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THE OAK RIDGE GASEOUS DIFFUSION PLANT
FUEL REPROCESSING PROGRAM*

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For the past few years, the Process Systems Development Department of the Oak Ridge Gaseous Diffusion Plant has participated with the national laboratories in a variety of projects related to the development of fluoride volatility processes for recovering values from irradiated fuel materials. The work at the ORGDP has covered both engineering studies and hardware development and testing. Our engineering studies have largely centered around conceptual plant designs. Earlier we were concerned with high enrichment fuel processing, but more recently we have focused our attention on the conceptual design and economic analysis of a 1 tonne per day LWR fuel reprocessing facility. Associated with the plant design work were a number of other fairly detailed studies which were required to supply design criteria and other auxiliary information for the plant designs; some examples of these study areas are the nuclear safety aspects of dry volatility

* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the United States Atomic Energy Commission.

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systems, cold trapping of uranium hexafluoride and plutonium hexafluoride, sorption of uranium hexafluoride on solid sorbent materials, and fission product compositions in spent fuel.

The experimental efforts at the ORGDP have been primarily keyed to process areas where large-scale testing or hardware development was considered necessary to provide bases for the design of full-size reprocessing plants. This work included semiworks processing of simulated fuel assemblies, i.e., hydrochlorination, oxidation, and fluorination of zircaloy clad uranium dioxide in a large fluid-bed reactor system; recycle compressor development and testing; corrosion studies; testing of valves, connectors, samplers, and filters; and investigations of the consequences of bromine pentafluoride spills.

Today, we would like to discuss each of these topics. The presentations will be somewhat abbreviated, since most of our work is described in the various AEC progress and topical reports listed below.

Progress Reports

Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies Summary Progress Report Fiscal Year 1964 through Fiscal Year 1965, October 29, 1965 (K-1649).

Smiley, S. H., Brater, D. C., and Pashley, J. H., ORGDP Fuel Reprocessing Studies Summary Progress Report July through December, 1965, June 28, 1966 (K-1669).

Smiley, S. H., Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report January through June, 1966, January 18, 1967 (K-1691).

Smiley, S. H., Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report July through December, 1966, June 12, 1967 (K-1717).

Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report January through June, 1967, May 9, 1968 (K-1738).

Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report June through December, 1967, July 17, 1968 (K-1744).

Pashley, J. H., and Schappel, R. B., ORGDP Fuel Reprocessing Studies Summary Progress Report January through June, 1968, Report in Progress (K-1769).

Topical Reports

Breton, D. L., Schappel, R. B., Merriman, J. R., Pashley, J. H., Littlefield, C. C., and Habiger, K. E., A Conceptual Study of a Fluoride Volatility Plant for Reprocessing Light Water Reactor Fuels, Report in Progress (K-1759).

Habiger, K. E., and Breton, D. L., Nuclear Safety Studies for Low Enrichment Fluoride Volatility Fuel Reprocessing Plants, September 4, 1968 (K-1734).

Dunthorn, D. I., The Design of Batch Desublimers, September 19, 1968 (K-L-6220).

Dunthorn, D. I., Design Considerations for a Plutonium Hexafluoride Cold Trap for the Bromine Halide Volatility Process, August 1, 1968 (K-L-2963).

Stephenson, M. J., A Design Model for the Dynamic Adsorption of Uranium Hexafluoride on Fixed Beds of Sodium Fluoride, M. S. Thesis, University of Tennessee, December, 1968.

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

Stephenson, M. J., Anderson, L. W., and Cates, P. S., Application of the Peripheral Compressor to the Fluoride Volatility Process, Report in Progress (K-1751).

CONCEPTUAL PLANT STUDIES

As noted, one of our major efforts in recent months has been a conceptual design study and economic evaluation of a fluoride volatility reprocessing plant for treating spent low enrichment power reactor fuel. The study was initiated in 1966 at the request of the U. S. Atomic Energy Commission, Division of Reactor Development and Technology, with two primary goals in mind. First, it was important to give guidance on the question of volatility process economics as applied to power reactor fuels; and second, it was expedient to supply an independent assessment of the technological feasibility of the process extrapolated to plant scale.

At the outset of the study, the plant throughput was assumed to be 300 tonnes of uranium per year, which was the expected processing load required by newly constructed and planned nuclear power reactors for the early part of the 1970's. The plant was to have a 300-day-per-year on-stream time with the remainder of the year allocated for downtime and major maintenance. Turnaround time, i.e., time needed to clean out the equipment between campaigns, was included in the 300 days of on-stream time.

Specifically, the study procedure involved the following steps:

- (1) review and evaluation of experimental data provided by Argonne National Laboratory, Brookhaven National Laboratory, Oak Ridge Gaseous Diffusion Plant, and Oak Ridge National Laboratory;
- (2) establishment

of line processing rates and preparation of process flow sheets; (3) conceptual design of the process equipment items and piping and instrumentation schemes; (4) conceptual design of the process buildings; (5) evaluation of the safety aspects, including analysis of criticality problems, shielding requirements, chemical hazards, and disposal of gaseous, liquid, and solid wastes; (6) sizing of the auxiliary facilities; and (7) preparation of a detailed cost estimate.

It should be stressed that the study was conceptual in nature, and that sufficient manpower and funding were not expended to prepare the equipment designs, process and building layouts, or auxiliary facilities in sufficient detail to achieve high precision in the cost estimate. The study results are, however, felt to be adequate to answer the basic economic questions concerning the competitiveness of the process with the established aqueous routes. Furthermore, it should be kept in mind that process technology, including scale-up from the relatively small test equipment and evaluation of problems for larger scale operation with irradiated fuels, is not in its final stages of development. In most cases, data were available only from small-scale experiments involving nonirradiated uranium dioxide.

The main reactor used in the process is a two-diameter fluid-bed unit, with 18- and 26-inch-diameter sections. The vessel is 30 feet high, excluding a slide valve, an expansion joint, and the plug penetration section. Fuel assemblies are charged into the upper 26-inch-diameter section, which is 22 feet long, in bundles containing about 1,500 kg of

uranium dioxide. Hydrochlorination of the zircaloy clad is performed at 400°C in a fluidized bed of inert alumina, with the assemblies completely submerged. Volatile chlorides of zirconium and tin leave the reactor, while the uranium dioxide, which is not attacked by the hydrogen chloride, falls to the lower section of the reactor.

The uranium dioxide is then oxidized to U_3O_8 before the uranium is selectively fluorinated with bromine pentafluoride. Oxidation is performed at 450°C, while the interhalogen fluorination is carried out at 300°C. The plutonium, which has been converted to plutonium tetrafluoride during the bromine pentafluoride fluorination step, is then volatilized with elemental fluorine at temperatures ranging from 300 to 550°C. The final bed material is conveyed pneumatically to annular waste storage bins.

A typical charge to the reactor, based on the dimensions of current fuel elements, would consist of either three 8-1/2-inch by 8-1/2-inch by 144-inch-long assemblies or seven 5-1/2-inch by 5-1/2-inch by 144-inch-long units; i.e., about 1300 kg of uranium. The time required for a complete batch cycle is about 60 hours. Two head-end reactors are thus provided to meet the scheduled throughput of 1 tonne of uranium per day. Process gas recycle equipment is designed to handle the off-gas load of only one of these reactors at a time, since operations in the two units can be phased so that simultaneous demands for the same reagents are avoided.

The zirconium and tin chlorides volatilized from the bed, the excess hydrogen chloride, and the hydrogen produced in the decladding reaction are first passed through a fluid-bed cooler-filter unit and a backup filter before being fed to a fluid-bed pyrohydrolysis reactor for conversion of the zirconium and tin compounds to solid waste with concomittant regeneration of the hydrogen chloride. The excess steam leaving the pyrohydrolyzer is condensed, along with part of the hydrogen chloride. This aqueous acid is vaporized and used again as pyrohydrolyzer feed gas. The remaining hydrogen chloride, except for a small amount lost with the hydrogen vent stream, is recirculated to the halogenator.

In the uranium dioxide oxidation step, dry air is used as the oxidant on a once-through basis. The off-gases are vented through a scrubber which also serves as the bromine pentafluoride fluorination vent gas scrubber.

Off-gases from the reactor during the bromine pentafluoride fluorination are directed to a bromine pentafluoride regenerator and then to a cold trapping system which collects the uranium hexafluoride as a solid and condenses most of the bromine pentafluoride as a liquid. The bromine pentafluoride liquid formed drains from the trap continuously and is subsequently vaporized and recycled to the halogenator. A portion of the process gases are vented immediately after the cold traps. After the bromine pentafluoride treatment has been completed, the trapped solid uranium hexafluoride is drained from the cold trapping

system and distilled. Two batch distillation columns are used in series to remove low and high boiling fission products, as well as bromine pentafluoride and any bromine trifluoride which may have formed. The uranium hexafluoride product is withdrawn as a vapor off the top of the second column and is condensed. Sorption traps containing sodium fluoride and magnesium fluoride, placed at strategic locations in the process, serve as the principal mode of selectively removing volatile fission product fluorides.

The plutonium recovery has been considered to the point where the plutonium has been fluorinated from the bed and collected in a cold trap. Plutonium technology for purification beyond this point by volatility methods is not available at present; however, an allowance for the cost of this processing step has been included in the cost estimate.

The fluid-bed volatility process for zirconium-clad uranium dioxide power reactor fuels was studied at Argonne National Laboratory on a 2- and 3-inch-diameter reactor scale using nonirradiated simulated uranium dioxide pellets. Also, the fission product removal aspects of the process were evaluated there on a 1-1/2-inch-diameter reactor scale. Initially, little was known on suitable hardware for the potential production-scale process; however, work at the ORGDP provided information in this area. Appreciable work in fluoride volatility has also been performed at ORNL.

The estimated capital cost for a 1 tonne of uranium per day fluoride volatility reprocessing facility is about 26 million dollars without contingency and 33 million dollars with a 25% contingency. With a depreciation charge of 15% per year, the unit capital cost becomes \$16.34 per kg of uranium. The operating cost is estimated to be \$10.98 per kg of uranium; therefore, the total unit processing cost is \$27.32 per kg of uranium. All costs are expressed in 1967 dollars.

The conceptual plant is located on a 200-acre site. Staff requirements were estimated to be 119 people. The facility requirements involve (a) a process building with a total floor area of 46,500 square feet and a volume of 1,030,000 cubic feet, including a process cell area of 2,650 square feet with a volume of 76,000 cubic feet; (b) a fuel receipt building 8,770 square feet in area and 339,000 cubic feet in volume; (c) a cell and process gas filtration system and a 400-foot-tall stack for disposal of cell ventilation air and process off-gases; (d) a utility, maintenance, and fluorine plant building having an area of 23,000 square feet; (e) an 8,000-square-foot warehouse; (f) miscellaneous structures for water pumping, water filtration and treatment, sewage disposal, and security operations; (g) waste storage areas; and (h) a number of the usual general outside improvements associated with a chemical processing plant.

NUCLEAR SAFETY STUDIES

One general conclusion from the ORGDP design effort is that the sizes of many of the process equipment items required in volatility plants must significantly exceed accepted nuclear guidelines for wet systems if throughput requirements are to be met economically. One of the principal advantages of the fluoride volatility route is that only gas-solids contacting operations are employed in the primary processing steps; consequently, aqueous solutions, with their good neutron moderating capabilities, are almost entirely avoided. Characteristically, aqueous plant design considerations include use of soluble neutron absorbers, concentration control, and stringent equipment size restrictions with concomitant multiline staging of vessels in order to avoid nuclear criticality situations. For the most part, however, such considerations do not apply to the volatility process. Of course, certain size and mass limitations do exist in a fluoride volatility plant, and fixed neutron absorbers might be necessary in some instances; however, there generally appears to be much more latitude in certain aspects of choice of equipment and/or batch sizes than for aqueous plant design.

Although a wealth of information on uranium and plutonium criticality does exist in the form of calculations and experiments; most of it is concerned with high uranium-235 enrichments, with aqueous or metal systems, or with systems of compounds which are of little value in evaluating volatility plant situations.

Thus, an essential part of our conceptual studies has been the establishment of reasonable criteria for equipment sizing and fissile material batching for dry volatility systems, which are generally moderated poorly relative to aqueous solution processing systems. Accordingly, a large number of criticality calculations have been made to ascertain the nuclear reactivities of various volatility process mixtures and geometries. Much of this work was related to both high enrichment and low enrichment uranium systems. In the high enrichment uranium cases, the limiting mass, considering pure uranium-235, was found to be about 118 kg. This value is for U_3O_8 at a density of 3 grams of uranium-235 per cubic centimeter in a 42 cm (16.6 inch) diameter sphere reflected with 30 cm of alumina. For low enrichment uranium, i.e., for uranium-235 assays below 5%, our studies indicated that there were no criticality problems due to uranium in any of the conceptual plant equipment items, as long as exclusion of water or other good moderators could be ensured.

The DTF-II and ANISN one-dimensional S_n transport codes were used to perform criticality calculations for the uranium and plutonium compounds expected in a low enrichment fluoride volatility plant. The codes were used in the S_4 option with 16-group cross sections and were shown, after some modification of uranium-238 cross-section data, to be sufficiently accurate for conceptual design studies by comparing code estimates with the results of critical experiments.

A summary of the results of criticality calculations performed for various uranium and plutonium systems is shown in Table I. Since, in most cases, a range of densities or concentrations was studied, the data in Table I are not complete, and the reports cited earlier should be consulted for other results and trends. In addition to the cases presented in the table, effective neutron multiplication factors were calculated versus infinite cylinder radii or sphere masses for systems of uranium hexafluoride and hydrogen fluoride, for plutonium dioxide, and for plutonium hexafluoride. Also not shown in the table are results for plutonium dioxide slab and spherical shell calculations; finite plutonium tetrafluoride cylinder and slab calculations, and comparisons of critical plutonium dioxide sphere masses for various plutonium isotopic distributions typical of fuel discharged from light water reactors.

It was concluded that mass limits for plutonium would be necessary in the main fluid-bed reactor and associated filters if plutonium segregation must be considered. With the possible requirement of neutron absorbing materials in certain other cases, it should be feasible to design the remaining equipment in the LWR fuel plant to be geometrically safe for both uranium and plutonium.

TABLE I

SUMMARY OF SELECTED CRITICALITY CALCULATIONS FOR URANIUM AND PLUTONIUM SYSTEMS

Fissile Material*	Density, g/cc	Diluent Material Compound	Density, g/cc	Reflector		Minimum Critical Conditions**			
						Infinite Cylinders		Spheres	
				Compound	Thickness, cm	Fissile Compound, vol %	Critical Radius, cm	Fissile Compound, vol %	Critical Mass, kg Pu
UO ₂	10.9	Al ₂ O ₃	2.5			All k _∞ 's less than 1.0			
UO ₂	10.9	H ₂ O	1.0	H ₂ O	30	20	12.8		
UF ₆	5.0	HF	1.0	H ₂ O	30	30	25.6		
UF ₆ ·2NaF	4.16	HF·NaF	2.16	H ₂ O	30	35	39.2		
PuO ₂	3.50			Al ₂ O ₃	30	100†			
PuO ₂	3.50			Al ₂ O ₃	30	100	8.0	100	43.9
PuO ₂	3.63	H ₂ O	1.0	Al ₂ O ₃	30			57.26	11.4
PuO ₂	3.63	Al ₂ O ₃	2.5	Al ₂ O ₃	30	20	21.1	20	113.7
PuF ₆	6.0			H ₂ O	30	100	6.9	100	25.8
PuF ₆	6.0	HF	1.749	H ₂ O	30	0.5	12.7	0.5	0.55
PuF ₆	6.0			Phenolic Foam	100	100	10.5		
PuF ₄ ·NaF	6.47	HF·NaF	2.16	H ₂ O	30	100	6.7		
PuF ₄ ·NaF	6.47			H ₂ O	30	100§			

* Uranium-235 isotopic composition = 5%. All plutonium is plutonium-239.

† Thickness of Infinite Slab = 3.22 cm.

§ Thickness of Infinite Slab = 3.98 cm.

** In most cases, the plutonium systems did not exhibit minima between the end points of the independent variables studied.

COLD TRAPPING STUDIES

During the initial development of the gaseous diffusion uranium isotope separation process, the fact that uranium hexafluoride sublimates at atmospheric pressure prompted the investigation of desublimation as a unit operation for the recovery of this gas from process streams. Recently, because of interest in the application of this operation to the collection of uranium hexafluoride, plutonium hexafluoride, and perhaps other similarly behaving halide gases present in fluoride volatility systems, a detailed phenomenological study of desublimation, or cold trapping, was undertaken.

A desublimer, used to separate a component from a noncondensable carrier gas by condensing it out as a solid, generally differs from a liquid condenser primarily in that condensed material is not drained continuously but is collected within the unit, eventually building up enough to stop the flow of gas. Hence, a cold trap is usually designed to operate batchwise, and the proper partitioning of the internal volume of the unit to allow for solids buildup is as important a design objective as the provision of sufficient cooling surface for condensation heat removal.

Usually, a gas stream entering a desublimer is superheated, i.e., it contains less than the saturation quantity of condensable component. Gas contacting the refrigerated cold trap walls, however, is cooled below saturation, causing solid to condense on the walls and setting up

a driving force for mass transfer between the bulk gas and the wall surface. At the same time, the bulk gas is being cooled by normal heat transfer. Generally, the gas tends to approach saturation, since in traveling down the trap, normal mass transfer to the wall does not remove condensables fast enough to keep the stream below the saturation concentration, which decreases rapidly as the temperature drops. After saturation is reached, this situation still exists, but, as the gas stream is cooled further, it must release enough condensable to prevent its becoming supersaturated. Thus, material in excess of the amount traveling to the wall by normal mass transfer freezes out in the gas stream itself as a mist or snow and must travel to the surface by falling or other mechanical means. Consequently, it would be expected that the solid deposit thickness would vary along the gas flow path and that an increase in deposit thickness would be observed at the point where the gas becomes saturated.

As a part of the cold trapping studies, a procedure for designing desublimers systems has been developed, and a design program has been coded and tested. As noted previously, there are two fluorination cycles in the bromine halide volatility process for nuclear fuel reclamation. In the first cycle, spent oxide fuel is treated with a bromine halide, producing volatile uranium hexafluoride. Plutonium is not volatilized by the bromine halide and remains in the reactor bed, along with some unconverted uranium. Even though small, the quantity of uranium would be expected to be comparable to that of the plutonium, which initially comprises somewhat less than 1% of the initial charge.

In the second fluorination cycle, fluorine is used to volatilize plutonium and the remaining uranium as the hexafluorides. The reactor off-gases may then be passed through a cold trap to recover plutonium hexafluoride and uranium hexafluoride.

Due to the plutonium hexafluoride-fluorine equilibrium relationship, a high mole ratio of fluorine to plutonium hexafluoride is required in the second fluorination cycle; when carried out at 400°C, the equilibrium mole ratio of plutonium hexafluoride to fluorine is $5.6 \times 10^{-3*}$. From tests at the Argonne National Laboratory, it appears that kinetics of the reaction require a substantial excess of fluorine above the equilibrium amount. An average plutonium hexafluoride concentration in the reaction off-gases equivalent to only 10% of the equilibrium concentration is assumed in this discussion; i.e., a mole ratio of plutonium hexafluoride to fluorine of 5.6×10^{-4} . Thus, for the purpose of heat transfer calculations, the stream entering the cold trap is so dilute in plutonium hexafluoride that it may be treated as though it were pure fluorine, and the unit may be designed as though it were just a gas cooler**. Consideration must be given to the buildup of desublimed material on heat transfer surfaces, of course, but the amount of condensable being trapped per cycle is quite small, and

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

** From a heat transfer standpoint, this assumption is essentially satisfactory for considerably higher plutonium hexafluoride concentrations, up to perhaps 1%.

almost any standard cold trap design providing sufficient heat transfer area would have individual gas flow passages large enough that plugging would not occur.

The design point of 0.1 mole percent plutonium hexafluoride-uranium hexafluoride* indicates that a maximum trapping temperature of minus 85°C, which is below normal refrigeration ranges, is required for 99% recovery of the plutonium. After a study of possible coolants, it was decided that liquid argon, which is readily available and inert, could be the best choice. The boiling point of argon is above that of fluorine, so that the fluorine itself will not condense, a problem that could occur with liquid nitrogen coolant. Since the temperature of argon is much below the required minus 85°C temperature for gas leaving the trapping system, a side effect is that the heat transfer area requirements are reduced substantially below those for a coolant nearer minus 85°C.

The heat transfer area required for a trapping system treating a flow of about 70 scfm varies somewhat with outlet temperature; however, as would be expected, the area requirements do not increase sharply with decreasing outlet design temperature, and a temperature lower than minus 85°C might be attractive in the event that the plutonium hexafluoride production rate is lower than expected.

* A study of plutonium hexafluoride properties indicated that, for the most part, it should act like uranium hexafluoride, and desublime with it.

Several plutonium hexafluoride cold traps arranged in parallel are required for the conceptual plant case due to a combination of criticality size limitations and a limitation on the velocity of the gas through the trap to minimize fuming losses. The fuming loss represents the percentage of condensables entering the trap which will be carried out, mechanically, in the gas stream. Actually, these stream-borne particles are removed by a nickel mesh filter rather than allowed to pass on downstream; however, it is not desirable to collect substantial amounts of plutonium hexafluoride on the nickel mesh, especially since the trap must later be heated for plutonium hexafluoride removal. A design velocity of about 0.5 ft/sec is generally used to avoid this problem.

An estimate was made of the rate of solid buildup on the trap cooling surfaces at the point in the trap where saturation occurs, which should also be the point of maximum deposition. For this particular example, the rate was found to be about 0.004 inch per hour; this rate should present no problems with operation of traps having this design.

URANIUM HEXAFLUORIDE FIXED-BED SORPTION STUDIES

Fixed beds of sodium fluoride pellets have been used rather extensively for the purification and collection of gaseous uranium hexafluoride, and several sorption units have been specified in the conceptual plant design. Currently, however, operational experience plays a predominant

role in the sizing of new sodium fluoride traps because the adsorption problem is relatively complex, involving a mechanism that employs variable reaction and diffusion rates. Consequently, the method of solution does not lend itself to hand calculation. For this reason, a theoretical investigation of the sorption process was begun recently, and a computer program for the design of fixed-bed sodium fluoride sorption traps for uranium hexafluoride service has been written.

The rate of removal of uranium hexafluoride from bulk gas flowing through a fixed bed of pelletized sodium fluoride has been found to be proportional to the effective diffusion rate, to the surface concentration of the reacting uranium hexafluoride, and to the effective radii of the pellets. The overall rate increases with temperature and decreases with the amount of uranium already complexed. The maximum loading of the pellet bed, in terms of pounds of uranium per pound of sodium fluoride, decreases with surface area and temperature, and increases with pellet porosity. Within the concentration limits of less than 8 to 9% uranium hexafluoride in the feed material, the maximum loading is, however, essentially independent of bulk gas concentration. For higher concentrations, temperature gradients within the pellets can be expected to increase the effectiveness of the pellets and thereby increase the loading capacity of the pellets. The computer program accounts for these variables in predicting trap design parameters. Preliminary checks of code results versus experimental data have been encouraging.

CALCULATION OF FISSION PRODUCT INVENTORIES IN SPENT FUEL

A detailed knowledge of the properties of spent fuel is very important to the reprocessor, who must deal satisfactorily with each of the problems caused by the presence of fission products and heavy elements in irradiated fuel. The problems are diverse and range from protecting personnel from penetrating radiation to designing the necessary equipment and procedures for product recovery and purification.

The type, as well as the detail, of fuel element information required for reprocessing studies varies somewhat both with the specific process and the specific problem considered. In general, however, a description of the spent fuel in terms of weights, activities, and heat release rates for each fission product and transuranic element is desirable for most engineering purposes. A high degree of accuracy, such as is needed for many nuclear reactor design calculations, is not required for fuel processing plant studies, primarily since individual reactor operating conditions are, within practical limits, arbitrary to each reactor operator. The basic fuel compositions chosen for the study cases, however, must instead be representative of a spectrum of fuels generated, and the recovery plant arrived at must be suited to process fuels of at least similar composition and burnup.

It is perhaps surprising that estimation of many irradiated fuel properties which are important in reprocessing studies has not received

a great deal of attention. This is especially true in view of the many techniques and computer codes which have been developed to aid in the analysis of several related fuel handling problems. While some existing reactor codes can be employed to provide certain parts of the desired data, such as transuranic element production during fuel exposure, none of the many techniques surveyed is focused directly on the problem of predicting the chemical composition of spent fuel elements, both in detail and with input requirements compatible with parametric studies. The problem can be simply stated as a lack of published information and calculation procedures prepared from the reprocessor's point of view.

Since the amount of information available in the literature concerning either calculated or experimentally determined fuel compositions is limited, it was felt that the development of a technique specifically aimed at providing isotopic weight, energy, and activity data was warranted. Consequently, a computer code was developed to aid in supplying fuel details. Since the goal was to develop a tool which could be easily utilized for a wide variety of case studies, probably the most important feature of the code is its simple input requirement. Nuclear data tables were used extensively, so that to run a case, only initial fuel compositions, burnup history, specific powers, cooling times, and a few easily obtained reactor parameters need be supplied. The output is a summary of data on the heat release and activity after irradiation, followed by an isotope-by-isotope listing of alpha, beta, gamma, and total heat release rates, activities, and concentrations.

In the present version, over 150 isotopes are included, and fissions due to uranium-235, plutonium-239, and plutonium-241 are considered. To generate results sufficiently accurate for fuel reprocessing work, a modified Westcott procedure is used to calculate and then update heavy element cross sections during the course of the exposure.

The code was designed for thermal reactor cases, with both high and low enrichment uranium fuel, and does not appear to be applicable, without substantial revisions of the data sets, to fast breeder fuel cases. For IWR cases, however, agreement with experimental data has been encouraging. For example, the plutonium concentrations predicted for Yankee fuel generally matched core evaluation data to within 15%. Tables II and III present similar comparisons for fission products.

GENERAL FLUID-BED EXPERIENCE

Turning now to the experimental phase of the ORGDP fluoride volatility program, we would like to discuss first some of our general fluid-bed experience. An engineering-scale semiworks system was built and has been operated to collect data on some of the more important processing steps. The equipment used in the oxidation, fluorination, and dechlorination work in the semiworks consists of a fluid-bed reactor, a filter cooler, an off-gas scrubber and attendant instruments for monitoring gas feed, for process control, and for collection of data. Several thousand pounds of uranium dioxide has been processed in over 50 runs, and material balances have been excellent.

TABLE II

PRODUCTION OF SELECTED FISSION PRODUCTS IN YANKEE FUEL

Nuclide	Burnup, GWD/MTU	Quantity Present, g/MTU Corrected to Reactor Discharge, as Determined from:		
		Yankee Data*	ORGDP Work	ALTHAEA† Computer Code
Sr-90	13.7	286	250	270
	17.7	312	317	315
	24.3	376	398	410
	31.8	488	483	495
Tc-99	13.7	340	350	355
	17.7	430	450	440
	24.3	590	610	620
	31.8	770	800	775
Cs-137	13.7	528	500	525
	17.7	645	645	675
	24.3	942	860	950
	31.8	1,205	1,130	1,200
Pm-147	13.7	131	150	115
	17.7	157	185	125
	24.3	158	225	130
	31.8	192	250	135
Total Pd	13.7	360	260	-
	17.7	410	360	-
	24.3	720	600	-
	31.8	-	-	-

* Roberts, F. P., and Van Tuyl, H. H., Promethium-146, Fission Product, and Transuranium Isotope Content of Power Reactor Fuels, Pacific Northwest Laboratory, March, 1965 (BNWL-45).

† Rohrmann, C. A., and Merrill, E. T., Formation of Selected Fission Products in Power Reactors, Pacific Northwest Laboratory, May, 1966 (BNWL-244).

TABLE III
CONCENTRATIONS OF SELECTED NUCLIDES
IN ANL SAMPLE FUEL PELLETS

Basis
100 g Uranium Dioxide Irradiated to 33,000 MWD/MTU in the Yankee
Reactor, then Cooled for 1 Year

<u>Isotope or Element</u>	<u>Calculated Concentration</u>	<u>ANL* Analyzed Value</u>
Kr 85	0.695 Ci	0.73 Ci
Ru 106	18.8 Ci	17.5 Ci
Cs 137	9.6 Ci	9.9 Ci
Mo	0.286 g	0.247 g
U	84.0 g	84.6 g
Pu	1.06 g	1.10 g
Ce	26.2 Ci	25.4 g

* Analytical Data obtained from A. A. Chilenskas, ANL.

Figure 1 is a schematic of the reactor and the filter cooler. Both vessels are constructed of low-carbon nickel. The reactor is approximately 16 feet 3 inches tall. The bottom zone of the reactor is 5 inches in diameter and 4 feet 8 inches tall; the upper section is 10 inches in diameter and 11 feet tall. The choice of different diameters for the lower and upper zones was primarily an experimental consideration but such a design could be used for a plant system. The basic idea was to allow a relatively high velocity in the pellet bed in the lower, smaller section without an undue increase in gas requirements or velocities in the upper section. Additional nozzles were, however, supplied along the height of the reactor to allow supplemental injection of gas and thus to permit control of velocity at several points on the reactor. Construction of the smaller diameter zone also allowed tests with deeper beds in view of fuel charge limitations due to fuel material availability and local criticality batching rules.

As shown in Figure 2, the reactor is wrapped externally with coils for cooling. The coolant supply to each 1-foot section is independently controlled. Electrical heaters are also mounted on the outside of the vessel at 1-foot intervals closely corresponding to the air cooling coil sections. Each heater is independently controlled and is automatically regulated based on the temperature of the reactor wall in each interval.

26
25

PHOTO NO. PH-67-95

Fig 1

27

PHOTO NO. PH-66-402

Figure *2*
SEMIWORKS REACTOR

The filter cooler, Figure 3, has an overall length of about 10 feet 3 inches and also has a two-diameter design. The lower section is 12 inches in diameter and is about 4 feet 3 inches high. The upper part of the filter cooler is 16 inches in diameter. To limit bed height in the lower section, the vessel is equipped with an overflow line which extends from the top of the 12-inch section to a receiving vessel. The lower part of the filter cooler is water cooled, while the upper zone is air cooled. The vessel temperature is also regulated with externally mounted electrical heaters, which are controlled from wall temperature measurements. A plate, serving as a vapor discharge manifold, is welded in the upper flange section of the filter and up to nine sintered metal filter tubes, 3 inches in outside diameter and 4 feet long, can be screwed into the plate. Although nine tubes could be accommodated in the vessel, only six filters were used for most of the tests. Each tube has an area of 2.7 square feet and a capacity to retain 95% of all particles with sizes greater than 3 microns. A nitrogen blowback system is provided for the filters; solenoid valves allow blowback of the tubes, three at a time.

Successful uranium dioxide oxidation in the 5-inch section has been demonstrated with gas velocities of from 2 to 3 ft/sec, with oxygen concentrations ranging from 5 to 40%, with alumina-to-uranium ratios from 0.8 to 2.0, and with oxidation temperatures between 850 and 1000°F. With gas velocities less than 2 ft/sec in the 5-inch-diameter pellet bed, fluidization was poor and bed plugging occurred. Similar results were obtained with alumina-to-uranium ratios less than 1.0.

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PHOTO NO. PH-66-893

Figure 73
FILTER COOLER

Limiting the oxidation reaction to the top of the bed was a key finding obtained from tests with deep pellet beds. Oxidation was deliberately localized at the top of the bed by keeping the temperature there at about 900°F, while the lower portion of the pellet bed was held at 600°F, a temperature too low for oxidation to proceed. This technique was developed to solve observed plugging problems.

Successful operation was also demonstrated for oxidation of pellet beds which were 8 to 12 inches deep and located in the 10-inch-diameter part of the reactor. Typical conditions for these tests were gas velocities of 1.3 to 2.5 ft/sec, oxygen concentrations of 10 to 21%, alumina-to-uranium ratio of 1.0, and oxidation temperatures between 850 and 950°F. Unlike the runs with the deeper beds, no problems were encountered when oxidation occurred uniformly throughout the pellet bed.

Cold PRTR* assemblies plus locally built simulated zircaloy-clad fuel elements, arranged in square assemblies, were used to test the hydrogen chloride treatment step. Decladding runs in which zircaloy was volatilized from the bed at a temperature near 750°F were controlled successfully using stepwise increases in hydrogen chloride concentrations from 20 to 60% over the course of the run. Gas velocities in the 10-inch reactor zone were between 0.5 and 0.9 ft/sec. In oxidation runs preceded by the zircaloy-hydrogen chloride reaction, both the selectivity for and the rate of uranium elutriation were increased.

* Uranium fuel assemblies from the Plutonium Recycle Test Reactor program.

Also, some fluorination tests were made with elemental fluorine. The equipment operated satisfactorily in these tests; however, large amounts of uranium were elutriated from the reactor to the filter cooler, where the temperature was maintained too low for fluorination.

Engineering-scale studies of a stirred fluid-bed sorption-screw desorption system for collection of uranium hexafluoride from a dilute, contaminated gas stream have also been made at the ORGDP. The process utilizes sodium fluoride to form a double salt with uranium hexafluoride at about 250°F. The double salt is decomposed at about 650°F in a screw desorber to release uranium hexafluoride gas and the regenerated sodium fluoride is recycled to the sorber for reuse. Such a system might have application in a fuel reprocessing plant to separate uranium hexafluoride from other constituents, such as bromine pentafluoride.

The main process vessel in the pilot plant used for this work is a 6-inch-diameter stirred fluid-bed reactor. Regenerated sodium fluoride is fed into the vessel just above a 36-inch-deep fluid bed through a solid-flight helical screw feeder. Gas flows into the fluid-bed unit through a conical bottom with a ball-check entrance section. The unit is cooled using coils attached to the shell. The agitator is triangular in shape with three vertical rods and four cross-brace sections. The stirrer rotational speed can be varied from 5 to 120 rpm.

The pilot plant has been operated successfully with a sorber fluidizing velocity near 0.5 ft/sec with weight ratios of uranium hexafluoride feed rate to sodium fluoride circulated in the range of 0.1 to 0.25. Most of the tests have been made with a stirrer speed of 38 rpm. It was judged in the tests that higher speeds only have a marginal advantage and that the use of the stirrer in the fluid bed improves contacting and tends to prevent loss of fluidization due to bed caking or channeling. The efficiency of collection of uranium hexafluoride was very good, generally being in excess of 99.5% with 2 mole percent feed material, and uranium hexafluoride collection rates have ranged from 5 to 15 pounds per hour per cubic foot of bed.

COMPRESSOR DEVELOPMENT AND TESTING

To reduce reagent usage and thereby lower operating costs in fluoride volatility reprocessing plants, reactant gas recycle appears to be preferred over once-through schemes for both the hydrochlorination and elemental fluorine fluorination steps of the process. The recycle compressor requirements for a 1 tonne of uranium per day reprocessing facility are summarized in Table IV. It can be seen that compression ratios of about 2 to 1 and flow rates as high as 150 scfm are needed. Additionally, the overall design of the selected compressors, as demanded by the nature of the process, must be highly reliable and troublefree, with remote or semidirect maintenance feasible.

TABLE IV

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

	Compressor in HCl Service	Compressor in F ₂ -UF ₆ Service
Suction Pressure, psia	14.7	14.7
Pressure Ratio	2:1	2:1
Volume Flow, scfm*	25 to 150	25 to 50
Suction Temperature, °F	-40 to +77	200
Process Gas Constituents	HCl, H ₂ , N ₂	F ₂ , N ₂ , UF ₆
Approximate Range of Molecular Weights	18 to 35	28 to 61
Maximum Inleakage, scfm	0.2	0.2

* Standard conditions are 32°F and 14.7 psia.

A commercial diaphragm compressor and a locally developed two-stage peripheral compressor were felt to be potentially suitable for the proposed process and therefore were employed in testing programs. The programs were set up to evaluate performance and operation and maintenance problems of each compressor while operating in a test loop under conditions similar to those of the fluorination step of the volatility process.

Diaphragm Compressor

A diaphragm compressor was tested in the first part of this program. The compressor, shown schematically in Figure 4, is a single-stage unit utilizing primary and remote pumping heads connected by a line filled with fluorocarbon oil. All parts of the remote head in contact with the process fluid are nickel and are therefore suitable for handling corrosive gases. The unit tested, driven by a 5 hp motor, has a rated capacity of 11 scfm at a suction temperature of 60°F and a maximum discharge pressure of 220 psig. The compressor, shown installed in the test loop in Figure 5, was operated for nearly 1,400 hours on mixtures of air, nitrogen, and fluorine.

As a recycle compressor for the volatility process, the major advantage of the diaphragm compressor is that the gas delivered will be free from lubricants, since only the metal diaphragm is contacted on the pumping side. There is no seal diluent necessary. Secondly, the remote head feature, which allows the process gas pumping head to be placed behind a protective barricade, offers a unique shielding feature for the handling of corrosive and radioactive gases, making it possible for

LEGEND

- 1 - REMOTE PUMPING HEAD
- 2 - PROCESS GAS INTAKE CHECK VALVE
- 3 - PROCESS GAS DISCHARGE CHECK VALVE
- 4 - PROCESS DIAPHRAGM SET
- 5 - INTERMEDIATE FLUOROCARBON OIL LINE
- 6 - PRIMARY COMPRESSOR HEAD
- 7 - PRIMARY DIAPHRAGM SET
- 8 - PRESSURE LIMITING DEVICE
- 9 - HYDROCARBON OIL CHECK VALVE
- 10 - MAIN DRIVE PISTON
- 11 - COMPENSATING OIL PUMP
- 12 - HYDROCARBON OIL STRAINER

COMPRESSOR SCHEMATIC

Fig. 4

direct maintenance of the drive section of the compressor. Thirdly, the machine is a relatively low-speed compressor and thereby requires only a conventional electrical power supply.

For the intended purpose, however, the disadvantages of the diaphragm compressor appear to outweigh the advantages. The test machine was large, yet it had a capacity of only 10 to 11 scfm. In the volatility process, pumping rates in excess of 100 scfm will conceivably be required for a 1 tonne of uranium per day plant. Thus, several diaphragm compressors operating in parallel would probably be needed to handle the load.

A second disadvantage of this type of machine results from the periodic replacement of diaphragms associated with all diaphragm-type compressors. The life of the diaphragm varies with the operational speed of the compressor, and the manufacturer recommends that, as a routine maintenance procedure, all diaphragms be changed after about 1,000 hours of operation. Although the test machine was operated for almost 1,400 hours and no mechanical failure of any kind was experienced with the compressor unit itself, it is felt that the diaphragm replacement would be the major periodic maintenance operation.

The operational problems associated with the remote head assembly present a third disadvantage. The accumulation of small amounts of gas in the intermediate hydraulic fluid continually threatens the pumping efficiency of the machine.

Still another disadvantage is associated with the hydrocarbon oil system. The hydrocarbon oil supplied to the compensating pump is drawn from the crankcase through a perforated tube which acts as a strainer. The blockage of these perforations with dirt will lower the efficiency of the compressor by reducing the volume delivered by the compensator to the head. Any foreign matter which becomes lodged under the seat of the pressure-limiting device also hampers satisfactory operation, since the primary diaphragm would not be forced into full contact with the confining head on each compression stroke of the driving piston. If the compressor has remained out of service for a long time, the moving parts in the crankcase above the oil level must be hand-lubricated before starting to avoid seizure or any failure because of a lack of lubrication.

On an overall basis, considering both the factors noted above and the rather severe vibration problems which must be dealt with, the diaphragm compressor does not appear particularly well suited for application in a large fluoride volatility plant.

Peripheral Compressor

From the standpoint of fabrication and maintenance costs; predicted operational characteristics; and the speed, impeller size, and number of stages required, the recently developed peripheral compressor appears to be a more suitable type of machine for the intended applications than either diaphragm or centrifugal units. Performance data from a single-stage experimental peripheral compressor demonstrated that

a two-stage machine, with a 10-inch-diameter impeller operating at 11,000 rpm, could probably be adapted to meet the volatility process flow and pressure requirements for the various gas mixtures of interest. Consequently, a prototype compressor was developed and built at the Oak Ridge Gaseous Diffusion Plant. The final compressor design, as derived from the development program, is shown in Figures 6 and 7. The machine is small and can be easily installed in a 3-foot by 3-foot by 3-foot space. Through the use of removable inserts to change the channel dimensions, it appeared that one basic compressor design could meet the requirements for both hydrogen chloride and fluorine recycle service. Thus, the basic design consists of an impeller and motor rotor mounted on a single shaft supported in grease-packed precision ball bearings. A nitrogen-buffered bushing seal isolates the bearings and motor from the process gas with only a small amount of nitrogen inleakage. Motor and bearing cooling is accomplished by a water jacket around the motor stator and an air thermal barrier between the compressor passages and the load bearing housing.

The prototype peripheral compressor, as evaluated from over 2 years of intensive testing, including over 6,200 hours of operation with corrosive gas mixtures, has proved worthy of high recognition as a potential recycle compressor for the proposed volatility process. The performance of the compressor was outstanding and exceeded the design criteria set forth for the fluorination step of the process. Although the machine was not actually tested under the conditions specified for the hydrochlorination step of the volatility process, it is felt that

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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

TWO-STAGE PERIPHERAL COMPRESSOR

Fig 6

DRIED PERIPHERAL COMPRESSOR

the prototype compressor could adequately handle the flow and pressure requirements. The ruggedness of the compressor was demonstrated during the first testing program where the load bearing and motor area of the compressor were inadvertently exposed to fluorine, and the compressor continued to perform for over 8 months* with periodic oil injections. The reliability of the machine was established during the second testing program in which the compressor was operated for 14 months* without need for maintenance. The compressor, being small and compact, could easily be disconnected and removed from the process site for bearing replacement or other desired maintenance service. In the event of a seal failure, contaminated or corrosive gases could not be expelled to the atmosphere because the compressor passages and the drive motor compose an integrally sealed package.

The peripheral compressor, however, is not without fault. First to be considered is the fact that the compressor is a close-tolerance machine, and as for any other precision equipment, a certain amount of care must be exercised in the construction and operation of the unit. Precision machining and balancing are mandatory, and special care must be employed in the assembly of the compressor to ensure that proper movement and tolerances are respected. Consideration must be given to the possibility that the impeller can contact the interstage seal during rapid startup due to uneven heating. Also, a filter similar to the sintered metal one used in the test loop is highly advisable upstream of the compressor to remove entrained solids from the pumping media.

* This is elapsed time of test period. Machine was started and stopped numerous times, including weekend and other shutdowns.

As noted, the impeller and motor rotor are mounted on a single shaft supported in grease-packed precision ball bearings. The bearings must be replaced periodically, probably around every 2,500 hours.* With experienced mechanics, the compressor could probably be removed from the process, disassembled, fitted with new bearings, and placed back into service within one day.

The prototype peripheral compressor was equipped with a bushing type shaft seal, and, therefore, a certain amount of nitrogen inleakage to the process must be tolerated. If the process system is a closed one, as was the test loop, provisions must be made to bleed off excess inventory and to maintain desired reactant concentration levels by makeup.

Lastly, since the peripheral compressor is driven by an alternating current synchronous motor, a variable frequency alternating current power supply is required to achieve selection of compressor speed. If variable speed is not desired, a source of 185 Hz power is needed.

CORROSION AND COMPONENT STUDIES

Materials of Construction - Corrosion Testing

To evaluate various materials proposed for use in the fluoride volatility process, coupon testing was done in a bench-scale controlled-atmosphere loop and also in a small fluid-bed unit. Of the many materials tested, nickel-200, nickel-201, and Duranickel appeared satisfactory for

* Actual running time.

multicycle-exposure to hydrochlorination, oxidation, and fluorination environments. Even these materials produced some assembly problems, however, and as a result, new welding procedures for joining nickel to nickel, nickel to Duranickel*, and Duranickel to Duranickel were developed.

Some exotic metals such as Berylco 440† were also studied, but high cost and non-availability in large amounts prohibited serious consideration.

Connectors

Since remote maintenance is a requirement at many points in the proposed fuel reprocessing facilities, custom designed connectors must be used to facilitate removal of equipment. The first approach to the 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. The Marman Conoseal clamp, made by Aeroquip Corporation, Los Angeles, California, showed promise for application in the larger process lines. Studies were also undertaken on a flat-faced flange design with crushable metal gaskets. The best design was found to consist of hardened Duranickel flanges compressing a multi-touchpoint soft nickel gasket with buffer connections between the

† Berylco 440 is a product of Beryllium Corporation of America, Reading, Pennsylvania. Its nominal composition is 1.95% beryllium and 0.5% titanium, with the remainder nickel.

* Duranickel is a product of the International Nickel Company, Huntington, West Virginia. It is commonly referred to as Alloy 501 and contains 93% minimum nickel and 4-4.75% aluminum.

touchpoints. Total flange bolt loadings in the order of 200,000 pounds are required to deform the gasket for proper sealing, thus necessitating the use of extra heavy flanges to reduce warping. Such a connector successfully withstood temperature cycling between 100 and 370°C. Attempts to increase the upper limit to 540°C usually resulted in gasket leaks.

Valves

It was felt that commercial bellows-sealed valves for gas stream application were satisfactory. Therefore, the valve studies were restricted to reactor charging and "dumping" units.

An 8-inch nickel-plated stainless steel slide valve was obtained from Mill Lane Engineering Company, Incorporated, of Burlington, Massachusetts, as a possible unit for the fuel element charger valve on the planned Oak Ridge National Laboratory hot pilot plant. Hold tests indicated satisfactory seat leakages, and performance testing indicated reliability in repeated operations.

Periodically, it would be necessary to empty the contents of the reactor bed to reduce the radiation level and to withdraw unreacted materials involved in the process. About thirty manufacturers were contacted requesting supply of a valve of the following specifications:

1. Straight-through configuration, radiation-resistant, hermetically sealed, remotely operated.
2. Two to 8-inch size with operating conditions of 20 psig and 540°C.

3. Construction of nickel, Duranickel, or halogen-resistant ceramics.

Most of the vendors admitted that the service was much too extreme for their standard units. Several companies offered to develop a valve on a best effort, development cost basis; however, an agreement was never concluded.

A 2-inch all-nickel plug valve was purchased from the Dezurick Company, for possible modification. This valve was designed to operate with a single-faced eccentric plug which rotates in a direction perpendicular to the direction of flow into position against a raised seat in the valve body. This seat is also eccentric to the axis of rotation; hence, the plug and seat make contact only in the fully closed position. The plug moves out of the flow path when the valve is open. The valve was modified to incorporate a hermetically sealed air-operated actuator. Tests indicated the valve would meet all specifications except for gas leakage through the seat. Powder leakage was nil, and high temperatures presented no apparent problem.

Samplers

A 6-inch Vezin solid sampler purchased from the Denver Equipment Company, Denver, Colorado, was tested for possible application in solids sampling in the process. Various materials were processed and analyzed. The unit was found to be satisfactorily accurate and reliable.

Filters

Commercially available sintered metal filters have been evaluated to determine if such units would give satisfactory service in removing solids from gas streams exiting from reactor units. Filter tubes of various shapes and materials were purchased for test in our filter test loop.

The first series of experiments was conducted on porous nickel tubes exposed to dilute hydrogen chloride at 315°C, air at 100°C, and dilute fluorine at 100°C in cycling phases. These gases were first used to fluidize a bed of tabular alumina (48 to 100 mesh) in a 4-inch reactor located ahead of the filters to simulate conditions expected in the volatility process. Basically, the following information was determined.

1. Powdered nickel bayonet filter units showed a 70 to 80% permeability loss after about seventeen cycles of exposure. Cracks developed in the tubes immediately adjacent to the welds.
2. Welded cylindrical porous powder tubes also cracked adjacent to the welds.
3. Molded nickel powder tubes exhibited some promise of success, but the particular manufacturer ceased production during the test period.

4. Porous nickel fiber tubes gave good results, with an average permeability loss of only 30 to 40%. The manufacturer was able to produce tubes of nickel-201, including weld material.

Upon completion of the gas exposure tests, the program continued adding a small charge of zircaloy to the reactor at the beginning of each exposure cycle. Excessive filter plugging developed almost immediately. Although laboratory analyses of filter coatings by means of wet chemistry, spectrochemical, and X-ray diffraction were unable to indicate that exact structure of the plugging media, it was thought to be either an intermetallic complex or an oxyhalogen compound.

All sources of oxygen were first eliminated during the hydrochlorination phase to no avail. The plugging was found to be somewhat reducible with hydrogen at 500°C, but excess hydrogen during hydrochlorination did not inhibit the reaction. Operation of two tubes in series gave plugging in both tubes, thus ruling out alumina as the cause.

Substitution of other bed diluent materials gave no improvement. Laboratory analyses of the filter coatings usually indicated high zirconium content.

In further studies, a series of tests was conducted using zirconium tetrachloride as a starting material in the reactor; this procedure eliminated other zircaloy constituents as the source of plugging. Briefly, the results of these studies indicated:

1. A mixture of zirconium tetrachloride and oxygen-free argon gave a 79% plug after ten cycles of exposure.
2. A mixture of zirconium tetrachloride and 50% hydrogen chloride in argon plugged the above filter beyond satisfactory use in six more cycles (98.8%).
3. Zirconium tetrachloride with 30% hydrogen in argon gave a 21% permeability loss in ten cycles of exposure.
4. The addition of 50% hydrogen chloride in mixture (3) gave a total plug (98.7%) after thirteen additional cycles.

In summary, it is believed that the plugging problem is largely caused by a combination of factors, the zirconium and the excess hydrogen chloride, probably enhanced by the high surface area of nickel. Other materials of construction for the filters, such as Inconel and stainless 316, were tested in the loop with only partial success. After nineteen cycles of exposure to the hydrochlorination and oxidation phases only, the stainless 316 tube experienced a 96% permeability loss; however, the final flow rate through the tube was about 8 scfm of air per square foot of surface area per pound per square inch pressure difference, which from a design standpoint, might be acceptable. Of course, this tube would not be acceptable for fluorination conditions and would lead to a two-vessel system.

LIQUID BROMINE PENTAFLUORIDE RELEASE TESTS

Field tests have been conducted to determine the resistance to attack and/or vigorousness of the reaction when various materials are contacted with liquid bromine pentafluoride. The materials included in the tests were those which might be found in the vicinity of volatility fuel reprocessing operations. Liquid bromine pentafluoride could conceivably come in contact with these materials in the event of a spill or break in a line. The tests were not intended to evaluate materials to be routinely exposed to bromine pentafluoride. Some items which obviously would be very reactive to bromine pentafluoride were included so that the importance of excluding them from operating areas could be assessed.

The tests were conducted in the ORGDP hazardous gas disposal area. Samples were placed in a shallow nickel pan, and a small amount of liquid bromine pentafluoride was drained into the pan via pipeline from a valving station located 150 feet upwind. The pan was tilted, and the contents were dumped by the use of a sling and a long rope after each test.

A list of the materials tested is given in Table V, along with the test results. Of the materials listed, the reaction with liquid bromine pentafluoride was the most violent for oils and greases, while no reaction was observed for metals, Transite, and Teflon.

TABLE V

BROMINE PENTAFLUORIDE SPILL TEST RESULTS

Material	Observed Reaction With Liquid Bromine Pentafluoride
Fabrication and Construction	
Selected Metals*	None
Transite	None
Concrete	No damage to sample
Glass	Etched
Asphalt	Burned, possibly exploded
Wood	Partially burned
Electrical Wiring	Completely burned
Lubricants and Oils	
Greases	Succession of explosions, fire
Grease-Covered Metals*	No reaction with metals. Grease exploded and burned vigorously
Hydrocarbon Oils	Explosion, fire
Fluorocarbon Oil	Reaction gave off orange-white smoke, but no flames or explosion; oil consumed
Wearing Apparel	
Leather, Neoprene Gloves	Completely consumed
Safety Glasses	Frames destroyed, lenses etched
Gas Mask	Burned vigorously, completely consumed
Paper and Cloth	Burned, completely consumed
Animal Flexh (sow's ears and gone)	Explosion, samples blown out of sample pan, but no further reaction
Insulation, Coatings, Gaskets	
Teflon	None
Rubber	Melted and burned
Cork	Burned, almost totally consumed
Yellow Tape and Plastic	Burned, completely consumed
Kel-F	None

TABLE V
(Continued)

BROMINE PENTAFLUORIDE SPILL TEST RESULTS

Material	Observed Reaction With Liquid Bromine Pentafluoride
Rubber Weather Stripping	Burned, almost completely consumed
Fire Retardant Coating (Gray)	Almost completely consumed
Heat Transfer Cement	Burned, residue exploded in two out of four tests
Reinforced Phenolic Foam Insulation	Partially burned and charred, discolored
Glass Wool Insulation	Burned, completely consumed in contacted areas
Urethane Insulation	Burned vigorously, almost completely consumed
Magnesium Oxide Insulation	Partially burned and charred, discolored
Foam Plastic Insulation (low temperature)	Reacted vigorously, totally consumed
Felt Insulation	Remained intact but partially consumed
Asbestos Strip (loose web)	Almost totally consumed
Asbestos Strip (tight weave)	Remained intact but partially consumed
Miscellaneous	
Gasoline	Explosion
Water	Reaction gave off orange-brown smoke with appreciable splattering of liquids
Alumina, Potassium Hydroxide, Soda Ash, Sodium Fluoride, and Magnesium Fluoride	Gave off orange-brown smoke, no apparent damage to materials

* The metals included stainless steel-304, stainless steel-316, Inconel, nickel, brass, copper, steel, zirconium, and Monel.

The extent of the reaction with asbestos cloth appears to be influenced by the weave. As can be seen in the listing, the reaction with a tightly woven mitten was far less than with a loosely woven strip.

Upon contacting liquid bromine pentafluoride with the heat transfer cement, there was a flame accompanied by large quantities of orange-brown smoke, but there were no explosions. Toward the end of the reaction, carbon particles or flakes were entrained in the smoke and were carried a few feet above the test sample. Since the reaction proceeded so vigorously, it was expected that the heat transfer cement had been totally consumed; however, upon investigation, it was found that a green-black residue, resembling congealed melt, remained. When the pan which contained the residue was tilted, particles began to break away, and it was evident that the residue was actually a powder. At this point, an explosion occurred, apparently detonated by mechanical shock or friction. The magnitude of the explosion was considered equivalent to about two "cherry bombs"; i.e., about one-eighth to one-fourth stick of dynamite. The explosive constituent is thought to have been an interstitial carbon-fluorine compound. Three additional tests with the heat transfer cement were performed. In all three cases, the initial reaction was similar to that in the first test; however, in only one case did an explosion occur when the residue was subjected to shock, and this explosion was quite mild and in no way approached the magnitude of that in the original test. It is apparent from these experiments that, in some cases, explosive compounds may be formed when

reacting the heat transfer cement with liquid bromine pentafluoride.

It is reasonable to assume that comparable reactions could occur between bromine pentafluoride and materials similar to the cement tested.