, No. 250; Wednesday, December 28, 1966.

TABLE XIII

SPECIFICATIONS FOR URANIUM HEXAFLUORIDE DELIVERED TO THE AEC

Item*	Numerical Value
Maximum vapor pressure of filled container at 200°F in pounds per square inch, absolute	75
Minimum weight percent of uranium hexafluoride in material	99.5
Maximum mole percent of hydrocarbons, chlorocarbons, and partially substituted halohydrocarbons	0.01
Maximum number of parts of elements indicated per million parts of total uranium:	
Antimony	1
Bromine	5
Chlorine	100
Niobium	1
Phosphorus	50
Ruthenium	1
Silicon	100
Tantalum	1
Titanium	1
Total of elements forming nonvolatile fluorides (having a vapor pressure of 1 atmosphere or less at 300°C), e.g., aluminum, barium, bismuth, cadmium, calcium, chromium, copper, iron, lead, lithium, magnesium, manganese, nickel, potassium, silver, sodium, strontium, thorium, tin, zinc, and zirconium	300
Maximum number of parts of elements or isotopes indicated per million parts of uranium-235:	
Chromium	1,500
Molybdenum	200
Tungsten	200
Vanadium	200
Uranium-233	500
Uranium-232	0.110
Maximum thermal neutron absorption of total impurity elements as equivalent parts of boron per million parts of total uranium	8

TABLE XIII
(Continued)

SPECIFICATIONS FOR URANIUM HEXAFLUORIDE DELIVERED TO THE AEC

Item*	Numerical Value
Maximum total of gamma activity due to fission products and uranium-237 as percent of gamma activity of aged natural uranium and as measured in a high-pressure ionization chamber (drawing D-AWM-8796 of Nuclear Division, Union Carbide Corporation)	20
Maximum beta activity due to fission products as percent of beta activity of aged natural uranium	10
Maximum number of parts of plutonium per billion parts of total uranium	1
Maximum alpha activity from all transuranic elements in disintegrations per minute per gram of total uranium	1,500
* All specification analyses on uranium hexafluoride shall be performed on samples removed in the liquid state from each cylinder while its contents are liquid and homogeneous.	

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

INTERNAL DISTRIBUTION

Administrative Office

Winkel, R. A.

Cascade Operations

Davis, W. A.

Monk, T. H.

Engineering Division

Dyer, R. H.

Patton, F. S.

Thompson, S. A.

Gaseous DiffusionDevelopment Division

Barber, E. J.

Burkett, D. L.

Burton, D. W.

Collins, W. T.

Kidd, G. J., Jr.

King, C. J.

McGill, R. M.

Melroy, P. E.

Nelson, T. E.

Pashley, J. H.

Stephenson, M. J.

Trammell, H. E.

Laboratory Division

Barton, J. C.

Smith, L. A.

Weber, C. W.

Operations Analysis and Long
Range Planning Division

Lang, D. M.

Operations Division

Anderson, L. W.

Cates, P. S.

Dykstra, J.

Legeay, A. J.

Plant LibraryPlant Records, RC (2)

Sommerfeld, K. W.

Technical Director

Wilcox, W. J., Jr.

Paducah

Clark, J. L.

Golliher, W. R.

Harris, R. L.

Hopkins, C. C.

Hull, G. T.

Levin, R. W.

Merriman, J. R.

Y-12 Plant

Griffin, J. D.

Jasny, G. R.

Vanstrum, P. R.

EXTERNAL DISTRIBUTION

TID-4500 (138)