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AEC RESEARCH AND DEVELOPMENT REPORT

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1966

AUTHORS:

S. H. Smiley
J. H. Pashley
R. B. Schappel

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IN NUCLEAR SCIENCE ABSTRACTS

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UNION CARBIDE CORPORATION
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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 third 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; (b) the composition of irradiated fuels; (c) the fates of fission products during volatility process; (d) the separation of mixtures of uranium hexafluoride-plutonium hexafluoride-fission product fluoride by distillation; (e) preliminary considerations in the sizing of a reactor to produce bromine pentafluoride from bromine; (f) sodium fluoride fluid-bed sorber criticality calculations; (g) some theoretical aspects of cold trapping; (h) corrosion testing and related studies; (i) process and reactor studies, including semiworks pilot-plant operation, sampling, a fluid-bed level indicator, and pressure drop measurements; (j) outlet gas filter studies; (k) sorption-desorption systems for product purification, using batch sodium fluoride pellet traps; (l) connector testing; (m) status of valve selections; and (n) evaluation of the ORGDP-designed peripheral compressor.

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ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1966

This report is the third 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. Much work still remains to be done by the National Laboratories in exploration of basic chemical and technical feasibility of new process opportunities and alternatives for low-enrichment power reactor fuels. 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

Emphasis continued to be placed, during this period, on the study of processes for zircaloy-clad power reactor fuels. The projects chosen were consistent with current fluoride volatility work at the National Laboratories, as well as the Argonne reference flow sheet. Because of the current interest in both fluorine and bromine pentafluoride as fluorinating agents in volatility processing, studies were made for both flow sheets.

Systems Analysis

Anticipated problems associated with volatility processing have been compiled in the form of questions. Detailed answers have been prepared for the hydrogen chloride declad-two zone oxidation-fluorination process, but much of the subject material is also applicable to the bromine pentafluoride flow sheet. It should be possible to make recommendations for

the scheduling and assignment of work after review and analysis of the collected information.

Composition of Irradiated Fuels

A study has been undertaken to modify the computer code which was recently prepared to obtain information on the fission products in spent fuels. Hopefully, computations on the uranium-232, plutonium-236, and plutonium-238 contents of the fuel can be included in the output, and the code can be revised to accept, as alternative input data, either time-flux information or the fuel exposure and operating specific power.

Fission Product Flow Sheet

The fission product and heavy element concentrations have been computed in power reactor fuel irradiated to about 20,000 Mwd./tonne. Preliminary estimates have been made of the fates of these elements during volatility processing. Current work is being directed at predicting the percentages of the various partially volatilized materials which may leave the bed during each phase of operation. The problem is complicated by synergistic, as well as independent, reaction mechanisms, and experimental work is necessary for an absolute evaluation.

Uranium Hexafluoride-Plutonium Hexafluoride-Fission Product Fluoride Separation

Regarding the process alternative that utilizes elemental fluorine for both uranium and plutonium volatilization, batch distillation can be used to remove fission products from the uranium hexafluoride-plutonium hexafluoride-fission product fluorides. A high-boiling compound may be necessary as a reboiler heel. Low-boiling fission product fluorides could be removed from the top of the still, and a side stream from the lower part of the vessel would be recycled through a thermal decomposer to remove the plutonium. Computations were made for (1) batch operation using niobium pentafluoride as the reboiler heel material; and (2) separation of molybdenum hexafluoride, which probably would be the low-boiling key component. The results for these calculations are described in detail.

Bromine Pentafluoride Converter

For a 24-inch diameter fluid-bed reactor system producing 75 pounds of uranium hexafluoride per hour per square foot, a converter 10 to 12 inches in diameter and about 15 or 20 feet long should be capable of regenerating the bromine pentafluoride if bromine trifluoride were the only product of the fluorination reaction. ANL has recently found that bromine pentafluoride is largely reduced to bromine when a substantial excess of urano-uranic oxide is present. Additional work is now required on design of a converter for fluorination of the bromine, but the vessel size may not differ greatly from that calculated for a bromine trifluoride and fluorine converter.

Criticality Calculations

Computations were made for a sodium fluoride sorption system through which large quantities of uranium would be processed. Previous work has been extended to include calculations for uranium-235 enrichments of 2 and 5%. A critical homogeneous assembly appears impossible for 2% uranium-235, since the infinite neutron multiplication factor was found to be less than 1.0. The maximum allowable diameter for the 5 or 6% assay was estimated to be about 2 feet, considering actual vessel length.

Calculations for reflected plutonium dioxide spheres of various densities have indicated that, for such cases, plutonium-239 alone is more nuclearly reactive than the mixtures of the plutonium isotopes which are expected in spent power reactor fuels. The plutonium densities which would be encountered in the volatility process in the fluid-bed reactor system are not known accurately but are estimated to be less than 3.2 grams of plutonium dioxide powder per cubic centimeter. Since the estimated critical mass for a plutonium dioxide powder density of 4.5 g./cc. is about 33 kg. of plutonium dioxide, it would appear conservative on a preliminary basis to suggest a mass limit of on the order of 20 kg. for a batch-limited system provided lack of light element moderation is assured and accountability inaccuracies are not excessive.

The assumption of lack of moderation may not be tenable for certain parts of a system, such as cold traps or sodium fluoride sorption beds, where hydrogen fluoride may accumulate. Additional calculations are being made for such situations.

Cold Trap Studies

About 100 square feet of heat transfer surface would be required in a plutonium hexafluoride cold trap for a fuel processing plant with a 24-inch diameter head-end reactor. Liquid argon or carbon tetrafluoride might be used as the refrigerant to get sufficiently low exit temperatures and reduced area requirements. Fin spacing as close as 1/8 inch would not be expected to plug in service over a 12-hour fluorination cycle.

A deposit thickness limit exists in a cold trap during solid buildup when the gas stream is superheated. The buildup rate tapers off as the limit is approached. This occurs for uranium hexafluoride typical cold trapping conditions after the deposit becomes thicker than 70% of the maximum possible for widely spaced fins. It is thus theoretically possible to choose fin spacing so that plugging would never occur at that point.

PROTOTYPE TESTING AND EVALUATION

Work was oriented toward the Argonne elemental fluorine volatility flow sheet processes. Among the highlights of the period was the completion

of construction of the semiworks facility. Studies were carried out on corrosion, solids sampling, filtering, sorption-desorption, connectors, valves, and the peripheral compressor.

PROCESS AND REACTOR STUDIES

Activities under this heading include the semiworks pilot plant, experiments for the determination of pressure drop in a fluidized bed reactor, solids sampling, and level indicator tests.

Cold Semiworks Pilot Plant

Semiworks construction was completed by the third week in June, and shakedown tests were begun. The reactor and filter cooler were fabricated and assembled in ORGDP shops according to Section VIII of the ASME Code for Unfired Pressure Vessels.

Fluidization of a charge of alumina, as viewed from the opened top of the reactor, appeared normal and satisfactorily turbulent for good mixing. In a 24-hour elutriation test with alumina, 31 pounds out of an original 180-pound filter-cooler charge was carried into the overflow vessel, while there was no decrease in the weight of alumina in the reactor. Future test plans include uranium dioxide pellet oxidation runs, followed by decladding and fluorination tests.

Pressure Drop Measurements in a Fluidized Bed

Pressure drops were determined in a test apparatus constructed to simulate the presently chosen design of the lower end of the fluidized bed reactor. Measurements were taken across the bottom cone and over various depths of the fluidized bed section. The equipment was filled with alumina, and for some of the runs, 5/8- or 9/32-inch metal balls were loaded into the bottom cone to act as a bed support for the powder.

Sampling

In monitoring the operation of the fluoride volatility plant for accountability and process control, sampling of solids will be necessary. Two solids samplers, a 6-inch Vezin type and a 20-inch Park type, were purchased. The Vezin sampler was tested for the sample cutting precision and ease of operation. Tests were conducted using 1/8-inch diameter by 1/8-inch long pellets of sodium fluoride and sodium bifluoride. A series of eight replicate runs resulted in sample cuts which ran 5.36 weight percent of the original with a standard deviation of 0.04%. Sequential cuts were made to reduce the sample size further; these ran 5.23 to 5.24 weight percent of the charge to the sampler.

Efforts to operate the 20-inch Park sampler on pellets were unsuccessful because of clogging.

Solids Material Level Indicators

One technique for evaluating the degree of completion of the hydrogen chloride decladding reaction involves measurement of the level of accumulated uranium dioxide pellet bed in the bottom of the reactor. Tests, using an Ohmart Nuclear Gauge with a 150-millicurie source of cesium-137, indicate that this type of equipment may be acceptable for measurement of pellet bed level in semiworks studies.

MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES

Nickel, Duranickel, Hastelloy B, and Hills-McCanna Company nickel alloy number 72 were submerged in a fluidized bed of tabular alumina and were subjected to 5 cycles of volatility process corrosive atmospheres containing hydrogen chloride-hydrogen-nitrogen, air, or fluorine at selected temperatures, typical of operations, between 400 and 540°C. A hard, yellow scale appeared on the samples of Hastelloy B and alloy number 72, and corrosion rates of 190 and 325 mils per year, respectively, were measured. In the same test, the corrosion rates for nickel and Duranickel were found to be about 30 mils per year.

Corrosion tests on INCO-61 welding wire and on low-carbon nickel weldments using INCO-61 wire indicated little attack by fluorine at 360°C. over a 69-hour exposure period.

OUTLET GAS FILTER STUDIES

Two Huyck Metals Company nickel filter tubes, fabricated from a mat of fibers in a wire mesh screen, were tested for 300 hours at an elevated temperature in 9 cycles of flowing corrosive atmospheres (hydrogen chloride, hydrogen, nitrogen, and fluorine). As the result of the test, there was a 25% loss in permeability. An additional 7% loss occurred in a 108-hour extension of the test. These losses are actually minor. A permeability decrease of this size normally is indicative of precoat-ing, and the filter is subsequently useful over a long operating period. At this point, the filters therefore appear to be acceptable for volatility processing.

PRODUCT PURIFICATION, SORPTION-DESORPTION SYSTEMS

A 4-inch diameter pellet trap was used to test the sorption capability of sodium fluoride pellets for trace quantities of uranium hexafluoride in process exhaust streams. The trap was charged with 34 pounds of freshly prepared sodium fluoride resulting in a bed 7 feet high. Nitrogen with 450 to 500 ppm. of uranium hexafluoride was fed to the trap, and the test was conducted at 121°C. at a velocity of 0.68 ft./sec. For the 300 hours before breakthrough, the concentration of the uranium hexafluoride in the off-gas stream averaged 10 ppm. The material in the trap was regenerated by heating to desorb the uranium hexafluoride.

The test was continued with a lower concentration of uranium hexafluoride in the feed stream, but the outlet gas contained 30 ppm. uranium hexafluoride.

The outlet gas concentrations are considered high but possibly satisfactory for plant use. Additional tests are planned employing lower superficial velocities, with correspondingly increased residual times.

CONNECTORS

Two connector assemblies were tested during this period, each consisting of a two-touchpoint, serrated nickel ring gasket and 150-pound, 4-inch Duranickel flanges joined using 5/8-inch diameter Inconel-X studs. The assemblies remained tight during heat cycling between 100 and 370°C., but leaked when temperatures were increased to 500 to 540°C. In all probability, the bolts expanded at the thread area or the nuts loosened when the temperature was raised.

Programs have been initiated to test temperature-compensating clamps and to redesign conventional basic joints for remote operation.

VALVES

Valving requirements for the fluoride volatility process are, in general, rather unique because of the unusual corrosive resistance specifications, the need for remote operation, and in some cases, the high temperatures at which the valves must function.

Initial efforts to find suitable valving have been devoted to a review of commercial units. A valve has been tested for possible use with the charger for the ORNL hot pilot plant. Efforts to find fuel element valves suitable for handling powder from the fluidized bed reactors in a volatility processing plant have been unsuccessful thus far, possibly because of material limitations due to expected high radioactivity and to corrosive environments. Modification of commercially available units is planned to allow testing to evaluate potential applicability in plant use.

COMPRESSORS

The ORGDP peripheral compressor appears to be suitable for recycling volatility process corrosive gases. More than 520 hours has been logged in an operational test, and continuous pumping of fluorine for a target of 2,000 hours is planned. Pumping rates of 70 std.cfm. have been attained. Additional work is planned on performance characteristics with mixtures of fluorine and nitrogen.

Although performance to date has been good, the bearing system will be tested on a separate rig at a speed of 11,000 rpm. to determine the extent of its service life in a continuous 7-day-per-week operation.

DISCUSSION

ENGINEERING STUDIES

J. H. Pashley, R. B. Schappel,
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LOW ENRICHMENT FUELS

During this period, the entire effort was placed on processes for zircaloy-clad uranium dioxide power reactor fuels. The projects chosen were consistent with the fluoride volatility work at the National Laboratories and the Argonne elemental fluorine volatility process flow sheet. Because of the current interest in both fluorine and bromine pentafluoride as fluorinating agents in volatility processing, studies were made for both schemes.

Systems Analysis

A systems analysis program has been initiated to highlight problem areas in the proposed fluoride volatility process flow sheet. Recognized problems have been written up in a compendium in the form of questions. Answers are being prepared in which the problem is discussed, related technology is assessed, and suggestions for further work are made if deemed necessary. The questions are organized in a matrix type format, i.e., by both process system and problem type, as shown in figure 1.

Formulation of write-ups was confined during this period to the original Argonne National Laboratory reference flow sheet for zircaloy-clad fuels; i.e., decladding by hydrogen chloride and two-zone oxidation-fluorine fluorination to remove uranium; however, much of the subject material is applicable to the alternative flow sheet which uses bromine pentafluoride for uranium volatilization.

Problems involving operations, process considerations, design, safety, and construction have been discussed for the main fluid-bed reactor, reactor off-gas cooling and filtration, pyrohydrolysis, and cold trapping. Work assignment and scheduling recommendations have not been made as yet, but plans are to include them with the program after grouping the questions according to experimental programs. Since a single experiment may provide the "answer" material for a number of questions in more than one vessel system, the scheduling feature is best pursued after the write-up information is reviewed and analyzed.

PROCESS SYSTEM	TYPE OF PROBLEM					
	Operation	Process	Design	Safety	Construction	Accountability
MAIN FLUID BED REACTOR						
Charging						
Declad						
Oxidation - Fluorination						
Bed Dumping and Sampling						
OFF-GAS COOLING & FILTRATION						
PYROHYDROLYSIS FLUID BED						
HCl RECOVERY SYSTEM						
COLD TRAPPING SYSTEM						
PuF ₄ PRODUCTION APPARATUS						
DISTILLATION SYSTEM						
GENERAL						

Figure 1
MATRIX FORMAT FOR SYSTEMS ANALYSIS QUESTIONS

Composition of Irradiated Fuels

In the previous summary progress report*, a new computer code was described which had been written to calculate heat release rates, activities, and weights of fission products found in spent power reactor fuels. This information is necessary for volatility process studies, and in particular, for the preparation of fission product flow sheets. In preliminary checks, the code output was in substantial agreement with published values; thus, it was concluded that the code can be used to provide reasonable estimates of spent power reactor fuel properties in a rapid manner.

Modifications to the code have been undertaken to make the code easier to use and to include computations on the transuranics uranium-232, plutonium-236, and plutonium-238. Significant amounts of these isotopes can be produced at the high fuel exposures which will be achieved in the future, and their presence could involve distinct problems because of large amounts of emitted radiation from daughters.

Time-flux and some reactor data are required at present as input for the code; i.e., the initial fuel composition, the exposure time increment and the associated flux, the effective temperature, the fuel rod diameter or mean chord length, and an assumed parameter indicating the fraction of the flux considered to be in the resonance region. A major programming change is under study whereby it would be possible to select fuel exposure and operating specific power as alternative input instead of the time-flux data.

Fission Product Flow Sheet

One of the most challenging problems of fuel reprocessing engineering studies is the prediction of the fates of radioactive fission products and actinides during the various processing steps. Straightforward analysis of this problem for a fluoride volatility process is complicated because volatilization of active nuclides depends on many factors and mechanisms which could conceivably act synergistically, as well as independently. For example, some of the factors which must be considered are accessibility of nuclides for reaction, carrier gas flow, thermodynamics, kinetics, interphase mass transfer, temperature conditions, and retention on environmental materials. Still another problem involves the behavior of the volatilized materials after their removal from the reactor. Radioactive decay to nonvolatile species, phase changes, solubilities, and reactions with sorbents and even with piping must all be dealt with.

It is clear that experimental work on an engineering scale is necessary for any absolute evaluation of fission product fate; however, to satisfy

* Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGD Fuel Reprocessing Summary Progress Report, July through December, 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, June 28, 1966 (K-1669).

immediate needs, a fission product flow sheet for the bromine pentafluoride process is being prepared using the fission product distribution obtained with the ORGDP spent power reactor fuel property code*.

Initial flow sheet calculations will use the preliminary fission product and heavy element concentrations listed in table I. These values were computed for a fuel sample irradiated to about 20,000 Mwd./tonne and cooled for 150 days. They are considered typical but not fixed. In actual cases, the concentrations will vary considerably from one case to another depending upon reactor operating conditions. Only a few thermodynamic calculations have been made to date, and the model for mass transfer has not been completely defined; however, preliminary estimates of fission product fates during the processing steps are as follows:

1. Hydrochlorination - 450°C.

Most Likely to be Volatilized. Radioactive cladding components (zirconium, niobium, small amounts of tin)

Less Likely to be Volatilized. Fission product zirconium, niobium, tin; plus xenon, krypton, iodine, bromine, indium, antimony, tellurium, selenium, molybdenum, technetium

2. Oxidation - 500°C.

Most Likely to be Volatilized. Remaining fission product gases

Less Likely to be Volatilized. Selenium, technetium, tellurium, cesium, ruthenium, and possibly molybdenum

3. Fluorination

a. Bromine Pentafluoride - 350°C.

Most Likely to be Volatilized. Niobium, molybdenum, technetium, ruthenium, tellurium, uranium

Less Likely to be Volatilized. Neptunium

b. Fluorine - 350 to 550°C.

Most Likely to be Volatilized. Plutonium, remaining neptunium

Less Likely to be Volatilized. Zirconium†, rubidium†

* A report on this code is in preparation.

† Although vapor pressure is relatively low, some volatilization may occur at higher temperatures.

TABLE I

TYPICAL FISSION PRODUCT AND HEAVY ELEMENT CONCENTRATIONS
EXPECTED IN 20,000 Mwd./tonne FUEL

Element	Concentrations, ppm.*	Element	Concentrations, ppm.*
Americium	87	Plutonium	8700
Antimony	7.4	Rare Earths	4800
Barium	730	Rhodium	320
Bromine	9.2	Rubidium	220
Cadmium	22	Ruthenium	1200
Cesium	2200	Selenium	17
Curium	11	Silver	50
Indium	19	Strontium	530
Iodine	180	Technetium	500
Krypton	210	Tellurium	320
Lanthanum	740	Tin	19
Molybdenum	2000	Xenon	2500
Neptunium	40†	Yttrium	270
Niobium	6.6	Zirconium	2100
Palladium	460		

* Initial total uranium basis.

† Recent experimental Yankee pellet data (BNWL-45) have indicated that this value is low by about a factor of 5. This is felt to be primarily due to the fact that the current version of the code, because of computer space limitations, does not consider all the production routes for this isotope.

4. Transferred with Bed to Waste Storage or Recycled for Further Processing

The rare earth fluorides, along with the fluorides of strontium, yttrium, rhodium, barium, lanthanum, silver, cadmium, etc., are expected to remain with the alumina bed.

At present, work is being aimed at predicting the percentages for the various partially volatile materials which might be removed from the bed during each phase of the chemical treatment. Also, attempts will be made to expand the scope of the work to include the disposition of fission products in recycle systems and in cleanup traps.

Uranium Hexafluoride-Plutonium Hexafluoride-Fission Product Fluoride Separation

Batch distillation can be used as a means of removing fission products from the uranium hexafluoride-plutonium hexafluoride-fission product fluoride mixture which is obtained in all-fluorine fluorination of spent oxide fuels. Subsequently, thermal decomposition of plutonium hexafluoride to solid plutonium tetrafluoride can be employed to provide a good separation of the plutonium from the uranium. In one processing scheme, a high-boiling compound would be added to the still prior to distillation to function as a reboiler heel. Low-boiling fission-product fluorides could then be removed from the top of the still, followed by uranium hexafluoride. Plutonium hexafluoride would be the final compound vaporized from the reboiler leaving behind a heel consisting of the added high boiler, together with the high-boiling fission products. During the operation, a side stream would be recycled from the still, through a thermal decomposer to remove the plutonium, and back to the overhead condenser or the upper part of the column.

The following batch distillation computations have been made during this report period:

1. A combined distillation-plutonium hexafluoride thermal decomposition operation when niobium pentafluoride is added as the reboiler heel.
2. The distillation column performance when molybdenum hexafluoride is the low-boiling key fission product in the mixture fed to the still.

Reboiler Heel Calculations. A digital computer program was prepared and debugged to perform the calculations necessary in the analysis of a dynamic batch distillation-thermal decomposition system through the use of column differential mass and enthalpy balances. This analysis requires the stepwise solution of a set of differential equations for the column flows, and the function evaluation for each step requires the solution of three nested transcendental equations for the overall column holdup, the liquid flow to each plate, and the bubble point temperature of each stream.

This program was initially employed to obtain performance estimates for a still system planned for the ORNL hot pilot plant. The following conditions were chosen:

Original Charge, g. mole	13.500
Plutonium Hexafluoride, g. mole	0.054
Uranium Hexafluoride, g. mole	13.108
Niobium Pentafluoride (Reboiler Heel), g. mole	0.338
Number of Theoretical Plates	20
Side Stream Plate, Counting Up from the Bottom, Excluding Reboiler	6
Holdup Per Plate (Constant), g. mole	0.118
Reboiler Holdup During Operation (Constant), g. mole	0.675
Vapor Flow From Reboiler (Boilup Rate), g. mole/hr.	24.03
Side Stream Flow to Decomposer, g. mole/hr.	3.375
Pressure, atmospheres	2.0

These conditions are met by a 1-inch column containing a high efficiency packing and operating at around 70% of flooding. It was assumed that the amount of niobium pentafluoride to be added to function as a reboiler heel would be about 2.5 mole percent of the original charge. The system holdup has been largely delegated to the condenser and upper portion of the column, leaving only 5% of the original charge in the reboiler. Since most of the plutonium hexafluoride inventory is contained in the reboiler side stream take-off region, the effect is to concentrate plutonium hexafluoride for the side stream.

The column was assumed to operate at total reflux until coming to steady state under the above conditions. At that point, the side stream flow to the thermal decomposer was begun for removal of plutonium, while the reflux operation was continued. The initial reboiler temperature was calculated as 99.4°C., corresponding to a mixture with uranium hexafluoride-niobium pentafluoride-plutonium hexafluoride mole fractions of about 0.46, 0.50, and 0.04, respectively. The initial side stream contained about 1.2 mole percent plutonium hexafluoride (against about 0.4% in the charge) and niobium pentafluoride on the order of 10-15 mole percent. About 60% of the plutonium hexafluoride was removed before a side stream concentration of less than 0.4% plutonium hexafluoride was observed 1.4 hours later. A total operating time of 7.6 hours was simulated in eighty time steps (requiring 9 minutes on the IBM 7090), resulting in a final calculated plutonium hexafluoride holdup in the column of 0.00051 gram mole, or less than 1% of the original charge.

At this point, the side stream contained about 0.01% plutonium hexafluoride. In spite of the fact that the final side stream concentration is low, it should be noted that the reboiler temperature and holdup were held relatively constant, and by decreasing the reboiler holdup, the plutonium hexafluoride side stream concentration could be increased. The 7.6-hour run described here is not necessarily typical but depends upon the side stream flow rate, which was arbitrarily chosen in this example.

It was assumed that appreciable plutonium hexafluoride decomposition or complexing does not take place in the column and that the decomposer itself removes essentially all of the plutonium hexafluoride. In this connection, the reboiler temperature was intentionally maintained below 100°C. to hold plutonium hexafluoride decomposition at a low level.

Low-Boiling Fission Product Calculations. Molybdenum is present in substantial amounts in irradiated power reactor fuel as a fission product. For this study, the concentration was estimated to be about 2,500 ppm. on a uranium basis for 20,000 Mwd./tonne of uranium burnup. This concentration is greater than the typical value given in table I. The number was chosen since it appeared to represent an upper limit and thus would be conservative for this study. Of the molybdenum isotopes present after 150-day cooling, the nonradioactive isotope predominates almost entirely; however, it is necessary to reduce the molybdenum concentration in the product uranium hexafluoride to less than 200 ppm. (uranium-235 basis) to meet the AEC specifications*. Most of the molybdenum is expected to be volatilized as the hexafluoride; however, some oxyfluorides will also be present. A modified version of the distillation digital computer program has been used to calculate the behavior of a batch column in which fission product molybdenum hexafluoride, diluted primarily with uranium hexafluoride, is separated from a plutonium hexafluoride-uranium hexafluoride-molybdenum hexafluoride mixture.

At 2 atmospheres' pressure, the boiling points of molybdenum hexafluoride and uranium hexafluoride are, respectively, 47 and 73°C. Because of the low molybdenum hexafluoride concentration and the fact that plutonium hexafluoride boils only about 12°C. higher than uranium hexafluoride at 2 atmospheres' pressure, relatively complete separation of the three in a batch production column would be difficult. Regardless of the number of distillation stages in a column, if the minimum volumetric holdup in the column condenser and reflux system is greater than the volume of molybdenum hexafluoride fed to the system, obviously a pure molybdenum hexafluoride product cannot be obtained.

The production of an overhead product of uranium hexafluoride-molybdenum hexafluoride containing as little plutonium hexafluoride as possible was studied as a step in the uranium-plutonium-fission product separation.

* Federal Register, 30, 232, p. 14938 (December 2, 1965).

Uranium hexafluoride in such a mixture may subsequently be recovered separately; therefore, the distillation problem centers about the stripping of plutonium hexafluoride from the mixture.

Calculations have been performed assuming that the column has been first brought to a steady-state, total reflux condition. A molybdenum hexafluoride-uranium hexafluoride mixture is then slowly withdrawn from the condenser holdup. In table II, specifications of the column simulated are shown for two cases involving different column holdups. To change the holdup, the condenser was drained in one hour in the first case and two hours in the second. Under these conditions, the initial product compositions were calculated to be 7.9 mole percent molybdenum hexafluoride and 0.0004 mole percent plutonium hexafluoride for the first case, and 4.4 mole percent molybdenum hexafluoride and 0.0004 mole percent plutonium hexafluoride for the second. In both cases, the calculations were discontinued when the condenser was fully drained. At each point, approximately 80% of the molybdenum hexafluoride had been removed from the column. It was found that, while slowly draining the condenser as described, the product composition changed very little over the course of the run, indicating no improvement by refluxing over a direct initial dumping of the condenser. At other product removal rates from the condenser, product composition may change so as to allow a decrease in the amount of uranium hexafluoride take-off and an increase in the molybdenum removal. In the current case, the plutonium hexafluoride concentration in the product was 0.1% of that in the feed; therefore, eventually all of the plutonium hexafluoride was left for subsequent separation from the uranium hexafluoride remaining in the column.

Bromine Pentafluoride Converter

Recent experiments at Argonne National Laboratory on the use of bromine pentafluoride as a fluorinating agent to produce uranium hexafluoride indicate that bromine pentafluoride is largely reduced to bromine when reacted with a substantial excess of urano-uranic oxide. These recent results differ from earlier information from Argonne that bromine trifluoride is generated in the interhalogen fluorination reaction. Actually, the reaction probably involves a two-step process in which bromine trifluoride is formed as an intermediate. This theory is based on ANL reports that bromine trifluoride reacts more rapidly than bromine pentafluoride with the uranium oxide. The bromine trifluoride can thus be expected to be consumed readily without accumulation.

Bromine trifluoride may also enter into the reconversion of bromine to bromine pentafluoride after the fluorination reaction. For such a case, it will be necessary to determine the controlling reaction rate. Up to the present, only the reconversion of bromine trifluoride to bromine pentafluoride has been considered in the conceptual interhalogen converter because work up to this point was based on the early information.

Additional work on the design of the interhalogen conversion equipment will be undertaken so that the fluorination of bromine to bromine

TABLE II
DESCRIPTION OF SIMULATED BATCH COLUMN

Initial Charge*, mole	1.000	
Plutonium Hexafluoride Charged, mole	0.004	
Molybdenum Hexafluoride Charged, mole	0.002	
Uranium Hexafluoride Charged, mole	0.994	
Number of Theoretical Plates	20	
Holdup Per Theoretical Plate, mole	0.00874	
Boilup Rate, mole/hour	1.78	
Product Removal Rates, mole/hour	0.02	
System Pressure, atmospheres	2.0	
	<u>Case I</u>	<u>Case II</u>
Time (Condenser Draining), hours	1.0	2.0
Reboiler Holdup, mole	0.8052	0.7852
Initial Condenser Holdup, mole	0.02	0.04

* Calculations are based upon a unit mole charge to the column.

trifluoride and bromine pentafluoride is included. Bromine trifluoride can be made by bubbling fluorine gas through liquid bromine at about 50°C. Bromine pentafluoride is not readily made in this manner. Bromine vapor combines vigorously with fluorine vapor below 50°C. to form bromine trifluoride. Bromine pentafluoride is formed above this temperature, and the reaction is reported to be rapid at 200°C.* The commercial method for preparing bromine pentafluoride has been stated to involve reacting an excess of fluorine with bromine diluted with nitrogen in a copper vessel at 200°C.† A somewhat higher temperature would be desirable to allow reduction in contact time and thus in reactor volume.

It appears that the converter for making bromine pentafluoride from bromine might be essentially the same as that used for making bromine pentafluoride from bromine trifluoride. For a 24-inch diameter fluid-bed system, processing fuel at 75 pounds of uranium hexafluoride per hour per square foot of cross-sectional area, a converter about 10 to 12 inches in diameter and about 15 or 20 feet long should be capable of giving the desired conversion of bromine trifluoride to bromine pentafluoride. The wall temperature would be controlled at about 400°C.; however, it is likely that the reaction temperature would be as high as 750°C.; thus giving relatively rapid conversion.

Criticality Calculations

There are many applications for sorption traps in the fluoride volatility process. For example, upon the proper choice of operating conditions, certain fission products or uranium hexafluoride may be absorbed on sodium fluoride solids and subsequently be selectively released. Criticality computations have been completed for sodium fluoride-uranium hexafluoride sorption systems with 2, 5, and 6% uranium-235 enrichments. The systems were moderated by the presence of hydrogen fluoride. The work was undertaken to shed light on an acceptable size for the plant absorber vessel.

Studies were also made on the critical properties of plutonium in order to provide information relative to a safe batch size for the spent power reactor fuel charge to the head-end reactor.

Sodium Fluoride-Uranium Hexafluoride-Hydrogen Fluoride Systems. Under consideration for application in fluoride volatility processing are (a) a fluidized bed of the sorbent to isolate and purify the uranium hexafluoride in the gases leaving the fluorination reactor during treatment with bromine pentafluoride, and (b) static bed traps to collect fission products or traces of uranium hexafluoride in streams to be vented.

* Kluksdahl, H. E., and Cady, G. H., "Reaction of Bromine Trifluoride and Fluorine to Form Bromine Pentafluoride", J. Amer. Chem. Soc., 81, p. 5285 (1959).

† Matheson Gas Data Book, The Matheson Company, Inc., East Rutherford, New Jersey, p. 39 (1961).

Criticality calculations have been made for process systems assuming uranium enrichments of 2, 5, and 6% and the formation of uranium hexafluoride-sodium fluoride ($\text{UF}_6 \cdot 2\text{NaF}$) and the hydrogen fluoride-sodium fluoride ($\text{HF} \cdot \text{NaF}$) complexes during the sorption. Hydrogen fluoride was included because of the possibility that it will be present in the process as an impurity. Two nuclear safety parameters were determined: the neutron multiplication factors for infinite media, k_∞ , and the radii of infinitely long cylinders having an effective neutron multiplication, k_{eff} , of 0.90. All cylinder calculations include a water reflector 30 cm. thick.

Calculations were based on a uniform homogeneous mixture of $\text{UF}_6 \cdot 2\text{NaF}$ and $\text{HF} \cdot \text{NaF}$ with no voids. The amount of hydrogen fluoride present would be small under normal circumstances, but in order to cover the optimum atomic hydrogen-to-uranium ratio ranges for each assay, a wide range of volume fractions of $\text{UF}_6 \cdot 2\text{NaF}$ was considered. The uranium density in the pure uranium hexafluoride complex was taken as 2.25 g./cc. based on the density of $\text{UF}_6 \cdot 2\text{NaF}$ being 4.13 g./cc.*, while the hydrogen density in its complex was assumed to be 0.035 g./cc. based on the density of $\text{HF} \cdot \text{NaF}$ being 2.16 g./cc.†

Neutron multiplication factors for infinite media are shown in table III. Since the maximum calculated k_∞ for the system with 2% enriched uranium is less than 1.0, a critical homogeneous assembly is probably not possible for the given system at that enrichment. The maximum k_∞ for 5% enrichment is about 1.24 and occurs at a moderating ratio of about 110 atoms of hydrogen per atom of uranium-235.

Calculated radii for infinitely long cylinders having an effective neutron multiplication factor of 0.90 are listed in table IV. The minimum radius is about 29.3 cm. for 5% enrichment. This is slightly larger than the minimum radius for 6% enrichment; i.e., about 27.4 cm. In actual practice in either case, the vessel diameter based on $k_{\text{eff}} = 0.9$, would probably be about 2 feet considering actual vessel length. The transport code indicates a larger diameter ($k_{\text{eff}} = 0.90$) for 6% than for 5% enrichment at a volume fraction of 0.5. This anomalous result may be due to the differences in moderating ratios, as well as the accuracy of the calculations.

Plutonium Dioxide Systems. Plutonium-239 is produced in nuclear power reactors as the result of radioactive capture of neutrons by the

* McNeese, L. E., An Experimental Study of Sorption of Uranium Hexafluoride by Sodium Fluoride Pellets and a Mathematical Analysis of Diffusion with Simultaneous Reaction, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, November 29, 1963 (ORNL-3494), p. 59-63.

† Oak Ridge Gaseous Diffusion Plant Physics Department personnel calculated this density from ASTM unit cell determinations by X-ray photography.

TABLE III

NEUTRON MULTIPLICATION FACTORS FOR INFINITE MEDIA

Volume Fraction $\text{UF}_6 \cdot 2\text{NaF}$	Neutron Multiplication Factors		
	2%	5%	6%
0.70	0.890	1.09	1.01
0.60	0.955	1.17	1.10
0.50	0.972	1.22	1.17
0.40	0.959	1.24	1.23
0.30	0.896	1.22	1.25
0.20	0.786	1.16	1.22
0.10	0.556	0.953	1.04

TABLE IV

RADII FOR INFINITELY LONG CYLINDERS* WITH AN
EFFECTIVE NEUTRON MULTIPLICATION FACTOR OF 0.90

Volume Fraction $\text{UF}_6 \cdot 2\text{NaF}$	Uranium Density, g./cc.	5% Enrichment		6% Enrichment	
		Moderating Ratio, H/U-235	Radius, cm.	Moderating Ratio, H/U-235	Radius, cm.
0.50	1.127	73.5	31.9	61.3	33.4
0.40	0.901	110	29.4	91.9	29.4
0.35	0.789	138	29.8	114	27.4
0.30	0.676	172	29.9	143	27.9
0.25	0.563			184	27.5
0.20	0.451	294	34.2	245	30.7

* 30 cm. water reflector.

uranium-238 in the fuel. In addition, plutonium isotopes 240, 241, and 242 are formed from plutonium-239 by the capture of additional neutrons. The uranium-235 concentration in power reactor fuel is relatively low. Therefore, for criticality control, when uranium and plutonium are both present, the allowable batch sizing will depend, for the most part, on the amount of fissile plutonium. Plutonium-239 and -241 are fissile nuclides; however, plutonium-240 and -242 are essentially nonfissionable.

Calculations have been reported previously for plutonium-239 dioxide spheres reflected with alumina*. Additional calculations have now been based on the mixtures of plutonium-239, 240, 241, and 242 isotopes which would be present in irradiated low uranium-235 enrichment fuel. Cross-sections were obtained from published sources†.

Plutonium criticality calculations were made for fluoride volatility processing of fuel elements subjected to burnups of 10,000, 20,000, and 30,000 Mwd./tonne of uranium. The three irradiation levels were selected to cover the expected range at which future power reactors may operate. The plutonium isotopic compositions for these irradiation levels are listed in table V and are based on the assumption that 20% of the neutron flux is in the resonance region‡. The 20% resonance flux represents a compromise between the expected flux distributions in boiling water and pressurized water reactors. Since the percentage of total fissile plutonium decreases as the burnup increases, it might be expected that the mass required for a critical assembly would correspondingly increase. Computations were made to check this point and to provide estimates of the magnitude of the increase in critical mass.

* Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies Summary Progress Report Fiscal Year 1964 through Fiscal Year 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, October 29, 1965 (K-1649), pp. 49,50.

† Plutonium-239 and plutonium-240 cross-sections were obtained from Hanson, G. E., and Roach, W. H., Six and Sixteen Group Cross-Sections for Fast and Intermediate Critical Assemblies, Los Alamos Scientific Laboratory, 1961 (LAMS-2543); plutonium-241 and plutonium-242 cross-sections were obtained from Joanou, J. D., and Dudek, J. S., GAM-II, a B₇ Code for the Calculation of Fast Neutron Spectra and Associated Multiplication Constants, General Atomic, 1963 (GA-4265).

‡ Dawson, F. G., et al, "Plutonium Buildup and Depletion", Nucleonics, 23, No. 8, p. 101 (1965).

TABLE V
PLUTONIUM ISOTOPE COMPOSITIONS

Isotope of Plutonium	Isotopic Composition at Indicated Irradiation Levels, atom percent*		
	10,000 Mwd./tonne of Uranium	20,000 Mwd./tonne of Uranium	30,000 Mwd./tonne of Uranium
239	75	65	59
240	15	18	19
241	9	15	17
242	1	2	5
Total Fissile	84	80	76

* A 20% resonance flux is assumed in accordance with the work of Dawson, F. G., et al., "Plutonium Buildup and Depletion", Nucleonics, 23, No. 8, p. 101 (1965).

Calculated critical radii of spheres containing plutonium dioxide at various densities, and with the plutonium isotopic composition corresponding to that estimated for the above irradiation levels, are given in table VI. The assumption of a 30 cm. thick alumina reflector is considered conservative, as compared to the more usual choice of a light water reflector in chemical processing studies. For comparison purposes, results are also included based on all the plutonium being the plutonium-239 isotope. The critical radii for irradiated plutonium at the burnups studied range from 3 to 6% greater than that for plutonium-239 alone. Thus, assumption that all plutonium is as the 239 isotope would apparently be conservative by 10 to 20% for the power reactor fuel compositions used.

The critical masses of plutonium in plutonium dioxide spheres have been computed from the above sphere data for plutonium-239 alone and for the various plutonium isotopes present at 10,000, 20,000, and 30,000 Mwd./tonne of uranium. The data are plotted in figure 2. The estimated critical masses for plutonium-239 are about 10 to 20% lower than for the irradiated cases. The computed results indicate the critical mass for plutonium-239 will be about 33 kg. at 4.5 grams of plutonium dioxide per cubic centimeter, while it would range from 37 to 39 kg. at that density for material subjected to burnups of 10,000 to 30,000 Mwd./tonne.

The limiting plutonium density which might be encountered in the volatility process has not been definitely stated; however, a comparison may be made with criticality assumptions concerning enriched uranium

TABLE VI

CRITICAL RADII FOR PLUTONIUM DIOXIDE SPHERES*

Plutonium Dioxide Powder Density, g./cc.	Plutonium Density, g./cc.	Critical Radii Assuming Only Plutonium-239 Present, cm.	Critical Radii for the Plutonium Isotope Composition at Indicated Irradiation Levels, cm.		
			10,000 Mwd./tonne of Uranium	20,000 Mwd./tonne of Uranium	30,000 Mwd./tonne of Uranium
4.5	4.0	12.6	13.1	13.1	13.3
4.0	3.5	13.7	14.2	14.3	14.5
3.5	3.1	15.0	15.7	15.7	15.9
3.0	2.6	16.8	17.5	17.6	17.8
2.5	2.2	19.0	19.9	20.0	20.2

* A 30 cm. alumina reflector at 2.5 g./cc. was assumed.

Figure 2
CALCULATED CRITICAL MASS OF SPHERES
CONTAINING PuO_2 POWDER

processing. The uranium density of bulk uranium salt powders encountered in salvage operations normally does not exceed 3.2 grams of uranium per cubic centimeter unless the material has been purposely pressed and/or sintered. Since the crystal densities of the oxide salts of uranium and plutonium are estimated to be the same, a logical hypothesis is that the plutonium density of bulk plutonium dioxide powder would also run less than 3.2 grams per cubic centimeter. For complete coverage, the calculations described previously were made for a powder density range of 2.5 to 4.5 grams of plutonium dioxide per cubic centimeter, which corresponds to a plutonium density range of 2.2 to 4.0 grams of plutonium per cubic centimeter. Of course, use of a still lower plutonium density in alumina diluted portions of the system might be justified if sufficient operational data were obtained.

The mass limit for plutonium in volatility reprocessing of present power reactor fuels would also depend upon the effective neutron multiplication factor to be applied as a safety factor in calculations. In an actual operating case, a mass limit on the order of 20 kg. of plutonium might be imposed providing the density and moderation assumptions for this study are verified for any mass-limited part of the system. Obviously, in determining permissible batch sizes, necessary system operating inventories must be considered, and allowances must also be made for potential input accountability inaccuracies and for operational errors. Moreover, while these computations are applicable to unmoderated systems, some degree of moderation must be assumed in volatility processing equipment. For example, hydrogen fluoride should be considered present in criticality calculations for sorption traps and cold traps. It may be desirable to use geometry control, perhaps also incorporating nuclear poisons, for these equipment items. Additional calculations are planned for the infinite cylinder case, including the assumption of variation with moderation and for k values less than 1; i.e., for subcritical situations.

Cold Trap Studies

Cold traps may be extensively used in the volatility processing of spent power reactor fuel elements where uranium hexafluoride, plutonium hexafluoride, or other desublimable materials are to be collected. A cold trap digital computer program has been developed and debugged using checks versus ORGDP operational experience with uranium hexafluoride. In use, it should improve the accuracy of cold trap design and should simplify cold trap applications to new materials, as well as to new conditions. A design study for a plutonium hexafluoride cold trap is described below.

In the early design procedures, transient effects were ignored and solid buildups were calculated by assuming that the buildup rate, calculated for the empty trap, remained constant until the trap plugged. This assumption was found to be reasonable for most of the test cases for the program, but exceptions were encountered. A study of the solid buildup rate in a cold trap, undertaken in an effort to explain these exceptions, is described in the second topic under this subject.

Plutonium Hexafluoride Cold Trap. In the bromine pentafluoride volatility process, the dilute plutonium hexafluoride evolved from the main reactor by treatment with fluorine may be recovered by low temperature desublimation.

The reaction producing plutonium hexafluoride is relatively inefficient in that it requires the presence of large excesses of fluorine to proceed. At 400°C., the equilibrium mole ratio of plutonium hexafluoride to fluorine is only 5.6×10^{-3} *. Based on ANL experience, it has been assumed that only 10% of equilibrium conversion will take place. At a reactor temperature of 400°C., the mole ratio of plutonium hexafluoride to fluorine in the outlet gas would then be 0.00056. On the other hand, the concentration of condensables in the off-gas from the reactor may be increased if small amounts of residual uranium oxides, unconverted by the bromine pentafluoride treatment, are volatilized during the fluorine treatment. As the gas is fed to the cold trap, coprecipitation of uranium hexafluoride and plutonium hexafluoride may then take place because of the closeness of the vapor pressures and the similarity of the crystals. To account for the expected amount of uranium conversion, as well as for the possible coprecipitation, the total effective concentration of condensables was assumed for calculation purposes to be 0.075 mole percent. The gas stream would have to be cooled to lower than minus 90°C. for 99.9% recovery to be theoretically possible.

The likelihood that codeposition of plutonium hexafluoride and uranium hexafluoride takes place implies that the addition of uranium hexafluoride to the reactor effluent stream could allow operation of a cold trap at a higher temperature at the expense of producing a more dilute mixture of plutonium hexafluoride in uranium hexafluoride.

Computations indicate that, for linear velocities of the gas through the cold trap of 0.5 to 0.9 ft./sec., the gas side heat transfer coefficient would be between 0.75 and 1.5 Btu./hr.-sq.ft.-°F. A value of 1.0 Btu./hr.-sq.ft.-°F. is assumed for the purpose of this report. Since the total amount of condensables to be collected is small, the cold trap for plutonium hexafluoride collection may be considered as essentially a gas cooler for fluorine for sizing purposes. Based upon a plant-scale fluorine flow of 11.5 pound-moles per hour, i.e., as for a 24-inch diameter head-end reactor, required heat transfer areas were calculated. These areas are shown in figure 3, plotted for various exit gas temperatures as a function of coolant temperature. The normal boiling points of three possible coolants, argon, carbon tetrafluoride, and ethane, are indicated on this plot. It can be seen that argon and carbon tetrafluoride coolants could be used with traps around 100 sq.ft. in area, while the use of ethane appears borderline at best.

In figure 4, the theoretical recovery of plutonium hexafluoride in cold trapping is plotted as a function of the temperature of the exit gases.

* Trevorrow, L. E., Shinn, W. A., and Steunenberg, R. K., J. Phys. Chem., 66, 398-403 (1961).

Figure 3
HEAT TRANSFER AREA REQUIREMENTS FOR
PLANT-SCALE PuF₆ COLD TRAP

DWG. NO. G-66-349

Figure 4
THEORETICAL PuF_6 RECOVERY BY COLD TRAPPING

Curves are given for plutonium hexafluoride mole fractions of 0.0005, 0.00075, and 0.001 in the inlet gas at a total pressure of 1 atmosphere.

To estimate fin spacing, the rate of solid buildup within the equipment was investigated. Assuming the effective uranium hexafluoride-plutonium concentration totaled 0.075 mole percent, the maximum rate of solid buildup was found to be in the saturated region and was calculated to be about 0.004 inch per hour. Under the circumstances, a trap with flow passages as narrow as 1/8 inch would not be expected to plug in service over a 12-hour fluorination cycle.

Solid Buildup Rate in a Desublimer. A simple balance of the heat flux through the deposited solids against the heat transferred from the gas flowing through the trap to the surface of the solids shows that, under some conditions, a deposit thickness limit exists. This occurs when the surface temperature of the solid-gas interface reaches the saturation temperature for the composition of the particular gas passing above it. For higher surface temperatures, material would sublime from the deposit back into the gas stream. This limiting height is expressed by the following equation:

$$b_{\max} = \frac{K_s (T_s - T_w)}{h(T_g - T_s)}$$

where $b_{\max}$ = limiting deposit height, ft.

K_s = thermal conductivity of solid deposit, Btu./hr.-ft.-°F.

h = gas-to-solid heat transfer coefficient, Btu./hr.-sq.ft.-°F.

T_s = saturation temperature of gas stream, °F.

T_w = temperature of trap metal wall, °F., and

T_g = bulk gas stream temperature, °F.

From this, it is apparent that a limiting height exists when the gas stream is superheated; however, if the gas is saturated, $T_g = T_s$, no maximum exists. Test calculations seemed to indicate that the rate of deposition was quite rapid until the deposit height was nearly at the maximum, whereupon it tapered off sharply.

To determine the shape of a typical buildup versus time curve, a calculation was performed assuming a low concentration of condensable in the gas phase and all physical properties except vapor pressure constant with temperature. In this case, from a material balance about the system,

$$\alpha \int_0^b \frac{d\beta}{\ln \left[\frac{1 - \frac{p_s}{p_T}}{1 - x} \right]} = \theta$$

where α = grouping of physical constants

p_s = vapor pressure of condensable at solid surface temperature

p_T = total system pressure

x = mole fraction of condensable in gas stream

θ = time, and

β = variable of integration.

Figure 5 shows a plot of this function for uranium hexafluoride under typical cold trapping conditions. The shape of the graph, with its tapering off of buildup rate as the limiting thickness is approached, is typical of desublimation from a superheated gas. It can be seen from this plot that tapering off of the rate is quite pronounced for deposits thicker than about 70% of the maximum when fins are widely spaced.

This behavior has two important applications in trap design. First of all, it is possible to design a unit which will not plug in the superheat zone by choosing the proper fin spacing. Further, as the deposits approach the maximum in the superheat zone, heat transfer is impaired, and gradually the zone where the gas first becomes saturated moves further down the trap. Since the maximum deposit rate is often found in the zone in which the gas first becomes saturated, the effect is to spread this peak deposit over a larger trap volume, allowing more material to be collected before the unit becomes plugged. Secondly, in designing traps to handle streams initially rich in condensables which become lean later in the trapping cycle, it is quite important to have good information concerning the limiting and actual deposit heights developed early in the cycle. In this case, material trapped from the rich stream early in the run would sublime back into the gas stream as the gas became leaner and would be redeposited further down the unit. Variation in deposit height and condensables concentration could easily cause a marked change in resublimation rate and consequently in the trap holding capacity.

Figure 5
TYPICAL SOLID BUILDUP VERSUS TIME CURVE
FOR THE SUPERHEAT SECTION OF A COLD TRAP

PROTOTYPE TESTING AND EVALUATION

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Program emphasis during the report period was centered on the hydrogen chloride decladding, uranium dioxide pellet oxidation, and uranium fluorination steps of the Argonne elemental fluorine volatility process flow sheet. Among the highlights of the period was the completion of construction of the semiworks facility. Studies were also undertaken concerning corrosion, solids sampling, gas filtering, sorption-desorption, connectors for high-temperature equipment, valving, and peripheral compressor operation.

PROCESS AND REACTOR STUDIES

Activities included the completion and shakedown of the semiworks pilot plant, experiments with solids sampling devices, and tests of flow versus pressure drop in a prototype fluidized bed reactor.

The need for engineering data from large-scale equipment, as well as the need for assurance that the main plant processing components will be properly designed and instrumented, has led to the construction of the semiworks unit and pilot plant described previously*. The pilot plant consists of a head-end reactor, a filter cooler, a scrubber, and cold traps. Feed systems are provided for the introduction of hydrogen chloride, air, nitrogen, and fluorine into the reactor. Construction was carried out during the past six months and completed by the third week in June. Shakedown tests were then initiated.

Using an 8-inch diameter Plexiglas fluid-bed test unit, the pressure drops were measured across the fluidized portion of a bed of alumina, a bed of alumina supported by steel balls, and across the conical process gas entrance piece for a reactor. The results are described below.

In recognition of the material control needs of a volatility processing plant and the problems inherent in good accountability, testing of various sampling techniques is being carried out. The initial experiments were aimed at equipment suitable for obtaining a small, representative sample from a large quantity of solid being fed to it. The potential application would be in sampling fluid-bed solid wastes and discarded sorbent. It is also planned to employ these sampling techniques in connection with semiworks experiments.

* Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies Summary Progress Report, July through December, 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, June 28, 1966 (K-1669), pp. 39, 45-46.

A test of a radiation gauge suitable for determining bed density was performed. Accurate pellet bed levels could be determined for mixtures of alumina and uranium dioxide pellets. The device may thus be useful in connection with the semiworks studies; however, the radiation level of irradiated fuel would probably be too high for utilization without drastic changes.

Cold Semiworks Pilot Plant

The construction of the semiworks pilot plant has been completed. The semiworks reactor (figure 6) and filter cooler (figure 7) were fabricated and assembled in the ORGDP shops in accordance with the provisions of Section VIII of the ASME Unfired Pressure Vessel Code. The vessels were pressure tested, welded, radiographed, and dye checked. Prototypes of proposed connectors were included in the plant piping for evaluation.

After preoperational testing of the equipment was completed, the reactor was charged with minus 60-mesh alumina and was fluidized with nitrogen at velocities up to 1-1/2 feet per second in the 5-inch diameter section. Gases were injected into the bottom, or simultaneously into the bottom and the side nozzle, just below the transition piece between the two diameters. Fluidization, as viewed from the opened top of the reactor, appeared normal, and turbulence was satisfactory in both cases.

A 24-hour elutriation test was carried out. The reactor was filled with 285 pounds of minus 48- plus 100-mesh alumina and the filter cooler with 180 pounds of the same material. The reactor was heated to 427°C. and the filter cooler to 100°C. These temperatures were maintained during the test except for an 8-hour period between 12 midnight and 8 a.m., when the power was off. The pressures were measured to be approximately 26 psia. in the bottom of the reactor and 18 psia. in the bottom of the filter cooler. Fluidization was continuous, using a flow averaging 600 std.cfh. of nitrogen. The 600 std.cfh. flow corrected for operating temperature and pressure gave a superficial velocity of 1.7 ft./sec. in the 5-inch diameter section of the reactor, a 0.42 ft./sec. velocity in the 10-inch diameter section of the reactor, and a 0.24 ft./sec. velocity in the cooling section of the filter-cooler. A total of 31 pounds of alumina was collected in the overflow from the filter cooler at the end of the test. There was essentially no decrease in the weight of alumina in the reactor, indicating that the overflow alumina came from the filter cooler.

In the first experimental runs, reactor grade uranium dioxide pellets now on hand will be used as feed material in a series of oxidation runs. The parameters to be studied will include the percentage of oxygen in the fluidizing gas, reaction temperature, fluidization velocity, and the ratio of alumina to uranium. When these tests are completed, it is then planned to study the decladding processes with mockup fuel elements prepared by filling zircaloy tubing with some of the uranium dioxide pellets. Separate fluorination tests or process cycle experiments will then follow.

Figure 6
SEMIWORKS REACTOR

Figure 7
FILTER COOLER

Pressure Drop Measurements in a Fluidized Bed

A test apparatus to simulate the bottom design of a fluidized bed reactor was constructed with a section of column and a flow distribution cone for the introduction of fluidizing air. The injection nozzle and the cone were constructed of stainless steel, while the column was fabricated from 8-inch diameter Plexiglas. A sketch of the equipment is shown in figure 8. Pressure drops were measured across the fluidized beds in the cone and in the column at various gas flows using a U-tube manometer. Pressure at the bottom of the cone was measured at the air inlet, while an adjustable probe mounted above the open top of the Plexiglas column was used to determine the pressures at various levels in the column.

Measurements were first made across the bottom cone. Since the current thinking for the hot pilot plant at ORNL is to use small metal balls in the conical gas entrance section to support the bed of powder, tests were made with two different sizes; $5/8$ inch and $9/32$ inch. For these runs, the conical bottom section was filled to the top with steel balls and 25 inches of Norton 90-mesh RR Alundum was added to the column. Pressure drops across the conical section are shown in figure 9 versus gas velocities from 0.5 to 2.72 ft./sec. The gas velocities were computed based on the larger cross-section of the cone (8 inches in diameter), a temperature of 25°C . and 1 atmosphere pressure. As the gas velocity was raised, the pressure drop across the ball-filled cone also increased and, at the higher velocities, audible indication of ball motion was noted.

Pressure drops were also measured across the cone when the cone was filled with alumina alone, and there was 25 inches of alumina in the 8-inch diameter column. The data are plotted on figure 9 to permit comparison with the initial data. The pressure drop across the powder-filled cone was constant between 0.5 and 1.8 ft./sec. velocities. In the velocity range of 0.5 to 1.0 ft./sec., the pressure drops for both ball sizes are essentially the same but lower than the drops for the cone filled with alumina powder alone. At superficial gas velocities above 1 ft./sec., the pressure drop across the powder-filled cone was lower than the pressure drop across either ball-filled cone. The supposition that the powder was probably not filling the spaces between the balls even at the low velocities, was verified when the charge was drained from the system. Very little alumina was observed until all the $9/32$ -inch balls were removed. It should be noted that the $9/32$ -inch balls drained easily but that rapping and rodding were required with the $5/8$ -inch balls.

Measurements of pressure drops were taken across various bed depths within the column section with and without the balls in the gas entrance cone. The data, taken at a superficial gas velocity of 0.7 ft./sec., are shown in figure 10. At each of several velocities, the pressure drops per foot of bed depth were calculated from pressure drop measurements at depths every 6 inches between $1/2$ foot and $2-1/2$ feet. These data were averaged and plotted in figure 11 versus the velocity. As can be seen in figure 10, the presence of the balls in the cone had no noticeable effect on the pressure drops in the upper section. In light of the direct relationship

Figure 8
FLUID BED TEST APPARATUS

Figure 9

PRESSURE DROP ACROSS BOTTOM CONE VERSUS THE GAS VELOCITY

Figure 10
PRESSURE DROP ACROSS FLUIDIZED BED SECTION
VERSUS BED DEPTH

Figure 1.1
EFFECT OF GAS VELOCITY ON THE PRESSURE DROP
PER FOOT OF ALUMINA BED IN THE COLUMN SECTION

between pressure drop and fluidized bed density, figure 11 also shows the relative decrease in fluidized bed density with increased gas velocity.

Sampling

In monitoring the operation of the fluoride volatility plant for accountability as well as for process control, sampling of solids will be necessary. Representative sampling of the large amounts of solids present in the main process equipment is considered to be a major problem. Two solids samplers, a 6-inch Vezin type and a 20-inch Park type, have been purchased from the Denver Equipment Company for testing.

The Vezin sampler employs a bucket-shaped cutter arm which rotates in a horizontal plane at a constant speed through a vertically flowing stream of the dry material to be sampled. The sample flows through the cutter arm to a collection tray, while the bulk of the stream is rejected. In the Park sampler, the stream to be sampled falls on a rotating disc and moves to the edge where a portion flows into a sample receiving tube. The remainder of the feed falls off the edge of the plate and passes out of the equipment.

The Vezin sampler was tested for the size of the sample cutting and the precision of the operation. The first series of tests was conducted using 1/8-inch diameter by 1/8-inch long pellets of sodium fluoride and sodium bifluoride. Twenty-five pounds of each compound was dumped together with no attempt to blend the mixture. This mixture was then fed to the Vezin sampler at the rate of 4.6 pounds per minute. A series of eight replicate runs resulted in sample cuts which ran 5.36 weight percent of the original throughput with a standard deviation of 0.04%. An average increase of $0.15\% \pm 0.14\%$ in fines concentration due to pellet degradation was experienced with each run in series. Since the size of each of the resultant samples was still relatively large, i.e., about 2.7 pounds, the sample was reduced by a second pass through the Vezin unit. A feed rate of 4.6 pounds per minute was employed. The result was a sample cut which was 5.23 weight percent of the first sample.

Next, a cursory test of the precision of the 6-inch sampler was undertaken. A mixture containing 20.0 weight percent yellow sodium fluoride-uranium hexafluoride complex pellets in white sodium fluoride pellets was processed through the sampler at a feed rate of 4.6 pounds per minute. The sample cut was 5.24%, and this sample was then rerun several successive times to reduce the size further. The yellow pellets were removed from each cut and weighed, and the mean complex concentration in the samples was found to be 20.32% by weight. Since the results of this test are encouraging, a multilevel sampling test will be designed to permit evaluation of the equipment on a statistical basis.

Efforts to operate the 20-inch sampler on pellets were unsuccessful as the pellets clogged the flow to a spinning sampling disc within the equipment. Further tests on this sampler will involve powder sampling.

It is planned to conduct the sampler evaluation program using various types and sizes of solids for the following purposes:

1. To determine if the basic sampler operational principle can be applied to the sampling of the various fluoride volatility process materials.
2. To determine the feed rate range of the samplers for various materials.
3. To assess the sampling capability, capacity, and efficiency, and to uncover possible biases.
4. To determine if the sampler is adequately self-cleaning.

Solids Material Level Indicators

During chemical decladding of fuel elements, the freed uranium dioxide pellets should fall to the bottom of the reactor unattacked by the anhydrous hydrogen chloride. Several techniques for evaluating the degree of completion of the decladding reaction are being investigated, one of which involves measurement of the level of accumulated uranium dioxide pellet bed in the bottom portion of the reactor. An available Ohmart Nuclear Gauge Model PG-100-6-090150, containing 150 millicuries of cesium-137 was modified for use as a level gauge. One end of a length of 5-inch Monel pipe was sealed and equipped with a gas inlet port. The assembly was installed so that it could be raised or lowered through the Ohmart unit. A 1-inch thick lead plate was installed in the gamma beam from the unit to reduce sensitivity and to obtain on-scale meter output readings. A bed of Alcoa tabular alumina (minus 48 to plus 100 mesh) was charged to the pipe. A series of tests was then conducted. A base reading profile was obtained for a static bed of alumina. The bed was then fluidized with air, and another set of readings was taken. The bed level was determined satisfactorily within an accuracy of ± 1 inch. About 10 kg. of uranium dioxide pellets (1/2 inch in diameter by 3/4 inch long) was then added to the fluidized alumina, and another set of readings was taken. Both the alumina and uranium dioxide pellet levels were determined within the ± 1 inch accuracy. Moreover, the accuracy was unchanged by varying the superficial fluidizing velocities from 0.28 to 0.37 ft./sec. The results of these tests indicate that this type of measurement may be acceptable for use on the semiworks equipment.

MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES

The program to study corrosion in process gas cycles was continued with tests on Hastelloy B and Hills-McCanna Company nickel alloy number 72. Samples of these metals, together with samples of nickel-201 and Duranickel, were submerged in a fluidized bed of minus 48- to plus 100-mesh Alcoa tabular alumina and were subjected to 5 cycles of corrosive atmospheres. Each cycle consisted of hydrogen chloride and hydrogen (composition by volume: 50% hydrogen chloride, 15% hydrogen, and 35% nitrogen) at 400°C. for 5 hours, air at 540°C. for 10 hours, and dilute fluorine

at 540°C. for 10 hours. Since nickel-201 and Duranickel had been tested before, they were run to permit comparisons with early work. The nickel alloy number 72 had been proposed as seat material for ball valves for the fluoride volatility environment. Hastelloy B, while suitable for the hydrogen chloride dechlorination step, had not been tested in the overall corrosive gas cycle. The corrosion results are listed in table VII. As in earlier tests, nickel and Duranickel exhibited relatively little corrosion. On the other hand, both the Hastelloy B and alloy number 72 samples were coated with a hard, yellow scale similar to the corrosion products formed on metals tested previously* which were unsuitable for the environment.

TABLE VII
RESULTS OF CORROSION TESTS
IN FLUORIDE VOLATILITY PROCESS GAS CYCLES

Sample	Initial Weight, g.	Final Weight, g.	Corrosion Penetration, mils/year
Nickel	103.9224	103.2443	37
Duranickel	91.6141	91.1446	32
Hastelloy B	93.5290	88.9479	190
Alloy No. 72	120.2243	116.3824	325

Although INCO-61 welding rod has been assumed to be acceptable for use on relatively low temperature locations in the fluoride volatility process equipment, some concern was registered as to possible attack during periods of plutonium cleanup. During plant operation, equipment would be exposed to fluorine at 350°C. to reconvert plutonium tetrafluoride to plutonium hexafluoride. Samples of INCO-61 welding wire and nickel-200 welded with INCO-61 welding rod were exposed to fluorine at 360°C. for 69 hours. The corrosion results are shown in table VIII. Both samples appeared to be unattacked by the exposure, although the weld area of the welded sample was slightly discolored.

* Smiley, S. H., Brater, D. C., and Pashley, J. H. ORGDP Fuel Reprocessing Studies Summary Progress Report Fiscal Year 1964 through Fiscal Year 1965, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, October 29, 1965 (K-1649), pp. 54-55.

TABLE VIII
RESULTS OF INCO-61 CORROSION TESTS

<u>Sample</u>	<u>Initial Weight, g.</u>	<u>Final Weight, g.</u>	<u>Corrosion Penetration, mils/year</u>
INCO-61 Wire	30.4969	30.4943	0.33
Ni-200 Welded with INCO-61 Welding Wire	61.2265	61.2214	0.90

A sample of nickel wool proposed for use as mist filter material in the outlet gas stream from the cold traps in the ORNL hot pilot plant was exposed to fluorine at 350°C. for 12 hours. No weight change was detected, and visual observation found little discoloration.

OUTLET GAS FILTER STUDIES

Considerable experimentation has been conducted with two Huyck Metals Company filter tubes. These tubes were fabricated from a mat of certified nickel fibers encased in a nickel wire mesh screen and were TIG (tungsten inert gas) welded using INCO-61 rod. The filter units were first subjected to an approximately 300-hour corrosion test involving 9 cycles of operation, each cycle consisting of hydrogen chloride and hydrogen (composition by volume: 50% hydrogen chloride, 15% hydrogen, and 35% nitrogen) at 315°C. for 5 hours, air at 100°C. for 10 hours, and dilute fluorine at 100°C. for 10 hours. The gases were first passed through a bed of Alcoa tabular alumina, nominally minus 48 to plus 100 mesh, and the bed was fluidized at a velocity of about 1 ft./sec.

The tubes appeared to be in good condition at the conclusion of this phase of the test. Flow tests made before and after the experiment indicated a 25% loss in permeability. No visible cracking or corrosion was observed.

The tubes were then reinstalled in the filter test loop and exposed to about 20% fluorine at 315°C. for an additional 108 hours. This phase of the testing was designed to simulate conditions that might be expected for plutonium cleanup in the fluoride volatility equipment. Air flow measurements indicated that the permeability had decreased by an additional 7% as the result of the extension of the experiment to give a total permeability decrease of 32%. Again no weld cracking or evidence of serious chemical attack was found.

Permeability decreases in the range of 25 to 32% are considered minor in industrial applications and are normally reflective of filter pre-coating. Such filters are subsequently useful over a long operating

period. It therefore appears that the Huyck filter tubes may be acceptable for service in volatility process environments.

Additional determinations have been made to establish the rate at which powder accumulates on filter tubes. A bed of minus 48- plus 100-mesh Alcoa tabular alumina was fluidized at 1 ft./sec., and the gases passed through two Huyck Metals Company tubes at 0.53 std.cfm. per square foot of filter surface area. An automatic blowback system provided a reverse flow of 0.12 cubic foot of nitrogen per square foot of filter area every 12 minutes. The filters were removed after 300 hours of service, and the powder coating was brushed off and weighed. The depth of the powder was computed to be 0.02 inch based on an assumed density of 0.8 g./cc.

PRODUCT PURIFICATION, SORPTION-DESORPTION SYSTEMS

Inert gases from cold trapping and purging operations, and from various process exhausts, may contain trace concentrations of uranium hexafluoride. Recovery of this uranium hexafluoride is desirable from the viewpoints of economics and health. The 4-inch diameter pellet trap was adapted to test the sorption capability of sodium fluoride pellets under these process conditions.

The trap was charged with 34 pounds of sodium fluoride which thus provided a bed 7 feet high and operated at 121°C. The sodium fluoride pellets were prepared by heating sodium bifluoride cylinders, 1/8 inch in diameter by 1/8 inch long, at 540°C. for 5 hours in an inert atmosphere. Nitrogen, with an average uranium hexafluoride concentration of 450 to 500 ppm., was fed to the trap using a gas flow rate of 2.5 std.cfm., i.e., a superficial gas velocity of 0.68 ft./sec. at the operating temperature. Analyses of the gas stream from the trap indicated an average concentration of about 10 ppm. of uranium hexafluoride during the 300 hours of testing before breakthrough. Up to that time, the pellets had sorbed about 19 pounds of uranium hexafluoride, giving a uranium hexafluoride-to-sodium fluoride ratio of 0.56.

After the trap was regenerated by heating to desorb the uranium hexafluoride, the sorption was resumed at the same gas flow but with a uranium hexafluoride concentration of about 130 ppm. During the next 340 hours of operation, the uranium hexafluoride concentration in the outlet gas held at 30 ppm., after which time breakthrough occurred. A total of 7.1 pounds of uranium was processed through the pellets, giving a uranium hexafluoride-to-sodium fluoride ratio of 0.21.

The concentrations of the outlet gases in these tests are possibly satisfactory for plant streams but are higher than expected. Further studies are planned employing lower superficial velocities and correspondingly increased residual times.

CONNECTORS

Studies of connector designs, involving the use of age-hardened Duranickel flat-faced flanges compressing various configurations of dead-soft nickel gaskets, have continued during this period. Provisions were made for double gasketing, thus creating a sealed annulus which could be pressurized and thus monitored to detect leaks.

Two connector assemblies were tested during this period, each unit compressing a two-touchpoint, serrated nickel ring gasket between two 150-pound, 4-inch Duranickel flanges using 5/8-inch diameter Inconel-X studs. A nitrogen pressure of 10 psi. within the buffer seal was used to detect leaks. The first joint was sealed using a total loading pressure of 150,000 pounds, and the second connector sealed at a loading of 190,000 pounds. The units were then heat cycled in an oven. The first joint remained tight for 8 cycles, fluctuating between 100 and 370°C. but developed leakage when the temperature was increased to 540°C. The second test unit successfully cycled between 100 and 370°C. for 15 complete cycles but leaked when the temperature was increased to 500°C. Measurements made before and after the tests indicate that either the bolts expanded at the thread area, or the nuts loosened during the heat cycling.

New joint concepts are also being developed incorporating the use of a temperature-compensating clamp which is designed to maintain a constant loading pressure over a wide temperature range. At the same time, a program has been initiated to redesign conventional basic joints for remote operation. Some of the design considerations are insertion, positioning and removal of gaskets, bolt layout and material selection, and parts reuse. A survey will also be made of electromechanical manipulators capable of performing the tasks required for connector operation and maintenance.

VALVES

Initial efforts to find suitable valving components for fluoride volatility processing have been directed to a survey of commercial items.

One of the special valve applications being considered is a fuel element charging valve for location on the top of the main reactor. An 8-inch nickel-plated stainless steel slide valve was obtained for inspection and testing. This valve is one being considered for charging use in the ORNL hot pilot plant. The test valve, supplied by Mill Lane Engineering Company, Inc., Burlington, Massachusetts, is air operated by means of a 4-way solenoid valve. A 100 psig. air supply drives the valve slide by means of a piston assembly. The valve seat seal is made by forcing the slide disc against a metal O-ring imbedded in the valve body.

The valve was opened and closed about fifty times with no malfunctioning of the components. A hold test indicated a seat leakage of about 0.1 std.cfd. which should be acceptable for the proposed use, since this

valve is not the ultimate seal to the atmosphere. This valve has been shipped to ORNL.

Bids were prepared for 2-inch ball, slide, or plug prototype valve to be applicable to handling bed solids removed from the semiworks reactor and the filter cooler. The valve was to be of all-metal construction with a hermetically sealed stem. There was little vendor interest, probably because of material limitations due to expected high radioactivity and corrosive environments. One company proposed a development contract. Pending procurement of all-metal valves, Monel plug or ball valves with Teflon sleeves and Teflon packing will be employed in the semiworks pilot plant for experimental convenience. The bodies will be cooled to prevent damage to the Teflon. Such valves would probably not be satisfactory in long-term plant applications because of the relatively poor radiation resistance of the plastic. Efforts to find valves suitable for use in volatility processing plants will continue. Commercially available units may be modified for testing to evaluate potential applicability to plant use.

COMPRESSORS

It is anticipated that in the volatility process, recycle of process gases will be required during the decladding and fluorination cycles. The pump showing the most promise for this application is the ORGDP peripheral compressor. Such a compressor, constructed of nickel and Duranickel, has been fabricated and installed in the volatility compressor test loop. It has been operated for more than 520 hours. Air was compressed during the initial stages of the test, but the last 230 hours has involved the pumping of mixtures of fluorine and nitrogen. Due to the high-speed instability of the presently used variable-speed motor-generator drive set, the speed of the compressor had to be maintained at about 10,000 rpm., or 1,000 rpm. less than the designed speed. This situation is to be corrected by use of a new motor-generator set. Even though the compressor speed is low, pumping rates of 70 std.cfm. of concentrated fluorine are being attained, with suction and discharge pressures of 1 and 2 atmospheres, respectively. Thus, even at the lower speed, the pump has met original design requirements. Additional studies on performance characteristics are planned with mixtures of fluorine and nitrogen.

Operating data with air indicate individual stage compression ratios of 1.4 and gas temperature increases of about 115°C. for each stage. The operating bearing temperatures appear to be steady at values of 60°C. for the load bearing and 40°C. for the outer bearing. Power requirements are about 6 kw.

It was discovered that a minor modification was required to assure bearing protection from exposure to the process gases in the event of emergency stops. A sudden shutdown of the pump would allow the process pressure inside the seal cavity to increase to a value greater than the seal feed supply pressure. Consequently, process gas could flow back

through the seal into the motor housing. By providing a higher nitrogen supply pressure, a temporary correction has been made; however, the entire seal arrangement for the final pump design will be reviewed.

Future testing of the peripheral compressor includes continuous service with fluorine for a target of 2,000 hours. The pump will be disassembled for inspection at the end of the test period. The same pump can be used for later hydrogen chloride recycle studies, providing it is in satisfactory condition. The channel inserts would probably be changed to obtain performance characteristics consistent with volatility processing plant conditions, and requirements.

Although performance to date in the fluorine recycle test operations with the present bearing system design has been good, the bearing system will also be tested on a separate rig to evaluate the full extent of its service life in continuous 7-day per week operation at 11,000 rpm.