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ORGBP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1968

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE GASEOUS DIFFUSION PLANT

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

**UNION
CARBIDE**

OAK RIDGE GASEOUS DIFFUSION PLANT
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Oak Ridge, Tennessee 37830

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Date of Issue: January 13, 1969

Report Number: K-1769

Subject Category: Chemical Separations \
Processes for
Plutonium and Uranium

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1968

J. H. Pashley
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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

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A B S T R A C T

The Oak Ridge Gaseous Diffusion Plant Gaseous Diffusion Development Division has participated in studies of a group of processes aimed at purifying and recovering valuable uranium and plutonium from spent nuclear reactor fuels. The program included two main phases: (a) preparation of conceptual plant studies with concomitant definition of problem areas associated with the process and technology and plant design; and (b) component development, including scale-up and testing of crucial process equipment and auxiliaries. The current report is the seventh and last in a series of progress reports issued semiannually. The topics covered include (1) the conceptual plant for the processing of spent, low enrichment LWR fuel; (2) scoping calculations for the volatility processing of spent Fast Breeder Reactor fuels in the areas of alumina usage economics, the increase in static bed with radioactive heat generation, the transfer of fission product heat from reactors, reagent requirements for plutonium fluorination, and nuclear safety; (3) process and reactor studies in the semiworks plant; (4) outlet gas filter studies; (5) uranium purification in a sorption-desorption system employing sodium fluoride; and (6) the testing of the ORGDP design peripheral compressor.

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ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1968

This report is the seventh and last in the series of semiannual summaries of Oak Ridge Gaseous Diffusion Plant work in the United States Atomic Energy Commission-sponsored volatility process development effort. The work has been performed in conjunction with development programs at Argonne National Laboratory and Oak Ridge National Laboratory. The ORGDP program supported and extended the national laboratory efforts in two ways. First, conceptual plant studies leading to statement of technology problem areas, program analysis, and economic comparisons of alternative flow sheets were performed, and the cost of a 1-tonne of uranium per day processing plant was determined. Second, a component development program was conducted to cover scale-up and testing of crucial process equipment and auxiliaries. Emphasis was placed on the study of low-enrichment power reactor fuel reprocessing systems. The possible applications of volatility techniques to fast reactor fuels were also considered, and some scoping studies in this area were conducted.

The program at the ORGDP was phased out as of July 1, 1968, in accordance with the AEC decision to discontinue studies on the application of volatility techniques to the processing of low enrichment power reactor fuels. Aqueous methods have been demonstrated to be successful and sufficiently economic to support this segment of the nuclear power industry; nevertheless, the dry processing route appears to be potentially competitive economically with the aqueous methods. Unfortunately, the advantages cannot be firmly established because development work is incomplete.

SUMMARY

ENGINEERING STUDIES

Topical reports were prepared for publication on the conceptual volatility processing plant, the design of cold traps, and plant nuclear safety studies. In addition, scoping calculations were made for volatility applications in Fast Breeder Reactor fuels reprocessing.

CONCEPTUAL PLANT STUDIES

The report on the 1-tonne of uranium per day conceptual plant is complete and will be published soon. Included in the report are sections on bases for the study, process technology, process description, process critique, general facilities, safety, plant staff, costs, and conclusions and recommendations. The capital cost of the plant is estimated at 33 million dollars when a 25% contingency is included. The total unit fuel reprocessing cost (capital charge plus operating cost) is \$27.32/kg of uranium.

FBR CALCULATIONS

Scoping type calculations for FBR fuels were made to provide input information for ANL volatility applications studies. The FBR fuel charges were assumed to be 50% core material (20% plutonium dioxide and 80% uranium dioxide) and 50% axial blanket material, while the core burnup and the specific power were 100,000 Mwd/tonne and 200 Mw/tonne, respectively. Calculations were made in the areas of alumina usage economics, the increase in static bed with radioactive heat generation, the transfer of fission product heat from reactors, reagent requirements for plutonium fluorination, and nuclear safety.

Alumina Usage Economics

Utilization costs, i.e., the total of alumina costs at \$0.19/lb, plutonium loss penalty at \$10/g, and waste storage investment, were computed for alumina usages of from 0.25 to 5.0 kg of alumina used per kilogram of uranium plus plutonium processed and for 30- and 120-day cooled fuel. The results indicate that a reduction in the amount of alumina used is desirable, as might be expected, and that some storage cost savings may be obtained by processing longer cooled fuel; however, the savings do not appear to be great.

Static Bed Temperature Increases Due to Radioactive Heat Generation

Estimates were made of the centerline temperature rise rates which might be encountered in various size solid cylindrical and annular beds containing FBR fuels if fluidization were lost during processing. Fuel cooling times of 30 and 180 days were considered. Calculations were made for the conservative case where fluidization is lost immediately after removing all the plutonium and uranium from the bed, with only the alumina and fission products left behind. The ratio of alumina to fuel prior to fluorination was assumed to be unity initially. The bed density, heat capacity, and thermal conductivity were taken to be 135 lb/cu ft, 0.26 Btu/lb-°F, and 0.26 Btu/hr-ft-°F, respectively.

The computed temperature changes are plotted versus time after loss of fluidization for cylindrical beds with radii of 0.5, 1.0, and 1.5 feet. The same type plots have been prepared for annular beds where the central diameters are 4, 8, and 12 inches, and the annulus dimensions are 3, 4, 6, and 8 inches. With such data, estimates can be made of permissible downtime limits before effective corrective action need be taken to avoid sintering.

Transfer of Fission Product Heat From Fluid-Bed Reactors

Computations indicate that fission product heat releases as high as 30,000 Btu/hr-cu ft of reactor bed are possible when FBR fuels are processed in fluid beds at low alumina usage ratios. The heat fluxes

required to remove this amount of heat was found to be no greater than 15,000 Btu/hr-sq ft of wall area for fluid-bed reactors up to 24 inches in diameter. Since fluid-bed heat fluxes in the range of 10,000 to 15,000 Btu/hr-sq ft can be achieved with a properly designed cooling system, reactor diameters up to 24 inches seem practical from the heat transfer standpoint.

Plutonium Fluorination Requirements

The production capabilities of 5- to 25-inch-diameter reactors were calculated for continuous fluid-bed fluorination of the plutonium from FBR fuels at bed temperatures from 300 to 500°C. Interest was focused, in particular, on the time requirement and the reaction rate for the step. A gas velocity of 1.0 ft/sec and a pressure of 1 atmosphere of fluorine were assumed. In addition, the product gases were assumed to contain equilibrium proportions of plutonium hexafluoride and fluorine at reaction bed temperatures.

Calculations were also made for overall fluorine requirements in batch fluorination with various plutonium charges and fluorine flow rates. The bed temperature was assumed to be 300°C initially and to rise to 400°C over the course of the reaction at a rate of 20°C/hr. During the latter stages of the reaction when the plutonium concentration in the fluid bed becomes small, the plutonium hexafluoride-to-fluorine ratio in the off-gas will likely become smaller than the equilibrium value because increased quantities of fluorine will be necessary to complete the step.

The results of the continuous and the batch process calculations are presented in graphical form. Each graph is arranged so that the average fluorination rate can be obtained as a function of the operating parameters within the ranges selected for the study.

Nuclear Safety

Studies were made of the nuclear reactivities of plutonium dioxide and plutonium tetrafluoride, at various densities, in spherical, infinite annular, infinite and finite slab, and infinite and finite cylindrical geometries.

The critical radii for spheres and infinite cylinders containing homogeneous mixtures of plutonium dioxide and alumina and also plutonium tetrafluoride in alumina were estimated by use of the ANISN Neutron Transport Code. The radii for spheres and infinite cylinders were found to be smaller for high density (9 g/cc) plutonium dioxide cases than for the fully dense (7 g/cc) plutonium tetrafluoride cases.

The critical inner radii were computed for vessels with 3, 4, 6, and 8-inch annular thicknesses containing homogeneous mixtures of plutonium dioxide and alumina. The effective neutron multiplication factor first increases as the radius of the inner cylinder is enlarged at constant annular thickness. The k_{eff} then reaches a maximum and eventually decreases and approaches the value for an infinite slab.

The Monte Carlo code was used to calculate the reactivities of finite cylinders and slabs of plutonium tetrafluoride. Bare vessels, as well as vessels with top and bottom reflection and nickel cladding, were considered. Reflected 10-inch-diameter cylinders containing plutonium tetrafluoride at 3 g/cc and 4-inch-thick by 2-foot-long slabs of plutonium tetrafluoride with compound densities of 3 and 5 g/cc were computed to be subcritical regardless of height.

PROTOTYPE TESTING AND EVALUATION

The projects during the final report period included runs in the semiworks facility, filter multiple exposure tests, product purification by sorption on sodium fluoride, and operation of the peripheral compressor. A movie showing results of bromine pentafluoride spill tests has been prepared.

PROCESS AND REACTOR STUDIES

The semiworks reactor system program was concluded with further elutriation tests and studies on semicontinuous pellet feeding during oxidation, the use of 40% oxygen instead of lower oxygen concentrations, and fuel element decladding.

Semiworks Plant Tests

Twelve new runs (UE-43 through -54) were conducted using annular EGCR or solid cylindrical Westinghouse uranium dioxide pellets, a PRTR fuel element, and an ORGDP-fabricated simulated fuel element. Alcoa tabular alumina was the bed diluent in all tests.

Several factors of possible influence on U_3O_8 elutriation during oxidation were studied. These included hydrogen chloride pretreatment of EGCR pellets, length of exposure to hydrogen chloride, and superficial velocity during oxidation.

A cold "normal" assay PRTR fuel element containing eighteen zircaloy-clad fuel rods and the second sixty-tube simulated fuel element fabricated in ORGDP shops were processed through decladding and oxidation. The PRTR test was the first in the semiworks plant with an actual reactor fuel assembly.

A series of runs featured semicontinuous pellet feeding during oxidation. In these runs, the pellets were fed to the reactor through a hold volume attached to the charging port at the top of the reactor. This mode of feeding is considered possibly applicable when preceded by a mechanical decladding process from which uranium dioxide pellets would be available for subsequent processing. Semicontinuous feeding of alumina to the filter cooler and removal of fluid-bed powder from the cooler during the oxidation process were also attempted.

In some of the oxidation tests, 40% oxygen was used instead of 21%. Westinghouse pellets and EGCR pellets were oxidized in separate runs to uncover possible differences in results at this high concentration.

The same six filters, which had been in use in most of the semiworks operation since the start of the program were used again in these tests. The filters were washed once during the test period to maintain permeability.

The current tests indicated the following:

1. The rate of U_3O_8 elutriation is increased by pellet exposures to hydrogen chloride of as little as 1 hour prior to oxidation, by raising the superficial velocity from 1.5 to 2.4 ft/sec, and by the use of 40% oxygen instead of concentrations in the range of 11 to 21% oxygen. Since U_3O_8 elutriation rates in excess of 7 kg per 1,000 scf of gas, deemed necessary for a plant operation, have been achieved; elutriation is probably a practical transfer technique for the two-vessel process.
2. The PRTR fuel element and the simulated fuel element were successfully processed in the semiworks reactor. Unreacted end caps and fragments of fuel cladding did not interfere with oxidation in the test with the PRTR fuel element.
3. When uranium dioxide pellets are fed semicontinuously to a fluid-bed reactor during oxidation, the temperature and pressure drop increases can be controlled and bed performance is not upset.
4. A concentration of 40% oxygen in nitrogen can be used from the outset of oxidation in shallow pellet beds. Vibration might be necessary to control high pressure drop buildup across the beds. The oxidized product with EGCR pellets appears to be fine enough for fluid-bed fluorination.
5. The comminution of solid Westinghouse pellets to minus 35-mesh particles is poorer than that obtained with cylindrical EGCR pellets when usual oxidation procedures are used. The differences might not be so pronounced with irradiated fuel processing.

In summary, the overall reactor system studies have indicated that (1) the removal of zircaloy cladding by reaction with hydrogen chloride proceeds satisfactorily and at sufficient rates for most purposes; (2) oxidation of uranium dioxide pellets can be performed satisfactorily, providing the proper gas velocity is employed and the reaction zone is located close to the top of the pellet zone; (3) fluid-bed fluorination with elemental fluorine can be performed readily at temperatures of 350 to 400°C and probably higher; and (4) a significant heat release will occur in the elemental fluorine fluorination step because of the failure of bromine pentafluoride to convert completely some of the fission product elements.

Outlet Filter Gas Studies

Studies were continued in the filter test loop in search of the cause of and a remedy for the plugging of sintered nickel fiber filter tubes in dechlorination off-gases. Activities were centered on the volatilization of zirconium tetrachloride from zircaloy tetrachloride powder charges to the reactor with hydrogen and with hydrogen and hydrogen chloride in the fluidizing gases. In addition, a 316 stainless steel filter was exposed to dechlorination off-gases; this material had been proposed for the filtration of the off-gases from the dechlorination and oxidation steps in a two-reactor process.

The exposure of zirconium tetrachloride plus a mixture of 30% hydrogen and 70% oxygen-free argon resulted in about a 20% permeability loss in the sintered nickel fiber filter; while hydrogen chloride, zirconium tetrachloride, and argon, with or without hydrogen, plugged the filter beyond satisfactory use, i.e., greater than 95%. The permeability loss for the stainless steel filter over the course of thirteen exposure cycles was likewise greater than 95%.

While the filter tube for general use with the fluoride volatility process has not been found, the use of separate filters for the operational steps might be desirable. For example, based on past corrosion tests, it might be possible to use stainless steel filters for chemical dechlorination and oxidation, while the fluorination off-gases would be routed through nickel filters.

Product Purification Sorption-Desorption Tests

New studies were made to cover high gas flow, low uranium hexafluoride concentration cases, such as might be encountered with exhaust gases from a cold trap backup system or to a sorption system in the event of a dilute gas release. The results indicate that an operating temperature of $93 \pm 8^\circ\text{C}$ should be satisfactory at a velocity of 1 ft/sec and a 200 ppm uranium hexafluoride concentration to reduce the outlet gas concentration to about 4 ppm. Since a bias might have been present during testing due to uranium hexafluoride background in the test system, it is possible that still lower outlet concentrations might be achievable.

PERIPHERAL COMPRESSOR

After 3,813 hours of operation, the compressor was shut down to replace bearings which were overheating. The bearing set nearest the compressor motor was found to have been damaged as the result of the degradation of the lubricating qualities of the grease. The bearings had performed well beyond the expected 2,500-hour life.

It is concluded that this compressor is potentially suited for the recycle of fluoride volatility process reagent gases.

DISCUSSION

ENGINEERING STUDIES

D. L. Breton, D. I. Dunthorn, K. E. Habiger,
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In keeping with the close-out plan for the Oak Ridge Gaseous Diffusion Plant fluoride volatility program, program engineering studies were concluded during this period. During the final report period, the conceptual processing plant study for light water fuels was completed; engineering calculations associated with that study and scoping calculations for the volatility reprocessing of spent FBR, i.e., Fast Breeder Reactor, fuels were made; and topical reports on (1) the design of cold traps, (2) nuclear safety studies for plants reprocessing high and low enrichment fuels, and (3) the conceptual plant engineering evaluation were prepared for publication.

CONCEPTUAL PLANT STUDIES

The completed report on the conceptual plant study contains sections on the bases for the work, process technology, process description, process critique, general facilities, safety, plant staff, costs, and conclusions and recommendations. The process rate was established at 1-tonne of uranium per day with the corresponding daily plutonium process rate being 9.7 kg. Conceptual drawings for important process equipment items are included, as well as layouts for fuel receipt and waste storage areas, process cells, and plant buildings. Since plutonium purification technology was not available, space and cost allowances, deemed adequate, were made for this portion of the process.

The plant is located on a 200-acre site. Staff requirements are 119 people. The facility includes (a) a process building with a total floor area of 46,500 sq ft, including a process cell area of 2,650 sq ft; (b) a fuel receipt building of 8,770 sq ft; (c) a cell and process gas filtration system and a 400-foot-tall stack; (d) a 23,000 sq ft utility, maintenance, and fluorine plant building; (e) an 8,000 sq ft warehouse; (f) waste storage areas; and (g) the usual utility and general improvements associated with process plants.

The capital cost of the plant has been estimated to be 33 million dollars with a 25% contingency included. With a depreciation charge of 15% per year, the unit capital charge becomes \$16.34 per kilogram of uranium. The operating cost is estimated to be \$10.98 per kilogram of uranium. The total unit fuel reprocessing cost would be the sum of the two, i.e., \$27.32 per kilogram. It should be stressed that, since the study was conceptual in nature, sufficient manpower and funding were not expended to prepare designs and layouts in sufficient detail to achieve high precision in the cost estimate.

FBR CALCULATIONS

The FBR scoping calculations were made to aid in assessing the applicability of the process to the treatment of irradiated fuels. The work was performed in cooperation with Argonne National Laboratory and was aimed at providing input information for their FBR fuel reprocessing studies. Calculations were made in five general areas. They were (1) the economics associated with alumina bed reusage, (2) static bed temperature increases due to radioactive heat generation, (3) the transfer of fission product heat from fluid-bed reactors, (4) the reagent requirements for plutonium fluorination, and (5) nuclear safety.

For the FBR calculations, it was assumed that the fuel assembly charged to the volatility process is comprised of 50% core material (20% plutonium dioxide-80% uranium dioxide) and 50% axial blanket material. Average FBR assembly radioactive heat generation rates were computed based on this split, assuming a core burnup and a specific power of 100,000 Mwd/tonne and 200 Mw/tonne, respectively; the axial blanket burnup and specific power were assumed to be 6,600 Mwd/tonne and 13.2 Mw/tonne, respectively. The average decay heats at various cooling times are shown in table I.

TABLE I
RADIOACTIVE DECAY HEAT FOR SPENT FBR FUEL

Cooling Time, days	Decay Heat*, Btu/hr-kg (U + Pu)		
	Core	Blanket	Average†
10	1,461	97	779
20	1,104	73	588
30	903	60	482
60	607	40	324
90	465	31	248
120	375	25	200
180	281	17	139

* Core burnup = 100,000 Mwd/tonne; specific power = 200 Mw/tonne;
Blanket burnup = 6,600 Mwd/tonne; specific power = 13.2 Mw/tonne.

† 50% core and 50% blanket.

Discussions of the calculations are presented in the following paragraphs.

Alumina Usage Economics

A few calculations were made to assess the bed diluent usage economics. The bed material was assumed to be alumina, and the computed utilization costs included alumina costs, plutonium loss charges, and waste storage investment based on bin storage costs developed at the Idaho Chemical Processing Plant*. The computed values are listed in table II for 30- and 120-day cooled fuel. The independent variable for these calculations was the alumina usage ratio; i.e., the kilogram quantity of alumina used per kilogram of uranium plus plutonium processed.

The cost of the alumina was taken as \$0.19 per pound, and the penalty for the plutonium losses was set at \$10 per gram. Plutonium retention on the discharge alumina was assumed to be 0.03 weight percent†. The results, in general, indicate that reduction of the alumina usage, perhaps by recycle, is desirable from an economic standpoint, as might be expected. They also show that storage capital costs are of the same order of magnitude as the value of plutonium losses. It should be noted that bin storage costs for bin thicknesses less than 3.0 inches were not available, so that the extrapolations to lesser thicknesses may be questionable.

The results also indicate that some storage cost savings may be obtained by processing longer cooled fuel; however, interestingly enough, this savings apparently is not large enough to be economically controlling in the cases studied. If processing of longer cooled fuel permitted reduction in waste volume, e.g., by allowing more recycles than possible with shorter cooled material, the economic significance would be greater.

Figure 1 shows the resultant volumetric heat generation rate in the waste alumina as a function of the alumina usage ratio, with cooling time as a parameter. The alumina density was taken to be 135 pounds per cubic foot. The bin thicknesses required to maintain a centerline-to-wall temperature difference of 650°C are indicated on the plot; they were calculated assuming a slab geometry and an alumina thermal conductivity of 0.2 Btu/hr-ft-°F.

* Stevens, J. I., An Economic Evaluation of Ultimate Disposal of Liquid Radioactive Wastes by the Fluidized Bed Calcination Process, Phillips Petroleum Company, October 30, 1962 (IDO-14595).

† The 0.03% plutonium retention value, although somewhat higher than average holdups experienced at ANL during treatment of dilute plutonium mixtures, was chosen on the basis of the high plutonium concentrations in FBR fuel charges.

TABLE II
ALUMINA USAGE ECONOMICS
IN PROCESSING SPENT FBR FUEL

Alumina Usage Ratio*	Bin Thickness, inch	Costs, \$/kg (U + Pu)			
		Waste Storage	Plutonium Losses	Alumina	Total
<u>Cooling Time = 30 days</u>					
0.25	1.54	0.92	0.75	0.10	1.77
0.50	2.16	1.01	1.50	0.21	3.32
1.00	3.06	2.77	3.00	0.42	6.19
2.00	4.33	4.74	6.00	0.84	11.58
3.00	5.32	6.48	9.00	1.26	16.74
4.00	6.11	8.11	12.00	1.67	21.78
5.00	6.84	9.65	15.00	2.09	26.74
<u>Cooling Time = 120 days</u>					
0.25	2.38	0.77	0.75	0.10	1.63
0.50	3.36	1.33	1.50	0.21	3.04
1.00	4.76	2.27	3.00	0.42	5.69
2.00	6.73	3.89	6.00	0.84	10.73
3.00	8.21	5.35	9.00	1.26	15.61
4.00	9.44	6.72	12.00	1.67	20.39
5.00	10.73	7.97	15.00	2.09	25.06

* The alumina usage ratio is the kilogram quantity of alumina used per kilogram of uranium plus plutonium processed.

WASTE ALUMINA
VOLUMETRIC HEAT GENERATION RATE

Figure 1.

Static Bed Temperature Increases Due to Radioactive Heat Generation

If fluidization were lost in a head-end reactor during processing, fission products present in the settled bed would cause heating which, if not checked, could eventually increase bed temperatures to the point where sintering or even melting of the contents could occur. Since this is an area of considerable concern, due to the possibly great difficulties which might be involved in removing plugs in an operating plant, estimates were made of the temperature increase rates which might be encountered for several FBR fuels. From these rates, estimates can be made of downtime before effective corrective action need be taken. These estimates would tend to be conservative, since it is probable that some gas could be passed through a plugged bed and with resultant increase in heat removal rate.

In this respect, it should be noted that the upper temperature permissible in the static bed is likely to be more a function of the caking tendencies of the minor constituents, i.e., fission product compounds, present rather than the caking tendencies of the relatively refractory aluminum oxide. Of course, tests to establish temperature limits for typical bed mixtures would certainly be valuable in setting the limits on the allowable static bed downtime. The results of the calculations described in the following sections should, however, provide approximate guides and comparisons for cylindrical and annular design cases.

Solid Cylinders Containing Fission Products Only. Calculations were made to estimate the centerline temperature rise rates of settled cylindrical alumina beds containing fission products from high burnup breeder reactor fuels. These calculations were made for the case where fluidization is lost immediately after removing all plutonium and uranium from the bed, with only alumina and fission products left behind. This should be the most conservative case, since, for initial alumina-to-fissile material weight ratios of 1, the volumetric heat generation rates are approximately doubled when the fissile material is removed.

The bed density, heat capacity, and thermal conductivity were taken to be 135 lb/cu ft, 0.26 Btu/lb-°F, and 0.26 Btu/hr-ft-°F, respectively. The initial ratio of alumina to fuel prior to fluorination was assumed to be unity, and it was assumed that the wall temperature could be held at its initial value. The results of the calculations are shown in figures 2 through 4 for cooling times from 30 to 180 days and for bed radii of 0.5, 1.0, and 1.5 feet.

Annular Cylinders Containing Fission Products Only. For comparison purposes, calculations were repeated for annular cylinders to estimate the maximum temperature rise rates of settled beds, again containing no uranium or plutonium. The values for bed density, heat capacity, and thermal conductivity were those which were used for the solid cylinder cases, and the starting bed alumina-to-feed ratio was once more taken as 1.0. Annulus dimensions of 3, 4, 6, and 8 inches were considered

CENTERLINE TEMPERATURE RISES FOR
SETTLED ALUMINA BEDS IN CYLINDRICAL VESSELS
CASE I: FUEL COOLED 30 DAYS

Figure 2

CENTERLINE TEMPERATURE RISES FOR
SETTLED ALUMINA BEDS IN CYLINDRICAL VESSELS
CASE II: FUEL COOLED 90 DAYS

Figure 3

CENTERLINE TEMPERATURE RISES FOR
SETTLED ALUMINA BEDS IN CYLINDRICAL VESSELS
CASE III: FUEL COOLED 180 DAYS

Figure 4

using central diameters of 4, 8, and 12 inches for each annular thickness. It was observed that temperature rises for a given annulus thickness were about the same for all of the central diameters considered at that thickness; accordingly, the results for the 4-inch-inside-diameter cases are the only ones presented here. Values for the other inside diameters considered differ from the plotted values by less than 5%. The results are shown in figures 5 through 7 for reference fuel cooling times of 30, 90, and 180 days.

Comparing figures 2 through 4, it can be seen that, for a 1-foot-diameter cylindrical reactor, a centerline-to-wall temperature difference of 800°C is reached in about 1.8 hours when the fuel has been cooled 30 days before processing. With an annular reactor having a 4-inch-inner pipe diameter, an annulus thickness of about 4.3 inches is required to achieve the same flow area as in the cylindrical case. For this annulus size, the 800°C temperature difference is not reached until after about 3 hours. This advantage can be increased by going to inside pipe sizes larger than 4 inches and, consequently, to smaller annulus thicknesses for the same cross sectional area; however, other considerations, primarily throughput demands and operational feasibility, limit the extent to which the annular thickness can be reduced.

Transfer of Fission Product Heat from Fluid-Bed Reactors

The burnup for fast breeder fuels will be considerably greater than the burnup for low enrichment LWR fuels. Consequently, fission product heat releases will necessitate more fluid-bed cooling capacity than envisioned for thermal reactor fuel plants. In fact, for very large diameters, the cooling requirements for removing the fission product decay heat alone, neglecting chemical reaction heat, may not be practical for high throughputs.

Table III shows typical heat fluxes required for removing fission product heat for four different volumetric heat generation rates. The volumetric heat generation rate is dependent on both the alumina usage and the fuel cooling time.

As presented earlier in figure 1, volumetric heat generation rates as high as 30,000 Btu/hr-cu ft are possible at low alumina usage ratios. Considering table III, then, it can be seen that, for several reactor sizes, the heat fluxes required to remove this amount of fission product heat are less than 15,000 Btu/hr-sq ft of wall area. Since fluid-bed heat fluxes in the range of 10,000 to 15,000 Btu/hr-sq ft can be achieved with a properly designed cooling system, fluid-bed reactor diameters up to 24 inches seem practical from the heat transfer standpoint. It should be pointed out, however, that other limitations may require use of smaller diameter reactors. For example, the quantity of plutonium contained in a 24-inch-diameter reactor would be about 43 kg, assuming a 6-foot bed depth and equal amounts of alumina and reference fuel material. Under certain conditions, this mass of plutonium could be critical, e.g., for plutonium dioxide at a powder density of 4.5 g/cc with 30 cm of alumina

TRANSIENT TEMPERATURE RISE IN STATIC ANNULAR BED
CASE I: FUEL COOLED 30 DAYS

Figure 5

TRANSIENT TEMPERATURE RISE IN STATIC ANNULAR BED
CASE II: FUEL COOLED 90 DAYS

Figure 6

TRANSIENT TEMPERATURE RISE IN STATIC ANNULAR BED
CASE III: FUEL COOLED 180 DAYS

Figure 7

TABLE III

FLUID-BED HEAT LOADS RESULTING FROM FISSION PRODUCT HEAT

Reactor Diameter, inch	Heat Flux at Indicated Volume Heat Generation Rates, Btu/hr-sq ft of reactor wall			
	10,000 Btu/hr-cu ft	15,000 Btu/hr-cu ft	20,000 Btu/hr-cu ft	30,000 Btu/hr-cu ft
6	1,250	1,880	2,500	3,800
9	1,870	2,810	3,750	5,600
12	2,500	3,750	5,000	7,500
15	3,120	4,690	6,250	9,400
18	3,750	5,630	7,500	11,300
24	5,000	7,500	10,000	15,000

reflection, the critical spherical mass of plutonium has been computed* to be in the range of 38 to 41 kg for the plutonium isotopic compositions arising from irradiation levels of 10,000 to 30,000 Mwd/tonne of uranium.

Plutonium Fluorination Requirements

In fast breeder fuels, the plutonium concentration at discharge is much higher than that for thermal fuels. Since the fluorination of plutonium tetrafluoride requires large quantities of fluorine, due to equilibrium limitations, the time requirements for processing large quantities of plutonium are of considerable interest. For scoping purposes, plutonium hexafluoride production capabilities for various diameter reactors were calculated by assuming that the product gases contained equilibrium proportions of plutonium hexafluoride and fluorine at the fluid-bed operating temperature. The results are plotted in figure 8. A gas velocity of 1.0 ft/sec and a pressure of 1 atmosphere of fluorine were assumed. The fluorination rates presented in figure 8 are for continuous operation of a reactor; however, semicontinuous or batch processing of the plutonium will probably be the route actually taken in the plutonium processing step. Semicontinuous or batch processing rates will, of course, be less than the rates predicted for continuous processing. Therefore, in an attempt to establish limits for the plutonium processing rate, calculations were also made for batch processing. Here, the bed temperature was assumed to be 300°C initially; upon beginning the plutonium fluorination step, the bed temperature was allowed to increase to 400°C at a rate of 20°C/hr. During the latter stages of batch fluorination when the plutonium concentration in the fluid bed becomes small, the off-gases leaving the bed will probably no longer contain plutonium hexafluoride and fluorine at their equilibrium ratio; it is likely that the plutonium hexafluoride-to-fluorine ratio would be less than the equilibrium value, and fluorination would require increased quantities of fluorine.

Data from ANL experiments on plutonium fluorination have been used to estimate the degree of equilibrium attained as a function of the plutonium concentration in the bed; the results are plotted in figure 9. The independent variable is the ratio of the moles of plutonium charged to the initial molar flow rate of fluorine (moles per hour), i.e., at 300°C. The fluidizing velocity is maintained at a constant value throughout the operation as the bed temperature is increased from 300 to 400°C at 20°C/hr. The parameter is the initial mass ratio of plutonium to alumina. Fluorine requirements are then expressed as the moles of fluorine required to fluorinate one mole of plutonium (tetrafluoride) with 99% plutonium recovery.

* Smiley, S. H., Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report January through June, 1966, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, January 18, 1967 (K-1691), p. 36.

CONTINUOUS PLUTONIUM FLUORINATION AS
A FUNCTION OF BED DIAMETER

Figure 8

PLUTONIUM BATCH FLUORINATION

Figure 9

As an example of the use of figure 9, consider a 12-inch-diameter reactor with a 6-foot bed operated at a gas velocity of 1.0 ft/sec, a system pressure of 1 atmosphere, and an alumina usage ratio of 1.0; i.e., one kilogram of alumina used per kilogram of uranium plus plutonium processed. These values correspond to a plutonium charge of approximately 9.4 kg, a molar ratio of plutonium charge to fluorine flow at 300°C of 0.02317 hour, and an initial mass ratio of plutonium to alumina of 0.0822. From figure 9, the moles of fluorine required per mole of plutonium tetrafluoride reacted is 310. The fluorination time will be 310 times 0.02317, or 7.2 hours, and the average fluorination rate will be about 1.3 kg of plutonium per hour. As a comparison, the fluorination time for the 9.4 kg plutonium charge would be 4.7 hours if equilibrium at 400°C were maintained through the fluorination step (figure 8). The fluorination rate for the equilibrium case would be about 2 kg/hr.

Nuclear Safety

The handling of FBR fuels poses difficult nuclear safety problems for a reprocessing plant treating sizable fuel loads, because of the large quantities of plutonium contained in the fuel. Even with its general advantage over aqueous schemes because of the absence of hydrogen moderation, the fluoride volatility process for FBR fuels is, nevertheless, faced with equipment size and batch limits which require considerable ingenuity on the part of the design engineer. To provide input for the FBR studies, then, several calculations have been made to ascertain the nuclear reactivities of several plutonium processing reactor designs; the cases studied have involved both plutonium dioxide and plutonium tetrafluoride, at various densities, containing in spheres, infinite cylinders, infinite annuli, infinite slabs, finite cylinders, and finite slabs.

Spheres and Infinite Cylinders. Critical radii for infinite cylinders and for spheres containing homogeneous mixtures of plutonium dioxide and alumina, and also plutonium tetrafluoride and alumina have been estimated using the ANISN neutron transport code. Presented in tables IV through VII, the results are also shown in figures 10 through 13 for easier inspection.

It was assumed for all cases that the cylinders or spheres were reflected with 30 cm of alumina. The alumina density, both in the reflector and in the fuel mixture was taken to be 2.5 g/cc. Fissile material compound densities assumed were 5, 6, and 9 g/cc for the oxide calculations and 3, 5, and 7 g/cc for the fluoride cases*. All plutonium was considered to be plutonium-239. Additionally, it was assumed that volumes of fissile

* These calculations are extensions of previous work summarized in tables A-VII and A-VIII of the ORGDP report: Habiger, K. E., and Breton, D. L., Nuclear Safety Studies for Low Enrichment Fluoride Volatility Fuel Reprocessing Plants, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, September 4, 1968 (K-1734).

TABLE IV

CRITICAL RADII FOR INFINITE CYLINDERS
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM DIOXIDE AND ALUMINA*

<u>Plutonium Dioxide, volume percent</u>	<u>Plutonium, weight percent</u>	<u>Critical Radius, cm</u>
<u>Plutonium Dioxide Density = 9 g/cc</u>		
10	25.20	18.54
40	62.25	7.58
70	78.81	5.16
100	88.19	4.02
<u>Plutonium Dioxide Density = 6 g/cc</u>		
10	18.57	23.54
40	54.27	10.07
70	74.82	6.94
100	88.19	5.44
<u>Plutonium Dioxide Density = 5 g/cc</u>		
10	16.03	26.21
40	50.40	11.44
70	72.63	7.92
100	88.19	6.22

* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.

TABLE V

CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM DIOXIDE AND ALUMINA*

<u>Plutonium Dioxide, volume percent</u>	<u>Plutonium, weight percent</u>	<u>Critical Radius, cm</u>	<u>Critical Mass, kg Pu</u>
<u>Plutonium Dioxide Density = 9 g/cc</u>			
10	25.20	30.334	92.80
40	62.25	13.522	32.88
70	78.81	9.514	20.04
100	88.19	7.518	14.13
<u>Plutonium Dioxide Density = 6 g/cc</u>			
10	18.57	37.398	115.93
40	54.27	17.667	48.89
70	74.82	12.691	31.71
100	88.19	10.214	23.62
<u>Plutonium Dioxide Density = 5 g/cc</u>			
10	16.03	41.532	132.32
40	50.40	19.895	58.18
70	72.63	14.390	38.53
100	88.19	11.682	29.45

* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.

TABLE VI
CRITICAL RADII FOR INFINITE CYLINDERS
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM TETRAFLUORIDE AND ALUMINA*

<u>Plutonium Tetrafluoride, volume percent</u>	<u>Plutonium, weight percent</u>	<u>Critical Radius, cm</u>
<u>Plutonium Tetrafluoride Density = 7 g/cc</u>		
10	18.00	23.20
40	49.41	9.88
70	65.80	6.79
100	75.87	5.30
<u>Plutonium Tetrafluoride Density = 5 g/cc</u>		
10	13.80	27.69
40	43.36	12.48
70	62.48	8.65
100	75.87	6.83
<u>Plutonium Tetrafluoride Density = 3 g/cc</u>		
10	8.93	35.68
40	33.72	17.58
70	55.91	12.51
100	75.87	9.98

* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.

TABLE VII

CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES
OF PLUTONIUM TETRAFLUORIDE AND ALUMINA*

Plutonium Tetrafluoride, volume percent	Plutonium, weight percent	Critical Radius, cm	Critical Mass, kg Pu
--	------------------------------	------------------------	-------------------------

Plutonium Tetrafluoride Density = 7 g/cc

10	18.00	36.638	109.41
40	49.41	17.119	44.64
70	65.80	12.143	27.88
100	75.87	9.660	20.05

Plutonium Tetrafluoride Density = 5 g/cc

10	13.80	43.942	134.83
40	43.36	21.318	61.58
70	62.48	15.392	40.56
100	75.87	12.454	30.70

Plutonium Tetrafluoride Density = 3 g/cc

10	8.93	55.144	159.88
40	33.72	29.330	96.23
70	55.91	21.866	69.78
100	75.87	18.069	56.25

* Reflected with 30 cm alumina at 2.5 g/cc. All plutonium was assumed to be plutonium-239.

CRITICAL RADII FOR INFINITE CYLINDERS
CONTAINING HOMOGENEOUS MIXTURES OF
PLUTONIUM DIOXIDE AND ALUMINA

Figure 10

CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES OF
PLUTONIUM DIOXIDE AND ALUMINA

Figure 11

CRITICAL RADII FOR INFINITE CYLINDERS
CONTAINING HOMOGENEOUS MIXTURES OF
PuF₄ AND Al_2O_3

Figure 12

CRITICAL MASSES FOR SPHERES
CONTAINING HOMOGENEOUS MIXTURES OF
PuF₄ AND Al_2O_3

Figure 13

material and alumina were additive in the fuel mixtures. For example, consider the case for a basic plutonium dioxide density of 9 g/cc, with the plutonium present in a mixture having a composition of 40 volume percent plutonium dioxide and 60 volume percent alumina. For each 100 cc of fuel mixture, the volume occupied by the plutonium dioxide and by the alumina would be 40 and 60 cc, respectively. The weight of plutonium dioxide in the mixture would then be 40×9 , or 360 grams, and thus, the resultant density of plutonium dioxide in the mixture would be 3.6 g/cc.

It can be seen from the results that the critical radii for infinite cylinders and the critical sphere masses are smaller for the high density (9 g/cc) plutonium dioxide cases than for the fully dense (7 g/cc) plutonium tetrafluoride cases.

Infinite Annuli. Calculations have also been made for homogeneous mixtures of plutonium dioxide and alumina contained in the annular space between two concentric cylinders. It was assumed for all cases that the inner cylinders were filled with alumina and that the outer cylinders were reflected with 30 cm of alumina. The alumina density was taken to be 2.5 g/cc, while the plutonium dioxide densities assumed were 3, 6, and 9 g/cc. All plutonium was considered to be plutonium-239. Annular thicknesses of 3, 4, 6, and 8 inches were investigated.

As the radius of an inner cylinder is increased while the annular thickness is kept constant, the effective neutron multiplication factor (k_{eff}) for the assembly first increases, then reaches a maximum, and finally decreases and approaches the value for an infinite slab (see figure 14).

The initial increase is due to the additional moderation as alumina is added to fill the expanding inner cylinder. As the inner radius is increased further, however, the system tends to uncouple, and the probability is reduced that neutrons emitted from one wall of the annulus in the direction of the center will reach the opposite annular wall. That is, as the spacing is increased, neutron interaction is reduced. Thus, at some point, the neutron multiplication factor begins to decrease.

A summary of calculated critical inner radii is presented in table VIII. In those cases in which it was not obvious that a critical radius existed, the ANISN transport code was used in the fixed radius option instead of the search option to avoid using excessive computer time. In the fixed radius option, the inner radius was specified along with the annular thickness and the fuel concentration, and the k_{eff} for the assembly was calculated. In subsequent calculations, the inner radius was progressively increased, and additional cases were run until a maximum k_{eff} was reached. Results for a typical subcritical assembly calculation are plotted in figure 14. The critical radius ($k_{eff} = 1.0$) was then found by interpolation; if the maximum k_{eff} was less than 1.0, it was, of course, concluded that the assembly would be subcritical for all inner radii. The critical radii determined in this manner, i.e., by interpolation, are denoted as approximate values in table VIII. For these cases, it is important to realize that only the first, or "smallest", critical radii

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EFFECTIVE NEUTRON MULTIPLICATION FACTORS FOR
INFINITE ANNULAR CYLINDERS OF
HOMOGENEOUS MIXTURES OF PuO_2 AND ALUMINA

Figure 14

TABLE VIII

CALCULATED CRITICAL INNER RADII FOR ANNULAR CYLINDERS
CONTAINING HOMOGENEOUS PLUTONIUM DIOXIDE AND ALUMINA MIXTURES*

Plutonium Dioxide, volume percent	First Critical Inside Radius, cm, for Given Annular Thickness			
	3 inches	4 inches	6 inches	8 inches
<u>Plutonium Dioxide Density = 9 g/cc</u>				
10	ca. 27.4	ca. 15.5	3.86	§
40	§	§	§	§
70	§	§	§	§
100	§	§	§	§
<u>Plutonium Dioxide Density = 6 g/cc</u>				
10	†	ca. 30.4	ca. 12.3	3.61
40	3.27	§	§	§
70	§	§	§	§
100	§	§	§	§
<u>Plutonium Dioxide Density = 3 g/cc</u>				
10	†	†	†	ca. 21.3
40	ca. 18.5	ca. 10	1.04	§
70	5.72	1.42	§	§
100	1.71	§	§	§

* The inner cylinder was filled with alumina and the outer cylinder was reflected with 30 cm of alumina. The alumina density was 2.5 g/cc. All plutonium was plutonium-239.

† Safe for all inner radii.

§ Supercritical for all inner radii.

are given. Since the k_{eff} 's reach maximum values and then decrease approaching the values for infinite slabs, it is obvious that for critical annulus cases where the k_{eff} for the infinite slab is less than 1.0, there will be a second radius, i.e., the "largest" critical radius, where the k_{eff} 's for the annular cylinders will again pass through 1.0. These values were not computed in this study, however, since most of the calculations were taken only to the point of locating the maximum k_{eff} . Additionally, for many of the cases summarized in table VIII, the assemblies were supercritical for all inner radii. These cases were those in which the annular thicknesses were larger than the radii of critical solid infinite cylinders of the same material, composition, and density.

Infinite Slabs. To aid in the annulus studies, criticality calculations were also made for infinite slabs containing mixtures of plutonium dioxide and alumina. The slabs were reflected on both sides with 30 cm of alumina. The fissile material densities assumed were the same as for the annular cases. In addition, the slab calculations were repeated for plutonium tetrafluoride at densities of 3, 5, and 7 g/cc. Results of these calculations are listed in tables IX and X and are plotted in figures 15 and 16.

Finite Cylinders. Reactivity estimates, made using the KENO Monte Carlo code, have been made for finite, 10-inch-diameter cylinders of plutonium tetrafluoride at densities of 3, 5, and 7 g/cc. Several cases of reflection were assumed* for each calculation; these are explained and the computation results are detailed in tables XI through XIV for plutonium tetrafluoride at 5 and 7 g/cc. For plutonium tetrafluoride at 7 g/cc, a plutonium isotopic distribution other than pure plutonium-239 was also assumed for one calculation series.

As can be seen from the tables, the addition of a bottom alumina reflector increases the effective neutron multiplication factor for the smaller cylinder heights, but has a lesser effect on longer cylinders. This is because the longer cylinders are approaching the point where they are essentially infinite and do not "see" the alumina reflectors at the ends. The addition of nickel cladding has an appreciable effect on the k_{eff} 's for all cylinder heights. For the cases shown, the cladding increased the k_{eff} 's from 5 to 10%. Also, as might be expected, a reduction in the percentage of fissile plutonium causes a corresponding decrease in reactivity.

All of the cylinders containing plutonium tetrafluoride at 3 g/cc were well below critical. For the most reactive case at this density, i.e., reflected on top and bottom with alumina and clad with nickel, the k_{eff}

* The basic approach was to begin with a bare cylinder and then add reflection in increments.

TABLE IX

CRITICAL THICKNESSES FOR INFINITE SLABS
CONTAINING HOMOGENEOUS PLUTONIUM DIOXIDE AND ALUMINA MIXTURES*

<u>Plutonium Dioxide, volume percent</u>	<u>Plutonium, wt %</u>	<u>Critical Thickness, cm</u>
<u>Plutonium Dioxide Density = 9 g/cc</u>		
10	25.20	11.37
40	62.25	3.12
70	78.81	1.80
100	88.19	1.26
<u>Plutonium Dioxide Density = 6 g/cc</u>		
10	18.57	16.06
40	54.27	4.65
70	74.82	2.70
100	88.19	1.89
<u>Plutonium Dioxide Density = 3 g/cc</u>		
10	10.38	26.92
40	39.20	9.07
70	64.98	5.37
100	88.19	3.79

* Slabs reflected on both sides by 30 cm of alumina at a density of 2.5 g/cc. All plutonium was plutonium-239.

TABLE X

CRITICAL THICKNESSES FOR INFINITE SLABS
CONTAINING HOMOGENEOUS PLUTONIUM TETRAFLUORIDE AND ALUMINA MIXTURES*

<u>Plutonium Tetrafluoride, volume percent</u>	<u>Plutonium, wt %</u>	<u>Critical Thickness, cm</u>
<u>Plutonium Tetrafluoride Density = 7 g/cc</u>		
10	18.00	15.73
40	49.41	4.59
70	65.80	2.67
100	75.87	1.88
<u>Plutonium Tetrafluoride Density = 5 g/cc</u>		
10	13.80	20.35
40	43.36	6.36
70	62.48	3.72
100	75.87	2.63
<u>Plutonium Tetrafluoride Density = 3 g/cc</u>		
10	8.93	29.30
40	33.72	10.32
70	55.91	6.16
100	75.87	4.38

* Slabs reflected on both sides by 30 cm of alumina at a density of 2.5 g/cc. All plutonium was plutonium-239.

CRITICAL THICKNESSES FOR INFINITE SLABS
CONTAINING HOMOGENEOUS MIXTURES OF
PuO₂ AND ALUMINA

Figure 15

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CRITICAL THICKNESSES FOR INFINITE SLABS
CONTAINING HOMOGENEOUS MIXTURES OF
PuF₄ AND ALUMINA

Figure 16

TABLE XI

INPUT PARAMETERS FOR CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 5 g/cc

Parameters	Case I	Case II	Case III
Top Reflector	100 cm Al_2O_3	100 cm Al_2O_3	100 cm Al_2O_3
Bottom Reflector	none	100 cm Al_2O_3	100 cm Al_2O_3
Wall Cladding	none	none	1.27 cm Ni
Isotopic Distribution	100% Pu-239	100% Pu-239	100% Pu-239

TABLE XII

RESULTS OF CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 5 g/cc

Cylinder Height, cm	Plutonium, kg	Effective Neutron Multiplication Factors		
		Case I	Case II	Case III
10	19.2		0.579 ± 0.003	0.634 ± 0.004
12	23.1		0.621 ± 0.003	0.669 ± 0.004
15	28.0		0.687 ± 0.004	0.738 ± 0.004
20	38.4		0.736 ± 0.004	0.802 ± 0.005
25	48.0	0.755 ± 0.004	0.774 ± 0.004	0.837 ± 0.004
35	67.3	0.812 ± 0.004	0.827 ± 0.004	0.905 ± 0.004
50	96.1	0.858 ± 0.004	0.874 ± 0.004	0.952 ± 0.004
100	192.2	0.919 ± 0.004	0.913 ± 0.005	1.000 ± 0.004
200	384.5		0.938 ± 0.004	

* Based on parameters in table XI.

TABLE XIII

INPUT PARAMETERS FOR CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc

Parameter	Numerical Value			
	Case I	Case II	Case III	Case IV
Top Reflector	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃
Bottom Reflector	none	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃
Wall Cladding	none	none	1.27 cm Ni	none
Isotopic Distribution	100% Pu-239	100% Pu-239	100% Pu-239	56% Pu-239 34% Pu-240 7% Pu-241 3% Pu-242

TABLE XIV

RESULTS OF CRITICALITY CALCULATIONS
FOR FINITE, 10-INCH-DIAMETER CYLINDERS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc*

Cylinder Height, cm	Plutonium, kg	Effective Neutron Multiplication Factors			
		Case I	Case II	Case III	Case IV
8	21.5		0.738 ± 0.004	0.776 ± 0.005	
10	26.9	0.741 ± 0.004	0.809 ± 0.004	0.859 ± 0.005	
12	32.3	0.818 ± 0.004	0.872 ± 0.005	0.930 ± 0.005	0.776 ± 0.004
15	40.4	0.897 ± 0.004	0.947 ± 0.005	1.004 ± 0.005	0.833 ± 0.004
20	53.8	0.985 ± 0.005	1.028 ± 0.005	1.087 ± 0.005	0.916 ± 0.004
25	67.3	1.065 ± 0.005			0.967 ± 0.004
100	269.1				1.117 ± 0.005

* Based on parameters in table XIII.

was $0.637 \pm 0.004^*$ at a cylinder height of 200 cm. It was concluded that 10-inch-diameter cylinders of plutonium tetrafluoride at a density of 3 g/cc would be subcritical for all heights under the reflection conditions assumed.

Finite Slabs. Monte Carlo calculations were also made for finite slabs, 4 inches thick by 2 feet long. Plutonium tetrafluoride densities of 3, 5, and 7 g/cc were again investigated with the same conditions of reflection as were assumed for the cylinder cases. The nickel cladding was assumed to be located on the faces of the slabs but not on the edges. The results for the 7 g/cc case are shown in tables XV and XVI.

All of the slabs of plutonium tetrafluoride at densities of 3 and 5 g/cc were found to be below critical. For the most reactive of these lower density cases, i.e., plutonium tetrafluoride at 5 g/cc, reflected on top and bottom with alumina and clad on the sides with nickel, the computed k_{eff} was 0.779 ± 0.004 at a slab height of 100 cm. It was concluded that 4-inch-thick by 2-foot-long slabs of plutonium tetrafluoride at 3 and 5 g/cc densities would be subcritical for all heights under the reflection conditions assumed.

* The k_{eff} value obtained by the Monte Carlo procedure represents an average of k_{eff} numbers computed for many different neutron batches. The qualification placed on this average (± 0.004 in this case) is one standard deviation based on the mathematics of the calculation. It is reported only to show the spread of the individually computed k 's and is not an indication of the absolute accuracy of the results.

TABLE XV

INPUT PARAMETERS FOR CRITICALITY CALCULATIONS
FOR FINITE 4-INCH-THICK BY 2-FOOT-LONG SLABS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc

Parameter	Numerical Value			
	Case I	Case II	Case III	Case IV
Top Reflector	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃
Bottom Reflector	none	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃	100 cm Al ₂ O ₃
Wall Cladding	none	none	1.27 cm Ni*	none
Isotopic Distribution	100% Pu-239	100% Pu-239	100% Pu-239	56% Pu-239 34% Pu-240 7% Pu-241 3% Pu-242

* The cladding was on only the two large faces of the slabs and extended to the levels of the top and bottom alumina reflectors.

TABLE XVI

RESULTS OF CRITICALITY CALCULATIONS
FOR FINITE 4-INCH-THICK BY 2-FOOT-LONG SLABS
OF PLUTONIUM TETRAFLUORIDE AT 7 g/cc*

Slab Height, Plutonium, cm kg	Effective Neutron Multiplication Factors			
	Case I	Case II	Case III	Case IV
12 39.5			0.744 ± 0.004	
15 49.3		0.714 ± 0.004	0.801 ± 0.004	
20 65.8	0.749 ± 0.004	0.776 ± 0.003	0.866 ± 0.004	
30 98.7	0.817 ± 0.004	0.822 ± 0.004	0.935 ± 0.004	
50 164.5	0.863 ± 0.004	0.857 ± 0.005	0.997 ± 0.004	
100 329.0	0.892 ± 0.005	0.895 ± 0.004		0.799 ± 0.004

* Based on parameters in table XV.

PROTOTYPE TESTING AND EVALUATION

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Activities were conducted according to the guidelines in the close-out plan for the Oak Ridge Gaseous Diffusion Plant fluoride volatility program. The work covered the zircaloy decladding, uranium dioxide oxidation, and fluorination phases of the process. Projects included runs in the semiworks facility, filter multiple exposure tests, a continuation of the long-term testing of the peripheral compressor, and product purification by sorption on sodium fluoride.

Formal topical reports will be issued shortly detailing the results of the major experimental work conducted during this program. The subjects which have been covered separately include semiworks plant tests, filter exposure tests, peripheral compressor work, and the bromine pentafluoride spill experiments which were conducted last year. In addition, a movie showing bromine pentafluoride spill tests in progress was prepared.

PROCESS AND REACTOR STUDIES

Additional semiworks tests were conducted under this phase of the program. The work encompassed the effect of various parameters on elutriation; the feasibility of semicontinuous pellet feeding during oxidation; fuel element decladding, followed by conversion of the released uranium to U_3O_8 ; and the use of 40% oxygen instead of lower oxygen concentrations in the oxidation step.

Semiworks Plant Tests

Twelve runs (UE-43 through -54) were conducted during this report period. In all the runs, 1/4- to 1/2-inch-diameter Alcoa T-164 alumina balls were added to position the uranium charge in the 10-inch-diameter section of the reactor about 1 foot above the top of the transition piece, while Alcoa T-61 tabular alumina powder, nominally minus 48- plus 100-mesh, was used in the reactor as bed diluent and in the filter cooler as a cooling bed. In all runs, 1/4- to 1/2-inch-diameter alumina balls were added to the reactor first, the uranium charge next, and the alumina powder last. Charges from various sources were involved in the testing, including annular EGCR or solid cylindrical Westinghouse pellets*, a PRTR fuel element containing vibratory compacted uranium dioxide, and an ORGDP-fabricated simulated fuel element containing solid cylindrical pellets.

* Obtained from scrap aluminum-clad fuel rods supplied by Bettis Atomic Laboratories. The normal assay, 1/2-inch-diameter by 3/4-inch-long pellets, were removed by physically peeling off the soft cladding. The rods had been utilized in a zero power critical facility operation.

Runs UE-43, -44, and -46, were made to study the effects of hydrogen chloride pretreatment of EGCR uranium dioxide fuel pellets, length of exposure to hydrogen chloride, and superficial velocity on U_3O_8 elutriation during the oxidation step. Run UE-43 was an oxidation run at the usual system backpressure and a superficial gas velocity of 2.4 ft/sec, which is the highest undertaken in tests in this program. With regard to operating steps, velocities, and reactant gas concentrations, UE-44 was similar to run UE-40, reported previously, in which the effect on U_3O_8 elutriation brought about by hydrogen chloride contacting a uranium dioxide pellet charge in the absence of zirconium was studied*. The hydrogen chloride treatment before oxidation lasted 4 hours in each case. The two runs differed only in that normal oxidation pressures were used in UE-44 while higher values were employed in UE-40. In UE-46, the time for the hydrogen chloride cycle was reduced to 1 hour to see if length of hydrogen chloride exposure is a major factor affecting elutriation.

Runs UE-45 and -48 were batch type tests with normal assay Westinghouse uranium dioxide fuel pellets. They were undertaken to see if the material from this new source could be processed without major difficulties. Because of the assay, this type of pellet could be tested in semiworks equipment without criticality limitations on the amount of uranium fed or accumulated; the material was ideally suited for use in planned semicontinuous feeding experiments with large charges. Operating conditions were chosen for run UE-45 to determine if good oxidation to U_3O_8 could be achieved in only 2 hours with air from the outset; and, for elutriation purposes, nitrogen was used for an additional 6 hours after cessation of air flow. Run UE-48 was conducted with the oxidation reaction time extended from 2 to 8 hours.

In UE-47, decladding and oxidation were carried out with a "cold" normal assay PRTR fuel element. This test was the first in the semiworks plant with an actual reactor fuel assembly. The PRTR fuel assembly was about 8 feet long and contained eighteen zircaloy-clad fuel rods. Each rod, which contained ceramic vibratory compacted uranium dioxide, was wrapped with wire to maintain spacing over the full length. The two end brackets were made of stainless steel, while the tubing, wire wrap, and end caps were zircaloy-2. The element originally had nineteen tubes in the cluster; however, the center rod was replaced with a thermowell so that, during the run, reaction temperatures at various positions along the longitudinal axis could be followed.

Runs UE-49, -50, and -52 featured semicontinuous pellet feeding during oxidation. This mode of feeding could be employed in a plant in which spent fuel rods would be declad mechanically with the pellets collected for salvage processing. In these runs, the pellets were fed to the

* Pashley, J. H., Schappel, R. B., ORGDP Fuel Reprocessing Studies, Summary Progress Report, July through December, 1967, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, July 17, 1968 (K-1744), pp. 46-47.

reactor through a hold volume attached to the charging port at the top of the reactor. This pellet charger is shown in figure 17 and consists of a 2-inch-diameter pipe, 2 feet 6 inches long, with ball valves on either end. Both valves were kept shut during the usual oxidation operation. When a batch of pellets was charged, the top valve was opened, pellets were loaded into the pipe, and the top valve was then closed. The lower valve was opened to allow the pellets to fall out of the pipe and into the reactor. In each run, an initial charge of pellets was placed directly in the reactor before startup so that an oxidation environment could be established before semicontinuous feeding commenced. EGCR pellets were used in UE-49, while Westinghouse pellets were fed to the reactor in both UE-50 and -52. Air was used as the oxidizing reagent in UE-49, but 40% oxygen was used in the two later runs.

Semicontinuous feeding of alumina to the filter cooler and removal of fluid-bed powder from the cooler were also attempted during oxidation in UE-50. A hold volume was mounted on the alumina fill port at the side of the filter cooler for the charging, while another volume for the collection of dumped powder was installed on the bottom valve. The overflow line on the filter cooler was shut off with a pipe cap before the run so that powder would leave the vessel only through the dump valve.

Runs UE-51 and -53 were made to study the oxidation reaction when 40% oxygen is used. The concentration was achieved by mixing air and oxygen at a 3.1 to 1.0 volume (flow) ratio. Westinghouse pellets were used in the first run and EGCR pellets in the second under identical operating conditions to highlight differences in material response to treatment.

In the final test, UE-54, the second of the two simulated fuel elements fabricated in the ORGDP shops* was processed through the decladding and oxidation steps. The dimensions of the element were the same as those reported for the first test†. Hydrogen chloride was used to volatilize the zircaloy cladding from the element, and the freed uranium dioxide pellets were oxidized with 40% oxygen.

The same six filter tubes were in use throughout this report period. Actually, these tubes had been used in most of the semiworks tests since the start of the program. Their permeabilities have been occasionally re-established by backflushing with water. After UE-49, the filters were inspected and found to be about 50% coated with a 1/16-inch-thick layer of gray powder. The filters were washed with water and reinstalled in the filter cooler for the remainder of the tests.

* Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies, Summary Progress Report, January through June, 1967, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, May 9, 1968 (K-1738), p. 56.

† K-1744, loc cit, p. 37.

PELLET CHARGER

Figure 17

Pertinent information on run conditions, including charge weights, operating conditions, and reagent concentrations, is contained in table XVII. Run results are summarized in table XVIII. Run commentary details are as follows:

Run UE-43. The restriction placed in the vent line for runs UE-39 through -42 to achieve higher-than-normal system backpressures was removed after the completion of run UE-42. After the system was charged for UE-43, heatup was begun with the bed of alumina powder in the reactor fluidized with nitrogen at a velocity of 0.5 ft/sec in the 10-inch-diameter section. When the system temperatures stabilized, the inlet flows were adjusted to give 11% oxygen and a velocity of 2.5 ft/sec in the 10-inch-diameter section of the reactor at operating conditions, i.e., 490°C and 2 psig. These conditions were maintained for 2 hours; all flows were then shut off, and the filter cooler and receiver were emptied. The recovered material (U_3O_8 and alumina) was weighed and sampled for analysis. System temperatures remained constant even though there was no flow through the system.

The filter cooler was recharged with 11.4 kg of fresh minus 48- plus 100-mesh alumina powder and oxidation was resumed using 21% oxygen and a velocity of 2.4 ft/sec in the 10-inch-diameter part of the reactor at operating conditions. After an additional 3 hours of oxidation, the filter cooler and receiver were again emptied, and the filter cooler was recharged as before. Operation was then resumed for the last 3 hours of oxidation with 21% oxygen and a velocity of 2.4 ft/sec at 460°C and 4.0 psig in the 10-inch-diameter section of the reactor. Again, at the end of the test, the material in the filter cooler and receiver was weighed and sampled.

No operational problems were encountered during the total 8 hours of the oxidation step. During this time, 97.5% of the pellet charge was oxidized and 73.5% of the uranium was elutriated to the filter cooler. The cumulative weights of U_3O_8 and alumina elutriated as a function of oxidation time are plotted in figure 18. Screen analysis indicated that 95.9% of the uranium charge was comminuted to minus 35-mesh material.

Run UE-44. As noted above, this run was made to provide additional data on the effect on elutriation during oxidation resulting from prior exposure of the pellets to hydrogen chloride in the absence of cladding material, i.e., zirconium. Hydrogen chloride flow was started after the temperatures in the fluid bed were established at 390°C during heatup. Flows were adjusted to give a 30% hydrogen chloride-70% nitrogen gas feed and a superficial gas velocity of 0.6 ft/sec in the 10-inch-diameter section based on operating conditions of 390°C and 0.9 psig. The scrubber water flow rate was maintained at approximately 1.9 gpm, and the hydrogen chloride analysis averaged about 1.52 weight percent. The hydrogen chloride step was discontinued after 4 hours, and the system was purged for 1 hour with nitrogen at a velocity of 0.5 ft/sec in the 10-inch-diameter section of the reactor while the pellet bed was heated to 480°C. After the system had been purged, all flows were shut off, and the filter cooler was emptied. About 10.4 kg of alumina powder was recovered. The overflow

SUMMARY OF SEMIWORKS RUN CONDITIONS

	Run Number													
	UE-43	UE-44	UE-45	UE-46	UE-47	UE-48	UE-49	UE-50	UE-51	UE-52	UE-53	UE-54		
<u>Reactor Charge</u>														
Support for Fluid Bed:														
1/4- to 1/2-Inch Alumina Balls, kg	79.5	79.5	79.5	79.5	79.5	80.0	79.5	79.5	79.5	79.5	79.5	79.5	79.5	
Bed Diluent:														
Alumina Powder (minus 48 plus 100 mesh), kg	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	56.8	45.4	
Uranium Dioxide Pellets, kg	64.9	64.9	64.9	64.9	46.6	64.9	63.6*	201.1†	65.0	201.1†	65.0	52.7	52.7	
Type of Pellet or Element‡	a	a	b	a	c§	b	a	b	b	b	a	a	d	
Pellet Charge Method**	a	a	a	a	a	a	b	b	a	b	a	a	a	
Zircaloy, kg	0	0	0	0	11.1	0	0	0	0	0	0	0	23.2	
Charge Weight Ratio, diluent powder-to-uranium	1.0	1.0	1.0	1.0	1.4	1.0	*	†	1.0	†	1.0	1.0	1.0	
<u>Initial Filter Cooler Charge</u>														
Alumina Powder (minus 48 plus 100 mesh), kg	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	
<u>Decad Cycle</u>														
Feed Gas Concentration in Nitrogen:														
Hydrogen Chloride, vol %		30		29	25 30 22 40 40								20 35 60	
Hydrogen, vol %		0		0	0 0 0 0 0								0 0 0	
Operating Time, hr		4		1	0.5 2.75 0.5 0.3 3.3								4 4 6	
Operating Temperature, °C		390		410	410 410 410 410 410								425 370 370	
Inlet Gas Temperature, °C		330		370	340 340 350 340 350								370 370 370	
Filter Temperature, °C					310								315	
Approximate Superficial Velocity in 10-Inch-Diameter Section, ft/sec		0.6		0.6	0.9 0.9 0.8 1.0 0.5								0.7 0.7 0.6	
<u>Oxidation Cycle</u>														
Oxygen Concentration in Nitrogen, vol %	11 21 21	11 21	21 0†† 0††	10 21 21	21 21 21	21 21 21	21	21	40	40	40	40	40	
Operating Time, hr	2 3 3	2 2	2 3 3	2 3 3	2 3 3	2 3 3	9	15.5	3	10	3	4	4	
Reaction Oxidation Temperature, °C	490 460 460	480 480	450 440 440	500 490 490	460 445 450	470 470 470	450	465	480	454	500	500	500	
Approximate Superficial Velocity in 10-Inch-Diameter Section, ft/sec	2.5 2.4 2.4	1.8 1.4	2.3 2.2 2.1	1.7 1.4 1.5	1.3 1.3 1.3	1.8 1.8 2.0	1.7	1.6	1.6	1.5	1.7	1.5	1.5	
Reaction Pressure Above Fluid Bed, psig	2.0 4.8 4.0	0.8 2.9	3.2 1.8 1.7	1.3 1.4 0.6	1.4 0.9 0.8	3.4 3.4 2.2	4.6	5.8	2.0	2.4	1.1	4.0	4.0	
* Only 31.8 kg of uranium dioxide was charged initially; thus, the initial diluent alumina-to-uranium ratio was 1.8. During oxidation, an additional 31.8 kg of uranium dioxide was added. A later alumina powder-to-uranium ratio, based on the full 63.6 kg charge, would be 1.0.														
† Only 64.9 kg of uranium dioxide was charged initially to the reactor; the initial diluent alumina-to-uranium ratio was 1.0. During oxidation, an additional 136.2 kg of uranium dioxide was added. A later alumina powder-to-uranium ratio, based on the full 201.1 kg charge, would be 0.3.														
‡ Pellet types are designated as follows: a - EOCR; b - Westinghouse solid cylinder; c - PRTR element; d - solid cylinders in simulated elements.														
§ The charge for this run was a PRTR fuel element containing vibratory compacted uranium dioxide.														
** The pellet charge method is coded as: a - batch; b - semicontinuous.														
†† Nitrogen flow only was used during these periods.														

TABLE XVIII
SUMMARY OF SEMIWORKS RUN RESULTS

	Run Number											
	UE-43	UE-44	UE-45	UE-46	UE-47	UE-48	UE-49	UE-50	UE-51	UE-52	UE-53	UE-54
Material Balances ($\frac{\text{weight recovered} \times 100}{\text{weight charge}}$), %												
Gross Weight Basis	99.9	98.4	100.1	100.3	100.4	99.8	100.3	95.9	107.2	99.2	100.0	95.0
Uranium Basis	99.5	95.3	103.0	102.8	97.3	105.0	103.8	98.0	104.2	98.9	103.3	98.3
<u>Declad Cycle</u>												
Zirconium Remaining in Bed, percent of original charge		*		*	16.2							7.4
<u>Oxidation Cycle</u>												
Pellet Charge Oxidized to U_3O_8 , %	97.5	97.1	98.2	96.0	93.5	98.3	97.8	99.2	95.9	99.5	99.1	97.1
Pellet Charge Comminuted to minus 35 mesh, %	95.9	95.6	76.7	98.3	100.0	88.7	98.5	71.4	55.2	75.1	95.5	99.4
Charge Elutriated from Reactor During Oxidation, %												
Diluent Powder plus Uranium Dioxide Pellets	55.4	40.3	42.9	58.1	48.1	60.6	38.2	28.0	36.0	34.1	28.2	62.0
Uranium	73.5	62.1	54.5	98.3	90.3	88.7	63.9	25.7	33.7	29.3	44.8	88.6
Diluent Powder	31.3	12.5	27.1	7.7	10.5	24.5	6.5	32.5	37.1	46.9	7.2	21.6
U_3O_8 Equivalent in Material Elutriated, weight percent	73.5	85.5	70.5	93.8	88.0	81.1	92.1	74.4	52.0	69.7	88.2	79.8
Elutriation Rate, kg U/hr of run time	5.2	7.1	3.9	7	4.6	6.3	4	2.9	6.4	5.1	8.5	10.3

* No zirconium charge to bed.

U_3O_8 AND ALUMINA ELUTRIATION DURING
OXIDATION IN UE-43

Figure 18.

receiver was not dumped. Only about 1 kg of the original filter cooler bed was transferred to the receiver in this case. Moreover, past tests indicate that very little to no uranium and alumina is normally transferred from the reactor to the filter cooler up to this point.

The recovered material plus an additional 1.0 kg of new alumina was recharged to the filter cooler, and oxidation flows were started with 11% oxygen and a velocity of 1.8 ft/sec at 480°C and 0.8 psig in the 10-inch-diameter section of the reactor. All flows were shut off after 2 hours of oxidation, and the filter cooler and receiver were again emptied, while the contents (a mixture of U_3O_8 and alumina) were weighed and sampled. The filter cooler was then recharged with 11.4 kg of fresh alumina and oxidation was resumed for three more hours with 21% oxygen and a velocity of 1.4 ft/sec at 480°C and 2.9 psig to give a total oxidation time of 5 hours. Again, at the end of the test, the filter cooler and receiver contents were weighed and sampled.

During oxidation, 97.1% of the uranium charge was oxidized, 62.1% of the uranium charge was elutriated to the filter cooler, and 95.6% of the uranium dioxide pellet charge was comminuted to minus 35-mesh material. The cumulative weights of U_3O_8 and alumina elutriated as a function of oxidation time are illustrated in figure 19.

Run UE-45. When temperatures in the pellet bed had stabilized at 480°C as the result of heatup, air was introduced into the reactor. The air flow was adjusted to give a comparatively high superficial gas velocity of 2.3 ft/sec based on average operating conditions of 450°C and 3.2 psig in the 10-inch-diameter section of the reactor. There was no observed temperature rise in the pellet bed even though air was used from the outset. When 2 hours of oxidation cycle had been completed, all flows were shut off, and the filter cooler was emptied. Only 5.0 kg of material was recovered even though the bottom of the vessel was rapped with a hammer several times. It was concluded that a portion of the cooler bed had bridged inside the vessel but the bridge had not been dislodged by rapping. A new alumina powder charge of 11.4 kg was added to the filter cooler, and the system was fluidized for 30 minutes with nitrogen at a velocity of 0.5 ft/sec in the 10-inch-diameter section of the reactor to try to loosen any bridged solids. The additional fluidization period was successful, and an additional 44.3 kg of material (a mixture of U_3O_8 and alumina) was recovered from the filter cooler and receiver.

The filter cooler was recharged with 11.4 kg of minus 48- plus 100-mesh alumina powder, and operations were resumed with nitrogen flow only. Air was not used for the remainder of the run so that the percentage conversion for the first 2 hours of oxidation could be determined. Continuation of the run at high gas velocities on the order of 2.2 ft/sec was thought to be desirable to obtain time versus elutriation data even though oxidation was not occurring. After 3 hours at 2.2 ft/sec based on operating conditions in the 10-inch-diameter section of the reactor, the nitrogen flow was shut off, and the filter cooler and receiver were emptied. The filter cooler was recharged with 11.4 kg of new minus 48- plus 100-mesh alumina powder. A nitrogen flow equivalent to a velocity of 2.1 ft/sec

U_3O_8 AND ALUMINA ELUTRIATION DURING
OXIDATION IN UE-44

Figure 19

at 440°C and 1.7 psig in the 10-inch-diameter section was continued for an additional 3 hours to give a total elutriation time of 8 hours. There was no indication that the U_3O_8 elutriation was any different with nitrogen than with oxygen.

During the 8 hours at 2.1 to 2.3 ft/sec fluidizing velocities, 54.5% of the uranium charge was elutriated. The weights of material elutriated versus oxidation time are shown in figure 20. In the short oxidation cycle (2 hours) with 21% oxygen, the oxidation rate appeared to be about twice the rate which is achieved when 10.5% oxygen is used for the first 2 hours and is followed by 21% oxygen to complete the reaction. Chemical analyses indicated that 98.2% of the pellet charge was oxidized to U_3O_8 ; however, only 76.7% of the pellet charge was comminuted to minus 35-mesh material.

The bulk of the plus 35-mesh material was roughly 1/16 inch or less in diameter but some pieces were found which were as large as one-fourth to one-half the original pellet size. Most of the smaller pieces were reduced to powder when hand pressure was applied, but the large pieces could not be broken up in this manner. Normally, considerably well over 90% of the uranium dioxide pellet charge is comminuted to minus 35-mesh powder during oxidation steps of the usual 4 to 8 hours duration.

Run UE-46. This run was similar to UE-44 in that pellet oxidation was preceded by hydrogen chloride treatment; however, the hydrogen chloride treatment of the pellets was reduced from 4 to 1 hour, and the oxidation cycle was increased from 5 to 8 hours to obtain elutriation data for an extended tail-off period. The hydrogen chloride step was shortened to see if length of exposure to hydrogen chloride influences elutriation.

After charging had been completed, heatup to simulated deacid temperatures of about 410°C was begun with the alumina bed fluidized with nitrogen. Hydrogen chloride flow was started when this temperature was reached. The flow was adjusted to obtain a 29% hydrogen-71% nitrogen mixture, and a velocity of 0.6 ft/sec in the 10-inch-diameter section of the reactor. The hydrogen chloride flow was checked by measuring the concentration of hydrogen chloride in the water from the scrubber. After 1 hour, the hydrogen chloride was valved out, and the system was purged with nitrogen while heating up to oxidation temperatures. The filter cooler and receiver were not emptied after the purging cycle, since data from runs UE-40 and -44 had indicated that no elutriation from the reactor occurred during the hydrogen chloride treatment and the subsequent nitrogen purge at the low velocities employed.

Oxidation was begun after 45 minutes of nitrogen purging, and the air and nitrogen flows were adjusted to give 10% oxygen and a velocity of 1.7 ft/sec in the 10-inch-diameter part of the reactor. Two hours after oxidation flows were begun, all flows were shut off, the filter cooler and receiver were dumped. The filter cooler was recharged with 11.4 kg of fresh minus 48- plus 100-mesh alumina powder, and oxidation was resumed for three additional hours at 21% oxygen and a flow corresponding to 1.4 ft/sec in

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U_3O_8 AND ALUMINA ELUTRIATION DURING
OXIDATION IN UE-45

Figure 20

the 10-inch-diameter part of the reactor based on average operating conditions. At the end of this time, the filter cooler and receiver were again emptied and recharged as before, and oxidation was continued for an additional 3 hours to give a total oxidation time of 8 hours. During this period, the oxygen concentration was maintained at 21%, and the velocity was kept at 1.5 ft/sec in the 10-inch-diameter section of the reactor. No operational problems were encountered in the run.

For the total 8-hour oxidation cycle, 96.0% of the uranium charge was oxidized to U_3O_8 , 98.3% of the uranium charge was elutriated, and 98.3% of the pellet charge was comminuted to minus 35-mesh material. After 5 hours, 89.3% of the uranium charge had been elutriated. A plot of U_3O_8 and alumina elutriation versus oxidation time is given in figure 21. For the same time in UE-44, only 62.1% of the uranium charge was elutriated. This may indicate that there is an optimum time for exposure to hydrogen chloride from the standpoint of maximizing elutriation, with this time being less than 5 hours. Data are considered too fragmentary to draw conclusions.

Run UE-47. When the element was charged, the top was located about 8 inches below the gas exhaust line. Alumina powder was added after the element was in place. When static, the alumina bed was about 2 feet deep.

The alumina powder was fluidized with nitrogen, and heatup was started with a gas velocity of 0.5 ft/sec. The declad step was begun when the temperature in the bed leveled out at 400°C. The gas concentration was kept at 25% hydrogen chloride and 75% nitrogen during the first 1/2 hour and at 30% hydrogen chloride and 70% nitrogen for the next 2-3/4 hours. The gas velocity in the 10-inch zone was maintained at 0.9 ft/sec. It took 1 to 1-1/2 hours for the reaction to start, as evidenced by a rise in the temperature of the element and the appearance of the scrubber effluent in that time period. The delay in the reaction may have been associated with some kind of treatment, such as autoclaving, to which the zircaloy rods had been exposed; unfortunately, the previous history of the tubes has not been established.

About 3-1/4 hours after the hydrogen chloride decladding was started, white vapor was observed escaping from the liquid drain line from the scrubber. Since the cause for this new occurrence was not apparent, all flows were shut off. Upon inspecting the system, a yellowish paste weighing about 1.0 kg was found on the roof of the pilot plant directly below the gas exhaust line from the scrubber. Chemical analysis of the paste indicated 24.3 weight percent zirconium and 15.6 weight percent chloride. The run was temporarily interrupted until the scrubber gas exhaust line could be taken down for inspection. It was considered possible that the line might be partially plugged with desublimed zirconium tetrachloride because of incomplete hydrolysis in the scrubber, but surprisingly enough, no plug was found.

During the period that the pipe was removed, the reactor was opened to inspect the partially reacted fuel element. Twelve of the eighteen fuel rods had dropped out of the top bracket, and the lengths of these twelve

U_3O_8 AND ALUMINA ELUTRIATION DURING
OXIDATION IN UE-46

Figure 21

tubes had been reduced to about 6 feet. Appreciable reaction was apparent on the lower 8 inches of the rods that had dropped out. All of the cluster wire wrap and cluster bands had been reacted completely, and calculations indicated that about 45% of the cladding had been volatilized from the reactor. The end brackets were still intact, and the top bracket was removed from the reactor before the top of the reactor was reinstalled. Figure 22 shows a photograph of the element at this time. Table XIX gives temperatures in the element and the fluid surrounding the element for the first 2-3/4 hours of the decladding cycle. As can be seen in this table, the maximum temperature difference between the element and the fluid was 61°C and was observed at the top of the element above the fluidized bed. The maximum temperature differences at the bottom and 32 inches up from the bottom of the element, i.e., positions where the fluidized bed was in contact with the element, were 22 and 25°C, respectively. Each time readings were taken after the first 1-1/4 hours of operation, the fuel element and fluid-bed temperatures were found to be the highest at the thermocouple 32 inches up from the bottom. This may mean that the maximum reaction is taking place above the bottom, the point of initial contact between the hydrogen chloride and the zircaloy.

TABLE XIX

TEMPERATURES DURING DECLADDING OF THE PRTR FUEL ELEMENT, UE-47

Hydrochlorination Time, hr	Temperature, °C, at Position* Noted						Temperature Difference, °C		
	Fuel Element			Fluid-Bed Gas Space					
	A	B	C	A	B	C	A	B	C
0	393	393	393	393	393	393	0	0	0
0.25	396	396	402	393	393	399	3	3	3
0.75	399	396	402	393	393	399	6	3	3
1.25	404	407	427	393	404	399	11	3	28
1.75	421	429	460	399	421	404	22	8	54
2.25	427	443	477	416	432	416	11	11	61
2.75	432	468	471	416	443	432	16	25	39

* Position A corresponds to the bottom of the element, B to about 32 inches up from the bottom, and C to the top of the element as positioned in the reactor; i.e., above the top level of the fluidized bed.

PRTR FUEL ELEMENT AFTER 3-1/4 HOURS OF EXPOSURE TO
HYDROGEN CHLORIDE IN UE-47

Figure 22

The reactor was again closed and was heated up to decladding temperature with the bed fluidized with nitrogen at 0.5 ft/sec. When the temperatures had stabilized, flows were adjusted to give 22% hydrogen chloride and a velocity of 0.8 ft/sec based on the average operating temperature and pressure. The scrubber effluent became milky within 5 minutes, thus indicating that reaction was in progress. The hydrogen chloride concentration was increased to 40% 30 minutes after decladding was resumed. The run appeared to be proceeding smoothly; however, vapor was again observed escaping from the liquid drain line from the scrubber. The gas flow was reduced to give a velocity of 0.5 ft/sec while the hydrogen chloride concentration was maintained at 40%, since it appeared that the scrubber was not large enough to handle the flow rate required for a 0.8 to 1.0 ft/sec velocity in the 10-inch zone. After the flow was reduced, no additional problems were observed; the declad cycle was terminated after a cumulative reaction time of 7.55 hours.

Following decladding, the system was purged with nitrogen, the filter cooler and receiver were emptied, the filter cooler was recharged with 11.4 kg of fresh alumina, and heatup to oxidation temperature was begun with the bed fluidized with nitrogen. When the temperature in the fluidized bed reached 480°C, air flow was started. The oxygen concentration was kept at 21%, and the gas velocity was kept at 1.3 ft/sec. The gas was cut off, and the filter cooler and receiver were emptied after 2, 5, and 8 hours of oxidation to obtain elutriation data. Fresh alumina powder, weighing 11.4 kg, was recharged to the filter cooler each time it was emptied. Oxidation was terminated after 8 hours.

By chemical analysis, conversion of the uranium dioxide charge to U_3O_8 was only 93.5% complete; however, all of the uranium was comminuted to minus 35-mesh powder. The elutriated material contained the equivalent of 88.0 weight percent U_3O_8 , with the amount of uranium elutriated corresponding to 90.3% of the uranium charged to the reactor. Only 10.5% of the alumina powder charge to the reactor was elutriated. The U_3O_8 and alumina elutriation during the progress of the oxidation are plotted in figure 23*.

On the other hand, the results for the declad cycle were not as good as was expected. The overall hydrogen chloride utilization was 18.8%, and only 83.8% of the zirconium charge was reacted during the 7.55-hour declad cycle. About 0.5 kg of unreacted zircaloy tubing and 1.3 kg of end caps were found in the bed after oxidation. Actually, none of the original thirty-six end caps were completely reacted. Figures 24 and 25 show these unreacted pieces. The progress of the zirconium reaction and the hydrogen chloride usage with time is given in figure 26.

* In a later decladding experiment in the filter test loop, it was concluded that the vibratory compacted uranium dioxide is largely pulverized during the decladding step. The large amount of U_3O_8 elutriated in the first 2 hours of the UE-47 oxidation phase supports this conclusion.

U_3O_8 AND ALUMINA ELUTRIATION DURING
OXIDATION IN UE-47

Figure 23

TYPICAL UNREACTED ZIRCALOY TUBING REMOVED FROM
REACTOR AFTER OXIDATION CYCLE IN UE-47

Figure 24

TYPICAL UNREACTED END CAPS REMOVED FROM
REACTOR AFTER OXIDATION CYCLE IN UE-47

Figure 25

ZIRCONIUM REACTED AND HCl CONSUMED IN RUN UE-47

Figure 26

If the hydrochlorination time had been extended, more zircaloy would undoubtedly have been reacted. The run was intentionally limited to 7.55 hours to observe the effects on subsequent oxidation when unreacted pieces remain in the fluid bed after decladding.

Run UE-48. In a previous run, UE-45, Westinghouse normal assay solid cylindrical uranium dioxide pellets were processed with air at 455°C for 2 hours to determine if 2 hours of oxidation with that high an oxygen concentration was sufficient for high conversion. Nitrogen was used for the last 6 hours of the run to obtain elutriation data. While 98.2% of the pellet charge was oxidized, only 76.7% of the uranium charge was comminuted to minus 35-mesh material. Since comminution was low in UE-45, it was decided to study the oxidation reaction with the Westinghouse pellets further by extending the reaction time with air to 8 hours.

After the system was charged for run UE-48, the alumina powder in the reactor was fluidized with nitrogen and the entire pellet bed was heated to 470°C. Sufficient air flow was started when this temperature was obtained to give a velocity of 1.8 ft/sec based on average operating conditions in the 10-inch-diameter section. These conditions were maintained for 2 hours, at which time, all flows were shut off, and the filter cooler and receiver were emptied. Oxidation was resumed for 3 hours more, with air at the same velocity, after the filter cooler had been recharged with 11.4 kg of fresh minus 48- plus 100-mesh alumina powder, and then the flows were again shut off to dump the filter cooler and receiver for the second time. The filter cooler was recharged with 11.4 kg of alumina powder, and oxidation was continued for a final 3-hour period to give a total oxidation time of 8 hours. No problems were encountered in the run.

By chemical analysis, the uranium dioxide pellet charge was 98.3% oxidized; however, only 88.7% of the material was converted to minus 35-mesh powder. With EGCR annular pellets, usually more than 95% of the uranium is comminuted to minus 35-mesh. Thus, the results from this run and from run UE-45 suggest that the solid cylindrical pellets are harder to break up during oxidation than are the EGCR pellets. During the 8 hours of oxidation, about 88.7% of the uranium charge was elutriated; i.e., essentially all of the minus 35-mesh material. This is the largest amount of uranium ever elutriated during the ORGDP runs which involved oxidation only. The material that was elutriated contained 81.1% U_3O_8 . The elutriation profile for this run is given in figure 27.

Run UE-49. After charging had been completed, the alumina powder was heated to 480°C, the air flow was started, and the nitrogen flow was valved out. Pellet charging was begun 3 hours 15 minutes after the air flow was started and was continued for the next 1 hour 45 minutes. During this time, 31.8 kg of EGCR pellets was charged to the reactor through the hold volume in about 1.4 kg batches.

When the pellet charger was loaded to capacity, i.e., with about 4.0 kg of EGCR pellets, it was difficult to get the pellets to fall out into the reactor, apparently because of bridging. Even with 1.4 kg batches, it

U_3O_8 AND ALUMINA ELUTRIATION DURING
OXIDATION IN UE-48

Figure 27

was necessary to beat on the pellet charger with a hammer to move the pellets out. The hammering caused the unions on the ball valves to loosen, and these had to be tightened during the charging to prevent powder leaks.

Over the course of the charging period, the pressure drop across the reactor rose from 6.0 to 6.4 psi. No further increase was observed during the remainder of the run. The velocity in the 10-inch-diameter section of the reactor was kept at 1.7 ft/sec and the oxygen concentration at 21% throughout the run. Total oxidation time was 9 hours. Analyses of the bed materials indicated that 98.5% of the uranium charge was comminuted to minus 35-mesh material and that 97.8% of the uranium charge was oxidized. During the oxidation cycle, 63.9% of the uranium charge and 6.5% of the alumina were elutriated to the filter cooler.

Run UE-50. As in previous runs, heatup was started with the alumina bed in the 10-inch-diameter zone. An attempt was made with the nitrogen flow on to empty the alumina from the filter cooler before oxidation started. Even though the flange on the bottom of the filter cooler was rapped with a hammer several times, no powder came out. The gas flow was stopped and a second attempt was made to empty the alumina but still no material was recovered. Nitrogen was again introduced, and another 11.4 kg of alumina was placed in the filter cooler, hopefully to break up a possible bridge. This technique was successfully used in run UE-45. The alumina was easily charged to the filter cooler even though nitrogen was flowing through the system. A third try to empty the filter cooler contents with the nitrogen flow on was successful after 10 minutes of fluidization and considerable hammering, and 23.3 kg of alumina was recovered.

The filter cooler was recharged with 11.4 kg of the recovered alumina powder, and the oxidation step was begun with air. The temperature in the pellet zone increased to 538°C within about 5 minutes, but cooling with air in the external coils reduced the temperature to 482°C, the desired level, in 15 minutes. Pellet charging had been started when air flow was resumed, and 13.6 kg of pellets was charged to the reactor in about 2.3 kg batches during the first half-hour of oxidation. A small powder leak developed at the union on the bottom valve of the pellet charger, probably because of the hammering necessary to get the pellets to fall out. After the 13.6 kg had been charged to the reactor, the air flow was stopped, and the leak was eliminated by tightening.

Pellet charging was continued, and nine additional 13.6 kg loads of pellets were added to the reactor at 1-hour intervals. Each time, it took about 15 minutes to dump the contents of the charge volume into the reactor.

The filter cooler was emptied and recharged with 11.4 kg of fresh alumina powder after 3, 6, 9, 12, and 15 hours of oxidation.

The run was terminated after 15-1/2 hours. The oxygen inlet concentration and the gas velocity in the 10-inch-diameter section were kept at 21% and 1.6 ft/sec, respectively, throughout the run. The nominal temperature in the 10-inch section was near 460°C. No reactor plugging problems were

observed in the run. The reactor pressure drop ranged from 4.2 to 7.8 psi with the nominal value near 4.8 psi. Pellet and alumina charging were successful; however, the dumping of the filter cooler contents with gas passing through the system was judged unsuccessful, since only 23.6% of the material that was elutriated during oxidation was recovered during the dumping attempt. The rest of the elutriated material was taken out of the filter cooler after the cooldown period.

During oxidation, 99.2% of the pellet charge was oxidized, and 25.7% of the uranium was elutriated to the filter cooler. Screen analysis indicated that only 71.4% of the uranium charge was comminuted to powder smaller than 35 mesh.

Run UE-51. This run was the first test in which an oxygen concentration greater than 21% was used. Oxidation of a single charge of Westinghouse normal-assay pellets was undertaken for 3 hours using a combined air-oxygen feed mixture with an oxygen concentration of 40%.

Nitrogen was used to fluidize the bed during heatup. When the temperature in the bed reached 482°C, 40% oxygen flow was started. An immediate increase in bed temperature was observed, and the temperature reached a maximum of 538°C, five minutes after oxygen flow was begun. Forced-air cooling through the external coils was used for the remainder of the run to keep the bed temperature at the desired level of 482°C. The pressure drop through the reactor fluctuated between 2 and 8 psi during the first hour of operation, and bed plugging tendencies were noted, apparently having been brought about by a buildup of power during the rapid reaction. After the first hour, the pressure drop leveled out at a nominal 7 psi, and there were no further indications of plugging or abnormal pressure variations.

Analysis of final bed materials obtained after the 3-hour oxidation cycle indicated 95.9% of the pellet charge was oxidized to U_3O_8 ; however, only 55.2% of the uranium charge was comminuted to minus 35-mesh material. Uranium dioxide elutriated to the filter cooler accounted for 33.7% of the uranium charged.

Run UE-52. This run was undertaken to study the combined effects of semi-continuous pellet charging and an oxygen concentration of 40% during the oxidation step. After the initial charge, Westinghouse normal-assay pellets weighing 136.2 kg were added semicontinuously to the reactor in 27.2 kg increments during the first 5 hours of the run.

Since there was a rapid increase in bed temperature in the previous run, once the 40% oxygen was introduced, the pellet bed was only heated to 427°C instead of the desired 482°C with the thought that the reaction heat would make up the difference. When the pellet zone temperature stabilized at 427°C, 40% oxygen flow was substituted for the nitrogen. The temperature in the bed increased to 482°C within 10 minutes. Semi-continuous charging was begun 1/2 hour after startup and 27.2 kg of the pellets were put in the reactor over the next 1/2 hour. The bed temperature increased to 504°C during this time. The second pellet charging was

started 1-1/2 hours after startup, and 27.2 kg of pellets was dropped into the bed between 1-1/2 to 2 hours. By this time, the pressure drop through the bed had increased to 9.5 psi and there was no indication that the pressure drop would level out or decrease. The bottom of the reactor was rapped with a hammer several times to open up the bed, and the pressure drop was reduced to 6 psi. Pellet charging was continued, and three additional 27.2 kg loads were put into the reactor at 1-hour intervals. The charging process took about 1/2 hour in each case.

Oxidation was terminated after 10 hours. The nominal gas velocity was near 1.5 ft/sec for the run. Although abnormal fluctuations in the reactor pressure drop were observed frequently in the run, the pressure drop was kept within reasonable bounds by rapping the bottom of the reactor with a hammer. Temperature control was good throughout the run.

When the run was terminated, the system contents were kept fluidized with nitrogen, and the system was cooled using the external air cooling. When cooldown was completed, the material in the reactor would not drain out through the bottom valve; therefore, the powder was taken out via the top of the reactor using a vacuum system. Once the powder was removed, the balls were drained from the bottom of the reactor by gravity discharge, while the remaining material had to be taken out through the top of the vessel with a vacuum system.

In the oxidation step, 99.5% of the uranium dioxide was oxidized, while only 75.1% of the uranium was converted to material smaller than 35 mesh. The plus 35-mesh powder shown in figure 28 consisted primarily of powder agglomerates, some of which could be reduced in size when light pressure was applied. Only 29.3% of the total uranium charge was elutriated to the filter cooler during the 10-hour oxidation test.

Run UE-53. Since only 55.2% of the uranium charge, i.e., Westinghouse pellets, had been comminuted to minus 35-mesh material in UE-51, similar operating conditions were employed in this run with EGCR pellets to determine if comminution is influenced by pellet source and/or geometry. The total oxidation time was 3 hours, and 40% oxygen in the feed gas was used from the outset.

The entire pellet bed was heated to 482°C. Once this temperature had been stabilized, the oxygen concentration was adjusted to 40%. As in UE-51, a rapid increase in pellet bed temperature was observed when the oxygen flow was begun. The temperature in the pellet bed increased from 482 to 560°C within 5 minutes, and air cooling with the external coils was used to bring the temperature down. The pressure drop through the reactor remained constant at 4.7 psi during the first 1/2 hour of operation and gradually increased to 5.0 psi over the next 2-1/2 hours. The run was terminated after 3 hours. Throughout oxidation, the inlet oxygen concentration and the 10-inch-diameter section velocity were kept at 40% and 1.7 ft/sec, respectively. No plugging tendencies were observed during the run, and the bed temperature was controlled with external cooling coils.

PLUS 35-MESH MATERIAL RECOVERED FROM REACTOR
AFTER OXIDATION STEP IN UE-52

Figure 28

Analysis of bed materials taken from the system after the run indicated that 99.1% of the EGCR pellet charge was oxidized, 44.8% of the uranium charge was elutriated, and that 95.5% of the uranium had been comminuted to minus 35-mesh material. The plus 35-mesh material shown in figure 29 contained hard pieces of oxidized pellets and fragments of alumina balls. The results of this test strongly suggest that EGCR pellets are easier to comminute to small sized material than are the Westinghouse solid cylindrical pellets. This fact is also confirmed by data obtained in the oxidation tests which have been made with 10-inch-diameter pellet beds at lower oxygen concentrations. For example, the comminution of EGCR fuel material has ranged from 90 to 99%, excluding the semicontinuous runs and the tests in which hydrogen chloride gas was used to volatilize zirconium or to simulate the decladding cycle. On the other hand, for the same kind of test, with the solid cylindrical Westinghouse pellets, comminutions of 55 to 89% were obtained.

Run UE-54. The bottom of the element was located approximately 1 foot above the top of the transition section. The depth of the alumina bed, when static, was 1 foot 11 inches and approximately 2 feet 8 inches of the element extended above the top of the alumina. The element was fitted with a thermowell lengthwise through the center of the tube array, and thermocouples were placed at each end and at the center of the element.

After charging had been completed, the bed was fluidized with nitrogen and heated to 425°C. The gas preheater outlet and the filter cooler outlet temperatures were held at about 315°C. Decladding was undertaken with stepwise increases in hydrogen chloride concentration and consisted of 4 hours with 20%, 4 hours with 35%, and 6 hours with 60% hydrogen chloride in nitrogen. Hydrogen was not used in the feed gases. The superficial gas velocity was kept nominally at 0.7 ft/sec during the 14-hour declad step.

The liquid effluent from the scrubber became opaque about 30 minutes after the 20% hydrogen chloride was introduced into the reactor. A significant slowdown in the reaction was not observed until after 13-1/2 hours, when the scrubber water began to clear up.

The three thermocouples placed within the element indicated temperatures which were somewhat higher than those of the bed itself. The maximum temperature, 560°C, or 100°C above the bed temperature, was measured in the middle of the element. Reaction and temperature control were judged good; furthermore, no problems were encountered with the scrubber at this velocity*.

The system was purged with nitrogen for an hour after the hydrogen chloride step, and the bed was heated to 482°C. Before oxidation was begun, the

* In run UE-47, the flow capacity of the scrubber was exceeded when gas was passed through the 10-inch-diameter section of the reactor at 0.8 to 1.0 ft/sec (see pp. 75 and 79 of this report).

PLUS 35-MESH MATERIAL RECOVERED FROM REACTOR
AFTER OXIDATION STEP IN UE-53

Figure 29

filter cooler was emptied and recharged with 11.4 kg of fresh alumina. Material weighing 8.8 kg was recovered, and only 0.04 kg was larger than 35 mesh. Chemical analysis indicated that both the plus and minus 35-mesh fractions contained 0.19 weight percent zirconium.

The oxidation cycle consisted of 4 hours with an oxygen concentration of 40%. An increase in bed temperature occurred shortly after the oxidation step was started, the maximum temperature being 537°C. The pressure drop through the bed stayed constant during the cycle, and plugging tendencies were not observed. The superficial gas velocity was held at 1.5 ft/sec throughout oxidation.

Oxidation was judged good both from the operational standpoint and from results obtained on the final bed materials. Various materials recovered from the reactor and filter cooler after the run are shown in figure 30. Chemical analysis and material balances indicated 97.1% of the uranium dioxide was oxidized to U_3O_8 , 88.6% of the uranium charge was elutriated, and 99.4% of the uranium was converted to material smaller than 35 mesh. The pulverization of 99.4% compared well with the 100.0% result obtained in the first semiworks test with a simulated fuel assembly, UE-33. Both the simulated fuel assemblies contained solid cylindrical fuel pellets; thus, the good comminutions obtained in these two runs suggest that decladding significantly improves pellet degradation to fine sized material during the subsequent oxidation step. The uranium elutriation rate of 22.2% per hour was the highest rate obtained in the ORGDP studies and confirmed the fact that decladding preceding oxidation also influences the rate of elutriation. In figure 30, the unusually large fraction of alumina ball fragments in the plus 35-mesh material taken from the reactor is ascribed to the prolonged reuse of balls in semiworks runs.

Results for the declad cycle indicated that 92.6% of the zircaloy charge was volatilized. Unreacted tie rods, shown in figure 30, weighing 1.5 kg, constituted the major portion of unreacted zircaloy. Bed analysis indicated that the minus 35-mesh and plus 35-mesh fractions of the reactor bed both contained 0.17 weight percent zirconium, and that the final filter cooler material had a zirconium content of 0.19 weight percent. The overall hydrogen chloride utilization was about 25% of the hydrogen chloride feed, and the maximum instantaneous utilization was slightly over 60%, as shown in figure 31.

In figure 32, the percentage of the uranium charge elutriated per hour of oxidation time is plotted versus the square of the time-weighted superficial velocity in the 10-inch-diameter section of the reactor. Two lines are shown, one for the runs in which the hydrogen chloride decladding or hydrogen chloride treatment preceded the oxidation step* and the other for runs involving oxidation only. The latter plot was originally

* Data for UE-24 have been omitted, since extremely low oxygen concentrations (1 and 3%) were used.

TYPICAL MATERIALS RECOVERED FROM SEMIWORKS SYSTEM
AFTER OXIDATION IN UE-54

Figure 30

ZIRCONIUM REACTED AND HCl CONSUMED IN RUN UE-54

Figure 31

Figure 32

published in the report for the previous period*, but new data points, i.e., from runs UE-43 and -45, have been inserted. The results of tests UE-43 and -45, where velocities were about 2.4 and 2.2 ft/sec, respectively, support the original curve. The graphs show the possible association of the elutriation rate with the Froude number and, in addition, make it evident that a higher elutriation rate is achieved after hydrogen chloride treatment. The elutriation rate remained essentially constant over the course of the runs which involved oxidation only. In contrast, the elutriation rates realized during the early part of the oxidation tests which were preceded by a hydrogen chloride treatment decreased if the tailout period was long. Since corrections for long-term tailout could not be readily made, only overall rates were plotted, and consequently, some of the long-run data might be somewhat biased in comparison with the rates from the shorter runs. The plot has not been established statistically but is shown as a broken line to reflect the uncertainties in the data.

The conclusions reached from the results of these tests are as follows:

1. Decladding Tests

- a. A simulated fuel element and a PRTR fuel element were successfully processed through decladding and oxidation in the semiworks reactor.
- b. Results of hydrogen chloride treatment-oxidation tests indicate that the rate of U_3O_8 elutriation is increased after pellet exposures to hydrogen chloride of as little as 1 hour prior to oxidation. These higher rates appear to be of about the same magnitude, regardless of whether the pretreatment consists of exposure to hydrogen chloride or a full zircaloy decladding cycle.
- c. The rate of uranium elutriation during oxidation after decladding the simulated fuel was greater than 10 kg U_3O_8 per 1,000 scf of gas. Since 7 kg of U_3O_8 per 1,000 scf of gas is deemed feasible for a two-vessel plant in which hydrogen chloride decladding is employed, elutriation is probably a practical transfer technique for the two-vessel process.
- d. Hydrogen chloride pretreatment also increases the elutriation selectively for uranium from an alumina- U_3O_8 mixture.
- e. The reaction temperature was controlled satisfactorily during the decladding of the PRTR fuel element. The assistance of the alumina in removing reaction heat during decladding was demonstrated in UE-47. The maximum temperature difference between the center of the fuel element and the fluid bed was only 25°C for the submerged portion of the fuel element during the first 2-3/4 hours

* K-1744, loc cit, p. 52.

of decladding. On the other hand, the temperature difference at the top of the element, i.e., above the fluid bed, reached a maximum of 61°C. With the breakup of the element, the circulation of the alumina between the rods would improve and better temperature control of the bed would result.

2. Oxidation Tests

- a. Although temperature and pressure drop increases are noted during oxidation when uranium dioxide pellets are fed semicontinuously, the effects can be controlled, and bed performance is not upset. In semiworks tests, material was elutriated from the reactor; however, the rate of uranium elutriation was less than the rate at which uranium was charged to the reactor. In a fuel recovery plant, local batching and criticality requirements would make control of fuel material buildup mandatory. Simple bed overflow would be a more reliable means of transferring the uranium in a two-vessel plant; however, it could have the shortcoming of also transferring more alumina than would otherwise be elutriated.
- b. A concentration as high as 40% oxygen in nitrogen can be used from the outset of oxidation in shallow pellet beds. No operational problems are expected when 21% oxygen is used. Indications are, based on bed performance in semiworks tests with solid cylindrical pellets, that some periodic vibration might be necessary to control high pressure drop buildup across the beds in plant-scale reactors when 40% oxygen is used. Of course, stepwise buildup to a high oxygen concentration, such as 40%, might be the superior oxidation procedure.
- c. Oxidizing EGCR pellets for 3 hours with a feed gas containing 40% oxygen produces a bed of U_3O_8 which appears to be fine enough for fluid-bed fluorination. The final bed obtained under these conditions is similar to that which is obtained with air feed and an oxidation time of 4 to 8 hours.
- d. The oxidation of Westinghouse solid cylinder uranium dioxide fuel pellets was conducted without difficulty, and no unusual conditions developed. The same degree of oxidation can be achieved with Westinghouse and annular EGCR pellets.
- e. When usual oxidation procedures are used, the comminution of the solid Westinghouse pellets to minus 35-mesh particles is poorer than that obtained with cylindrical EGCR pellets. Some of the smaller lumps are rather soft and might possibly either break up during bed removal and handling or at least might not be stable in the fluidized bed. Others, however, are hard and constitute something of a potential operating problem since good comminution is important in achieving good fluidization, in expediting transfer of fissile material by elutriation, and in preventing sintering during the highly exothermic uranium fluorination step. The

differences observed with solid cylindrical and EGCR pellets might not be so pronounced in an irradiated fuel reprocessing plant, since it is expected that irradiated materials will be more reactive and tend to pulverize more easily because of the cracking and density decreases occurring during irradiation.

- f. The rate of uranium elutriation appears to have been improved by about 50% when 40% oxygen was used for oxidation instead of 11 to 21% oxygen.
- g. An increase in superficial velocity from 1.5 to 2.4 ft/sec increases the uranium elutriation rate when EGCR pellets are oxidized. Runs UE-41, -42, and -43 were conducted under similar conditions except that the higher velocity was used in the last run. The elutriation rate in UE-43 was approximately twice as great as those of the earlier two runs.
- h. The rate of oxidation appears to be doubled when air is used for the entire oxidation cycle instead of using 10.5% oxygen for the first 2 hours and 21% oxygen afterward for final conversion.
- i. The cumulative weight of U_3O_8 elutriated during batch runs involving uranium dioxide oxidation at fluidization velocities as high as 2.0 ft/sec increases approximately linearly with time for runs with oxidation cycles up to about 5 hours when the oxidation is not preceded with hydrogen chloride treatment.
- j. Most of the alumina elutriation during a batch oxidation generally occurs during the first 2 hours of the run.
- k. High semiworks system backpressure does not significantly increase the U_3O_8 elutriation rate from the reactor. This conclusion was made after a comparison of previously obtained high pressure run data with current tests.

Summary of Semiworks Plant Results. The overall reactor system studies from the viewpoint of the ORGDP experimental program might be summarized as follows:

1. Removal of zircaloy cladding by reaction with hydrogen chloride appears to proceed satisfactorily and at sufficient rates for most purposes. Evaluation of the effects of fuel assembly submergence in the fluid bed on chemical de-clad rate and temperature control indicates that complete submergence of the material in the fluidized bed of alumina is not required. Off-gas filtering remains a problem, with no satisfactory solution of the filter plugging difficulty presently in hand.
2. Oxidation of uranium dioxide pellets can be performed satisfactorily in batch operations with bed depths from several inches to over 3 feet, providing sufficient gas velocity is employed to remove the

formed powdered material from the pellet zone and the reaction zone is localized in the upper few inches or so of the pellet zone. Superficial gas velocities required range from 1 ft/sec in shallow beds to 2.5 to 3.0 ft/sec for the deepest ones tried. Pretreatment of pellets with hydrogen chloride with or without concurrent zircaloy reaction appears to aid comminution and increase elutriation rates in the subsequent oxidation step.

3. Fluorination with elemental fluorine can be performed readily in the fluid bed at temperatures of 350 to 400°C and probably higher. The main difficulty would appear to be elutriation of unreacted material to the filter zone. This probably can be minimized by use of lower gas velocities.
4. Fluorination studies with synthetic beds made by Argonne by processing spiked uranium dioxide through the bromine pentafluoride step indicated that a significant heat release will occur in the elemental fluorine fluorination step due to the failure of bromine pentafluoride to completely convert some of the fission product elements.

Bromine pentafluoride fluorination was not done in the semiworks. A system for testing this phase of the operation, including regeneration of bromine pentafluoride, collection and separation of uranium hexafluoride and bromine pentafluoride, and recycle of bromine pentafluoride, had been designed and some of the equipment had been built when the close-out order necessitated suspension of this phase of the program.

One limitation of the semiworks test program was the inability to process actual irradiated elements. This part of the program was to have been covered at ORNL in a hot pilot plant which was also cancelled by the program close-out decision. Variability arising from different starting materials and from effects of changes in pretreatment can certainly affect results, as has been indicated to a limited degree in some of the semiworks oxidation tests.

Outlet Gas Filter Studies

Filter permeability losses of 95 to 99% are encountered when sintered nickel filter tubes are subjected to multicycle exposure to hydrogen chloride-stannous chloride-zirconium tetrafluoride-hydrogen-inert gas mixtures typical of the reactor off-gases during the decladding of zircaloy clad power reactor fuels in a fluidized alumina bed. Depending on initial permeability, the maximum tolerable loss for this type of filter in decladding-oxidation-fluorination plant operations is established to be about 90%, if adequate flow in long-term use under exposure to a wide variety of dusts is to be assured.

Since nickel is potentially the most suitable material of construction for a single filter handling the gases from the three-step operation, efforts have been made to determine the plugging mechanism in the hope

that, once the causes were identified, they could be circumvented. Of course, other alternatives might be considered, e.g., separate filters for each process step (thus permitting the use of different materials of construction) or other types of gas cleanup equipment, such as bed filters and cyclones.

Recent tests with the nickel filters have been centered on the volatilization of zirconium tetrachloride from zirconium tetrachloride powder charges to the reactor while the bed was fluidized with hot inert gases. Zirconium tetrachloride sublimate in the gas was thus substituted for dechlorination off-gases, i.e., the hydrogen, hydrogen chloride, and alloy constituents, are eliminated. This technique permits the selective study of the influences of zirconium tetrachloride alone, as well as combinations of zirconium tetrachloride with hydrogen and/or hydrogen chloride. Details of tests with zirconium tetrachloride in argon, and zirconium tetrachloride with argon and hydrogen chloride were given in the previous report*.

During the current test period, nickel filter permeability loss tests were made with hydrogen and with hydrogen and hydrogen chloride in the fluidizing gases, together with the zirconium tetrachloride. In a final test, a sintered powder 316 stainless steel filter was exposed to the off-gases from the dechlorination and oxidation reactions. This material of construction had been proposed for the filtration of reactor off-gases prior to fluorination in a two-reactor process.

A single sintered nickel fiber filter was installed in the test loop in the primary position. The filter loop reactor was then charged with 7.5 kg of minus 48- plus 100-mesh Alcoa tabular alumina and 1.8 kg of zirconium tetrachloride. The bed was fluidized with 70% argon and 30% hydrogen at a superficial gas velocity of 0.75 ft/sec. After the filter had been heated to 315°C, the reactor bed was heated to 425°C at a rate of 50°C per hour, thereby volatilizing the zirconium tetrachloride. To complete a full cycle, the bed was then exposed in succession to air and to 20% fluorine, each at a gas velocity of 1 ft/sec at 480°C for 1 hour. Argon was used as the gaseous diluent. The filter temperature was maintained at 100°C during the oxidation and fluorination. Heated argon blowback of the filter was utilized during all phases of operation.

The reactor was recharged at the start of each cycle. At the completion of ten cycles of operation, the filter appeared to be quite serviceable but was removed for inspection. A very light coating of gray-white powder was noted which analyzed 41.0% zirconium, 12.0% aluminum, 0.41% nickel, 0.16% chloride, and 33.6% fluoride. Flow measurements indicated a 21% permeability loss, which is comparable to the loss experienced when a filter tube is subjected to simulated reaction off-gases without zirconium.

* K-1744, loc cit.

The filter tube was subsequently reinstalled in the filter loop, the reactor was charged, and the exposure cycling was resumed with hydrochlorination fluidizing gases composed of 50% hydrogen chloride, 30% hydrogen, and 20% argon. After fourteen more cycles of operation, the filter tube was again removed for inspection. The usual filter coating was observed, and the laboratory analyses gave 45.9% zirconium, 6.4% aluminum, 0.66% nickel, 0.12% chloride, and 35.9% fluoride*. X-ray diffraction analysis indicated 70% zirconium tetrafluoride and 30% unknowns. Flow measurements indicated a total permeability loss of 98.7%.

In summary, the results of all the zirconium tetrachloride experiments made with sintered nickel fiber filters are that (1) zirconium tetrachloride plus a mixture consisting of 30% hydrogen and 70% oxygen-free argon resulted in little filter plugging, i.e., about 20% in ten cycles; (2) zirconium tetrachloride and oxygen-free argon gave a 79% permeability loss in ten cycles; and (3) hydrogen chloride, zirconium tetrachloride, and argon, with or without hydrogen, plugged a filter beyond satisfactory use; i.e., in fourteen cycles caused permeability losses of 95% and greater, which are comparable to the plugs experienced with zircaloy-hydrogen chloride reactions. Previous tests with hydrogen chloride and hydrogen, but not zirconium, indicated 25 to 30% permeability losses in nickel fiber filter tubes. It is therefore believed that the difficulty is caused by the presence of both zirconium tetrachloride and hydrogen chloride, and probably involves formation of a complex between these materials and the nickel in the relatively high surface area filter environment. The higher permeability loss with zirconium tetrachloride diluted with argon than with zirconium tetrachloride diluted with both argon and hydrogen is unexplained.

In the exposure test with the 316 stainless steel filter, the test loop was charged with 7.5 kg of minus 48- plus 100-mesh tabular alumina and 0.9 kg of zircaloy tubing. The bed was fluidized for 8 hours with hydrogen chloride in hydrogen and argon† at 400°C and a superficial gas velocity of 0.75 ft/sec, then with air at a velocity of 1 ft/sec and a temperature of 480°C for 10 hours. The filter temperature was maintained during the hydrochlorination and oxidation phases of the cycle at 315 and 100°C, respectively.

* The major difference between the two filter coating analyses in this report lies in the aluminum content; however, the filter pressure drop does not appear to be affected by the aluminum content. In addition, the aluminum in the coating probably results from elutriation of bed diluent rather than from deposition of a volatile aluminum compound.

† The hydrogen chloride concentration started at 10% and was increased 10% each hour to a maximum of 70% by volume. The hydrogen concentration was held at 30%.

The pressure drop across the filter measured 0.12 psi during the hydrochlorination phase of the first cycle and increased to about 1.5 psi by the sixth cycle. The pressure drop continued to average 1.5 psi during the next thirteen cycles of exposure. Laboratory flow measurements made on the filter tube indicated an initial flow rate of 216 scfm/sq ft-psi pressure drop and a flow rate of 8.5 scfm/sq ft-psi pressure drop at the end of the nineteenth cycle. The permeability loss over the course of the test was 96%. Although this loss appears large, it should be noted that the final flow rate exceeds the 4 scfm/sq ft-psi pressure drop factor used in design calculations for the process gas filters in the conceptual plant.

Samples of a light gray powder coating found on the surface of the tube were sent to the laboratory for analysis. Wet chemistry analyses indicated the presence of 29.08% zirconium, 17.26% aluminum, 8.84% nickel, 12.81% chloride, and 91.3% fluoride. The nickel analysis is higher than that found in most of the previous tests; this magnitude may be attributable to the corrosive action of the hydrogen chloride on the stainless steel material of construction. The material also analyzed semiquantitatively, by X-ray diffraction, at about 60% zirconium dioxide, 20% alumina, and 20% unknown. The diffraction patterns exhibited by this unknown component are similar to the patterns for the unknown component in the coatings on nickel fiber filters in past tests. It was therefore concluded that the plugging mechanism may be similar to that for sintered nickel tubes.

The filter tube for general use with volatility process off-gases has obviously yet to be found. Separate filters for dechlorination and fluorination might, in the long run, prove to be most practical from the corrosion standpoint. There would probably be no problems with the use of nickel filters for fluorination off-gases, and stainless steel should be suitable for chemical dechlorination. There are no foreseen difficulties with either of these materials in filtering off-gases from the oxidation step.

Product Purification Sorption-Desorption Tests

In volatility operations, uranium hexafluoride sorption on sodium fluoride can be effectively employed for uranium product purification and recovery, as well as the decontamination of process exhaust streams. The sorption has been demonstrated in ORGDP tests with gas streams containing from 130 ppm to 10% uranium hexafluoride. A trap 4 inches in diameter was used, 120°C was chosen as the operating temperature, and gas velocities ranged from 0.08 to 1 ft/sec. The sorbed uranium hexafluoride was removed by heating and collected in a relatively pure form, leaving the

sodium fluoride regenerated for future use. The results have been published in previous progress reports*.

In the tests with low concentrations of uranium hexafluoride, a velocity of 0.7 ft/sec was employed. During the current report period, two new studies were made to cover higher gas flow, low uranium hexafluoride concentration cases, such as might be encountered with exhaust gases from a cold trap backup system to a sorption system in the event of a dilute gas release. The sorbent material was prepared by heating 1/8 inch cylindrical commercial sodium bifluoride pellets at 538°C for 5 hours. The resultant sodium fluoride had a surface area of 1.44 sq m/g, a void fraction within the pellet of 0.505, and a pellet density of 1.43 g/cc. For each test, approximately 18 kg of the sodium fluoride pellets was charged to the 4-inch-diameter trap to form a 7-foot-deep bed, and a superficial gas velocity of 1 ft/sec was employed. The gas flowed through the trap in the downward direction.

The first run lasted 1,820 hours. The operating temperature was 120°C, and the uranium hexafluoride concentration in the inlet stream was maintained at about 120 ppm. Although breakthrough did not occur during the test, the uranium hexafluoride analyses of the outlet gas stream averaged 30 ppm. This concentration was higher than expected. Pellet descriptions and analyses of uranium content at the conclusion of the test are given in table XX as a function of bed location.

A study of the test temperature data indicated that the middle section of the trap averaged about 4 to 6°C higher than at the ends. The uranium content of the pellets was lowest in this area of the bed, and it is possible that sorption was poor there because of the higher temperature. Reduction of test temperature is suggested as a possible means of improving sorption efficiency. The 120°C condition was chosen as a condition that would minimize hydrogen fluoride sorption in the event significant quantities were present. Sufficient hydrogen fluoride rejection might be achieved at slightly lower temperatures. On the other hand, selective regeneration may be possible so that the hydrogen fluoride and uranium hexafluoride may be separated in spite of the sorption of both on the sodium fluoride.

* Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies, Summary Progress Report, Fiscal Year 1964 through Fiscal Year 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, October 29, 1965 (K-1649), pp. 74 to 80; Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies, Summary Progress Report, July through December, 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, June 28, 1965 (K-1669), pp. 48 and 49; K-1691, loc cit, p. 57; K-1738, loc cit, pp. 83 to 85; and K-1744, loc cit, pp. 61 and 62.

TABLE XX

SODIUM FLUORIDE PELLET SORPTION DATA
AFTER 1,820-HOUR RUN AT 120°C*

<u>Pellet Location in Bed</u>	<u>Uranium Concentration, %</u>	<u>Color of Pellet</u>
Top	25.0	Dark yellow
6 Inches from Top	25.0	Dark yellow
1 Foot from Top	24.7	Dark yellow
1-1/2 Feet from Top	22.1	Dark yellow
2 Feet from Top	21.0	Dark yellow
2-1/2 Feet from Top	6.3	Light yellow
3 Feet from Top	2.9	White
3-1/2 Feet from Top	2.7	White
4 Feet from Top	1.8	White
4-1/2 Feet from Top	2.6	White
5 Feet from Top	2.4	White
5-1/2 Feet from Top	3.3	Light yellow
6 Feet from Top	4.6	Light yellow
6-1/2 Feet from Top	7.1	Light yellow

* The inlet uranium hexafluoride concentration was about 120 ppm, the sodium fluoride bed was 7 feet high, and the nominal residence time was 7 seconds.

The second run consisted of a series of tests at temperatures between 66 and 135°C to determine the effect of temperature on the outlet concentration of uranium hexafluoride. The inlet uranium hexafluoride concentration was adjusted for a target value of about 200 ppm and the resultant uranium hexafluoride concentrations in the outlet gas were determined.

The results, shown in table XXI and plotted in figure 33, indicate that an operating temperature of $93 \pm 8^\circ\text{C}$ should be satisfactory and would result in an exit gas containing about 4 ppm uranium hexafluoride. As shown in the data, even though the bed temperature was reduced to 66°C, outlet concentrations of greater than 1 ppm were observed. It may be that these last results are biased high because the trap used has seen long-term uranium hexafluoride service, and some uranium hexafluoride background may exist throughout the system.

The observed uranium hexafluoride concentrations were compared with computed gas concentrations based on equilibrium pressure equations from ORNL-2661* and ORNL-3497† for uranium hexafluoride over the $\text{UF}_6 \cdot 2\text{NaF}$ complex. Extrapolation down to test temperatures was necessary, since the reference data were obtained at much higher temperatures. The uranium hexafluoride concentrations observed in this run fell between the values obtained from the two references.

It seems that outlet concentrations close to equilibrium are being achieved with the nominal 7-second residence time. Thus, use of a deeper bed or lower gas flow rate would probably not result in significant reduction of the outlet concentration.

PERIPHERAL COMPRESSOR

After 3,813 hours of operating, including 2,340 hours of pumping mixtures of gas containing small amounts of uranium hexafluoride and fluorine, the compressor was shut down to inspect and replace the bearings. In the 54 hours of operation prior to shutdown, the load bearing temperature had increased from 54 to 79°C. One cubic centimeter of oil was injected into the bearing area, but there was no substantial decrease in temperature.

The unit had been in service on the second set of bearings since January, 1967, and had required no maintenance. Over the report period until shutdown, the compressor was operated at 9,500 rpm, the suction and

* Cathers, G. I., Bennett, M. R., and Jolley, R. L., The Fused Salt-Fluoride Volatility Process for Recovering Uranium, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, April 1, 1959 (ORNL-2661).

† Katz, S., Apparatus for the Gasometric Study of Solid-Gas Reactions: Sodium Fluoride with Hydrogen Fluoride and Uranium Hexafluoride, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, October 29, 1963 (ORNL-3497).

TABLE XXI

SODIUM FLUORIDE PELLET SORPTION DATA
AT TEMPERATURES FROM 66 TO 135°C*

Temperature, °C	Uranium Hexafluoride Inlet Concentration, ppm	Uranium Hexafluoride Outlet Concentration, ppm
66	180	1.5
66	177	1.5
80	156	2
80	172	1.5
93	182	4
93	176	3
102	233	8
107	232	8
107	115	9
113	178	11
113	180	12
121	312	14
121	345	15
121	274	21
135	330	31
135	347	41

* Inlet uranium hexafluoride concentration was approximately 200 ppm, the sodium fluoride bed was 7 feet high, and the nominal residence time was 7 seconds.

URANIUM HEXAFLUORIDE CONCENTRATION IN OUTLET GAS
AS A FUNCTION OF SORPTION TRAP TEMPERATURE

Figure 33

discharge pressures were 12 and 28 psia, respectively; the corresponding power requirement was 5.75 kw, and the load and rear bearing temperatures had been 54 and 43°C.

The compressor was removed from the test loop and was disassembled. Unusual difficulty was encountered in disassembling the process side with the cover plate and the impeller especially hard to remove. All surfaces which had been in contact with the process were covered by an adhering layer of uranium salts, principally uranyl fluoride. This type of deposit is not unusual for equipment used in uranium hexafluoride service. There had been no dusting. The metal surfaces coming into contact with the corrosive gases were easily cleaned with water, and inspection showed no signs of attack.

The general condition of the rear bearing was excellent. The grease that was packed throughout the bearing, although slightly stiff, appeared to possess much of its initial lubricity. The balls, phenolic retainer, and bearing races looked especially clean.

Inspection of the load bearing assembly showed that the bearing set nearest the compressor motor was responsible for the overheating. The forward bearing set was deficient in the amount of grease packed around the balls, but was not dry. The oil injected into the bearing area just before shutdown had obviously reached this point. The second bearing set, on the other hand, contained grease but was very dry. The phenolic retainer was found to have been broken at one place. The surfaces of the inner and outer races on which the balls ride were found to be moderately damaged. All of the balls of the second bearing set were slightly marred, with one ball being galled. The evidence classified the bearing failure as a normal one, resulting from degradation of the lubricating qualities of the bearing grease through routine use.

The grease-lubricated bearings performed well beyond the expected life of 2,500 hours. The compressor was designed for remote maintenance in an operating cell. The grease system was chosen over more conventional recirculating oil lubrication for design simplicity and for ease of removal of the entire compressor from a remote location, such as a processing cell, for maintenance purposes. In more conventional applications, an oil system would probably have been used.

The compressor was reassembled, with all new bearings, and was returned to service for 586 additional hours prior to conclusion of the long-term durability tests. Throughout this final test period, operation was again normal, and there were no unscheduled shutdowns.

It has been concluded as the result of these tests that the compressor is potentially suited for the recycle of reagent gases in volatility process applications. Test performance with mixtures of fluorine has exceeded the design criteria, and the long-term durability test program has demonstrated the mechanical reliability of the unit.

A formal report will soon be published which will give detailed information on the entire development and testing program. An analysis of the results of tests comparing design performance curves with actual performance data will be included.