AEC RESEARCH AND DEVELOPMENT REPORT

NOV 2 1965

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
FISCAL YEAR 1964 THROUGH FISCAL YEAR 1965

AUTHORS:

S. H. Smiley
D. C. Brater
J. H. Pashley

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

**UNION
CARBIDE**

UNION CARBIDE CORPORATION
NUCLEAR DIVISION

Operating the

OAK RIDGE GASEOUS DIFFUSION PLANT	• OAK RIDGE NATIONAL LABORATORY
OAK RIDGE Y-12 PLANT	• PADUCAH GASEOUS DIFFUSION PLANT

*For the Atomic Energy Commission
Under U.S. Government Contract W7405 eng 26*

DISCLAIMER

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

DISCLAIMER

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

Printed in USA. Price \$4.00. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U.S. Department of Commerce, Springfield, Virginia

— LEGAL NOTICE —

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Date of Issue: October 29, 1965

Report Number: K-1649

Subject Category: Chemical Separations
Processes for
Plutonium and Uranium
TID-4500 (45th Ed.)

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
Fiscal Year 1964 Through Fiscal Year 1965

S. H. Smiley
D. C. Brater
J. H. Pashley

Engineering Development Department
Technical Division

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

A B S T R A C T

During the past several years, the Atomic Energy Commission has been sponsoring technical and scientific studies of a group of processes aimed at recovering valuable uranium and plutonium from spent nuclear reactor fuels by dry gas techniques. In essence, these elements are volatilized as the hexafluorides, and most of the undesirable fission products are left behind. Purification from volatile fission products is accomplished by distillation or selective sorption.

Basic technology for recovering both high and low enrichment fuels by volatility methods is being provided by the Argonne, Oak Ridge, and Brookhaven National Laboratories. During the past two years, the Oak Ridge Gaseous Diffusion Plant Technical Division has supported the main effort of the National Laboratories in two ways. First, conceptual plant studies have been performed, including economic comparisons of alternative process flow sheets. These evaluations have attempted to define process problem areas and to point to the optimum route to a successful commercial enterprise. Second, a components development program has been initiated covering scale-up and testing of crucial process equipment and auxiliaries. The report which follows is primarily a summary presentation of the Oak Ridge Gaseous Diffusion Plant work carried out during fiscal years 1964 and 1965.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	17
SUMMARY	18
ENGINEERING STUDIES	18
HIGH ENRICHMENT FUELS	18
LOW ENRICHMENT POWER REACTOR FUELS	19
Zircaloy-Clad Fuel Process	19
Stainless Steel-Clad Fuel Process	19
Interhalogen Flow Sheet	20
Head End Fluid-Bed Reactor	20
Radioactive Heat Generation	20
Alumina Diluent and Bed Storage Costs for Power Reactor Fuel Processing	20
CRITICALITY CALCULATIONS	21
High Enrichment Fuels	21
Low Enrichment Fuels	21
Plutonium	21
COLD TRAPS	21
PROTOTYPE TESTING AND EVALUATION	21
MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES	22
PROCESS AND REACTOR STUDIES	23
OUTLET GAS FILTER STUDIES	24
PRODUCT PURIFICATION, SORPTION-DESORPTION SYSTEM	24
CONNECTORS	25
COMPRESSORS	25

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS (Contd.)

	<u>Page</u>
REACTOR FABRICATION PROCEDURES - WELDING STUDIES	25
DISCUSSION	26
ENGINEERING STUDIES	26
HIGH ENRICHMENT FUELS	26
LOW ENRICHMENT POWER REACTOR FUELS	30
Zircaloy-Clad Fuel Process	30
Stainless Steel-Clad Fuel Process	34
Interhalogen Flow Sheet	35
Head End Fluid-Bed Reactor	39
Radioactive Heat Generation	41
Alumina Diluent and Bed Storage Costs for Power Reactor Fuel Processing	43
CRITICALITY CALCULATIONS	45
High Enrichment Fuels	45
Low Enrichment Fuels	47
Plutonium	49
COLD TRAPS	50
PROTOTYPE TESTING AND EVALUATION	53
MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES	53
Filter Materials	53
Flange and Reactor Materials	59
PROCESS AND REACTOR STUDIES	62
Decladding and Fluorination Studies	67
Inert Gas Fluidization	67

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS (Cont'd.)

	<u>Page</u>
Semiworks Reactor	68
OUTLET GAS FILTER STUDIES	70
PRODUCT PURIFICATIONS, SORPTION-DESORPTION SYSTEM	74
Cylindrical Pellet Trap	74
Annular Pellet Trap	80
Fluidized Bed	80
CONNECTORS	85
Marman Conoseal	85
Flat-Faced Flange Connectors	89
COMPRESSORS	89
Peripheral Compressor	96
Seal Development	98
Compressor Aerodynamics	98
Test Rig Evaluation of Design Features	104
Diaphragm Compressor	106
REACTOR FABRICATION PROCEDURES - WELDING STUDIES	107

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Cycle Times for Zirconium and Aluminum Fuels	28
II	Physical Properties of Bromine Pentafluoride, Bromine Trifluoride, and Uranium Hexafluoride	37
III	Temperature Rise in a 20-Inch Diameter Settled Bed with Volume Heat Generation	42
IV	Element Temperature Transients in Settled Bed for 14 x 14 Pseudo-Westinghouse Module in 16-Inch Diameter Bed	44
V	Alumina Usage Economics	45
VI	Critical Size of Urano-Uranic Oxide Spheres for Different Multiplication Factors, k_{eff}	46
VII	Infinite Medium Neutron Multiplication Constants for Uranium Dioxide-Alumina Mixtures	47
VIII	Critical Radii of Infinite Cylinders Containing Uranium Dioxide-Water Mixtures	48
IX	Critical Spheres of Uranium Dioxide-Water Mixtures	49
X	Critical Mass of Plutonium Dioxide Spheres Reflected with Alumina	50
XI	Calculated Uranium Hexafluoride Capacity for 10-Inch Diameter, "Egg-Crate" Type Cold Trap	52
XII	Results of Corrosion Tests	54
XIII	Results of 4-Inch Diameter Sodium Fluoride Trap Sorption Tests	76
XIV	Effect of Preparation Temperature on Sodium Fluoride Pellet Characteristics	77
XV	Results of Annular Trap Sorption Tests	84
XVI	Design Criteria for Fluid-Bed Volatility Loop Compressors, 1 Tonne of Uranium Per Day Line	96
XVII	Performance of 1.9375-Inch Diameter Bushing Seal	104
XVIII	Corblin Compressor Performance Specification	106

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Decladding and Chemical Pretreatment	31
2	Fluorination and Product Recovery	32
3	Power Reactor Fuel Reprocessing Plant	33
4	Interhalogen Reference Flow Sheet	36
5	Corrosion of Porous Nickel	57
6	Porous Nickel Exposed to Fluorine at 550°C.	58
7	Electroless Nickel Plate Corrosion Attack	60
8	Duranickel Corrosion Attack	61
9	Corrosion Results (Test No. 8)	63
10	Corrosion Results (Test No. 8)	64
11	Corrosion Results (Test No. 7)	65
12	Corrosion Results (Test No. 7)	66
13	Semiworks Fluid-Bed Reactor	69
14	DRD Filter Test Loop	71
15	Porous Nickel Filter Failures	73
16	4-Inch Sorber Loop	75
17	Sodium Fluoride Pellets	79
18	Annular Trap	81
19	Annular Trap Loop	82
20	Continuous UF_6 Sorption System	83
21	Marman Conoseal Single Seal	86
22	Marman Conoseal Double Seal	87
23	Nickel Marman Conoseal After Heat Cycling	90
24	Double Ring Gasket	91

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

LIST OF FIGURES (Contd.)

<u>Figure</u>		<u>Page</u>
25	Serrated Gasket	92
26	Milled Multiple Touchpoint Gasket	93
27	Multiple Touchpoints on Flange - Flat Gasket	94
28	Duranickel Fractures	95
29	Single Stage Peripheral Compressor	97
30	Two-Stage Peripheral Compressor	99
31	Peripheral Compressor Dual Stage Results	100
32	Peripheral Compressor Dual Stage Results	101
33	Peripheral Seals	102
34	Peripheral Compressor Channel Characteristics	103
35	Peripheral Compressor Impellers	105
36	Corblin Pump Loop	108
37	Corblin Compressor	109
38	Corblin Vibration Measurements	110
39	Corblin Fluorocarbon Oil Pressure Measurements	111

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ORGDP FUEL REPROCESSING STUDIES
SUMMARY PROGRESS REPORT
Fiscal Year 1964 Through Fiscal Year 1965

INTRODUCTION

Competitive nuclear power depends upon the realization of certain technological and economic successes, and an important part of the overall picture is the fuel cycle. With the development and demonstration of economically sound systems for reprocessing nuclear fuels as its stated objective, the AEC's Chemical Separations and Development Branch has supported comprehensive development programs at the Argonne, Oak Ridge, and Brookhaven National Laboratories.

The design of the first commercial reprocessing plant to be built, i.e., Nuclear Fuel Services, was based on the aqueous separations technology which had a history of use at government plants at Hanford, Savannah River, and Idaho Falls and major long-term technical support from ORNL, ANL, and BNL, as well as from the processing sites themselves. During the past several years, the AEC has also been sponsoring technical and scientific studies of a basically different group of processes aimed at recovering valuable uranium and plutonium by dry gas techniques. In essence, these nuclear fuels are volatilized as the hexafluorides, and most undesirable fission products are left behind. Purification from volatile fission products is accomplished by distillation or selective sorption.

Basic technology for recovering both high and low enrichment fuels by volatility methods has been and is being provided by the three National Laboratories already named. Particularly, at this writing, participating groups are fully occupied exploring the chemical and technical feasibility of the various process alternatives for handling low enrichment fuels. Laboratory development programs on high enrichment fuels are essentially complete.

During the past two years, the Oak Ridge Gaseous Diffusion Plant Technical Division has supported the main effort of the National Laboratories in two ways. First, conceptual plant studies have been performed, including economic comparisons of alternative volatility process flow sheets. These evaluations have attempted to define process problem areas and to point to the optimum route to a successful commercial enterprise. Second, a components development program has been initiated covering scale-up and testing of crucial process equipment and auxiliaries. In some cases, e.g., the process recycle compressor, the complete development and design program has been undertaken at the ORGDP.

The report which follows is primarily a summary presentation of the work carried out during fiscal years 1964 and 1965. Bimonthly progress reports have been issued regularly during this period to a limited AEC distribution. Henceforth, ORGDP work will continue to be reported bimonthly and summarized semiannually.

SUMMARY

ENGINEERING STUDIES

Studies of the economic and technical feasibility of processes for recovery of fissile material from irradiated nuclear fuels are being performed at the Oak Ridge Gaseous Diffusion Plant to provide guidance for the associated laboratory and engineering experimental programs supported by the Chemical Separations and Development Branch of the Division of Reactor Development. The tangible result of such evaluations is the development of conceptual plant designs with associated costs accompanied by realistic appraisals of potential scale-up problems. Coupled with this engineering effort is a comprehensive systems analysis study designed to summarize the large number of process alternatives and problems and to indicate those work areas that should be emphasized in the integrated overall DRD program.

A brief resume of ORGDP feasibility studies (both completed and in progress) concerned with reprocessing of spent high enrichment uranium fuels and power reactor clad uranium dioxide materials appears in this report. Included also are more detailed calculations relating to specific problems, such as alumina bed usage economics, bed temperature rises due to radioactively generated heat, criticality considerations for high and low uranium enrichment fuels, and cold trapping equipment.

Historically, the ORGDP participation began with the evaluation of processes for high enrichment fuels, since National Laboratory development programs were considerably more advanced for this class of fuel. The emphasis has now shifted almost completely to the low enrichment power reactor fuels; however, much of the component work and, to a lesser extent, the engineering analyses is applicable to either high or low enrichment materials.

HIGH ENRICHMENT FUELS

Survey analyses were first made for classified fuel flow sheets, including both different volatility process approaches and comparison aqueous routes. These engineering evaluations of technology and economics were used for program planning purposes. The major conclusions were that volatility processes were at least competitive with aqueous routes and that the fluid-bed volatility approach coupled more versatility than the major competitor, molten salt processing, with a high probability of ultimate success. Additionally, fluid-bed processes were deemed to be more adaptable to power reactor fuel treatment, including plutonium recovery.

Accordingly, it was requested by the AEC that a definitive evaluation covering aluminum, zirconium, and graphite-base fuels and using the latest estimates of generation rate be performed for a fluid-bed volatility plant. This study is now in progress.

LOW ENRICHMENT POWER REACTOR FUELS

The present volatility program emphasis is on developing processes for recovery of uranium and plutonium by volatilization as the corresponding hexafluorides from low enrichment zircaloy and stainless steel-clad fuels. Since it appears that the zircaloy-clad fuels may predominate in the future, the initial study is aimed at these materials.

Many decisions regarding basic technology application still remain to be made, as well as others involving more strictly economic optimization. The discussion in the body of this report covers selected alternative process routes which may be considered reference flow sheets, since they have been accepted by the participating groups as such.

Zircaloy-Clad Fuel Process

The present flow sheet for zircaloy-clad fuel calls for removal of the clad by volatilization with hydrogen chloride gas at about 400°C. The reaction with the fuel charge takes place in a head end reactor containing a fluid bed of alumina grain. Pyrohydrolysis at 350°C. is used in a second fluid bed to convert the zirconium and tin compounds to the oxide form for storage as solids. Although the oxide fuel fragments will be relatively unattacked by the hydrogen chloride, some radioactive material will be volatilized during the hydrochlorination; however, except for the noble gases, these substances are expected to be retained in the hydrolysis reactor bed. The uranium oxide fuel fragments remaining in the head end fluid bed are oxidized to a fine powder at about 400°C., and the resulting uranium and plutonium oxides are fluorinated using elemental fluorine at temperatures graded from 400 to 550°C. Since most of the elements comprising the bulk of the fission product activity and transuranic elements (except neptunium and plutonium) form nonvolatile fluorides which remain in the fluid bed, considerable decontamination of the uranium and plutonium is achieved by the volatilization as the hexafluorides. Plutonium tetrafluoride is produced by thermal decomposition of the plutonium hexafluoride in the absence of fluorine. The uranium hexafluoride is then purified of remaining fission products and traces of plutonium and neptunium by distillation and sorption on magnesium fluoride and hot sodium fluoride.

Although much basic information remains to be developed with regard to this flow sheet sequence, ANL work to date has given a degree of confidence that plutonium can indeed be volatilized and transferred. The uranium recovery aspect certainly appears technically feasible; however, additional scale-up work is required.

Stainless Steel-Clad Fuel Process

The present preferred process for stainless steel-clad uranium dioxide fuels utilizes a hydrogen fluoride-oxygen gas at 600°C. to spall off the cladding in rusty fragments. The uranium dioxide pellets are concurrently broken up into fine powder and are converted to uranyl fluoride and uranium tetrafluoride.

The uranium and plutonium recovery and purification aspects of stainless steel-clad fuel reprocessing would be about the same as for the zircaloy materials.

Interhalogen Flow Sheet

Flow sheets employing bromine pentafluoride for removal of the uranium are now being evaluated. Uranium salts can be readily converted to uranium hexafluoride with this reagent, while for thermodynamic reasons, plutonium hexafluoride should not be formed. Thus, a clean separation of uranium and plutonium in the fluid-bed fluorinator should be possible, and simplifications in the product handling system may be achievable.

Several flow sheets involving different arrangements of the bromine halide recycle and uranium hexafluoride purification equipment are being considered.

Head End Fluid-Bed Reactor

A two-diameter fluid-bed reactor is contemplated for the conceptual plant unit. The lower section would be of small diameter to allow attainment of higher gas velocities for improvement of heat transfer and powder carry-out during the oxidation of pellet fragments and reaction of other fuel constituent pieces. The larger, upper diameter permits insertion of the fuel charge and sufficient reduction of exit gas velocities to prevent excessive elutriation.

Radioactive Heat Generation

Radioactive heat generation poses a problem in (a) fuel charging machinery, (b) the fluid bed in removal of heat from newly charged elements should fluidization fail, and (c) the contaminated bed solids if bed caking or settling occurs. Calculations made for various possibilities indicate that temperature rise at the bed centerline can be generally assumed to be adiabatic for the contemplated plant reactor size.

One conclusion from the calculations is that temperature rise rates are large enough to impose significant problems, particularly with short cooled, high burnup material. Temperature rise rates on the order of 50 to 100°C. per hour may be typical. Obviously, this is not a serious problem in the same way that a nuclear reactor transient hot spot might be; however, it would require corrective action to "unstick" the bed in a fairly short time, in chemical plant operating terms.

Alumina Diluent and Bed Storage Costs for Power Reactor Fuel Processing

Calculations have been made relating to the economics of bed recycling, including alumina cost, fuel cooling time before processing, and waste storage investment, using bin storage costs developed at the Idaho Chemical Processing Plant. Ultimately, waste disposal might require different hardware; however, storage in bins appears most reasonable at present. The conclusion is that waste storage capital costs are of the same order of magnitude as the value of plutonium losses of 1%.

There is a sizable incentive from both waste storage and plutonium loss economic viewpoints of holding the ratio of diluent alumina used to uranium throughput as low as possible. Presently, the target value for this ratio is 0.4.

CRITICALITY CALCULATIONS

High Enrichment Fuels

Criticality calculations are presented for highly enriched uranium. Considerable operational advantage is derived from elimination of homogeneous moderation from the process system, and the minimum critical mass for a uranium density of 3.2 g./cc. or less appears to be in excess of 109 kg.

Low Enrichment Fuels

Critical mass calculations for uranium dioxide pellet charges for dry systems and in the presence of liquid water are presented for uranium-235 assays of 2 and 5%. According to the calculations, dry systems are inherently safe for these enrichments, since the infinite medium neutron multiplication constants are less than 1. With liquid water present, however, criticality could be achieved with masses substantially less than those proposed for batch charges. Precautions in design, such as avoidance of water cooling for the reactor and use of temperature interlocks, will essentially eliminate the possibility of water accumulation in the equipment.

Plutonium

Critical mass calculations were made for plutonium oxide spheres reflected with alumina to provide orientation for problems involved in power reactor fuel reprocessing. At a plutonium density of 4.6 g./cc. with a 50 cm. alumina reflector and assuming all plutonium is as the 239 isotope, the critical radius was indicated to be 10.79 cm. with a corresponding critical mass of 24.2 kg. of plutonium.

COLD TRAPS

Batch desublimers (cold traps) are used to collect uranium hexafluoride from gas streams. To aid in the design of such units, a desublimer design digital computer program is being developed. Preliminary computer results agree well with available experimental data.

PROTOTYPE TESTING AND EVALUATION

Development work is proceeding in a number of areas where additional information is required for design of a production facility. Of primary importance is extension of the Argonne National Laboratory, Oak Ridge National Laboratory, and Brookhaven National Laboratory work on volatility processes by studies in larger equipment. In some cases, scale-up from relatively small experimental equipment may be possible; in

others, tests in up to half or even full size reactors will be required. Also of major importance are materials of construction, outlet gas filters, product purification systems, remotely operable connectors, gas compressors, cold traps, and reactor fabrication procedures. As the work progresses, need for investigation in other areas may become apparent.

At the time the ORGDP program was started, the AEC's primary interest was in design and evaluation of plants for reprocessing high enrichment fuels. Therefore, the initial studies were made in problem areas concerned mainly with the hydrogen chloride-fluorination procedure for reprocessing zircaloy and aluminum alloy fuels. A small amount of experimental work was also done on the oxidant fluorination method of processing graphite type fuels. With the change of emphasis to low enrichment power reactor fuel recovery, the ORGDP components program is now centered on the three-step hydrogen chloride decladding, uranium dioxide pellet oxidation, and fluorination method developed for zircaloy clad uranium dioxide fuels. As time permits, experimental studies related to the hydrogen fluoride-oxygen decladding procedure for stainless steel or zircaloy clad fuels are also being carried out.

Program results and status are summarized below.

MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES

Because of the unusual sequence of atmospheres in a single system, only scant corrosion data are available in the literature. For this reason, exposure tests are being made to determine which materials are suitable for the various volatility processes described earlier. To date, nickel-201 appears to be the only choice for a fluid-bed reactor in which fluorination is to be carried out at temperatures up to 550°C. Nickel-200 has good corrosion resistance, but the ASME pressure vessel code allows nickel only as the low carbon nickel-201 at the temperature level of the process. Both nickels appear satisfactory from a corrosion standpoint for alternating hydrogen chloride-fluorine atmospheres. Tests have not yet been made to simulate the conditions for the three-step hydrogen chloride plus oxygen-fluorine process for low enrichment zircaloy-clad fuels.

Duranickel, a nickel alloy containing a small amount of aluminum, is slightly less corrosion resistant to the hydrogen chloride-fluorine exposure than nickel-200 and nickel-201 but should be acceptable for flange material. Flanges should operate at a somewhat lower temperature than that required for the reaction vessel.

Corrosion rates of nickel-201, nickel-200, and Duranickel are also adequately low under the process conditions expected in the hydrogen fluoride-oxygen fluorination process.

Commercially available porous nickel filter material has good corrosion resistance in alternating hydrogen chloride-fluorine atmospheres. Monel filters are satisfactory for the hydrogen fluoride plus oxygen-fluorine system.

Corrosion resistance of all molybdenum and chromium containing alloys was relatively poor in both the hydrogen chloride-fluorine and the hydrogen fluoride plus oxygen-fluorine atmospheres.

PROCESS AND REACTOR STUDIES

The program in this area is related to the various chemical methods involved in converting reactor fuels to the desired volatile form. Since the chemistry of the various processes has in general been proved feasible by National Laboratory investigations, ORGDP work will be concerned mainly with establishing firm engineering information regarding reactor performance, configuration, and sizing. In the course of this work and during evaluation of system components, information on the flow sheet reactions will also be accumulated.

In conjunction with studies of filters for a high enrichment zirconium alloy element reprocessing system, tests were made which indicated that the small amount of oxygen contaminant in nitrogen or argon diluents will convert uranium metal to a finely divided oxide in the presence of hydrogen chloride and hydrogen. In other filter tests related to the hydrogen fluoride plus oxygen-fluorine process, a by-product of the filter investigation was a verification of the stainless steel oxidation results obtained at Argonne and Brookhaven National Laboratories.

To aid in the design of larger fluid-bed reactors for low enrichment fuels, fluidization of the various materials concerned is being observed in transparent columns. In one test, it was shown that complete separation of alumina and stainless steel oxidation residue by elutriation was not feasible. Removal of the coarse stainless steel oxidation products before fluorination would probably have made control of that step easier in addition to lowering fluorine costs and decreasing certain contaminants which form volatile fluorides, such as chromium and molybdenum.

Another study with a bed of simulated oxide pellets and alumina indicated that movement of the alumina diluent around most of the pellets was very poor. Channeling of a major portion of the gas through a small part of the bed was observed, thus indicating that heat transfer and gas contact problems may be serious in a large reactor during the pellet oxidation step. Although the total quantity of heat released by this reaction is relatively small (compared with the fluorination step), National Laboratory experience has shown that temperature excursions can still occur and that incomplete attrition of the pellets results.

A semiworks scale head-end fluid-bed reactor is being designed and will be constructed to study the decladding, fuel pellet oxidation, and fluorination operations. The unit will be 10 inches in diameter by 11 feet high with a 3-1/2-foot long, 5-inch diameter section at the bottom. The purpose of the reduced diameter of the lower portion of the bed is to provide a relatively high gas velocity through the settled bed of oxide fuel pellets, thus improving heat transfer and mobility of the alumina diluent. Tests will also be made without the 5-inch diameter section for purposes of comparison, and if indicated desirable, various gas

entrance configurations will be evaluated, as well as different bottom section designs. Outlet gas cooling and filtering will also be studied in this system. In addition to the semiworks fluid bed, an 8-inch diameter Plexiglas unit is being assembled to study gas entrance configurations and to observe fluidization characteristics with various types of fuel modules.

OUTLET GAS FILTER STUDIES

Studies are being made in a small fluid-bed loop to evaluate sintered metal filters for use in the fluid-bed reactor gas outlet. Both bench-scale corrosion tests and fluid-bed tests indicate that commercially available sintered nickel filter material will withstand cyclic exposure to hydrogen chloride and then to fluorine at the expected temperatures. Fabrication of a tube by rolling and welding appears to be a problem, however, as all welds have cracked after exposure. Preliminary tests on a molded (seamless) tube made by the Purolator Corporation are encouraging.

A test was also made which showed that sintered Monel filter tubes are suitable for the hydrogen fluoride plus oxygen-fluorine atmospheres required for stainless steel clad-ceramic fuels.

PRODUCT PURIFICATION, SORPTION-DESORPTION SYSTEM

As contemplated, a portion of the fission product contamination will be removed from the uranium hexafluoride product by sorption on sodium fluoride heated to 400°C. Further purification is also possible by sorbing all the uranium hexafluoride on sodium fluoride held at 100°C. and allowing other impurities to pass through the bed. Studies are being made to determine the best type of sodium fluoride pellet to use for a batch sorber, to optimize both sorption and desorption conditions, and to evaluate traps designed for production use. At the present time, a temperature of 100 to 120°C. appears best for complete sorption of the uranium hexafluoride, while 400°C. is ample for desorption. All types of sodium fluoride pellets studied to date gradually break down into powder with repeated sorption-desorption cycles. Tests are also in progress to evaluate a production-scale pellet trap of annular design.

A fluid-bed system which appears capable of continuously sorbing large quantities of uranium hexafluoride has been developed for another project at the ORGDP. The uranium hexafluoride-containing gas is passed through a stirred fluid bed into which sodium fluoride powder is added continuously. Essentially complete stripping of the uranium hexafluoride is effected, and the powder overflow is transported to a ribbon flight screw where it is heated to recover the uranium hexafluoride. The regenerated sodium fluoride is then returned to the fluid bed to complete the cycle. The pilot-plant unit has been operated for a sufficient time to show that the process is workable; additional studies are required to determine capacity and optimum operating conditions.

CONNECTORS

Remotely operable connectors capable of maintaining gas-tight seals under process conditions will be required on major equipment items. Flange and gasket type seals utilizing double gaskets with a pressured buffer to monitor leakage are being considered for this use. Age hardened Duranickel appears to have adequate corrosion resistance and hardness for use as a flange with a nickel gasket. Preliminary temperature cycling tests in an inert atmosphere indicate that commercially available Marman Conoseal flanges made of this material are satisfactory for the alternating high and low temperature conditions. In view of the high cost of these units, however, studies are in progress to evaluate standard flat-faced flange designs.

COMPRESSORS

To reduce reactant usage in a reprocessing plant, gas recycle will probably be used in both the hydrochlorination and fluorination steps. The only commercially available compressor which will meet the process requirements is the diaphragm type unit. Such a machine, a Corblin compressor, has been purchased and is undergoing performance tests.

The diaphragm compressor has several undesirable features for use in a remote maintenance plant. These are (a) amplitudes of vibration are inherently high, making use of flexible connectors mandatory; (b) periodic replacement of diaphragms is necessary; and (c) flow rates are easily affected by malfunctioning of the check valves or by accumulations of small amounts of gas in the hydraulic fluids. In addition, flow rates are basically low, and relatively large and expensive units would be required.

A potentially better compressor from the standpoints of initial cost and maintenance is the peripheral type which is being studied at the ORGDP for other applications. Performance data have been obtained which demonstrate that a two-stage peripheral machine utilizing a 10-inch diameter impeller operating at 11,000 rpm. will meet the requirements for hydrogen chloride and fluorine recycle systems. In addition to the impeller, the compressor will include a shaft seal and an externally mounted bearing system and driving motor. Tests indicate that a low clearance bushing seal and grease packed high precision angular contact bearings should give satisfactory performance. A prototype unit is presently under construction and will be evaluated under process conditions.

REACTOR FABRICATION PROCEDURES - WELDING STUDIES

A procedure has been developed for making welds of nickel-201 rod which will meet the conditions specified in pressure vessel codes.

DISCUSSION

ENGINEERING STUDIES

J. H. Pashley, D. L. Breton, D. I. Dunthorn
J. A. Iacovino, C. C. Littlefield, J. R. Merriman

Studies of the economic technical feasibilities of various processes for recovery of fissile material from irradiated nuclear reactor fuels are being performed to provide guidance for the associated development programs. These studies are aimed at arriving at conceptual plant designs with estimates of cost and evaluations of potential scale-up problems.

Coupled with this effort is a systems analysis program designed to summarize the large number of process alternatives and problems and to indicate work areas which should be emphasized in the integrated overall program.

Engineering studies for power reactor fuels and high uranium enrichment materials are described briefly in this report. Included also are more detailed calculations relating to specific problems, such as alumina bed usage economics, bed temperature rises due to radioactively generated heat, and criticality considerations for high uranium enrichment fuels.

Historically, the ORGDP development programs began with evaluation of processes for the high enrichment fuels. This followed logically from the National Laboratory volatility programs which had been largely aimed at the spent high enrichment fuels because of their relatively early availability for processing. It is not surprising, however, that the volatility technology, engineering, and experimental results for high enrichment fuels are, to a substantial degree, useful in the low enrichment power reactor fuel program.

HIGH ENRICHMENT FUELS

Engineering studies have been performed for the aluminum-uranium, zirconium-uranium, and graphite matrix high enrichment fuels. Processing of these materials using the fluid-bed reactor systems bears many similarities to work for low enrichment fuels. The major difference is, of course, the necessity for recovering plutonium from the low enrichment fuels. Technology, however, for low enrichment fuels processing has been relatively incomplete because much remains to be learned about plutonium hexafluoride handling and conversion to solid product.

Initial engineering analyses were carried out on the technology and economics of high enrichment fuel processing because of the advanced

"state-of-the-art". The analyses were used primarily for program planning purposes. The general conclusions were that volatility processes were at least competitive with aqueous routes and that the fluid-bed volatility approach coupled a high probability of ultimate success with more versatility than is available with the major competitor, molten salt processing. Additionally, fluid-bed systems were recognized to be more adaptable than the molten salt sequence to low enrichment fuel treatment for plutonium recovery.

Following these initial analyses, a more comprehensive study was undertaken covering highly enriched aluminum, zirconium, and graphite base fuels and using the latest estimations of generation rate. This study is now in progress, and a few details relating to the processing schemes and time cycles follow.

The processes for both the aluminum and zircaloy fuels involve hydrochlorination to remove the aluminum or zirconium and tin as volatile chlorides. The hydrochlorination off-gas is fed to a fluid-bed pyrohydrolyzer for conversion of the clad compound to solid oxide in oxychloride form. The uranium remains behind as a nonvolatile chloride and may be fluorinated immediately or after treatment of the bed with hydrogen fluoride to replace the chloride with fluoride. This latter step is included to prevent generation of chlorine trifluoride or chlorine which could lead to problems in the off-gas caustic scrub system. Both single-vessel and multiple-vessel reactor lines are being considered.

Some fission products, notably zirconium, ruthenium, niobium, iodine, and the noble gases, are expected to be wholly or partly volatilized in the hydrochlorination. The zirconium, ruthenium, and niobium are expected to be retained in the pyrohydrolysis reactor bed, while the noble gases will pass through to the vent. Iodine may tend to accumulate in the hydrogen chloride recycle system until blown down to the neutralization system.

Technetium, ruthenium, molybdenum, and tellurium, as well as plutonium and neptunium, are the primary contaminants expected to be found in the reactor off-gases during fluorination. A combination of sodium fluoride and magnesium fluoride sorption is expected to be effective in removing these elements excepting tellurium. Although tellurium is expected to be partially removed by caustic scrubbing and exposure to hot nickel or carbon, it may pose a vent problem.

In the single-vessel process, hydrochlorination, hydrofluorination, and fluorination steps are all carried out in the same fluid bed. The multiple vessel line originally considered had three separate units, one for each chemical step; however, it is now felt that equipment use scheduling will permit both hydrofluorination and fluorination to be carried out in the same vessel.

Table I compares time schedules for the two schemes. In each case, three charges of elements are hydrochlorinated before hydrofluorinating for chloride removal in the single-vessel case or transfer to the hydrofluorinator-fluorinator in the multiple-vessel case.

TABLE I
CYCLE TIMES FOR ZIRCONIUM AND ALUMINUM FUELS

Operation	Reactor Time Required, hours	
	Single-Vessel System	Multiple-Vessel System
Transfer Aluminum Oxide In, Charge Fuel, Adjust Temperature	2	2
Hydrochlorinate	12	12
Purge, Charge Fuel, Adjust Temperature	2	2
Hydrochlorinate	12	12
Purge, Charge Fuel, Adjust Temperature	2	2
Hydrochlorinate	15*	15*
Purge, Adjust Temperature, or Transfer Bed Material Out	<u>1</u>	<u>2</u>
Total Hydrochlorination Time	46	47
Transfer Bed Material In, Adjust Temperature	0	1
Hydrofluorinate	3	3
Purge, Adjust Temperature	1	1
Fluorinate	4	4
Purge, Sample, and Analyze†	0	3
Purge, Transfer Bed Material Out	<u>1</u>	<u>1</u>
Total Hydrofluorination and Fluorination Time	9	13
Cycle Controlling Time	55	47

* A 3-hour tailoff period is included in the final hydrochlorination time to assure complete reaction of the thicker sections of the fuel modules.

† The bed material from the single vessel system is transferred to a surge hopper for sampling and analysis; the bed material from the multiple vessel process is sampled in the fluorinator and is held there until sample results are obtained.

The overall cycle time for the single-vessel option is 55 hours. This allows processing of aluminum fuels in a single line at the rate of 5.13 kg. of uranium per day. With an assumed load of 1,000 kg. of uranium per year from this source, about 195 on-stream days per year are thus required. Assuming only 260 on-stream days are available per year to allow for downtime for maintenance, inventory, and campaign accountability purposes, 65 on-stream days per year are left for the zirconium-base fuels. This appears sufficient, so a single line is used to handle both loads.

The overall cycle time for the hydrochlorinator in the two-vessel plant is only 47 hours. The hydrofluorinator-fluorinator reactor processing time is only 13 hours per overall cycle; thus, the hydrochlorinator scheduling is controlling. Using the same size reactor for the hydrochlorination step as in the single-vessel plant, the processing rate is 6.01 kg. of uranium-235 per day for the aluminum fuels. This would apparently allow processing of about 17% more fuel in the two-vessel plant, thus making a nominal decrease in reactor size possible.

In the event that processing loads are increased, another possibility for the two-vessel flow sheet calls for one hydrofluorinator-fluorinator servicing two or more hydrochlorinators; however, this arrangement might be undesirable from the standpoints of accountability and criticality control. Perhaps the biggest advantage of the two-vessel system would be to remove some of the restrictions on the material of construction. For example, Inconel can be considered for use in both the reactor and porous metal filter systems for hydrochlorination if not subsequently exposed to fluorine. Sintered Inconel filter tubes have been used at ANL in some of the hydrolyzer work. The corrosion performance of both porous and structural nickels may be improved if exposed only to hydrogen fluoride containing a small amount of hydrogen chloride and to fluorine. Monel may even be satisfactory for this last combination.

The graphite fuel reprocessing is best done in a separate line. The fuel may be broken into chunks and fed semicontinuously to a relatively small oxidizer fluid bed; i.e., perhaps 10 inches in diameter. Combustion proceeds readily at 700°C., and little unconsumed graphite, other than newly fed chunks, is present. When enough uranium has accumulated in the alumina diluent, the bed is transferred to a fluorination fluid bed. Most of the uranium comes off readily in fluorination; however, there is a decreasing rate at the end so that several hours are required for the removal of the last few percent.

The present concept of a multipurpose volatility plant thus includes one reactor line for processing zircaloy and aluminum alloy fuels and a second reactor line for handling the graphite-base material. Each line would have its own specific auxiliaries, such as the pyrohydrolysis reactor and hydrogen chloride recycle for the zircaloy and aluminum alloy fuels and combustion off-gas system for the graphite-base materials. Since the lines would be expected to be operated at the same time during a substantial portion of the year, each would have its own cold trap system.

Process flow sheets and conceptual equipment designs and layouts have been essentially completed. Estimates of cost and preparation of the report are in progress.

LOW ENRICHMENT POWER REACTOR FUELS

The present volatility program emphasis is on developing processes for recovery of uranium and plutonium by volatilization as the corresponding hexafluorides from low enrichment zircaloy and stainless steel-clad uranium dioxide power reactor fuels. Consistent with this goal, the major part of the engineering study effort is now being directed toward processes for the low enrichment fuels. Since it appears that the zircaloy-clad fuels may predominate in the future, the initial study is aimed at these materials. Before describing a tentative view of the conceptual plant system, a brief look at process alternatives is warranted. Figures 1 and 2 show the major potential flow sheet routes in simplified schematic fashion, omitting decisions which may be settled on an essentially economic basis; e.g., recycle requirements for gases and bed solids, process equipment necessities such as filters and heat exchangers, number of reactors in a processing line, and order of purification and recovery steps. The heavy connecting line shows the path of the present reference flow sheet for the zircaloy-clad uranium dioxide fuels.

Zircaloy-Clad Fuel Process

In the present reference flow sheet for zircaloy-clad fuels, figure 3, the initial processing step after mechanical removal of end hardware is hydrochlorination at 400°C. with the fuel element(s) immersed in a fluidized bed of inert powder; i.e., alumina. This treatment volatilizes zirconium as the tetrachloride and tin as the bichloride. Reaction with the uranium dioxide is expected to be minimal. The decladding off-gas is conducted to a second fluid-bed reactor where the volatile cladding compounds are reacted with water vapor at about 350°C. to convert them to solids for ease in storage. Except for the noble gases and iodine, radioactive substances vaporized by the hydrochlorination would be expected to be fixed on the pyrohydrolysis bed material, thus leaving a relatively clean hydrogen chloride-containing effluent stream. Since the hydrogen chloride is not expected to attack the uranium dioxide to a significant degree, most of the fission product activity is not expected to be reacted. That remaining after fluorination could be volatilized in the subsequent hydrochlorination in the likely event that the bed material is reused. The hydrogen chloride consumed in the head-end fluid bed is reconstituted in the hydrolysis process and, along with the excess hydrogen chloride, may be recycled back to the head-end fluid bed.

After conclusion of the declad step, the uranium dioxide solids will be in an essentially static bed at the bottom of the reactor due to their high density and relatively large size. A diluent oxygen stream is used to convert the uranium dioxide to fine urano-uranic oxide powder which will fluidize along with the diluent. The pellet breakup will also allow conversion of the plutonium and fission products to fine powders. Fluorine is used to react with these materials to produce the uranium hexafluoride

Figure 1
DECLADDING AND CHEMICAL PRETREATMENT

Figure 2
FLUORINATION AND PRODUCT RECOVERY

Figure 3
POWER REACTOR FUEL REPROCESSING PLANT

and plutonium hexafluoride. The fluorination reaction is initially conducted at 400°C. to remove most of the uranium along with a relatively small proportion of the plutonium. The temperature is then increased to 500 to 550°C., and the remainder of the plutonium is volatilized.

As subsequently discussed in more detail, it is presently planned to use a two-diameter fluid bed such that high gas velocities can be utilized in the lower smaller diameter in which the pellets will fall after de-cladding. This high velocity should result in improved powder carryout and heat transfer in this zone, while at the same time, the velocity will be less in the upper bed section with the larger diameter so that excessive elutriation does not occur.

The product gas stream is passed through a cold-trapping system for removal of plutonium hexafluoride and uranium hexafluoride. The plutonium hexafluoride-uranium hexafluoride mixture, along with fission product fluorides also removed at this point, is fed to a thermal decomposer in which plutonium tetrafluoride solid product is deposited. The uranium hexafluoride is then distilled, and the product fraction is passed through sorbent traps for final cleanup. The fission product streams from the distillation may be packaged for storage by chemisorption on a suitable solid or by other suitable means.

Some basic information remains to be developed with regard to this flow sequence. The uranium processing aspect seems to be demonstrated from a technical standpoint, although additional information is needed for proper scale-up. The ANL work to date has also given a degree of confidence that the plutonium can indeed be volatilized and transferred. Additional effort will be required to show that actual fuel materials can be so treated and to provide better operational parameters. Further, studies of distillation of plutonium hexafluoride-bearing material and of thermal decomposition for plutonium tetrafluoride production necessary to provide design data are incomplete. Fission product chemistry investigations on a process scale with irradiated fuel water are required to validate predictions as to which will be volatilized in each step and where these will come out in the process.

Stainless Steel-Clad Fuel Process

The present preferred process for stainless steel-clad uranium dioxide fuels utilizes a hydrogen fluoride-oxygen gas at 600°C. to spall off the cladding and rusty fragments. The uranium dioxide pellets are currently broken up by oxidation into fine powder and are then converted to uranyl fluoride and uranium tetrafluoride. The maximum reaction rate appears to occur when a 40% hydrogen fluoride concentration is employed; however, plant operation may require use of lower or higher concentration for reaction and heat release control. The clad is not volatilized except for a portion of the chromium converted to fluoride. A large part of the clad residue is relatively coarse, even containing slivers as long as 1/2 inch or so. The degree of conversion of the clad and the uranium to oxyfluorides and fluorides depends on the length of exposure to hydrogen fluoride. The fluorination step proceeds readily enough,

except that some difficulty may be encountered in control of reaction heat removal in the zone in which the coarse material accumulates. Use of the two-diameter fluid bed and careful control of the fluorine concentration in the early stages of the reaction should minimize operating difficulties. Fluorination breaks up the coarse clad material to a fine powder so that bed transfer should not be impeded.

The uranium and plutonium recovery and purification aspects of stainless steel-clad fuel reprocessing would be about as stated for the zircaloy materials.

Interhalogen Flow Sheet

Flow sheets employing bromine pentafluoride for removal of the uranium, as indicated by figure 4, are now being evaluated. The thermodynamics indicate that plutonium cannot be volatilized in significant amounts by reaction with bromine pentafluoride, while uranium can be essentially completely removed*. Plutonium would be volatilized by reaction with elemental fluorine in the subsequent step. Thus, a clean separation of uranium and plutonium in the fluid-bed fluorinator should be possible, and simplifications in the product handling system could be achievable as compared to that for the reference flow sheet which uses fluorine only. Additionally, the rate of fluorination of uranium salts with bromine pentafluoride is apparently faster than with fluorine, and the heat release is also lower. This last feature of use of bromine pentafluoride may not be exploitable in two-zone oxidation-fluorination, since the oxidation step may well be controlling. Against these advantages must be weighed the complications involved in having (a) an off-gas stream containing bromine pentafluoride, bromine trifluoride, and uranium hexafluoride; (b) a reaction system for conversion of bromine trifluoride to bromine pentafluoride; and (c) a sorption or distillation separation system for purifying the uranium hexafluoride from bromine compounds.

The use of bromine fluorides for nuclear fuel reprocessing had been studied previously but mainly for metallic uranium or alloy type fuels. From these efforts, data are available for many of the component properties†, table II.

* Experimental studies are in progress at Argonne National Laboratory to verify this conclusion and provide kinetic data.

† Stoller, S. M., and Richards, B. B., editors, Reactor Handbook, Volume II, Fuel Reprocessing, Interscience Publishers, Inc., New York (1961).

Figure 4

INTERHALOGEN REFERENCE FLOW SHEET

TABLE II

PHYSICAL PROPERTIES OF
BROMINE PENTAFLUORIDE, BROMINE TRIFLUORIDE, AND URANIUM HEXAFLUORIDE

Property	Uranium Hexafluoride	Bromine Pentafluoride	Bromine Trifluoride
Molecular Weight	352	174.92	136.92
Melting Point, °C.	64.02	-60.5	8.77
Normal Boiling Point, °C.	56.54*	41.3	125.75
Triple Point Pressure, mm. Hg	1137	1.7	2.4
Critical Constant (estimated)			
Temperature, °C.	230	213	340
Pressure, atmospheres	45.5	47	70
Heat of Fusion, kcal./mole	4.588	1.74	2.875
Heat of Vaporization, kcal./mole	6.82	6.88	10.235
Density, g./cc.			
Solid	5.06(25°C.)	3.09(-61°C.)	3.23(8.8°C.)
Liquid	3.67(64°C.)	2.4604(25°C.)	2.803(25°C.)
Solubility of Uranium Hexafluoride in Bromine Pentafluoride at -40°C., g.UF ₆ /g.BrF ₅	0.163	-	-
Vapor Pressure of Pure Component at -40°C., mm. Hg†	0.3	8.5	0.05

* Uranium hexafluoride sublimates at normal atmospheric pressures.

† This should be about the same as partial pressure of solute above a saturated solution at this temperature.

Liquid-solid phase diagram information is available for the binary systems uranium hexafluoride-bromine pentafluoride and uranium hexafluoride-bromine trifluoride. Liquid-vapor equilibrium diagrams are available for the binary systems but not for low total pressures. Ternary phase equilibrium data have not been found in the literature. Based on the available data, the following comments can be made:

1. Cocurrent condensation of a liquid mixture of bromine pentafluoride, bromine trifluoride, and uranium hexafluoride with high recovery

from a dilute gas stream requires that the bromine pentafluoride be in high concentration in the mix. For a reactor off-gas containing 3% uranium hexafluoride, 10% bromine trifluoride, and 3% bromine pentafluoride, precipitation of uranium hexafluoride and bromine trifluoride would probably occur at temperatures not much below the uranium hexafluoride triple point; however, a mixture containing 90 mole percent bromine pentafluoride, 5 mole percent bromine trifluoride, and 5 mole percent uranium hexafluoride is expected to be a liquid at minus 30°C., at which temperature, the total vapor pressure of the solution would be about 10 mm. Hg, and the uranium hexafluoride partial pressure would be about 1 mm. Hg. The freezing point of a liquid containing 95% bromine pentafluoride and 5% uranium hexafluoride would, however, be about minus 53°C., at which point, the uranium hexafluoride vapor pressure would be about 0.05 mm. Hg.

2. Continuous distillation of a bromine pentafluoride, bromine trifluoride, and uranium hexafluoride mix to produce purified uranium hexafluoride with high recovery would appear to require two columns, since the uranium hexafluoride is intermediate in volatility.
3. Obtaining a purified uranium hexafluoride product from the bromine pentafluoride-uranium hexafluoride mix may be relatively simple, since the relative volatility of bromine pentafluoride to uranium hexafluoride at the low bromine pentafluoride end exceeds two. Purifying the bromine pentafluoride from uranium hexafluoride by distillation will be more difficult but probably less important, since some recycle of uranium hexafluoride in this stream may be tolerated. British reports of an azeotrope at a significant uranium hexafluoride concentration are discounted by Argonne National Laboratory work*.
4. Stripping of the lower boiling bromine trifluoride from uranium hexafluoride to achieve concentrations of 1 ppm. bromine† may require a considerable number of transfer units in a continuous distillation unit. Further data as to the activity coefficient of bromine trifluoride at the low bromine trifluoride concentration end may be needed.
5. Kinetics of conversion of bromine trifluoride to bromine pentafluoride by reaction in a gaseous state with fluorine are such that moderately high conversion efficiencies, i.e., 95 plus percent, may be obtained even from fairly dilute streams. Ultrahigh conversions, i.e., so that less than 1 ppm. bromine as bromine trifluoride (uranium basis) remains, may require a fairly large reactor or may even be prevented by equilibrium considerations. It appears that the best solution of the distillation problem would be to eliminate bromine

* Ellis, J. F., Johnson, K. D. B., J. Inorg. Nucl. Chem., 6, 194 (1958).

† This is the present specification limit for return of uranium hexafluoride to the AEC. Recycle directly to fuel fabrication operations might allow a considerably higher specification limit and considerably ease the separation problem.

trifluoride from the system by prior reaction possibly helped along by injection of some fluorine into the still reboiler to ensure reaction completion.

The selection of a process flow sheet depends not only on feasibility but also on economics. Accordingly, several flow sheet arrangements which are all thought to be technically feasible have been prepared for preliminary evaluation.

These flow sheets all presume hydrogen chloride decladding for removal of the zircaloy clad and then two-zone oxidation-fluorination, using bromine pentafluoride, for volatilization of the uranium. Plutonium would then be recovered by fluorination with elemental fluorine. The differences among the arrangements lie in the off-gas handling portion of the two-zone oxidation-fluorination step. The oxidation-fluorination operation in the main reactor would be essentially the same as before except that bromine pentafluoride would be used, and thus no plutonium would be volatilized. The off-gas will be mostly oxygen and nitrogen with, on the average, about 3 mole percent uranium hexafluoride, 3 mole percent bromine pentafluoride, and 10 mole percent bromine trifluoride.

The variations are related to the location of the step for fluorination of bromine trifluoride to bromine pentafluoride in the process scheme, i.e., before and after separation of the condensables from the head-end fluid-bed reactor off-gas, and to the selection of the major uranium hexafluoride purification process; i.e., sorption or distillation. An additional variant can be introduced depending on whether a flash cooler-condenser requiring substantial amounts of bromine pentafluoride liquid recycle is employed to remove condensables from the gas stream at such high relative bromine pentafluoride concentrations that uranium hexafluoride and bromine trifluoride are dissolved. In some flow sheets, particularly if distillation is the purification method, this strategem would probably reduce the size of the necessary cold-trapping systems.

Work is in progress to complete the conceptual sizing of the equipment required for each of these flow sheets. Comparison of the equipment requirements will hopefully lead to elimination of some of the alternatives so that more detailed comparisons can be made, including the reference flow sheet using fluorine alone in this group.

Head-End Fluid-Bed Reactor

The fluid-bed halogenator is probably the key unit in the volatility process for power reactor fuels. It must serve satisfactorily in processing highly radioactive material through rigorous chemical treatment under conditions that are far from those usually considered ideal for fluidization. These conditions include the heterogeneous situation during decladding when the fuel bundle is immersed in the fluidized bed of alumina. Furthermore, for the zircaloy fuels, the oxidation of uranium dioxide takes place in a packed bed of fuel pellet fragments with the alumina grain fluidized in the interstices.

In the first case noted above, the main question appears to be how freely the fluidized alumina bed and the gas move through the tube bundle. This circulation is necessary for both heat removal and reaction reasons. Test work to date has been limited and on a relatively small scale; i.e., nine tubes*. In the zircaloy-clad class, a single Dresden-type module has 36 tubes, and proposals are being made for still larger modules. Oyster Creek is scheduled to have 64 tubes per module. Stainless clad fuels have as many as 169 tubes per module. A production reprocessing batch charge for the zircaloy-clad fuels as presently contemplated would be on the order of 150 tubes. With nine tubes, the center tube has only one tube between it and the free bed. Thus, the dynamic and reaction situation of interior tubes located many rows from the free bed has probably not been achieved. The pellet oxidation studies have been mainly on a 3-inch diameter bed with some work on a 6-inch diameter unit.

As discussed in the component section that follows, a semiworks reactor intermediate in scale between the plant unit and the present test units has been proposed.

A two-diameter reactor is contemplated so that high gas velocities may be attained in the pellet oxidation zone while having a normal velocity in the upper portion of the bed. For example, the present conceptual plant reactor is 24 inches in diameter in the upper part of the bed which gives room for charging fuel elements side by side to a total of 500 to 1000 kg. of uranium and allows operation with an outlet gas velocity less than 1 ft./sec. for the flow sheet gas quantities. At the same time, the lower portion of the reactor is only 1 foot in diameter which, after giving effect to pressure drop, still permits operation at 1.5 to 2.0 ft./sec. gas velocity to aid in fines carryout from this zone. The smaller diameter also allows for a greater wall-area-to-bed-volume ratio for heat transfer.

Disadvantages of the two-zone approach that will have to be considered in the final optimization analyses are (a) an adverse effect from the greater overall reactor height on equipment and building expense, (b) the higher gas pressure drop that would be incurred, (c) possible compaction of the pellets at the bottom of the deep pellet bed, and (d) prevention of fines transfer from the deeper pellet bed to the upper fluid-bed zone by an impingement filtration action.

With regard to mechanical details, it appears that nickel is the leading and virtually only candidate material of construction on a corrosion resistance basis for a vessel in which hydrochlorination, oxidation, and fluorination are performed; i.e., where the single-vessel approach is used for the reactions in the fluid bed. If fluorination were carried out in a separate vessel, Inconel could probably be employed for the hydrochlorination and oxidation phases. The fluorinator would be a

* ANL experiments on a 25-tube bundle were scheduled as this report was in preparation.

second fluid bed, and the process would be called a two-vessel process. Either Inconel or nickel should have moderately good resistance to the hydrogen fluoride-oxygen gas mixture used for decladding stainless steel-clad fuels.

For the single-vessel process, the present specification concept is that low carbon nickel will be used for surfaces in contact with the process. Welding will be performed using low carbon nickel rod and a modified Helium arc process. Except if needed for corrosion resistance, stress relief may not be required, particularly since the operating temperature will be near that used for stress relief. Inspection of welds will include dye penetrant and full X-ray. Pressure and leak testing will be required. The vessel design will be subjected to stress analyses per section III of the ASME code; however, stress values from section VIII will be employed.

Radioactive Heat Generation

Radioactive heat generation poses a problem in (a) fuel charging machinery, (b) the fluid bed in removal of heat from newly charged elements should fluidization cease in this area, and (c) the contaminated bed solids should fluidization fail for the whole bed.

Results of calculations covering the centerline temperature rise rate for the settled alumina bed are given in table III. The 9-watt per liter case is valid for 1 to 2 bed cycles with fuel which has been cooled 130 to 165 days after irradiation to 10,000 to 25,000 Mw.-day/metric ton of uranium. With the present shipping regulations, this much cooling time would probably be required for safety and economy. The 90-watt per liter case was chosen to represent five bed recycles for processing the 30-day cooled fuel. Since the bed material conductivity is not known, values of 0.25, 0.5, and 1.0 pcu./hr.-ft.-°C. were used in the calculations.

TABLE III
TEMPERATURE RISE IN A 20-INCH DIAMETER
SETTLED BED WITH VOLUME HEAT GENERATION

Time, hr.	ΔT , °C.					
	$Q = 9$			$Q = 90$		
	$k = 0.25$	$k = 0.50$	$k = 1.0$	$k = 0.25$	$k = 0.50$	$k = 1.0$
1	13.9	13.9	13.9	139	139	139
2	27.8	27.8	27.5	278	278	275
4	55.0	55.0	48.6	550	550	486
8	113.9	97.2	70.5	1,139	972	705
16	194.4	141.6	80.5	1,944	1,416	805
Steady State	335.6	167.8	83.4	3,356	1,678	834

Notes: ΔT = Centerline Temperature Rise, °C.

k = Thermal Conductivity of Bed, pcu./hr.-ft.-°C.

Q = Heat Generation in Bed, w./l.

Specific heat used was 0.26 pcu./lb.-°C.

Density used was 135 lb./cf.

For the first 4 hours, the centerline temperature rise is about that which could be calculated for adiabatic conditions. Accordingly, for this period of time for the centerline temperatures, the actual value of the thermal conductivity is not important so long as it is less than 1.0 pcu./hr.-ft.-°C., and it does not matter if the wall temperature is held constant; i.e., whether heat is removed at the wall or not. While it is not feasible to put an upper limit on allowable alumina temperature now because the effect of solids residues (both radioactive and nonradioactive) on the caking tendency has not been established, it is reasonable that a temperature of perhaps 700°C. would be limiting. If the charging commences with the bed initially at 400°C., the numbers in table III indicate that the bed may be settled for 2 hours before centerline temperatures get too high, even with the higher power level alumina. It is also apparent that difficulties with sintering and even alumina melting could occur under extreme circumstances with the lowest value assumed for thermal conductivity of the bed. Calculations were also made to determine the temperature rise rate for a module immersed in a settled bed. A machine program was written to compute rod temperatures for a fuel element having an even, square array with the element being immersed in a bed of greater diameter than the diagonal of the array.

Calculations were made for a pseudo-Westinghouse module, 14 x 14 rods in dimension. The module was considered to be immersed in a bed 16 inches in diameter; i.e., about 6 inches longer than the diagonal of the cluster. The bed was assumed to be initially at a uniform temperature of 350°C. and to be cooled through the wall by a heat transfer media at a tempera-

ture of 100°C. with a heat transfer coefficient of 10 pcu./hr.-sq.ft.-°C. The bed conductivity was taken at 0.25 pcu./hr.-ft.-°C., and the density and specific heat again approximated those for alumina. Although the chosen model does not precisely duplicate the contemplated reactor sizing, i.e., a bed of about 2 feet in diameter containing two 173-rod clusters side by side, it is thought to be sufficiently close to provide usable information. The calculation results are given in table IV. The two cases simulate the 130- to 165-day cooled material in a bed recycled about two times and the 30-day cooled element in a bed recycled five times. Significantly, for both cases for the innermost rod, the temperature rise is essentially adiabatic for at least 6 hours. The adiabatic temperature rises per hour are about 78 and 228°C. for case I and case II, respectively.

One conclusion from the calculations is that the temperature rise rates are large enough to impose significant problems, particularly with the shorter cooled, higher burnup material. Certainly the melting point of stainless steel, i.e., about 1400°C., would be a circumstance resulting in unusual operating difficulty, and the sintering of bed material, perhaps 700°C. or slightly higher, might be used as the restriction for more usual operating difficulty situations. A second conclusion is that calculation of adiabatic temperature rise rates is probably adequate for consideration of the problem; thus, much use of the machine program is not required. A few additional situations may be explored to determine the effect of use of a higher bed material conductivity, probably $k = 1$ pcu./hr.-ft.-°C., of smaller bed diameter, and of smaller modules. A memorandum has been prepared to cover in detail the radioactive heat generation calculations made to date.

Alumina Diluent and Bed Storage Costs for Power Reactor Fuel Processing

Calculations relating to the economics of bed recycling, including alumina cost, fuel cooling time before reprocessing, and waste storage investment using bin storage costs developed at the ICPP*, have been made. Some of the results are presented in table V. The 0.4 kg. alumina per kg. of uranium usage rate corresponds to about six bed recycles or, equivalently, a 16% drawoff after each cycle. The results in general indicate that, as might be expected, reduction of alumina usage is desirable from an economic standpoint. They also show that storage capital costs are of the same order of magnitude as the value of plutonium losses of 1%, which is the presently envisioned process loss limit. For example, for a fuel containing 10 kg. of plutonium per MTU, a high value for slightly enriched uranium fuels, a loss of 1% amounts to 100 grams per MTU, or about \$1,000 per MTU. Thus, the incentive for increasing alumina utilization may lie as much in reduction in waste storage costs as in further increases in plutonium recovery efficiency.

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

TABLE IV

ELEMENT TEMPERATURE TRANSIENTS IN SETTLED BED
FOR 14 × 14 PSEUDO-WESTINGHOUSE MODULE
IN 16-INCH DIAMETER BED*

Time, hr.	ΔT , °C.			
	Case I†		Case II‡	
	Innermost Rod	Outermost Rod	Innermost Rod	Outermost Rod
0	0	0	-	0
0.5	40	36	115	109
1.0	80	67	230	211
2.0	160	117	460	401
3.0	240	161	690	577
4.0	320	202	920	745
6.0	479	284	1,380	1,062
8.0	638	366	-	-
11.5	911	507	-	-

* Rod diameter is 0.340 inch, and the rods are in a square pitch array with a center-to-center distance of 0.452 inch. The actual element contains 173 rods with the same center-to-center spacing and rod diameter but with two offset rows accounting for the deviation from a 13 × 13 array. The boundary condition employs a wall heat transfer coefficient of 10 pcu./hr.-sq.ft.-°C. to a cooling media with a temperature of 100°C. The starting condition is a uniform bed temperature of 350°C. The cooling was sufficient to reduce the wall temperature below 350°C. in each case. The bed material is assumed to have a density of 135 pounds per cubic foot, a specific heat of 0.25 pcu./lb.-°C., and a thermal conductivity of 0.25 pcu./hr.-ft.-°C.

† Heat generation in rods is equivalent to 1 kw. per 100 kg. of uranium; heat generation in bed solids, 9 watts per liter. This may be considered to be the case for about two bed recycles for processing 130- to 165-day cooled material.

‡ Heat generation in rods is equivalent to 2.81 kw. per 100 kg. of uranium. Heat generation in bed solids is 90 watts per liter. This may be considered to be the case for perhaps five bed recycles for processing 30-day cooled material.

TABLE V
ALUMINA USAGE ECONOMICS

Cooling Time, days	Heat Release*, Btu./hr.-MTU	Al ₂ O ₃ Requirements, kg./kg. U	Storage Volume, cu.ft./MTU†	Storage Cost‡, \$/MTU	Al ₂ O ₃ Cost§, \$/MTU	Total, \$/MTU
30	87,000	0.4	8.5	1,037	160	1,197
60	58,500	0.4	8.5	961	160	1,121
90	45,000	0.4	8.5	893	160	1,053
150	30,000	0.4	8.5	833	160	993
30	87,000	1.0	19.1	1,967	400	2,367
150	30,000	1.0	19.1	1,643	400	2,043

* As estimated using PHOEBE code for fuel with burnup of 10,000 Mw.-days/MTU as a specific powder of 20 kw./kg. of uranium.

† Based on 125 pounds of alumina per cubic foot and 1.5 cubic feet of cladding fines per MTU.

‡ Based on cost table in IDO-14595 and calculation of annular bin thickness assuming that 90% of fission product powder in feed goes to storage and that bed centerline-to-wall ΔT is 1000°C. with a thermal conductivity of 0.3 Btu./hr.-ft.-°F.

§ Assuming cost of \$0.40 per kg. of alumina.

It is also indicated that some storage cost saving may be made by processing longer cooled fuel; however, this saving apparently is not large enough to be economically controlling at the same waste volume. If processing of longer cooled fuel allowed reduction in waste volume, the economic significance would be much greater.

Finally, the cost of alumina is not a large factor for the \$0.40 per kg. (or less) variety; however, one grade has been considered which would cost about \$1.50 per kg. The cost differential for the more expensive alumina is certainly important at 1.0 kg. of alumina per kg. of uranium and is not insignificant at the 0.4 ratio. Nevertheless, use of the higher priced grade would well be justified if it can be employed through more recycles.

CRITICALITY CALCULATIONS

High Enrichment Fuels

One advantage of a volatility process is that the critical mass for the poorly moderated systems is high relative to that for aqueous solution.

processing. Calculations were made for the purpose of estimating the critical mass for highly enriched uranium processing. The limiting case was considered to be the fully reflected sphere.

Accordingly, sizes and uranium masses for urano-uranic oxide spheres reflected with alumina or water were calculated for several values of k_{eff} from 0.9 to 1.0. The uranium-235 density was taken as 3.0 g./cc., which is felt to be the maximum conceivable value for the processes and fuels being considered. The DTK and DDK transport codes were used for the calculations. The results are given in table VI.

TABLE VI
CRITICAL SIZE OF URANO-URANIC OXIDE* SPHERES
FOR DIFFERENT MULTIPLICATION FACTORS, k_{eff}

k_{eff}	Radius, cm.	Uranium-235 Mass, kg.	Reflector†
1.00	24.58	186.6	Water
0.95	22.68	146.6	Water
1.00	21.08	117.7	Alumina
0.98	20.58	109.5	Alumina
0.95	19.80	97.55	Alumina
0.90	18.60	80.86	Alumina

* Uranium is 100% uranium-235 at a density of 3.0 g./cc.

† The reflector thickness is 30 cm., with water and alumina densities of 1.0 and 2.5 g./cc., respectively.

The reflected sphere at 3.0 g./cc. uranium-235 density has been taken as the controlling case, since spheres or cylinders of lower uranium density have somewhat higher critical masses. The possibility of obtaining a sphere or sphere-like geometry with the assumed uranium density is thought to be very slim; accordingly, this assumption is probably quite conservative.

The results also indicate that, for the large reflector thicknesses used, spheres have somewhat lower masses for the same k_{eff} for alumina reflection than for water reflection. Usually, the equivalent of the water-reflected situation might be expected to hold; however, pending analysis of possible effective reflection by furnace and vessel components, as well as alumina contained in the process vessels, the more restrictive alumina-reflected cases are being used.

With the estimated potential calculation error of 2% in k_{eff} , the critical mass of uranium would appear to be greater than 109 kg. As the uranium-235 is diluted with uranium-238 to hold a uranium-235 density of 3.0 g./cc., the critical uranium mass will increase; however, the mass of uranium-235 required for criticality will decrease slightly.

The calculations also indicate that, for either water or alumina reflection, the neutron spectrum is quite fast. For example, at k_{eff} equal to 1, 99% of the neutrons has an energy greater than 10 KEV.

Low Enrichment Fuels

During reprocessing of low enrichment nuclear reactor fuels by fluid-bed fluoride volatility methods, large quantities of uranium dioxide will be contained in the fluid-bed reactors proposed. Several calculations were made using the DTK transport code to determine nuclear properties of uranium dioxide systems for criticality control purposes*. In order to obtain mass limits, homogeneous mixtures of materials were assumed. The ultraconservative case where minimum critical masses result from optimum spacing of feed in a matrix arrangement was not employed. Such a condition is highly unlikely here, particularly considering the relatively small size of the fuel fragments and the random arrangement implied for dumped beds.

Since processing will take place in the dry state at elevated temperatures, assumption of water moderation is unnecessarily restrictive; therefore, neutron multiplication factors in infinite media, i.e., k_{∞} , are listed in table VII for mixtures containing alumina granules and pellets of uranium dioxide at 2 and 5% uranium-235 enrichment.

TABLE VII
INFINITE MEDIUM NEUTRON MULTIPLICATION CONSTANTS
FOR URANIUM DIOXIDE-ALUMINA MIXTURES

Uranium Concentration, g./cc. bulk*	k_{∞}	
	2% Enrichment	5% Enrichment
8.814	0.551	0.843
7.051	0.538	0.828
5.289	0.552	-

* The density of alumina was assumed to be 2.5 g./cc.

Since all the k_{∞} 's are less than 1, a finite system containing any of the above mixtures presents no criticality problem according to the calculations.

* In the event that unirradiated or very short burnup fuels were processed, plutonium would be essentially absent; additional calculations for high burnup fuels are planned in which the largely compensatory effects of uranium-235 depletion and plutonium buildup are considered.

As just noted, elevated temperatures and the sequence of processing steps, no water in liquid form should be present in the equipment. Nevertheless, computations were made in order to evaluate the "order-of-magnitude" of limits for uranium dioxide-water systems. Infinite multiplication factors were determined for uranium dioxide concentrations between 10 and 60 volume percent. In all cases involving 2 and 5% enrichment, k_{∞} was close to or greater than one.

The study was extended to include determinations of critical properties of geometric systems (cylinders and spheres) containing uranium dioxide pellets and water. The cylinder calculations assumed infinite length with 30 cm. of water reflection. Critical radii are shown in table VIII.

TABLE VIII
CRITICAL RADII OF INFINITE CYLINDERS*
CONTAINING URANIUM DIOXIDE-WATER MIXTURES

Uranium Dioxide, volume percent	Uranium Concentration, g./cc.	Critical Radius, cm.	
		2% Enrichment	5% Enrichment
60	5.765	-	29.80
40	3.843	30.91	17.61
30	2.882	25.67	15.28
20	1.992	26.59	14.11
10	0.9608	-	15.37

* Reflected with 30 cm. of water.

Table IX gives the critical masses and critical radii of several spheres containing uranium dioxide-water mixtures, assuming 30 cm. of water reflection. The minimum critical masses appear to be about 370 kg. of 2% enriched uranium at 21 volume percent uranium dioxide in water and 37 kg. of 5% enriched uranium at 9.4 volume percent uranium dioxide in water.

TABLE IX
CRITICAL SPHERES* OF URANIUM DIOXIDE-WATER MIXTURES

Uranium Dioxide, volume percent	Uranium Enrichment, Percent Uranium-235	Uranium Concentration, g./cc.	Critical Radius, cm.	Critical Mass, kg. of U
25	2	2.402	33.93	393.02
20	2	1.992	36.04	376.89
15	2	1.441	41.65	436.1
13	2	1.249	49.41	631.1
15.5	5	1.489	19.68	47.54
12	5	1.153	20.37	40.82
8	5	0.7684	22.81	38.20
6	5	0.5764	26.72	46.06

* Reflected with 30 cm. of water.

When a k_{eff} of 0.90 is employed for mixtures of uranium dioxide pellets in water, computations indicate that a sphere containing 21 volume percent uranium dioxide at 2% enrichment should be limited to a radius of 25.88 cm. The mass limit for the above set of conditions is thus 146 kg. of uranium; i.e., the amount of uranium contained in such a sphere at the optimum hydrogen-to-uranium ratio. Likewise, a sphere with 9.4 volume percent uranium dioxide at 5% enrichment should have a radius of 17.60 cm. and a mass of 20.62 kg. of uranium.

Since these critical quantities for liquid water-uranium dioxide mixtures are less than the conceptual design point batch charge of about 500 kg. of uranium, the contemplated precautions in design and the use of operating interlocks which will, to a satisfactory degree, prevent liquid water interjection appear to be mandatory. These precautions include use of air cooling for the reactor and auxiliaries, and provision of sensor activated interlocks to prevent operation at temperatures which would allow liquid hydrogenous material accumulation.

Plutonium

Four critical mass calculations have been made for spherical plutonium salt assemblies reflected with alumina. The resultant numbers provide some orientation for critical mass problems involved in power reactor fuel processing. Table X gives the results of these computations. At a reflector thickness of 50 cc. and a plutonium density of 4.6 g./cc., the critical radius was 10.79 cm., and the critical mass was 24.2 kg. of plutonium. The total diameter of the core reflector assembly was about 123 cm. The critical mass for the high density spheres of plutonium

dioxide is about 20% of that found for spheres of urano-uranic oxide with 3.0 grams of uranium per cubic centimeter.

TABLE X
CRITICAL MASS OF PLUTONIUM DIOXIDE SPHERES
REFLECTED WITH ALUMINA

Plutonium Density*, g./cc.	Reflector Thickness†, in.	Critical Radius, cm.	Critical Mass of Plutonium, kg.
3.0	12.8	15.14	43.6
4.6	0	17.86	109.8
4.6	12.8	11.20	27.1
4.6	20.0	10.79	24.2

* The plutonium densities of 3.0 and 4.6 g./cc. are based on 30 and 45% of the theoretical crystal density of plutonium dioxide, respectively.

† The density of alumina reflector was taken as 2.5 g./cc.

It should be realized that the assumed plutonium densities and reflector thicknesses may be unnecessarily restrictive. Additionally, it should be recognized that plutonium-239 was used for the calculation rather than the probably less reactive mixture of the 239, 240, 241, and 242 isotopes present in the irradiated low assay enriched uranium dioxide power reactor fuels.

COLD TRAPS

Final collection of uranium hexafluoride in any of the volatility processing methods will be accomplished by desublimation in a refrigerated heat exchanger; i.e., cold trap. Batch desublimers have been generally used for condensation of uranium hexafluoride as a solid since the inception of the uranium isotope separation program in the early 1940's. A design procedure* was worked out at that time which, in essence, is still being used. This procedure utilized the basic heat and mass transfer equations which were interrelated by the application of the Chilton-Colburn j-factor equations. One of the biggest difficulties was prediction of the holding capacity of a trap, since the point accumulation rates for the empty exchanger were assumed to hold to plugging without correction for the effects of the deposit or the increase in gas velocities. Experimental work on several sizes of traps of similar geometry, however, allowed formulation of empirical correction factors.

* Thompson, W. I., "Theory of Heat and Mass Transfer in Batch Condensation of Solids", Engineering Developments in the Gaseous Diffusion Process, U.S.A.E.C., Technical Information Service Extension, Oak Ridge, Tennessee, 1949 (NNES-II-16).

Because of the emerging requirements for new cold trap designs for the uranium hexafluoride and plutonium hexafluoride in volatility programs, coupled with the ready availability of high speed data processing equipment, improvements to this historic procedure are now both justified and possible. Accordingly, a desublimer design digital computer program is being developed.

A series of checks of the computer program is being made for a 10-inch diameter, "egg-crate" type trap design*. This trap is employed in the facility used for reprocessing uranium scrap returns at ORGDP. The theoretical uranium hexafluoride capacity is being calculated for various inlet concentrations of uranium hexafluoride, noncondensable flow rates, and inlet temperatures. In the future, such investigations will be of importance in the design of cold traps, not only for uranium hexafluoride, but for other desublimable materials. Availability of ready calculation techniques will potentially allow study of the basic characteristics of desublimer designs at a much lower cost than pilot plant testing.

Before such computer simulation studies can be accepted and given credence, it must, of course, be shown that the results are consistent with those observed on operating systems. Accordingly, comparison of available data from both experimental testing and production operation of various traps with corresponding calculated results is planned.

Preliminary results of calculations are shown in table XI. The estimated operating conditions for this size trap in the ORGDP scrap reprocessing area are inlet temperature, about 60°C.; flow rate, about 0.4 pound per mole inert per hour; and inlet concentration of uranium hexafluoride, about 15 mole percent. The calculated capacity for these conditions is lower than the reported operational experience of approximately 270 pounds of uranium hexafluoride, although it can be seen that calculations for somewhat lower uranium hexafluoride concentrations and somewhat higher noncondensable flow rates tend toward this figure. As with any other batch desublimation problem, assumptions made as to the thermal conductivity and, particularly, density of the deposit are relatively crucial in estimating batch capacity. Unfortunately, accurate information as to the values of these deposit characteristics for various conditions of deposition appears to be scarce.

* Such a trap is depicted in the following reference: Smiley, S. H., Brater, D. C., Littlefield, C. C., and Pashley, J. H., "Quantitative Recovery of Uranium Hexafluoride from a Process Gas Stream", Ind. Eng. Chem., 51, 191-196 (1959).

TABLE XI
 CALCULATED URANIUM HEXAFLUORIDE CAPACITY
 FOR 10-INCH DIAMETER, "EGG-CRATE" TYPE COLD TRAP

<u>Inlet Uranium Hexafluoride, mole percent</u>	<u>Inert Flow Rate, lb. mole/hr.</u>	<u>Inlet Gas Temperature, °C.</u>	<u>Uranium Hexafluoride Holding Capacity*, pounds</u>
15	0.4	60	218
15	0.6	60	246
15	0.4	40	233
15	0.4	90	253
30	0.4	60	211
5	0.4	60	259

* Calculated using a nitrogen inert, trap cooling temperature of minus 48°C., desublimed solid thermal conductivity of 0.1 pcu./hr.-ft.-°C., and bulk density of 135 pounds per cubic foot.

More exact plant trap performance data will be obtained when the reprocessing system is next operated. Additionally, improvements are being made to the program which should increase calculation accuracy.

PROTOTYPE TESTING AND EVALUATION

D. C. Brater, L. W. Anderson, P. S. Cates,
B. L. Geldmeier, H. L. Kaufman, V. H. Kiplinger

MATERIALS OF CONSTRUCTION - CORROSION TESTING AND RELATED STUDIES

For a commercial reprocessing facility, it may be desirable to use a single fluid-bed reactor for all types of low and high enrichment fuels. Thus, the reactor must be able to withstand the conditions for (a) the hydrogen chloride-fluorine procedure for high enrichment zircaloy and aluminum alloy fuels, (b) the hydrogen chloride-oxygen-fluorine process for low enrichment zircaloy-clad ceramic fuels, and (c) the hydrogen fluoride plus oxygen-fluorine system for stainless steel and zircaloy-clad ceramic fuels. Because of the high temperatures during oxidation, a separate system would be required for graphite-type fuels.

To evaluate various materials, tests are being conducted in a bench-scale controlled-atmosphere loop. Samples are sealed in an electrically heated vessel, and gas of the desired composition is passed through the system at a low rate. To minimize the possibility of inleakage, an all-welded system is used. Additional data are being accumulated in conjunction with filter performance evaluation in a fluid-bed system. The results of the studies completed to date are presented in table XII. For convenience, the tests are divided into two groups, i.e., filter materials and flange and reactor materials, and will not necessarily be discussed in the numerical order shown in the table. Conditions expected for the high enrichment zircaloy and the low enrichment stainless steel-clad fuels have been studied to date. Tests with alternating hydrochlorination, oxidation, and fluorination atmospheres have been started to obtain data for the low enrichment zircaloy-clad fuel recovery process.

Filter Materials

In run 1, samples of porous nickel and Monel filter materials and a porous alumina disc were subjected to cyclic exposures at 315°C. to a mixture of zirconium tetrachloride, stannous chloride, hydrogen chloride, and hydrogen, and then to a fluorination atmosphere of uranium hexafluoride, fluorine, and nitrogen. These conditions are expected when high enrichment zircaloy fuels are reprocessed. Twenty-two cycles of alternating 16-hour hydrochlorinations and 4-hour fluorinations were made. As was anticipated, no apparent attack of the alumina was noted, while the Monel sample deteriorated extensively. Microscopic examination of the nickel sample indicated that it withstood the exposure well, as there was no evidence of cracking. Flow tests showed that the permeability was acceptable for filtering purposes.

Run 2 was made to investigate further the corrosion effects of hydrogen chloride and fluorine on sintered nickel filter material. Two samples cut from a Micrometallic type-G nickel bayonet filter tube were exposed

TABLE XII
RESULTS OF CORROSION TESTS

Test No.	Materials	Total Number of Cycles	Phase I		Total Exposure, hr.	Phase II		Total Exposure, hr.	Corrosion Penetration*, mils/year	Corrosion Description and Remarks
			Gas Components	Exposure Temp., °C.		Gas Components	Exposure Temp., °C.			
1	Porous Nickel-200 Porous Monel Alundum	22	HCl, H ₂ , ZrCl ₄ , SnCl ₂	315	228	F ₂ , N ₂ , UF ₆	315	81		Good condition Badly contaminated No apparent attack
2	Porous Nickel-200	20	HCl, H ₂	315	216	F ₂ , N ₂	205	80		Good condition
3	Duranickel Low P Electroless Ni Plate High P Electroless Ni Plate	20	HCl, H ₂	400	246	F ₂ , N ₂	540	87		Good condition Heavily corroded Heavily corroded
4	Porous Nickel-200 Duranickel	20	HCl, H ₂ , ZrCl ₄ , SnCl ₂	315	218	F ₂ , N ₂ , UF ₆	200	80	6.9	Good condition Good condition
5	Aluminum Wire Anodized Aluminum Nickel-Coated Steel Al ₂ O ₃ -Coated Steel	1	HCl, H ₂	200	100					Disintegrated Disintegrated Slight weight gain Slight weight gain
6	Hastelloy-C Hastelloy-F Hastelloy-G Hastelloy-N Duranickel Nickel-200	20	HCl, H ₂	400	235	F ₂ , N ₂	540	80	477 195 90.5 48.0 8.8 1.1	Yellow, brown flakes Heavy, yellow powder Heavy, yellow powder White, brown flakes Light, white powder Light, white powder
7	Hastelloy-C Hastelloy-F Hastelloy-G Hastelloy-N HyMu-80 Duranickel	10	HF, O ₂	590	95	F ₂ , N ₂	540	40	1,970 238 376 117 39	Entirely consumed Heavy, yellow flakes Heavy, yellow powder Light, yellow scale Light, yellow powder Light, white powder

TABLE XII (Contd.)
RESULTS OF CORROSION TESTS

Test No.	Materials	Total Number of Cycles	Phase I		Total Exposure, hr.	Phase II		Total Exposure, hr.	Corrosion Penetration*, mils/year	Corrosion Description and Remarks
			Gas Components	Exposure Temp., °C.		Gas Components	Exposure Temp., °C.			
8	INCO-61 Fod	20	HCl, H ₂	400	236	F ₂ , N ₂	540	77	182	Yellow powder
	Silver Solder									Entirely consumed
	Welded Inconel								79.3	Heavy, yellow powder
	Inconel								55	Heavy, yellow powder
	Welded HyMu-80								41	Heavy, yellow powder
	HyMu-80								21	Heavy, yellow powder
	Welded Nickel-200								7.1	Light, yellow powder
	Nickel-200								5.1	Light, yellow powder
	Welded Nickel-201								4.9	Light, yellow powder
	Nickel-201								4.2	Light, yellow powder
	Welded Duranickel								8.2	Light, white powder
9	Porous Nickel	1				F ₂ , N ₂	550	12		Material was heavily corroded and brittle
10	Porous Nickel	1				F ₂ , N ₂	550	21		Material was heavily corroded and brittle

* Based on weight change and sample surface area.

alternately to hydrogen chloride in hydrogen at 315°C. and to dilute fluorine at 205°C. for twenty cycles involving 80 hours of fluorination and 216 hours of hydrochlorination. The experiment was started with a fluorination cycle and was concluded after a hydrochlorination cycle. One of the porous nickel samples was subsequently fluorinated for 4 hours before analyses were made.

Visual inspection showed that both samples had darkened in color with a thin, reddish deposit on the bayonet weld area. Laboratory analysis of the sintered nickel showed 81 ppm. fluoride and 398 ppm. chloride after hydrochlorination and 1,170 ppm. fluoride and 130 ppm. chloride after fluorination. These low fluoride and chloride values were considered acceptable for fluoride volatility applications. Flow measurements indicated a 20% plug of the material caused by the exposure treatment, but this loss is not considered serious. Figure 5 shows the grain structures of the exposed and unexposed samples involved in this test.

A qualitative spectrographic analysis of the reddish deposit on the areas and also of the weld material itself showed unexpectedly high concentrations of iron and manganese. Modification of vendor welding procedures may be necessary if this type filter is to be used.

Another study of the Micrometallic type-G porous nickel material was made in test 4 wherein samples were subjected to twenty cycles of exposures to hydrogen chloride, hydrogen, and zirconium tetrachloride at 315°C. and to fluorine, uranium hexafluoride, and nitrogen at 200°C. Small weight gains of less than 1% were experienced during this test, and again the sample appeared undamaged.

It was thought originally that, in a low enrichment fuel reprocessing facility, treatment of the fluoride volatility equipment periodically with fluorine at 550°C. might be necessary to convert any reduced plutonium tetrafluoride in the system back to plutonium hexafluoride. One of the concerns of such a procedure was the effect of the treatment on the porous nickel filters. In test 9, two samples of Micrometallic porous nickel were exposed to fluorine at 550°C., one for 12 hours and one for 21 hours. Examination of the exposed materials, figure 6, showed that both samples were heavily corroded, had become very brittle, and were not acceptable as filter material. The present opinion of Argonne National Laboratory personnel is that the plutonium cleanup will be satisfactory at 350°C.; therefore, the test is to be repeated at that temperature level.

A problem which might be encountered in fluorinating a filter is that uranium deposits could react rapidly resulting in high localized temperatures and filter failure. Prediction of the magnitude of such a problem is difficult; however, it should be noted that, in a low enrichment zircaloy-clad fuel system using simultaneous oxidation and fluorination, uranium dusts should not reach the filter. Uranium accumulation on the filter would be expected with the present flow sheets for high enrichment alloy fuels and low enrichment stainless steel-clad fuels. Temperature measurements on the filter may be necessary to evaluate this

Unexposed

After Final HCl Treatment

After Final F₂ Treatment

Figure 5
CORROSION OF POROUS NICKEL

21 Hours
Exposure

12 Hours
Exposure

1-1/4 X Magnification

12 Hours Exposure

21 Hours Exposure

50 X Magnification

Figure 6

POROUS NICKEL EXPOSED TO FLUORINE AT 550°C.

problem.

One test was also made early in the program (not shown in table XII) to investigate the suitability of various filter materials for alternating oxygen-fluorine exposures, both at 315°C. These atmospheres would be encountered in a volatility system for reprocessing graphite-type fuels. Sintered nickel, porous alumina, fine nickel wire, and nickel wool all appeared satisfactory.

Flange and Reactor Materials

The search for a hard surface for gasket compression in connector design for the process was the reason for test 3. Samples of Duranickel (a nickel alloy containing about 4-1/2% aluminum), low phosphorus electroless nickel plate, and high phosphorus electroless nickel plate were subjected to cyclic exposures of hydrogen chloride in hydrogen at 400°C. and dilute fluorine at 540°C. Twenty cycles were completed involving 246 hours of hydrochlorination and 87 hours of fluorination.

Both of the electroless nickel plate samples became heavily corroded; thick, powdery deposits formed on the surfaces. Microphotographs, figure 7, revealed that, while a considerable amount of the electroless plate remained after the exposure treatment, there was corrosion penetration into the plate.

The Duranickel sample withstood the corrosion attack well. A very light, white, powdery film was visible on the surface after exposure, and microphotographs, figure 8, showed a slight surface attack but no intergranular attack. These results were supported in subsequent tests, 4, 6, and 8, which indicate a corrosion rate of less than 10 mils per year under similar exposure conditions.

In test 5, parts of a proposed canned rotor pump having possible application for gas recycle during fuel reprocessing was subjected to a flow of hydrogen chloride in hydrogen at 200°C. for 100 hours. As expected, samples of aluminum and anodized aluminum disintegrated. Steel and electroless nickel-plated steel parts darkened in color, but very little weight change was noted. Electroless nickel-plated steel plasma-coated with aluminum oxide appeared unaffected.

Tests 6 and 8 were made to evaluate possible materials of construction for the head-end fluid-bed reactor where high strength at elevated temperatures is required in addition to corrosion resistance. In test 6, samples of Hastelloy-C, Hastelloy-F, Hastelloy-G, Hastelloy-N, Duranickel, and nickel-200 were exposed to cyclic hydrochlorination at 400°C. and fluorination at 540°C. The corrosion penetration of the Hastelloys was found to be high compared with Duranickel and nickel-200 under the conditions of the test.

In test 8, samples of silver solder, INCO-61 welding rod, welded and unwelded Inconel, HyMu-80 (80% nickel, 4% molybdenum, and 16% iron), nickel-200, and nickel-201 were subjected to twenty cycles of alternating

Plastic

Corrosion Product

Nickel Plate

Substrate

Magnification 500 X

High Phosphorus

Plastic

Corrosion Product

Nickel Plate

Substrate

Magnification 500 X

Low Phosphorus

Figure 7

ELECTROLESS NICKEL PLATE CORROSION ATTACK

Plastic

Duranickel

Unexposed

Magnification 500 X

Plastic

Duranickel

Exposed

Magnification 500 X

Figure 8
DURANICKEL CORROSION ATTACK

exposures to hydrogen chloride and hydrogen at 400°C. and to dilute fluorine at 540°C. All nickel welds were made with INCO-61 rod, while the Inconel and HyMu-80 samples were welded with INCO-82T rod. Nickel again exhibited the best corrosion resistance. The weight losses for the welded samples were greater than those for unwelded samples of the same materials, and microscopic inspection showed the corrosion penetration of the weld material to be several times that of the base metal. Some of the samples after exposure are illustrated in figures 9 and 10.

Stainless steel-clad fuel elements require decladding in a hydrogen fluoride-oxygen atmosphere; therefore, in test 7, samples of Hastelloy-C, Hastelloy-G, Hastelloy-N, HyMu-80, and Duranickel were suspended in the filter loop fluid-bed reactor above the powder bed and were subjected to ten cycles of alternate exposures to hydrogen fluoride and oxygen at 590°C. and to dilute fluorine at 540°C. Again, the Hastelloys exhibited poor resistance to the exposure conditions. The Hastelloy-C sample corroded to the extent that it fell from its support into the fluid bed during the sixth cycle and was assumed to be consumed during the test. Microphotographs of the HyMu-80 and Hastelloy-N samples, figure 11, show the attack on these materials. While Duranickel exhibited fair resistance to corrosion, based on penetration data, some intergranular attack was present, as shown in figure 12.

In summary, it is apparent that nickel-200, nickel-201, and Duranickel are the most corrosion-resistant materials tested to date. As new alloys become available, they will be exposed to similar conditions; e.g., samples of an alloy called Berylco Nickel-440 are being prepared for testing. This metal contains small quantities of beryllium and titanium and has age hardening properties which might be useful in flange face application.

PROCESS AND REACTOR STUDIES

Extension of studies made at the National Laboratories will be necessary to prove the volatility processes on a larger scale and to obtain good engineering design data for a production facility. The major uncertainty in basing plant design on the present small-scale work arises from the fact that good fluidization and bed homogeneity are probably not achieved during the decladding and pellet oxidation steps for recovery of low enrichment zircaloy or stainless steel-clad fuels. Predictions of heat transfer and gas contact problems, therefore, are difficult if not impossible. To obtain the required design information, process work on a larger scale is planned. The initial tests will be made in a 10-inch diameter head end reactor. Still larger equipment will be used if necessary. In addition, the decladding and fluorination reactions will be observed in the filter test loop in conjunction with that test program. Inert gas fluidization will also be studied in transparent columns to evaluate proposed reactor sizing and configuration.

Plastic

Corrosion

Hy Mu-80

Hy Mu-80

Magnification 500 X

Plastic

Corrosion

Hastelloy N

Hastelloy N

Magnification 500 X

Figure 9
CORROSION RESULTS (TEST #8)

Magnification 250 X

Ni-200

Magnification 250 X

Ni-201

Figure 10
CORROSION RESULTS (TEST #8)

Plastic

Corrosion

Hy Mu-80

Hy Mu-80 Magnification 500 X

Plastic

Corrosion

Hastelloy N

Hastelloy N Magnification 500 X

Figure 11
CORROSION RESULTS (TEST #7)

Plastic

Corrosion Products

Intergranular Attack

Duranickel

Magnification 500 X

Duranickel

Figure 12
CORROSION RESULTS (TEST #7)

Decladding and Fluorination Studies

Some studies related to the hydrogen chloride reaction with high enrichment zirconium alloy fuels have been made in conjunction with filter tests which are described later. In these studies, where expected conditions at the filter must be simulated as nearly as possible, information on the performance of the fluid-bed reactor for the various process steps is generated at little or no additional cost. Uranium metal was added to the fluid bed before halogenation to simulate more nearly conditions which might increase filter loading, either from volatile uranium tetrachloride or from fine uranium trichloride particulates. Inspection following hydrochlorination showed that the bed was black instead of the green uranium chloride color expected. Analyses of the bed material detected the presence of uranium dioxide.

Although the formation of uranium dioxide was unexpected, it is known that uranium will react readily with oxygen and even preferentially in basically chloride systems; therefore, a series of test runs was conducted to determine the oxygen source. The tests included (a) substituting magnesium fluoride as a fluid-bed media instead of alumina, (b) drying the hydrogen with Molecular Sieves, (c) drying the hydrogen chloride with refrigerated silica gel, and (d) substituting argon for the nitrogen diluent. In all cases, oxidation of the uranium still occurred, thus indicating that the oxygen contents of the nitrogen and argon diluents were higher than could be tolerated. This assumption was verified when a test run made with undiluted hydrogen and hydrogen chloride gave a green reaction product in the bed.

During the testing of sintered Monel filters in the hydrogen fluoride-oxygen system proposed for decladding stainless steel-clad uranium dioxide fuel elements, a number of observations relating to performance of the fluid bed were made. Several test decladding runs were made using stainless steel 347 and 304L tubing. Hydrogen fluoride concentrations were varied from 15 to 80%, and reaction temperatures covered a wide range of 540 to 620°C. In general, the observations reported by ANL and BNL were verified. A hydrogen fluoride concentration of 40% and a bed temperature of 590°C. appeared to be the optimum. In all cases, the decladding reaction produced a hard, coarse oxide scale that was slightly magnetic and insoluble in hydrochloric acid. Fluorination treatment broke the scale into fine particles.

Presently, studies of pulverizing uranium dioxide pellets by oxidation and of fluorinating the resulting urano-uranic oxide to uranium hexafluoride are being made in conjunction with Purolater filter unit tests.

Inert Gas Fluidization

Two brief investigations were made with fluid beds utilizing glass columns for visual observation. The first of these was carried out to determine the possibility of simplifying low enrichment stainless steel clad fuel reprocessing by separating the stainless steel oxide scale from the alumina bed by elutriation. The bench-scale unit consisted of

a 2-inch diameter glass column mounted below a 5-inch diameter glass column. Air for fluidizing and elutriation entered at the bottom of the 2-inch column. The columns were filled with minus 100-mesh tabular alumina to a height of about 6 inches in the 5-inch column, and 500 grams of coarse stainless steel oxide scale was inserted on the top of this bed.

When an air flow was established, the stainless scale moved downward through the two glass sections and collected in the 2-inch portion; however, complete separation could not be accomplished with gas velocities as great as 10 feet per second. A velocity of 20 feet per second in the 2-inch column elutriated both the alumina and the scale.

In a second test, the 5-inch glass column was used to observe fluidization in a simulated bed of uranium dioxide pellets. The conical bottom was filled with 1/2- and 1/4-inch steel balls. Minus 60-mesh tabular alumina was then added to the column to a depth of 1 foot. This bed fluidized nicely at a gas velocity of 0.2 to 0.6 foot per second, and some elutriation was evident at about 1 foot per second. Stainless steel pellets, 1/2 inch in diameter by 1 inch long (simulating oxide fuel pellets), were then inserted on top of the alumina bed to a depth of 4 to 5 inches. The pellets moved downward through the bed during fluidization to the ball bearing base; however, movement around the pellets was essentially nil even with gas velocities as high as 3 feet per second. Some evidence of gas channeling through the pellets was observed.

The test was repeated using 60- to 100-mesh Norton RR Alundum. Although a higher fluidization velocity was required (0.75 to 1.0 foot per second), the results were essentially the same as with tabular alumina.

An 8-inch transparent plastic column is being fabricated to study fluidization and gas flows in beds containing simulated reactor fuel modules.

Semiworks Reactor

The design of the planned semiworks head-end reactor is shown in figure 13. The 10-inch diameter reactor will be provided with a 3-1/2-foot long, 5-inch diameter lower section for the initial tests. The reduction in diameter at the bottom of the reactor will increase the gas velocity through the portion of the bed which will contain the nonfluidizable chunks of stainless steel oxides and/or uranium dioxide pellets. Improved heat transfer and gas contact should result. If the two-diameter concept proves to be undesirable, this lower section can be removed easily. Furthermore, bottom sections of different dimensions can be fabricated and evaluated if program results indicate the expediency of such an approach.

The reactor dimensions are almost half those estimated for a production unit capable of processing about 500 kg. of uranium dioxide per batch. A charge of 65 to 85 kg. of uranium dioxide will be used. Studies of both the hydrogen chloride and hydrogen fluoride-oxygen decladding methods will be possible, and fluorine introduction will be provided at several

Figure 13
SEMI-WORKS FLUID-BED REACTOR

points so that simultaneous oxidation and fluorination can be evaluated. The system could also be modified to test the bromine pentafluoride fluorination flow sheet.

Based on an anticipated specific reaction rate of $34 \text{ kg. of uranium hexafluoride per hour per square foot of cross-sectional area}$, about 20 kg. of uranium hexafluoride will be produced per hour in the 10-inch diameter bed with a heat generation of about 50,000 Btu./hr. Setting the bed depth at 5 feet, the heat flux at the inside wall is about 3,800 Btu./hr.-sq.ft. which should be removed easily, since the high temperatures of the operation, 400 to 500°C., allow a correspondingly high temperature differential between reactor and coolant.

The rate of oxidation of the uranium dioxide is expected to be stoichiometrically equivalent to the rate at which urano-uranic oxide is fluorinated; therefore, the oxidation rate of the uranium dioxide pellets will be about $34 \text{ pounds of urano-uranic oxide reacted per hour}$ with an associated heat generation of 5,600 Btu./hr. Using a 3-foot packed bed depth in the oxidation section, the average heat flux at the inside wall is about 1,400 Btu./hr.-sq.ft. The point heat release rate is expected to be somewhat greater owing to the difficulty of achieving good fluidization and corresponding evening of temperatures in the pellet zone. Despite this factor, the high temperature differential attainable, coupled with the ability to vary the oxygen content of the feed gas, hopefully will allow reasonable control.

Off-gases from the reactor will be cooled to 100°C., probably in a fluid-bed cooler, and will be filtered through sintered nickel filter tubes. Cooling to 100°C. is specified, since in the end application, such a temperature limit is expected to minimize thermal decomposition of the plutonium hexafluoride. From a filter life standpoint, cooling to 200°C. should be ample. The product uranium hexafluoride will be collected in cold traps for accountability purposes.

For stainless steel-clad fuels, the declad procedure of present choice is hydrogen fluoride-oxygen treatment at about 600°C. Although this treatment breaks up the uranium dioxide itself into fine powder, it leaves much of the clad in the form of relatively coarse, i.e., greater than 20 mesh, shards which tend to sink to the bottom of the fluid bed. The ability to use a high gas velocity and to control reagent concentrations in the smaller diameter section of the semiworks bed should be of advantage in minimizing hot spots by control of the reaction of these pieces.

OUTLET GAS FILTER STUDIES

Commercially available sintered metal filters are being evaluated in the test loop shown in figure 14. The loop includes a 4-inch diameter fluid bed, an inlet gas preheater, an internally finned outlet gas cooler, and a filter section. The purpose of this work is to determine if sintered metal filters mounted directly above the fluid bed will give satisfactory service in the proposed volatility processes. Packed bed filters scaled

Figure 14

FILTER TEST LOOP

from laboratory studies would be quite large in a plant system and would increase the possibility of uranium and/or plutonium holdup and loss. Also, since a considerable amount of uranium dust would probably be transported to the filter during decladding and/or pellet oxidation, generation of heat at the filter during fluorination could present difficulties.

The first series of tests was made with type-G Micrometallic nickel bayonet filter tubes. During hydrofluorination, an operating temperature of 315°C. at the filter was selected because this is the minimum safe temperature necessary to prevent condensation of stannous chloride. At the flow sheet fluorination conditions, condensation will not be a problem provided the temperature is above 100°C. Based on past ORGDP experience, a maximum filter temperature of 200°C. was chosen for the fluorination step.

Two 3-inch wide by 3-foot long filter tubes were subjected to fourteen cycles in which first dilute hydrogen chloride-hydrogen and then fluorine-nitrogen mixtures were passed through a bed of Alcoa T-61 tabular alumina and through the filters. Fluidizing velocities were varied from 0.5 to 2.0 feet per second, and fluid-bed temperatures were 400°C. for the hydrochlorination step and 540°C. during fluorination. Filter temperatures were maintained at the levels noted earlier.

During the 183 hours of hydrochlorination and 56 hours of fluorination, the performance of the filters appeared normal. The pressure drop across the tubes increased rapidly and then leveled out at an acceptable value requiring only infrequent blowback. Inspection of the tubes after the runs showed a coating of fine powder which was primarily alumina containing some aluminum fluoride and nickel fluoride. Measurements on the two tubes showed air flows of 7.6 and 6.6 std. cfm., with a pressure differential of 1 psi., as compared with a flow of 28.5 std. cfm. for a new tube. Such initial plugging was anticipated. Similar results were obtained in a second series of tests during which 157 hours of hydrochlorination and 23 hours of fluorination were accumulated. In the latter test, uranium metal turnings were added to the bed before each cycle to provide uranium hexafluoride in the gas passing through the filter during fluorination.

Slight cracking at the welds of the bayonet tubes was noted after the tests just described, and the next evaluations were made with Micrometallic cylindrical tubes of the same material. After 150 hours of hydrochlorination and 20 hours of fluorination, the cylindrical tubes were inspected and were found to be badly cracked on each side of the longitudinal weld, figure 15. Analyses of the weld material showed some titanium, about 1%, indicating that INCO nickel-61 welding rod had been used.

In view of the weld cracking problems, molded (seamless) nickel filter tubes manufactured by the Purolator Corporation were obtained and are being evaluated. In these tests, an oxygen exposure has been added after hydrochlorination to simulate more nearly the process for low enrichment fuels. The exposure treatment consists of hydrogen chloride and hydrogen

Figure 15
POROUS NICKEL FILTER FAILURES

for 5 hours at 315°C., oxygen for 10 hours at 100°C., and fluorine for 10 hours at 100°C. At the recommendation of Argonne National Laboratory, the filter temperature during fluorination was lowered from 200 to 100°C., the temperature necessary to lower plutonium decomposition to an acceptable value during actual processing. The bed in the reactor consists of minus 60-mesh tabular alumina. After four cycles, the tubes were inspected and were found to be in excellent condition. Testing is continuing.

One series of tests was made to determine the suitability of cylindrical Micrometallic Monel tubes for the alternating hydrogen fluoride-oxygen and fluorine atmospheres encountered when stainless steel-clad fuels are reprocessed. As would be expected from production experience in uranium hexafluoride manufacturing plants developed and operated by Union Carbide Corporation, these tubes were in excellent condition following 10 cycles of exposure involving about 50 hours with each gas. The filter temperature was held at 200°C. Stainless steel tubing was charged to the bed before each cycle to simulate chemical conditions during decladding. Monel tubes were not tested for the hydrochlorination-fluorination system because bench-scale corrosion tests showed rapid deterioration of the Monel.

Following the tests currently in progress, use of Inconel tubes will be studied. At the lower filter temperature of 100°C. during fluorination, Inconel may be equal to, or even better than, nickel for the combined service.

PRODUCT PURIFICATION, SORPTION-DESORPTION SYSTEM

In the flow sheets for the proposed volatility processes, there are several applications for solid sorbent traps. With high enrichment fuels where the plutonium content is negligible, fluorination off-gases are passed through high temperature (400°C.) sodium fluoride pellet traps to remove some fission products. The partially purified uranium hexafluoride is then collected on low temperature (120°C.) sodium fluoride pellets allowing other impurities, such as molybdenum, to pass through. Similar uranium hexafluoride purification in the low enrichment cases might also be possible following plutonium removal.

Studies are being made in three different systems. Investigation of operating conditions and testing of various types of sodium fluoride pellets are proceeding in a simple cylindrical trap. Trap design is being evaluated by testing a prototype annular unit; and finally, a continuous uranium hexafluoride collection system involving a fluidized bed of sodium fluoride powder and a screw regenerator is being considered. A pilot-scale unit of this latter type is available from other programs.

Cylindrical Pellet Trap

The test loop, figure 16, constructed to study pellet characteristics and effects of operating conditions consists of a vertical length of 4-inch nickel pipe providing a 7-foot deep bed of pellets. The trap is electrically heated and water-cooled and is installed with a gas metering station, cold traps, and an outlet gas uranium hexafluoride detection unit.

Figure 16
4" SORBER LOOP

The first series of tests, runs 1 through 24 in table XIII, was made to study the effects of various gas compositions on uranium hexafluoride sorption capability. Effects of uranium hexafluoride, fluorine, and chlorine trifluoride concentrations were determined; chlorine trifluoride will be encountered in the high enrichment process when chlorides are converted to fluorides. The sodium fluoride used was prepared from commercially available*, 1/8-inch, cylindrical pellets of sodium bifluoride by heating at 540°C. for 5 hours in an inert atmosphere. Operation was carried out using a sorption temperature of 120°C., a gas retention time of 80 seconds (assuming 100% voids), and a desorption temperature of 400°C. During the sorption cycle, the gas flows were maintained constant with the gas entering the top and leaving the bottom of the bed until uranium hexafluoride breakthrough was indicated by the detection unit in the trap outlet line. Concentrations in excess of 1 ppm. of uranium hexafluoride were considered breakthrough.

TABLE XIII
RESULTS OF 4-INCH DIAMETER SODIUM FLUORIDE TRAP SORPTION TESTS

Run Number	Total Flow, std.cfm.	Inlet Gas Concentration, %				Average Sorption Time, hr.	Average Desorption Time, hr.	Average Sorption Ratio, lb. UF ₆ /lb. NaF
		UF ₆	F ₂	ClF ₃	N ₂			
1	0.3	10	15	30	45	27.7	12	0.49
2 thru 14	0.3	10	15	30	45	6.3	12	0.28
15 thru 18	0.3	10	15	60	15	5.1	14	0.28
19 thru 23	0.3	10	15	0	75	8.3	14	0.47
24	0.3	10	15	30	45	5.0	14	0.25
A-1	0.3	10	15	30	45	8.2	14	0.45
A-2 thru A-6	0.3	10	15	30	45	5.2	14	0.26
A-7 thru A-10	0.3	10	15	0	75	3.9	14	0.21
B-1 thru B-6	0.3	10	15	30	45	2.9	14	0.10
B-7 thru B-15	0.3	10	15	0	75	3.0	14	0.11
C-1 thru C-5	0.3	10	0	0	90	3.9	14	0.13
D-1 thru D-5	0.3	10	15	0	75	12.1	14	0.67

On completion of the sorption cycle, the trap was purged, valved to reverse the gas flow through the bed, and heated to 400°C. A small flow of fluorine was used to sweep the desorbed uranium hexafluoride and to convert any uranium pentafluoride to uranium hexafluoride.

* Harshaw Chemical Company, Technical Grade No. Na-0101T-1/8.

As can be seen from the data, the sorptive capability of fresh pellets was approximately twice that of used material. The average capacity for used pellets in the first fifteen runs was about 0.28 pound of uranium hexafluoride per pound of sodium fluoride. Runs 15 through 18 show that increasing the chlorine trifluoride concentration from 30 to 60% had little effect on sorption. When the chlorine trifluoride flow was stopped in runs 19 through 23, the sorptive capacity almost doubled; resumption of the chlorine trifluoride flow in run 24 decreased the sorption to the earlier values. This phenomenon did not occur in the A and B series of test runs with different pellets. Run 25 was made to obtain breakthrough data for use in trap sizing and configuration. After the uranium hexafluoride detector showed a trace amount in the outlet gas, bulb samples were withdrawn periodically and were analyzed for uranium hexafluoride. Outlet uranium hexafluoride analyses were 0.3 mole percent 1 hour after breakthrough, 0.7 mole percent after 1-2/3 hours, and 5.5 mole percent after 2-1/2 hours. Data of this type should allow prediction of the performance of traps of various lengths.

The pellets were removed and inspected after run 25. The top 6 inches of the bed was found to be a powder, and the remainder of the bed was a mixture of powder and pellets. Inspection of individual pellets revealed that, while the pellets were quite hard, they were considerably smaller than when charged. In search of a material that would be more resistant to surface degradation, sodium fluoride pellets were heat treated for 5 hours at different temperatures. The properties of these pellets are summarized in table XIV.

TABLE XIV
EFFECT OF PREPARATION TEMPERATURE ON
SODIUM FLUORIDE PELLET CHARACTERISTICS

Treatment Temperature, °C.	Surface Area, sq.m./g.	Void Fraction	Stokes Hardness, div.*
540	2.149	0.406	1.0
590	0.118	0.120	5.5
650	0.061	0.104	6.5
700	0.031	0.038	8.0
760	0.060	0.097	8.0

* Comparative scale.

In the B and C series of tests, pellets were used that had been prepared by heating Harshaw sodium fluoride pellets to 650°C. for 5 hours. These pellets had a surface area of 0.110 sq.m./g. and a void fraction of 0.136. Temperatures and gas flows were similar to those in the original series of tests. It is apparent from the data that the sorptive capacity of

the 650°C. pellets was approximately one-half that of pellets treated at 540°C.

When the trap was emptied and the pellets were inspected, surface degradation was evident, although not so severe as with pellets treated at 540°C. There appeared to be some bonding between pellets; however, the clumps were easily broken apart, and no hard caking was observed. The small decrease in pellet degradation was probably more than offset by the loss in sorptive capacity.

A special sorbent pellet prepared at the Paducah Gaseous Diffusion Plant by pelletizing sodium bifluoride and furnacing at 760°C. was used in the D series of test runs. Gas flows and trap temperatures were again the same as those used previously. The data indicate that the sorptive capacity of this material is nearly three times that of the Harshaw type pellet used in all other runs; however, the fresh Paducah pellets sorbed less than used pellets which is contrary to experience with Harshaw pellets. When the trap contents were inspected on completion of the tests, severe pellet degradation was evident. The upper two-thirds of the trap was nearly 50% powder, and those pellets remaining were easily crumbled. Photographs of the two types of pellets before and after use are shown in figure 17.

After the Paducah pellet material was removed, the trap was filled with Harshaw sodium fluoride pellets which had been heat treated at 540°C. The bed was then subjected to temperature cycling in a nitrogen atmosphere to determine the effect of thermal shock on the pellet. An average cycle consisted of (a) maintaining a temperature of 120°C. for 2 hours, (b) heating to 400°C. in about 3 hours, (c) maintaining a temperature of 400°C. for 4 hours, and (d) cooling to 120°C. in approximately 1-1/2 hours. After seventeen cycles, the trap was opened, and the bed was inspected. No abnormal dusting was evident, and a Stokes pellet test showed no apparent change in hardness. Not surprisingly, these data and inspections of pellets used previously in the 4-inch trap support the belief that pellet degradation is chiefly, if not completely, a function of the amount of sodium fluoride-uranium hexafluoride complex made and decomposed each cycle.

The above pellets were then exposed to a flow of 0.3 std.cfm. of gas consisting of 10% uranium hexafluoride, 15% fluorine, and 75 % nitrogen at varying sorption temperatures. Under these conditions, the sorption ratios, pound of uranium hexafluoride per pound of sodium fluoride, at temperatures of 85, 120, and 175°C. averaged 0.32, 0.37, and 0.10, respectively.

It is apparent from the above tests that occasional changeout of trap charges will be necessary if sodium fluoride pellets are used for uranium hexafluoride sorption. The effective trap operating time will be influenced by the type of pellet used and the uranium hexafluoride loading. When there is no uranium hexafluoride sorption, as in the high temperature fission product removal trap, no pellet deterioration problems would be expected.

Figure 17
SODIUM FLUORIDE PELLETS

Trapping studies will be continued with different type pellets. Some tests are planned with pellets of mixed compositions.

Annular Pellet Trap

The primary problem encountered in designing large pellet traps for production use is one of heat transfer and resultant long desorption cycles. At this time, it is judged that large traps should be of annular design to minimize the distance from the center of the bed to the wall. A prototype unit consisting of concentric 5- and 12-inch diameter Monel pipes having a 60-inch bed height has been constructed. The annulus is baffled so that both the inlet and outlet pipes can be located at the top of the trap, and the bottom is coned to a central discharge port to facilitate removal of the pellets. The unit is heated electrically and is air cooled with the heating and cooling applied to the outside surface of the 12-inch pipe and to the inside surface of the 5-inch pipe. The trap and a flow diagram of the sorber loop are shown in figures 18 and 19.

The results of the annular trap sorption tests are shown in table XV. A total of 184.5 pounds of 540°C. treated sodium fluoride pellets was used as a charge for the first series of runs. In all runs, a sorption temperature of 120°C. and a desorption temperature of 400°C. were used. As was expected, the fresh pellets sorbed more uranium hexafluoride per pound of sodium fluoride than did the used pellets; however, the average sorption ratio amounted to only 0.17 pound of uranium hexafluoride per pound of sodium fluoride. Since this ratio was somewhat lower than expected, the pellets have been put in storage. At a later date, 4-inch trap tests will determine whether the low value is associated with pellet properties or with trap design.

To investigate the possibility of gas channeling in the upflow section, the annular trap was modified for the B series of runs to allow a separate parallel downflow of gases through each side of the annulus and a rejoined flow outlet at the bottom of the trap. Flows through each half were not measured and were dependent on the pressure drops through each of the pellet beds. The sorption ratios for a third charge of pellets were slightly lower than those obtained with the trap used as designed originally. Modifications to the trap and operating conditions are being formulated in an attempt to improve the performance capability.

Fluidized Bed

Pilot-plant studies are being made of a continuous system, figure 20, for the sorption of uranium hexafluoride from a process gas stream. Uranium hexafluoride diluted with nitrogen is first passed through sodium fluoride powder in a 6-inch diameter, 30-inch deep stirred fluid bed held at 120°C. Sodium fluoride is fed continuously, and the overflow powder is transported by the outlet gases to a filter mounted above the feed hopper for a ribbon flight screw desorber. The uranium hexafluoride-laden powder is fed from this hopper to the 6-inch diameter, 8-foot long screw, where it is heated to 400°C. to drive off the uranium hexafluoride. A small flow of fluorine is maintained through the screw to prevent formation of

Figure 18
ANNULAR TRAP

Figure 19
ANNULAR TRAP LOOP

Figure 20
CONTINUOUS UF_6 SORPTION SYSTEM

uranium compounds other than the hexafluoride. The regenerated sodium fluoride falls into the fluid-bed hopper to complete the cycle. The total sodium fluoride inventory in the system is about 200 pounds.

TABLE XV
RESULTS OF ANNULAR TRAP SORPTION TESTS

Run Number	Total Gas Flow, std.cfm.	Inlet Gas Concentration, %			Sorption Time, hr.	Desorption Time, hr.	Sorption Ratio, lb. UF ₆ /lb. NaF
		UF ₆	F ₂	N ₂			
1	2.6	10	15	75	5.2	14	0.41
2	2.6	10	15	75	3.0	14	0.24
3	2.6	10	15	75	2.5	14	0.21
4	2.6	10	15	75	2.0	14	0.16
5	2.6	10	15	75	3.2	14	0.23
6	4.0	10	15	75	1.2	14	0.11
7	4.0	10	15	75	1.5	14	0.17
8	4.0	10	15	75	2.2	14	0.24
9	5.0	2	5	93	3.0	14	0.11
10	5.0	2	5	93	5.0	14	0.13
11	5.0	2	5	93	4.0	14	0.15
12	5.0	2	5	93	4.0		0.15*
B-1	2.6	10	15	75	3.7	14	0.32
B-2	2.6	10	15	75	2.1	14	0.18
B-3	2.6	10	15	75	2.2	14	0.15
B-4	2.6	10	15	75	2.0	14	0.12
B-5	2.6	10	15	75	2.0	14	0.16
B-6	2.6	10	15	75	1.8	14	0.15

* From flow measurements only. Not confirmed by cold trap weight on desorption.

Performance of the system has been very good for the range of conditions studied to date. The fluid bed has been operated with gas velocities of 0.15 to 0.70 foot per second, inlet gas uranium hexafluoride concentrations of 1 to 4%, and a bed temperature of 120°C. No problems have been noted with stirrer speeds as low as 20 rpm., and the average uranium hexafluoride concentration in the outlet gas has been consistently below 50 ppm. Essentially complete desorption of the uranium hexafluoride has been accomplished in the screw reactor at 400°C. with only a small flow

of buffering gas. Screw outlet gases containing as high as 40% uranium hexafluoride have been obtained. The rotational speed of the screw flight is 1 to 2 rpm.

The sodium fluoride used in the tests just described was prepared by heating sodium bifluoride crystals (100% through 20 mesh, 5% through 325 mesh) to 815°C. for 2 hours. The resulting crystals meet essentially the same particle size specifications as the starting material, have bulk and packed densities of 1.3 and 1.6 g./cc., respectively, and have a surface area of 0.2 to 0.3 sq.m./g. In the studies to date, only a small decrease in particle size to 10 to 15% through 325 mesh has been noted, and no effect on fluidization has been observed. If the powder is heated to only 535°C., however, rapid attrition occurs.

Continued operation of the pilot-plant system is planned. Studies will be made to determine the maximum capability of the unit and to investigate the effects of operating variables and of fission product accumulation. Since, for reprocessing use, the system must be essentially maintenance free, extended operation of the pilot plant at the expected conditions is necessary.

CONNECTORS

Since remote maintenance will be a requirement at many points in the proposed fuel reprocessing facilities, custom designed connectors must be used to facilitate removal of equipment. Service conditions for connectors at some points in the system will be quite rigorous because of the high temperatures and the corrosive gas atmospheres, particularly in view of the large size of some of the connectors, possibly up to 36 inches in diameter.

The first approach to the connector problem was to contact possible commercial suppliers. Several manufacturers of couplings were found who could deliver what appeared to be satisfactory products for electrical, instrument, and small process line use; however, only the Marman Conoseal clamp made by Aeroquip Corporation showed promise for application in the larger process lines. To broaden the possibilities for success, design work on adapting standard flat-faced flange closures for the required service was initiated. Results of the studies on the two types of connectors are described below. For both types, it was thought that double gaskets should be used so that the pressure between the seals could be monitored to detect leaks.

Marman Conoseal

A standard single gasket Marman Conoseal connector is shown in figure 21; a double seal unit is shown in figure 22. The initial problem faced in adapting the Marman connector for the intended service was selection of suitable materials for the flange and the gasket. Use of nickel for both parts was undesirable from the standpoint of galling. Duranickel which can be age hardened appeared to be the logical flange material based on corrosion data given in an earlier section of the report. Gaskets would

Figure 21
MARMAN CONOSEAL SINGLE SEAL

PHOTO NO. PH-65-715

Figure 22
MARMAN CONOSEAL DOUBLE SEAL

then be made of the softer nickel. Another possibility was plating of a hard flange material with nickel, either by electroless or electrolytic means. Accordingly, 1-1/2-inch Marman couplings made of nickel, Duranickel, and stainless steel were ordered for testing. Larger units were not obtained because of the high price quoted for single custom-built units.

Good sealing was obtained with an electroless nickel-plated flange if a soft aluminum gasket was used. With a stainless steel gasket, however, spalling of the plate occurred. Electrolytic plating was not attempted because it was felt that deposition of an even coating on the contemplated flange face was improbable. The decision to omit the electrolytic plating possibility from the program was further strengthened by good results with the Duranickel flange.

A-nickel and Duranickel 1-1/2-inch Conoseal joints were checked for seating at room temperature using nickel gaskets. The as-received hardness of the components were Rockwell B-75, B-95, and B-54 for the A-nickel flanges, the Duranickel flanges, and the gasket, respectively. The Duranickel flanges were subsequently heat treated to a hardness of Rockwell C-40 before testing.

Both joints sealed effectively at a bolt torque loading of 20 foot-pounds. Each joint was opened and closed six times using the same gasket and resealed satisfactorily each time. It was somewhat difficult to join the two flanges with the provided clamps due to the bevel angle of the gasket. Considerable prying was also necessary to open the clamps to inspect the joint after each test.

The two Conoseals were then subjected to a heat cycling procedure. Both joints were torqued to a bolt loading of 30 foot-pounds, pressured internally to approximately 10 psig., and then placed in a muffle wherein the temperature was cycled between 95 and 540°C. and held at the maximum and minimum temperatures for 1 hour. After the sixth cycle, the A-nickel joint developed a leak and was subsequently retorqued to a bolt loading of 85 foot-pounds. Both connectors sealed for the remaining of the twenty-nine cycles of the test.

It was very difficult to open the joints at the conclusion of the experiment. The clamps on both assemblies required hammer force to separate them from the joint flanges. The A-nickel Conoseal appeared to have fused together at the gasket surfaces; however, the Duranickel flanges separated readily after the clamps were removed. Material hardness checks of the components gave a Rockwell B-58 for the A-nickel and Rockwell C-39 for the Duranickel flanges. This indicates that annealing of the A-nickel occurred, while the Duranickel hardness remained constant.

Results of the tests on their units have been discussed with Marman Conoseal representatives. It is their opinion that the clamp problem will probably be eliminated when the final design incorporates remote operator features and the use of dissimilar metals. The galling and fusing of the inner flanges and gaskets, resulting from the tests

described, figure 23, however, are not so readily explainable, and the Marman engineers are reviewing their design for possible modifications.

Flat-Faced Flange Connectors

Four typical flange arrangements were chosen for the test program. Basically, these units consist of two standard 150-pound, 4-inch flanges machined and drilled for buffer connections to accommodate the various style gaskets. The joint arrangements include (a) a double wire ring gasket made of 1/16-inch nickel wire, figure 24; (b) a serrated type nickel gasket, figure 25; (c) a multiple touchpoint style nickel gasket, figure 26; and (d) a flat nickel gasket with a double ring serration milled into the flange, figure 27.

Compression tests showed that nickel was an unsatisfactory flange material with nickel gaskets. Severe scoring of flanges was noted under pressures required to give good sealing. Scoring was even observed with soft copper gaskets which had been nickel plated.

Efforts were then concentrated on the use of Duranickel for the flat-faced flanges. The first flanges made of this material were welded to nickel stubs and were age hardened by the following procedure:

1. Heat to 595°C. in hydrogen atmospheres and maintain at that temperature for 16 hours.
2. Slow cool at 5°C. per hour to 480°C.
3. Cool at furnace cooling rate to room temperature.

Inspection of the flanges after hardening showed severe cracking, figure 28. At the recommendation of the International Nickel Company, the assembly was annealed by heating to 815°C. under hydrogen and then water-quenching before hardening. Use of this procedure has eliminated the cracking.

The flange assemblies described earlier have been fabricated from Duranickel, and testing is in progress.

COMPRESSORS

In the volatility flow sheets, recycle of process gas will be required in the fluorination steps and probably during hydrogen chloride decladding. The only commercially available pump application for these services is the diaphragm type unit. Accordingly, bids from various vendors of such units were requested, and a Corblin compressor was purchased through the American Instrument Company, Inc. The lack of choice of commercial compressors, coupled with the inherent low capacity of the diaphragm machines, made it desirable to consider utilization of ORGDP compressor development experience to fill the process needs. Accordingly, work was started at the ORGDP in designing a peripheral type compressor, a unit that has many potential advantages over the diaphragm type machine.

Figure 23
NICKEL MARMAN CONOSEAL AFTER HEAT CYCLING

Figure 24
DOUBLE RING GASKET

Figure 25
SERRATED GASKET

Figure 26
MILLED MULTIPLE TOUCHPOINT GASKET

Figure 27
MULTIPLE TOUCHPOINTS ON FLANGE - FLAT GASKET

Magnification 1X

Magnification 10X

Figure 28
DURANICKEL FRACTURES

Peripheral Compressor

Compressor requirements for a 1-tonne of uranium per day production line are summarized in table XVI. Studies at the ORGDP on the peripheral compressor indicated that it had attractive possibilities for meeting these requirements and would also operate reliably with satisfactorily low maintenance. A photograph of an experimental single-stage peripheral (sometimes called drag or regenerative) compressor is shown in figure 29. Positive displacement compressors, such as the reciprocating piston, the rotary lobe, and the diaphragm, are generally inferior because of problems associated with lubrication, wear, sealing, diaphragm life, and vibration. Compared with the centrifugal compressor, the peripheral type has simpler construction, operates stably throughout its flow range, and develops higher heads or pressure ratios for a given impeller speed and size.

TABLE XVI
DESIGN CRITERIA FOR
FLUID-BED VOLATILITY LOOP COMPRESSORS
1 Tonne of Uranium Per Day Line

	<u>Compressor No. 1</u>	<u>Compressor No. 2</u>
Suction Pressure, psia.	14.7	14.7
Pressure Ratio	2:1	2:1
Volume Flow, std.cfm.	50 to 150	25 to 50
Suction Temperature, °C.	-40 to +25	95
Process Gas Constituents	HCl, H ₂ , N ₂	F ₂ , N ₂ , UF ₆ , ClF ₃
Approximate Range of Molecular Weights	18 to 35	28 to 61
Maximum Inleakage, std.cfm.	0.2	0.2

In addition to selection of compressor type, it was necessary to choose the type of drive, bearing, and seal system. Two methods considered were (a) use of conventional bearings and motor with a shaft seal for protection from the process gas, and (b) use of process gas lubricated bearings with the motor operating in the process gas. Although the latter method has the advantage of a totally enclosed system with no inleakage, the technology, especially with regard to materials and motor protection, was considered insufficiently advanced to ensure a satisfactory compressor in the desired time.

The project therefore consisted of (a) development of the compressor aerodynamics; (b) development of a shaft seal design; and (c) combination of the aerodynamic, seal, shaft, bearing, and motor designs into a reliable, complete compressor. The goal was to evaluate the component and integrated designs and to construct a prototype compressor by July 1, 1965.

Figure 29
SINGLE STAGE PERIPHERAL COMPRESSOR

The component development and testing, the integrated design evaluation, and the design of a prototype compressor have been completed. Construction of the prototype is in progress and is scheduled for completion by June 30, 1965. The compressor, shown in figure 30, will have two stages on a single impeller, and an interstage cooler will be used to remove the heat of compression from the first stage. Through the use of removable inserts to change the channel dimensions, one basic compressor design will meet the requirements of both compressors operating at 11,000 rpm. The design consists of the impeller and motor rotor mounted on a single shaft supported in precision ball bearings. A nitrogen-buffered bushing seal will seal the process gas with a small amount of nitrogen inleakage. Motor and bearing cooling will be accomplished by a water jacket around the motor stator and an air thermal barrier between the compressor passages and the bearing housing. The expected compressor performance curves based on results of tests conducted in air are shown in figures 31 and 32. Descriptions of the work involved in arriving at the design of the compressor follow.

Seal Development. For the relatively high shaft speed necessary for these compressors, a positive clearance seal was considered more feasible than a contact seal. Three seal types studied in the program were (a) labyrinth, (b) screw, and (c) bushing. A stand for conducting the seal tests were constructed, and several designs of each type were evaluated using a 1.9375-inch diameter shaft size. Figure 33 is a photograph showing each seal type studied. All tests were made in air at speeds of 0, 8,600, or 11,000 rpm. Capacitance-type clearance probes were used at monitor shaft position during various operating conditions. Radial clearances of 0.002 inch and 0.003 inch were tested; other geometric variables included length of seal, eccentricity of hub to sleeve, number and shape of labyrinth teeth, and design of screw seal grooving.

Designs of all three seal types which would meet the inleakage requirements were tested, and the best was the bushing seal. Table XVII summarizes the performance of the bushing seal. The flows reported are actual cfm. at 1 psi. differential pressure. The effect of eccentricity was studied to predict the result of any misalignment upon assembly or operation. As may be seen in the table, even with a 3.2-mil radial clearance and a 0.5 eccentricity, a 2-inch long seal is adequate. The shorter length and larger clearance increase the freedom from assembly and operating difficulties. With precision ball bearings, a 3-mil radial clearance is considered quite practical. Also, the pressure differential of 1 psi. is considered adequate to prevent any back diffusion of the process gas outward through the seal past the buffer gas (nitrogen).

Compressor Aerodynamics. Part of the ORGDP peripheral compressor program included studies of channel and impeller geometries. Of the impellers tested, one with 0.500-inch deep blading was judged best. Stationary flow channel dimensions were systematically varied and tested with this impeller. Figure 34 summarizes the results obtained on nine channels which were closest to those required. Pressure ratio is plotted as a function of a dimensionless flow parameter which accounts for different fluid properties. Assuming two-stage operation, the approximate design points

MATERIALS

IMPELLER- DURANICKEL 301

SHAFT- 4340 STEEL, NICKEL-PLATED
IN SEAL AREA

PARTS EXPOSED TO PROCESS GAS-
NICKEL 200

OTHER PARTS- MONEL, STAINLESS STEEL,
OR MILD STEEL

Figure 30
TWO-STAGE PERIPHERAL COMPRESSOR

Figure 31
 PERIPHERAL COMPRESSOR DUAL STAGE RESULTS

Figure 32
 PERIPHERAL COMPRESSOR DUAL STAGE RESULTS

Figure 33
PERIPHERAL SEALS

Figure 34
 PERIPHERAL COMPRESSOR CHANNEL CHARACTERISTICS

for each stage of each compressor were included in the figure. These curves point out an important advantage of the peripheral compressor. With a basic impeller and housing design, the performance at a given speed can be varied greatly by the use of simple inserts to change the channel dimensions. These channel data were obtained with 0.015-inch impeller-to-casing clearance, which has proved to be satisfactory both aerodynamically and mechanically.

TABLE XVII
PERFORMANCE OF 1.9375-INCH DIAMETER BUSHING SEAL

Design	Leakage Flow, cfm. at 1 psi.	
	2 Inches Long	3-1/2 Inches Long
1. Required*	0.155	0.155
2. 0.0020-Inch Radial Clearance (Concentric)	0.018	0.010
3. 0.0032-Inch Radial Clearance		
a. Concentric	0.096	0.054
b. Eccentric ($\epsilon = 0.5$)†	0.130	0.075

* Maximum permissible leakage based on 18 psia. average process pressure.

† ϵ is eccentricity ratio which is zero when hub is concentric with sleeve and unity when hub is touching sleeve.

It became apparent early in the program that two stages of compression would be necessary to permit reasonable operating speeds. Since the two sides of a peripheral impeller are independent of each other, mounting two stages on a single wheel with some interstage sealing device seemed feasible. This dual stage, single impeller concept would reduce the overhang moment on the shaft and would improve the rotor dynamic characteristics. The concept proved successful in performance tests and has been incorporated in the compressor designs. The data in figures 31 and 32 were obtained with a single impeller and a labyrinth seal to reduce cross-leakage between stages. This concept, along with a comparison of two impeller designs, is shown in figure 35. The new impeller design on the right is only 60% as heavy and has maximum stresses 59% as great as the conventional solid disc type impeller shown at left. The new type impeller is included in the prototype compressor design.

Test Rig Evaluation of Design Features. In addition to the development of the seal and compressor aerodynamic designs, it was considered important to study other design features of the compressor in an assembled configuration. These included rotor dynamic characteristics, bearing performance, motor and bearing cooling schemes, and motor performance.

Figure 35
PERIPHERAL COMPRESSOR IMPELLERS

A test rig, built for other ORGDP programs, was ideally suited for this evaluation. The rig was instrumented with capacitance clearance probes to monitor rotor movement and with thermocouple and stick-on temperature indicators to determine thermal conditions under various modes of operation. The studies to date have verified the mechanical and thermal integrity of the compressor designs. Performance of the high precision angular contact ball bearings packed with Andok-260 grease has been good, and the motor and bearing cooling methods have proved satisfactory. Bearing temperatures less than 80°C. can be maintained at 11,000 rpm. under full load conditions (temperatures less than 95°C. are considered acceptable for these applications). Sizing of the motor, 26 hp., was adequate, and sufficient motor cooling is provided with a flow of 2 gallons of water per minute. By maintaining close but practical machining tolerances and by achieving a high quality of rotor balance, no difficulties with rotor performance were encountered. Testing is still in progress to confirm the aerodynamic performance of the new impeller design, figure 35, but preliminary data indicate the performance to be satisfactory. Actually, any discrepancies in either the compressor requirements or the correlation of performance from air to the particular process gas should be easily resolvable by adjustments in channel dimensions in the final installation.

Diaphragm Compressor

Performance specifications for the experimental diaphragm compressor are outlined in table XVIII. Multiple compressors would be needed for a production line capable of reprocessing 1 tonne of uranium per day, since there is no available commercial unit capable of satisfying flows and pressures shown in table XVI. The fluorine service application calls for a dual head assembly with a fluid media inert to fluorine, uranium hexafluoride, hydrogen fluoride, and chlorine trifluoride between the diaphragms. All parts exposed to the process gas are constructed of nickel. For hydrogen chloride service, a single diaphragm in contact with the process gas is sufficient. The diaphragms for the experimental machine are 26 inches in diameter.

TABLE XVIII
CORBLIN COMPRESSOR PERFORMANCE SPECIFICATION

<u>Condition</u>	<u>Fluorine Service</u>	<u>HCl Service</u>
Capacity, std. cfm.	12	20
Suction Pressure, psia.	14.7	14.7
Suction Temperature, °C.	95 Maximum	- 30 to + 25
Discharge Pressure, psia.	30	30
Gas to be Pumped	F ₂ , N ₂ , UF ₆	HCl, H ₂ , N ₂
Molecular Weight Range	28 to 61	18 to 35

The compressor was installed in a test loop as shown in the flow diagram, figure 36. A photograph of the unit is presented as figure 37. The system was arranged to test the remote head arrangement first, i.e., with the fluid volume between the diaphragms in the primary and remote heads filled with a fluorocarbon oil. As received from the vendor, no provision was made to compensate for fluorocarbon oil volume expansion and contraction resulting from temperature fluctuation; therefore, it was necessary to install pressure and vacuum relief valves for liquid volume control.

From the beginning, the pump exhibited an inherent vibration that required several revisions to the loop to provide flexible couplings on the pump and service headers. Calibrated reactance probes were installed at various positions on the primary and remote heads, and the vibration frequency and amplitude were measured on an oscilloscope. Four vibration pulses per pump revolution are detectable as shown in figure 38. Vibration movements as great as 0.100 inch on the remote head and 0.060 inch on the primary head were measured. Representatives of the pump vendor were informed of these results, and they stated that such vibration amplitudes were considered normal.

The maximum flow rate obtainable with the remote head was 10 to 15% lower than that obtained in the manufacturer's tests before shipment; therefore, transducers were installed at points in the fluorocarbon oil section to investigate the possibility of harmonic pressure pulse development in the length of pipe connecting the primary head to the remote head. Such a condition could affect the pumping performance of the unit. Evidence of some minor wave action was present; however, a maximum pressure pulse occurred simultaneously at all points in the oil system, figure 39. At this writing, it is concluded that the lower rate is probably caused by a small amount of air in the hydraulic fluid in the primary head.

The compressor loop is now being readied for a life test of the pump. It is planned to compress dilute fluorine at the maximum flow rate under suction and discharge pressures of 14.7 and 30 psia., respectively.

REACTOR FABRICATION PROCEDURES - WELDING STUDIES

The present specification concept for the primary fluid-bed reactor is that low carbon nickel will be used for surfaces in contact with the process. All welds on the equipment should be made using welding rod of the same material so that corrosion problems can be minimized. Considerable experimentation has shown the need for stringent preparation and welding procedures if acceptable welds of nickel-201 with nickel-201 rod that will meet the condition specified in pressure vessel codes are to be produced.

Many welding attempts were made in developing the recommended TIG weld. First, it was found that cleanliness of all components must be of the highest degree, since any nickel oxide present will cause welding difficulties and will create a porous weld. Flash pickling of all materials was found necessary. By dipping the work in a solution of 20% water-30% sulfuric acid-50% nitric acid containing 60 grams of sodium chloride per

Figure 36
CORBLIN PUMP LOOP

Figure 37
CORBLIN COMPRESSOR

Vibration Amplitude
19 mils per Division

Primary Head

Vibration Amplitude
19 mils per Division

Remote Head

Figure 38
CORBLIN VIBRATION MEASUREMENTS

Figure 39
CORBLIN FLUOROCARBON OIL PRESSURE MEASUREMENTS

liter and following this with a hot water dip, a bright, lustered surface was attained. Clean, white gloves were worn when handling the components.

Inasmuch as the filler rod is virtually unalloyed, melting and solidification occur abruptly without the incidence of a sluggish puddle. For this reason, the best welding control combination was found to be a high heat input with a fast travel rate. Arc amperages were varied between 50 and 120 amperes; arcs of 100 amperes for the root weld and increasing to 120 amperes for the face welds were necessary in butt welding 3-inch nickel pipe. The rod was fed into the puddle in fast, short jabs, but the tip was never removed from the inert gas shield of the torch, thus reducing the possibility of oxide formation.

A joint bevel angle of 75 degrees and a 1/8-inch gap were found to be the ideal conditions for a good weld. Both argon and helium torch and purge gases were employed in the tests with helium superior for both applications. A much higher back purge flow was required for the root pass to prevent oxidation and to provide adequate cooling.

Nickel-201 rods are not available commercially; therefore, nickel-201 sheet was slit, and the strips were swaged to provide a 3/32-inch diameter wire.

Successful welds have been made joining 3-inch nickel-201 pipe in the 2G and 5G welding positions. Face bend and root bend tests on these welds showed no cracking. Radiographs of the joint indicated no porosity or other defects. Tensile strength tests gave ultimate strengths of 55,000 to 60,000 psi. and elongations of about 20%. All of the above tests meet the ASME requirements for an acceptable weld; at the present, a formal welding procedure is being prepared for training and qualifying welders.

The future program will include studies of welding Duranickel to nickel-200 and to nickel-201.