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AEC RESEARCH AND DEVELOPMENT REPORT

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JULY THROUGH DECEMBER, 1966

AUTHORS:

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NUCLEAR DIVISION**

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Engineering Development Department
Technical Division

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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 Technical Division is participating with Argonne and Oak Ridge National Laboratories in studies of a group of processes aimed at purifying and recovering valuable uranium and plutonium from spent nuclear reactor fuels. The ORGDP portion of the program includes 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 fourth in a series of progress reports to be issued semiannually. The topics covered include (a) the status of the current low-enrichment fuel flow sheet studies, including the systems analysis project, conceptual plant studies, and sizing of the main fluid-bed reactor; (b) the separation and purification of uranium hexafluoride-interhalogen mixtures; (c) the fates of fission products during volatility process; (d) the composition of irradiated fuels; (e) criticality calculations; (f) the preparation of an interhalogen flow sheet for the semiworks facility; (g) process and reactor studies, including semiworks pilot plant operation, fluidization, and sampling studies; (h) corrosion testing; (i) outlet gas filter studies; (j) connector testing; (k) work on a powder discharge valve; and (l) evaluation of the ORGDP designed peripheral compressor.

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ORGDP FUEL REPROCESSING STUDIES
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JULY THROUGH DECEMBER, 1966

This report is the fourth in the series of semiannual summaries of Oak Ridge Gaseous Diffusion Plant work in the AEC-sponsored volatility process development effort. As stated previously, the work is performed in conjunction with National Laboratory programs, particularly those at Argonne National Laboratory and Oak Ridge National Laboratory. The ORGDP program supports and extends 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 are performed. Second, a component development program is being conducted to cover scale-up and testing of crucial process equipment and auxiliaries. Perhaps the most significant item is a semiworks fluid-bed reactor system to provide scale-up data for the main (head-end) fluid-bed reactor.

Emphasis has continued to be placed on the study of low-enrichment power reactor fuel reprocessing systems. Reporting will continue to be on a semiannual basis but, as substantive completion is achieved in various areas, topical reports will be issued.

SUMMARY

ENGINEERING STUDIES

LOW ENRICHMENT FUELS

Two major changes were made in the Argonne National Laboratory reference flow sheet. The two-zone oxidation-fluorination reactor concept was abandoned to allow use of lower uranium fluorination temperatures than thought to be achievable with this concept, and bromine pentafluoride was chosen over elemental fluorine for the conversion of U_3O_8 to uranium hexafluoride.

Since plutonium dioxide is not converted by bromine pentafluoride to plutonium hexafluoride because of thermodynamics, the use of the interhalogen results in a uranium hexafluoride vapor stream containing a negligible amount of plutonium. The U_3O_8 fluorination with bromine pentafluoride proceeds more rapidly at temperatures below 350°C . than with elemental fluorine. The use of such low temperatures for uranium fluorination permits a higher plutonium recovery efficiency on subsequent fluorination with elemental fluorine.

Engineering studies were focused on the bromine pentafluoride fluorination process, including the preparation of flow sheets for (1) the eventual full-scale processing plant, (2) fission product distribution, and

(3) adaption of the semiworks pilot plant to interhalogen fluorination. The systems analysis work is being pursued concurrently with the flow sheet work, and additional computations have been made on criticality control limits.

Systems Analysis

The question-and-answer format has been retained in the current realignment of the systems analysis program for the interhalogen volatility flow sheet. The questions are grouped in nine major categories, which include eight process systems and general considerations. New guidelines have been prepared to highlight important considerations in answer preparation. Questions on the Main Fluid-Bed Reactor and the Reactor Off-Gas Cooling and Filtration Systems have been revised, and answer write-ups have begun. The questions on the remaining systems will be restructured with some, such as those under the Pyrohydrolysis Fluidized Bed and the Hydrogen Chloride Recovery and Recycle Systems, not expected to require much revision.

Conceptual Plant Studies

Plant flow sheets were modified to include the reference flow sheet changes resulting from the adoption of interhalogen volatility. The lower amount of heat released when uranium hexafluoride is fluorinated with bromine pentafluoride instead of elemental fluorine simplifies temperature control problems in the main reactor. In addition, better reaction rates are achieved with the employment of interhalogen fluorination.

For the plant study, the fuel processing rate chosen is nominally 1 Mtu/day. Arrangement options with the main fluid-bed reactor are being considered. In a single vessel system, all the process steps involving the fuel element would be conducted in a single reactor. In the two-vessel system, a fuel element would be declad, and the oxidation would take place in the first reactor. The U_3O_8 and plutonium dioxide would then be transferred to another vessel for fluorination. The success of this option appeared to be contingent on successful development of a technique to achieve a partial separation of the U_3O_8 and the plutonium dioxide from the alumina. For the two-vessel system, a single line of equipment would be satisfactory to attain throughput goals but, if the single vessel system is used, two lines of equipment would probably be employed.

Main Fluid-Bed Reactor Sizing

Preliminary vessel sizing calculations were made based on the sizes of fuel assemblies for the TVA Brown's Ferry, Alabama (GE-BWR), and the Turkey Point, Florida (Westinghouse-PWR), reactors.

For the single-vessel system, two reactors, each about 26 inches in diameter, would be required to meet the planned production rate of 1,000 kg of uranium per day, including allowance for off-stream time.

Separation and Purification of Uranium Hexafluoride-Interhalogen Mixtures

The scheme for recovery of uranium hexafluoride and bromine pentafluoride from the gas stream leaving the bromine pentafluoride regenerator involves condensation, followed by distillation, to separate the two materials. Both liquid-solid cold trapping and liquid condensation of the two vapors in a multistage condenser system were considered during the report period.

A cold trap can be designed to condense concurrently a solid uranium hexafluoride condensate and a liquid composed of 90 to 96 mole percent bromine pentafluoride. The liquid phase would be continuously drained to a receiver and then recycled to the fluid-bed reactor. The solid product, which might contain as much as 10 mole percent bromine pentafluoride, would be liquefied and charged to the still. If cold trapping is employed, rather than single-stage liquid condensation, flows and equipment sizing requirements in the distillation system are decreased, and the equipment should be less complex.

Multistage liquid condensation is an improvement over single-stage liquid condensation because of reductions in the sizes of the equipment in the system and the lower requirements for bromine pentafluoride as a diluent. Two of three stages would be sufficient for a 1,000 kg uranium per day plant. Nevertheless, cold trapping remains the preferred choice because less bromine pentafluoride is fed to the still with that method.

A digital computer program has been written to perform design calculations for a continuous distillation operation with the uranium hexafluoride-bromine pentafluoride mixture. To make the program useful for any of several design arrangements, features are being incorporated which permit study of the theoretical effects of sidestreams; multiple feeds, the presence of several condensables, as well as a stream of fluorine; the rates of chemical reactions within the column (for example, the reaction of fluorine with bromine and bromine trifluoride); and pressure drop. The method for obtaining multicomponent vapor-liquid equilibria has not been chosen, but a simple interim model is currently being used by which binary system data are modified for multicomponent use.

The basic program has been debugged for three condensable components with chemical reaction rates of zero. A small amount of additional debugging may be necessary when the multicomponent and reaction rate features are included. A second version of the program will be prepared to perform batch column calculations on a quasi-steady-state basis.

Fission Product Flow Sheet

Recent work associated with the fates of fission products and actinides during volatility processing has been confined to equilibrium calculations for volatilization of various nuclides, release of normally gaseous fission products, and distribution of fission products within the pellets.

A computer program has been written to calculate specific nuclide distributions at equilibrium under various processing conditions. Ideal behavior was assumed for gases and mixtures, as well as for complete saturation of the carrier gas by the volatile fission product species. Although somewhat inaccurate, the results are assumed to represent the upper limits of the quantities of nuclides volatilized.

Krypton and xenon will be major gases released from the fuel assemblies during the de-clad step. The gas escapes from uranium dioxide during irradiation and is trapped in the voids between the cladding and the fuel until the cladding is removed. When the cladding is breached, the gas escapes into the process stream.

The preparation of the gas formed as a result of irradiation which so escapes appears to be a function of the fuel temperature developed during reactor operation. Calculations for several power reactors indicate that from 1 to 27% of the total amount produced may be released, depending on fuel operating conditions.

Information is being gathered on the distribution and chemical form of fission products within individual uranium dioxide pellets. These data are of value in assessing fission product fate during processing because of accessibility for reaction and susceptibility to chemical attack.

Composition of Irradiated Fuels

Except for the relatively minor constituent, plutonium-242, the results from the ORGDP computer code for estimating the properties of irradiated fuel checked within 10% with uranium and plutonium experimental data from the Yankee reactor. The discrepancy in the plutonium-242 results is felt to be due to inaccuracies in the cross-section data employed in the calculations.

Criticality Calculations

Calculations were made for plutonium dioxide spheres and infinite cylinders. Only plutonium-239 was considered present. For a plutonium density of 3.2 g/cc, the critical radius of an infinitely long cylinder was estimated to be 7.87 cm. Results from a set of calculations, involving the theoretical water absorption by plutonium dioxide and the critical properties of spheres at various hydrogen-to-plutonium atom ratios, indicate that powder containing plutonium dioxide might be handled in slightly humid atmospheres without serious criticality limitations.

Critical radii for infinitely long cylinders of plutonium hexafluoride-hydrogen fluoride mixtures reflected with 30 cm of water were computed to decrease monotonically from 12.69 cm at 0.5 volume percent plutonium hexafluoride to 6.87 cm at 100 volume percent plutonium hexafluoride (no hydrogen fluoride present). The unit safe diameter for a plutonium hexafluoride cold trap reflected with 30 cm of water would probably be about 5 inches; i.e., 6.35 cm radius.

Checks have been made on the accuracy of criticality calculations performed using the ANISN computer code with the S4 option. The calculation results are compared with criticality experimental data from Hanford on plutonium nitrate-water and plutonium dioxide-polystyrene systems and from Los Alamos on a plutonium metal assembly. The error in the calculated effective multiplication factor was less than 1% for the two plutonium nitrate cases. The errors for the plutonium metal and plutonium dioxide-polystyrene calculations were plus 4.6 and plus 3.0%; i.e., they were in the conservative direction. It was concluded that the accuracy of the calculation method appears to be satisfactory for both the moderated and relatively poorly moderated situations.

Semiworks Reactor Interhalogen Flow Sheet

Conceptual schemes to adapt the ORGDP semiworks facility for interhalogen volatility processing have been evaluated, and material balance computations have been made. A flow sheet employing a cold trap-distillation column arrangement has been selected for the semiworks system.

The reaction between U_3O_8 and bromine pentafluoride in the main reactor will liberate uranium hexafluoride, bromine, and oxygen. The gases will flow into a regenerator where the bromine will be converted back to bromine pentafluoride in a flame type reaction. The regenerator off-gases will then be cooled, and the bromine pentafluoride and uranium hexafluoride will be separated in a cold trap operating at about minus 40°C. The liquid bromine pentafluoride will be vaporized and reused in the main reactor, while the uranium hexafluoride will be purified in a distillation column.

PROTOTYPE TESTING AND EVALUATION

The test runs in the semiworks facility are among the highlights of the period. Studies were also carried out in sampling; corrosion testing; off-gas filtration; elutriation; fluidization; and the evaluation of connectors, valve, and the peripheral compressor.

PROCESS AND REACTOR STUDIES

A series of oxidation runs has been completed in the semiworks facility. In support of the test programs planned for this large-scale equipment, fluidization and elutriation scoping tests and sampling experiments have been conducted.

Cold Semiworks Pilot Plant

Fifteen oxidation tests have been conducted in this equipment since start-up in July, using charges of unirradiated reactor-grade uranium dioxide pellets, about 3/8 inch in diameter, and powdered sintered alumina (minus 48 plus 100 mesh) as the bed diluent. One-half-inch alumina balls were used in all but the first two tests to position the pellet bed within the

heated zone of the reactor. The bed was fluidized and oxidized with air or air diluted with nitrogen.

After initial exploratory tests, emphasis was placed on finding reliable operable oxidizing conditions consistent with attaining satisfactory bed properties and cycle times.

It was found that essentially complete oxidation of uranium dioxide pellets can be accomplished under controlled conditions. A gas velocity of 3 ft/sec in the pellet zone and control of bed and gas preheat temperatures so that oxidation consumes the pellet bed starting at the top appear to be desirable to avoid plugging of the pellet bed with fine U_3O_8 .

Fluidization Studies

Tests in a 2-inch Plexiglas column 4 feet long show that, when an alumina (minus 48 plus 100 mesh) bed is restrained by having a coarse uranium dioxide pellet charge loaded on top of it, more pressure is needed to initiate fluidization than to sustain it.

In a series of tests in the same equipment using minus 35-mesh bed material taken from the semiworks reactor after selected oxidation runs, a velocity of 1.6 ft/sec appeared to be suitable for U_3O_8 elutriation. A relatively small amount of alumina is also carried over.

Sampling

Additional sampling tests have been conducted in the 6-inch Denver Vezin solids sampler. The feeds used were mixtures of powder, consisting of one relatively coarse and one fine component, to simulate the bed material from the main fluid-bed reactor.

Sample cuts of 5.38 and 5.5 weight percent were obtained using feed rates of 12 and 1.33 kg/min, respectively. Sampling biases on the order of 0.25 to 1% were found which may have been influenced by the feed rate to the unit.

MATERIALS OF CONSTRUCTION - CORROSION TESTING

Coupons of nickel and Duranickel were exposed to the volatile chlorides produced during the zircaloy dechlor step and then to the process environments occurring during the oxidation and elemental fluorine fluorination steps. A 5-cycle test was conducted with the results indicating corrosion rates of 42 and 48 mils per year for the nickel-201 and Duranickel, respectively. These results compare favorably with those from previous tests conducted in the absence of zircaloy and indicate that the zircaloy reaction products have no significant effect on corrosion of the materials of construction for the head-end fluid-bed system.

OUTLET GAS FILTER STUDIES

Sintered nickel fiber tubes, manufactured by Huyck Metals Company, were exposed to the off-gases produced during the decladding of zircaloy-clad fuels by hydrochlorination. The overall volatility processing cycle was then simulated by subsequently exposing the tube to air and then to fluorine-containing gas.

Air flow tests, made on the filter tubes before and after exposure, have indicated permeability reductions on the order of 85% for three exposure cycles, as compared with previously determined filter permeability losses of about 30% for multiple exposure cycles to process chemicals, not including the off-gas constituents coming from the zircaloy reaction. Considering the relatively high flow capacity of the new tubes, tubes retaining as much as 5 to 10% of the original permeability would probably be usable in process applications. Nevertheless, reduction of permeability loss is certainly desirable at this permeability level, and the relatively high loss indicated for such short exposure time is a matter of present concern.

Laboratory analysis indicated that alumina, zirconium tetrafluoride, and an unknown compound, possibly a complex, were the chief constituents of the filter coating at the end of a cycle. It has been concluded that the plugging is probably due to the interaction of zirconium tetrachloride with the filter media. Filter permeability has been largely recovered by treatment with 10 to 15% hydrogen at 540°C.

CONNECTORS

New 2- and 4-inch connectors, employing a DSD Company temperature-compensating clamp, have been fabricated and tested. Various gasket and flange facing designs were tried. The connectors were cycled between 100°C and temperatures as high as 540°C for 10 to 19 cycles before leaks developed. In two out of three tests undertaken, the bolts on the clamps were retorqued and a leak-tight seal was regained. In the last case, the bolt retainers broke during tightening.

VALVES

A commercial all-nickel plug valve might be satisfactorily applied, after modification, to handle the powder discharge from a fluid-bed reactor. The leakage of air at room temperature through a 4-inch-diameter bed of alumina, with a closed valve on the bottom, was measured at about 2.5 cfm, but there was no leakage of alumina. Several modifications are to be made to the valve at ORGDP.

PERIPHERAL COMPRESSOR

A 2,000-operating-hour continuous service test with fluorine has been completed. During the run, occasional lubrication was necessary to keep the temperature of the load bearing at the normal 60°C. No other operating difficulty of any significance was encountered after the nitrogen seal pressure was boosted to prevent exposure of the bearings to fluorine. A detailed inspection of the interior of the compressor is planned. Preliminary indications are that the metal surfaces of the unit are clean and uncorroded, and that the unit is in excellent condition.

DISCUSSION

ENGINEERING STUDIES

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LOW ENRICHMENT FUELS

Major Argonne National Laboratory reference flow sheet changes were made during the report period. These were (1) dropping of the two-zone concurrent oxidation-fluorination concept in favor of sequential steps, and (2) use of bromine pentafluoride instead of fluorine for conversion of U_3O_8 to uranium hexafluoride.

Laboratory work at ANL indicated that the uranium fluorination temperature must be well below the pellet oxidation temperature, i.e., less than $350^{\circ}C$ as compared to greater than $450^{\circ}C$, if plutonium recovery in excess of 99% is to be attained. This is necessary regardless of whether fluorine or bromine pentafluoride is the fluorinating agent for uranium removal. Since achievement of this temperature gradation in a single bed does not appear to be feasible, it seems that separate oxidation-fluorination steps must be employed if a single reactor is used, and the two-zone concept must be discarded.

The use of bromine pentafluoride for uranium oxide fluorination has several advantages. Foremost, perhaps, is the fact that conversion of the plutonium dioxide to plutonium hexafluoride is apparently not thermodynamically possible with bromine pentafluoride; therefore, significant amounts of volatile plutonium are not introduced into the main uranium hexafluoride product vapor stream. In addition, bromine pentafluoride and the intermediate product, bromine trifluoride, both react more rapidly with U_3O_8 than does fluorine at room temperatures below $350^{\circ}C$, thus allowing production of the uranium hexafluoride under conditions most conducive to increased plutonium recovery efficiency during the subsequent fluorination with elemental fluorine.

Because of the change in the ANL reference flow sheet to utilize the interhalogen route, engineering studies during the report period were focused on fluorination with bromine pentafluoride.

The systems analysis work is being carried along at the same time as the flow sheet studies. The systems analysis is aligned in a question-and-answer format. Since the elemental fluorine reference flow sheet had been used as the basis for stating the questions, the shift to a bromine pentafluoride flow sheet and the elimination of the two-zone oxidation-fluorination has necessitated that all questions be reviewed and those no longer applicable be eliminated. Second, the bromine pentafluoride flow sheet is being studied, and necessary additional questions are being

added to the list. The preparation of answer material is proceeding concurrently with the latter work in the reoriented program.

Interhalogen flow sheets were started for conceptual plant studies. Fission product flow sheet calculations were made for the bromine pentafluoride process. Process flow sheets were in preparation for adaption of the semiworks pilot plant for interhalogen fluorination. Additional computations were carried out on the criticality control limits for plutonium dioxide spheres and cylinders.

Systems Analysis

Realignment of the question-and-answer format for the interhalogen volatility flow sheet is in progress. The following breakdown of process systems is being used:

1. Main Fluid-Bed Reactor
2. Reactor Off-Gas Cooling and Filtration
3. Pyrohydrolysis Fluid Bed
4. Hydrogen Chloride Recovery and Recycle
5. Bromine Pentafluoride Feeding, Regeneration, Recycle, and Handling
6. Uranium Hexafluoride Separation and Purification (Cold Trapping-Distillation)
7. Plutonium Hexafluoride Separation, Cold Trapping and Fluorine Recycle
8. Plutonium Product Preparation System
9. General Considerations

The problems being considered under each heading are further subdivided according to the following categories:

1. Operations
2. Process Technology
3. Design
4. Safety
5. Construction
6. Accountability

New guidelines have been prepared to highlight important considerations in answer preparation. The format for answer preparation includes the

headings: Discussion, Work Required, Suggested Schedule, References, and Related Questions. Several areas which are to be covered under Discussion include the statement of the problem, the reasons for considering it, the seriousness, the degree of precision of information needed; the status, i.e., who is or has worked on it and how useful is available information; the variability of problem with flow sheet and fuel charge changes; and an assessment of the degree of difficulty, including the kind of work involved in getting needed information. The Work Required area is to cover not only present experimental plans, but also assessment as to what experimental work and scale of effort are needed, and which site is best prepared for such effort. Under Suggested Schedule, points at which information is needed in the program are considered, as well as current schedules. The category, Related Questions, allows cross referencing and thus provides for interrelationship of questions and simplification of answers.

The questions on the Main Fluid-Bed Reactor and the Reactor Off-Gas Cooling and Filtration Systems have been revised, and concurrently, a number of operational and process technology "answers" have already been prepared for the decladding, oxidation, and the two fluorination steps. There are over 150 questions listed under the Main Fluid-Bed Reactor. Since this is the most important system in the plant, the number of questions can logically be expected to be greater than for any of the other eight major categories.

Restructuring of the remaining systems will continue. The Pyrohydrolysis Fluidized Bed and the Hydrogen Chloride Recovery and Recycle Systems questions, written previously for the two-zone oxidation-fluorination process, are not expected to require much revision. Previous work may also be helpful in updating the Cold Trapping-Distillation and General Considerations questions.

Conceptual Plant Studies

Flow sheets were modified as necessary to encompass the reference flow sheet changes agreed upon at the September Volatility Process Advisory Committee meeting.

The major reference flow sheet change involves the use of bromine pentafluoride for the production of uranium hexafluoride. Since bromine pentafluoride for thermodynamic reasons will not fluorinate plutonium salts to give significant concentrations of plutonium hexafluoride, the uranium hexafluoride produced is essentially free of plutonium. Minute trace quantities of plutonium present in the uranium hexafluoride should readily be eliminated at the same time as other radioactive impurities are removed from the uranium hexafluoride.

This clear-cut separation of the uranium hexafluoride and plutonium hexafluoride production operations should be a very substantial advantage, but it is not gained without some complication of the flow sheet associated with the recovery of the uranium hexafluoride, separation of the uranium hexafluoride and the interhalogen materials, and reconversion of

the reduced bromine and bromine compounds to bromine pentafluoride.

Substitution of bromine pentafluoride for fluorine does have additional advantages beyond that relating to plutonium-uranium separation. Fluorination of the U_3O_8 with bromine pentafluoride results in a lower heat release, thus simplifying temperature control problems in the fluid-bed reactor. Also, bromine pentafluoride is a better fluorinating agent at low temperatures, thus minimizing accumulation of U_3O_8 in cooler parts of the apparatus.

Another process change involves the elimination of the two-zone oxidation-fluorination operation for simultaneous comminution of the uranium dioxide by conversion to U_3O_8 , and fluorination of the U_3O_8 to produce uranium hexafluoride. The reason for this change is that the uranium fluorination temperature must be well below the pellet oxidation temperature, i.e., less than 350°C as compared to greater than 450°C , if plutonium recovery in excess of 99% is to be achieved. This is necessary regardless of whether fluorine or bromine pentafluoride is the fluorinating agent for uranium removal. Since achievement of this temperature gradation in a single bed appears to be unfeasible, it seems that separate oxidation and fluorination steps must be employed.

The separation of oxidation and fluorination steps opens up other equipment arrangement options:

1. All process steps could be carried out sequentially in the same vessel, as usually suggested with the two-zone reference flow sheet.
2. After decladding and oxidation, all or perhaps only part of the bed, if it contained substantially all the uranium, could be transferred to another vessel for the fluorination steps. If the U_3O_8 could be transferred as it was formed by oxidation, the uranium fluorination might be conducted in a separate fluid bed in series with the oxidizer.

Thus, by having the separate fluid beds, the time cycle advantage of the two-zone oxidation-fluorination sequence might be retained and the temperature adjustment problems would be solved.

The equipment arrangement could be similar to that of the semiworks where the fluid-bed cooler is in juxtaposition with the reactor.

These options could be employed with a straight fluorine flow sheet, and some consideration had been given to the various possibilities in the past. The employment of bromine pentafluoride for uranium fluorination is, however, advantageous to any of the schemes because, as previously mentioned, better reaction rates can be achieved at temperatures below 350°C and the heat release is lower.

Both single-vessel and two-vessel main reactor system flow sheets are being considered. The two-vessel option appears to have some advantages if a satisfactory technique for making a bulk separation of alumina and U_3O_8 can be devised. In this flow sheet, part of the bed containing the

bulk of the uranium is transferred to another reactor for fluorination. This leaves the declad vessel free to accept another fuel charge.

The separation of the process steps also allows a little more flexibility in materials choice, i.e., Inconel as well as nickel for declad-oxidation, and Monel as well as nickel for fluorination. Somewhat better corrosion resistance may be possible in this way, but this is probably not too important except possibly in connection with the choice of the filter materials. On the other hand, the single-vessel flow sheet may have some advantages in relation to criticality control and accountability.

The plant study is aimed at a fuel processing rate equivalent to 1 Mtu/day throughput. It is anticipated that a one-line, two-vessel plant, i.e., one declad-oxidation reactor and one fluorination reactor, would be practical to attain throughput goals. On the other hand, if the single-vessel system is used, i.e., all steps performed in the same vessel, it appears that a two-line plant would probably be employed, thus requiring duplication of the more expensive declad vessel and fuel charging station. Discussions of the fluid-bed reactor sizing and various other aspects of flow sheet development follow.

Main Fluid-Bed Reactor Sizing

Preliminary sizing calculations have been made for the main fluid-bed reactor in the conceptual volatility process plant. The reactor size and the necessary gas inlet and outlet flows serve as the basis for the interhalogen process flow sheets now in preparation.

The main fluid-bed reactor used for decladding and subsequent process steps is expected to contain about 1,500 kg of uranium in a single charge. For the single-vessel flow sheet, two reactors would be installed to meet the planned 1,000 kg of uranium per day production rate. Each reactor would have a diameter of about 26 inches, assuming the sizes of the fuel assemblies to be charged lie within the range covered by the fuel planned by General Electric for the TVA Brown's Ferry, Alabama reactor and that planned by Westinghouse for the Turkey Point, Florida reactor. Descriptive data for these fuel assemblies and the fluid-bed reactor charge that would result are shown in table I.

If the fuel elements are to be covered with the fluid bed, about 2,000 kg of alumina is required in the reactor. Under these conditions, the pressure drops across the fluid bed after the hydrochlorination, oxidation, and fluorination steps are expected to be about 10, 15, and 18 psi, respectively, not considering the possible effects due to internal bed supports and feed baskets or to the removal of material by elutriation and/or by partial bed withdrawal after decladding to reduce aluminum oxide-to-uranium ratio for the subsequent oxidation step.

TABLE I

CHARGE DATA FOR THE MAIN FLUID-BED REACTOR*

	<u>General Electric</u> <u>Fuel Assembly TVA,</u> <u>Brown's Ferry, Alabama</u>	<u>Westinghouse</u> <u>Fuel Assembly,</u> <u>Turkey Point, Florida</u>
Fuel Assembly Descriptions		
Cross-Section of Fuel Assembly, inches	5.44 x 5.44	8.43 x 8.43
Fuel Rod Array	7 x 7	15 x 15
Fuel Rod Outside Diameter, inches	0.562	0.422
Number of Fuel Rods Per Assembly	49	205†
Number of Control Rod Guide Thimbles Per Assembly	none	20
Length of Assembly, ft.	12	12
Uranium Dioxide Per Assembly‡, kg.	221.1	517.2
Zircaloy-2 Per Assembly, kg.	41	103
Number of Assemblies Per Main Fluid-Bed Reactor Charge	7	3

* Data were obtained from Preliminary Safety Analysis reports which are available at the U. S. A. E. C. Public Reading room in Washington, D. C. The docket numbers are 50-259 and 50-260 for the Brown's Ferry reactor, and 50-250 and 50-251 for the Turkey Point 3-4 installation.

† Some assemblies have an instrumented rod.

‡ These numbers are for the unirradiated fuel assemblies.

Separation and Purification of Uranium Hexafluoride-Interhalogen Mixtures

After the effluent gases from the fluid-bed reactor during the interhalogen cycle have been treated with fluorine to regenerate the bromine pentafluoride, the uranium hexafluoride and the bromine pentafluoride must be removed from the gas stream. Emphasis has been placed on schemes to separate the bromine pentafluoride and uranium hexafluoride by condensation from the remainder of the stream (primarily nitrogen, oxygen, and fluorine), and then distilling the condensate to separate the bromine pentafluoride and uranium hexafluoride. Both liquid condensation and cold trapping to produce a part liquid-part solid condensate have been considered as methods for removing the bromine pentafluoride and uranium hexafluoride from the noncondensable gas stream.

Liquid-Solid Cold Trapping of Uranium Hexafluoride-Bromine Pentafluoride Mixtures

A cold trap has been proposed for removal of uranium hexafluoride and bromine pentafluoride from the gas stream leaving the bromine pentafluoride regenerator during interhalogen fluorination. The uranium hexafluoride-bromine pentafluoride system forms a simple eutectic at about 4 mole percent uranium hexafluoride, so that a cold trap could be designed to collect concurrently a solid uranium hexafluoride condensate and a liquid in the range of 90 to 96 mole percent bromine pentafluoride, while the remainder of the gas stream would flow through and out of the equipment. The condensed bromine pentafluoride is sufficiently depleted of uranium hexafluoride that continuous recycle of it to the main reactor should be feasible throughout the interhalogen fluorination cycle. After isolation and heating of the cold trap, the collected material, primarily uranium hexafluoride, can be charged to the distillation system by vapor transfer or draining.

Design information for such a unit is quite limited, but there is reason to expect that the liquid produced would be quite close to the equilibrium composition at the chosen operating temperature. Although the outlet liquid nozzles may require heating to eliminate possible plugging due to solid entrained in the liquid, the amount of such entrainment, and thus the difficulty arising from this cause, should be small. The final solid product in the trap is expected to contain bromine pentafluoride in an amount less than 10 mole percent, although the possibility of a 15 mole percent entrainment will be considered in the design of the distillation system.

This two-phase cold trapping method has two basic advantages over single-phase condensation. First, cold trapping provides a partial separation of uranium hexafluoride and bromine pentafluoride, and the charge to the distillation system is smaller, since it contains much less bromine pentafluoride. As a result, flows and equipment sizes in the distillation system are decreased. Second, although initial design is somewhat less certain for two-phase cold trapping, the equipment should be less complex.

Multistage Condenser System

A multistage condenser system could be used as an alternative to the cold trap. The system would consist of a number of condensers arranged for series flow of the process gases. The condensate from each stage would be cooled and recycled in that stage, with the product flow being toward the gas input stage. This type of system differs from the single-stage type* which utilizes one coolant temperature and only allows recycle around the entire unit, rather than around individual stages. Both types of condenser arrangements are primarily concerned with handling dilute product streams containing about 20 mole percent condensables. The main aim of either condenser system is to avoid precipitation of solids in the equipment because plugging could possibly result.

Multistage condensation is an improvement over single-stage condensation because of the advantages gained by operating the stages at different temperatures. For example, there would be lower amounts of bromine pentafluoride and uranium hexafluoride vented from the system with the off-gases, and reductions in equipment sizes as compared to the single-stage system because of lower recycle requirements for bromine pentafluoride as a diluent. Two or three stages appear to be sufficient for the expected plant feed system.

For the time being, the condenser systems are being shelved in favor of the main cold trapping arrangement previously discussed. Perhaps the main disadvantage of the condenser systems; in comparison to the cold trapping arrangement, is that more bromine pentafluoride must be handled through the associated distillation system and the resulting uranium hexafluoride concentration in the feed to the still is correspondingly lower.

Distillation Column for Uranium Hexafluoride Purification

The distillation system for bromine pentafluoride-uranium hexafluoride separation will treat the cold trap product stream, containing about 85 to 90 mole percent uranium hexafluoride; the remainder being primarily bromine pentafluoride, with small quantities of bromine trifluoride, bromine, and fission product fluorides. The distillation column will produce a tops product of bromine pentafluoride, containing as much as 10 mole percent uranium hexafluoride, which can be recycled to the fluid-bed reaction system. The remaining uranium hexafluoride may be removed from this column either in a side stream or as a bottoms product, and if necessary, the stream may then be sent to a second column for final

* Dunthorn, D. I., Liquid Condensation of a Uranium Hexafluoride-Bromine Pentafluoride Mixture from a Noncondensable Carrier Gas Stream, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, February 1, 1967 (K-L-2223).

purification of the uranium hexafluoride to meet specifications*. Fluorine will be fed at the bottom of the first column to eliminate traces of bromine and bromine trifluoride by conversion to bromine pentafluoride. Removal of small amounts of fission products and other impurities from uranium hexafluoride by passing it through solid sorbents is also probably practical. This technique might be used as an adjunct with either a one- or two-column distillation system.

A digital computer program has been written to perform the calculations required for the design of a continuous column for uranium hexafluoride-bromine pentafluoride distillation. Considerable flexibility is included in the program so that it can be utilized for any of several design arrangements, and so that the theoretical effect of various process situations can be studied. Several condensable components may be considered present in the column, as well as a stream of noncondensable fluorine. Calculations may include effects of removal of side streams, multiple feeds, and reactions of process fluids with materials of construction and with fluorine. Since one column may require on the order of 50 stages, provision has been made for taking pressure drop into account. Because a plate rather than a packed column may be used, a simple plate efficiency model has been incorporated.

Chemical reaction rate is important where bromine pentafluoride is reduced to bromine trifluoride. Bromine pentafluoride is more volatile than uranium hexafluoride, while bromine trifluoride is considerably less volatile. The reversal of this reaction with fluorine and the fluorination of traces of elemental bromine are important considerations in the distillation problem.

The most significant theoretical problem that has not been resolved is that of multicomponent vapor-liquid equilibria. Measurements and estimations of many of binary system equilibria are available, and a simple interim model is currently being used to modify these for multicomponent use. A number of methods are available for estimating multicomponent equilibria from binary data but these are primarily applicable to organic systems. The ultimate choice of the method to be used will rest not only on the ability to work with inorganic compounds, but equally important, to operate well at low concentrations, since all components except bromine pentafluoride and uranium hexafluoride are likely to be present in relatively small amounts.

The basic program makes use of two subroutines, one for vapor-liquid equilibria and the second for the calculation of reaction rates in the liquid and gas phases. These routines may be tailored to the requirements of the system being analyzed, and the main program need not be altered. As input, the main program accepts information concerning the column feed, bottoms product, boilup rate, number of plates, physical properties of

* The current specification for bromine content in uranium hexafluoride is 5 ppm on a uranium basis; i.e., an atom ratio of bromine-to-uranium of 1.5×10^{-5} .

the components, and other information required to specify the column. The bottoms compositions are then guessed, and the operation of the column is calculated on this basis. Any mismatch of calculated tops composition serves as a basis for modifying the bottoms composition guesses, and the calculation is repeated until a match is achieved at the top of the column. Usually, only five or six such cycles are required to obtain a high precision (0.005%) match. The calculated time required for convergence is somewhat more than 1 minute of IBM-7090 time for a three-component system with 40 column plates. For each plate in the column calculation, equilibrium is used to establish the plate temperature, while the vapor flow from the plate is found by satisfying an enthalpy balance.

The program has been debugged and has tested quite satisfactorily on several process-oriented design examples. These examples have included only three condensable components with chemical reaction rates of zero. Because of the manner in which the multicomponent and reaction rate features are incorporated into the program, however, there will be no changes in the basic calculations when these features are used, and little, if any, additional debugging should be required to employ them. The major problem in including additional condensable components will be, as stated above, in obtaining and combining the required data. It is likely that approximations will have to be devised in some instances, especially for chemical reaction rates, as previously mentioned, involving reduction of the higher bromine halides by corrosion of surfaces and in situ regeneration of these compounds with elemental fluorine, are important reactions taking place in the distillation system.

As an example of the program calculations, in one of the test cases, a 20-plate column was tried with a vapor feed, containing 85 mole percent uranium hexafluoride, entered at the tenth plate. The pressure was 2.8 atmospheres at the top of the column, with a pressure drop of 10 mm of mercury per plate. A high boilup rate of ten times the feed rate was used, and a bottoms product was withdrawn at 0.9 times the feed rate. The bottoms product composition was calculated as 94.02 mole percent uranium hexafluoride, 2.22 mole percent bromine trifluoride, and 3.76 mole percent bromine pentafluoride; and the overhead product composition was calculated as 3.85 mole percent uranium hexafluoride, 0.0003 mole percent bromine trifluoride, and 96.15 mole percent bromine pentafluoride*. Liquid and vapor flow rates departed only slightly from equimolal overflow, as would be expected from the relative closeness of molal latent heats of vaporization for bromine pentafluoride and uranium hexafluoride. Heat loads for the reboiler and condenser were not calculated; but for similar examples, they proved to be about 40,000 Btu/lb mole of feed, based upon a boilup-to-feed ratio (bottom reflux ratio) of ten.

* The concentrations achieved according to this example are certainly not satisfactory from a plant standpoint; however, the example does demonstrate qualitatively the difficulty of the separation. More stages are indicated to be required in the column to remove bromine pentafluoride from the uranium hexafluoride. A higher reflux ratio might also be needed. It may also be necessary to use a second column to achieve satisfactory separation of the uranium hexafluoride from bromine trifluoride.

Studies are now centered upon using the program to analyze possible designs for the column to be employed with the interhalogen flow sheet. In this connection, a second version of the program is being prepared to perform batch column calculations for the same system on a quasi-steady-state basis. In actuality, this is a minor modification in terms of program operation. All that need be done is to change the basis of the column-matching function from overhead product composition to column holdups and make provisions for restarting the calculation as overhead product is withdrawn and the column content changes.

Fission Product Flow Sheet

A major study has been undertaken to determine the fates of radioactive fission products and actinides during the various process steps of the bromine pentafluoride volatility flow sheet. Because of the large variety of nuclides present and the multiplicity of factors which can influence distribution, a comprehensive effort is required. Recent work associated with the fission product flow sheet has been confined to equilibrium calculations for nuclides volatilized during processing, fission gas release from fuel pellets, and fission product distribution within the pellets.

Equilibrium Calculations. On the assumption that upper limit estimates of the quantities of specific nuclides volatilized can generally be obtained from equilibrium distributions, a computer program has been written to perform the calculations for a variety of operating temperatures and carrier gas flow rates. The principal assumptions were (1) ideal behavior for gases and mixtures, and (2) complete saturation of the carrier gas by the volatile fission product species. It should be noted that the results may not describe the true processing situation accurately. First, the program probably overestimates the quantities volatilized because no reaction or diffusion rate limitations are considered. Second, in cases where well-established vapor pressure data were not available, estimated values were used, thus possibly resulting in additional inaccuracies. Currently, a search for more complete vapor pressure data is being conducted, and the general computation procedure is being checked.

Preliminary calculations were made for the oxidation and bromine pentafluoride fluorination steps. Similar estimates for the hydrogen chloride decladding step will involve assessing the amounts of various fission products which are occluded within the fuel pellets and thereby are unavailable for reaction, at least on the initial hydrochlorination. Recycling of the alumina will also allow some reaction of fission products not eliminated by oxidation or fluorination.

Fission Gas Release from Fuel Pellets. The fission gas released from the main fluid-bed reactor during the declad step will be primarily krypton and xenon, which escape from the fuel during irradiation. This gas is trapped in the fuel rod plenum and in the voids between the cladding and the fuel, and the gas escapes when the cladding is punctured. For burnups below 45,000 Mwd/Mtu, the amount of fission gas released appears to be a function of fuel temperature. It has been suggested that more than 95% of the fission product gas produced in a uranium dioxide

pellet during irradiation will be released in that portion of the fuel in which the temperature is greater than 1600°C, 60% will be released in that portion which is between 1300 and 1600°C, and less than 1% will be released where the temperature is below 1300°C*.

A computer code was written to calculate the temperature distribution in clad uranium dioxide fuel during irradiation. Fission gas releases from the fuel were then computed for power reactor fuel elements exposed in peak or average flux regions of the core. The results of these calculations for several reactors are shown in table II. The estimated percentages of fission gas released vary from approximately 1 to 27%, depending on the reactor and the fuel position during irradiation.

Fission Product Distribution in Fuel Pellets. Information is being gathered concerning the distribution and chemical form of fission products within individual uranium dioxide pellets. Location in the fuel and the compound form can affect fission product fate during processing because of changes in accessibility for reaction and susceptibility to attack. Most solid fission products, instead of being uniformly dispersed in the fuel, tend to segregate into annular rings of high concentration, with the more volatile fission product generally migrating to the outer, cooler fuel regions. In particular, cesium and ruthenium show tendencies to move toward the pellet surface. One report surveyed† suggested the interesting conclusions that (1) molybdenum, technetium, ruthenium, and rhodium probably segregate as metals; (2) barium and strontium segregate as oxides which are, in turn, associated with some fission product zirconium and cesium; and (3) neodymium and unassociated zirconium are uniformly dissolved as oxides.

Composition of Irradiated Fuels

Results of the computer code developed at ORGDP‡ for estimating the properties of irradiated fuel were checked versus experimental data obtained from the Yankee reactor§. A summary of the comparisons is given in table III, where values for uranium-235 and uranium-238 depletions and for uranium-236 and plutonium isotopic buildups are presented for fuel

* Scott, J. L., "Fuel Element Performance Limitations", Nuclear Safety, 7 (3), 302-313 (Spring, 1966).

† Bradbury, B. T., Demant, J. T., and Martin, P. M., Solid Fission in Irradiated Uranium Dioxide, Atomic Energy Research Establishment, January, 1966 (AERE-R-5149).

‡ Merriman, J. R., "Estimation of Irradiated Reactor Fuel Properties for Reprocessing Studies", M. S. Thesis, University of Tennessee (December, 1966).

§ Nodvik, R. J., Evaluation of Mass Spectrometric and Radiochemical Analyses of Yankee Core I Spent Fuel, Westinghouse Electric Corporation, Atomic Power Division, March 1966 (WCAP-6068).

TABLE II
URANIUM DIOXIDE FISSION GAS RELEASES
FOR POWER REACTOR FUEL ELEMENTS

Plant*	Contractor	Power, Mwe Net	Hottest Fuel Element		Average Fuel Element	
			PCT†, °C	FGR‡, %	PCT†, °C	FGR‡, %
Turkey Pt. 3-4	Westinghouse	760	2332	26	1688	7
H.B. Robinson	Westinghouse	760	2332	26	1688	7
Dresden 2-3	General Electric	809	2132	20	1321	1
Quad-Cities	General Electric	809	2132	20	1321	1
Palisades	Comb. Engr.	810	2210	23	1393	2
Indian Pt. 2	Westinghouse	873	2393	27	1754	9
Brown's Ferry	General Electric	1,100	2316	27	1732	8

* Information on these plants was obtained from preliminary safety analysis reports, which are available at the U.S.A.E.C. Public Reading room in Washington, D. C. The docket numbers for these reports are as follows: Turkey Point 3-4, 50-240 and 50-251; H. B. Robinson, 50-261; Dresden 2-3, 50-237 and 50-249; Quad-Cities, 50-254; Palisades, 50-255; Indian Point 2, 50-247; and Brown's Ferry, 50-259 and 50-260.

† Peak central temperature

‡ Fission gas release.

TABLE III

COMPARISON OF EXPERIMENTAL DATA WITH COMPUTER CODE OUTPUT
(BUILDUP AND DEPLETION OF SPECIFIC ISOTOPES IN YANKEE REACTOR)

Burnup, Mwd/Mtu	Data Source	Isotopic	Depletion	Isotopic Buildup, kg/Mtu				
		U-235, %	U-238, kg/Mtu	U-236	Pu-239	Pu-240	Pu-241	Pu-242
10,000	Yankee	28.5	8.30	1.85	4.60	0.61	0.30	0.02
	Predicted	28.8	8.10	1.89	5.00	0.70	0.40	0.03
15,000	Yankee	38.8	12.6	2.49	5.96	1.50	0.64	0.07
	Predicted	39.7	12.1	2.60	5.90	1.10	0.72	0.09
20,000	Yankee	47.5	17.2	3.03	6.95	1.47	0.99	0.14
	Predicted	48.8	16.1	3.20	6.60	1.55	1.10	0.21
25,000	Yankee	55.5	22.0	3.45	7.70	1.79	1.29	0.25
	Predicted	57.0	20.0	3.72	6.96	1.91	1.40	0.33

exposures of 10,000, 15,000, 20,000, and 25,000 Mwd/Mtu. The agreement between experimental and calculated numbers is encouraging and, except for plutonium-242 production, is usually within 10%. Plutonium-242 errors are felt to be due primarily to the cross-section data used in the calculations.

Criticality Calculations

Evaluation of process criticality problems was centered on those due to plutonium. Calculations were made to provide values for plutonium dioxide and plutonium hexafluoride systems under various conditions in order to obtain information on which to base estimates of safe batch sizes and to size equipment where control by geometry restriction was contemplated.

In order to evaluate the accuracy of the DTF code as applied to plutonium criticality computations, a series of checks of code output versus plutonium criticality experimental results was undertaken.

Plutonium Dioxide Systems. Criticality calculations have been made for plutonium dioxide powders contained in spheres and infinitely long cylinders, where the plutonium present is the plutonium-239 isotope, using the ANISN code.

Assuming a bulk density for plutonium dioxide powder equivalent to 3.2 grams of plutonium per cubic centimeter*, mass computations were performed for spheres at various effective neutron multiplication factors, k_{eff} . The results are presented in table IV. Critical radii for infinitely long cylinders, containing plutonium dioxide powder at several different bulk densities, are shown in table V. For a plutonium density of 3.2 g/cc, i.e., a plutonium dioxide density of 3.6 g/cc, the criticality radius of an infinitely long cylinder was estimated to be 7.87 cm.

Also, criticality calculations were made for spheres of plutonium dioxide to determine the effect of small amounts of water that might be picked up by the powder. The amount of water which might be picked up by plutonium dioxide powders is dependent on surface area, relative humidity, and time. The results, along with calculated plutonium masses, are given in table VI. At 22% relative humidity and a specific surface area of 20 sq m/g, plutonium dioxide powder gains only about 0.2 weight percent as water; however, when the humidity exceeds 95% relative humidity, as much as 3.5 weight percent as water may be picked up in 24 hours†. In accordance

* The plutonium density of bulk plutonium dioxide has been estimated to be less than 3.2 g/cc; e.g., 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. 37.

† Moseley, J. D., and Wing, R. O., Properties of Plutonium Dioxide, The Dow Chemical Company, Rocky Flats Division, August, 1965 (RFP-503), pp. 21-23.

TABLE IV
CRITICALITY CALCULATIONS FOR PLUTONIUM DIOXIDE SPHERES

k_{eff}	Radius, cm	Plutonium Mass, kg
0.80	11.75	21.74
0.90	13.16	30.55
0.95	13.89	35.92
0.98	14.34	39.53
1.00	(14.66)*	42.23

* This radius was interpolated from earlier calculations of the critical radii for plutonium dioxide spheres having various plutonium dioxide powder densities.

Note: These calculations are based on a bulk density of 3.2 grams of plutonium per cubic centimeter and a 30 cm thick alumina reflector with a density of 2.5 g/cc.

TABLE V
CRITICAL RADII OF INFINITELY LONG
CYLINDERS OF PLUTONIUM DIOXIDE

Plutonium Dioxide Density, g/cc	Critical Radius, cm
4.5	6.69
4.0	7.29
3.5	8.04
3.0	9.00
2.5	10.29
2.0	12.12
1.5	14.98
1.0	20.29

Note: All calculations were performed assuming an effective neutron multiplication factor, k_{eff} , of 1. It was also assumed that the cylinders were reflected by 30 cm of alumina with a density of 2.5 g/cc.

TABLE VI
CRITICAL RADII OF
PLUTONIUM DIOXIDE SPHERES* CONTAINING WATER

<u>Water, weight percent</u>	<u>Atom. Ratio, H/Pu</u>	<u>Critical Radius, cm</u>	<u>Critical Mass Plutonium, kg</u>
0	0	14.66†	42.2
2.94	0.91	13.49	32.9
5.76	1.84	12.27	24.9
8.48	2.79	11.18	18.7
11.1	3.76	10.26	14.5
13.6	4.75	9.46	11.4

* The spheres contain plutonium dioxide at 3.2 grams of plutonium per cubic centimeter and have a 30 cm alumina reflector at 2.5 g/cc.

† Estimated.

with the results, it appears that powders containing plutonium dioxide may be handled in atmospheres which are slightly humid without serious criticality limitations.

Plutonium Hexafluoride Systems. Critical radii for infinitely long cylinders of plutonium hexafluoride-hydrogen fluoride mixtures, reflected with 30 cm of water, have been calculated for varying plutonium hexafluoride concentrations. These mixtures could be present in unusual circumstances in the plutonium hexafluoride cold trap, where the temperature will be as low as minus 180°C. The densities of plutonium hexafluoride and hydrogen fluoride used for the calculations at this temperature were extrapolated to 6.0 and 1.749 g/cc, respectively, and all plutonium was assumed to be plutonium-239. As shown in table VII, the smallest critical radius is 6.87 cm and occurs for 100% plutonium hexafluoride; i.e., when no hydrogen fluoride is in the system. Based on these rather conservative assumptions, the unit safe diameter for a plutonium hexafluoride cold trap would probably be greater than 5 inches; i.e., more than 6.35 cm radius.

Computer Code Calculations Versus Critical Experiments. The ANISN computer code, used with the S4 option for the criticality computations, is presently being checked for plutonium cross-section accuracy by comparing criticality calculations with the results of critical experiments. Checks made to date have been confined to plutonium nitrate* and plutonium dioxide-polystyrene data† of the Hanford Laboratories and the Jezebel plutonium metal data of Los Alamos‡. The experimental data and calculated results for the Jezebel and plutonium dioxide-polystyrene assemblies are shown in table VIII. Each assembly was unreflected, and in both cases, critical dimensions were used as input to the code, and effective multiplication factors were calculated. As shown in table VIII, the percentages of error in the calculated effective multiplication factors were 4.6 and 3.0% for the Jezebel and plutonium dioxide-polystyrene assemblies, respectively. Moreover, in each instance the error is conservative; i.e., k_{eff} is overestimated.

The experimental data and calculation results for two plutonium nitrate spheres reflected with water are shown in table IX. Again, critical

* Physics Research Quarterly Report, July, August, September, 1962, General Electric, Hanford Atomic Products Operation, October 15, 1962 (HW-75228), p. 34; Physics Research Quarterly Report, October, November, December, 1962, General Electric, Hanford Atomic Products Operation, January 15, 1963 (HW-76128), p. 60.

† Richcy, C. R., White, J. D., Clayton, E. D., and Lloyd, R. C., "Criticality of Homogeneous Plutonium Oxide-Plastic Compacts at H:Pu = 15", Nuclear Science and Engineering, 23, 150-158 (1965).

‡ Jarvis, G. A., Linenberger, G. A., Orndoff, J. C., and Paxton, H. C., "Two Plutonium-Metal Critical Assemblies", Nuclear Science and Engineering, 8, 525-531 (1960).

TABLE VII

CRITICAL RADII FOR INFINITELY LONG CYLINDERS
OF PLUTONIUM HEXAFLUORIDE-HYDROGEN FLUORIDE*

<u>Plutonium Hexafluoride, volume percent</u>	<u>H/Pu</u>	<u>Critical Radius, cm</u>
0.5	1,024	12.69
1.00	509	10.06
1.25	406	9.56
1.50	338	9.24
2.00	252	8.86
2.50	201	8.62
3.00	166	8.48
5.00	98	8.15
10.0	46	7.72
100.0	0	6.87

* Reflected with 30 cm of water.

TABLE VIII
COMPUTER RESULTS VERSUS CRITICAL EXPERIMENTS
FOR UNREFLECTED ASSEMBLIES CONTAINING PLUTONIUM

	<u>Jezebel Assembly</u>	<u>Plutonium Dioxide- Polystyrene Assembly</u>
Plutonium Density, g/cc	15.66	1.12
Plutonium-240, %	4.5	2.2
H/Pu	0	15
Critical Mass, kg	16.28 ± 0.05	-
Critical Radius, cm	-	18.58 ± 0.22
Reflector	None	None
Experimental k_{eff}	1.0	1.0
Calculated k_{eff}	1.046	1.030
Percentage of Error in k_{eff}	4.6	3.0

TABLE IX

COMPUTER RESULTS VERSUS CRITICAL EXPERIMENTS
FOR PLUTONIUM NITRATE SOLUTIONS

<u>Plutonium Concentration, g/l.</u>	<u>Acid Molarity</u>	<u>Water, g/l.</u>	<u>Total Nitrate, g/l.</u>	<u>Specific Gravity</u>	<u>H/Pu</u>	<u>Calculated k_{eff}</u>	<u>Percentage Error in k_{eff}</u>
140*	2.2	882	284	1.307	171	0.994	0.6
44.5†	5.49	825	386	1.261	521	0.991	0.9

* Contained 4.6% plutonium-240 and reflected with water plus 0.049-inch stainless steel.

† Contained 4.6% plutonium-240 and reflected with water plus 0.044-inch stainless steel.

dimensions were used as input to the code, and effective multiplication factors were calculated. The error in the calculated effective multiplication factor is less than 1% in each case. It was concluded that the accuracy of the calculation method appears to be satisfactory for both the moderated and relatively poorly moderated situations; nevertheless, additional validation is desirable.

Accordingly, the ANISN code is now being checked with other Hanford plutonium nitrate critical data. Of the available data, only those experiments which are consistent and require a small extrapolation to the critical volume are used for checking purposes. Some experiments do not have consistent material balances, and some are significantly subcritical and require relatively large extrapolations to get the critical volume.

Semiworks Reactor Interhalogen Flow Sheet

Material balance computations have been made for several interhalogen flow sheet schemes which might be employed in semiworks pilot-plant operation with bromine pentafluoride. The presently installed reactor and filter cooler would be used for the reaction and off-gas filtration. The filtered reaction product gases would be fed to a regenerator for reconversion of the bromine and bromine trifluoride to bromine pentafluoride. Consideration has been given to processing the gases leaving the regenerator via each of the three following routes for the separation and purification of uranium hexafluoride and bromine pentafluoride: (1) a two-stage partial condenser for liquefaction of the condensables (uranium hexafluoride and bromine pentafluoride), followed by distillation to separate and purify these materials; (2) a fluid-bed sorber-desorber system; and (3) a cold trap for the separation of the bromine pentafluoride as a liquid from solid uranium hexafluoride, followed by distillation for purification of uranium from entrained bromine pentafluoride. The cold trap-still scheme has been selected as the tentative flow sheet because distillation has become the primary method of interest for uranium hexafluoride purification and because, of the two schemes employing distillation, the smaller size still is required for this case; thus, it is the method of choice at present in conceptual plant studies.

The conceptual flow sheet for all but the distillation unit operation is presented in figure 1, along with the expected material flows during the initial reaction period.

After oxidation of uranium dioxide pellets, the semiworks fluid-bed reactor will contain about 67.6 kg of U_3O_8 . Gaseous bromine pentafluoride will be obtained from a vaporizer to which the recycle bromine pentafluoride, including some contained uranium hexafluoride, is fed. The bromine pentafluoride will be diluted with nitrogen, then fed into the fluid-bed reactor operating at about 300°C. In the main reactor, the fluorination proceeds according to the stoichiometric relation

COMPONENT	STREAM NUMBER										
	1	2	3	4	5	6	7	8	9	10	11
BrF ₅ , kg./hr.	22.5					22.5	1.3		21.2		22.5
Br ₂ , std. cfh.		51		51							
UF ₆ , kg./hr.	3.6	41.4		41.4		41.4	Trace	37.9	3.5		3.6
N ₂ , std. cfh.	400	400	3	403	31	434	434			400	
O ₂ , std. cfh.		113		113		113	113				
F ₂ , std. cfh.					281	26	26				
TOTAL, std. cfh.	510	657	3	660	312	768	579.01	85.19	103.8	400	110

FLOW SHEET FOR INTERHALOGEN ADDITION TO THE SEMIWORKS REACTOR

Figure 1

Off-gases from the fluid-bed reactor will be fed to the filter cooler for removal of entrained solids prior to being fed to the regenerator for the reconversion of bromine via its reaction with fluorine back to the pentafluoride. It is anticipated that the reactions involved in regeneration of the bromine pentafluoride will proceed rapidly and that a flame reactor may be employed. Thermodynamically, several bromofluorides (bromine monofluoride, trifluoride, and pentafluoride) can be produced. Equilibrium calculations indicate that the bromine trifluoride would be the predominate product in the flame; however, as the reacting gases are cooled, the equilibrium is shifted in the pentafluoride direction. The gases will leave the regenerator at about 375°C. Equilibrium calculations indicate that essentially 100% of the bromine will have been converted to bromine pentafluoride at this temperature. A heat exchanger in the line after the regenerator will then cool the process stream to about 100°C before the gases enter the cold trap, which will be maintained at about minus 40°C. In the cold trap, solid uranium hexafluoride and a liquid mixture of 92.5 mole percent bromine pentafluoride and 7.5 mole percent uranium hexafluoride will be formed. The liquid will be drained into an accumulation tank for reuse in future experiments. At the end of the run, the solid uranium hexafluoride will be vaporized and fed to the distillation system.

PROTOTYPE TESTING AND EVALUATION

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Program emphasis was centered on the zircaloy decladding, uranium dioxide oxidation, and uranium fluorination phases of the volatility process. Among the highlights of the report period was the startup of tests in the semiworks facility. Programs on sampling, corrosion testing, off-gas filtering, and the evaluation of connectors and valves were continued, while a new study was undertaken on fluidization with emphasis on elutriation. The first phase of tests with the ORGDP peripheral compressor was completed as over 2,000 operating hours with elemental fluorine was logged.

PROCESS AND REACTOR STUDIES

Operations in the semiworks facility have been initiated with oxidation tests using unirradiated uranium dioxide pellets. A series of fifteen runs has been completed. Test details are presented below.

Problems associated with fluidization in the semiworks reactor, together with interest in the separation of the U_3O_8 product from the alumina bed diluent by elutriation, have led to new fluidization studies in small-scale equipment. All tests are run at ambient temperature, thus permitting the use of transparent construction materials for easy viewing.

Volatility processing material control needs and the problems inherent in good accountability have prompted continued sampling tests with mixed solids. Since product residues in solid waste streams cannot be completely recovered economically, there are potential applications for representative sampling techniques at those points.

Cold Semiworks Pilot Plant

Semiworks construction was completed in June, 1966, and operational tests were started the following month. A schematic drawing of the system, together with pictures of the reactor and filter cooler, are shown in figure 2. Views of the installation are shown in figure 3. The first phase of the volatility process operation to be investigated was the fluid-bed oxidation. The objectives of this series of tests were (1) to establish processing conditions and equipment requirements for optimized batch oxidation of uranium dioxide pellets to form a product suitable for fluid-bed fluorination, and (2) to obtain information which could be utilized in conceptual plant and engineering analyses studies.

The uranium charge for each of the tests consisted of slightly enriched salvage unirradiated reactor-grade cylindrical pellets approximately $3/8$ inch in diameter by $3/4$ inch long. The design reactor capacity is 65 kg of uranium dioxide; however, generally half-size charges, i.e., about 35 kg, were employed in the interest of fuel economy. The bed diluent used in each case was Alcoa T-61 tabular alumina, nominally

SEMIWORKS REACTOR SYSTEM

Figure 2

PHOTO NO. PH-67-427

PHOTO NO. PH-67-428

PHOTO NO. PH-67-430

PHOTO NO. PH-67-42

VIEWS OF SEMIWORKS REACTOR INSTALLATION

Figure 3

minus 48- plus 100-mesh size. As shown in figure 2, 1/2-inch-diameter T-164 Alcoa tabular alumina balls were used in most of the tests to position the pellet bed in the heated zone of the reactor and to improve fluidizing gas distribution. The oxidizing medium in all runs was either air or air diluted with nitrogen.

In general, the first of these tests was largely exploratory in nature, indicating the benefit of having an internal support for the reactor bed, the need for an inlet gas preheater, and the desirability of an oxygen analyzer to supplement the bed thermocouple readings employed in monitoring the course of oxidation. Subsequent operations concentrated on finding reliable operable oxidizing conditions concurrent with attaining satisfactory bed properties and cycle times. The effects of variation of gas velocity, oxygen concentration, gas preheat temperatures, and the ratio of alumina-to-uranium were examined.

Pertinent information on these runs, i.e., the charge weights, operational temperatures, oxygen concentrations, run results, etc., is listed in table X and in the run commentaries, while conclusions are listed at the end of this section. Run commentaries are as follows:

Run UE-1. Reactor heatup was begun while a mixture of air and nitrogen was injected to fluidize the bed and to react the charge. As anticipated, the uranium dioxide pellets loaded on top of the bed gravitated to the bottom of the reactor early in the run. The starting pellet bed depth was estimated to have been 18 inches in the 5-inch-diameter section of the reactor. The total initial bed height, including alumina, was 93 inches. Heatup of the pellets was difficult because most of the alumina which would normally be expected to expedite heat transfer was apparently blown out of the interstices between the pellets. Moreover, a portion of the pellet zone was located below the bottom reactor heating zone. Because of the heat transfer difficulties, the superficial gas velocity was changed from the 1.5 ft/sec planned to 0.5 ft/sec to decrease the gas heating load and thus to obtain hotter gas. Nitrogen dilution of the feed gas stream was terminated. It appeared that a temperature of about 400°C was necessary to initiate the reaction. The pellet temperature then climbed at a faster rate than that of the main part of the fluidized bed, again indicating relatively poor heat transfer. Since the pellets in the very bottom could not be heated to 400°C, only partial oxidation was achieved, and the run was discontinued. Based on the coarse (plus 35 mesh) material found in the bed, only about 80% of the 35.2 kg charge of uranium dioxide was indicated to be pulverized in the test and thus was presumed to be converted to U_3O_8 .

Run UE-2. The materials in the reactor and filter cooler at the end of the first run constituted the charges to the respective vessels for this run. A 3 kw air preheater was inserted in the air line to the bottom of the reactor. Reaction in the pellet zone was obvious when the temperature reached 471°C. About 1.6 kg of broken pellets and chunks was found in the reactor at the end of the test. Thus, oxidation was computed to be about 95% complete at the end of this

TABLE X

SUMMARY OF SEMIWORKS URANIUM DIOXIDE OXIDATION RUNS

	UE-1	UE-2	UE-3	UE-4	UE-5	UE-6	UE-7	UE-8	UE-9	UE-10	UE-11	UE-12	UE-13	UE-14	UE-15
Charge to Reactor															
Alumina, kg	90.8	UE-1 Recharge	90.8	45.5	UE-4 Recharge	22.7	34.1	UE-7 Recharge	34.1	UE-9 Recharge	36.36	65.9	UE-10 Recharge	54.5	56.8
Uranium Dioxide Pellets, kg	35.2	32	32.7	64.8		33.3	33.0		32.8		34.97	36.9		31.2	32.5
Alumina Balls, kg	None	None	3.2	3.2	3.2	3.2	3.2		3.2		3.2	3.2	14.2	10.0	8.9
Weight Ratio, Alumina- Powder-to-Uranium	3.0		3.2	0.8		0.8	1.2		1.2		1.2	2.0		2.0	2.0
Oxygen Concentration, %	21	21	21	21	21	21/10.5	10	10	5	5/15/21	5/10/15/21	21	10.5/15/21	10.5/15/21	21
Pellet Bed Temperature, °C															
At Apparent Initiation of Reaction	400	471	332	566		332	454	454	510	510	454	343	454	454	454
Maximum	504	482	582	1038	510	793	593	593	621	716	554	582	556	565	565
Approximate Superficial Velocities*, in.															
5-Inch-Diameter Section, ft/sec	0.5-1.5	0.5	1.2		2.0	1.5	1.5	1.5	1.5	1.5	1.5	1.0	3.0	3.0	3.0
10-Inch-Diameter Section, ft/sec†	0.6	0.6	0.53		0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.75	0.75	0.75
Apparent Oxidation Time, hr	2	3	4	2		2	5.5	1.5	9	5	10.75	1	6.5	6	6
Inlet Temperature of Fluidizing Gas, °C	Ambient	371	371	545	510	454	454	454	510	510	459/566	316	316	316	316
Run Results															
Percentage of Charge Reacted								90.9	84.4	100	96.7	-	99.1	99.1	100
Percentage of Charge Comminuted (minus 35 mesh)	79.4	95.5	92.8	58.3	65.4	95.2	71.1	91.4	68.6	84.7	64.5	31.6	86.0	83.2/100	78.6/100

* At 454°C, the target temperature of the run.

† The velocity in the 10-inch-diameter zone was maintained by injecting, when necessary, additional nitrogen at the bottom of that zone.

run based on the amount of coarse material found.

Run UE-3. Alumina balls, 1/2 inch in diameter, were added to the reactor prior to charging the alumina powder and uranium dioxide in order to support the pellets within the heated zone of the reactor. In addition, six thermocouples were added to the 5-inch section, four were mounted vertically from the bottom flange of the reactor, so that the temperatures at various points within the pellet beds could be observed. Fresh materials were charged to the reactor in the following sequence: balls, pellets, and then alumina. Attempts to fluidize were unsuccessful when a plug developed somewhere in the pellet zone. The reactor was dumped and then reloaded, while air was admitted to the bottom of the reactor to fluidize the charge. The starting pellet bed depth for run UE-3 was estimated to have been 17 inches in the 5-inch-diameter section of the reactor. The total initial bed height, including alumina, was 98 inches. The reactor was brought to temperature, and dilute oxygen was injected at the same time. As a result of the various improvements made, the temperatures necessary to initiate the reaction were obtained more easily than previously. Reaction was noted when the temperature at one point in the bed rose from 332 to 582°C in 30 minutes. The operation was relatively smooth. While the pellets were essentially all converted to powder (presumably U_3O_8), 2.7 kg of coarse material (plus 35 mesh) was also found. Tests indicated that this material was largely U_3O_8 , but the cause of the coarse particle formation was not established.

Run UE-4. Prior to run UE-4, the plant was equipped with a new air preheater and an oxygen analyzer (paramagnetic type). The air preheater was designed to heat 800 scfh of air to 650°C, and the oxygen analyzer was installed in the process off-gas line to provide a direct measure of the progress of the reaction. The reactor was charged in the following sequence: 1/2-inch alumina balls, alumina powder, uranium dioxide pellets. A small amount of air was introduced into the bottom during addition of the pellets to agitate the bed. After the charging was completed, air was introduced into the reactor at the operational velocity for the run, and the contents were heated to temperature. From the outset, an inlet air pressure of about 20 psig was required to maintain fluidization of the bed. The pressure drop across the bed was over twice as high as in earlier runs. While the amounts of materials charged in this run were different by comparison with previous tests, the increase in the pressure drop indicated that a plug possibly existed in the bed. The starting pellet bed depth for run UE-4 would have been 35 inches in the 5-inch-diameter section of the reactor. It appears, however, from the fluidization behavior that the pellet layer remained in the 10-inch-diameter section in which its depth was about 9 inches. The total initial bed height, including alumina, was 79 inches. As the reactor was heated, the plugging appeared to become worse because increasingly higher air feed pressures were necessitated. No reaction was evident until the bed reached a temperature of approximately 566°C. At this point, the oxygen consumption increased as indicated by oxygen analysis of the

off-gases, and the bed and reactor wall temperatures near the top of the bed in the reactor began to rise very sharply. The air cooling coils on the exterior of the reactor were effective in holding the reactor wall temperature at about 510°C but were ineffective in controlling the temperature surge within the bed. Nitrogen was substituted for air as the fluidizing gas, but the temperature at the top of the bed reached about 1038°C before the temperature trend was reversed. When the bed dropped to 496°C , air again was used as the fluidizing medium. The temperature at the top rose immediately to 543°C and then gradually decreased over the next 2 hours. Air was fed to the reactor for an additional hour to ensure completion of the reaction. Unfortunately, the oxygen analyzer, while giving qualitative indication of reaction progress, was not functioning accurately enough to allow precise determination of the reaction end point.

The contents of the reactor were removed and examined. About 42% of the pellets charged had remained as coarse material greater than 35 mesh. The bulk of the uranium was found at the top of the bed, and much of the alumina appeared to have not mixed with the U_3O_8 powder produced during the oxidation. Most of the pellet charge had apparently remained at the top of the bed in some sort of bridge. With this kind of arrangement, much, if not all, fluidization was effectively inhibited. Thus, most of the reaction took place in the vicinity of the top of the bed.

Run UE-5. The material removed from the system at the end of run UE-4 constituted the charge for run UE-5. Air was used for fluidization. The alumina was first added to the reactor, followed by the uranium coarse and fine fractions. Attempts to fluidize the charged material failed, although air pressures up to 40 psig were used. Fluidization was achieved after material had been removed from the reactor from the top down to the middle of the 5-inch-diameter section. A cause for the apparent plugging was not found.

The reactor was recharged in 13.6 kg increments, and after each addition, air was injected into the bottom nozzle to ensure that fluidization was possible. After the addition was completed, fluidization could be easily initiated in the static bed.

Initial bed and preheater air temperatures were 427°C . When no reaction was indicated by either oxygen consumption (using the oxygen analyzer) or bed temperature rise, the bed and preheater temperatures were increased in 28°C increments until 510°C was reached, but there was no evidence of any reaction. Examination of the system contents showed that 34.6% of the original charge remained in the plus 35-mesh range. Laboratory analysis by X-ray diffraction verified that both the powder and the coarse material, some of which was in the form of lumps as large as the original pellets, were essentially 100% U_3O_8 .

In retrospect, it appeared likely that the lump material from UE-4 had already been converted to U_3O_8 and sintered and thus was largely

unsusceptible to further attack in UE-5. This was subsequently confirmed by laboratory oxidation tests on a few lumps which had been removed from the UE-4 coarse fraction. By that time, the UE-5 run, which was made very shortly after UE-4, was already over.

Run UE-6. The 33.3 kg uranium dioxide charge for this run brought the bed level just to the top of the transition section between the 5- and 10-inch diameter portions of the reactor. The starting pellet bed depth was estimated to have been 17 inches in the 5-inch-diameter section of the reactor. The total initial bed height, including alumina, was 63 inches. A pressure of about 85 psig was required to start fluidization after the pellets were added to the top; however, after the bed was fluidized, the inlet pressure necessary to sustain fluidization dropped to about 4 psig. Oxygen consumption, as indicated by the decrease in oxygen content of the off-gases, was first noted when the temperature of the bed was 332°C. A temperature excursion then took place in the pellet area of the bed, but the rise was arrested when the air was diluted to 10.5% oxygen with nitrogen. The temperature peaked at 793°C. After the temperature had been reduced to approximately 500°C, the nitrogen dilution was discontinued, and the run was completed using air alone for fluidization. No temperature difficulties were experienced during the final portion of the run. During the first 4 hours of the run, fluidization appeared normal; but during the last 2-1/2 hours, the pressure oscillations across the bed, which are characteristic of fluidization, were missing; rather, there was a constant small pressure drop across the bed. Pressure oscillations could be attained for a short period of time by rapping the bottom of the reactor. Examination of the reaction product showed that essentially all the pellets (99.1%) were converted to powder, but the bed material appeared damp and somewhat cohesive as opposed to a free-flowing dry material. The alumina-to- U_3O_8 ratio of 0.8 was relatively low as compared with the 2.0 figure most used in ANL studies. Bed properties would be expected to be better with more of the coarser diluent present; however, more bed recycles or perhaps utilization of some means of separation of U_3O_8 from the alumina would be needed to reduce alumina throughput for economic reasons.

Six new Huyck Metals Company nickel fiber filters had been installed in the new filter cooler before run UE-3. After run UE-6, the filters were removed and examined. There was a thin, somewhat uneven coating of material on the filters, probably less than 1/32 inch on the average. Filter operation has been trouble-free during the four runs in which these filters have been used, and the pressure drop across the filters has been consistently about 0.03 psi. A photograph of the filters as they were removed from the filter cooler is shown in figure 4.

Runs UE-7 and UE-8. Because of the temperature excursion in UE-6, it was decided to make a run using a lower oxygen concentration in order to control the reactor temperature and a higher ratio of alumina-to- U_3O_8 to improve fluidization properties of the bed. Run

FILTER TUBES AS REMOVED FROM FILTER COOLER
FOLLOWING RUN UE-6

Figure 4

UE-7 was made using an oxygen concentration of 10.5% in the inlet gas as compared to air for UE-6. An alumina-to- U_3O_8 ratio of 1.2 was employed instead of 0.8 as in UE-6. The starting pellet bed depth for run UE-7 was estimated to have been 17 inches in the 5-inch-diameter section of the reactor. The total initial bed height, including alumina, was 68 inches.

The bed was heated to 454°C using nitrogen as the fluidizing gas, and air was then admitted and the gas flows were regulated to give 10.5% oxygen in the feed gas. The velocities were nominally 1.5 and 0.6 ft/sec in the 5- and 10-inch-diameter sections, respectively. As soon as the diluted air was admitted to the reactor, the oxygen analyzer indicated consumption, and the bed temperature began to rise; however, within 10 minutes, the rate of oxygen usage decreased, and within 30 minutes, the indication was that only about 7% of the oxygen was being used. In addition, the reactor inlet and pressure drops had increased by approximately 50%, and there were some wide fluctuations in these pressures. The rate of oxygen usage continued to decrease, and the run was terminated after a total time of 6-1/2 hours. Upon removal of the bed and screening, it was found that 30% of the uranium dioxide had not been pulverized; i.e., was plus 35-mesh in size.

The material from UE-7 was used as the charge for UE-8. Conditions for UE-8 were essentially the same as those for UE-7. Additional oxidation was obtained, and after a total run time of 5 hours, the run was terminated. After run UE-8, approximately 91.5% of the original pellet charge had been converted to powder.

Runs UE-9 and UE-10. The action of the fluid bed in run UE-7 had indicated a tendency to plug, and an attempt was made to circumvent this problem by reaction at higher temperature and lower oxygen concentrations. For UE-9, the reactor bed was preheated to 510°C, using nitrogen, and then air was admitted to give an inlet concentration of 5%. Gas velocities were the same as in UE-7 and UE-8. As in UE-7, the starting pellet bed depth for UE-9 was estimated to have been 17 inches in the 5-inch-diameter section of the reactor, and the total initial bed height, including alumina, was 68 inches. The action of the bed in UE-9 was similar to that described for UE-7 except that the reactor plugged twice. Air pressures of 42 and 37 psig were required to dislodge the two plugs. At the end of the run, only 68.6% of the pellet charge had been converted to minus 35-mesh powder.

The bed material from UE-9 was used as the charge for run UE-10. The conditions for this run were essentially the same as those for UE-9, except that each time the reaction appeared to stop, the oxygen concentration in the feed gas was raised. Concentrations of 5, 15, and 21% were used. After this run, 84.7% of the original pellet charge was found to have been converted to minus 35-mesh powder.

Run UE-11. The starting pellet bed depth for run UE-11 was estimated to have been 18 inches in the 5-inch-diameter section of the reactor.

The total initial bed height, including alumina, was 70 inches. Run UE-11 was made following the pattern of UE-10; however, after the reaction had nearly stopped with 21% oxygen at 454°C, the bed temperatures were raised in 28°C increments until a final temperature of 566°C was reached. Examination of the bed following this run showed that 64.5% of the pellet charge had been converted to minus 35-mesh powder, although some of the material in the plus 35-mesh range had been agglomerated to form pieces larger than any of the original pellets. X-ray analysis indicated that these pieces were 65% uranium dioxide. Photographs of the sieve fractions of the plus 35-mesh material are shown in figure 5.

Runs UE-12 and UE-13. Review of all the prior runs indicated that the only ones in which 99% of the charge was converted to powder (minus 35 mesh) were runs UE-3 and UE-6. In each of these runs, 21% oxygen was used as the oxidizing agent, and the superficial velocity in the 5-inch-diameter section was 1 to 1.5 ft/sec. Run UE-12 was carried out at a velocity of 1.0 ft/sec in the 5-inch-diameter section. Prior to making the run, the four internal thermocouples which were mounted vertically from the bottom of the reactor during UE-3 were removed because it was suspected that the incomplete reaction observed in previous runs could be due to channeling of the gas alongside the thermocouple wells. The starting pellet bed depth was estimated to have been 20 inches in the 5-inch-diameter section of the reactor. The total initial bed height, including alumina, was 85 inches. The reactor bed was heated to 316°C, using nitrogen as the fluidizing gas; and then the nitrogen was replaced with air, and the temperature set point was raised to 454°C. When the temperature reached 343°C, reaction was indicated; however, within 20 minutes after oxidation began, plugging problems were encountered, and within 65 minutes after oxidation began, a plug had developed which could not be removed by use of feed gas pressures of 40 to 50 psig at 482°C or 90 psig at 200 to 260°C. Examination of the reactor contents showed that 31.6% of the charge had been converted to minus 35-mesh powder. The powder appeared to be concentrated in the 5-inch-diameter section, and the plug apparently was caused by tightly packed powder and pellets. It was theorized that the velocity in the 5-inch-diameter section was not sufficient to remove the powder from the pellet zone and mix it with the alumina.

UE-13 was made using all the material left after UE-12 as the charge. A superficial velocity of 3.0 ft/sec was tried in order to move the powder out of the pellet section into the alumina as quickly as possible. The initial stages of the run consisted of preheating the reactor bed to 454°C, with nitrogen injected in the reactor bottom at 1.5 ft/sec, and then feeding air into the first nozzle up from the reactor bottom. Additional 1/2-inch-diameter alumina balls had been added to raise the pellet zone to a level so that half of the pellets were above the nozzle and half were below it; the total depth of the pellet bed was 12 inches. The air injected through the nozzle in the pellet zone could not be preheated, and very little reaction was detected. After approximately 1 hour, the air inlet point was

PHOTO NO. PH-66-1632

-6+12 MESH

15.7%

PHOTO NO. PH-66-1633

-12+20 MESH

15.2%

PHOTO NO. PH-66-1634

-20+35 MESH

15.0%

PHOTO NO. PH-66-1635

+6 MESH

54.1%

FRACTIONS SCREENED FROM A SAMPLE TAKEN FROM
THE PLUS 35-MESH MATERIAL AFTER RUN UE-11
(Percentages noted are of the plus 35-mesh fraction)

Figure 5

shifted from the pellet zone nozzle to the bottom of the reactor, and reaction was immediately apparent. At the end of the test, 86% of the total charge had been converted to minus 35-mesh powder. The coarse material which remained was in the form of flat platelets, the largest being approximately 1/4 inch in diameter and 1/8 inch thick.

Runs UE-14 and UE-15. The results of run UE-13 indicated that the high superficial gas velocity was effective in reducing the tendency of the reactor to plug. In addition, it was thought desirable to attempt to oxidize the upper section of the pellet bed first and proceed downward.

In both runs UE-14 and UE-15, the amount of 1/2-inch alumina balls was adjusted to fix the position of the pellet bed so that it was divided between two reactor heating sections. The starting pellet bed depths for both runs UE-14 and UE-15 were estimated to have been 17 inches in the 5-inch-diameter section of the reactor. The total initial bed heights, including alumina, were 81 inches in each case. The temperature of the upper half of the pellet bed was controlled at 454°C, and the lower half and the preheated gas were controlled at 316°C. The above conditions were attained using nitrogen as the fluidizing gas.

When the above conditions were reached in UE-14, the gas flows were adjusted to give 10.5% oxygen concentration. Reaction was immediately indicated in the upper section of the pellet bed. As oxidation of the upper section was nearly completed, the rate of oxygen usage began to decrease; therefore, heat was applied to the lower section to raise its temperature to 454°C. As the temperature of the lower section increased, oxygen usage increased and the reaction proceeded. To finish the run, the oxygen concentration was increased to 15% and finally to 21%, and the bed temperature was raised to 565°C, but little additional reaction was evident.

Run UE-15 was conducted following the pattern of UE-14, except that the initial oxygen concentration was 21% rather than 10.5%.

Examination of the system after runs UE-14 and UE-15 showed that each of the beds still contained plus 35-mesh lumps amounting to about 20% of the expected weight of U_3O_8 . This material did not, however, consist of hard particles as in the previous runs but was mostly soft powder balls less than 5 mm in diameter. When the balls were gently rubbed over a 35-mesh screen using pieces of flexible plastic, most of the material passed through, leaving only 27 and 26 grams of hard material, respectively, in UE-14 and UE-15.

During these two runs, there was no indication of bed plugging or temperature excursion. Fluidization was good, as indicated by reactor pressure and bed pressure drop oscillations, and temperature uniformity in the bed above the pellet zone. The filter cooler and other downstream equipment performed quite satisfactorily.

The oxidation runs performed indicate the following:

1. Essentially complete oxidation of uranium dioxide pellets can be accomplished under controlled conditions in the semiworks plant. The product is a powder which, in mixtures with alumina, fluidizes well and appears to be suitable for fluid-bed fluorination. A ratio of diluent alumina-to- U_3O_8 as low as 0.8 can be utilized; however, the fluidization properties of the resultant bed appear to be relatively poor at that ratio.
2. A superficial gas velocity of 3 ft/sec is satisfactory for prevention of plugging of the pellet bed. In addition, control of bed and gas preheat temperatures so that oxidation consumes the bed starting at the top appears to expedite elutriation of fines from the oxidation zone. This technique is therefore desirable as a guard against plugging of the pellet zone with fine U_3O_8 .
3. An oxygen analyzer measuring the oxygen content of the reactor off-gases by the paramagnetic principle can be used to follow the start and the progress of these pellet oxidation tests. Reasonably accurate estimates of the extent of the reaction could be made based on the instrument readings, and the readings could also be used to regulate feed concentration if excessive oxygen consumption was shown.
4. Major operational temperature excursions in the pellet bed cannot be controlled by use of the air cooling coils on the exterior of the reactor. Since temperature excursions in well-mixed, fluidized beds can usually be readily controlled from the wall, there is apparently little bed circulation in the pellet zone.
5. A layer of 3/8-inch-diameter pellets can form a compact bridge over as large a cross-section as a 10-inch diameter. The bridge can form an obstruction which causes so much backpressure that the alumina below cannot fluidize. This prevents mixing of the alumina bed and also makes it impossible for the pellets to drop to the desired position in the bottom of the reactor.
6. In the presence of the 3/8-inch-diameter uranium dioxide pellet bed, a sizable pressure may be required to initiate fluidization of an alumina bed in comparison with the pressure requirement to maintain that fluidization. This is especially noticeable if the pellets are present in a separate layer.

Plans call for additional oxidation runs to validate the above conclusions and to explore the operating range, including the effect of use of larger charges. One or two fluorination tests using elemental fluorine may be made to test system performance in that mode. Several simulated decladding tests are then planned for the remainder of the next 6-month period.

Fluidization Studies

A series of test runs in a transparent column has been made to investigate various facets of fluid-bed operations, including elutriation of the U_3O_8 for separation from the alumina.

The experimental column used in this study consists of a 4-foot length of 2-inch Plexiglas tubing with a removable conical section on the bottom. A metered air supply furnishes the fluidizing gas, and pressures are measured with a mercury manometer. A sketch of the apparatus is shown in figure 6.

The first group of test runs conducted was specifically designed to determine the gas velocity required to cause uranium dioxide pellets to drop down through a bed of alumina. Interest in information of this nature stemmed from the pellet bridging which apparently developed during the charging of semiworks oxidation run UE-4 and never did break up during processing. The column was initially filled with a known weight of alumina (minus 48- plus 100-mesh T-61 Alcoa tabular alumina) to a height of 24 inches, and then a known amount of 3/8-inch-diameter by 3/4-inch-long uranium dioxide pellets was added to the top of the bed while it was static. The minimum velocities and the pressures to fluidize the alumina, together with the velocities required to drop the uranium dioxide pellets to the base of the column, were observed. The results of the experiment were as follows:

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>
Minimum Velocity to Fluidize Alumina, ft/sec	0.3	0.2	0.4
Weight Ratio, Alumina-to-Uranium Dioxide	3	6	1
Inlet Pressure to Initiate Fluidization, psig	12	12	12
Inlet Pressure to Maintain Fluidization, psig	5 to 8	5 to 8	5 to 8
Velocity Required to Settle Uranium Dioxide Pellet, ft/sec	0.4	0.4	0.5

In one run, as air was added, the column of pellets separated into two parts. The lower portion settled to the bottom of the bed, while the upper portion remained in place. The latter portion was then dislodged by increasing the velocity from 0.5 to 1.0 ft/sec. In general, the tests show that, when a bed is restrained by having a coarse charge loaded on top of it, more pressure is needed to initiate fluidization than to sustain it. Changing the ratio of the alumina-to-uranium dioxide did not appear to influence the results.

Charges of about 3 kg of the bed material produced in semiworks oxidation runs UE-6 and UE-11 were elutriated at various gas velocities in a series of elutriation tests. The top of the column was piped to a glass filter chamber in which a porous nickel filter was installed. Uranium analyses

FLUIDIZATION APPARATUS

Figure 6

of the bed in the column before and after elutriation and of the material collected in the filter indicate the efficiency of the separation of the U_3O_8 from alumina.

Bed expansions of 30 to 40% were experienced during the elutriation conditions. Inlet pressures of 3.9 to 4.8 psi were required to initiate fluidization. Pressure drops across the fluid bed during elutriation averaged 1.4 to 1.7 psi. The experimental results, which are given in table XI, are interpreted as encouraging when related to the goal of separation by elutriation, especially since the fluid-bed material used was taken from the minus 35-mesh fraction removed from the 5-inch section of the semiworks reactor after completion of the reaction. This material may be even slightly coarser than that found in the 10-inch section of the reactor. In tests 5 and 6, over 80% of the U_3O_8 was elutriated, but relatively little of the alumina was transferred.

It appears that the most desirable elutriation velocity based on the test conditions may be close to 1.6 ft/sec. At 1.6 ft/sec, a significant but tolerable amount of alumina carryover was noted. At lower velocities, the rate of elutriation of the U_3O_8 tends to drop off substantially.

Additional elutriation tests are planned with materials from current semiworks runs to establish elutriation rate coefficients for the U_3O_8 and alumina. Some semiworks tests will be operated with high exit gas velocities from the main bed during the oxidation reaction to evaluate this elutriation procedure. Efforts will be made to evaluate data from each source and compare with a view toward being able to estimate effect of changes in the various design and operating parameters, such as system geometry, disengaging space, gas density, gas viscosity, gas velocity, and controllable powder properties. It is hoped that, from this information, it will be possible to make reasonable extrapolations to plant-scale operations.

SAMPLING

Tests have been conducted with a 6-inch Denver Vezin solids sampler to evaluate the equipment for representative sampling of large amounts of solids. In monitoring the fluoride volatility plant for accountability, as well as for process control, solids sampling will be necessary. The results of sampling tests with pellets 1/8 inch in diameter and 1/8 inch long were reported previously*. Two additional sampling tests have now been conducted in the sampler aimed at assessing sampling capability and uncovering biases. The feeds used were mixtures of powder consisting of one relatively coarse component and one fine component, thus simulating the bed material from the main fluid-bed reactor. The particle sizes of the materials were chosen to permit use of screening in obtaining analysis of the sample cuts.

The first mixture was prepared using 60- to 325-mesh sodium fluoride crystals and 20- to 40-mesh graded quartzite. The two components were

* K-1691, loc. cit., p. 53.

TABLE XI
RESULTS OF ELUTRIATION TESTS*

Test Number	Feed Material Source (Material from Semiworks Run Numbers Noted)	U ₃ O ₈ in Charge, %	Superficial Velocity, ft/sec	Elutriation Time, hr	U ₃ O ₈ Transferred, %	Alumina Transferred, %
1	UE-3	22	0.75	5	56	3.3
2	UE-3	22	1.0	1	61	27
3	UE-6	65	1.1	2	40	7
4	UE-6	65	1.3	0.75	14	3
5	UE-11	55	1.22	1.75	57	6
6	UE-11	59	1.25	2	56	2
7	UE-11	57	1.25	4	89	2
8	UE-11	50	1.60	1.5	81	4

* The material charged for a fluidization run was obtained from the minus 35-mesh fraction collected from the 5-inch-diameter section of the semiworks fluid-bed reactor after the oxidation run noted.

poured together but were not mixed in a blender or in any other such device. A $5.38 \pm 0.11\%$ sample cut was obtained using a feed rate of about 12 kg/min. The sample results gave 67.78 and 32.22% for the quartz and sodium fluoride concentrations, respectively, whereas the concentrations based on the original formulation should have been 66.67 and 33.33%, respectively. Analysis of the data indicated a slight bias toward preferential sampling of the coarse material.

A second test was performed at a much lower feed rate, i.e., about 1.33 kg/min, using mixtures of Norton RR Alundum (minus 60 plus 200 mesh) and quartz gravel (minus 20 plus 30 mesh). A sample cut averaging about 5.5 weight percent was obtained. The fines (the Alundum) concentrations of the material fed were 33.60, 49.85, and 67.15%. The analyses indicated sampling biases for the three mixture compositions of 0.24, 0.64, and 0.51%, respectively, toward preferential sampling of fines.

The difference in the direction of the sampling biases for these tests may possibly be attributable to the difference in feed rate. Additional tests are planned to confirm the findings and to determine the effects of various feed rates and particle sizes on the sampling bias.

MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES

Corrosion tests reported previously* have been made in the presence of the process reagents; i.e., hydrogen chloride, oxygen, and fluorine. Now, tests have been made in which nickel and Duranickel have been exposed to the volatile chlorides produced in the reaction of hydrogen chloride with zircaloy in a fluidized bed of alumina. During recent dechlorination off-gas filtering tests, coupons of both nickel and Duranickel were submerged in the fluid-bed reactor of the test loop. Corrosion rates were determined during five cycles of chemical exposure where each cycle consisted of hydrochlorination, oxidation, and fluorination with elemental fluorine.

The reactor was filled with 7.7 kg of minus 48- plus 100-mesh Alcoa tabular alumina, and the coupons were submerged in the top portion of the fluid bed.

During the hydrochlorination treatment, a 0.9 kg charge of zircaloy-2 in the alumina was reacted at 400°C with 30% hydrogen chloride for 2 hours, 50% hydrogen chloride for 3 hours, and 70% hydrogen chloride for 3 hours. The hydrochlorination phase was followed by an exposure to 15% oxygen at 475°C for 10 hours and then to 20% fluorine at 540°C for 10 hours. On completion of the hydrochlorination treatment during the fourth and fifth cycles, the samples were exposed to 12% hydrogen in argon for 1 hour while an attempt was being made to unplug the porous metal filter tubes located on the outlet of the fluid bed.

The indicated corrosion rates of 42 and 48 mils per year for the nickel-201 and Duranickel samples, respectively, based on weight losses and

* K-1691, loc. cit.

surface areas. These results compare favorably with corrosion experimental data in the past and indicate that the zircaloy reaction products have no apparent adverse effect on reactor materials of construction proposed for the volatility process.

OUTLET GAS FILTER STUDIES

Sintered nickel fiber filter tubes, manufactured by Huyck Metals Company, have been installed in the filter test loop and exposed to hydrogen chloride-zirconium tetrachloride-stannous chloride-inert gas mixtures typical of the off-gases produced during the decladding of zircaloy-clad power reactor fuels. Such exposure was subsequently followed by dilute oxygen treatment as for the uranium dioxide pellet oxidation and then by dilute fluorine to simulate the volatility processing cycle. The decladding operation gas mixtures were obtained by reacting 0.91 kg of zircaloy-2 with diluted hydrogen chloride in a fluidized bed of 7.7 kg of 48- to 100-mesh tabular alumina in the filter loop reactor. Six separate test runs have been undertaken. Details of the exposure conditions and the results of the runs are shown in table XII.

In the first test, a set of two new filter tubes was subjected to three complete exposure cycles. The off-gas filtering temperature for the decladding operation was approximately 315°C. The diluent employed in the hydrochlorination was a mixture of nitrogen and hydrogen. The hydrogen was included, since it is produced by the reaction and might be expected to be a significant constituent of a plant hydrogen chloride recycle gas stream. The hydrogen concentration is, however, probably substantially lower than it would be in a plant operation. The zirconium tetrachloride and stannous chloride gases leaving the filter were passed through a high temperature steam nozzle to form the oxides for easy disposal. Considerable plugging was encountered during the first cycle, particularly in the outlet gas line from the filter chamber. The system was opened for cleanout, and additional heat was applied to the line to eliminate the plug. The exothermic reaction with zircaloy produced temperature surges of 30 to 50°C within the fluidized bed. These were controlled by decreasing the hydrogen chloride concentration from the original 60 to 30 volume percent.

Air flow tests made on the filter tubes before and after the three-cycle exposure indicated an 85% permeability reduction as compared with previous filter permeability losses of about 30% for multiple exposure cycles to process chemicals, not including the off-gas constituents coming from the zircaloy reaction. A hot water wash reduced the loss to about 65%, but additional washing with ammonium carbonate and hydrogen peroxide failed to improve the flow conditions. Hot water readily dissolves zirconium compounds, such as the chloride and oxychloride. The failure of the carbonate-peroxide mixture suggested that the difficulty was not due to reduced materials or to those which would be complexible in moderately basic solution.

Bed and filter scraping samples contained 1,350 and 2,500 ppm of zirconium and 70 and 10 ppm of tin, respectively. The filter scraping was

TABLE XII

EXPOSURE ENVIRONMENT FOR FILTER STUDY

	Run Number					
	1	2	3	4	5	6
Total Number of Cycles*	3	3	1	1	1	5
Initial Filter Plug, %	0	32	60	40	60	0
Final Filter Plug, %	85	80	85	60	75	90
<u>Hydrochlorination</u>						
Hydrogen Chloride Supplied, volume percent†	60	60	60	60	30 to 70	30 to 70
Hydrogen Supplied, volume percent	5	5	5	5	0	0
Hydrogen Chloride Exposure Time, hr	5	5	5	5	8	8
Filter Temperature, °C	315	325	340	340	355	355

* Complete cycles included exposure to hydrogen chloride, oxygen, and fluorine in turn. The bed temperature during hydrochlorination was 400°C, and a gas velocity of 0.75 ft/sec was used. Filter temperatures, gas compositions, and exposure times are shown in the table. The oxidation consisted, each case, of 10 hours at 100°C filter temperature with an oxygen concentration of 15 volume percent and a reactor gas velocity of 1 ft/sec. The fluorination portion involved 10 hours' exposure at 100°C filter temperature, fluorine concentrations of 20 to 25 volume percent, and reactor gas velocity of 1 ft/sec.

† Average concentrations in the gas passing through the filters for the first four runs were calculated as 51% hydrogen chloride, 5% hydrogen, and 2.5% zirconium tetrachloride. Two-, three-, and three-hour exposures at 30, 50, and 70% hydrogen chloride, respectively, were used in each of runs 5 and 6. Assuming the major portion of zircaloy reaction occurred in the first 2 hours, approximate gas concentrations passing through the filters at that time were 17.5% hydrogen chloride, 6.7% hydrogen, 3.3% zirconium tetrachloride, 0.1% stannous chloride, and 72.4% inerts.

also found to contain 1,100 ppm of nickel. The remainder of both samples was presumed to be largely alumina.

Since the permeability loss was much less when the zircaloy was not added to the fluid bed, it was presumed that the difficulty was due to the presence of zirconium, tin, or some minor constituent. Tin did not appear to be present in large enough quantities in the bed sample or in the filter scrapings to cause the difficulty. It was conjectured that the high loss of permeability in this test might have been due to zirconium oxide formation when the system was opened to clean out the filter outlet line plugs. Another possible explanation was that the zirconium tetrachloride might have been left behind on the filter by adsorption or even condensation and then fluorinated.

In the next test, two filters, each with a 32% permeability loss from previous hydrogen chloride, oxygen, and fluorine exposures, were subjected to the test conditions used in run 1. The filter operating temperature was, however, raised slightly from 315 to 325°C in order to guard against the possibility of zirconium tetrachloride or stannous chloride condensation in the filter pores. After the three-cycle exposure test, the total filter permeability loss was found to have increased to 80%. Laboratory analyses indicated a zirconium concentration of 20% and a tin concentration of 20 ppm in the filter coating. Anionic constituents were not determined, and the material was presumed to contain considerable aluminum from the alumina bed diluent. The filter tubes were washed with hot water, and the permeability loss was reduced to 60%.

In run 3, a one-cycle exposure test was conducted under conditions similar to runs 1 and 2, except that the filtering temperature for the dechlorination phase was increased to 340°C. The filter plugging increased from 60 to 85% during the run, and the resultant filter coating was found to contain 45% zirconium, 1.2% nickel, 7.3% aluminum, and 10 ppm tin. X-ray diffraction and optical analyses indicated that alumina and zirconium tetrafluoride were the chief constituents of the filter coating. The tubes were washed with hot water and 50% sulfuric acid, reducing the permeability loss to about 40%.

Since the nitrogen used in the runs thus far as an inert gas diluent occasionally contained up to 1% oxygen, the oxide or oxychloride of zirconium could have been produced in the bed during hydrochlorination. It was thought that the route could be either by direct reaction of the oxygen or perhaps by the hydrolysis of zirconium tetrachloride after the oxygen had been converted to water by reaction with the hydrogen present. The loss of permeability could, in part, be attributed to the collection of this material as it was blown up on the filter surfaces, and it is conceivable that the oxide coating might have been converted to a fluoride during the subsequent fluorination exposure. An available deoxidizer for argon was used instead of nitrogen in the next run (number 4). The one-cycle exposure test at a hydrochlorination phase filter temperature of 340°C was repeated using the washed filters. The permeability loss rose from 40 to 60%, and the filter coating was found to contain 39% zirconium. Analysis of the bed in the filter loop reactor at the conclusion of the

test indicated a zirconium concentration of 6.3%, together with 0.19% nickel, 46% aluminum, and 15 ppm tin. The conversion of the zirconium metal to the tetrachloride had apparently been incomplete, apparently due to the bed temperature in the bottom of the reactor being slightly low.

To reduce the possibility of incomplete hydrochlorination of the zircaloy, the hydrogen chloride exposure phase in run 5 was extended to include operation at 30% hydrogen chloride for 2 hours, 50% hydrogen chloride for 3 hours, and 70% hydrogen chloride for 3 hours. The use of excess hydrogen in the reacting gas was eliminated, and the filter temperature during the hydrochlorination phase was increased to 355°C. After one complete treatment cycle, the filter permeability loss had increased from 60 to 75%. Filter coating analyses indicated a zirconium concentration of only 3% with nickel, aluminum, and tin concentrations of 1%, 48%, and 20 ppm, respectively. X-ray diffraction inspection found zirconium tetrafluoride, alumina, and a considerable amount of an unknown compound, possibly a complex. Samples of the final reactor bed gave zirconium, nickel, and aluminum concentrations of 0.06, 0.09, and 52%, respectively, which indicate a relatively complete zirconium reaction.

In order that the filter plugging rates could be studied more thoroughly, modifications were made to the filter loop to indicate more accurately filter internal temperatures and filter differential pressures. A new single Huyck Metals Company filter tube was flow tested and installed in the test loop. Internal thermocouples were positioned at the top, center, and bottom of the tube. The positioning of these thermocouples prohibited the use of filter blowback during the following tests. Instrumentation capable of indicating the pressure differential across the filter with sufficient sensitivity for following in-process permeability changes was added to the system.

Run 6 was then initiated. At the completion of the first cycle, little change had been noted in the filter pressure drop. During the hydrochlorination phase of the second cycle, the filter differential pressure increased to about 18 inches of water and then decreased to 10 inches by the end of the oxidation and fluorination phases. A significant filter temperature rise was noted during the fluorination treatment but was of short duration. During the third cycle, the filter pressure differential increased to 28 inches of water during the hydrochlorination phase, and a significant temperature excursion developed during the fluorination exposure. The filter internal temperature rose from 100 to 370°C, and the fluorine flow was stopped for several minutes for cooling purposes.

The test loop was shut down after the third cycle, the reactor bed was removed, and the filter was retested in the laboratory. The flow data indicated that the tube had developed no holes or cracks from the temperature excursions, but a permeability loss of about 90% had resulted from the three-cycle exposure.

It was theorized that possibly a nickel-zirconium chloride compound or complex might be the cause of the high permeability loss during the hydrochlorination phase of the process. Such a complex might be decomposed with heat, and the permeability might be recovered if zirconium tetrachloride were to escape. Testing was resumed, and at the end of the hydrochlorination portion of the next cycle, during which the filter pressure differential had increased to 1 psi, the filter chamber was heated to nearly 540°C. After 1 hour, little indication of unplugging was noted, and it was decided to feed hydrogen at a stream concentration of about 10 to 15%. The filter pressure differential began to decrease immediately, and after 2 hours, it had reached about 0.5 psi, which was the value logged at the beginning of the process cycle. Little change was observed after the oxidation and fluorination treatments. The above procedure was repeated in the next cycle with more uniform temperature control but provided the same indications and results.

In a plant operation, the hydrogen chloride would be recycle and would contain considerable hydrogen, perhaps as much as 50 mol percent of the gas stream at the filter location. It is possible that this excess hydrogen would be helpful in minimizing the filter plug in the hydrogen chloride step.

When the significance of permeability figures is evaluated, it is also necessary to consider the high flow capacity of the new tubes and, of course, the process requirements. At 1 atmosphere pressure and 25°C, a new tube will pass about 3 to 4 cfm of air per square foot per inch of water pressure drop. Considerable permeability loss is expected in service, although it is obviously desirable for the filter to retain as much flow capacity as possible to minimize the number of tubes provided in a filter. It is difficult to draw a precise conclusion as to acceptable flow capacity per tube because of the variables in the problem; nevertheless, it is thought that tubes of the type tested which have as much as 5 to 10% of the original flow capacity could be usable, and it is common practice to operate at the 10 to 20% range of values.

Since no plugging difficulties were experienced when the exposure cycle was repetitively performed in the absence of the zircaloy, it appears definite that the recently observed high plugging rates are due to the interaction of clad residues with the nickel filter tubes. There are several investigative approaches which may yet be pursued. First, the effect of excess hydrogen, which would be present in the plant recycle, can be tested. Also, a second filter may be installed in series with the first to determine if the plugging rate is the same and, from this, whether the plug constituent is volatile or nonvolatile or possibly present in only trace amounts. Finally, variation in blowback procedure and operating temperature can be evaluated.

At present, the filter loop system is being studied to determine what modifications are required (a) to observe the effect of excess hydrogen on filter plugging, (b) to observe the plugging rates of two filters in series, and (c) to install a heated filter blowback system.

CONNECTORS

New 2- and 4-inch connectors designed to maintain a constant gasket loading pressure over wide temperature ranges have been fabricated and tested. A unit, as shown in figure 7, consists of a two-ring touchpoint nickel gasket compressed between Duranickel flanges by means of a DSD Company temperature-compensating clamp.

The 2-inch connector was assembled using a torque of about 25 foot-pounds on the two clamp bolts provided. The buffer zone between the two rings of the gasket was then pressured to 10 psia with air, and the connector was placed in an oven. The assembly was cycled five times between 100 and 370°C and ten times between 100 and 540°C. A decrease in buffer pressure was noted during the tenth cycle, indicating that a small leak had developed. The connector was removed from the oven to retorque the bolts to 50 foot-pounds. Two additional leak-tight heat cycles were then run between 100 and 540°C.

The 4-inch joint was successfully subjected to nineteen heat cycling tests between 100 and 540°C before a small leak developed. A new gasket was placed in the unit, but efforts to apply sufficient torque to the joint to maintain a buffer seal resulted in a failure of the clamp bolt retainers. The clamp was repaired, and the connector was subjected to an additional three cycles between 100 and 540°C.

Another 4-inch flanged joint, consisting of two Duranickel flanges having two concentric and matching ring projections on each face and assembled to compress a flat nickel gasket by means of the DSD Company temperature-compensating clamp, was successfully thermocycled between 100 and 540°C for twelve cycles before a small leak developed. The clamp bolts were then torqued to about 50 foot-pounds to obtain the original seal.

Contacts are being made with the manufacturer of the clamps for recommendations on means to strengthen the bolting arrangement.

VALVES

The search for a vendor to supply a valve that would meet all the desired operating requirements for handling powder discharged from the fluid-bed reactors has met with very limited success. Several standard plug and ball type valves appeared promising if some modifications could be made, but manufacturers were reluctant to enter into the development program necessary on the small order involved. Therefore, a study was made of commercially available "shelf-item" valves that might be modified at ORGDP for testing purposes. One of the most promising units is an all-nickel plug valve. This valve is designed for straight-through flow with no cavities to fill with powder and operates with a single-faced eccentric plug (i.e., cam-shaped in horizontal cross-section) which rotates perpendicular to the direction of flow into position against a raised-seat in the valve body. This seat is also eccentric to the axis of rotation; hence, the plug and seat make contact only in the fully closed position. The plug moves out of the flow path when the valve is open.

PHOTO NO. PH-66-909

CONNECTOR WITH TWO RING TOUCHPOINT GASKET
AND TEMPERATURE COMPENSATING CLAMP

Figure 7

One of these valves was installed on the bottom of a 4-inch-diameter hopper. Alcoa tabular alumina (minus 48- plus 100-mesh) was added to the hopper to a depth of about 32 inches. Air at 15 psig pressure was then applied to the bed. Air leakage through the bed of alumina and valve was measured to be approximately 2.5 cfm, which was both unexpectedly high and considerably higher than allowable for the proposed application. One unusual test result was that no measurable amounts of alumina passed through the valve with air flow. Studies are in progress to determine what modifications can be made to reduce the leakage.

The valve, as produced, contains a Teflon stem seal which is unsuitable for the proposed application. A design has been proposed which should provide a hermetic seal for the stem assembly of this or similar valves.

It may be necessary to apply a dry lubricant to the bearing surfaces of the movable plug. Various coatings and powders are being considered.

PERIPHERAL COMPRESSOR

The continuous service test for a target of 2,000 operating hours with fluorine* was completed during the report period. A total of over 2,400 hours was actually logged, 2,016 of which involved mixtures of fluorine and nitrogen. The fluorine concentration was maintained between 20 and 50%, and the compressor speed averaged between 9,600 and 9,700 rpm. Over the course of the run, some lubrication problems developed from time to time (these may have been solved as discussed below), but other than minor instrumentation malfunctions, no operating difficulties were encountered after the nitrogen seal pressure was boosted to prevent exposure of the bearings to process gases.

Events of importance during the course of the test were as follows:

1. A study was made to evaluate the change in pumping rates and power requirements with gases of varying molecular weights. A series of test runs was made at a compressor speed of 9,955 rpm and a compression ratio of 2:1, while the fluorine gas concentrations in nitrogen were varied from zero to 75.4%. The results of the experiment are shown in table XIII. Thus, it can be seen that, as the fluorine concentration was raised from zero to 75%, pumping rates increased to about 50% with a corresponding 15% increase in power requirement.
2. Calibrated rotameters were installed in the nitrogen seal feed and exhaust lines to determine the seal flow distributions. These results are presented in table XIV. The net inleakage of nitrogen through the pump seal into the process stream is indicated to be only about 0.1 scfm. This is about one-half the rate assumed acceptable for design purposes.

* This test was begun during the first half of 1966. The initial phases of the test were covered in K-1691, pp 59-60, the Semiannual Progress Report for January Through June, 1966. For most of the test period, the compressor operated on a 13-shift, 104-hour per week basis.

TABLE XIII
PERIPHERAL COMPRESSOR CHARACTERISTICS*

Fluorine, %	Pumping Rate, scfm	Power Requirement, kw
0.0	51.0	5.60
25.7	62.5	6.16
30.4	63.3	6.18
45.7	67.1	6.20
52.0	71.9	6.24
66.4	73.2	6.30
75.4	73.8	6.40

* Peripheral speed = $9,955 \pm 15$ rpm and a 2:1 compression ratio.

TABLE XIV
PERIPHERAL COMPRESSOR SEAL FEED-SEAL EXHAUST FLOWS

Pressure Drop Between Seal Feed And Process, psi	Pressure Drop Between Seal Feed And Seal Exhaust, psi	Seal Feed Flow, scfm	Seal Exhaust Flow, scfm	Estimated Inleakage To Process, scfm
1.5	0.5	0.15	0.05	0.10
1.5	0.2	0.09	0.00	0.09
2.0	0.5	0.15	0.04	0.11
1.0	0.5	0.09	0.05	0.04

3. After the compressor had been operated about 600 hours, the temperature of the load bearing of the pump began to fluctuate periodically from the normal 60°C to 70 or 75°C and back to 60°C. In the following 48-hour period, the bearing temperature cycled a total of 27 times. Since a lack of bearing lubrication was indicated, attempts were made to add a small quantity of oil to the grease-packed bearing. The main oil supply port was found plugged, but 7 cc of oil was successfully added through an auxiliary lubrication line. The bearing temperature dropped to normal within 5 hours.
4. After a total of 1,830 hours of operation, the load bearing of the compressor suddenly began operating a relatively steady 7 to 10°C hotter than normal. Since the temperature did not drop after oil injections, it is considered possible that the observed heating may have resulted from loss of desirable lubricating properties of the grease originally packed in the bearing. Fluorine attack (there were several known exposures during emergencies) may have decomposed a significant amount of the grease. Addition of the auxiliary oil lubricant may have not rejuvenated the grease. On the other hand, the amounts of oil added to the grease over the several months of operation may have been too great, resulting in severe thinning or dilution of the grease.
5. After almost 400 hours of operation at the higher temperature, the load bearing temperature rose to 87°C, at which point, an alarm circuit shut the compressor down. The input power recorder indicated that the overheated load bearing was grabbing just before shutdown, but the shaft was rotated freely by hand after shutdown, thus alleviating fears of burned or warped bearings.

Two centimeters of oil was then injected into the bearing area, and the compressor was restarted. The only abnormality observed in the startup was the rapid rate at which the load bearing approached its operational temperature as the load was imposed on the compressor. The load bearing temperature leveled off at $60 \pm 1^\circ\text{C}$ and then remained approximately constant.

The unit has now been removed from the test loop and disassembled. A detailed inspection has not yet been undertaken; however, preliminary indications are that the unit is in excellent condition. Metal surfaces appear clean and uncorroded. After completion of the inspection, the compressor will be reassembled and installed in the loop for additional fluorine exposure tests.