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ENGINEERING DEVELOPMENT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part 14. Processing Experience in Fluorinating Plutonium Materials and Thermally Decomposing Plutonium Hexafluoride in the Engineering-scale Alpha Facility

by

N. M. Levitz, G. J. Vogel, E. L. Carls,
I. E. Knudsen, D. E. Grosvenor, R. W. Lambert,
E. L. Youngblood, W. A. Murphy, B. J. Kullen,
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for Plutonium and Uranium

ARGONNE NATIONAL LABORATORY
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Chemical Engineering Division

November 1969

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ABSTRACT

The applicability of fluoride-volatility methods to the reprocessing of light-water-reactor fuels was demonstrated in a program of fluid-bed fluorination studies and fluid-bed thermal-decomposition studies conducted in an engineering-scale alpha facility. Studies were conducted on nonirradiated UO_2-PuO_2-F.P. pellet materials and PuF_4 powder charges. Key features of this work were the production and transport of PuF_6, and the demonstration of good plutonium material balances. The results of these studies are considered applicable to processes for high-plutonium materials, such as fast-breeder-reactor fuels and plutonium scrap materials.

1. SUMMARY

Fluid-bed fluoride-volatility processes based on the conversion of uranium and plutonium to volatile hexafluorides show considerable potential for reprocessing spent light-water-reactor oxide fuels. Both all-fluorine and interhalogen-fluorine flowsheets have been proposed. Development studies on the main fluorination recovery step and on fluid-bed thermal decomposition as a means of separating and partially purifying the plutonium fraction were conducted on simulated, nonirradiated fuel materials. The primary purpose of this program (which was achieved) was to demonstrate that the production and manipulation (transfer and recovery) of PuF_6 was feasible. Of a total of 635 g of PuF_6 handled in these experiments, over 90% was produced directly in fluorination experiments. Material balances were satisfactory, accounting for about 98% of the plutonium.

Experimentation was carried out in two pilot-plant systems installed in an engineering-scale alpha facility. The fluorination process equipment, essentially all of nickel, included a 3-in.-dia fluid-bed reactor, large cold traps for collecting the UF_6 and PuF_6, a diaphragm gas compressor for circulating unused fluorine, sintered-metal filters, and sorption traps for trapping residual quantities of hexafluorides and fluorine from the off-gas. Thermal-decomposition studies were conducted in a 2-in.-dia Inconel fluid-bed reactor system.

Fluorination studies were conducted on three types of materials: (1) pellets containing UO_2-0.5 wt % PuO_2-simulated fission products, (2) powdered PuF_4, and (3) PuF_4 remaining after the uranium in oxidized pellets was fluorinated by BrF_5. The fluid bed comprises a charge of inert, high-fired alumina (which serves as a heat-transfer medium) and the fuel material.

The UO_2-0.5 wt % PuO_2-simulated fission-product (F.P.) pellets (8.8 kg per charge) were processed by a two-zone reaction scheme in which the fuel was pulverized by reaction with oxygen in the lower portion (a fluidized-packed bed) of the reactor; the resulting fine U_3O_8-PuO_2 material was elutriated by the fluidizing gas to the fluidized-bed region, which was above and contiguous with the pellet region where reaction with fluorine converted the oxides to the volatile hexafluorides. Oxidation was carried out at about 400-450°C, and fluorination at 450-550°C. Average UF_6 production rates ranged from 24 to 51 lb/(hr)(sq ft). Rates as high as 100 lb/(hr)(sq ft) were achieved for short periods. With bed reuse for the three experiments, overall plutonium and uranium removals of 98.7 and 99.9% were achieved.

The data show that preferential fluorination of uranium was achieved in the initial fluorination period, suggesting a means of achieving at least a partial separation of uranium from plutonium, if this separation is desirable. The use of BrF_5 as a selective fluorinating agent for the uranium, followed by the use of fluorine to recover the plutonium, represents an alternative approach.

Fission product behavior during fluorination was as expected, elements such as molybdenum and ruthenium forming volatile fluorides, while the bulk of the fission products were converted to nonvolatile fluorides, which remained in the fluorinator bed. It is not clear that a single volatile species formed, since about 30 and 15% of the molybdenum and ruthenium, respectively, were recovered by fluorinating the cold traps and hexafluoride storage cylinders at 300°C after the contents (mainly UF_6 and PuF_6) were vapor transferred to other vessels at 80°C. No significant changes in the particle-size distribution of the alumina bed in the fluorinator were noted during a run.

Fluorination experiments with 135-g batches of PuF_4 demonstrated that (1) plutonium could be volatilized quantitatively from a fluid bed of alumina, (2) satisfactory material balances were obtained, and (3) practical fluorination rates and fluorine utilization were realized. Fluorination was started at 200 and 300°C and was completed at 550°C.

Two experiments involving bed reuse and simulating the plutonium recovery step of the interhalogen flowsheet gave residual plutonium and uranium values in alumina of 0.015 and 0.002 wt %. These values represent 98.7 and 99.9% removal of plutonium and uranium from alumina. The beds were prepared in a separate facility by oxidation and a BrF_5 treatment of UO_2-0.5 wt % PuO_2-F.P. pellets to remove the uranium. Fluorination with fluorine was started at 300°C and was completed at 550°C. Fluorine efficiencies greater than 50% were measured at the start of the run. Efficiency diminished as the plutonium level in the bed decreased. The cold traps, operating at about -60°C, collected the relatively small quantities of PuF_6 efficiently from the recycled gas stream.

The fluid bed was readily sampled during the experiments, but results indicated that the samples were often not representative of the column inventory. Elutriation of fines and holdup of this material above the bed region in the upper parts of the column must be considered in developing reliable sampling procedures. The system can apparently be optimized from the alumina particle-size-distribution standpoint.

On the basis of the present work, separation of plutonium as PuF_4 from UF_6-PuF_6-F.P. mixtures by thermal decomposition in a fluid-bed system appears feasible. Separations of over 99% were achieved at 300°C in the single fluid-bed stage using the 10-kg batches of UF_6-PuF_6 mixture provided by the companion fluorination experiments. Calculated gas-residence times in the decomposer were less than 10 sec. Decontamination factors of $>10^3$ and $>10^2$, respectively, were obtained for ruthenium and molybdenum, which were in the UF_6-PuF_6 feed as volatile fluoride species.

Plutonium deposited in lines and equipment by alpha- or thermal-decomposition mechanisms or because of interaction with the system was shown to be recoverable by a simple fluorination treatment at 300°C using high (~90%)-concentration fluorine on a recycle basis.

The value of neutron survey meters as semiquantitative plutonium monitors was clearly demonstrated in this program. Their further use as a quantitative instrument should be exploited.

Although this program was directed at the reprocessing of light-water-reactor fuels, much of the results and information derived from it should be applicable to the processing of high-plutonium materials such as fast-breeder-reactor fuels and scrap materials.

2. INTRODUCTION

Since nuclear-reactor fuels suffer physical damage and lose nuclear reactivity during irradiation, the fuel elements are periodically discharged from the reactor in a partially spent condition. These fuel elements must be processed to separate the valuable fissionable and fertile materials, and to reconstitute the fuel into new fuel elements for return to the reactor. An extensive program has been carried out at U.S. national laboratories and foreign research centers to develop new processing methods that use fluoride-volatility techniques for the recovery of uranium and plutonium from spent reactor fuel materials. These processes are based on the ability to convert the uranium and plutonium to volatile hexafluorides, which can be readily separated from associated fuel materials (cladding, fission products) and purified by established techniques. A significant feature of fluoride-volatility processes is the application of gas-solids fluidization.

The major objectives of the fluoride-volatility program were to establish process feasibility and to develop the technical data required for the design of a commercial fluoride-volatility reprocessing plant for both low- and high-enrichment power-reactor fuels. The present report discusses process studies directed toward the processing of low-enrichment UO_2-PuO_2 fuels clad in Zircaloy or stainless steel of the type used in water-cooled power reactors. The results of this work are considered pertinent to processes for fast-breeder high-plutonium fuels, as well.

Two process flowsheets have been under study (see Section 3). One is referred to as the two-zone process, the other the interhalogen process. Both processes have the same basic steps:

a. Decladding.

b. Transformation of the uranium-plutonium oxides to hexafluorides by an oxidation-fluorination reaction sequence.

c. Purification of the hexafluorides.

d. Reconversion of the hexafluorides to oxides.

Conceptually, the fuel elements are charged to a fluid-bed reactor. Inert, high-fired alumina comprises the bed, which serves primarily as a heat-transfer medium. The decladding and fluorination steps (a and b) are carried out successively in batch operations in this reactor. Steps c and d are carried out in other equipment.

A major difference between the two flowsheets is the use of BrF_5 in the interhalogen flowsheet as a selective fluorinating agent for the uranium, followed by fluorine to recover the plutonium, as opposed to fluorine alone being used in the two-zone process to recover both the uranium and plutonium. Alternatively, plutonium can be separated from UF_6-PuF_6 mixtures by thermal decomposition as described in Section 8.

Two types of studies were undertaken in an engineering-scale alpha facility directed toward the development of these flowsheets--fluorination studies on simulated fuel materials, and a study on thermal decomposition as a means of separating plutonium as PuF_4 from UF_6-PuF_6-F.P. mixtures. Fluorination studies were conducted on three types of material, all non-irradiated:

1. UO_2-0.5 wt % PuO_2 pellets containing simulated F.P. oxides.
2. PuF_4 powder.
3. Plutonium-bearing residues from treatment of UO_2-0.5 wt % PuO_2-F.P. pellets with BrF_5.

The UF_6-PuF_6-F.P. mixtures produced in the fluorination of the oxide pellets (1 above) served as feed for the thermal-decomposition experiments.

Among the objectives of these studies were to (1) demonstrate the ability to produce and transport practical quantities of plutonium as PuF_6, (2) account for all of the materials processed (show good material balances), (3) show that uranium and plutonium recovery from the alumina bed material was adequate (the goal was 99% removal), and (4) explore the behavior of molybdenum and ruthenium (key fission products in the fluorination and thermal-decomposition steps). Neutron activity from the (α,n) reaction of fluorine with plutonium permitted the extensive use of neutron survey meters as plutonium monitors.

Section 4 presents sources of information on prior work. The remainder of the report describes the present work. A considerable amount of procedural information is presented in the appendixes.

3. VOLATILITY PROCESS DESCRIPTION

3.1 Two-zone Flowsheet

In the application of the two-zone flowsheet (shown in Fig. 1) to Zircaloy-clad UO_2-PuO_2 fuel, the fuel assemblies are charged to a fluid-bed reactor (primary reactor), where they are immersed in a bed of high-fired alumina. The Zircaloy cladding is removed by reaction with HCl gas at a temperature above the sublimation point of $ZrCl_4$ (331°C). The $ZrCl_4$ gas is pyrohydrolyzed to a solid oxide waste by reaction with steam in a second fluid-bed reactor (pyrohydrolyzer).

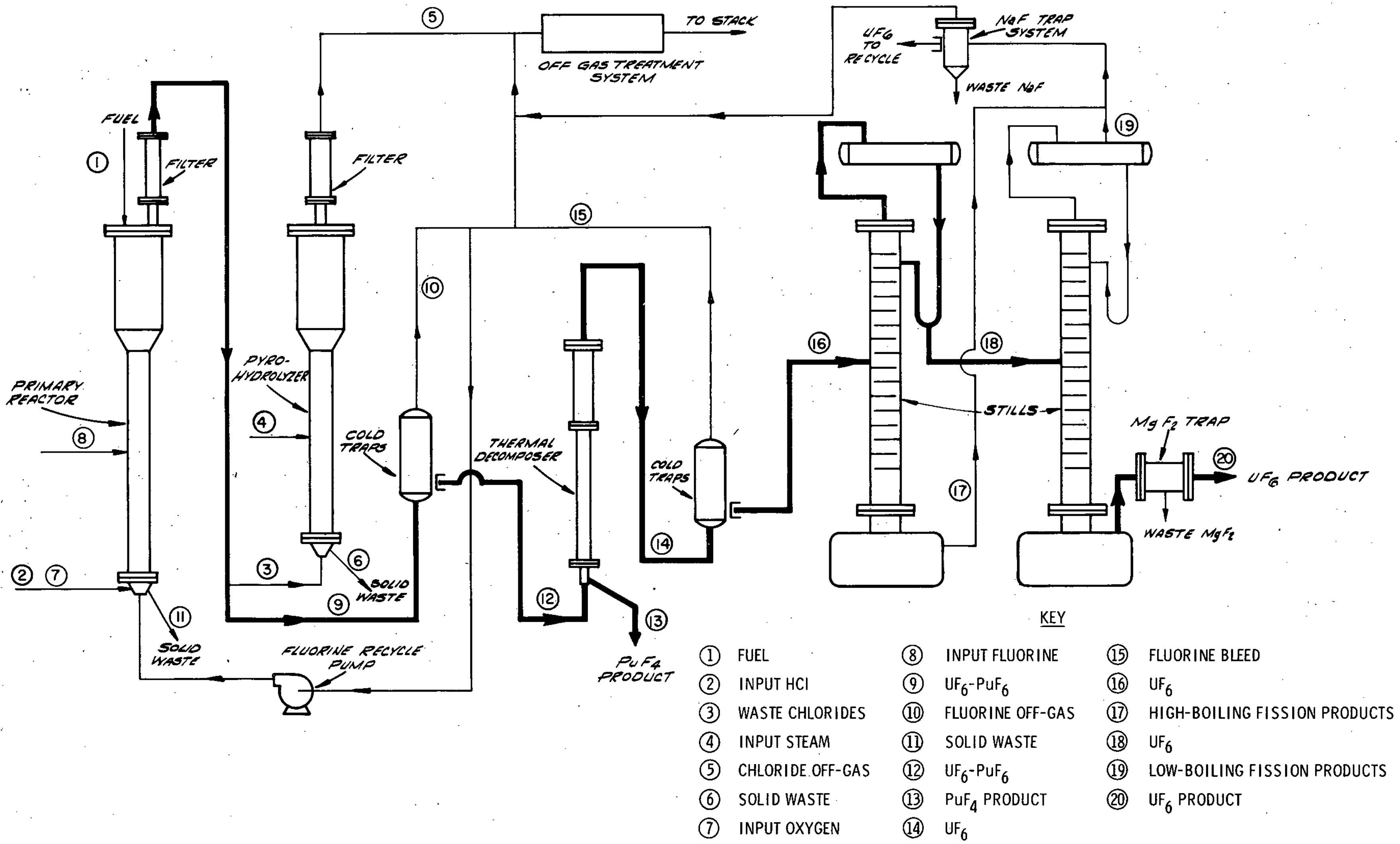


Fig. 1. Reference Flowsheet (Jan. 1, 1965) for Fluid-bed Fluoride-volatility Process. ANL Neg. No. 108-8171.

The uranium dioxide and plutonium dioxide are unattacked during decladding and accumulate in the lower zone of the primary reactor. The fuel is in the form of pellets or pellet fragments. The characteristics of this fluidized-packed-bed system (fluidized alumina grain in the free space of the pellet bed) were studied by Gabor and Mecham.[1] The fuel is next reacted with diluted oxygen, which oxidizes the UO_2 and thereby converts the fuel pieces to a finely powdered mixture of U_3O_8 and PuO_2. The mixing action of the fluid bed transports the powdered fuel to the upper (unhindered fluid bed) zone of the bed, where fluorine is continuously injected. Fluorination reactions in the upper zone result in the formation of UF_6 and PuF_6, which are volatilized from the reactor and collected in refrigerated traps. Some control over relative fluorination rates of uranium and plutonium can be exercised by control of fluorine concentration to effect a partial initial separation of uranium. Excess fluorine gas is recycled during the later stages of fluorination in order to conserve fluorine.

The mixture of hexafluorides, together with the fission products whose fluorides are volatile, is next revaporized and fed continuously from the cold traps to a second reactor, the thermal decomposer, in which the less stable PuF_6 is thermally decomposed to nonvolatile PuF_4. The ultimate use of the plutonium is not specified.

The UF_6 and the remaining volatile fluorides pass into cold traps, where they are again condensed, and are later fed to fractional-distillation columns for separation of the F.P. fluorides from the UF_6. The UF_6, after reenrichment, may be reconverted to the oxide by a fluid-bed process developed by Knudsen[2,3] and co-workers at Argonne National Laboratory.

The impurities, NpF_6 and TeF_6, which may not be separated by distillation, are removed from the UF_6 gas stream by sorption on granular MgF_2.

The bulk of the fission products are removed as solid waste with the alumina bed from the primary reactor. Other lower-level radioactive waste streams are removed from various process vessels.

3.2 Interhalogen Flowsheet

The interhalogen flowsheet is shown in Fig. 2. In this case, uranium and plutonium are separated in the primary reactor by selective fluorination. After decladding, the uranium in the fuel is oxidized to U_3O_8 and is fluorinated with BrF_5 gas to UF_6 (Fluorination I), which is volatilized from the vessel and collected in a condenser, together with the excess BrF_5 and the reaction product, bromine. In this step, plutonium reacts to form nonvolatile PuF_4, which remains in the primary reactor. The UF_6 and the interhalogens, together with those F.P. fluorides that are volatile, are separated by fractional distillation, resulting in a completely decontaminated uranium hexafluoride product. The Br_2 is refluorinated to BrF_5, which is recycled.

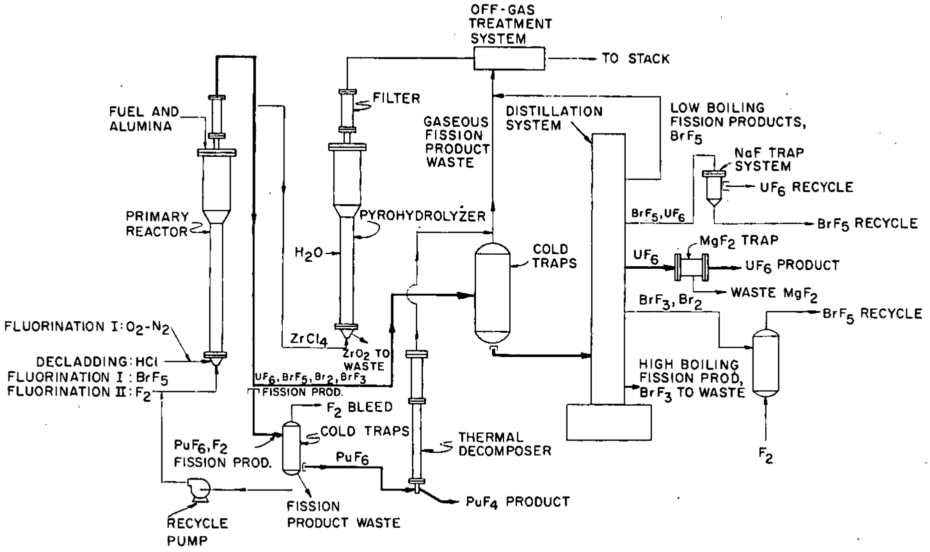


Fig. 2

Reference Flowsheet (Feb. 1, 1965) for Interhalogen Fluid-bed Fluoride-volatility Process. ANL Neg. No. 108-8381 Rev. 6.

In the second fluorination step (Fluorination II), the plutonium, as PuF_4, is fluorinated with fluorine gas to PuF_6, which is volatilized from the vessel and collected in separate cold traps. After collection, the PuF_6 is revaporized and passed into a heated vessel, where it is thermally decomposed to nonvolatile PuF_4 product.

The subsequent treatment of the plutonium and uranium would depend on their end use.

4. SOURCES OF INFORMATION ON VOLATILITY PROCESS

Jonke[4] has reviewed the recovery of uranium and plutonium from spent nuclear-reactor fuel elements using processes based on volatilization, fractional distillation, and selective adsorption. His article presents a history of volatility-processing methods and describes the steps in processing both low- and high-enrichment fuels by the fused-salt process, the fluid-bed fluoride-volatility process, and the nitrofluor process; the steps in separating the F.P. elements from uranium and plutonium products; the method of converting UF_6 to UO_2; data on corrosion; and the status (in 1964) of the fluid-bed fluoride-volatility process.

Experimental results on volatility process studies obtained by both American and foreign investigators are reported in the quarterly issues of Reactor and Fuel-Processing Technology (earlier titles: Reactor Fuel Processing; Power Reactor Technology and Reactor Fuel Processing). These are published by the Technical Information Division, United States Atomic Energy Commission.

At ANL, laboratory-scale investigations are reported with the general title, Laboratory Investigations in Support of Fluid-bed Fluoride Volatility Processes. Reports on engineering-scale investigations are issued with the general title, Engineering Development of Fluid-bed Fluoride Volatility Processes. This report is Part 14 of the latter series. Other reports in this series are listed at the front of this report.

5. ENGINEERING FACILITY AND EQUIPMENT

Because the engineering alpha facility and pilot-plant equipment have been described in detail in a previous report,[5] only the more important details are repeated here. The automatic data-logging system, used fully only in the later runs, has not been discussed in previous reports.

5.1 The Alpha Facility

Figure 3 shows the location of the alpha boxes and the panelboard in the Alpha Facility. Plutonium processing equipment is housed inside the large alpha box, which is inside a concrete cell in the room. Auxiliary equipment that might become plutonium-contaminated is housed in a smaller alpha box in the room. Fluorine cylinders are stored in a ventilated enclosure in the room. The room is serviced by an overhead crane having a rail elevation of 25 ft.

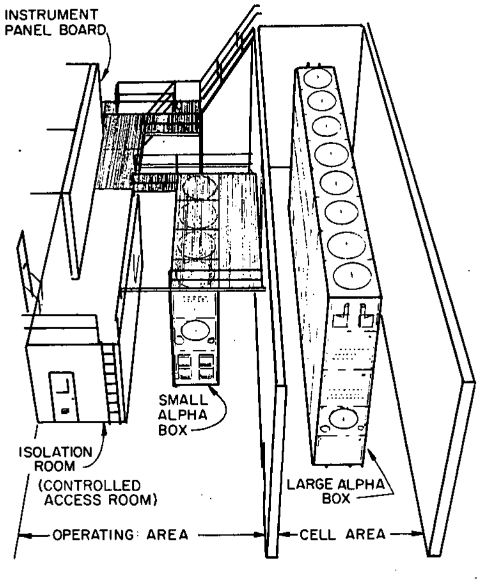


Fig. 3. Room Layout of Pilot-scale Alpha Facility

The panelboard, containing the remote process control and recording instruments, overlooks the operating area from its position above the controlled access room. Access from the main building corridor to the facility is provided through this room, where personnel radiation monitoring instruments are stationed.

Ventilation air flows through the area once (it is not recycled) from the least to the most contaminated areas (i.e., from the building corridor to the isolation room to the operating area to the process cell) and also from the inlet ventilation ducts to the operating area to the process cell. Air flow through the larger box is up to 600 cfm; through the smaller box, 150 cfm.

All air entering the facility is humidified to 40% relative humidity and is water-scrubbed and filtered at least once before being exhausted from the building. For air exhausted from the larger alpha box, this treatment is performed twice (in sequence). All air exhausted to the building stack is monitored continuously for radioactivity, using a recorder. Figure 4 shows the path of ventilation air flows.

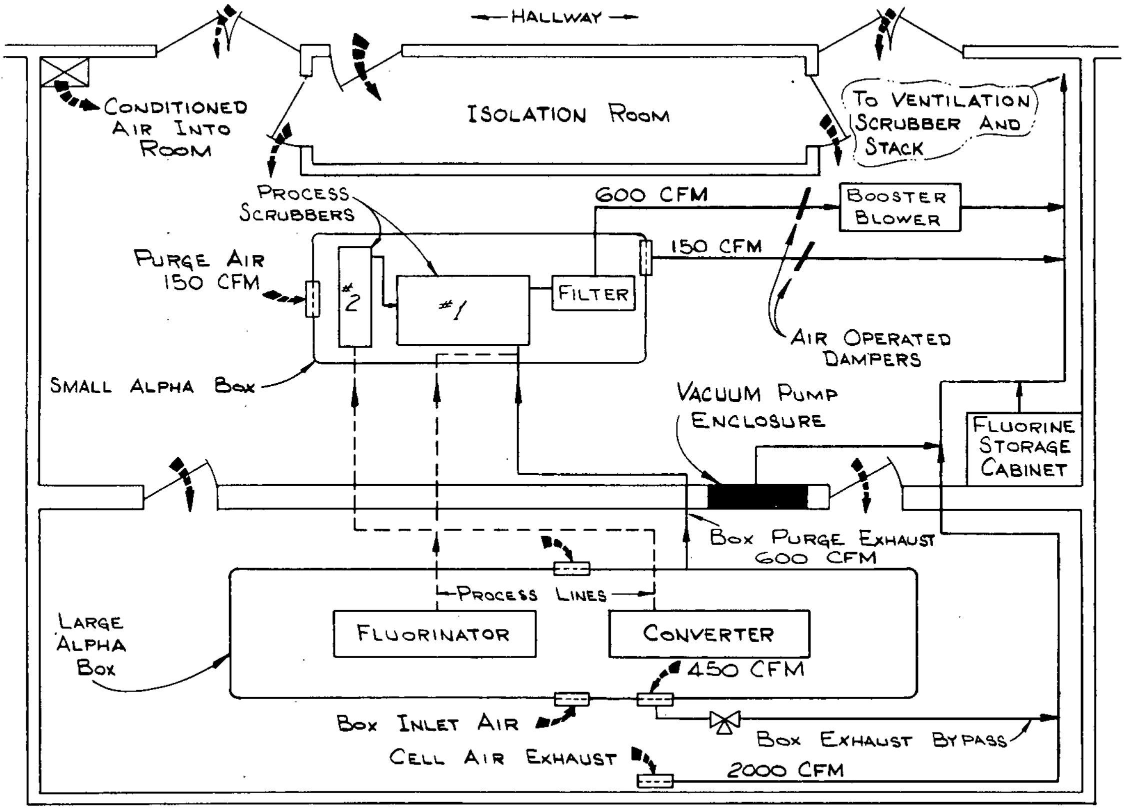


Fig. 4. Ventilation Air and Process Off-gas Flows for Alpha Facility

The large alpha box is $17\frac{1}{3}$ ft high, $26\frac{1}{2}$ ft long, and $3\frac{1}{2}$ ft wide; the small alpha box is $10\frac{1}{2}$ ft high, $13\frac{1}{4}$ ft long, and $3\frac{1}{2}$ ft wide. Construction is modular, each section being essentially a $3\frac{1}{2}$-ft cube; the large alpha box is eight sections long and five sections high. Windows are located at all but three of the 80 face positions (40 on each side of the large alpha box); the exceptions are the two ventilation-air inlets and an emergency-air exit-duct connection. The side sections of the boxes are fabricated from 1/8-in.-thick, cold-rolled sheet steel; the end panels, from 3/16-in.-thick steel. The alpha box windows, 3/8-in.-thick laminated glass, are sealed to the framework by Neoprene channel stripping and a plastic sealant that sets at room temperature. Inside and outside metal surfaces of the boxes are painted with chemical resistant finishes.

Equipment and materials are brought into or removed from the boxes through 8-, 22-, or 30-in.-dia openings with a bag-sealing technique using polyvinylchloride bags and a dielectric sealer. Eight 30-in. openings are located at the top of the box for removing large equipment items, since vertical (but little lateral) movement of such equipment is possible. In addition to the above openings, 4-in.-dia sphincter-type openings are available for adding items of small size.

Hydraulically operated lifts elevate personnel to working positions on each face of the larger glovebox. The 7-ft-long, 2-ft-wide lift platforms are large enough to accommodate more than one person at a time.

Figure 5 is an overall view of the process equipment in the large alpha box. Figures 6 and 7, respectively, are equipment-instrumentation flowsheets of the fluorination and decomposer pilot plants.

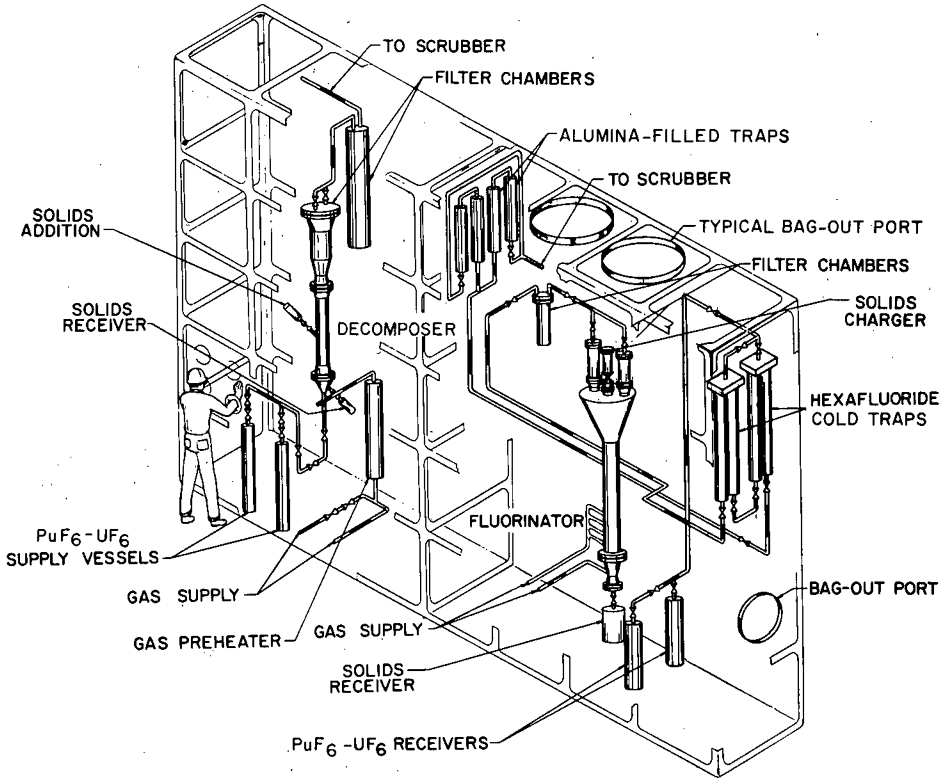


Fig. 5. Overall View of Process Equipment in Large Glovebox (Not to scale)

5.2 Fluorination Pilot-plant Equipment

The fluorination system includes gas supplies, a fluid-bed fluorinator with connected off-gas filters, a secondary off-gas filter, hexafluoride cold traps, a pump for circulating part or all of the fluorine-containing process off-gas, a gas-analysis system, chemical traps for removing fluorine and hexafluorides, and UF_6-PuF_6 product receivers. Most process components of the fluorination system are located in the large alpha box, the exceptions being the pump for recirculating fluorine and the control valves for the gas supplies. The fluorine pump head is enclosed in its

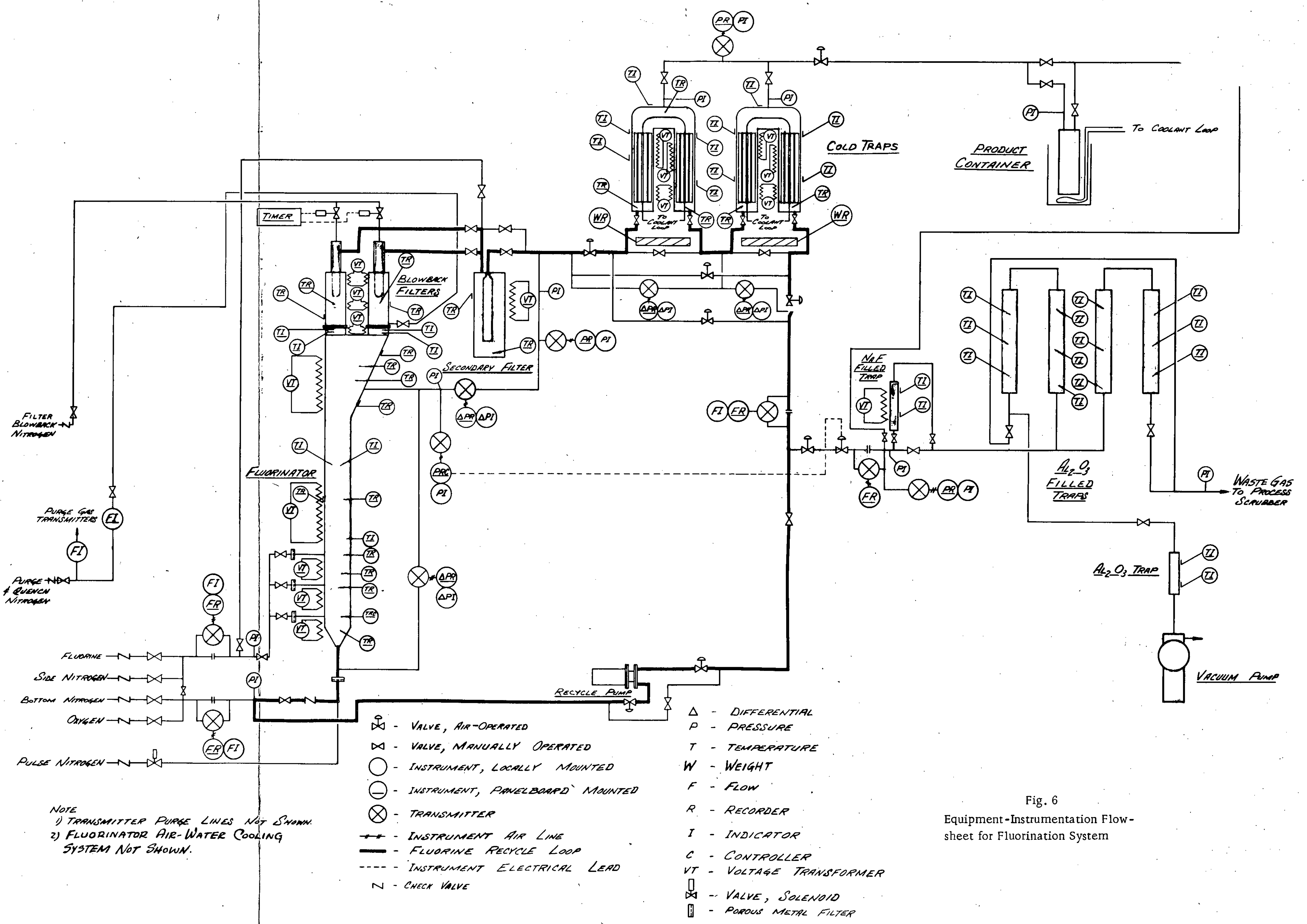
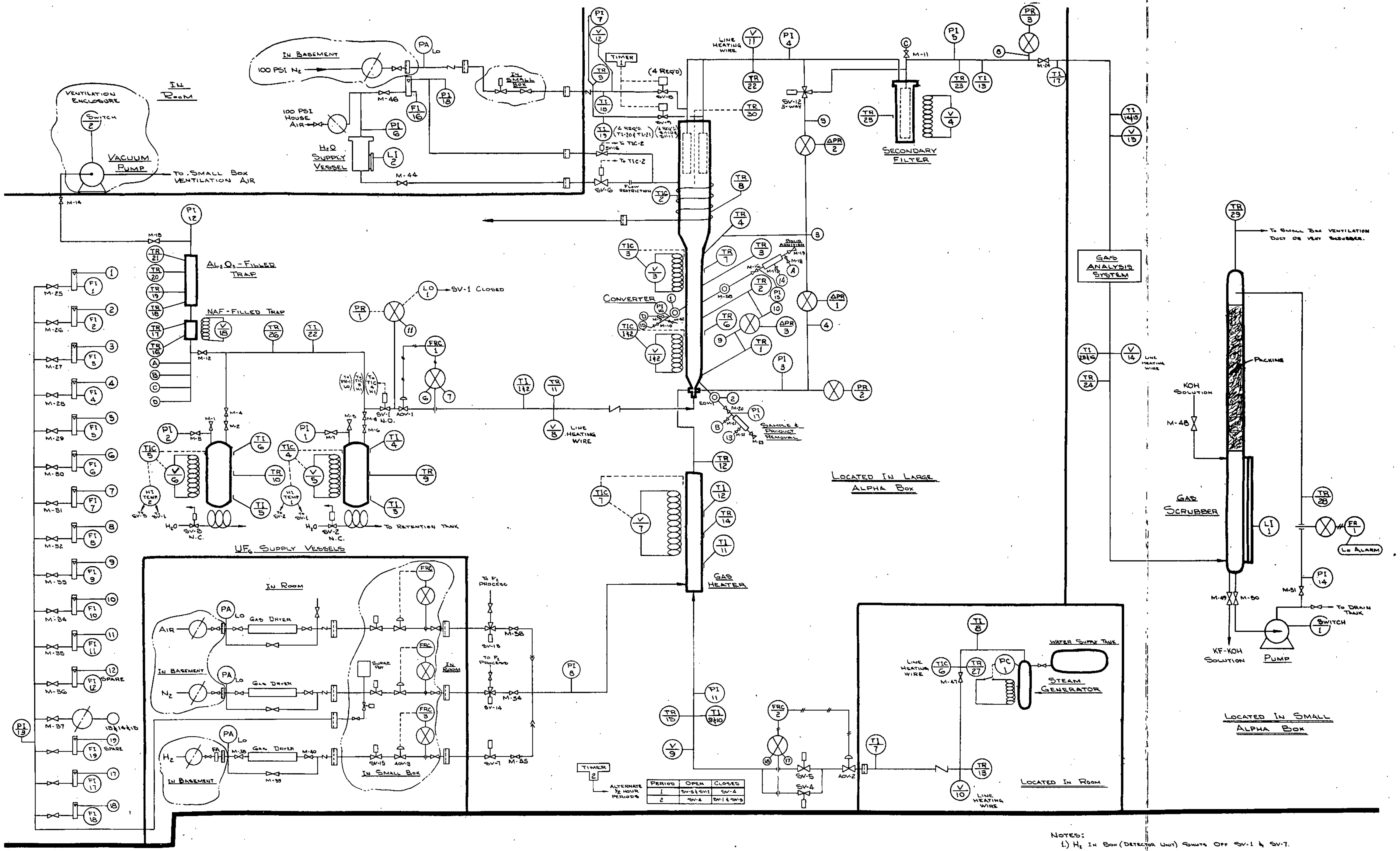


Fig. 6
Equipment-Instrumentation Flowsheet for Fluorination System



Notes:
1.) H_2 In Box (Detector Unit) Shuts Off SV-1 & SV-7.
2.) Emergency Button (Panelboard) Shuts Off SV-1 & SV-7.

Legend

○	Instrument, Local Mount
⊖	Instrument, Panelboard Mount
⊗	Transmitter, Local Mount
∅	Pressure Reducer Plus PI
⋈	Valve, Manual
⋈	Valve, Air-Operated
⋈	Valve, Solenoid
◎	Valve, Plug
▯	Flowmeter, Rotameter
⊣⊢	Flowmeter, Orifice
▯	Filter
N	Valve, Check
------	Signal Line, Electric
—+—+—	Signal Line, Pneumatic
ꝏꝏ	Heating Coil
ꝏ	Cooling Coil

T - Temperature
P - Pressure
L - Level
F - Flow
W - Weight
I - Indicator
R - Recorder
V - Variac
SV - Solenoid Valve
C - Controller
N.C. - Normally Closed
N.O. - Normally Open
M - Manual
A - Alarm
AOV - Air-Operated Valve
EOV - Electrically Operated Valve
FA - Flame Arrestor

Fig. 7

Equipment-Instrumentation Flowsheet for Decomposer System own small alpha enclosure, which is connected to the large alpha box via a welded duct. The control valves for the gas supplies are located in the small alpha box.

The fluorinator shown in Fig. 8 with its three sections--fluidizing, disengaging, and gas distributing--is of welded A-nickel construction, except for the disengaging section, which is L-nickel for added strength. The fluidization section of the fluorinator consists of a 4-ft section of 3-in. Schedule 40 pipe. The conical disengaging section, fabricated from 3/16-in. plate, is welded to the top of the fluidization section. The disengaging section is in the form of an inverted, oblique, truncated cone, 20 in. long and 14 in. in diameter at the top. All internal angles are greater than 60° from the horizontal in order to minimize powder holdup. The gas distributor, a baffled-cone unit, is connected to the flanged bottom of the fluidization section.

The fluorinator is provided with both heating and cooling systems. The heaters and the cooling coils are wrapped together on each reactor section. Heat is supplied from tubular, electric-resistance heaters wrapped on the separate reactor sections. To aid conductive heat transfer, the heating elements are bonded to the walls by copper applied by flame spraying; an overlay of stainless steel, similarly applied, protects the copper from oxidation. The lower 24 in. of the reaction zone is cooled using a two-phase mixture of air and water, which is passed through an external coil attached to the wall of the fluorinator. Air is passed continuously through the coil; water injection into the cooling coil at each of three locations in the coil is controlled by a temperature controller for each of three cooling zones. Internal reactor temperatures are measured by Chromel-Alumel thermocouples.

The filter chambers are mounted atop the disengaging section of the fluorinator unit. These chambers ($3\frac{1}{2}$-in.-dia, 40-in.-long Schedule 40 pipe) house sintered-Monel, bayonet-type filters, which retain dust entrained from the fluid bed by the fluorinator off-gas. The lower 18-in. portions of the filter chambers are wrapped with water-cooling coils and have internal fins to aid in cooling the off-gas to below 150°C, the desired filter operating temperature. The porous, sintered Monel filter elements are 9-in.-long bayonet type, and have a filtering area of 0.18 sq ft per element and a nominal porosity rating of 20 μ. The filter units operate in parallel. To prevent buildup of filter cake, each filter is equipped with an automatic blowback system, which supplies a pulse of 80-psig nitrogen gas intermittently. One filter is blown back at a time.

A secondary filter chamber (shown in Fig. 6), containing an 18-in.-long bayonet filter, is located downstream from the primary units to trap any entrained solids in the event of failure of the primary filter elements. The filter chamber is provided with electrical heaters.

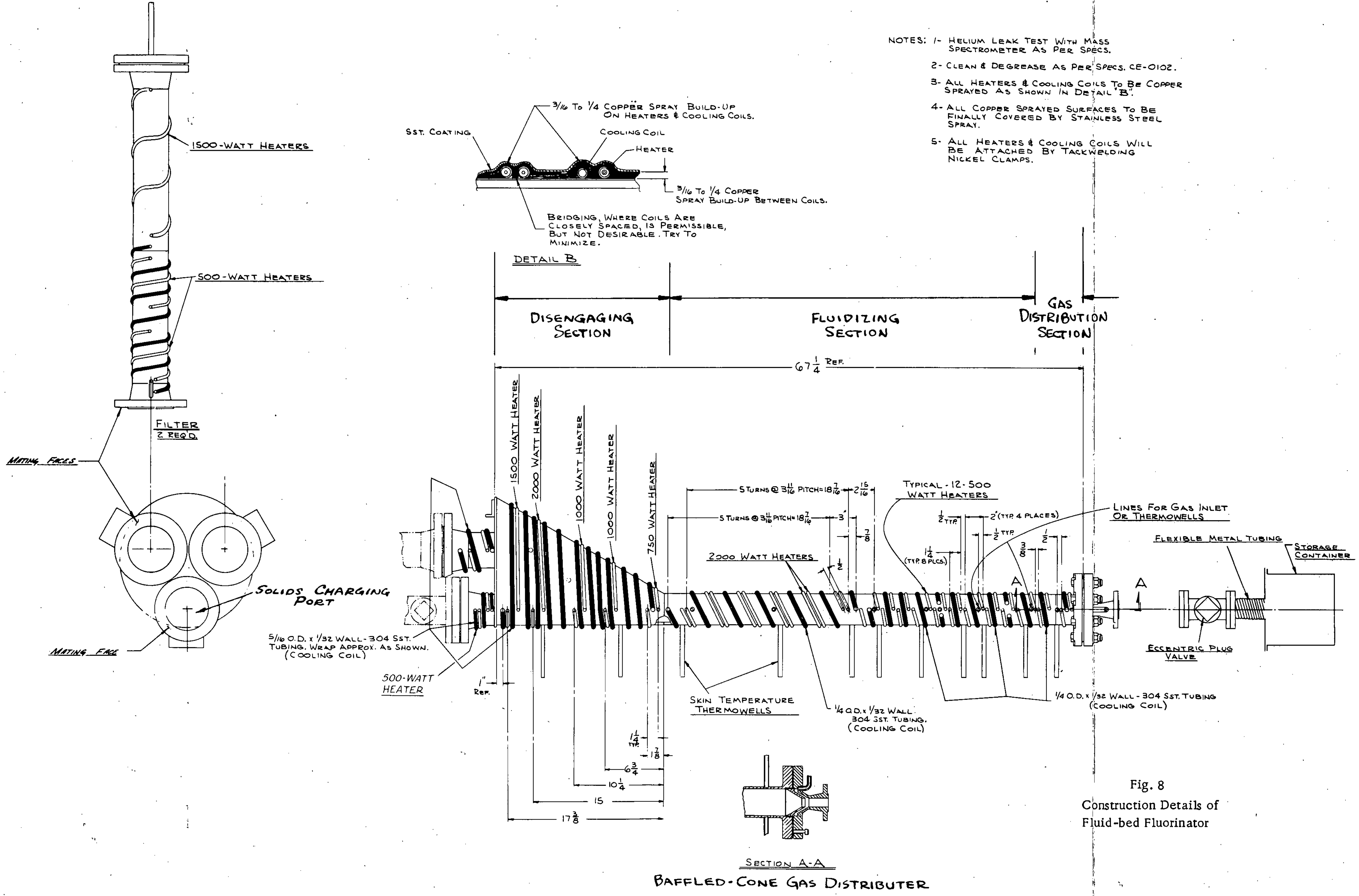

NOTES: 1- HELIUM LEAK TEST WITH MASS SPECTROMETER AS PER SPECS.
2- CLEAN & DEGREASE AS PER SPECS. CE-0102.
3- ALL HEATERS & COOLING COILS TO BE COPPER SPRAYED AS SHOWN IN DETAIL "B".
4- ALL COPPER SPRAYED SURFACES TO BE FINALLY COVERED BY STAINLESS STEEL SPRAY.
5- ALL HEATERS & COOLING COILS WILL BE ATTACHED BY TACKWELDING NICKEL CLAMPS.

Fig. 8
Construction Details of
Fluid-bed Fluorinator

Uranium and plutonium hexafluoride from the fluorinator off-gas are collected in two series-connected, U-shaped cold traps, made of nickel and Monel. In each leg of the cold traps, the coolant flows through a central tube to which longitudinal fins are welded. The solid hexafluoride products are collected on the fins. (The U shape eliminates the need for expansion joints.) The central coolant tubes are double-walled pipes, consisting of an outer 3/4-in.-dia pipe to which the fins are welded, and an inner tube ($1\frac{1}{16}$-in.-thick wall) swaged in place. The double wall reduces the possibility of contaminating the coolant if a leak should develop in the finned tube. The trichloroethylene heat-exchange liquid flowing through the central tubes is cooled by a 6000-Btu/hr mechanical refrigeration unit designed to maintain the coolant at -70°C. Hexafluorides can be transferred from the cold traps by vaporization by heating the heat-exchange trichloroethylene fluid to approximately 80°C and heating the outer walls with resistance heaters.

Each cold trap is weighed continuously, the weight being recorded remotely on a millivolt recorder at the panelboard. The weighing system consists of a platform-type beam scale coupled to an automatic chain-balancing system. Movement of the beam from the null balance point is detected by a photocell. The photocell circuit actuates a reversible electric motor, which moves a sprocketwheel and adds or subtracts chain to rebalance the beam. A 10-turn precision potentiometer turns with the sprocket wheel, providing a millivolt signal that is in direct proportion to the weight.

The off-gas from the cold traps can be recycled to the fluorination reactor by a remote-head diaphragm compressor. This recirculation pump has a rated capacity of 2.0 scfm at 15-psia inlet and 30-psia discharge pressure. The remote head contains a nickel diaphragm sealed between heavy nickel flanges, 18 in. in diameter. An alpha box encloses this remote head, and a 4-in. vent duct connects this enclosure to the large alpha box. Pneumatic control of the variable-speed electric motor of the pump unit allows variation of pumping flow by remote operation from the panelboard.

Sodium fluoride and activated-alumina chemical traps in the off-gas line downstream from the cold traps remove any hexafluorides and fluorine in the process off-gas before the gas is sent to the process scrubber. The traps, fabricated from 4-in.-dia brass tubing, are each 5 ft long. The bed of active material is supported by a perforated plate inside the trap, and nickel wool prevents solids from entering the connecting lines at either end. Thermocouples are mounted on the outside wall to indicate bed temperature. Consumption of the activated alumina is monitored by following the reaction zone with these thermocouples.

Analysis of fluorine in the process gas is based on the thermal conductivity of the gas that flows through the analyzer continuously at flows of 100 to 500 cc/min. The gas to be analyzed is removed from the process-gas stream either before or after the cold traps. The gas conductivity is measured before and after chlorine is substituted for the fluorine in the gas stream by reaction with sodium chloride:

$$2NaCl(s) + F_2(g) \rightarrow 2NaF(s) + Cl_2(g).$$

The analyzer is installed in the large alpha box; electrical controls and recorded outputs of the thermal conductivity cells are located at the panelboard. (A complete discussion of this gas analysis method is presented in Part 11 of this series of reports.)

Two types of process valves are used. The first is a manually operated, 1/4-in., Monel diaphragm valve, which is used for low gas flow-rate applications and where temperature or pressure requirements are not stringent. The second and major type of process valve is a 1/2-in. Monel bellows-seal type. This valve is either manually or air-operated and has either a metal-to-metal seat for 350°C service, or a Teflon-to-metal seat for lower-temperature service. The valve bonnet is bolted to the valve body and can be removed for cleaning and repairing the plug or seat. The valve bellows withstands a static load of 200 psi. When installed, the process shutoff valves had a leakage rate of less than 0.1 micron-cu ft/hr (1×10^{-6} standard cc/sec) across the seat.

5.3 Thermal-decomposer Pilot-plant Equipment

The decomposer process equipment (shown in Fig. 7) includes gas supply sources, a gas preheater, a fluid-bed reactor with integral filter section, a secondary filter, an off-gas analysis system, an exit-gas scrubber, and dry chemical traps. The reactor is fabricated of Inconel; other equipment and lines are of nickel and Monel.

The reactor is composed of three sections connected by flanges: a 60° cone bottom, a fluid-bed section, and a cooling and filtering section (disengaging section). The cone bottom (shown in Fig. 9) has an opening at the apex for the gas feed: The hexafluoride feed mixture enters through a 0.125-in.-ID nozzle extending $2\frac{1}{2}$ in. into the cone; the fluidizing nitrogen or steam and hydrogen reactants enter through the annulus around the hexafluoride nozzle. The side opening in the cone bottom is for product takeoff and sampling.

The fluid-bed section (shown in Fig. 10) is of 2-in. Schedule 40 pipe and 24 in. long. Three 1500-W and two 750-W alloy-sheathed tubular electric-resistance heaters (includes one spare of each size) are bonded to the outside wall with a coating of copper and an overlay of stainless steel. Thermocouples are inserted through side inlets, which also serve as pressure taps. One side inlet is available for adding seed particles to the fluid

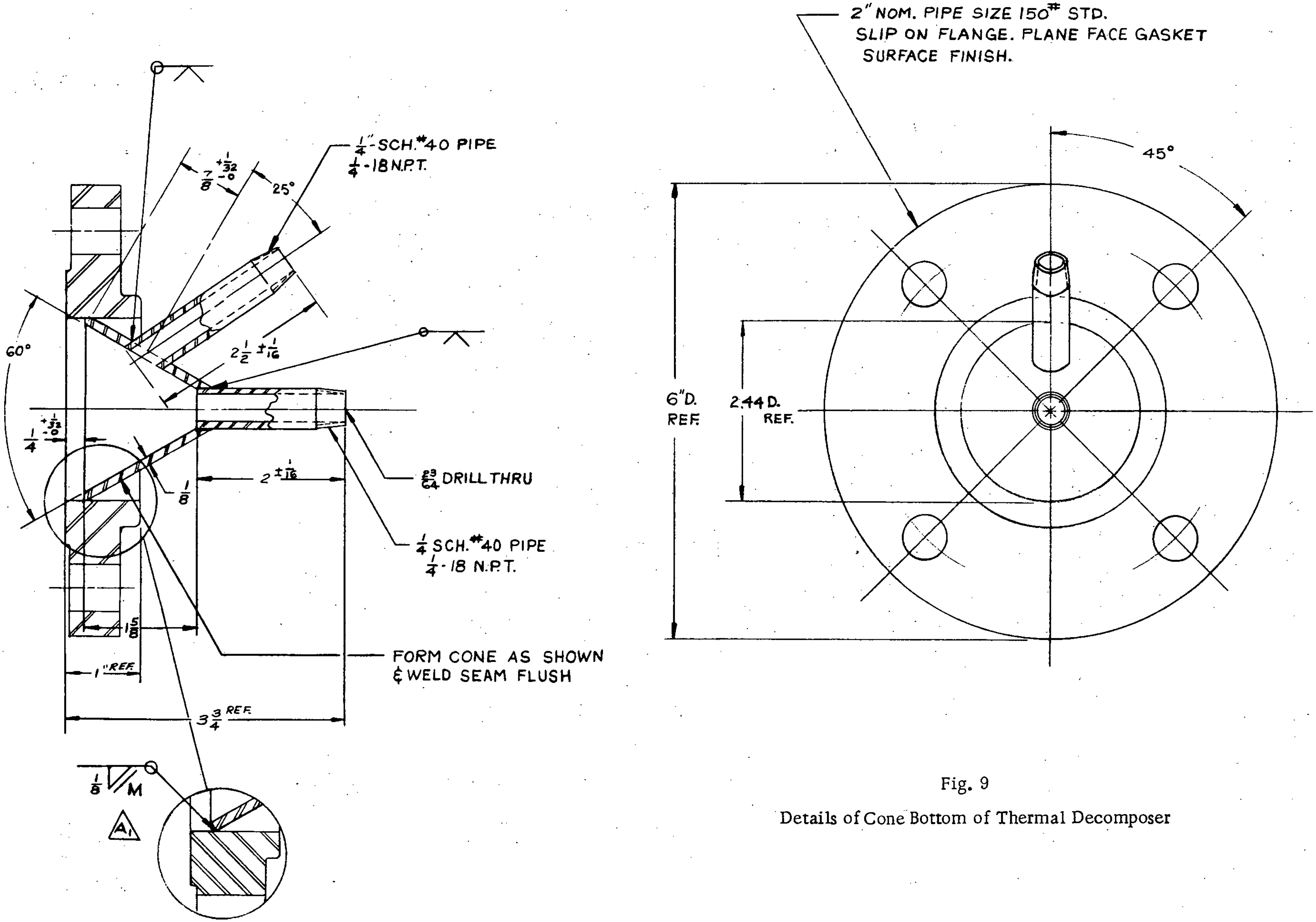


Fig. 9

Details of Cone Bottom of Thermal Decomposer

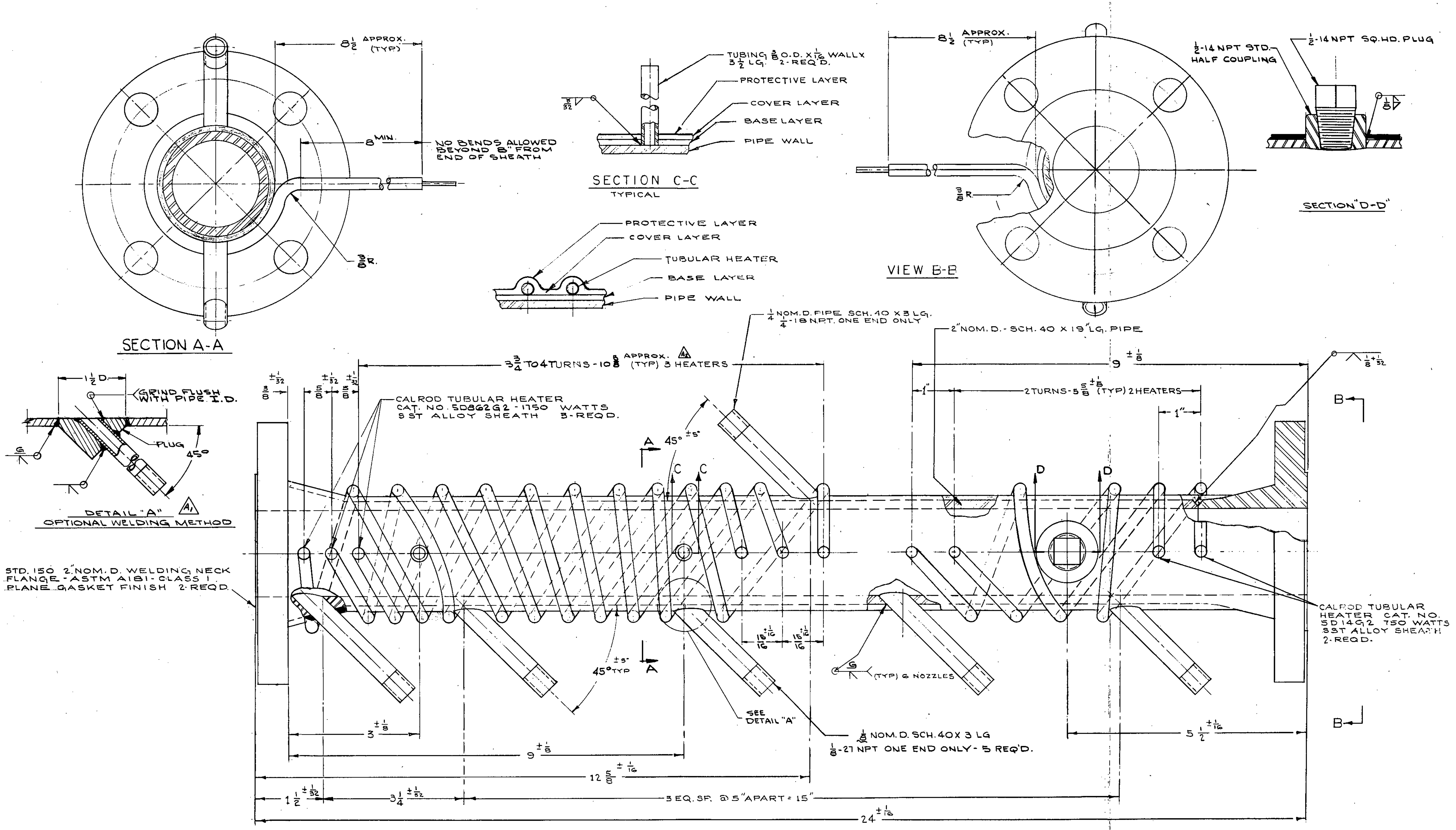


Fig. 10. Details of Fluid-bed Section of Thermal Decomposer

bed. Other openings include a solids-overflow pipe and a port, normally plugged, through which a Borescope* can be inserted for examining the interior of the reactor. Two thermowells are located on the lower half of the wall of the fluid-bed section for measuring skin temperatures.

The cooling and filtering section (shown in Fig. 11) of the reactor has a 26-in. length and a 4.03-in. ID. The lower half of the cooling and filtering section is wrapped with cooling coils, which are bonded the same way that the coils are bonded to the main reaction section. A two-phase air-water mixture is the coolant. At the middle of this section, a port is provided for viewing the interior of the reactor. The cover flange is provided with a central opening for a thermowell and four couplings for the four bayonet filters, $1\frac{3}{4}$ in. wide by 12 in. long, of porous nickel (mean pore size, 10 μ). A filter blowback device (jet pump), using high-pressure nitrogen, is provided for each filter.

The secondary (backup) filter vessel, 21 in. long with a 3.55-in. ID, is wrapped with a 1500-W tubular heater. In this vessel is a single cylindrical filter, 18 in. long and $2\frac{3}{4}$ in. in diameter as a backup to the primary filters and fabricated of a similar grade of porous nickel.

The UF_6-PuF_6 mixture is fed from 4-in.-dia, 31-in.-long cylindrical vessels, each heated by two 200-W band heaters. Cooling coils are provided for emergency cooling. Air, nitrogen, and hydrogen are supplied from high-pressure cylinders and pass through driers. Steam is supplied by a constant-pressure, electrically heated steam generator. All gas flowrates are metered and automatically controlled by orifice-differential pressure systems. The gases entering the decomposer (nitrogen, steam, hydrogen, or oxygen) are preheated in a 33-in.-long, $1\frac{1}{2}$-in.-dia pipe section packed with 1/2-in.-dia nickel Raschig rings; heat is supplied by automatically controlled clamshell heaters.

The off-gas from the secondary filter vessel passes to a scrub tower. The scrubber is a countercurrent, packed tower constructed of 4-in.-dia pipe of Monel alloy 400 in which caustic is circulated. The packed section, containing 1/2-in.-dia Monel Raschig rings, is 3 ft long and is finned on its outer surface for heat dissipation. Caustic solution is pumped from the hold tank and sprayed onto the top of the packing; the off-gas enters the bottom of the tower and passes through the packed section to a liquid deentrainment vessel and then is discharged into the ventilation-air treatment system.

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*Product of the American Cystoscope Makers, Inc., New York.

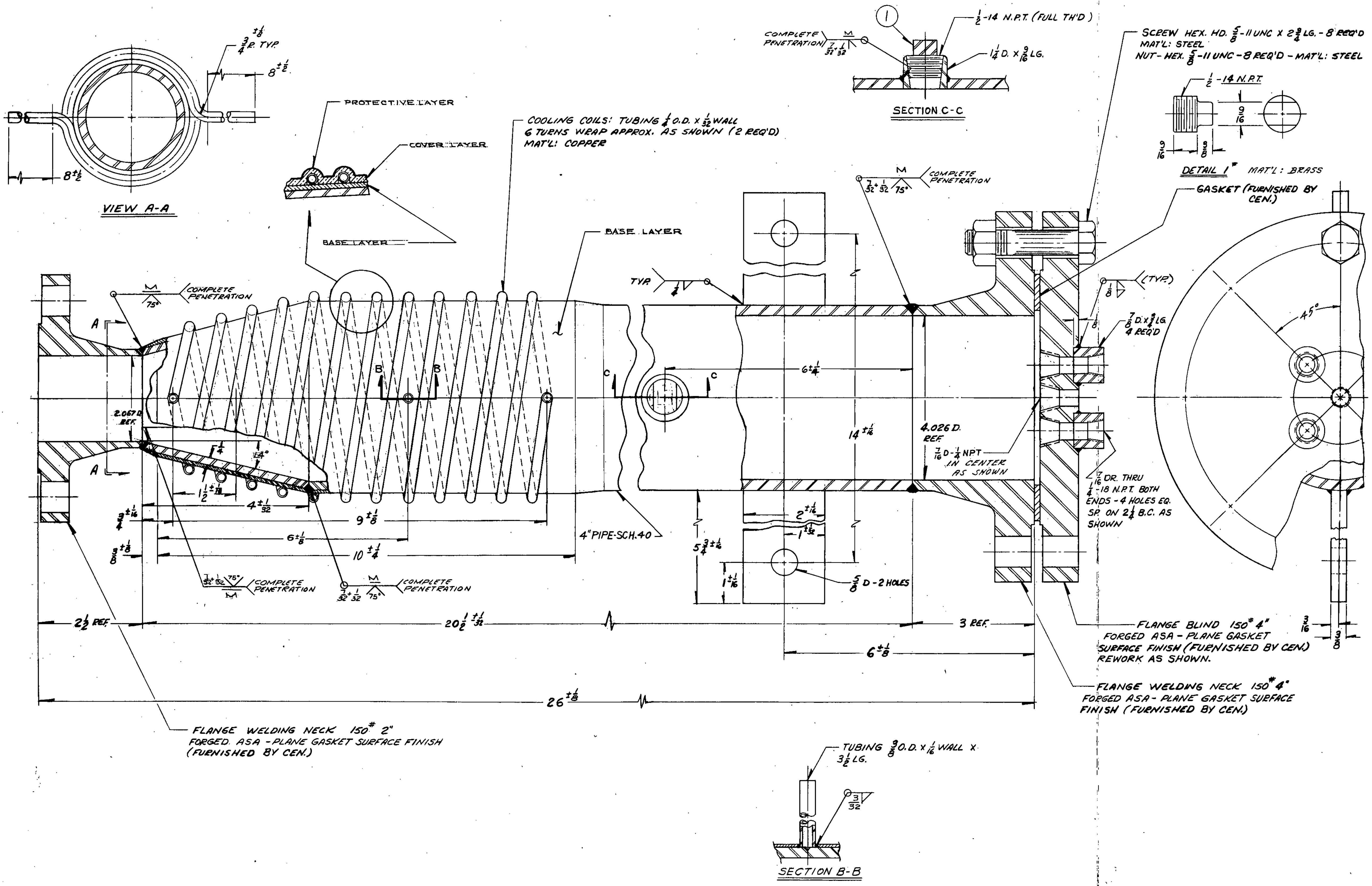

Fig. 11. Details of Disengaging Section of Thermal Decomposer

5.4 Data-handling Equipment

The data-handling equipment includes a Minneapolis Honeywell data logger with its associated Flexowriter typewriter* and paper tape punch unit. Data on the paper tape are transferred to magnetic tape on a Control Data Corporation (CDC) 160A, and the information on the magnetic tape is processed on the CDC 3600. All plotting of information is on a Calcomp 580 plotter.** Figure 12 is a schematic diagram of the data-handling system.

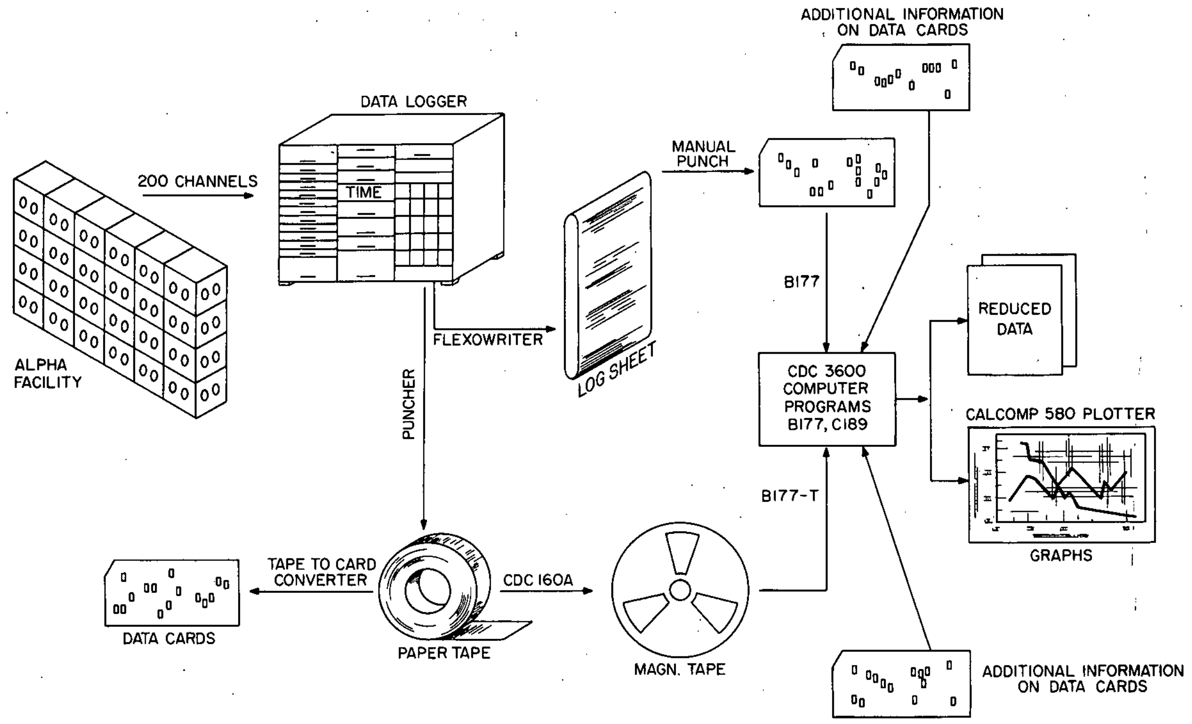

Fig. 12. Handling of Data from the Logger

The data logger, a relatively old (1958) unit, can accept 175 Chromel-Alumel (0-1000°C) thermocouple signals, 19 (3-15 psig) pneumatic signals, and 6 (0-20 mV) electrical signals. The thermocouple channels are compensated to give a linear temperature output. Pneumatic signals are transduced to millivolt signals by pressure-to-current, force balance units.

Two modes of logger operation are possible--(1) a scanning of all data points to find those outside a preselected range and a logging of these points, or (2) a logging of all points. The former has not been used here and will not be discussed further. The logging cycle consists of digitizing

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* A product of the Commercial Controls Corporation, Rochester, New York.

** A product of California Computer Products, Inc., Anaheim, California.

each variable at a rate of about one second per point and printing the data on a roller-type log sheet with a time signal recorded every 50 points. The logging cycle can be initiated either manually or automatically by a time-clock relay. A 5-min interval between logging cycles has been used generally. Figure 13 shows a part of a typical log sheet (the right side has been cut off).

A computer program for calculating results was written, and a typical output data sheet showing the input and computed values is shown in Table 1. A graph of any calculated data can be obtained; Fig. 14 shows typical plots.

Any variable that is logged can be selected for plotting as a function of time using another computer program. Figure 15 is a typical plot of temperatures in the fluorinator filter zone.

6. MATERIALS OTHER THAN PLUTONIUM-CONTAINING MATERIALS

Properties of plutonium-uranium-containing materials--UO_2-PuO_2-F.P. pellets, PuF_4, and BrF_5 bed residues--are discussed separately in other sections. Properties of other process materials are discussed below.

Six-pound cylinders of fluorine gas were obtained from Allied Chemical Company, Industrial Chemicals Division. From chemical analyses supplied by them, the gas, considered typical of December 1966 production, contained 98.81% fluorine, 0.43% HF plus CF_4, and 0.76% oxygen plus nitrogen. Any residual HF was sorbed on NaF, in a trap installed in the fluorine supply line.

Nitrogen and oxygen were obtained from Argonne National Laboratory supplies of 2000-psig cylinders containing 200 scf. Minimum guaranteed compositions were 99.9% nitrogen and 99.5% oxygen.

The dense alumina grain for the fluid bed was Alumina Company of America Tabular 61, nominal 48-100 mesh. Sieve data are given in Table 2. The alumina, prepared by heating it to 3700°F (the fusion point of Al_2O_3), is composed of tablet-like crystals. This material is distinctly different from the fused alumina, which is prepared by heating to 4000°F. According to the Alcoa specification sheet, the alumina after discharge from the converter contains 99.5% Al_2O_3, 0.06% SiO_2, 0.06% Fe_2O_3, and 0.02% Na_2O and has a bulk density of 125 lb/cu ft, a hardness of 9 on the Moh scale, and a porosity* of 13%.

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*Porosity represents a measurement of the pore volume as determined by water absorption.

Time	Calibration	1	2	3										← Channel Numbers →											24	25	26	27
1926	0496	0075	0193	0084	0092	0142	0078	0041	0327	0055	0039	0046	0051	0032	0029	0630	0690	0048	0635	0029	0030	0632	0058	0679	0688	0024	0314	0313
1936	0496	0075	0197	0085	0091	0143	0078	0041	0342	0054	0039	0045	0052	0030	0030	0618	0677	0048	0651	0029	0030	0631	0059	0619	0676	0024	0313	0312
1946	0497	0075	0198	0086	0090	0144	0078	0040	0334	0054	0040	0046	0051	0031	0030	0673	0675	0048	0618	0029	0029	0638	0058	0644	0677	0024	0313	0313
1956	0497	0074	0200	0086	0089	0145	0078	0040	0354	0055	0040	0046	0051	0031	0030	0636	0686	0048	0621	0030	0029	0633	0059	0618	0677	0024	0313	0312
2006	0497	0073	0202	0086	0089	0146	0078	0041	0332	0054	0038	0045	0051	0030	0030	0630	0663	0048	0635	0029	0029	0649	0058	0673	0686	0024	0313	0312
2016	0498	0074	0203	0086	0088	0146	0078	0042	0339	0054	0040	0046	0051	0030	0030	0616	0674	0047	0656	0030	0030	0620	0058	0635	0690	0024	0313	0312
2026	0497	0073	0204	0087	0087	0148	0078	0040	0344	0054	0039	0045	0050	0031	0029	0636	0661	0047	0646	0029	0029	0630	0058	0668	0681	0025	0312	0312
2037	0497	0073	0208	0087	0086	0149	0078	0041	0334	0054	0039	0045	0050	0030	0030	0619	0688	0047	0623	0030	0029	0666	0058	0623	0693	0024	0313	0312
2047	0497	0072	0207	0087	0086	0149	0078	0041	0348	0054	0039	0045	0050	0030	0030	0676	0688	0048	0619	0030	0030	0667	0058	0657	0694	0024	0313	0311
2057	0494	0072	0210	0087	0085	0151	0078	0040	0322	0054	0039	0045	0051	0031	0030	0676	0693	0048	0637	0030	0030	0642	0058	0622	0691	0025	0312	0311
2107	0497	0071	0212	0087	0084	0152	0078	0040	0327	0054	0039	0045	0050	0032	0030	0646	0687	0047	0647	0029	0029	0638	0058	0676	0683	0025	0313	0311
2117	0497	0071	0212	0088	0084	0153	0078	0040	0326	0054	0038	0045	0050	0030	0030	0613	0687	0047	0650	0029	0029	0633	0058	0635	0675	0024	0312	0311
2127	0497	0070	0212	0088	0084	0153	0078	0041	0328	0054	0039	0045	0050	0031	0030	0630	0685	0048	0635	0030	0030	0620	0058	0653	0698	0025	0312	0311
2137	0497	0070	0214	0089	0083	0154	0078	0040	0326	0054	0038	0044	0050	0030	0030	0623	0694	0048	0677	0029	0030	0675	0058	0635	0651	0024	0312	0311
2147	0496	0070	0226	0089	0082	0161	0079	0041	0340	0054	0038	0045	0049	0031	0030	0677	0694	0048	0655	0029	0030	0618	0059	0671	0678	0024	0312	0311
2157	0497	0070	0235	0091	0083	0169	0079	0040	0329	0054	0039	0045	0050	0031	0030	0628	0693	0047	0638	0030	0030	0635	0059	0640	0681	0024	0311	0311
2207X	0496	0070	0237	0093	0083	0173	0080	0041	0306	0054	0038	0045	0050	0030	0030	0625	0650	0047	0638	0030	0030	0618	0059	0669	0685	0024	0312	0311

		51	52												← Channel Numbers →										74	75	76	77
1927	0496	0665	0671	0656	0671	0653	0657	0661	0672	0656	0670	0672	0667	0663	0652	0660	0660	0670	0666	0663	0662	0672	0667	0675	0652	0024	0089	0502
1937	0497	0663	0665	0653	0653	0656	0674	0670	0674	0664	0656	0672	0656	0669	0654	0657	0652	0658	0655	0644	0675	0660	0657	0657	0654	0024	0084	0502
1947	0494	0661	0658	0645	0656	0655	0656	0651	0656	0653	0657	0654	0673	0658	0665	0651	0664	0675	0653	0661	0657	0664	0667	0667	0670	0025	0092	0502
1957	0494	0663	0663	0657	0660	0670	0659	0670	0654	0663	0669	0665	0660	0658	0652	0669	0669	0654	0665	0650	0658	0651	0665	0667	0668	0024	0091	0502
2007	0495	0668	0667	0668	0656	0659	0661	0655	0657	0656	0668	0657	0665	0656	0656	0662	0652	0660	0663	0647	0650	0646	0671	0658	0653	0024	0085	0502
2017	0497	0665	0663	0665	0663	0677	0656	0664	0657	0654	0647	0650	0671	0655	0656	0649	0660	0657	0654	0668	0655	0653	0663	0665	0648	0024	0087	0502
2028	0497	0660	0660	0653	0668	0657	0656	0654	0656	0654	0657	0655	0656	0672	0658	0650	0658	0666	0657	0665	0668	0670	0672	0673	0658	0024	0090	0502
2038	0497	0660	0670	0671	0667	0656	0667	0654	0663	0648	0663	0667	0652	0658	0670	0656	0664	0671	0655	0641	0662	0673	0657	0651	0669	0024	0083	0502
2048	0497	0663	0663	0653	0662	0653	0664	0651	0665	0667	0663	0653	0652	0660	0654	0655	0654	0660	0655	0669	0661	0656	0666	0655	0670	0024	0084	0502
2058	0497	0661	0673	0662	0667	0667	0659	0668	0655	0652	0673	0658	0654	0672	0654	0660	0658	0668	0666	0663	0663	0657	0656	0667	0664	0024	0089	0502

Fig. 13. Portion of a Log Sheet

TABLE 1. Computer Output Data Sheet for Pilot-plant Fluorinator

TIME	TEMPERATURE LOWER (C)	TEMPERATURE UPPER (C)	PRES PSIG	INPUT FLOW RATES (SCFM) F2	INPUT FLOW RATES (SCFM) O2	CUM. F2 (SCF)	F2 IN OFF GAS (0/0)	VELOCITY (FT/SEC) UPPER	VELOCITY (FT/SEC) LOWER	PERCENT UTILIZATION O2	PERCENT UTILIZATION F2	RATE OF UF6 VOL. SCFH	RATE OF UF6 WT. LB/HR	CUM. UF6 (GM)	UF6 LB/HR/ SQ.FT.	PERCENT TOTAL UF6
0	420	440	6.1	0.000	0.000	0.0	0.0	1.108	0.786	0.0	0.0	0.000	0.000	0.0	0.0	0.0
10	420	440	6.1	0.153	0.388	1.5	7.6	1.108	0.786	0.4	9.1	0.278	0.272	20.6	5.3	0.2
20	420	440	6.1	0.172	0.391	3.2	8.9	1.108	0.786	0.2	4.2	0.145	0.142	31.3	2.8	0.3
30	465	435	4.6	0.208	0.384	5.3	6.4	1.178	0.898	2.7	44.9	1.867	1.830	169.8	35.7	1.5
40	465	435	4.6	0.096	0.037	6.3	0.5	1.179	0.898	26.1	90.0	1.722	1.689	297.6	32.9	2.7
50	465	435	4.6	0.216	0.000	8.4	4.1	1.174	0.898	0.0	66.6	2.878	2.822	511.2	55.0	4.6
100	465	420	4.6	0.194	0.000	10.4	12.7	0.834	0.606	0.0	14.3	0.556	0.545	552.4	10.6	4.9
110	465	420	4.6	0.068	0.071	11.1	-0.9	0.831	0.606	12.4	117.2	1.589	1.558	670.3	30.4	6.0
120	465	420	4.6	0.178	0.000	12.9	9.8	0.833	0.606	0.0	29.0	1.033	1.013	746.9	19.8	6.7
130	410	442	5.8	0.115	0.054	14.0	4.6	0.999	0.664	8.3	35.3	0.811	0.795	807.1	15.5	7.2
140	410	442	5.8	0.209	0.225	16.1	10.8	1.000	0.664	1.7	16.2	0.678	0.665	857.4	13.0	7.7
150	410	442	5.8	0.218	0.107	18.3	2.9	0.990	0.664	18.0	80.0	3.489	3.421	1116.3	66.7	10.0
200	405	440	4.1	0.230	0.065	20.6	-0.4	1.144	0.743	40.5	102.6	4.711	4.620	1465.8	90.1	13.1
210	405	440	4.1	0.234	0.000	22.9	0.0	1.144	0.743	0.0	99.9	4.678	4.587	1812.9	89.4	16.2
220	405	440	4.1	0.290	0.000	25.8	-2.0	1.137	0.743	0.0	110.8	6.434	6.308	2290.3	123.0	20.5
230	390	465	6.8	0.328	0.000	29.1	-6.3	1.017	0.645	0.0	128.0	8.412	8.248	2914.3	160.8	26.0
240	390	465	6.8	0.309	0.104	32.2	0.5	1.025	0.645	32.0	97.3	6.012	5.894	3360.3	114.9	30.0
250	390	465	6.8	0.181	0.104	34.0	3.7	1.037	0.645	12.7	65.8	2.389	2.343	3537.6	45.7	31.6
300	400	440	6.4	0.042	0.104	34.4	-0.3	1.032	0.748	5.1	114.1	0.956	0.937	3608.5	18.3	32.2
310	400	440	6.4	0.053	0.107	35.0	2.3	1.034	0.748	1.4	26.1	0.278	0.272	3629.1	5.3	32.4
320	400	440	6.4	0.196	0.107	36.9	9.1	1.032	0.748	4.0	19.6	0.767	0.752	3686.0	14.7	32.9
330	460	457	6.7	0.251	0.107	39.4	12.1	1.160	0.809	1.8	7.1	0.356	0.349	3712.4	6.8	33.2
340	460	457	6.7	0.250	0.107	41.9	9.7	1.157	0.809	6.8	26.5	1.322	1.297	3810.5	25.3	34.1
350	460	457	6.7	0.241	0.107	44.3	3.6	1.150	0.809	18.0	72.5	3.489	3.421	4069.4	66.7	36.4
400	445	445	7.2	0.242	0.107	46.7	2.0	1.090	0.776	21.4	85.5	4.145	4.064	4376.9	79.2	39.1
410	445	445	7.2	0.210	0.107	48.8	0.2	1.090	0.776	21.4	98.6	4.134	4.053	4683.5	79.0	41.9
420	445	445	7.2	0.234	0.107	51.2	2.5	1.092	0.776	19.6	81.2	3.800	3.726	4965.5	72.6	44.4
430	460	460	7.6	0.304	0.283	54.2	0.3	1.077	0.749	11.8	98.4	5.978	5.862	5409.0	114.3	48.3
440	460	460	7.6	0.330	0.054	57.5	-2.5	1.073	0.749	76.0	112.4	7.423	7.278	5959.7	141.9	53.3
450	460	460	7.6	0.321	0.051	60.7	1.7	1.078	0.749	63.9	90.8	5.834	5.720	6392.5	111.5	57.1
500	442	450	7.9	0.325	0.047	64.0	-3.4	1.037	0.714	89.5	117.2	7.612	7.463	6957.3	145.5	62.2
510	442	450	7.9	0.237	0.256	66.4	-2.7	1.043	0.714	12.3	119.5	5.667	5.557	7377.7	108.3	65.9
520	442	450	7.9	0.057	0.365	66.9	-1.8	1.055	0.714	2.8	159.3	1.822	1.787	7512.9	34.8	67.1
530	440	435	8.0	0.018	0.356	67.1	-1.8	1.028	0.827	1.6	286.8	1.033	1.013	7589.6	19.8	67.8
540	440	435	8.0	0.017	0.355	67.3	-2.7	1.027	0.827	2.1	406.4	1.345	1.318	7689.3	25.7	68.7
550	440	435	8.0	0.011	0.356	67.4	-1.1	1.029	0.827	1.0	298.8	0.633	0.621	7736.3	12.1	69.1
600	445	435	8.1	0.010	0.354	67.5	-0.8	1.419	1.245	1.0	298.5	0.611	0.599	7781.7	11.7	69.5
610	445	435	8.1	0.010	0.355	67.6	-1.0	1.419	1.245	1.1	352.8	0.722	0.708	7835.3	13.8	70.0
620	445	435	8.1	0.198	0.351	69.6	0.3	1.410	1.245	6.0	95.8	3.789	3.715	8116.4	72.4	72.5
630	450	440	8.8	0.156	0.350	71.1	1.5	1.013	0.791	4.1	82.6	2.578	2.528	8307.7	49.3	74.2
640	450	440	8.8	0.144	0.354	72.6	0.0	1.012	0.791	4.5	99.8	2.878	2.822	8521.2	55.0	76.2
650	450	440	8.8	0.171	0.351	74.3	-2.8	1.008	0.791	7.0	128.7	4.400	4.315	8847.7	84.1	79.1
700	447	438	9.1	0.111	0.349	75.4	2.9	0.999	0.776	1.8	50.1	1.111	1.090	8930.1	21.2	79.8
710	447	438	9.1	0.113	0.349	76.5	1.8	0.998	0.776	2.5	70.4	1.589	1.558	9048.0	30.4	80.9
720	447	438	9.1	0.075	0.349	77.3	2.0	1.000	0.776	1.1	48.2	0.722	0.708	9101.6	13.8	81.3
730	435	440	9.0	0.091	0.350	78.2	-1.3	0.989	0.764	3.6	126.1	2.300	2.255	9272.2	44.0	82.9
740	435	440	9.0	0.082	0.349	79.0	3.9	0.996	0.764	0.2	9.5	0.156	0.153	9283.8	3.0	83.0
750	435	440	9.0	0.108	0.348	80.1	-1.9	0.988	0.764	4.5	131.1	2.822	2.767	9493.2	53.9	84.8
800	440	440	9.1	0.168	0.348	81.8	1.6	1.077	0.860	4.3	81.0	2.722	2.669	9695.2	52.0	86.6
810	440	440	9.1	0.178	0.351	83.5	6.6	1.082	0.860	1.4	24.3	0.867	0.850	9759.5	16.6	87.2
820	440	440	9.1	0.204	0.000	85.6	6.9	1.081	0.860	0.0	32.1	1.311	1.286	9856.7	25.1	88.1
830	447	442	2.1	0.226	0.000	87.8	-6.8	0.785	0.814	0.0	126.9	5.723	5.611	10281.3	109.4	91.9
840	447	442	2.1	0.294	0.000	90.8	-8.8	0.778	0.814	0.0	125.1	7.367	7.224	10827.9	140.8	96.8
850	447	442	2.1	0.300	0.000	93.8	23.5	0.804	0.814	0.0	17.8	1.067	1.046	10907.0	20.4	97.5
900	440	440	1.8	0.262	0.000	96.4	26.0	0.710	0.712	0.0	8.1	0.422	0.414	10938.4	8.1	97.8
910	440	440	1.8	0.258	0.000	99.0	27.2	0.711	0.712	0.0	1.1	0.056	0.055	10942.5	1.1	97.8
920	440	440	1.8	0.152	0.000	100.5	16.0	0.711	0.712	0.0	1.1	0.033	0.033	10945.0	0.6	97.8
930	456	456	1.7	0.137	0.000	101.9	16.1	0.654	0.654	0.0	1.2	0.033	0.033	10947.5	0.6	97.8
940	456	456	1.7	0.139	0.000	103.3	16.3	0.654	0.654	0.0	1.2	0.033	0.033	10949.9	0.6	97.9
950	456	456	1.7	0.139	0.000	104.6	16.3	0.654	0.654	0.0	1.2	0.033	0.033	10952.4	0.6	97.9

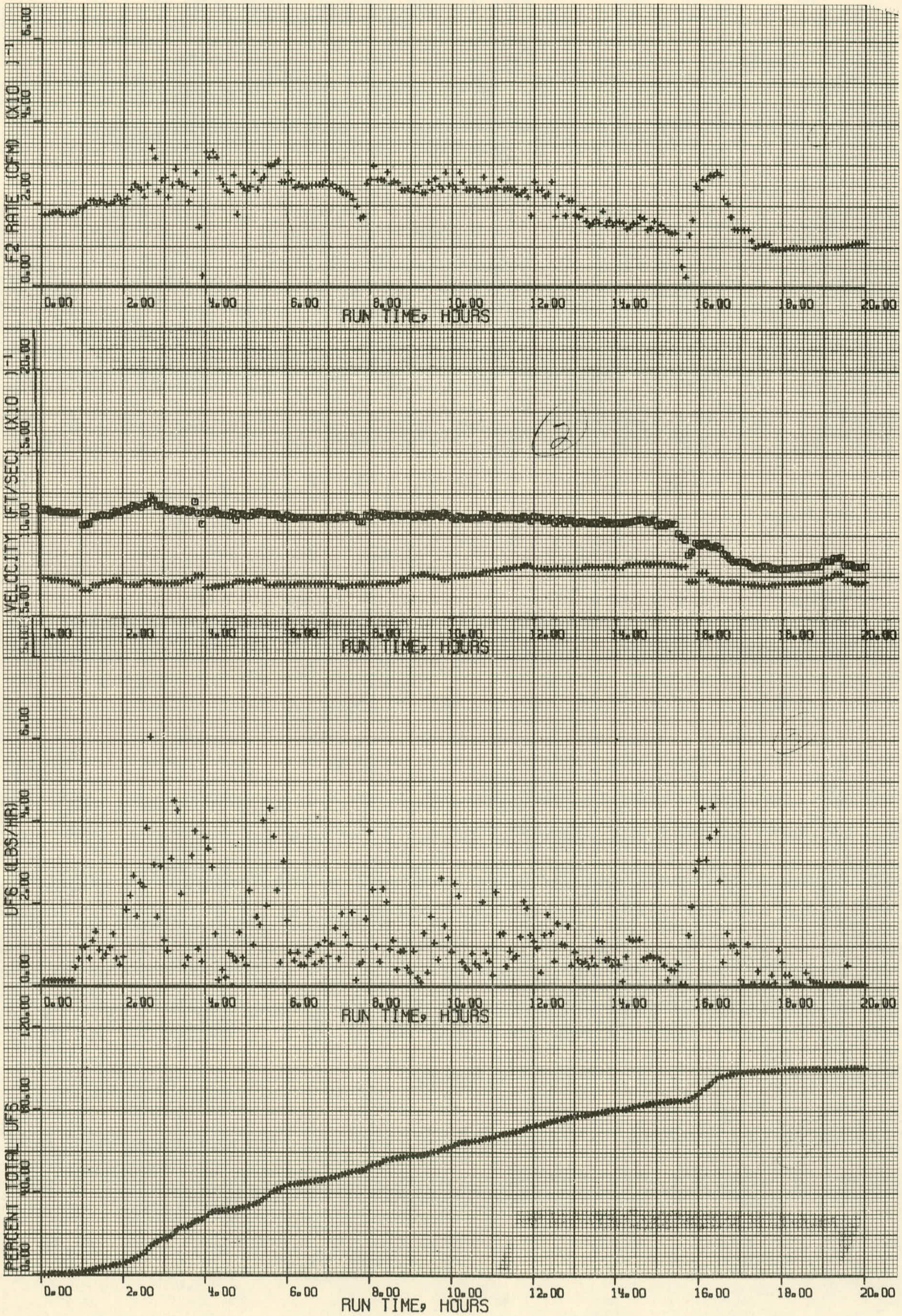


Fig. 14. Graphical Output from Automatic Data Plotter for Pilot-plant Fluorinator

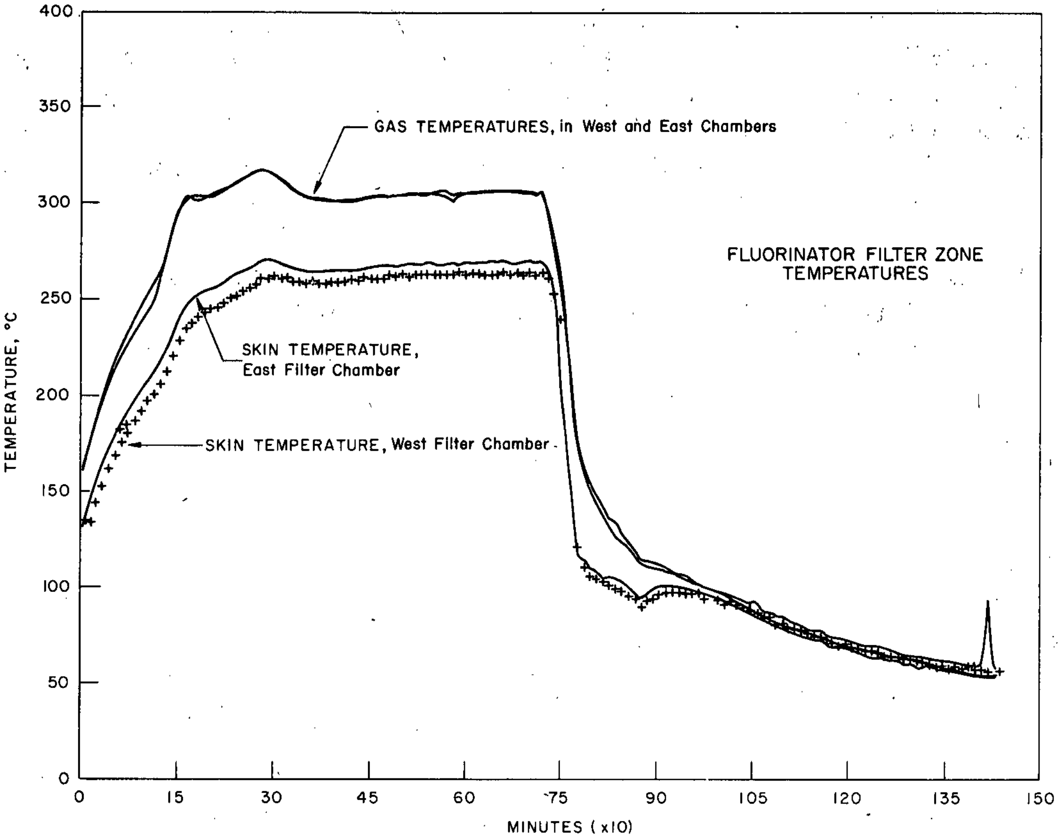


Fig. 15. Typical Computer Plot of Selected Logged Data

TABLE 2. Sieve Analysis[a] of Alcoa Tabular T-61, Nominal 48-100 Mesh Alumina

USS Sieve	wt %	USS Sieve	wt %
+45	0.1	-120 +170	4.4
-45 +60	7.3	-170 +230	0.5
-60 +80	57.1	-230 +325	0.4
-80 +120	30.0	-325	0.2

[a] Sample sieved by placing screens on shaking tray for 15 min.

Alcoa F-1 grade, 8-14 mesh, activated Al_2O_3, which has surface areas greater than 200 m^2/g and a bulk density of about 52 lb/cu ft, is the reactant or sorbent for fluorine and fluorides in the process gas leaving the pilot-plant fluorination equipment. The Alcoa specification sheet states that the activated alumina typically contains 92% Al_2O_3, 0.90% Na_2O, 0.08% Fe_2O_3, and 0.09% SiO_2. Loss on ignition at 1100°C is 6.5%. The material is prepared by thermal treatment of rock-like granules of hydrated alumina and is used to sorb gases and vapors.

NaF pellets (1/8 in. in diameter by 1/8 in. high), prepared by desorbing HF from pellets of NaF·HF (a process that produces a high-porosity pellet), were used as sorbents for uranium hexafluoride and plutonium hexafluoride. Batches of as-received NaF pellets from Harshaw Chemical Company contained 0.02% to 1.7% residual HF. Pellets desorbed by us contained 0.05% HF.

Cesium fluoride used in the PuF_4 fluorination experiments was obtained from City Chemical Company as a fine powder, 99.9% pure.

7. PLUTONIUM FLUORINATION RUNS

7.1 Two-zone Oxidation-Fluorination Experiments

7.1.1 UO_2-PuO_2-F.P. Pellets

Numec Corporation prepared the 1/2- by 1/2-in. right cylinders of UO_2-PuO_2-F.P. oxide pellets. The concentration specified for PuO_2 in these pellets was 0.49 wt % and for the F.P. oxides as shown in Table 3. Concentrations are typical of those for a fuel kept in a Dresden-type reactor for 4 yr (10,000-MWd/ton burnup) and then cooled for 30 days. In the preparation of the pellets, plutonium metal was oxidized and this powder was mechanically blended with other oxide powders. This mixture was pressed into pellets, which were sintered in 6 vol % hydrogen in nitrogen for 8 hr at 1600°C. The production contract specified that the finished pellets should have O/U and O/Pu ratios between 1.90 and 2.08, and that the minimum pellet density should be greater than 10.2 g/cc, or about 93% of theoretical.

TABLE 3. Concentration of F.P. Oxides Added by Pellet Fabricator

F.P. Oxide	Concentration, wt %	F.P. Oxide	Concentration, wt %
SrO	0.0510	La_2O_3	0.0750
BaO	0.0870	Ce_2O_3	0.1350
ZrO_2	0.2720	Pr_2O_3	0.0630
MoO_3	0.2800	Nd_2O_3	0.2620
RhO_2	0.0340	Sn_2O_3	0.0600
PdO	0.0180	Eu_2O_3	0.0030
RuO_2	0.1380	Gd_2O_3	0.0008
Ag_2O	0.0012	Nb_2O_5	0.0004
CdO	0.0030	Y_2O_3	0.0039
Ir_2O_3	0.0004		

For material-balance purposes, it was necessary to know the amounts of elements, particularly plutonium, in the pellets. Wet analyses to determine concentrations of plutonium and some fission products, and spectrochemical analyses for all fission products, indicated that there was wide variation in plutonium and F.P. concentrations from batch to batch of pellets and also between pellets within a given batch. A nondestructive test method for plutonium was developed to supplement the costly wet analysis. This test was based on measuring the gamma radiation emitted mainly by the 60-keV gamma from the ^{241}Am decay. Ten pellets from each of the 12 batches were examined. The conclusions reached were:

1. There was a wide variation in concentration between batches and also between pellets of a batch, as wet analyses suggested.

2. The test could not disprove the contention that the pellets contained an average of 0.49 wt % PuO_2.

The equipment, technique, and data for this radiation analysis method are presented in Appendix A. For material-balances purposes, it was assumed that the pellets contained the amounts of uranium, plutonium, and fission products specified in the contract.

7.1.2 Procedure

Before each fluorination run, any leaks in lines or equipment were detected by pressurizing isolated sections of the pilot-plant system (excluding the off-gas scrubbing system) to 15 psig. In those sections in which a pressure drop was observed after the supply nitrogen was isolated, any suspected joints were covered with soap solution, and any leaks found were repaired. The procedure was continued until the rate of pressure drop (if any) was less than the maximum specified for the particular section. The value for the maximum allowable pressure-drop rate was determined by considering the concentration of plutonium in the gas phase, the volume of the system, and the assumed decontamination of the ventilation air that could be obtained in the two in-series scrubber systems. Details for arriving at the values for each section are given in Appendix B.

Table 4 shows the weights of the alumina and pellet charges to the fluorinator in each run. The new alumina was 48-100 mesh, except in Run Pu-2 where finely divided (mostly less than -325 mesh) alumina was added to the 48-100 mesh material in an attempt to increase the filter cake buildup, and thereby achieve better return of this elutriated material to the reaction zone when the filters were cleaned by blowback. Table 4 also shows the particle-size data for the alumina feed of Run Pu-2.

After a satisfactory leak-test result was obtained, materials were charged to the reactor while it was at room temperature and atmospheric pressure. The alumina was charged to the fluorinator through a charging flange at the top of the disengaging section. The alumina was fluidized with nitrogen, and the nickel balls (which served as the support bed for the oxide pellets) were dropped through the alumina to the bottom of the fluorinator. Fluidizing-gas velocity was then increased to 2.2 ft/sec so that the oxide pellets that were added next would sink through the alumina to the nickel-ball support bed. The distance from the charge port to the top level of the pellets was measured to ensure that the pellets were in place. Adding pellets to a fluidized bed greatly decreases the breakage that occurs when they are dropped directly onto the nickel-ball bed. The cone and bottom 3 in. of the fluorinator contained the nickel balls, and the next 13 in. of the fluorinator contained the pellets. Figure 16 shows the locations of the nickel balls, the pellets, and the control and indicating thermocouples. The flange cover of the charge port was sealed and leak-checked after the pellets had been added and flow of the fluidizing gas was stopped.

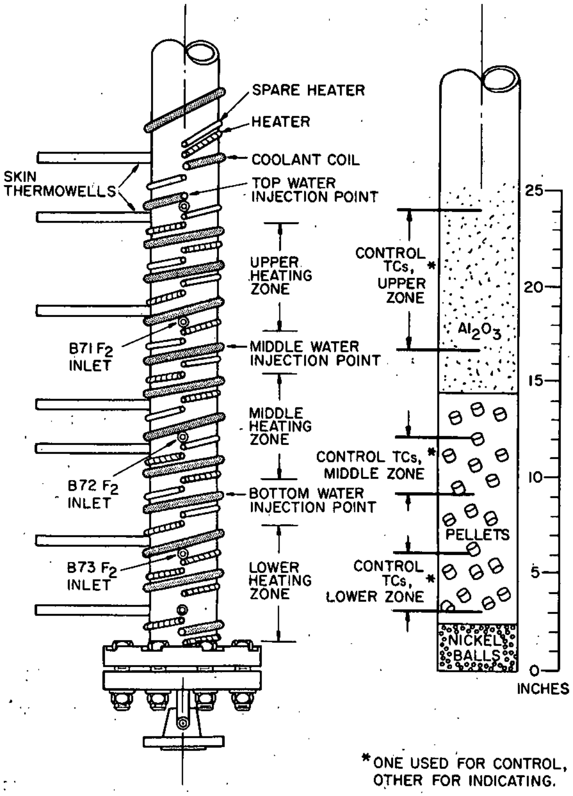
TABLE 4. Weights of Al_2O_3 and Pellet Charges to Fluorinator

Run No.	New Al_2O_3, g	Reused Al_2O_3, g	0.5 wt% PuO_2-UO_2-F.P., g	100% UO_2, g
Pu-1	6758[a]	0	6532	2267
Pu-2	356[b]	5895[b]	8530	-
Pu-3A	2578[a]	5478	8340	-
Pu-3B	500[a]	6251	-	-

[a] Alcoa Tab 61, 48-100 mesh.

[b] Sieve size data, starting bed material, Run Pu-2:

Mesh	5895 g Reused Alumina, wt %	356 g Fines Added, wt %	6251 g Composite, wt %
+25	0.2		0.2
-25 +35	1.4		1.3
-35 +45	32.8		30.9
-45 +60	20.7		19.5
-60 +80	25.1		23.7
-80 +120	14.3		13.5
-120 +170	2.7		2.5
-170 +230	1.6		1.5
-230 +325	0.7	31.5	2.5
-325	0.5	68.5	4.4
Total	100.0	100.0	100.0



*ONE USED FOR CONTROL, OTHER FOR INDICATING.

Fig. 16

Location of Heating and Cooling Zones on Lower Fluorinator Section

The nitrogen fluidizing-gas flow was restarted, and the bed was heated to the operating temperature before addition of oxygen and fluorine in Run Pu-1. Because the PuF_6 yield in the first run made with plutonium materials (Run Pu-1) was poor, the upper part of the fluorinator, the secondary filter, and the gas line connecting the fluorinator to the cold traps were treated with ClF_3 before the main fluorination in Runs Pu-2 and -3. This had two purposes: to remove moisture that may have entered the apparatus in the charging step, and to remove uranium (as UF_6) that may have been present from the equipment shakedown experiments. Both moisture and uranium compounds can react with PuF_6 to form a nonvolatile fluoride.

Before the ClF_3 treatment, any sorbed moisture on the pellets and alumina was removed by heating the charge to 250°C for 1 hr with nitrogen flowing through the system. The column was then cooled to 35°C, and the nitrogen flow was reduced. This nitrogen bleed served as a diluent for the ClF_3 (which was added near the top of the fluorinator disengaging section) and prevented ClF_3 from diffusing down to the pellets. After the surfaces to be treated had been heated to 100-150°C, ClF_3 was added, and its concentration was increased from 5 to 80% in five steps of 15 min each, and then kept at 80% for 1/2 hr. The maximum ClF_3 flowrate was 0.2 scfm. Any UF_6 produced by reaction with ClF_3 was collected on NaF. Purging of the ClF_3 with nitrogen completed the ClF_3 treatment, and the pellets and alumina were next heated to the scheduled oxidation and fluorination temperatures.

Each run comprised three fluorination periods: a two-zone oxidation-fluorination period, during which the bulk of the UF_6 was collected; a single-zone fluorination period, mainly for completing uranium removal; and finally, a bed-cleanup fluorination period, characterized by total fluorine recycle and gradually increasing bed temperatures, to volatilize the bulk of the plutonium from the alumina bed. In the two-zone oxidation-fluorination period, oxygen diluted with nitrogen entered at the bottom of the fluorinator and passed through the oxide pellet bed. Oxide fines produced were reacted with fluorine added through an inlet in the side of the fluorinator above the level of the pellet bed. Since the height of the pellet bed decreased as the pellets were oxidized, lower fluorine addition points were used, in turn, after about 8, 40, and 75% of the UF_6 had been collected. After 85% of the UF_6 had been collected, the single-zone fluorination period was started by stopping the oxygen flow, adding fluorine through the bottom inlet, and allowing the fluorine to pass directly through the remaining pellets. At about the same time, part of the process gas--all of which had been leaving the fluorination system after passing through the fluorinator once--was recycled to the fluorinator to conserve fluorine. The fluorine concentration in this recycle gas was increased gradually to 80-90%, as the temperature in the reaction zone permitted. After 100% of the UF_6 had been collected (no further weight change could be noted on the UF_6 weight recorders, WR, Fig. 6), the bed-cleanup fluorination period was started by increasing the temperature in the fluidized bed.

The fluorine content of the process off-gas was determined by a thermal-conductivity cell unit during the one- and two-zone fluorination periods. In these periods, the input fluorine concentration was relatively low and fluorine consumption was high. Input fluorine to the fluorinator was adjusted to give a measurable concentration in the process off-gas. The concentration was kept above zero to ensure that enough was being fed to react with the oxide, but below about 10% to conserve fluorine. The thermal-conductivity unit was calibrated before and after the run with 3 and 9% standard mixtures of fluorine in nitrogen.

The UF_6 and PuF_6 products were desublimed from the gas stream on passage through the cold traps, which were cooled with recirculated -60 to -70°C trichloroethylene. After the run, the hexafluorides were transferred to a storage receiver in the following manner: After evacuation of the chilled cold traps, the transfer line, and the storage cylinder, transfer was started by cooling the storage cylinder to -60°C and heating the cold traps to about 80°C. Progress of the transfer was monitored by noting the weight change on the cold-trap scales. After the transfer, liquid hexafluoride samples were taken from the storage cylinder, hydrolyzed in HNO_3-$Al(NO_3)_3$, and analyzed for uranium and plutonium.

Solids samples were taken from the fluidized bed, from the dumped alumina bed after the run, and from the NaF and activated Al_2O_3 in the off-gas trapping system. In all runs, duplicate samples were removed from the fluidized bed of alumina at intervals during the plutonium-cleanup fluorination period. In addition, duplicate samples were taken during the one- and two-zone fluorination periods in Run Pu-3. To minimize cross contamination, the first of the duplicate samples was discarded since it may have contained solids from the previous sample. The second sample was reduced to a 10-g sample size using a 2- by $2\frac{1}{2}$-in. riffler, then ground to a fine powder suitable for the X-ray analysis, using a motorized mortar-pestle. The dumped alumina bed (approximately 6 kg) was reduced to a 10-g sample in two stages using a 10- by 4-in. riffler, then a $2\frac{1}{2}$- by 2-in. riffler; the sample was then ground to a fine powder. The activated alumina (10 kg) and NaF (3 kg) from the process off-gas traps were riffled with the larger riffler to give a 1-kg sample and then coarse-ground with a disk mill. This material was split, using both rifflers, to a 10-g sample, which was ground and submitted for analysis.

7.1.3 Operating Conditions

Figure 17 shows operating conditions--gas flowrates and concentrations, and nominal temperatures in the alumina fluidized bed and the pellet zone--for all periods in each run. Because of operational difficulties, these conditions were different from those planned in some cases.

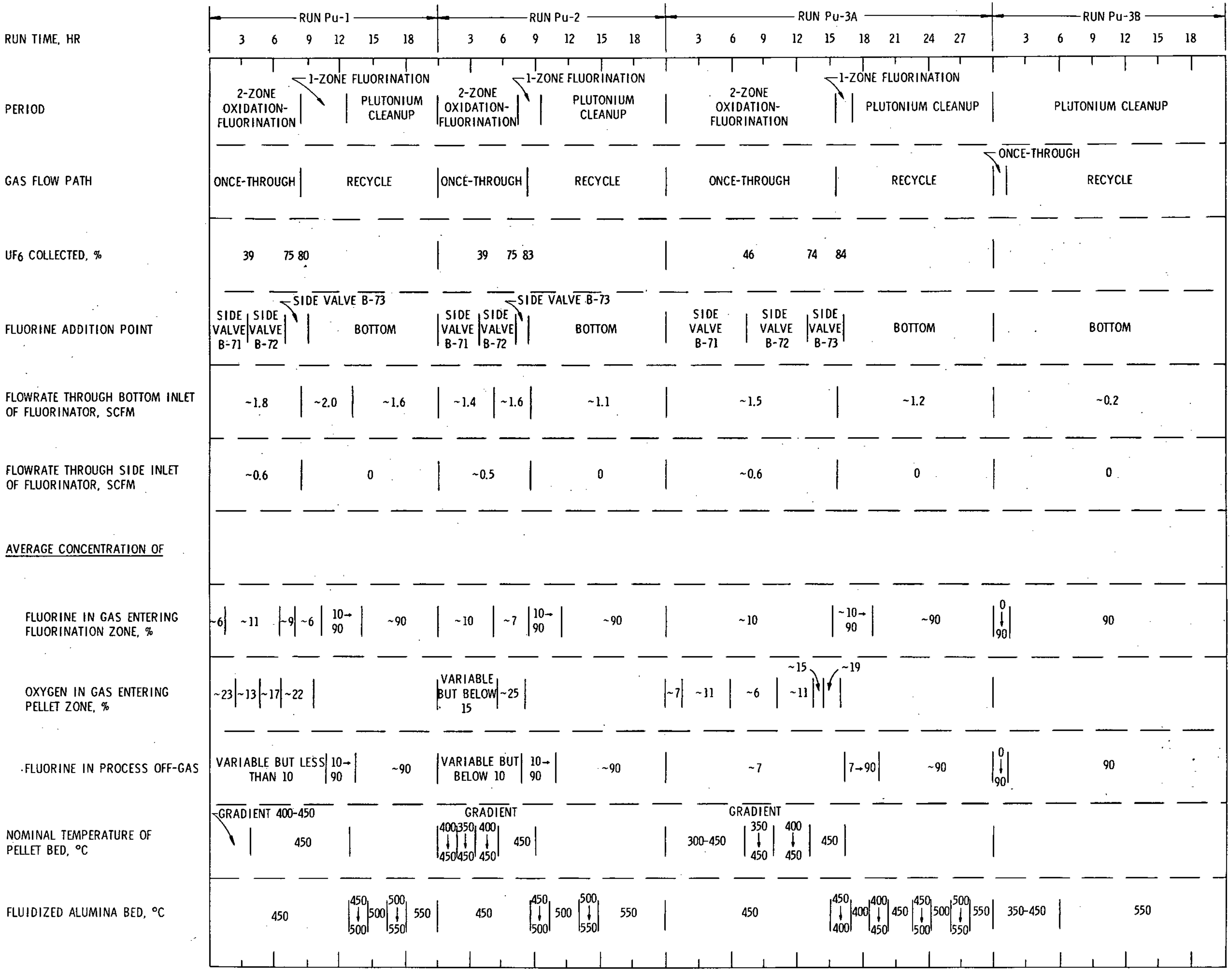


Fig. 17. Operating Conditions for Runs Pu-1 through -3B

The first run was a baseline run in which uranium fluorination conditions were based on experience gained in processing UO_2 pellets in the shakedown runs; plutonium fluorination conditions were picked to provide a significant decrease in the plutonium content of the bed.

In the second run, conditions were scheduled so that fluorination time could be reduced; oxygen and fluorine flowrates were to be higher than in the first run, and the fluorine was to be introduced into the bottom of the fluorinator at an earlier time to eliminate a period of low hexafluoride production rate. Because of a plug in the oxide pellet bed, which forced a shift in the operating procedure, these conditions were not entirely achieved.

In the third run, the objective was to produce the UF_6 at a more uniform rate. The rate of producing fines (U_3O_8) was lowered by decreasing the oxygen flowrate and increasing the temperature gradient in the pellet zone. The amount of fluorine available for fluorination was also increased.

7.1.4 Results and Discussion of Results

7.1.4.1 Operations. In Run Pu-1, oxidation of the pellets and fluorination of the U_3O_8 and PuO_2 proceeded smoothly. The pellets oxidized readily; a 400-450°C gradient was used in the pellet bed until about one-third of the charge had reacted; a uniform temperature of 450°C was maintained for the remainder of the two-zone reaction period. Fluorine utilization was very high in the first few hours, and the fluorine rate, being limited by the initially installed orifice-flow measurement system, apparently was not high enough for the existing U_3O_8 fines production rate, permitting oxide fines to accumulate in the fluidized bed. The oxygen input rate was reduced gradually during the first to fifth hour to limit production of fines.

After the run, the alumina bed was dumped without difficulty through the bottom valve of the fluorinator. No solids agglomeration was evident in the dumped bed, and no cakes were found on the fluorinator or filter chamber walls.

In Run Pu-2, except for a partial plug, which probably occurred in the oxide pellet bed at about 0030 (run time), the operation proceeded smoothly. The blockage never stopped the gas flow, but flow was reduced because the pressure at the inlet of the fluorinator (normally 5 to 10 psig) gradually increased to 25 psig. At the time of the partial plug, the temperature of the pellet bed at a point 3 in. from the bottom of the bed increased to 510 from 400°C. The nitrogen flow (the oxygen had been turned off) was pulsed, and the fines agglomerate was gradually broken up, being complete at 0130. To limit fines production in the lower level of the pellet bed, the temperature was reduced from 400 to 350°C. Also, the oxygen flowrate was reduced until 60% of the pellets had reacted.

In Run Pu-2, as in Run Pu-1, the off-gas analyzer indicated that all the fluorine was being consumed during the early stages of the experiment. Apparently a good balance had not been achieved between the oxidation and fluorination rates (fluorine input was deficient), and a considerable quantity of oxide fines accumulated in the alumina bed without being detected. Increasing the fluorine rate incrementally gave a correspondingly higher UF_6 production rate, but did not result in a fluorine excess--the off-gas detector still gave a zero-fluorine indication. Finally, at 0155 (run time), the oxygen flow was shut off to stop the production of fines. With the oxygen off and a sustained fluorine input, the hexafluoride production rate continued to average about 5 lb/hr for the next 45 min, indicating that about 3 lb of U_3O_8 fines had been present and undetected in the bed. Detection might be possible if the oxygen content of the process off-gas is measured. The volume of oxygen calculated from this concentration could be compared with the volume of oxygen fed to the fluorinator. Since the net effect of the oxygen-fluorine reaction with UO_2 is to produce oxygen, this increased volume should be detected in the process off-gas if the fines are being fluorinated when formed. This type of operation should show improvement if the system was automated.

After Run Pu-2, a 475-g soft agglomeration of fines was found on the disengaging section wall of the fluorinator where the wall joins the 3-in. pipe. In this run, 356 g of mostly -325 mesh fines had been added to build a thicker cake on the filter, so that the cake, on blowback, would drop into the fluidized bed. Most of the 356 g of fines was probably in this agglomerate. Plutonium content was high (about 20%).

Operations proceeded smoothly in Runs Pu-3A and -3B. At the end of Run Pu-3A, the main portion of the bed dropped freely from the fluorinator, but the nickel balls appeared to be cemented together with alumina. An agglomerate of about 297 g was removed from the fluorinator after Run Pu-3A, but none was found after Run Pu-3B. The 475-g agglomerate from Run Pu-2 had been reground and added to Run Pu-3A, and the 297 g found in Run Pu-3A was reground and added in Run Pu-3B.

7.1.4.2 UF_6 Production Rate and Fluorine Utilization. The UF_6 production rate during the two-zone fluorination period depends primarily on:

1. Rate of oxidation of the UO_2 in the pellets to U_3O_8 fines.
2. Rate of transfer of the U_3O_8 fines from the pellet bed zone to the fluorination zone above.

3. Temperature of the fluidized bed.
4. Availability of fluorine.

The rate is changed also by factors affecting gas-solid mixing--e.g., gas velocity, solids particle-size distribution, and projections (such as thermowells) that interfere with fluidization. Also dependent on many of these factors is fluorine utilization, which is defined as the ratio of fluorine used in producing UF_6 to that added to the fluorinator.

Most of the listed factors changed during a fluorination run and from one run to the next. Therefore, the UF_6 production rate and fluorine utilization could not be expected to be constant. Table 5 gives average UF_6 production rates and fluorine utilization for the two-zone fluorination step of all three runs and for periods in Runs Pu-2 and -3.

TABLE 5. Average and Hourly Uranium Hexafluoride Production Rates and Fluorine Utilization in the Two-zone Fluorination Step

Run Number	Production Rate, lb/(hr)(sq ft)	Fluorine Utilization, %
Pu-1	41	~55
Pu-2	51	66
Pu-3	24	26

Run Interval	Run Pu-2 Production Rate lb/hr	Run Pu-2 Production Rate lb/(hr)(sq ft)	Run Pu-2 Fluorine Utilization, %	Run Pu-3 Production Rate lb/hr	Run Pu-3 Production Rate lb/(hr)(sq ft)	Run Pu-3 Fluorine Utilization, %
0000-0100	1.21	23.6	32	0.25	5	7
0100-0200	2.01	39.2	52	0.85	17	21
0200-0300	4.71	91.8	95	2.64	52	52
0300-0400	1.69	32.9	36	2.34	46	56
0400-0500	5.68	110.7	102	1.06	21	20
0500-0600	1.81	35.3	80	2.32	45	43
0600-0700	2.52	49.1	80	0.73	14	15
0700-0800	1.68	32.7	64	1.28	25	28
0800-0900				1.08	21	21
0800-0910	2.35	45.8	54			
0900-1000				1.01	20	19
1000-1100				0.96	19	20
1100-1200				1.24	24	28
1200-1300				1.03	20	23
1300-1400				0.67	13	21
1400-1500				0.78	15	26
1500-1530				0.44	9	19
Average	2.63	51.2	66	1.22	24	26

In Run Pu-1, a baseline run, the two-zone fluorination period lasted 8 hr, and the average UF_6 production rate and fluorine utilization were 41 lb/(hr)(sq ft) and 55%, respectively. The fluidized-bed temperature was kept at 450°C, and the oxide pellet bed at a 400-450°C gradient for the initial 3 hr, and then at 450°C for the remaining 5 hr.

In Run Pu-2, the aim was to decrease the overall processing time for the two-zone period and thus increase both the production rate and the fluorine utilization. The plan had to be revised and the oxygen and fluorine input rates reduced because a partial plug in the pellet bed resulted in high pressures in the fluorinator inlet gas line. Apparently, U_3O_8 fines accumulated in the interstices of the pellets and were not transported to the fluorination zone. The input nitrogen was pulsed until pressure at the fluorinator inlet decreased, indicating that the U_3O_8 plug had been eliminated. Normal two-zone operations were then resumed. The production rate was 51.2 lb/(hr)(sq ft), about 20% higher than in the first run, and the fluorine efficiency was about 66%, compared to 55% in the first run.

The aim in the third fluorination run was to make the UF_6 production rate uniform without being concerned about achieving either high production rates or high fluorine efficiencies. A lower production rate was achieved by decreasing the amount of oxygen and by increasing the temperature gradient across the pellet bed. The fluorine flowrate was also correspondingly reduced. As expected, the UF_6 production rate and fluorine efficiencies were lower than in the other runs. A uniform production rate was not achieved, as can be seen in Figs. 18 and 19, which show the UF_6 production rates in Runs Pu-2 and -3, respectively. Smooth production rates may be difficult to achieve in the two-zone process unless fines movement from the pellet bed to the fluorination zone and the amount of fines in the zone can be measured.

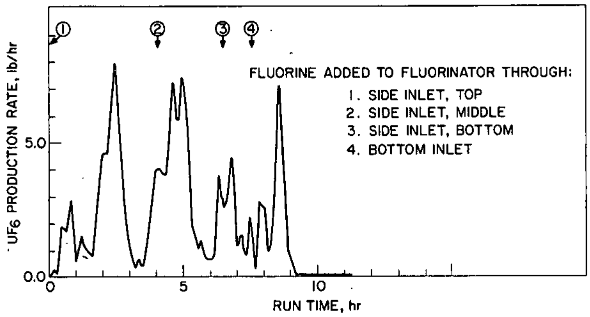


Fig. 18. UF_6 Production Rate for Run Pu-2

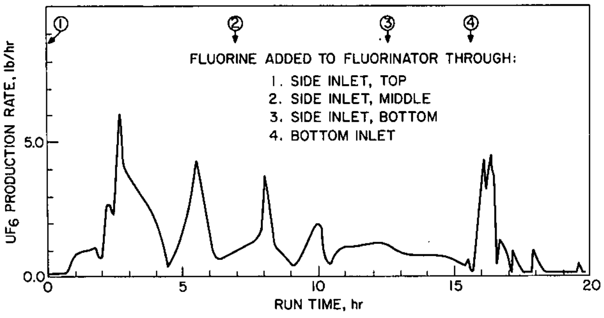


Fig. 19. UF_6 Production Rate for Run Pu-3

7.1.4.3 The Lower Plutonium Fluorination Rate Relative to Uranium. In concurrent oxidation-fluorination of uranium-plutonium oxides in Runs Pu-1 through -3, the oxide fines leaving the oxidation zone passed into the fluorination zone, where they were fluorinated. Analytical data on samples removed from the fluorination zone soon after the start of the bed cleanup step show that the uranium was preferentially fluorinated from the bed. From 21 to 37% of the plutonium and only 0.1% or less of the uranium charged was present in the bed at the start of the cleanup period, as shown in Table 6. As indicated earlier, concentrations in these samples are not true bed compositions, although they should reflect the ratio of uranium to plutonium in the bed.

TABLE 6. Preferential Fluorination of Uranium from Fluorinator

	U, Pu in Bed Charged to Fluorinator, g		U, Pu in Bed Sample Shortly after Start of Plutonium Cleanup Step, g		Percent of Charged Amount Remaining in Bed	
Run	U	Pu	U	Pu	U	Pu
Pu-1	7757	29.5	3.1	10.8	0.04	37
Pu-2	7757	43.9	4.6	4.6	0.06	36
Pu-3	7757	40.1	2.6	2.6	0.03	21

Two factors may account for the slower removal of plutonium from the bed:

1. A large equilibrium amount of fluorine is required to fluorinate the plutonium. For example, at 500°C, 100 moles of fluorine per mole of plutonium is required; even more fluorine is required at lower temperatures. The available fluorine reacts with the uranium present, leaving little for reaction with the plutonium.

2. PuF_6 is a good fluorination agent. Soon after its formation, it might react with uranium compounds in the bed and be reduced by this mechanism.

Consequently, the fluorination might be split into two periods to obtain a uranium concentrate during the first period and a plutonium concentrate during the second period.

7.1.4.4 Uranium and Plutonium Removal from the Bed. Nearly complete removal of plutonium from the final alumina bed of the fluorinator is desirable, since the bed is discarded as process waste. Removal data for uranium and plutonium (Tables 7 and 8, respectively) show that 98.7% of the plutonium and greater than 99.9% of the uranium were removed from the bed. Not all the plutonium removed was volatilized as the hexafluoride from the fluorinator and collected as product. Some plutonium (as PuF_4) was contained in samples removed from the bed, in solids from cleanout of the equipment, in cakes, and in filter coatings. (See Fig. 32 for amount and location of nonvolatilized plutonium.) Most of this plutonium is recoverable. The alumina bed contained 3.1 g of plutonium (97.1% removal) at the end of Run Pu-3B, the last run in this series. Part of this bed was refluorinated for an additional 12 hr at a maximum temperature of 550°C in a 2-in.-dia fluorinator. The final plutonium content (calculated for the total bed) was 1.3 g or an overall removal of 98.7% of the plutonium charged for all runs.

TABLE 7. Uranium Removal from Fluorination Bed: Runs Pu-1, -2, -3A, and -3B

	Uranium Charged, g					Cumulative Removal Data	
Run	In Pellets[a]	From Previous Run[b]	Total	Uranium in Final Bed, g	Removed in Run, %	Cumulative Uranium Charge in Pellets, g	Cumulative Removal, %
Pu-1	7634	0	7634	12	99.8	7634	99.8
Pu-2	8360	12	8372	1	>99.9	16006	>99.9
Pu-3A	7206	4	7210	195	97.3	23216	99.1
Pu-3B	0	201	201	1	99.5	23216	>99.9

[a] Pellets assumed to contain 0.49 wt % PuO_2, 1.5 wt % fission products, and the remainder UO_2.
[b] In bed of previous run, plus ground caked solid.

TABLE 8. Plutonium Removal from Fluorination Bed: Runs Pu-1, -2, -3A, and -3B

	Plutonium Charged, g					Cumulative Removal Data	
Run	In Pellets	Previous Run	Total	Plutonium in Final Bed, g	Removed in Run, %	Cumulative Plutonium Charge in Pellets, g	Cumulative Removal, %
Pu-1	29.5[a]	0	29.5	6.5	78	29.5	77.3
Pu-2	37.5[b]	6.5	44.0	2.2	95	67.0	96.2
Pu-3A	35.2[a]	4.9	40.1	12.6	69	102.2	87.7
Pu-3B	0	13.2[c]	13.2	3.1	67	102.2	97.1
2-in.-dia reactor				1.3		102.2	98.7

[a] Data from the fuel supplier and our analytical group.
[b] Data from our analytical group.
[c] Bed plus ground caked solid.

Reuse of the bed in batch processing would be desirable, since the volume discarded as waste would be reduced. Reuse is limited by the F.P. heat generated in the bed by the nonvolatile fission products remaining in the bed after fluorination. Use may have to be limited to three batches, as in these experiments.

The analytical data for all dumped-bed samples, presented in Table 9, show that there is better agreement in the results of samples from the same split than in the results of samples from different splits. To obtain these samples, the dumped-bed material was first riffled to obtain a 10- to 15-g portion, from which at least two samples were removed for analysis. The riffled-solids fractions were recombined, and the solids again riffled to obtain another 10- to 15-g portion from which two samples were removed. This procedure was repeated to obtain samples for the third split.

TABLE 9. Analytical Data for Final Fluidized-bed Samples and Dumped-bed Samples

	Dumped-bed Sample				Final Fluidized-bed Sample[a]	
Run	Split No.	Sample No.	% Pu	% U	% Pu	% U
Pu-1	1	1	0.115	0.29	0.025	0.039
	1	2	0.130	0.31		
	2	1	0.087	0.16		
	2	2	0.085	0.17		
	2	3	0.090	0.17		
	3	1	0.096	0.089		
Pu-2	1	1	0.032	0.024	0.030	0.016
	1	2	0.040	0.023		
Pu-3A	1	1	0.220	2.12[b]	0.040	0.018
	1	2	0.224	3.34		
	2	1	0.211[c]	3.18		
	2	2	0.209[c]	3.18		
Pu-3B	1	1	0.0596	0.0262	0.042	0.0282
	1	2	0.0605	0.0271		
	2	1	0.0644	0.0256		
	2	2	0.0603	0.0243		

[a] Taken within 5 min of end of run.

[b] Colorimetric method; other results obtained by fluorometric methods.

[c] Liquid scintillation method; other results obtained by X-ray spectrographic method.

7.1.4.5 Plutonium and Uranium Concentrations in the Fluidized Bed during the Bed-cleanup Fluorination Period. Solids samples were removed from the fluidized bed during the plutonium cleanup portion of all runs and during the two-zone oxidation-fluorination step in Run Pu-3A. The results of the plutonium and uranium analyses are plotted against time in Figs. 20 and 21, respectively.

The above data may be useful for showing a trend, but misleading results may be obtained if production rates and fluorine efficiencies are calculated from the data. Data from later experiments, presented in

Section 7.2.4.3, indicate that the actinide concentrations in the analyzed samples are probably not the true bed concentrations (the bed is not homogeneous) and that other factors, such as the fluorination of plutonium from a wall surface above the bed, contribute to the production rate and fluorine efficiency. Only at the end of the run, when the alumina bed was dumped, could the plutonium contents of the bed and the final fluidized-bed sample be compared. In all cases, the concentrations in the dumped-bed samples were higher than in the final fluidized-bed samples. Whether this is a result of fines from the upper disengaging and filter areas dropping onto the alumina bed after the gas flow had stopped or a sample being taken from a nonhomogeneous fluidized bed cannot be determined from our data.

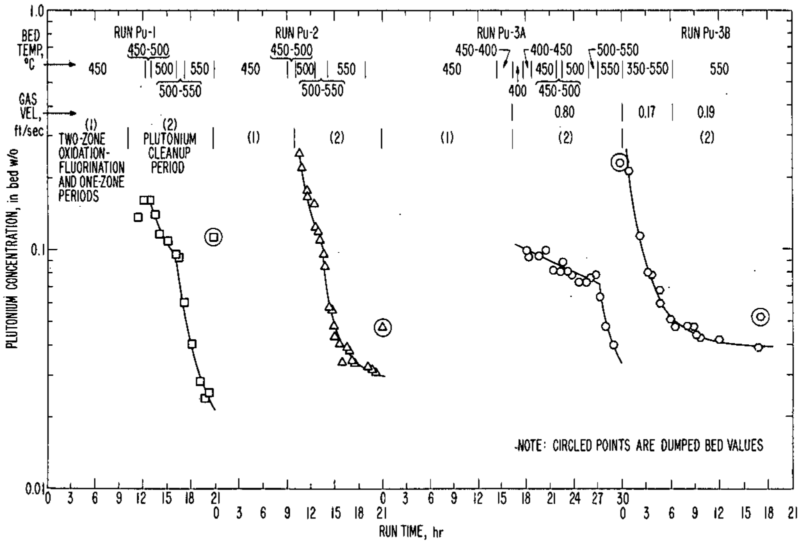


Fig. 20. Plutonium Concentration in Samples Removed from Fluidized and Dumped Beds: Runs Pu-1, -2, -3A, and -3B

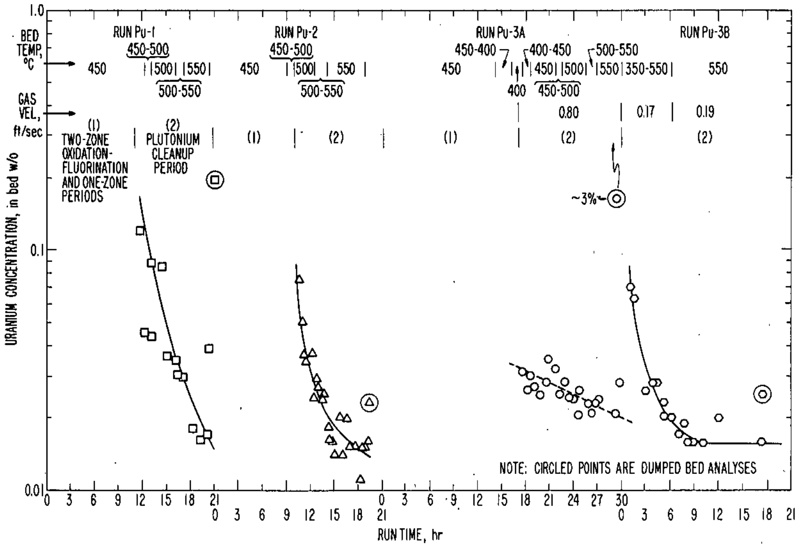


Fig. 21. Uranium Concentration in Samples Removed from Fluidized and Dumped Beds: Runs Pu-1, -2, -3A, and -3B

7.1.4.6 Particle-size Changes in Alumina Fluidized Bed during Fluorination Runs. For satisfactory fluidized-bed operations, the size distribution of the bed particles should not change radically with time. Change is expected, however. Sieving data (Table 10) show that particle growth occurred in the first, but not in succeeding, fluorination runs. During Run Pu-2, there was little change in the particle-size distribution, except that fewer -170 mesh fines were found in the final bed as a result of a cake formed of the fines added at the start of the run. In Runs Pu-3A and -3B, there was little change in particle-size distribution, although there was an increase in -230 mesh material in Run Pu-3A, for which there is no explanation. Although the bed was reused in successive runs, the particle-size distribution in the final bed cannot be compared directly with that of the starting bed (next run), since (1) alumina was added to the final beds to replace that removed in samples and (2) after Run Pu-1, alumina fines were added to the bed.

TABLE 10. Particle-size Distribution of Bed Samples, wt %

Mesh Size Range	Run Pu-1 Starting Bed	Run Pu-1 Final Bed	Run Pu-2[a] Starting Bed	Run Pu-2 Bed after ClF3 Treatment	Run Pu-2 Final Bed	Run Pu-3A Starting Bed	Run Pu-3A, Sample 6 at 0522 hr	Run Pu-3A, Sample 10 at 1121 hr	Run Pu-3A, Sample 14 at 1659 hr	Run Pu-3A, Sample 26 at 2118 hr	Run Pu-3A, Sample 46 at 2750 hr	Run Pu-3A, Sample 52 at 3030 hr	Run Pu-3A Final Bed	Run Pu-3B Starting Bed	Run Pu-3B Final Bed
+25	0	0.2	0.2	0	0.6	0.4	↑	↑	↑	↑	↑	0.4	0.8	0.7	0.4
-25 +35	0	0.8	1.3	0.7	0.7	0.5	22.7	23.9	32.4	18.4	20.3	0.9 } 22.5	0.6	0.6	0.4
-35 +45	0.1	33.7	30.9	29.8	30.8	20.8	↓	↓	↓	↓	↓	21.2	20.0	18.5	20.6
-45 +60	7.3	20.4	19.5	21.0	18.5	14.9	20.4	21.8	21.9	16.2	17.6	15.6	16.8	16.1	15.1
-60 +80	59.1	24.8	23.7	26.3	27.2	37.0	31.3	29.9	24.3	29.7	27.4	34.7	33.1	34.9	34.6
-80 +120	30.0	15.2	13.5	17.9	15.3	20.1	20.0	18.4	16.1	20.0	23.2	18.9	14.8	16.0	18.3
-120 +170	4.4	3.0	2.5	3.2	3.4	3.7	↑	↑	↑	↑	↑	4.3	4.1	4.1	4.6
-170 +230	0.5	0.6	1.5	0.3	0.9	0.7	5.1	5.8	4.9	14.8	11.2	1.2 } 7.3	1.3	1.2	0.7
-230 +325	0.4	0.7	2.5	0.5	1.5	1.1	↓	↓	↓	↓	↓	1.8	3.6	3.4	3.5
-325	0.2	0.2	4.4	0.3	1.1	0.8	0.5	0.2	0.4	0.9	0.3	1.0	4.9	4.5	1.7
ρ Bulk, g/cc	1.63														
ρ Pack, g/cc	2.0												2.3	2.3	2.2
F^-, %		2.38			5.60							7.5	11.3	11.3	12.6

[a] Calculated values.

Changes in particle-size distribution in samples removed from the fluidized bed during the run (Table 9) are difficult to interpret, because the fluidizing-gas velocity was not constant during the runs. Higher gas velocity would elutriate more fines from the bed, leaving a coarser mixture. A change in particle-size distribution was indicated for samples 14 and 26, apparently because the gas velocities were different. The decrease in fines concentration after sample 26 may have been due to gradually increasing gas velocities near the end of the run when the temperature was being increased with a constant gas throughput.

7.1.4.7 F.P. Accountability. Most of the added fission products form nonvolatile fluorides, which remain in the fluorinator alumina bed. The behavior of the volatile F.P. fluorides is of interest, since they represent product contaminants and must be separated from the UF_6 and PuF_6.

Good accountability for two of the simulated fission products--molybdenum and ruthenium--that were volatilized from the fluorinator could not be achieved, because the concentration levels in samples were near the lower limits of the analytical methods. However, some distribution information was obtained.

Since the hexafluoride product from the fluorination runs served as the feed material in the thermal-decomposition experiments, distribution data are for both the fluorination and thermal-decomposition experiments. After each oxide fluorination, the actinide hexafluorides and other fluorides that had been collected in the cold traps were vapor-transferred to separate hexafluoride product pots, which served as feed cylinders for thermal-decomposition experiments. In the latter experiments, fluorides were fed into a heated alumina bed, and the PuF_6 decomposed to PuF_4. Nondecomposed fluorides passed through the bed and were collected in the fluorination-system cold traps and later transferred to another cylinder. After the final experiment in the series, all the vessels and piping were fluorinated to recover PuF_4 and other deposited compounds. (This operation is referred to as the equipment cleanup fluorination step, which is distinct from the bed-cleanup fluorination step conducted as part of each fluorination experiment.)

Based on analyses of selected samples, the following were found for molybdenum:

1. Less than 6% (limit of detectability) remained in the final bed of the fluorinator.

2. About one-third was collected during plutonium cleanup of the equipment and hexafluoride containers, and of this one-third, most (about 70%) was collected from the cold traps.

This suggests two possibilities:

a. MoF_6 was formed in the fluorinator and was reduced to a nonvolatile fluoride by reaction with metal or another compound. This reduced compound was refluorinated during the equipment-cleanup fluorination step, or

b. A high-boiling compound (an oxyfluoride or MoF_5) was formed in the fluorination step and collected in the cold traps, but did not transfer with the UF_6 and PuF_6 at 80°C. This compound was eventually recovered when the cold traps were heated to 300°C during the plutonium cleanup step.

3. Most of the molybdenum was collected in the overhead UF_6 product of the thermal-decomposition runs. This suggests that mainly MoF_6 was formed during the fluorination of the oxide fines.

For ruthenium, the following were found:

1. Approximately 3% was found in the final alumina bed removed from the fluorinator.

2. About 20% (±50%) was found in the UF_6 product of the thermal-decomposition step.

3. About 10% was collected during the refluorination of equipment. About four-fifths of this was from cold-trap equipment, and the remainder from the hexafluoride feed cylinders used in the thermal-decomposition runs.

4. Detectable amounts were found in samples of the alumina and NaF process off-gas traps.

5. None was detected in the unfed hexafluoride in the feed cylinders for the thermal-decomposition runs (limit of detection 1% of the ruthenium charged, as for the pellets).

6. The decomposer bed contained less than 0.01% of the ruthenium charged.

The percentage figures are based on the assumption that the pellets contained the specified concentration of ruthenium. Our own analytical data suggest that only half the specified quantity was present; on this basis, the percentages given above should be doubled. The general behavior of ruthenium was similar to that for molybdenum: (1) The bulk of the ruthenium formed a volatile compound and was transported to the primary cold traps with the UF_6 and PuF_6, and (2) the bulk of the volatile ruthenium material remained with the UF_6 through the thermal-decomposition step, affording some degree of decontamination of the plutonium product.

7.2 PuF_4 Fluorination Runs

7.2.1 Introduction

In view of the poor PuF_6 yield results in the initial set of experiments on plutonium-bearing materials (see Section 10), a set of fluorination experiments was planned specifically to demonstrate high plutonium recovery. The experiments were conducted with mainly PuF_4 as the charged material in an alumina bed, but can be considered as a simulation of the plutonium-recovery step of the interhalogen flowsheet. The objectives of these experiments were: (1) to demonstrate that plutonium could be volatilized quantitatively from the fluorinator, (2) to demonstrate that satisfactory material balances could be obtained, and (3) to obtain data on PuF_4 fluorination rates and fluorine efficiency.

Four fluorination runs were made--Pu-6, -10, -11, and -13. A fifth, dummy run (Pu-12) was made, which involved no fluorination but only the fluidization of a PuF_4-alumina charge with nitrogen to establish the distribution of the PuF_4 in the reactor as a function of time, i.e., to determine whether the PuF_4, which was of relatively fine particle size (virtually all -325 mesh), remained distributed in the nominal 48-100 mesh alumina bed, or was elutriated rather quickly from the bed and deposited on the filters or on other upper surfaces of the reactor. The movement of the PuF_4 was followed with neutron survey meters, and by analysis of bed grab samples. Appendix D discusses the procedure and results obtained in this run, which illustrates the potential of the neutron survey meter in such applications.

In addition, the feasibility of transporting PuF_6 from the main process cold traps to a second, smaller product receiver was examined in three experiments--U-7, U-8, and Pu-9. Runs U-7 and -8 were made first using UF_6 as a stand-in for the PuF_6, and then Run Pu-9 was made with PuF_6 alone. The transfer experiments are discussed in Appendix C.

7.2.2 PuF_4 Properties

The PuF_4 powder, mostly less than -325 mesh, was of high purity. Microphotographs showed that the individual particles were about 4 μ in diameter, although a few agglomerates as large as 100 μ were present. Analytical and sieve size data are given in Tables 11 and 12.

TABLE 11. Impurity and Isotopic Analyses of PuF_4

Spectrographic Analysis (parts per million parts of plutonium)

Ag	Al	As	B	Be	Bi	Ca	Cd	Cr	Cu	Fe	Ge	K	Li	Mg
1	20	-	-	-	-	50	-	5	1	130	-	20	-	20

Mo	Mn	Na	Ni	P	Pb	Si	Sn	Tl	V	Zn	Ti	C	wt % Pu
-	10	100	50	-	5	21	2	-	-	-	20	205	74.8

Isotopic Analysis by Mass Spectrometer, wt %

239	240	241	242
90.948	8.183	0.830	0.039

TABLE 12. Screen Analysis of Plutonium Tetrafluoride
Used in Runs Pu-6, -10, -11, -12, and -13

USS Sieve Size	wt % Solids on Sieve	USS Sieve Size	wt % Solids on Sieve
+170	1.9	-230 +325	2.2
-170 +230	2.2	-325	93.7

7.2.3 Operating Conditions and Procedure

7.2.3.1 Charging of Materials and Conditioning of Alumina. Before the charging of the materials, the entire system was checked for leaks as in the earlier runs using the criterion given in Appendix B. The nickel balls and alumina charge were then added to the fluorinator, using the procedure described in Section 7.1.2. For three of the four runs (Pu-6, -11, and -13) a fresh bed of Al_2O_3 was charged; in the fourth run (Pu-10), the bed from Run Pu-6 was reused. The fresh charges of Al_2O_3 were conditioned by passing 90% fluorine through the Al_2O_3 for 24 hr at 450°C in Runs Pu-6 and -11, and for 4 hr at 550°C in Run 13. The PuF_4 charge was dumped on top of the Al_2O_3 in Runs Pu-6, -11, and -13; in Run Pu-10, the PuF_4 was mixed with the reused bed of Run Pu-6 and then charged. The reactor was sealed and again leak-checked just before fluorination.

7.2.3.2 Operating Conditions and Procedures for Fluorination Runs. The operating conditions for the four fluorination runs are listed in Table 13. The starting procedure differed slightly, but in all runs, gas with a high concentration of fluorine was recycled through the PuF_4-Al_2O_3 bed, and the PuF_6 that formed was collected by direct sorption on NaF or by desublimation in cold traps. To begin Runs Pu-10 and -13, the PuF_4-Al_2O_3 bed was heated to the starting fluorination temperature with nitrogen circulating through the bed. Then fluorine was added to the recycle gas stream. The concentration of fluorine in the recycle stream was increased gradually. To begin Runs Pu-6 and -11, the entire system was evacuated when the desired starting bed temperature was reached (200°C in Pu-6, and 100°C in Pu-11). The system was then filled with fluorine, and the gas recycle pump was next started. In Run Pu-11, after the gas recycle pump was started, the temperature was increased as rapidly as possible to 200°C.

The PuF_6 product was sorbed directly on NaF in Run Pu-6 and desublimed from the gas stream in the cold traps in the other three runs. The collection of PuF_6 was monitored with a neutron survey meter, increased activity (neutron emission rate) indicating accumulation of PuF_6. Characteristic of all runs, the neutron count rate diminished and finally plateaued for each temperature setting, indicating a cessation in the production and collection of PuF_6. When the count rate leveled, the fluorination temperature was increased 25°C. An almost immediate response (an increased neutron count rate) was noted, indicating that additional PuF_6 was being produced and accumulated. Essentially the same time-temperature cycles were used for Runs Pu-6 and -11. The same technique was used for Run Pu-13, but the time sequence varied somewhat from the above. For Run Pu-10, a more arbitrary, shorter time-temperature cycle was used in exploring the effect of this variable on overall plutonium recovery.

TABLE 13. Operating Conditions for Runs Pu-6, -10, -11, and -13

	Run Pu-6	Run Pu-10	Run Pu-11	Run Pu-13
Charge				
Weight of Al_2O_3 (48-100 mesh) before pretreatment with F_2, g	6751	4848[a]	6758	6258
PuF_4, g	134.2	138.0	135.4	137.7
UF_4, g	0	41.5	0	0
CsF, g	0	41.8	39.2	0
Gas Flow				
Total scfm (90 vol % F_2 in N_2)	~0.29	~0.1	~0.1	~0.8
Makeup F_2, scfm	0.1	0.1	0.1	0.1
Superficial fluidizing-gas velocity for temperature range 300-550°C, ft/sec	0.2-0.28	0.86-1.21	0.2-0.28	0.4-0.8
Hours at Stated Bed Temperature,°C				
200	3.5		3.5	4.0
225	2.0		2.0	6.0
250	1.5		1.5	3.6
275	1.5		1.5	1.6
300	1.5	3.0	1.5	1.2
325	1.5		1.5	1.6
350	1.5		1.5	0.5
375	3.0		3.0	0.8
400	2.0	5.0	2.0	0.5
425	2.0		2.0	0.8
450	2.0		4.5	0.5
475				0.5
500	2.5		2.5	0
525				1.5
550	25.0	6.0	25.0	5.2
Hours at Stated Filter Temperature				
~125°C	27.5	7.0	30.0	
Increasing to ~300°C	4.5	1.0	4.5	
300°C	17.5	6.0	17.5	

[a] The final bed from Run Pu-6 was reused as the starting bed for this run.

After the fluorination step in Runs Pu-11 and -13, the PuF_6 collected in the cold traps was transferred in a stream of inert gas into smaller (weighable) chilled containers to determine yield. In Run Pu-10, the PuF_6 was inadvertently transferred to sorbent NaF, which was then analyzed.

To recover a greater overall fraction of each plutonium charge as PuF_6 during a given run, the temperature of the filter zones was increased from the normal operating temperature (125°C) to 300°C to fluorinate any PuF_4 in this region. Earlier experience indicated some accumulation of PuF_4 (perhaps equivalent to 10% of a charge) occurred there. Fluorination of the filter zone was started when fluorination of the bed was essentially complete (e.g., after 27.5 hr of fluorination in Run Pu-6). To remove still further plutonium from the bed, however, the bed was kept at the final operating temperature (550°C) while the filter-zone plutonium-removal step was being completed. The filter-zone fluorination time was shorter in Run Pu-10 (6 hr) than in Runs Pu-6 and -11 (17.5 hr). In Run Pu-13, filter cleanup was conducted separately from the cleanup of all lines and equipment that had been exposed to PuF_6.

Duplicate samples were removed from the fluidized bed during each run, but only the second sample of the duplicate was analyzed. The first sample was considered to have purged the sample lines of residual solids. After a run, the bed was dumped and sampled using the riffler-splitting technique.

7.2.3.3 Transfer of PuF_6. In Runs Pu-10 and -13, the PuF_6 collected in the cold traps was inert-gas transferred to a 2.5-in.-dia, 10-in.-high product container. The system was similar to the system (described in Appendix C) in which UF_6 was transferred. The gas train included, in series, cold traps, the product container, the backup NaF trap, and the process NaF trap. Nitrogen gas at 2 scfh was passed through the train, and the trichloroethylene coolant, circulating through the cold traps at -60°C, was gradually warmed to 70°C. The skin heaters on the cold traps were also turned on to improve the rate of transfer. The product container was chilled to about -78°C with a trichloroethylene-dry ice slush mixture. After transfer was completed, the container was evacuated, removed, allowed to warm up, and then weighed. The NaF was dumped and sampled for plutonium content.

7.2.3.4 Recovery of Deposited Plutonium from Equipment after Run Pu-13. For material-balance purposes, parts of the system that "saw" plutonium and possibly contained plutonium deposits were treated with fluorine at 300°C; any recovered PuF_6 was sorbed on NaF. Procedure and data on the equipment-cleanup fluorination step are discussed in Section 9 of this report.

7.2.4 Results and Discussion of Results

7.2.4.1 Operating Experience. Operating experience was good in these runs, but a few problems developed that had not been encountered earlier, such as difficulty in starting the fluidizing gas through the bed, sticking of check valves in the recycle gas pump, and a filter burnout. The fluidizing-gas flow problem, one of not being able to pass gas through the bed except at very high forepressures, was encountered in Run Pu-6. In this run, the system, with the bed at 200°C, had been evacuated and refilled with fluorine. During the evacuation step, some solids from the bed may have been sucked into the fluorinator inlet gas line, forming a partial plug, which limited the gas flow. A pressure of 30 psig finally dislodged this plug.

When the pump check valves stuck, gas flow through the reactor virtually stopped. To correct the problem, the pump was isolated by valving;

meanwhile, fluidization was continued with once-through nitrogen, and the bed was maintained at temperature. The check valves were removed, cleaned, and reinstalled. Overall, only a 2-hr delay was suffered, before fluorination was resumed.

Examination of the fluorinator filters after Run Pu-11 disclosed that they had failed. One of the filters showed evidence of nickel-fluorine reaction--a heavy fluoride scale and two holes (each about 1-in. in diameter), with evidence of nickel melting. The other filter was in better condition, although two small holes were found. Both filters were warped longitudinally. Subsequent examination of filter-zone temperature data indicated that destruction probably occurred during the 13th hour of Run Pu-10--in the filter cleanup step when the programmed filter-zone temperature was 300°C. A temperature spike to 450°C was found on the temperature trace for a thermocouple located about 1 in. below the filter. The filters had not been inspected after this run. Data on the gas flowrate through the filter as a function of pressure drop across the filter would have been useful in pinpointing the problem, but were not available. Since both filters apparently were not functioning after having failed, blowback was ineffective. High-plutonium-concentration solids were found inside one of the filters, so data on plutonium removal from the bed for both Runs Pu-10 and -11 are suspect. New sintered-metal filters were installed, and no further difficulty with filters was experienced.

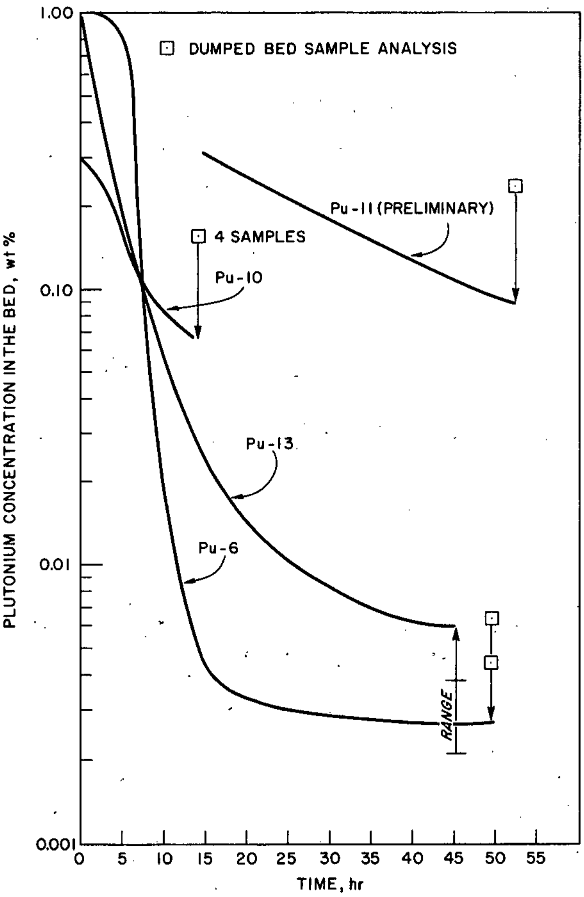


Fig. 22. Plutonium Concentration in Samples Removed from Fluidized Bed during and after Runs Pu-6, -10, -11, and -13

7.2.4.2 Plutonium Concentration in Bed Samples during and after the Run.

Figure 22 summarizes the concentrations of plutonium in the samples removed from the fluidized bed and from the dumped beds. The results of these four runs cannot be compared, since the amounts of alumina, uranium, and cesium present in the charges differed, the operating conditions (the time-temperature cycle and the gas velocity) changed, and the operating procedures (starting with 100% fluorine, or gradually increasing the fluorine concentration in the recycle gas) differed.

Figure 22 also shows the average plutonium concentrations of the dumped-bed samples. These would be a measure of the effectiveness of fluorination in Runs Pu-6 and -13, but not for Runs Pu-10 and -11 because of the filter burnout problem. For Run Pu-6, the data show that over 99.7% of the plutonium was removed from the bed. Also, as in previous experiments, the dumped-bed samples (in three of the four runs) had a higher concentration of plutonium than the final fluidized-bed samples.

7.2.4.3 Relation of Plutonium Concentration of Fluidized-bed Samples to PuF_6 Production Rate and Fluorine Efficiency. Solids samples were removed from the fluidized alumina bed during the runs and analyzed for plutonium content to determine PuF_6 production rates and allow calculation of fluorine efficiencies for different run periods. (Fluorine efficiency is defined as the ratio of PuF_6 produced to the theoretical amount that could be produced from fluorine input and equilibrium considerations.)

In both calculations, the amount of PuF_6 produced in a given period must be known. Techniques providing data for this determination included weighing the product receivers, direct sorption on NaF and analysis of the NaF, measurement of the neutronic activity at the collection point, and indirectly, analysis of fluorinator bed samples, which under ideal conditions should show a plutonium depletion rate corresponding to the PuF_6 collection rate. Each method had some limitations. Direct sorption of PuF_6 on separate beds of NaF in successive run periods, then analysis of the NaF, would provide the necessary information, but transfer of PuF_6, which was an objective of these experiments, could not be demonstrated. Therefore, this technique was not used at this time. This method was successfully used in subsequent work.

Direct measurement by weight was not possible, since the sensitivity of the scales on which the product cold traps were mounted was 25 g, large in comparison to the 125-150 g of PuF_6 collected. The quantitative measurement of neutron emission was just being investigated and shows considerable promise, but needs some development.

Finally, the problem of determining PuF_6 production rate from plutonium analyses of fluidized-bed samples requires these considerations:

1. One aspect of the problem is the ratio of plutonium in the bed to the total column inventory of plutonium at the time of sampling. A fraction of the plutonium can be out of the bed, collected on the filter surfaces, and periodically returned to the bed when the filters are blown back. Filter blowback timing can be controlled, and if bed samples are consistently taken a certain interval after blowback, the analytical results might not be biased. However, if some plutonium-bearing solids are returned to the bed at irregular times, unreliable data may be obtained. For example, solids do accumulate on the sloping wall of the disengaging section and may return to

the bed at irregular times, due to column vibrations induced by fluidization of the bed alone. Accumulation and sliding-off of powder in this region was observed in mockup fluidization tests.

2. Plutonium fines can reside on surfaces (e.g., disengaging section walls) that are hot enough so that plutonium can be fluorinated and contribute to the PuF_6 production rate without this being reflected by changes in bed-sample composition. Evidence that plutonium is transported to such surfaces during the initial fluidization periods was found during the mock run (Run Pu-12) through the use of the neutron survey meter.

3. If the fluidized bed is not homogeneous, obtaining a representative sample may be impossible. In the present case, the use of fine-mesh PuF_4 and a relatively coarse alumina was far from ideal as regards mixing, and some of the PuF_4 may have segregated into a plutonium-rich layer at the top of the bed.

Data used in an attempt to define the sampling problem are next reviewed, starting with information obtained in the initial plutonium experiments. As indicated earlier, in Runs Pu-1 through -3 the plutonium concentration of the dumped-bed samples and the final fluidized-bed samples differed. This suggested that some plutonium was held in the gas phase above the fluidized bed during a run and dropped when the fluidizing-gas flow was stopped. Also, some solids could have been dislodged from the walls above the bed during the bed-dumping operation when the column was rapped. In Run Pu-6 (the first run in the PuF_4 fluorination series), a similar concentration difference in the dumped-bed samples and final fluidized-bed samples was noted.

In the runs with PuF_4 powder, since a known amount of PuF_4 was added to the alumina, the plutonium concentration in a fluidized-bed sample taken before fluorination started should be comparable with the concentration calculated from the known amounts of plutonium and alumina added to the fluorinator, if the system is homogeneous. The plutonium concentration in the fluidized-bed samples was 0.77% as compared with the calculated concentration of 1.6%. This suggested that a large proportion of the plutonium was out of the fluidized bed--in the gas phase or adhering to the upper surfaces of the fluorinator--or that the bed was nonhomogeneous when sampled.

In Run Pu-12, neutron probes were placed along the length of the fluorinator to locate the plutonium during the experiment. (This was a qualitative method, since an exact relationship between the amount of plutonium and the neutron emission rate had not been established.) Fluidized-bed samples were taken of the PuF_4-Al_2O_3 at time intervals throughout the run. The bed was fluidized with nitrogen and kept at room temperature, since temperature changes shift the calibration curve of the neutron meters. The results (see Appendix D for experimental details) showed the following:

1. At gas velocities of 0.3 to 0.7 ft/sec, little plutonium (estimated to be less than 10% of that charged) was in the filter-zone region.

2. The disengaging section contained significant amounts of plutonium, the amount increasing with time of fluidization.

3. When the gas flow was stopped, or the filters blown back, or the fluorinator hammered to dislodge particles, the neutron count dropped significantly in the filter and disengaging zones.

4. Successive fluidized-bed samples contained 0.06, 0.1, and 0.7 wt % plutonium. These concentrations are less than the 2% they would have contained had all plutonium been in the bed and had the bed been homogeneous. Data show that homogeneity increased with time.

Concurrently with the above neutron-monitoring tests, experiments were made using a mixture of fine nickel powder (instead of PuF_4) and alumina and a plastic column to allow the degree of homogenization of the bed particles to be observed. These tests confirmed results from the neutron probe test. Sectioning of the bed after the run showed that the nickel was not uniformly distributed. Since the plastic column did not have a filter, over 30% of the fines were transported from the bed. Homogenization could be promoted by the addition of alumina fines, and this was the basis for adding fines in some of the later runs.

Efforts to show the extent of fines holdup in the gas phase by the fluidizing gas proved inconclusive. The beds of Runs Pu-14 and -15 were drained through the bottom valve of the fluorinator in three portions (some mixing of the three portions could have easily occurred in using this procedure). The top portion of the Run Pu-15 bed did have a higher plutonium concentration than the lower portions, which would be the case if material dropped onto the bed when fluidization was stopped. However, results of Run Pu-14 do not show a higher plutonium concentration in the topmost portion. Consequently, the data presented and discussed in Section 7.3.3.2 are inconclusive.

Further evidence of bed inhomogeneity was observed in a comparison of analytical results of samples taken from two elevations--10 and 27 in. above the nickel-ball support. Results and the experimental details, given in Appendix E, show poor agreement of uranium and plutonium concentrations for samples taken at two levels, demonstrating that the bed was not homogeneous.

The runs that followed Run Pu-15 (results of these are to be presented in a subsequent report[6]) established that there was little correlation between the PuF_6 collected (on NaF in these runs) in a given period and plutonium depletion data obtained from analysis of the bed samples. Thus, from the available data we concluded that with the PuF_4/Al_2O_3 mixture and operating conditions used:

1. PuF_6 production rates calculated from the concentrations of plutonium in fluidized bed samples would be incorrect.

2. Of the two factors that prevent calculation of PuF_6 production rates from fluidized-bed compositions, the nonhomogeneity of the bed has been demonstrated in the tests. The amounts of plutonium in the gas phase above the bed and on the wall surfaces during a run have not been determined.

7.2.4.4 Change in Particle-size Distribution of Alumina Fluidized Bed during a Fluorination Run. The dumped beds of Runs Pu-6, -10, and -11 were sieved to detect any change in the particle-size distribution. The data (given in Table 14) show that there was no significant change in the particle-size distribution.

TABLE 14. Particle-size Distributions before and after Fluorination Runs

Mesh Size Range	Starting Al_2O_3, % in Size Range	Final Al_2O_3 Beds, % in Size Range		
		Run Pu-6	Run Pu-10	Run Pu-11
+25	0	0.2	1.2	0.3
-25 +35	0	0.1	0.2	0.1
-35 +45	0.1	0.2	0.2	0.1
-45 +60	7.3	9.4	11.1	12.1
-60 +80	57.1	53.4	56.7	55.9
-80 +120	30.0	30.4	25.9	26.2
-120 +170	4.4	4.3	4.0	4.7
-170 +230	0.5	0.7	0.3	0.5
-230 +325	0.4	0.8	0.2	0.4
-325	0.2	0.4	0.2	0.2

7.2.4.5 PuF_6 Transfer Data. In two of the runs (Pu-11 and -13), the PuF_6 product that was collected in the cold traps was inert-gas-transferred to a small product container (0.03 cu ft) using procedures developed earlier (see Appendix C). About 86 and 88%, respectively, of the PuF_6 were collected in the product container. The remainder passed through the chilled product container and was sorbed on NaF. Recovery of the PuF_6 would be increased if the surface area of the product container was increased or if the gas flowrate was reduced to increase the contact time in the product container.

7.3 Fluorination of Beds Processed through O_2-BrF_5 Steps

Two additional fluorination experiments (Runs Pu-14 and -15) were carried out as part of the development effort on the interhalogen flowsheet. These experiments were intended to provide a basis for comparing fluorination results obtained in the pilot-scale unit with those obtained in the 2-in.-dia laboratory fluid-bed unit;[7] this would be useful in developing scale-up information. Since the alpha facility was not yet equipped with BrF_5, the plutonium charges for the pilot-scale unit were prepared by processing UO_2-PuO_2-F.P. pellets through the oxidation and BrF_5 steps in the laboratory unit.

7.3.1 Materials

The bed for Run Pu-14 consisted of residual beds from laboratory-scale runs (designated Purse in Table 15) in which synthetic fuel materials were processed through the entire sequence of oxygen, BrF_5, and fluorine steps. The plutonium was contained in the residual bed from a laboratory experiment (Run J-2) that included only the O_2-BrF_5 steps. The final bed from Run Pu-14 served as the starting bed for Run Pu-15. A separate plutonium-containing bed from Run J-3 was charged for Run Pu-15.

The charge in each laboratory experiment consisted of 1100 g of 48 to 100 mesh Alcoa T-61 alumina and about 650 g of 1/2- by 1/2-in. cylindrical pellets containing 5 wt % PuO_2, 93.5 wt % UO_2, and 1.5 wt % fission products. In addition, about 0.6 g of 99.9% pure CsF powder, 0.15 g of RbF, and 0.48 g of NpO_2 were added to the bed.

Reaction conditions in Runs J-2 and -3 were similar. The pellets were oxidized in 4 hr at 450°C with 20-23% oxygen in nitrogen flowing at a superficial velocity of 0.75 ft/sec. Then 10-12% BrF_5 in nitrogen, at a gas velocity of 0.65 ft/sec, was passed through the 300°C bed for 2 hr. The bed was packaged and moved to the engineering-scale alpha facility for further processing with fluorine.

The J-2 and -3 beds were tumbled, and grab samples taken before being charged to the alpha-facility fluorinator. Table 15 lists the concentrations of uranium, plutonium, and cesium, where available in the beds used in Runs Pu-14 and -15. The J-2 and -3 beds contained 1.86 and 1.99% plutonium and 0.76 and 1.01% uranium. Standard deviations (σ) were 10, 5, 21, and 14%, respectively, at the 95% confidence level. Particle-size distribution data and uranium and plutonium contents of the sieved fractions of the J-3 bed (given in Table 15) show that the bulk of the uranium and plutonium was in the -60 +120 range fraction.

TABLE 15. Bed Charges for Runs Pu-14 and -15

Run	Material Weight, g	Plutonium		Uranium		Cesium	
		%	g	%	g	%	g
			Run Pu-14				
Purse 2	829.3	0.028	0.232	0.018	0.149		
Purse 3	729.3	0.022	0.161	0.006	0.044	0.051	0.40
Purse 4	621.1	0.005	0.031	0.005	0.031	0.029	0.19
Purse 5	632.3	0.006	0.038	0.007	0.044		
Purse 7	567.6	0.006	0.034	0.004	0.023		
Purse 8	676.6	0.012	0.082	0.014	0.094		
Purse 9	646.0	0.005	0.032	0.003	0.019	0.034	0.25
Purse 10-12	712.1	0.005	0.032	0.002	0.014	0.073	0.54
J-2 bed	995.2	1.86[a]	18.51	0.79	7.86		
Total	6409.5		19.18	0.13	8.28		
			Run Pu-15				
Pu-14 bed	5751	0.011	0.63	0.002	0.12		
J-3 bed[b]	1042	1.99[c]	20.73	1.01	10.52		
Total	6793		21.36		10.64		

[a] Results of plutonium analyses, J-2 bed samples:

Sample		
1	1.71	
2	1.83	
3	1.90	Average, 1.86% Pu
4	1.99	σ = ±10% (95% C.I.)

[b]

J-3 Bed USS Sieve Size	Gram Fraction	% Pu in Fraction	g Pu/100 g of Bed	% U in Fraction	g U/100 g of Bed
+60	0.0221	1.76	0.039	2.70	0.060
-60 +80	0.6105	1.50	0.916	0.56	0.341
-80 +120	0.3084	1.52	0.469	0.64	0.197
-120 +170	0.0513	1.80	0.092	0.89	0.046
-170	0.0077	16.65	0.128	15.10	0.116
	1.0000		1.644		0.760

[c] Results of plutonium analyses, J-3 bed samples:

Sample		
1	1.91	
2	1.98	
3	2.03	Average, 1.99% Pu
4	2.05	σ = ±5% (95% C.I.)

7.3.2 Procedure

Prerun preparations, fluorination, and carrier-gas transfer of product PuF_6 from the cold traps to a NaF-filled trap are discussed. Although operating conditions for the two runs were similar, some differences did exist, and these are indicated.

7.3.2.1 Prerun Preparations. The prerun steps of system leak testing and powder charging were similar to those described in Section 7.1.2. A special procedure was used to remove sorbed moisture from all the materials charged. Nitrogen flow in a once-through path was started, and the fluorinator was heated until the bed temperature reached 150°C. This step allowed surface moisture to be removed from the bed particles. The gas flow was then recycled through the bed until the bed temperature reached 300°C. During the preheat period, the cold traps were bypassed to avoid collection of moisture. Total times to reach reaction temperature (300°C) were 1.7 and 2.7 hr in Runs Pu-14 and -15, respectively.

7.3.2.2 Fluorination Step. After the bed temperature reached 300°C, 0.1 scfm of fluorine was added to the recycle gas stream and fluorine addition continued for the remainder of the fluorination period, except for one unplanned interruption in each run. In Run Pu-14, in which the process-scrubber pump motor failed, the makeup fluorine flow was interrupted from 1046 to 1118 (run time), but recycle gas flow was continued. In Run Pu-15, at 0010, the flow was interrupted for 7 min while the bed temperature (which had reached 370°C) was reduced to the desired 300°C (the indicating needle on one of the three temperature-indicating controllers used on the bed zone had stuck on the set-point indicator). The fluorine concentration in the recycle loop ultimately reached approximately 80%, the diluent being nitrogen from the transmitter line-purge flows and from the filter blowback-gas flow.

In Run Pu-14, the total gas flowrate (about 1.0 scfm) was not changed during the run. Consequently, the superficial gas velocity in the fluorinator increased as the bed temperature was increased. In Run Pu-15, the superficial gas velocity was held constant (at about 0.6 ft/sec) by reducing the recycle-gas flowrate as the bed temperature increased. Consequently, more fluorine was passed through the bed in Run Pu-14. Figure 23 shows total flowrates (including fluorine) and makeup-fluorine flowrates into the fluorinator for Runs Pu-14 and -15. Figure 24 shows the superficial gas velocities through the bed.

In Run Pu-14, the bed temperature (initially at 300°C) was increased incrementally 25°C whenever the rate of PuF_6 collection at the cold traps (as measured by the neutron flux from the α-n reaction) appeared to decrease. The maximum bed temperature of 550°C was held arbitrarily for 5 hr.

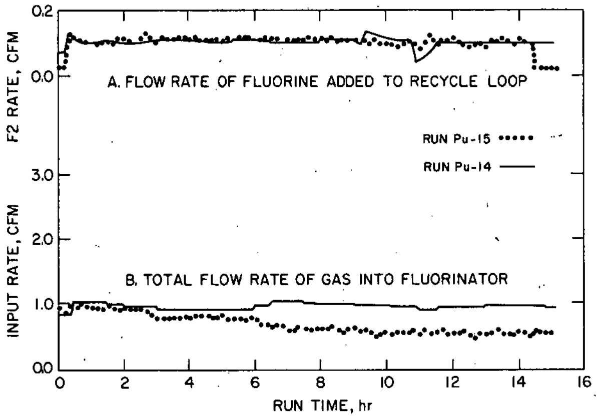


Fig. 23. Flowrates in Runs Pu-14 and -15 (fluorination periods)

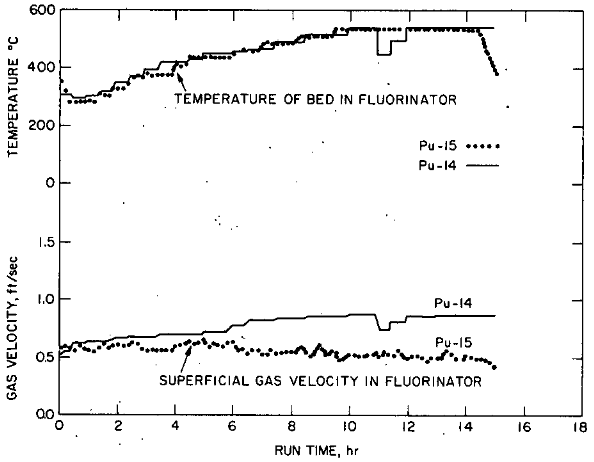


Fig. 24. Gas Velocity and Bed Temperature in Runs Pu-14 and -15 (fluorination periods)

Bed temperatures in Run Pu-15 were programmed similarly to Run Pu-14; neutron count-rate data were also recorded. Indicated bed temperatures, shown in Fig. 24 for Runs Pu-14 and -15, were about 15-20°C below the control temperature. Since the lower temperatures were used in the gas-velocity calculations, the calculated values are understated slightly.

When a run was finished, nitrogen was substituted for fluorine, the fluorinator heating circuits were shut down, and the bed was cooled by increasing the fluorinator coolant flow to the maximum.

The gas temperature in the filter chambers in the fluorinator was held near 125°C in each run. Gas and skin temperatures in Run Pu-15 are shown in Fig. 25. Each of the two filters was blown back every 30 min, using a 1-sec pulse of 92-psig nitrogen.

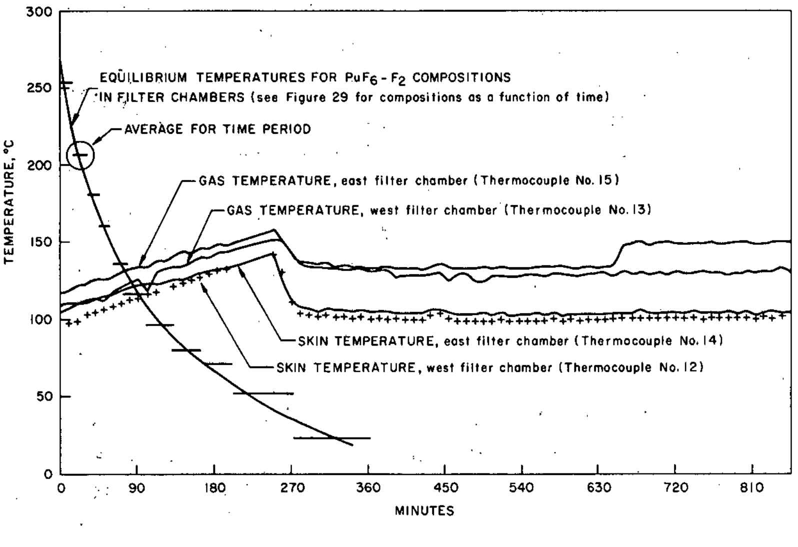


Fig. 25. Filter-chamber Gas Temperatures in Run Pu-15

The temperature of the coolant circulating through the cold traps was lower than -65°C in both runs. Cold-trap skin temperatures were kept at 50°C to prevent premature desublimation, which might cause plugging at the inlet.

After the fluorination step, the carrier-gas transfer of PuF_6 from the cold traps to a NaF-filled trap was completed. Next, the lines and equipment were fluorinated to recover any plutonium deposits. During this 12-hr cleanup fluorination period, the fluorinator bed was maintained at 550°C to determine how low a level of plutonium could be reached. The additional bed fluorination was carried out in both runs.

7.3.2.3 Carrier-gas Transfer of PuF_6 from the Cold Traps to a NaF-filled Trap. The PuF_6 that had been collected in the cold traps was transferred onto sorbent NaF by the following procedure: Nitrogen at 2 scfh was passed through the in-series cold traps, which at the start of this operation were still being cooled, and through a NaF-filled trap located in the exit line of the second cold trap. Cold-trap temperatures were gradually increased by heating the coolant to 80°C and simultaneously raising the skin temperature of the cold trap to 80°C. The nitrogen flow was continued for 7 hr, probably an excessively long time since neutron count data indicated that transfer was complete within 2 hr. Samples were removed from each of three 900-g portions in the NaF trap.

7.3.3 Results and Discussion

7.3.3.1 Plutonium and Uranium Removal from the Bed. The data for bed samples taken in Runs Pu-14 and -15 are plotted in Fig. 26. Although fluidizing-gas flowrates differed slightly, these two experiments were considered a replicate pair, and, in general, the results were similar. The rates of plutonium removal from alumina were nearly identical, and both experiments showed final plutonium concentrations in the range 0.010 to 0.015 wt %. A small buildup of plutonium in the final bed was evident after bed reuse in Run Pu-15.

On the basis of bed-sample analysis, the plutonium concentration reached a steady-state value when the reactor was at 500°C; no additional plutonium was removed from the bed during the 17-hr period at 550°C (including the 12-hr cleanup period). If the operating temperature during the final period of the recycle-fluorination step could be reduced from 550 to 500°C, a significant process improvement would be achieved in terms of reducing corrosion and high-temperature stress of materials.

The final plutonium concentration in the alumina bed from Run Pu-13 (0.005 wt %) using PuF_4 powder as the feed material was lower than that achieved in runs simulating the interhalogen flowsheet (Runs Pu-14 and -15). The presence of other elements, such as uranium and fission products in

Runs Pu-14 and -15, and a different form of the PuF_4 may have accounted for this difference. However, the level of residual plutonium in the bed from Run Pu-15 is considered satisfactory, since this bed had been used in the processing of about 75 g of plutonium. A final value of 0.015 wt % represents the retention of about 1 g of plutonium or about 98.7% removal. Corresponding values for overall plutonium removal achieved in experiments with PuF_4 alone were about 99.7%.

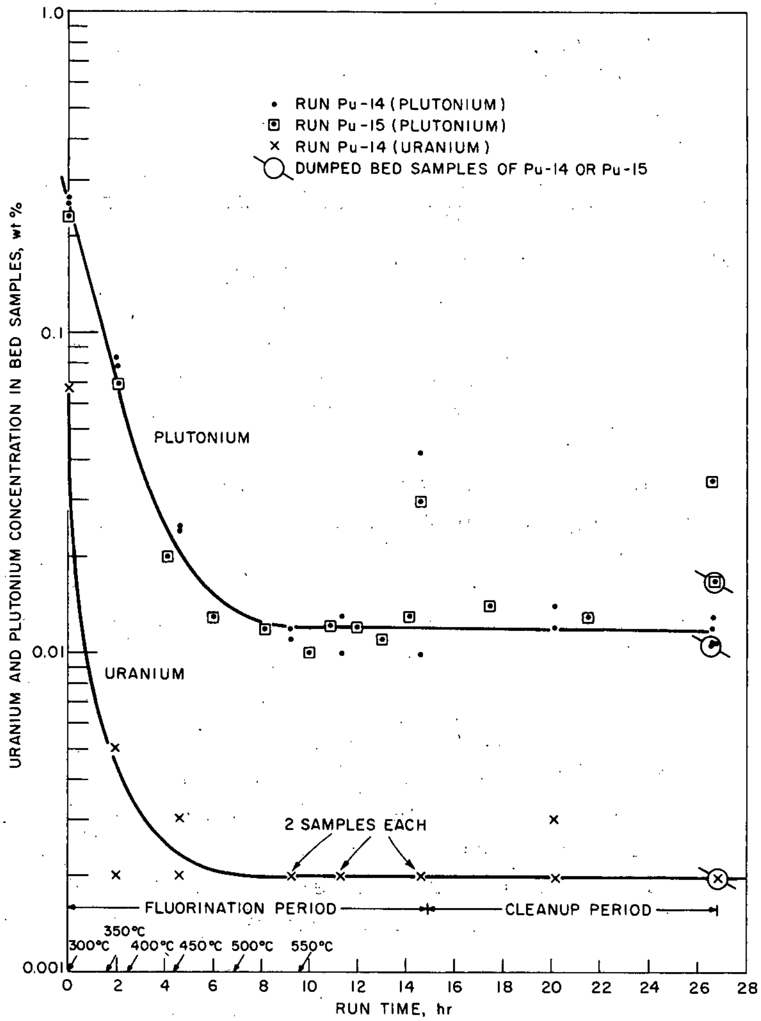


Fig. 26. Uranium and Plutonium Concentrations in Bed Samples. ANL Neg. No. 308-864.

Removal of the uranium that remained after the BrF_5 step was rapid and complete. The concentration of uranium in the final alumina bed for Run Pu-14 was 0.002 wt %, representing more than 99.9% removal. In all runs performed in the facility, the uranium concentrations in the final beds have been less than the plutonium concentrations.

Samples taken from the fluid bed before Runs Pu-14 and -15 showed plutonium concentrations of 0.26 and 0.23 wt % (see Fig. 27). Calculated

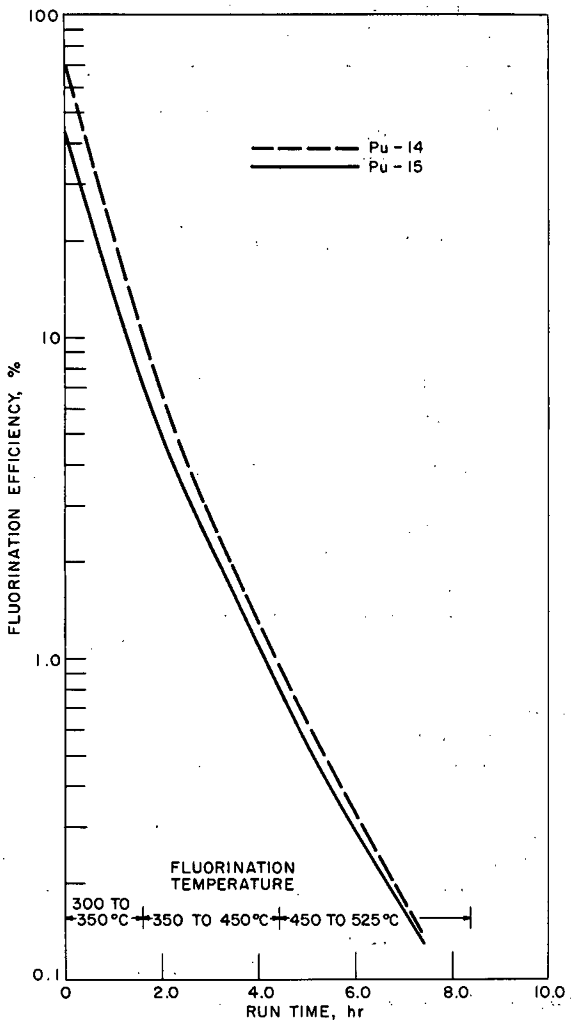


Fig. 27. Fluorination Efficiency vs Time: Runs Pu-14 and -15. ANL Neg. No. 308-863.

values for plutonium concentrations based on analyses of the feed were 0.30 and 0.31 wt %, respectively. The difference between the observed and calculated values is attributed to the more general problem of sampling a nonhomogeneous bed. Most of the plutonium charged in Runs Pu-14 and -15 was in material in the 60 to 120 mesh range, rather than in a -325 mesh fraction as in the earlier runs with PuF_4. However, even with this coarser plutonium material, there appears to be a bed sampling problem when the bed is fluidized.

7.3.3.2 Analysis of Final Samples from Top, Middle, and Bottom of Bed.

Previous work indicated that analyses of grab samples of the fluidized bed showed significantly lower plutonium concentrations than analyses of samples taken from the final bed after the bed was withdrawn from the reactor and blended. This behavior was attributed to return of the plutonium fines from the upper section of the reactor to the bed after fluidization was terminated. To test this postulate, the bed of each run was emptied through the bottom valve of the fluorinator in three portions. Some mixing between portions might have occurred, since the core of the bed would tend to drop out first. The data (Tables 16 and 17) show that, in Run Pu-15, analyses for the upper portion (10% of the bed) were 0.014 and 0.027 wt % plutonium and that the remainder of the bed analyses were about 0.015 wt % plutonium. In contrast, in Run Pu-14, the samples from the top and bottom of the bed had identical plutonium concentrations. Therefore, more data would have to be obtained to corroborate the behavior. If the top portion did indeed contain more plutonium than lower sections, a method for reducing the loss of plutonium with the alumina bed would involve withdrawing only the lower portion of the bed and retaining the upper portion for further processing in the fluorination of subsequent fuel charges. A better understanding of mixing as a function of particle-size distribution would be helpful in attaining homogeneity in the bed and therefore facilitate obtaining representative bed samples.

TABLE 16. Uranium and Plutonium Concentrations in Top, Middle, and Bottom Portions of Pu-14 and -15 Final Beds

		Run Pu-14		Run Pu-15	
		% Plutonium	% Uranium	% Plutonium	% Uranium
Top portion of	Sample 1	0.010	0.002	0.027	0.011
	Sample 2	0.011	0.002	0.014	<0.001
	Sample 2 (Sum of sieved fractions)			0.029	0.015
Middle portion of	Sample 1	0.011	0.003	0.017	0.005
	Sample 2	0.011	0.002	0.013	0.002
Bottom portion of	Sample 1	0.012	0.001	0.015	0.003
	Sample 2	0.011	0.002	0.015	0.004

TABLE 17. Uranium, Plutonium, and Fluoride Concentrations in Sieved Fractions of Sample 2 of Top Portion of Run Pu-15 Final Bed

		Plutonium		Uranium		
Sieve Fraction Size	Weight Fraction	%	Grams per 100 g	%	Grams per 100 g	Fluoride, %
+25 Mesh	0.0027	0.002	0.00001	0.009	0.00003	Not submitted
-25 +60	0.0986	0.017	0.00167	0.003	0.00030	2.92
-60 +80	0.6058	0.037	0.02241	0.021	0.01272	2.68
-80 +120	0.2429	0.022	0.00534	0.009	0.00219	3.26
-120	0.0050	0.037	0.00018	0.014	0.00007	6.49
Total	1.0000		0.02961		0.01534	

The top portion of the Pu-15 final bed was sieved, and the fractions chemically analyzed. Only 0.005 of the final bed was smaller than -120 mesh. Therefore the present test of the postulate that sufficient fines fall back onto the bed after fluidization has stopped, confounding sampling results, may not be fully valid. No trend in plutonium or uranium concentration was observed with decreasing particle size, but the fluoride content did increase with decreasing particle size. About 6% of the larger-sized Al_2O_3 was converted to AlF_3, but about 10% of the -120 mesh material was converted. The Al_2O_3 had been contacted with fluorine for about 50 hr at temperatures mostly above 450°C.

7.3.3.3 Fluorination Efficiency. Fluorination efficiency is defined as the amount of PuF_6 produced in a given period divided by the theoretical amount produced at equilibrium considering the reaction

$$PuF_4 + F_2 \rightarrow PuF_6.$$

Fluorination efficiencies were calculated for the fluorination periods for Runs Pu-14 and -15 using fluidized-bed sample analyses as the basis (see Fig. 27). Since this calculation considered all plutonium that had left the bed, including the plutonium that had been elutriated but not necessarily fluorinated, the values shown represent the maximum expected efficiencies. The efficiency was high (~50%) initially and decreased rapidly as the PuF_4 was fluorinated. The slightly higher efficiencies for Run Pu-14 than for Run Pu-15 may be the result of the slightly higher fluorine throughput rates in Pu-15.

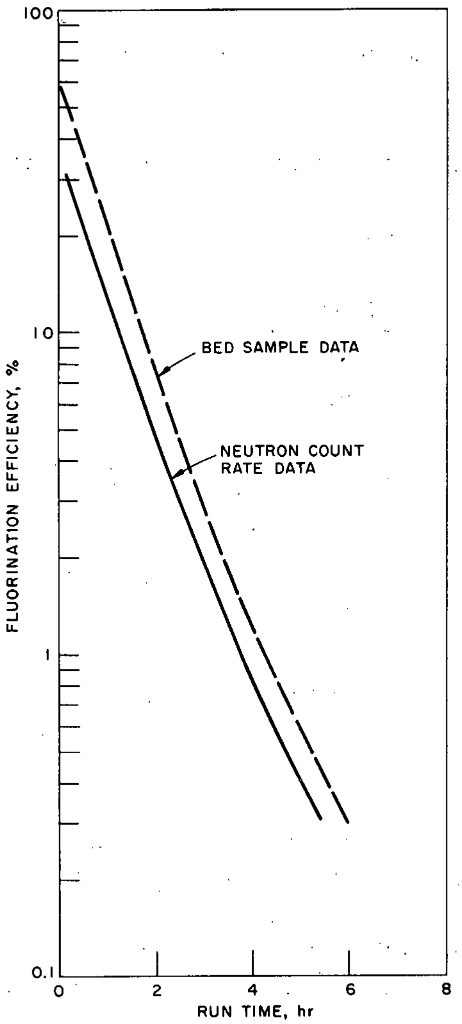


Fig. 28

Fluorination Efficiency in Run Pu-14 as Determined from Neutron-count-rate Data and as Calculated from Bed-sample Analyses. ANL Neg. No. 308-844 Rev. 1.

Figure 28 compares fluorination efficiencies calculated on the basis of bed-sample analyses and on the neutron count rate at the PuF_6 cold trap for Run Pu-14. The neutron count rate was considered to be directly proportional to the plutonium level. As expected, efficiencies calculated from the neutron data are lower, since they reflect only the PuF_6 recovered, as opposed to the bed data, which reflect plutonium removed by both fluorination to PuF_6 and elutriation of PuF_4. The accuracy of the values obtained by neutron counting cannot as yet be established. With experience, the neutron counter may provide direct quantitative information about the PuF_6 collection rate, and efficiencies may then be calculated as the run proceeds.

7.3.3.4 Efficiency of PuF_6 Cold Traps. The efficiency of the cold-trap system for condensing PuF_6 from the recycle gas stream was determined in Runs Pu-14 and -15. The system consists of two inverted U-shaped cold traps in series, chilled by recirculating trichloroethylene (coolant temperature, -65 to -70°C). A NaF trap (at ~100°C) served as a backup trap to collect any PuF_6 that passed through the cold trap as vapor. The backup trap was assumed to be 100% efficient, since in previous experiments little plutonium has been found downstream of this trap (in either the activated alumina towers or the scrubbing system).

Efficiency of cold trapping was determined indirectly by the following method:

a. The PuF_6 collected during each fluorination experiment was vaporized from the cold trap in a nitrogen carrier-gas stream at 70°C and collected in a NaF trap. The plutonium content of the NaF was then determined.

b. The cold traps were then exposed to fluorine for 12 hr at 300°C to remove any residual plutonium. This PuF_6 was sorbed on a separate NaF trap.

c. The plutonium content of the backup NaF trap was determined.

The amount of plutonium collected (in grams) in a, b, and c was:

	a	b	c	Efficiency
Run Pu-14	15.9	1.0	1.9	90%
Run Pu-15	18.9	0.6	0.7	96%

The total plutonium input was assumed to be the sum of a, b, and c; efficiency was expressed as

$$\frac{a + b}{a + b + c} \times 100.$$

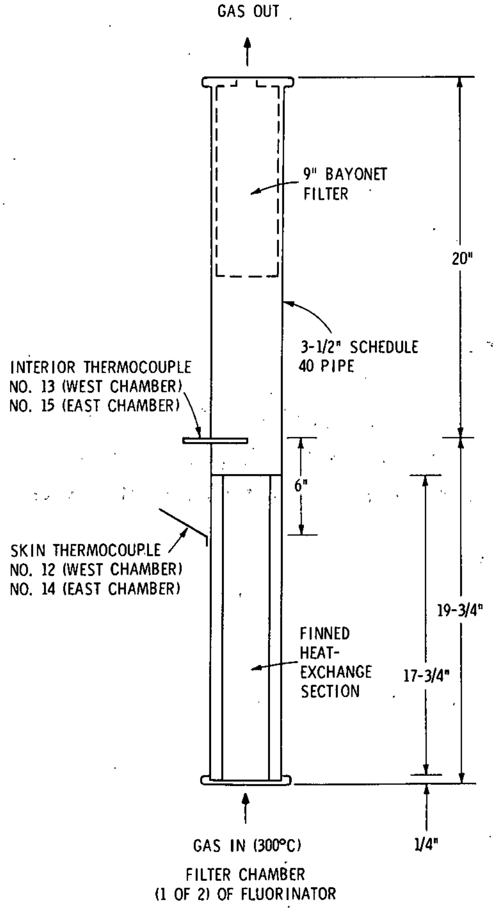
Efficiencies of 90 and 96% were obtained for the two runs. The higher efficiency in Run Pu-15 may reflect the lower overall gas velocity and the observed lower coolant temperatures.

The "loss" of PuF_6 to the backup NaF trap corresponded to the amount of PuF_6 that would remain as vapor in a saturated gas stream at about -60°C, calculated by extrapolation of vapor-pressure data.[8,9] This implies that the cold traps actually operated at 100% efficiency during the run and that a higher fraction of the input PuF_6 can be collected by operating at lower temperatures.

On the basis of this calculation, the loss of PuF_6 through the cold trap appears to be a function of cold-trap temperature and not due to "snow" formation. Since the temperature of the cold trap is near the minimum for the existing refrigeration system, the limit of trapping efficiency appears to have been reached.

7.3.3.5 F.P. Data. No information could be obtained on the movement of molybdenum and ruthenium during the fluorination step, because the concentrations of these elements in the as-received beds (J-2 and -3) were below the detectable limit of 0.005 wt %. More than 95% of the molybdenum and 90% of the ruthenium had already been removed in the oxidation and BrF_5 steps conducted in the laboratory unit. No detectable amounts of these elements were found in the PuF_6 product or in any samples taken from the sorbent traps. The cesium concentration in the bed was constant during the run at approximately 0.35 wt %.

7.3.3.6 PuF$_6$ Thermal Decomposition. In the heat-exchange section of the filter chambers of the fluorinator, the gas from the fluorination zone is cooled from the fluorination temperature (usually 300°C or above) to approximately 150°C to prevent corrosion damage to the filters. During the early part of the fluorination run, it is possible to have the PuF_6/F_2 ratio in the gas from the fluorination zone exceed the PuF_6/F_2 equilibrium ratio[10] for the temperature at which the filters are operating, a condition that might result in decomposition of some PuF_6 to PuF_4 with the release of fluorine. In Fig. 25, the equilibrium temperature for the PuF_6/F_2 gas mixture entering the filter chamber is plotted as are the temperature curves of the four thermocouples in the two filter chambers. (The relative positions of the thermocouples are shown in Fig. 29.) Since, in the first 80 min of the run, the gas-mixture equilibrium temperature is higher than the temperature in the filter chamber, almost 50% of the plutonium (20 g) should be decomposed to PuF_4 (from equilibrium considerations).



	Average Temp in Zone, °C	0000-0015	0015-0030	0030 0045	0045-0060	0100-0115	Fluorination Run Time
		5.44	3.39	2.38	1.16	1.13	Plutonium Fluorinated in This Time Period, g
		Fraction of Plutonium Passing through Zone (1 - F)[a]					
0.3'	122	>0.9999	>0.9999	>0.9999	>0.9999	>0.9999	
0.3'	133	>0.9999	0.9999	>0.9999	>0.9999	>0.9999	
0.3'	157	>0.9999	>0.9999	>0.9999	>0.9999	1.0000	
0.3'	197	>0.9994	>0.9994	1.0000	1.0000	1.0000	
0.3'	260	1.0000	1.0000	1.0000	1.0000	1.0000	

[a] $F = \frac{R_0 - R_t}{R_0(1 + R_t)}$, where F is the fraction PuF_6 decomposed; for definitions of other terms see p. 76.

Fig. 29. Decomposition of PuF_6 in Heat-exchange Section of Fluorinator Filter Chamber during Run Pu-15

Actually, when the kinetics of the decomposition are considered using the model proposed by Trevorrow and Steindler, less than 0.1% should decompose. The equations for the rate calculations are

$$\log \frac{R_t - K}{R_0 - K} = -kt\left(1 + \frac{S}{V}\right)^*$$

and

$$\log k = -\frac{3750}{T} + 5.625,$$

where

R_t = PuF_6/F_2 molar ratio at time t,

R_0 = PuF_6/F_2 molar ratio at time t_0,

K = equilibrium constant, moles PuF_6/moles F_2,

k = rate constant, moles PuF_6/moles F_2,

T = temperature, °K,

t = time, min,

S/V = surface to volume ratio of system, cm^{-1},

and

$$F = \frac{R_0 - R_t}{R_0(1 + R_t)},$$

where F is the fraction of PuF_6 decomposed.

Figure 29 is a drawing of the heat-exchange section of the filter chambers. For the calculation, the chamber volume was divided into five temperature zones, and the gas temperature profile along the length was calculated from the formula

$$\frac{T_{gas} - T_{wall}}{T_{gas\ inlet} - T_{wall}} = e^{CL},$$

where

C = -1.63,

T = temperature, °C,

and

L = distance from the gas inlet, ft.

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[*] This equation has been modified slightly since the calculations were made. Conclusions are the same using the modified equation. See Ref. 11.

The table in Fig. 29 shows the calculated values for 1 - F, the fraction of PuF_6 passing through the zones, as a function of the operating conditions. For a portion of the length, no PuF_6 would decompose, since the equilibrium ratio at the zone temperature would not be exceeded. In the remaining zones, the rate would be so low that less than 0.1% of the PuF_6 would decompose, or less than 0.2 g in each of the Runs Pu-14 and -15. However, in each run, about 3 g of plutonium was recovered from the upper part of the fluorinator. The conclusion would be that, if the proposed model is correct, the plutonium present in the filter regions must be there, (1) because of elutriation of PuF_4 from the bed, or (2) because of a reduction reaction of PuF_6 with metal or some other system constituent, since thermal decomposition of PuF_6 is negligible under present operating conditions.

7.4 Miscellaneous

7.4.1 Sorption of PuF_6 by NaF

Sorption of PuF_6 on NaF at 100-150°C proved to be a highly efficient method for collection of the PuF_6 product. Although plutonium cannot be readily recovered from the NaF bed, this method of collecting the plutonium was more convenient than condensation of PuF_6 in refrigerated traps, because it facilitated the obtaining of samples for analysis.

Sorption performance data are summarized in Tables 18 and 19, respectively, for the traps used in the plutonium cleanup step following Run Pu-3 and those used in Runs Pu-14 and -15. As shown in both tables, most of the plutonium was sorbed in the inlet third of the NaF bed. In one trap (Table 18, Trap 5), for which the bed was at 50°C because of heating problems, the sorption efficiency was lower than with traps held at 100°C. Within the ranges used in these tests, sorption efficiency was not affected by gas velocity or by the quantity of PuF_6.

TABLE 18: Distribution of PuF_6 in NaF Traps in Run Pu-3

Trap No.	Superficial Gas Velocity through Trap, ft/min	Trap Temperature Range,[a] °C	Total Pu Content of Trap, g	Percent of Pu Found in Given Portion of Trap: Inlet Third	Middle Third	Exit Third
1	2	90-96	2.1	99.5	0.2	0.3
2	2	90-96	2.4	93.9	0.4	5.7
3	2	90-96	3.0	94.7	<0.1	5.3
4	2	124-160	4.0	98.2	0.6	1.2
5	2	50-50	6.7	63.1	34.5	2.4
6	6	107-130	17.4	96.3	3.7	<0.1
7	7	80-150	97.4	96.8	3.1	0.1
8[b]	7	100-136	0.8	82.9	7.3	9.8

[a] Range determined from two or three skin-temperature measurements.
[b] In series with Trap 7.

TABLE 19. Sorption of PuF_6 on NaF in Runs Pu-14 and -15

NaF Trap Location	Trap Section	Superficial Gas Velocity, ft/min	Run Pu-14 Plutonium Concentration of NaF, wt %	Run Pu-14 Weight of NaF, g	Run Pu-14 Superficial Contact Time, sec	Run Pu-15 Plutonium Concentration of NaF, wt %	Run Pu-15 Weight of NaF, g	Run Pu-15 Superficial Contact Time, sec
Process off-gas line (5-3/4-in. ID by 11 in.)	1	0.8	0.151	1260	45	0.320	1177	45
	2		0.080	1466		0.005	1132	
	3		0.030	1784		0.027	2196	
Downstream of cold traps, used in inert-gas PuF_6 transfer step (2-7/8-in. ID by 24 in.)	1	1.0	1.850	873	120	2.578	909	120
	2		0.003	878		0.003	876	
	3		<0.001	900		<0.001	879	
In exit line of fluorinator during cleanup step (2-7/8-in. ID by 24 in.)	1	20-36	0.313	878	Varied 3.3-6.0	3.189	1000	Varied 4.3-6.2
	2		0.002	864		0.002	657	
	3		<0.001	874		0.002	952	
In exit line of cold trap during cleanup step (2-7/8-in. ID by 24 in.)	1	20-36	0.110	874	Varied 3.3-6.0	0.088	880	Varied 4.3-6.2
	2		0.001	874		0.002	873	
	3		0.006	879		0.001	880	

In obtaining the data shown in Table 19, the plutonium hexafluoride was sorbed on NaF in two sizes of traps. The process off-gas trap (located downstream of the cold traps) had a $5\frac{3}{4}$-in. ID and about an 11-in. height; the other traps had a $2\frac{7}{8}$-in. ID and a 24-in. height. All traps were operated at about 100°C. Flow was upward in the process NaF trap and downward in the others. As shown in Table 18, the PuF_6 was removed effectively in the smaller-diameter traps in the first 8-in. section of NaF (average contact time of about 5 sec). Sorption efficiency was poorer in the $5\frac{3}{4}$-in.-ID trap--possibly because of poor gas distribution. Consequently, a smaller-diameter, taller trap was preferred. A consideration in design, of course, is the pressure drop through the trap.

7.4.2 Plutonium Concentration in Samples Removed from Reactor Surfaces and Filters

Wall scrapings from the fluorinator and secondary filter chamber and the fine layer of powder on the primary filters were sampled for plutonium analysis. Analytical data (Table 20) indicate that the concentration of

TABLE 20. Plutonium Concentration in Samples Removed from Internal Reactor Surfaces of Fluorinator

Run		Pu, %	U, %	Comments
Pu-2	East filter	3.19	19.6	
Pu-4	Scrapings removed from fluorinator filters during the plutonium cleanup step. Filters had been at 250°C in concentrated fluorine for 19 hr.			
	West filter, upper section	1.11	0.16	
	lower section	0.15	0.03	
	East filter, upper section	1.43	0.13	
	lower section	0.65	0.06	
Pu-11	Sample removed from secondary filter	6.6	0.03	Probably high plutonium content because of holes in filters used in Runs Pu-10 and -11
Pu-1	Disengaging section	15.6	29.2	
Pu-2	Disengaging section	20.2	3.8	
Pu-11	Disengaging section	1.8	-	
Pu-11	Disengaging section	0.59	0.006	
Pu-11	Main reaction section	0.67		41.2% fluoride
Pu-11	Charge port	1.00	0.002	
Pu-11	West filter chamber	10.6	0.02	
Pu-11	East filter chamber	0.98	0.04	
Pu-11	Secondary filter chamber	8.0	0.11	0.03% fluoride

plutonium in the samples was relatively high and covered a broad range, 3-20%. Many of the samples were taken after Run 11, the experiment in which filter burnout occurred, so some of the data may be atypical. Even though the concentrations are high, the total quantity of plutonium on the entire upper wall area was small, because the coating was quite thin. A cleanup fluorination treatment would be expected to reduce the plutonium levels, as indicated in the samples removed from the filters after Run Pu-4, in which the filters were exposed to concentrated fluorine at 250°C for 19 hr; the plutonium concentration in these samples ranged from 0.15 to 1.43%.

8. THERMAL DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE

8.1 Introduction

The fluoride-volatility flowsheet described in the introduction of this report produces a mixed plutonium-uranium hexafluoride product. The type of further processing of this material is dictated by the end use of the fissile and fertile components. Both separation and purification steps may be needed. In either case, conversion of the plutonium to a form more stable than the hexafluoride such as solid PuF_4 or PuO_2 is required.

Separation of the plutonium from the uranium, with simultaneous conversion of the PuF_6 fractions to solid PuF_4 by thermal decomposition, appeared feasible on the basis of kinetic and mechanistic laboratory studies.[10,12,13] Technology and experience with fluidized beds in studies[2] on the conversion of UF_6 to the dioxide suggested that a fluid-bed approach be explored.

A brief but successful proof-of-principle program on fluid-bed thermal decomposition was carried out in a 2-in.-dia fluid-bed reactor installed in the engineering-scale alpha facility. Mixed PuF_6-UF_6 feeds containing representative F.P. fluorides were produced in the fluorination system in the same facility (Runs Pu-1, -2, and -3). Details and results of the work are described below.

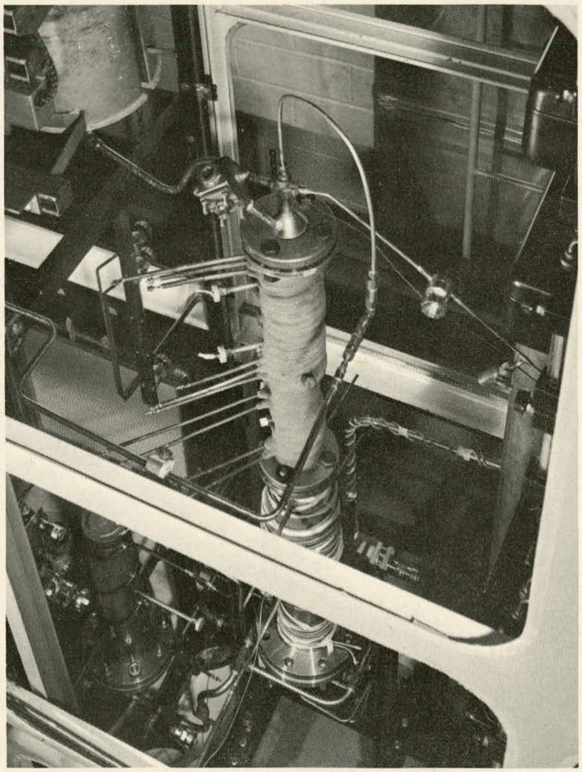

Fig. 30. Fluid-bed Thermal Decomposer Mounted in Large Alpha Box. ANL Neg. No. 108-7889.

8.2 Equipment

The equipment train consisted of a hexafluoride feed station, a 2-in.-dia fluid-bed reactor, a secondary filter, and cold traps (used in common with the fluorinator) for collection of the UF_6. The off-gas was vented through the fluorinator vent system, which consisted of a NaF trap, activated alumina traps, scrubbers, and filters. A separate off-gas system installed for use with the 2-in.-dia reactor for studies on the conversion of the mixed hexafluorides to oxides was bypassed for the thermal-decomposition work. Figure 30 shows a view of the fluid-bed column as installed in the Alpha Facility. Details of the equipment were described in Section 5.3.

8.3 Operating Conditions

Operating temperatures and flows were selected mainly on the basis of the earlier laboratory work. These conditions were tested in an equipment shakedown experiment with UF_6. Conditions were similar for the subsequent experiments with the UF_6-PuF_6 mixtures, except for the bed temperature, which was tested at 350 and 300°C. The lower temperature was used after the first plutonium experiment (see Table 21) in an effort to reduce the level of uranium codeposition with the PuF_6 product.

TABLE 21. Average Operating Conditions for Fluid-bed Thermal-decomposition Studies

Equipment: 2-in.-dia Inconel reactor

Bed material:[a] 2.4 kg of Alcoa T-61, -100 mesh alumina (18-in. static-bed height)

Run	Bed Temp, °C	Hexafluoride Feed Rate, g/min	Superficial Fluidizing-gas Velocity, ft/sec	Run Duration, hr	Inlet Gas Composition, % Hexafluoride in Nitrogen
Shakedown	300	19	0.15	6.8	40
DUP-4	350	18	0.17	9.6	37
DUP-5	300	20	0.17	8.2	37
DUP-6	300	21	0.15	7.6	45

[a] Fresh alumina beds were used for the first three experiments. The final bed from Run DUP-5 was used as the starting material for Run DUP-6.

The starting bed consisted of -100 mesh Alcoa T-61 alumina (average particle size ~90 μ; minimum fluidizing velocity ~0.05 ft/sec); the sieve analysis of this material is given in Table 22. A relatively fine mesh alumina was chosen so that a low gas velocity could be used for fluidization, thus maximizing gas residence time in the bed. The calculated residence time, based on the superficial velocity of ~0.15 ft/sec, was about 10 sec. Fresh alumina beds were used for the shakedown experiment, and again for the first and second plutonium experiments. The bed from the second plutonium experiment was reused in the last experiment. Since the bed would be coated with PuF_4 after a single use, the present scheme simulated the use of a bed of PuF_4.

The reactor and associated lines and the starting bed were prefluorinated with fluorine as a part of the shakedown run to minimize interaction between the hexafluorides and the materials of construction. Final prefluorination conditions were 300°C and 75% fluorine in nitrogen for 1 hr. The filter-region temperature did not exceed 100°C during prefluorination.

TABLE 22. Physical Properties of Alumina Used for Fluid-bed Thermal-decomposition Studies

USS Sieve Size	Run DUP-5 Start	Run DUP-5 Final	Run DUP-6 Final, % on Given Sieve
	% on Given Sieve		
80	1.3	1.0	3.7
120	4.7	4.4	2.5
170	21.3	20.0	18.3
230	18.6	17.5	15.2
325	18.6	18.6	16.1
-325	35.5	38.5	44.2
Tapped bulk density, g/cc	2.3	2.2	2.2
Surface area, sq m/g	0.17[a]	0.22[a]	0.19

[a] Data for the earlier run, DUP-4, which employed similar alumina to that used in Runs DUP-5 and -6.

Separate 10-kg batches of UF_6-PuF_6 mixtures produced in the fluorination of nominally 0.5 wt % PuO_2-UO_2-F.P. pellets were processed in the three thermal-decomposition experiments. Small quantities of molybdenum and ruthenium fluorides were present, having been formed in the fluorination process. The feeds for the first two decomposition experiments contained less than the expected quantities of plutonium, as a result of low plutonium yield in the preceding (fluorination) step. This became known only after these two decomposition experiments were completed and analytical results were received. Additional PuF_6 was spiked into the final batch of UF_6-PuF_6 feed to ensure a reasonable plutonium input. Manipulation of the PuF_6 "spike" material involved several small nickel vessels and auxiliary piping. As a precautionary measure to minimize interaction of the PuF_6 with these materials, the equipment used in the transfer was pretreated, first with ClF_3, then with PuF_6 itself. The amount of PuF_6 actually fed during an experiment was determined by the change in the weight of the feed vessel, by plutonium analysis, and by the change in the weight of the hexafluoride feed cylinder due to the "spike."

Average values for the concentrations of plutonium in the successive feeds were 0.02, 0.13, and 0.43 wt %. These values were calculated on the basis of plutonium accounted for (sum of bed and off-gas content) rather than being obtained by direct analysis of the feed hexafluoride, since there was considerable scatter in the analyses of feed samples. Liquid sampling of mixed hexafluorides containing PuF_4 particulate material remains problematical. Vapor sampling appeared promising, but needs further study.

8.4 Operating Procedure

Detailed check sheets were used for each experiment to ensure that equipment and instrument inspection was conducted properly. Leak-testing was done carefully; also, since several systems were common to the fluorinator and the decomposer, particular attention was given to setting valves to ensure that the appropriate gas path had been set.

With the reactor bed charged, fluidization was started using nitrogen. The reactor was brought to temperature. Meanwhile, the 10-kg batch of hexafluoride had been sampled while installed in a heated rocker-sampler box (see Fig. 31 and Appendix F). The sample was hydrolyzed, preparatory to analysis (see hydrolysis procedure, Appendix G). The feed cylinder was then positioned in the feed manifold and was brought to temperature (~80°C). Hexafluoride flow was started, initially at a low rate, but flow quickly was brought up to the desired rate and placed on automatic control.

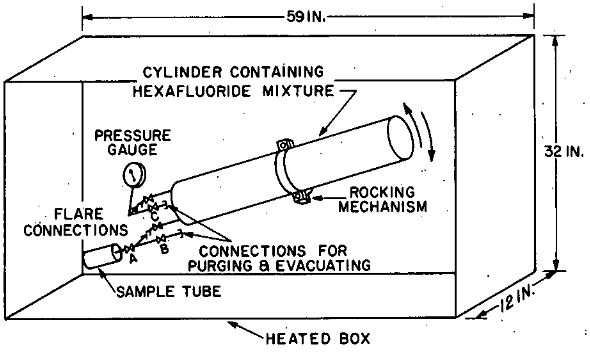

Fig. 31. Heated Rocker-Sampler Box

The bed and the off-gas were sampled on a preset schedule. Operating data were logged automatically with the data logger; in addition, selective data were taken manually on a given schedule.

The procedure also included sampling of the final bed after it was withdrawn from the reactor and sampling of powder recovered separately from the filter regions or other internal reactor surfaces. The overhead (UF_6) product was sampled after it had been transferred from the cold traps to a fresh receiver; UF_6-PuF_6 remaining in the feed vessel was also sampled for material-balance purposes.

8.5 Results

The success of the thermal-decomposition process was measured in two ways: by the low plutonium content of the overhead UF_6 product stream, and by the plutonium inventory in the bed. Results of only the last two experiments (Runs DUP-5 and -6) were used in this analysis, since the feed for Run DUP-4 apparently contained little volatile plutonium.* Samples

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*Data from Run DUP-4 indicate that less than 0.1 g of plutonium was fed to the reactor.

of the bed taken during the runs gave information on the rate of plutonium buildup on the particles. Final bed analyses and overall inventories allowed back-calculation of the input plutonium concentrations. Analysis for molybdenum and ruthenium in the various streams gave some insight into F.P. behavior in the decomposition process.

8.5.1 Plutonium Content of the UF_6 Product Stream

The plutonium content of the overhead UF_6 product stream served as a measure of the completeness of separation of plutonium from uranium. Overhead vapor samples taken at approximately hourly intervals in Runs DUP-5 and -6 contained very low levels of plutonium, the average of six samples in one case and seven samples in the other being less than 0.001 wt %. In contrast, calculated feed values were 0.13 and 0.34 wt %, respectively. Analyses of these samples, reported in Table 23 as uranium-to-plutonium ratios, also showed no trend of increasing or decreasing plutonium concentration as the run progressed. The ratios ranged from 0.9×10^5 to 2.9×10^5 for Run DUP-5 and from 1.0×10^5 to 1.8×10^6 for Run DUP-6. The analysis of a liquid and a vapor sample from the UF_6 product receiver for Run DUP-6 confirmed the low (<0.001 wt %) plutonium content of this stream. The variance of the U/Pu ratios was considered acceptable at these low plutonium levels.

TABLE 23. UF_6 Product-stream Analyses

Elapsed Run Time, hr:min	10^{-5} x U/Pu in Overhead Grab Samples	
	Run DUP-5	Run DUP-6[a]
1:05	-	0.96
1:18	1.3	-
2:02	1.5	9.5
3:01	1.2	4.6
4:01	2.9	6.4
5:01	2.9	18.0
7:00	0.9	1.4
7:34	-	6.6
Average	1.4	6.8

[a] Liquid and vapor hexafluoride samples taken from the UF_6 product after transfer from the cold traps to a receiver showed U/Pu ratios of 7.6×10^5 and 1.9×10^5, respectively, and are in agreement with these grab-sample data.

8.5.2 Bed Composition

Runs DUP-5 and -6 were considered as a unit, since a single alumina bed charge was used and run conditions were similar. Samples taken from the reactor after the bed had been fluidized but before feed was started showed initial plutonium, uranium, and fluoride contents of 0.001, 0.12, and 0.07 wt %, respectively, as a result of slight contamination from the previous experiment. After Run DUP-5, the corresponding values were 0.46, 0.24, and 0.19 wt %; after Run DUP-6, the values were 1.47, 0.40, and 0.68 wt %. The increase in plutonium concentration from ~0.001 to 0.46 wt % and then to 1.47 wt % represents plutonium accumulations of 9.2 and 22.6 g.

Codeposition of uranium appeared to be low at 300°C; about 6 g of uranium was deposited in Run DUP-5 and only an additional 3 g in Run DUP-6. In contrast, about 30 g was found after the earlier experiment (Run DUP-4), made at 350°C.

The mechanism by which uranium deposits in this process is not understood; thermal decomposition of UF_6 is not thought to be the cause. Uranium hexafluoride is considered reactive and could readily react with system impurities and the Inconel reactor itself. In any case, this small degree of contamination may not be significant in any plutonium recycle scheme. In fact, plutonium is likely to be used in combination with uranium in applications such as nuclear fuel materials for power reactors.

8.5.3 Separations Efficiency

The efficiency of separating plutonium from a UF_6-PuF_6 mixture was determined by comparing the ratios of uranium to plutonium in the feed to those in the UF_6 product stream (see Table 24). The input value

TABLE 24. Results of Fluid-bed Thermal-decomposition Studies

	Uranium/Plutonium Ratio	
Stream	Run DUP-5	Run DUP-6
Feed	700	290
Final bed	0.6	0.3[a]
Off-gas	0.9×10^5 to 2.9×10^5	1.0×10^5 to 1.8×10^6
UF_6 product		6.2×10^5 and 8.9×10^5 (liquid) 1.9×10^5 (vapor)
Separations efficiency, %[b]	99.2 to 99.8	99.7 to 99.99

[a] Cumulative value for Runs DUP-5 and -6.

[b] Based on range of off-gas analyses and calculated feed content:

$$\frac{\left(\frac{U}{Pu}\right)_{out} - \left(\frac{U}{Pu}\right)_{in}}{\left(\frac{U}{Pu}\right)_{out}} \times 100.$$

was calculated on the basis of the total plutonium found in the reactor plus that found in the UF_6 product container. Analysis of the series of vapor samples taken of the flowing UF_6 product stream provided the ratio of uranium to plutonium in the exit gas. Samples of the UF_6 in the product receiver for Run DUP-6 provided data that served as a check on the grab-sample results.

Input uranium-to-plutonium ratios for Runs DUP-5 and -6 were 700 and 290, respectively, based on 9.2 g of plutonium accounted for in Run DUP-5 and 22.6 g of plutonium accounted for in Run DUP-6. The final bed showed the accumulation of these amounts, or 31.8 g of plutonium.

Separations efficiencies* calculated on the basis of these data ranged from 99.2 to 99.8% for Run DUP-5 and 99.7 to 99.99% for Run DUP-6.

8.5.4 Hexafluoride Material Balances

Hexafluoride material balances were made for each experiment on the basis of the weights of material fed and collected. The bulk constituent was the UF_6, which was recovered in cold traps and then vapor-transferred to new receivers. The amounts of uranium and plutonium in bed and hexafluoride samples were included in these balances. Balances ranged from 98.7 to 100.5%, as follows:

Experiment No.	Net Input, kg	Net Collected, kg	Material Balance, %
DUP-4	10.04	9.92	98.7
DUP-5	9.32	9.34	100.5
DUP-6	9.76	9.71	99.6

8.5.5 Bed Properties

The particle-size distribution appeared to change only slightly during the approximately 16 hr of operation in Runs DUP-5 and -6; the extreme sizes of particles, +80 and -325 mesh fractions, both showed slight increases. The calculated average particle size remained about the same. If the average particle size is considered to be about 60 μ, the total amount of plutonium involved in these two experiments would represent an average coating thickness of only 0.1 μ. Decomposition on a surface provided by the fluidized-bed particles as opposed to gas-phase decomposition appeared to be preferential; only 1-2% of the plutonium was found in filter and column brushings.

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*Separations efficiency $= \dfrac{\left(\frac{U}{Pu}\right)_{out} - \left(\frac{U}{Pu}\right)_{in}}{\left(\frac{U}{Pu}\right)_{out}} \times 100.$

Surface areas determined by Brunauer-Emmett-Teller[14] (BET) measurements* on bed samples taken before and after Run DUP-4 showed an increase from 0.17 to 0.22 sq m/g, but the final value after two successive runs (DUP-5 and -6) with the same bed showed a value within this range, 0.19 sq m/g; therefore it is not certain that a significant change occurred.

It is difficult to extrapolate these data to what might be expected from long-term continuous operations with a PuF_4 bed, although the alumina base material, after its initial coating with PuF_4, can be considered as behaving like a bed of PuF_4. The major difference in materials would possibly be the density (crystal density of Al_2O_3 is 3.99 g/cc; that of PuF_4 is ~6.5 g/cc); the density of the deposited layer of PuF_4 was not determined.

8.5.6 Sampling of Hexafluorides

Reliable sampling of batches of mixed uranium-plutonium hexafluorides remains problematical, because of the instability of PuF_6. Particulate PuF_4 material is present, formed by the decomposition of PuF_6, and the problem is one of getting a representative sample of a very dilute slurry. The current technique of using a rocker assembly for mixing proved inadequate. Vapor sampling was expected to circumvent the problem of solids interference and appeared promising, particularly as the work progressed and the equipment was used repeatedly. Evidence of this lies in the results of the final experiment (Run DUP-6); vapor samples agreed within about ±10%; previously, differences ranged from a factor of two to several orders of magnitude. Proper pretreatment of lines and equipment with PuF_6 as a fluorinating agent may be necessary before sampling becomes reliable.

Sampling results depend also on the completeness of hydrolysis of the samples in the gas bulbs. A laboratory shaker, which was modified to handle the sample bulbs, was installed in the large alpha box to facilitate the hydrolysis work. Analysis of successive rinses with the standard hydrolysis solution showed that little additional plutonium was being recovered by rinsing, indicating that hydrolysis techniques were satisfactory. More than 99% of the plutonium (and uranium) was recovered in the initial hydrolysis, except for very low-level samples containing 0.001 to 0.005 mg of plutonium per sample. In these cases, rinses contained 10-50% of the amount of plutonium found in the original hydrolysis solution. The hydrolysis procedure that evolved is presented in Appendix G.

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*A Perkin-Elmer-Shell Model 212 Sorptometer (Perkin-Elmer Corp., Norwalk, Conn.) was used.

8.6 Discussion

8.6.1 Maximum PuF_4 Separation as Calculated from Equilibrium Considerations

The maximum separation of plutonium from the UF_6-PuF_6 feed is determined by the equilibrium of the reaction $PuF_6 \rightarrow PuF_4 + F_2$. Since there are three temperature zones in the reactor (300°C in the bed zone, 100°C in the filter zone, and a thermal transition zone between these two), the equilibrium shifts as the gas passes through the column. Decomposition occurs rapidly at the temperature of the bed, but is further promoted in the transition zone by the equilibrium shift.

Calculations of the maximum PuF_4 separation were based on the final experiment (Run DUP-6), since it involved the largest amount of plutonium. Considering only the bed zone, the equilibrium uranium-to-plutonium ratio was calculated to be 9.2×10^4. Using a calculated feed value based on the final bed analyses, we obtained a separation efficiency of 99.7%. Since the actual off-gas analyses showed ratios of $\sim 1 \times 10^5$ to 2×10^6 for the uranium-to-plutonium ratio, giving observed separation factors greater than 99.9%, further decomposition may have occurred in the gas phase. By direct extrapolation to a fast-reactor case involving 20 wt % plutonium feed, calculations give a separation efficiency of 99.5% for similar operating conditions, except that higher temperatures may be required.

Gas residence time in the bed in the present work, as determined from the superficial gas velocity of 0.15 ft/sec at column conditions, was less than 10 sec, and equilibrium was considered attained. For comparison, the minimum residence time to reach equilibrium at 300°C, as determined from work by Trevorrow,[15] is about 15 sec. A combination of process parameters that will maximize gas residence time and increase the efficiency of gas-solid contact is thus needed for good separations. Variables such as bed temperature, particle-size distribution, gas velocity, and feed concentration (diluent effect) are important in optimizing this process.

8.6.2 Effect of Surface Area

A good correlation between the surface area available in a given bed-size fraction and the amount of uranium in that fraction was found in Run DUP-4, although the mechanism for uranium deposition is not known. Bed samples were not analyzed for plutonium, since very little plutonium was present, nor was the analysis for plutonium performed in subsequent experiments. However, since thermal decomposition of the PuF_4 also resulted in deposition on the bed-particle surfaces, one may assume a similar correlation for plutonium.

The uranium content in this case was about 1.5%, about equal to the final plutonium content of the bed after Run DUP-6. The final bed from Run DUP-4 was divided into three portions, the +170 mesh fraction, the -170 +325 mesh fraction, and the -325 mesh fraction. Average particle diameters for these fractions were 132, 66, and 22 μ, respectively, as determined by averaging sieve sizes. From these values, the corresponding relationship of surface areas is approximately 0.46:0.91:2.73; these are in the ratio of 1:2:6. Upon analysis of the three fractions, the uranium contents were found to be in a 1:2:3.7 relationship, approaching that of the surface-area ratio. Deposition thus appeared to be directly associated with the available surface area.

8.6.3 Plutonium Decontamination from Ruthenium and Molybdenum in the Thermal-decomposition Process

The behavior of fission products in the thermal-decomposition process is of interest in recovery processes for plutonium. In the current process, ruthenium and molybdenum* fluorinated along with the uranium and plutonium to a volatile fluoride form. A fraction of this ruthenium and molybdenum was present in the feeds to the decomposer, having been transferred out of the cold traps with the UF_6 and PuF_6 at 80°C. (Unimportant to the present discussion, but perhaps of future interest, is that a fraction of the molybdenum and ruthenium remained in the cold traps as fluorides of lower volatility.)

Ruthenium analyses were given more attention in this investigation, since this element represents a long-lived gamma-active contaminant that would be of concern in fuel refabrication; molybdenum mainly represents a metallic impurity. As determined by analysis of the UF_6 in the product receivers, approximately 5.2 ± 2.6 g of ruthenium was fed to the decomposer during Runs DUP-5 and -6 along with the 31 g of plutonium. Analysis of bed samples by a sensitive spark-source mass-spectrometric method at the Rocky Flats Laboratory showed ruthenium values of 0.2 ppm, equivalent to 0.0008 g of ruthenium for the total bed content. Based on these input and output values, including a 50% uncertainty in the input value, decontamination factors of 10^3 to 10^4 for ruthenium were realized, which are considered satisfactory.

Similarly, substantial amounts of molybdenum were found in the UF_6 product receivers in all three experiments. Considering data from only the latter two experiments, the UF_6 product contained about 23 g of molybdenum while the final bed contained less than 0.2 g. (Bed analysis showed <0.01 wt %, the limit of the analytical method used.) These values give a decontamination factor greater than 10^2 for molybdenum. These

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*These fission products were among the 19 inactive F.P. oxides added to the synthetic oxide fuel charged to the fluorinator.

results suggest that the decomposition process shows promise as a means of partially purifying PuF_6 streams from undesirable contaminants. Further investigations are recommended to confirm these results.

8.7 Conclusions

Thermal decomposition by a fluid-bed technique appears satisfactory for separating plutonium as PuF_4 from PuF_6-UF_6 mixtures. Since the decomposition occurs preferentially on surfaces, the use of fluid beds for this process is attractive in that the bed represents a medium with a large surface area. Furthermore, the process can be made continuous, and the product is uniform.

Bed temperatures of 300-350°C appear adequate for low-plutonium-content (~0.5 wt %) feed materials. Higher temperatures may be needed for plutonium-rich systems, such as the 20 wt % plutonium materials contemplated for fast-reactor fuels. Separation of plutonium from other volatile fluoride contaminants, such as F.P. ruthenium, appears possible by the thermal-decomposition process and should be explored further.

9. RECOVERY OF PLUTONIUM DEPOSITED IN LINES AND EQUIPMENT

9.1 Introduction

Plutonium tetrafluoride can be deposited in lines and equipment by alpha and thermal decomposition of PuF_6 or by chemical reaction of PuF_6 with metal or a chemical compound. Studies of the rate of decomposition by alpha decomposition showed that the rate varied from 0.06 to 1.8% per day for PuF_6 in the gas phase.[16] The rate decreased with time, in the presence of helium or krypton, and with lower vapor pressure of the PuF_6. Decomposition in the solid phase has been estimated to be 1.5% per day.[8] In our experiments, the largest quantities of PuF_4 produced from alpha decomposition of PuF_6 would be recovered from the equipment holding the PuF_6--the cold traps and the product containers.

The amount of PuF_6 decomposed thermally is a function of time, temperature, and the amount of PuF_6 and fluorine present. Under some conditions, but not those used in the pilot-plant experiments, very high decomposition rates, above 95% per day, are possible.[11] In the pilot plant, PuF_6 might be thermally decomposed in the fluorinator when the fluorine-nitrogen-PuF_6 mixture leaving the fluidized bed at 500°C is cooled to 150°C before being passed through the fluorinator filters. As noted in Section 7.3.3.6, little (<0.1%) of the plutonium decomposes as PuF_4 by this mechanism and collects on the filters.

The fraction of PuF_6 converted to PuF_4 by chemical reaction alone during these studies can be assessed if the amounts contributed by alpha and thermal decomposition can be isolated. Because PuF_6 is a strong fluorinating agent, reaction with materials of construction and chemical compounds (uranium oxides and fluorides, F.P. fluorides or oxyfluorides) is likely.

9.2 Procedures and Conditions

For recovering PuF_4 deposited by decomposition or chemical reaction of the PuF_6, the equipment and the process line were heated to about 300°C while fluorine was recycled through the system. The PuF_6 formed was sorbed on NaF placed in containers located strategically so that the amounts of PuF_6 collected could be assigned to specific items of equipment.

The PuF_4 cleanup fluorinations were made after Runs Pu-3, -6 (fluorinator filters only, since the cold traps were not used), -13, -14, and -15. The fluorination time-temperature conditions of the first cleanup run are shown in Table 25. Sorption traps were analyzed after arbitrary periods of 8, 25, and 24 hr. A separate period (Period 4) was used during the cleanup of the hexafluoride transfer line. Temperatures in some cases were less than the desired 300°C, because of heater problems, which were later solved. In the first cleanup run, the fluorination was interrupted after 8 and 33 hr to replace the NaF sorption traps so that information could be obtained on the rate of plutonium removal from the equipment. On the basis of data obtained, a fluorination time of 12 hr was used in other cleanup runs.

TABLE 25. Plutonium Cleanup Runs (Pu-4 and Pu-5).* Summary of Fluorination Times and Approximate Average Equipment Temperatures

	Period 1 ⟷ Period 2 ⟷ Period 3
Time (hr)	5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 57
Temp of Equipment (°C)	
Fluorinator	440 + B.T.** + 445
Primary filters for fluorinator	260 + B.T.** + 200
Secondary filter for fluorinator	270 + B.T.** + 200
Cold-trap A	~300 + ~350 + ~350
Cold-trap B	~300 + ~350 + ~350
Hexafluoride transfer line†	260
Hexafluoride receiver No. 1	<100 + 190 + B.T.** + 285 + 350 – 150 (DECREASING) + 350 + DECREASING TO 150
Hexafluoride Receiver No. 4	<100 + 185 + B.T.** + 245 + 330 + 310 + 355 + 325
Hexafluoride Receiver No. 5	140 + 280 + 265 + 330
Inlet line of thermal decomposer (converter)	<100 + 185 + B.T.** + <100 + 150 + 180

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*The main fluorinator reaction zone containing the alumina bed was heated to 550°C for 15 hr during the cleanup of the bed (Run Pu-3A) before Run Pu-4. The primary filters were heated to about 300°C for the last 6 hr of Run Pu-3A.

**At ambient temperature of alpha box; equipment not heated.

†Fluorinated during a separate cleanup period, Period 4 (see Table 26).

After the cleanup fluorination, the NaF-filled traps were removed and sampled. The NaF was removed from the equipment area, and the equipment was then surveyed with neutron meters to locate any plutonium deposits; when the neutron counting rate was near background, the equipment was considered to be free of plutonium.

9.3 Results and Discussion

Detailed data from the first cleanup run (Table 26) show the amounts of plutonium removed in successive fluorination periods from the different equipment items. Most of the plutonium was recovered within 33 hr. On the basis of the results, the quantities of plutonium that had deposited in the equipment in the course of the initial campaign may be categorized as small, intermediate, or large as follows:

a. Small (~1 g or less)--lines and secondary filter (probably as a result of reaction with the nickel equipment).

b. Intermediate (several grams)--product receivers, primary filters.

c. Large (decagrams)--cold traps.

TABLE 26. Plutonium Deposits Recovered in Fluorination Cleanup Runs

	Plutonium Recovered, g			
	Period 1 of 8 hr	Period 2 of 25 hr	Period 3 of 24 hr	Total for Periods 1-3, 57 hr
Fluorinator including primary filters	1.8	0.1	0.3	2.2[a]
Secondary filter for fluorinator and line	0.3	0.1	0.2	24.3
Cold trap A[b]	4.0	11.4		
Cold trap B[b]	6.8	1.5		
Hexafluoride transfer line	Negl.	Negl.	Negl.	Negl.
Hexafluoride receivers (total of three)	9.3		-	9.3
Inlet line of thermal decomposer	0.2		-	0.2
Subtotal				36.0
Hexafluoride transfer line (49.5-hr Period 4)				0.9
Total				36.9[a]

[a] An additional 8.1 g was recovered from the filters during the last 6 hr of cleanup Run Pu-3A (conducted on the alumina bed from Run Pu-3).

[b] Cold trap A was first in line for Runs Pu-1 and -2 and served as a backup to cold trap B for Run Pu-3. Cold trap B was first in line for Run Pu-3 and served as a backup to cold trap A for Runs Pu-1 and -2.

The quantity of plutonium recovered from the cold traps was over 20% of that charged in the oxide pellets. The plutonium recovered from the fluorinator filter was probably PuF_4 that had been elutriated from the bed and not dislodged by blowback of the filters. The amounts recovered from other items reflect plutonium deposited by alpha decomposition (and possibly chemical reaction), which is a function mainly of the amount of PuF_6 present and the time.

Table 27 summarizes the amounts of plutonium recovered from the different equipment items in all cleanup runs. Recovered amounts varied from 8 to 36% of the plutonium charged in a given experiment. The highest percentage is for the first cleanup run, in which the PuF_6 was kept in the cold traps for a longer time than in succeeding runs. In later runs, the PuF_6 was transferred from the cold traps to sorbent NaF almost immediately after the run. Also contributing to the high percentage value for the first cleanup run was the transfer of PuF_6 with UF_6 to product containers, where the PuF_6 was stored until used as feed for thermal-decomposition experiments. During the storage period, considerable plutonium decomposed. Also, some PuF_6 (an unknown quantity) was reacting with the new metal surfaces of the equipment, and this probably contributed to the high percentage recovered from equipment after the first run.

TABLE 27. Plutonium Collected from Equipment Items in Plutonium Cleanup Step

	Cleanup Step Following Run				
Equipment Item	Pu-3	Pu-6	Pu-13	Pu-14	Pu-15
Fluorinator filter, g	10.3	[a]		2.7	3.2
Cold traps, g	23.9				
Misc. lines and secondary filter, g	1.5	Not used	26.4	1.0	0.6
Product containers, g	9.3		Not used		
Total, g	45.0		26.4	3.7	3.8
Plutonium charged, g	123.8	100.4	351.7	19.2	21.4
Percent of plutonium charged	36	-	8	19	18

[a] Not collected separately. The PuF_6 from both the fluorination period and the plutonium cleanup period were collected on the same bed of NaF.

After the plutonium cleanup fluorination, one of the 4-in.-dia product containers was sectioned, its inside metal surface was washed with dilute HNO_3-$Al(NO_3)_3$ solution, and the washings were analyzed for plutonium. From the data obtained, the plutonium surface concentration was calculated to be only 0.2 to 1.2 mg/sq ft.

Neutron survey data indicate that the equipment was free of plutonium deposits. From these and material balance data, it was concluded that plutonium could be removed easily from surfaces of the equipment by fluorination at 300°C.

Pretreatment of the equipment with some strong fluorinating agent is recommended to minimize interaction and subsequent deposition of PuF_6 (as PuF_4); ClF_3 may be convenient for this purpose. In the present work, however, a ClF_3 treatment in addition to the prefluorination with fluorine did not appear to affect the level of interaction with the equipment surfaces, which remained small.

10. PLUTONIUM MATERIAL-BALANCE DATA

In the course of fluorination experiments involving charges of 20 to 100 g of plutonium, 635 g of plutonium was introduced into the fluorinator system in the following materials:

103 g	as unirradiated 0.5 wt % PuO_2-UO_2-F.P. pellets (Runs Pu-1 to -3)
410 g	as PuF_4 powder (Runs Pu-6, -10, -11, and -13)
41 g	as PuF_4 in the beds resulting from oxidation and BrF_5 fluorination of unirradiated 5 wt % PuO_2-UO_2-F.P. pellets (Runs Pu-14 and -15)
81 g	as a PuF_6 "spike" in a fluid-bed thermal-decomposition experiment (DUP-6) and in transfer experiments (Pu-9)
635 g	Total

A separate plutonium material balance was made after Runs Pu-3, -6, -13, -14, and -15 (i.e., after each plutonium cleanup run). These data are shown in Table 28. Figure 32 presents additional data for the oxide pellet fluorination runs (Pu-1, -2, and -3) and thermal-decomposition runs (DUP-4, -5, and -6).

TABLE 28. Plutonium Material Balances

	Plutonium, g								
	Pu-1 through -3	Pu-6	Pu-9	Pu-10	Pu-11	Pu-12 and -13	Pu-14	Pu-15	Total
Plutonium Charged									
Al_2O_3 bed of previous laboratory runs							0.67	0.65	
As pellets, PuF_4, or in BrF_5 residues	103.2	100.4		103.6	101.3	105.3	18.51	20.73	
PuF_6 spike added to PuF_6 product of Run Pu-3	20.6								
PuF_6 charged in transfer experiment			60.5						
Total plutonium charged	123.8	100.4			370.7		19.18	21.38	635
Plutonium Recovered									
Volatilized plutonium									
Sorbed on NaF during fluorination step		97.4							
Collected in cold trap and then transferred to NaF or used in thermal-decomposition experiments	31.9 + 20.6-g spike					76.3	15.88	18.92	
Collected in PuF_6 transfer experiment									
In product container and in NaF backup trap			58.5	67.8	57.1				
Collected in NaF and Al_2O_3 off-gas traps				8.7	15.0	5.4			
Collected in plutonium cleanup step							1.92	0.74	
From fluorinator filter and disengaging zones	45.0					26.4	2.76	3.22	
From secondary filter, cold trap, and connecting lines							1.03	0.58	
Nonvolatilized plutonium									
In bed samples	6.8	2.0		1.3	6.2	2.0	0.19	0.17	
In bed dumped from fluorinator	3.1	0.3		6.4	8.0	0.2	0.65	1.01	
From brushing walls and cleaning lines of fluorinator		0.1		3.9	13.4	0.1			
Miscellaneous	1.6						0.34	0.10	
Total recovered	109.0	99.8			357.7		22.77	24.74	614
Accounted for, %	88	99.4			96.5		119	116	97

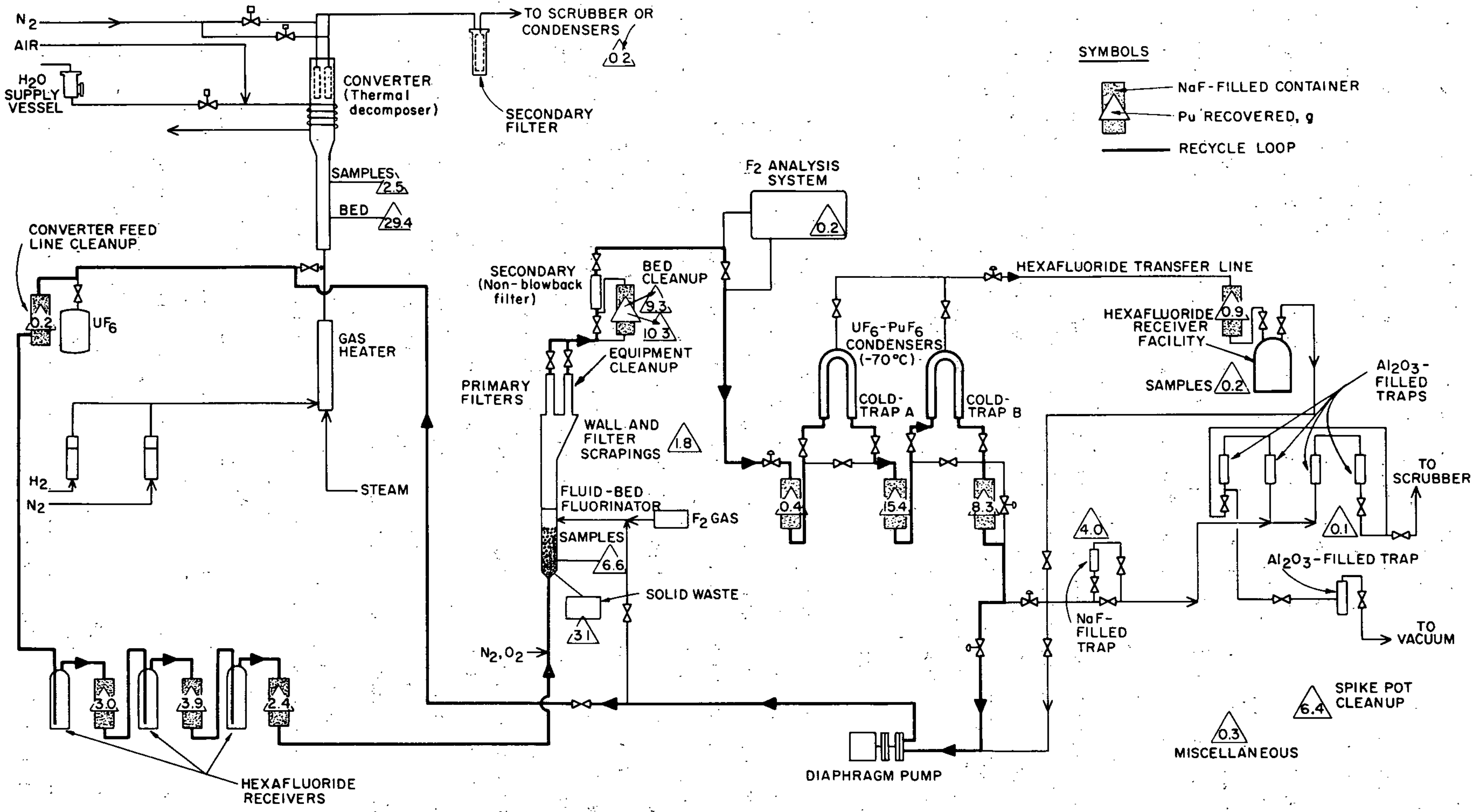

Fig. 32. Location of Plutonium after Runs Pu-1 through -3. ANL Neg. No. 308-475 Rev. 1.

Of the 544 g of plutonium fluorinated, over 90% was converted to PuF_6 during fluorination operations and this, plus the 81 g added as a "spike," was transported through the pilot-plant system of filters, valves, and associated piping to cold traps and subsequently to NaF sorption traps or product containers. About 8% of this 90% was recovered in the cleanup step and represents plutonium decomposed by radiation or thermal mechanisms, reacted with metal or compounds, or elutriated from the fluidized bed to the filters during the fluorination run. Of the 10% of the plutonium not volatilized, most was contained in the alumina bed samples and in the final bed of the fluorinator. As determined by neutron surveys, little plutonium remained in the equipment after Run Pu-15.

The material-balance data show that 97% was accounted for in these runs. This value was considered satisfactory, since with sampling techniques and with our analytical errors, a balance within the 96-104% range is acceptable. Experimental details and results of the sampling test to support this conclusion are given in Appendix H. In the sampling test, two separate quantities of NaF containing 1.9 and 0.06% plutonium were riffled and sampled six times, and each sample was analyzed three times to establish the sampling error.

Table 29 shows sampling-error data for both input and output solids with the amounts of plutonium handled and the percent accounted for. In the runs in which most of the plutonium was handled (Pu-6 and also Pu-9 through -13), satisfactory balances were obtained. The balance for the first set of runs (Pu-1 through -3) shows only 88% accounted for, but in this case the variability in the plutonium content of the pellets in a given batch and among batches precluded obtaining an accurate value for plutonium input (as discussed in Appendix A). Therefore, the balance was based on an input plutonium value of 0.49 wt %, which was specified for the fabrication of the pellets. In Runs Pu-14 and -15, larger amounts were accounted for than were added: 119 and 115%. Here the input analysis data show high standard deviations at the 95% confidence interval, and more samples should have been analyzed. Since relatively small amounts of plutonium were involved, the high accountability (119 and 115%) may be due to recovering a few grams of unrecovered plutonium from earlier runs.

TABLE 29. Summary of Information Available on Errors in Sampling and Analyzing Input and Output Plutonium-containing Materials

Run	Amount of Plutonium Handled, g	Percent of Plutonium Accounted For	Analytical and Sampling Standard Deviation (95% C.I.)	
			Input Materials	Output Materials
Pu-1 to -3	123.8	88	<2% (laboratory standard deviation)	±4%
Pu-6	100.4	99	<2% (laboratory standard deviation)	±4%
Pu-9 to -13	370.7	96	<2% (laboratory standard deviation)	±4%
Pu-14	19.2	119	±10%[a]	±4%
Pu-15	21.4	115	±5%[a]	±4%

[a] Analysis of four samples, 95% confidence interval.

APPENDIX A

Nondestructive Test for Plutonium Content of Pellets

Early analyses of the UO_2-PuO_2-F.P. pellets fluorinated in Runs Pu-1, -2, and -3 showed that the plutonium and F.P. concentrations varied widely from pellet to pellet. Analysis of a sufficiently large number of pellets was desirable to establish the plutonium concentration range accurately. Analysis of pellets by wet (dissolution) methods was destructive and therefore not attractive economically. The basis for the nondestructive test was the measuring of the gamma radiation emitted by ^{241}Am.

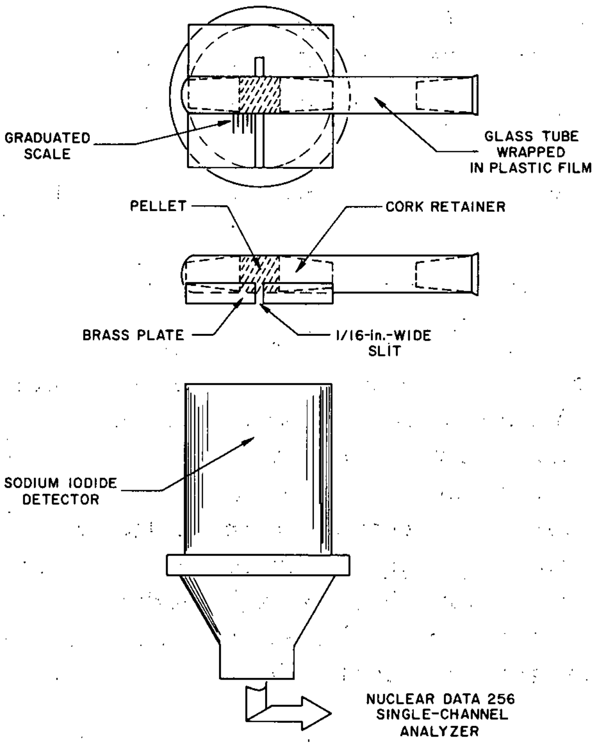

Fig. A.1. Oxide Pellet Mounting and Positioning for Gamma Counting

Figure A.1 shows the method of mounting the pellet before making the gamma-radiation count with a sodium iodide (NaI) detector and a Nuclear Data 256 single-channel analyzer.* The pellet was contained in a glass tube, which was wrapped with a plastic film. Cotton plugs held the pellet in position inside the tube. The glass tube was positioned above the counter head on a brass plate, which had a graduated scale for centering the pellet. A slit in the plate allowed radiation to pass to the NaI detector head. The sample was moved to a lead enclosure before being counted. Each pellet was counted twice for a 10-min period. Ten pellets were selected from each of the 12 batches processed in Runs Pu-1, -2, and -3.

The gamma-counting results (given in Table A.1) show that there was considerable variation among pellets of a given batch and among the means of the 12 batches. For the 10 samples of each batch, the error in the estimate of the mean (95% confidence interval) is a minimum of ±0.6% and a maximum of ±15%. If the two highest error estimates (±15.0 and ±6.0%) are eliminated, the range of the remaining error estimates is ±0.6 to ±1.7%. If the means of all the batches are compared, the error in the estimate of the mean of the batches again at the 95% confidence interval is 31%, which is excessively high.

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*Product of Nuclear Data Co., Inc., Schaumburg, Illinois.

TABLE A.1. Gamma Count Rate (10^3 counts/min) Obtained from UO_2-0.5 wt % PuO_2 Feed Pellets Processed in Runs Pu-1 through -3

	Batch											
Pellet No.	20	24	13	19	10	17	25	33	2	5	7	4
1	7.794	9.92	8.43	8.43	10.86	10.07	9.261	10.22	10.80	10.91	9.961	10.47
2	7.758	10.8	8.35	8.31	10.85	10.14	9.408	10.13	10.82	10.98	10.41	10.89
3	7.583	10.2	8.39	8.39	10.65	10.15	9.494	10.24	10.87	10.59	9.784	10.60
4	7.720	15.3	8.13	8.45	10.83	10.11	9.192	10.32	10.04	10.78	10.10	10.51
5	7.710	10.4	7.96	8.29	10.95	10.18	9.359	10.13	10.89	10.69	9.980	10.65
6	7.670	10.1	8.28	8.44	11.00	10.12	9.679	10.13	10.82	10.85	10.26	10.86
7	7.733	15.7	8.33	8.36	11.00	10.41	9.405	10.13	10.86	11.08	9.989	10.74
8	7.744	15.3	8.32	8.38	10.79	10.45	9.158	12.90	10.75	10.95	10.09	10.86
9	7.747	10.4	8.24	8.36	10.96	10.15	9.460	10.20	10.82	11.18	10.20	10.72
10	7.783	10.8	8.32	8.11	10.74	10.32	9.395	10.10	10.83	10.87	10.00	10.56
Batch mean	7.73	11.89	8.28	8.35	10.86	10.21	9.38	10.45	10.75	10.89	10.08	10.69
Estimate of error from the mean 95% C.I., %	±0.6	±15.0	±1.2	±0.8	±0.8	±0.9	±1.3	±6.0	±1.7	±0.8	±1.2	±1.9

Mean, all pellets--9.96

Estimate of error from the mean, 95% C.I.--±31%

Eleven of the 120 pellets that had been counted were selected for wet analysis to obtain a correlation between the gamma count and the concentration of plutonium in the pellet. A line having a least-squares fit was drawn through the data plotted in Fig. A.2. Considerable scatter is apparent, and no satisfactory conclusion can be made. For the average gamma count of 9,960 counts/min, the plutonium concentration of the pellet would be 0.54%, or higher than the 0.49% the pellets supposedly contained. This high value is unlikely, since the pellets were made by weight additions. Therefore, for material-balance calculations, it was assumed that the plutonium concentration was 0.49%, the original concentration specified to the manufacturer.

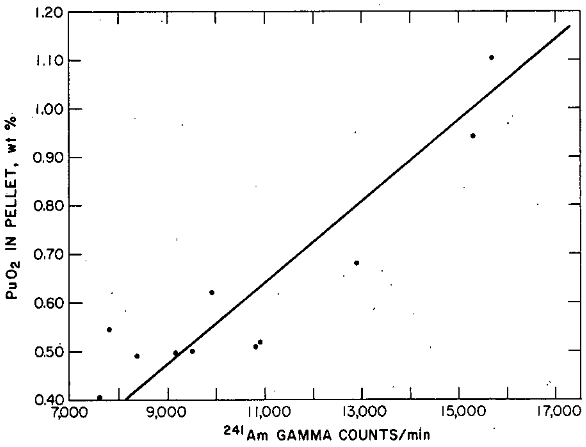

Fig. A.2

Least-squares Plot of Pellet Gamma Count Rate vs PuO_2 Concentration Obtained from Wet Analysis

APPENDIX B

Leak Testing of the Fluorination System

The need for having prescribed limits on the rate of leakage from the fluorination system is apparent, since leakage of PuF_6 could cause the plutonium concentration in air leaving the building to exceed the maximum permissible concentration.* Criteria for establishing these limits were based on the following assumptions:

1. Maximum leak rates acceptable at 15 psig from the isolatable equipment sections and their approximate volumes

   a. 10 cc/min from the inlet-gas system (1400-cc volume), the fluorinator (24,000 cc), or the fluorinator off-gas and secondary filter system (2000 cc).

   b. 30 cc/min from the process off-gas trapping system (60,000 cc). (Note: The process off-gas trapping system should contain no volatile plutonium. Therefore, the limit for leak rate from this system was raised from 10 to 30 cc/min.)

2. Amount of plutonium fluorinated: 50 g/batch

3. Fluorination time: 18 hr

4. Volume of gas passing through fluorination system during run: 2 scfm

5. Plutonium concentration in gas stream: 100%

6. Plutonium isotope fluorinated: 239.

From these assumptions, the amount of plutonium escaping through a 10 cc/min equipment leak would be 1×10^{-5} g/min or 165 μCi/min. Leakage into the glovebox would be diluted first with 600 cfm of box ventilation air, and this 600 cfm would be further diluted to 4000 cfm with room ventilation air before leaving the building. The plutonium concentration in this 4000 cu ft of air would then be 1.5×10^{-6} μCi/cc. The air is actually scrubbed and filtered (through high-efficiency AEC filters**) twice after leaving the large alpha box and before leaving the building. First, the 600 cfm of box ventilation air is scrubbed and filtered in equipment installed in the smaller alpha box; after combining with the room ventilation air, the

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* For reference, the off-site air MPC for ^{239}Pu is 5×10^{-12} μCi/ml.

** Manufactured by Flanders Filter Corporation, Riverhead, N.Y.; Cambridge Filter Manufacturing Corporation, Syracuse, N.Y.; and American Air Filter Corporation, Louisville, Kentucky.

entire 4000 scfm is scrubbed in a second scrubber and filtered a second time. With a very conservative decontamination factor of 10^6 for these operations,[17] the plutonium concentration in the exhaust air would be 1.2×10^{-12} μCi/cc, or approximately one-fourth the maximum permissible concentration limit, 5×10^{-12} μCi/cc.

Before each run, the entire system was leak-checked to satisfy the leak-rate requirements. In establishing a leak-test procedure, we related the 10-cc/min leak rate to the pressure drop that would occur in the volumes of the four parts of the system (valved off into four convenient parts to quickly detect a loss in pressure during leak testing and to help pinpoint the leak). System volumes were determined from gas-volume calibrations and by calculated values obtained from construction drawings. Pressure drop was read on $4\frac{1}{2}$-in.-dia, 0- to 30-psig gauges. A value for the maximum pressure drop per unit time was established. A leak test could be completed in a 1-hr period, and the smallest change specified (1/2 psi/hr) could be easily read on the gauges.

Operating experience with the leak-testing procedure was good. Check sheets ensured that the operations were carried out in the proper order.

APPENDIX C

Transfer of Hexafluoride from Cold Trap to Product Receiver

In Runs Pu-10, -11, and -13, the 100 to 135 g of PuF_6 collected in the pilot-plant cold traps was to be transferred to a small product receiver. To establish a transfer procedure for PuF_6, transfers were first made with UF_6. The first test, Run U-7, was aborted; Run U-8 was completed. A PuF_6 transfer experiment (Run Pu-9) followed under similar conditions.

A carrier-gas transfer method was selected because experience had shown that a rapid transfer of relatively small amounts of material from the pilot-plant cold traps to a small surface-area product container by pressure alone was impractical. Large amounts (10,000 g) of UF_6-PuF_6 mixture had been transferred satisfactorily under its own vapor pressure.

The UF_6 and PuF_6 for these tests were prepared by fluorinating the respective tetrafluorides. Product purity was not determined, but crude vapor-pressure measurements indicated that no highly volatile species other than the hexafluorides were present.

The equipment for the transfer experiments (shown schematically in Fig. C.1) consisted of a supply container of UF_6 (or PuF_6), a cold trap (4-in. diameter, 1-cu ft volume), and a receiving container (0.03-cu ft volume) for hexafluoride transferred from the cold traps. All equipment was constructed of Monel or nickel.

In Run U-8, 160.2 g of UF_6 from the supply vessel was transferred into the cold trap in 28 min. The cold-trap temperature was -52°C. The supply vessel, transfer line, and cold-trap skin temperatures were maintained at 75 ± 5°C. Completion of the transfer was indicated by a near-zero absolute-pressure reading in the system.

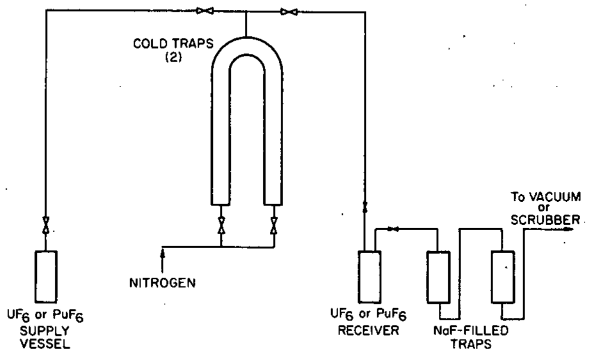

Fig. C.1. Schematic Diagram of Hexafluoride Transfer Test Equipment

Transfer from the cold trap to the UF_6 receiver was started by passing nitrogen at 2.5 cfh through both legs of the cold trap while the trap was still chilled. The UF_6 receiver was chilled, and then the cold trap was gradually heated. The receiver was maintained between -38 and -57°C throughout the transfer. After the cold-trap temperature reached 75°C, parallel flow through both legs of the cold trap was maintained for 6 hr. An additional 3 hr, with nitrogen flowing alternatively through one leg then the other leg of the cold trap, was used to ensure complete transfer. A total of 15 volume throughputs of nitrogen were passed through each leg of the cold trap with satisfactory results. This is probably much in excess of the required quantity, since the bulk of the transfer occurred in the early part of the run (based on the results of the plutonium transfer experiment).

Receiver and NaF trap weighings showed that 122.8 and 35.2 g of UF_6, respectively, were collected in the product receiver and the small backup NaF trap during the transfer. This total of 158.0 g of UF_6 represented a recovery of 98.7% of the hexafluoride from the cold trap. The average deviation in weighing the receiver (total approximate weight of 4 kg) introduced a precision of ±0.8% in the recovery figure.

The PuF_6 transfer experiment (Run Pu-9) was conducted using the same procedures and temperatures as in the UF_6 transfer experiment. The net weight of the PuF_6 and PuF_4 (from decomposition) in the supply vessel was 100.9 g. Three hours were allowed for vacuum transfer of the PuF_6 from the supply vessel into the large cold trap. The slower transfer rate than for the UF_6 transfer was used to minimize entrainment of PuF_4 particulate material. After the transfer, less than 1 g of PuF_6 remained in the supply vessel (calculated from vapor-pressure measurements). Only 89.4 g of hexafluoride was transferred, the remainder of the 100.9 g being PuF_4 formed by alpha decomposition of the PuF_6 while the PuF_6 was in the supply vessel. Residual PuF_4 in this container was not of concern for the purposes of this experiment.

After the PuF_6 transfer into the large cold trap, transfer from this trap into the small product receiver was begun. The nitrogen flowrate and the total transfer time were identical to those used in the UF_6 transfer experiment.

The PuF_6 supply vessel, receiver, and small NaF trap were weighed with an analytical balance of 5-kg capacity located in an alpha box. The experimental results are as follows:

Weight of PuF_6 transferred from the supply vessel into the large cold trap:	89.4 g
Weight of PuF_6 transferred from the large cold trap into the small product receiver:	74.0 g
Weight of PuF_6 collected in the backup NaF trap:	13.4 g
Actual recovery of PuF_6 from the large cold trap:	97.8%
Recovery of PuF_6, allowing for 8 hr of alpha decomposition (2%/day) in the large cold trap:	98.4%

Neutron readings were taken at various times during the transfer. Insufficient data were accumulated to justify graphic presentation. However, the readings did show the movement of PuF_6 into the cold trap and then into the receiver and the NaF trap. Transfer into the product receiver appeared to be complete in about 2 hr. Additionally, the readings indicated that plutonium (probably PuF_4 from PuF_6 decomposition) remained in the cold trap after the PuF_6 transfer from it was completed. Neutron count rates near the inlet line (where most of the PuF_6 would be expected to condense) increased from 42-events/min background before the transfer to 51 events/min after the transfer. The quantity of plutonium represented by this increase was relatively small, since the neutron reading was 1280 events/min with 89.4 g of plutonium in the trap.

APPENDIX D

The Use of Neutron Probes in Fluidization Tests

The success of neutron counting as a tool to determine the movement of PuF_4 and PuF_6 in the fluorinator equipment has led to several experiments involving fluidizing PuF_4 and alumina at room temperatures. The tests were designed (1) to determine the distribution of PuF_4 in the fluorinator during fluidization with nitrogen gas at room temperatures, (2) to determine the rate and extent of the removal of PuF_4 from the bed at several fluidization rates, (3) to determine whether PuF_4 deposited on the fluorinator filters is dislodged during filter blowback, and (4) to determine the usefulness and sensitivity of portable neutron survey meters* as a means of determining the location and amount of PuF_4 in the fluorinator bed, disengaging section, and filter sections.

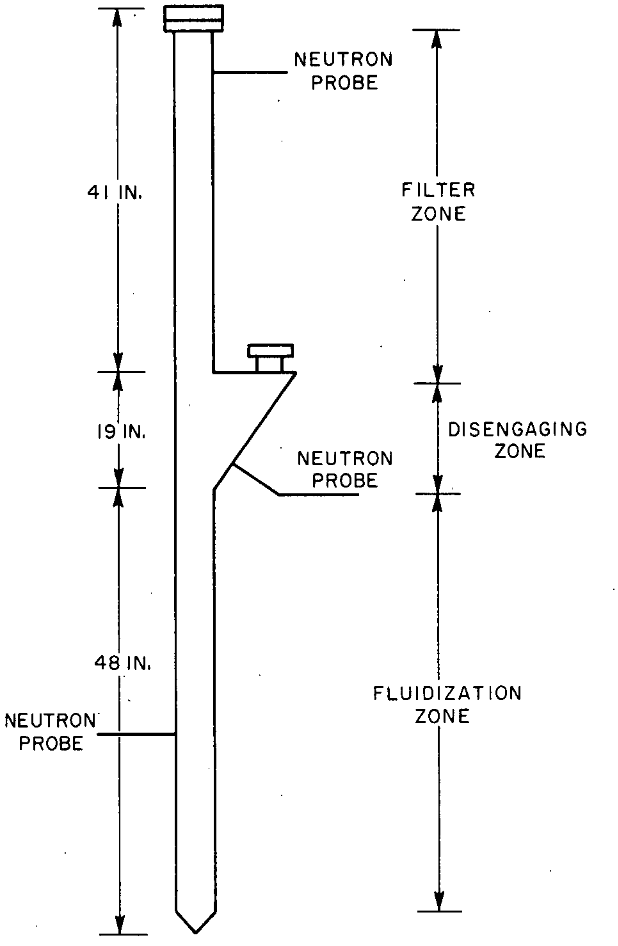

Fig. D.1. Positions of Neutron Probes on Fluorinator

1. Fluidization Tests with PuF_4 and Alumina

The charge to the fluorinator consisted of 6760 g of 48-100 mesh alumina (Alcoa Type Tab-61) and about 139 g of -325 mesh PuF_4 powder. The static-bed height of the Al_2O_3 in the fluorinator was about $2\frac{3}{4}$ ft. Microphotographs of PuF_4 show the individual particles to be about 4 μ with PuF_4 agglomerates (present in large numbers) varying in size from 15 to 100 μ. A screen analysis of the PuF_4 showed that about 1 wt % remained on a 270 mesh screen with 99% through the 325 mesh screen. The material caught on the 270 mesh screen appeared to be scale.

The bed was fluidized for approximately 4 hr in each test. Neutron counting data were recorded about every 15 min from the probes positioned at the fluorinator. Four neutron monitors were used--three at the locations shown in Fig. D.1, a fourth for surveying the column during or after each experiment. The neutron monitors each consist of a BF_3 probe, a paraffin moderator, and a cadmium shield. In the final test,

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*Type PNC-1, Eberline Instrument Corporation, Santa Fe, New Mexico.

the paraffin moderator was replaced with Lucite. Since the survey meters were used with a scaler, count rates were obtained.

Preliminary interpretation of the results of the tests show that when the bed was fluidized at 0.3 or 0.7 ft/sec, little PuF_4 was elutriated from the bed to the filters; since little PuF_4 reached the filters, variations in blowback procedure had little effect.

The PuF_4, charged initially to the top of the alumina bed, was not distributed uniformly in the bed, even after 4 hr of fluidization, and was at or near the top of the bed when the bed was either fluidized or static. This interpretation of the neutron data is supported by plutonium analysis of bed samples taken in Runs Pu-12A, -12B, and -12C. The point of sampling was approximately 12 in. from the bottom of the bed. Samples taken after 4, 8, and 12 hr of fluidization contained 0.06, 0.1, and 0.7 wt % plutonium, respectively. Based on the quantity of plutonium in the charge, the average value should have been ~2.0 wt % plutonium. These results indicate uneven distribution of plutonium in the bed at the beginning of the series of experiments, although there was some mixing as fluidization continued over an extended period of time (about 12 hr). At no time was there a uniform distribution of PuF_4 in the alumina bed. An undetermined but significant amount of PuF_4 was in the disengaging section during fluidization, as indicated by the neutron counts taken with a probe located at several positions on the disengaging section.

Figure D.2 is typical of the results of the tests. A slight increase in neutron counts was noted at the filter section when fluidization began. There was very little variation in neutron counts during the tests, despite various filter blowback tests. At the start of a test, the bed showed an immediate drop in neutron level; the count rate continued to drop slightly during the test. At the end of a test, when fluidization was stopped, the neutron level in the bed increased immediately. With vibration of the fluorinator, the neutron level in the bed returned to about its original level.

The neutron level of the disengaging section increased when fluidization began and increased slightly during the tests; at the end of the tests, the count rate dropped to its original value.

Additional tests were made with the neutron counters to determine the effect on count rate of (1) a 10-g source of PuF_4, and (2) a source consisting of 8 g of PuF_4 distributed in about 800 g of NaF. No significant difference in count rate was noted for these two sources when they were placed in the reactor at the filter location. An increase of about 4000 events per minute was noted, which is consistent with the previous estimates of about 40 events/(min)(g plutonium).

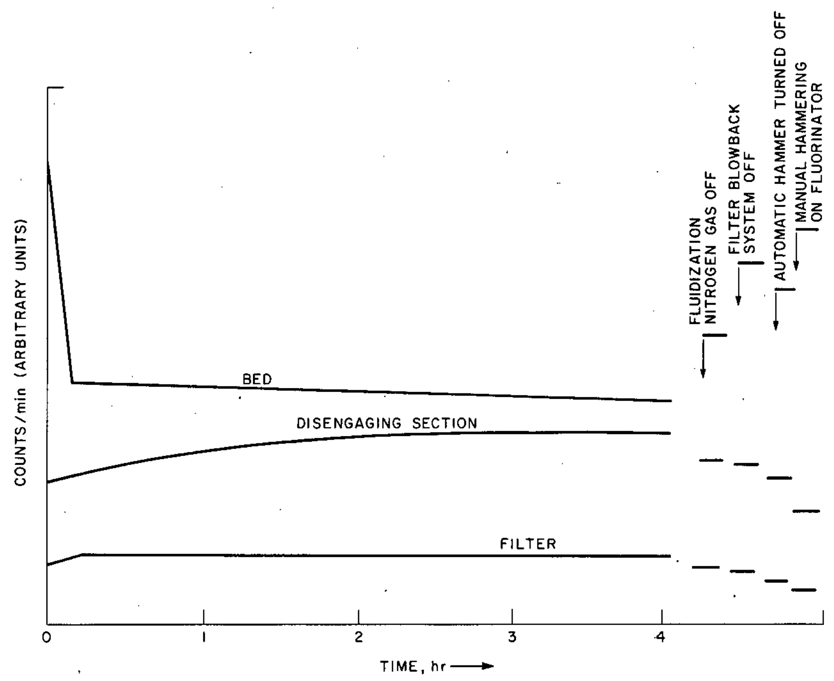

Fig. D.2. PuF_4 Distribution in Unheated Reactor during Fluidization of -325 Mesh PuF_4 and 48-100 Mesh Alumina with Nitrogen

The probes were also positioned at the disengaging section while the PuF_4 samples were held in the filter section. No increase in count rate above background was observed. Any change in the counting rate measured with the probes indicates a change in plutonium content in the immediate area of the probe. Probes 2 ft away from a plutonium source are not affected.

2. Mockup Fluidization Tests with Nickel Fines

In support of fluidizing tests made in the fluorinator using PuF_4 and 48-100 mesh alumina, three tests were made in a $2\frac{5}{8}$-in.-ID brass column. In these tests, 135 g of 500 mesh nickel was fluidized in a bed of alumina (5935 g) to observe the rate of mixing of the nickel and alumina, its distribution throughout the bed, and weights of nickel and alumina elutriated from the bed at several gas velocities. In Tests A and C, the nickel was dumped onto the top of the static alumina bed; in Test B, a layer of nickel was sandwiched in the middle of the alumina.

Figure D.3 is a schematic drawing of the column and filter and shows the method of collecting the elutriated fines so they may be collected and weighed, not accidentally returned to the bed. Table D.1 summarizes the results of the three tests and shows that at a gas velocity of 0.3 ft/sec (Test A), the nickel did not distribute evenly through the column in a 30-min fluidization period. When the test was finished, about 40 wt % of the nickel was in the bottom third of the column and about 7 wt % of the nickel remained on the surface of the bed.

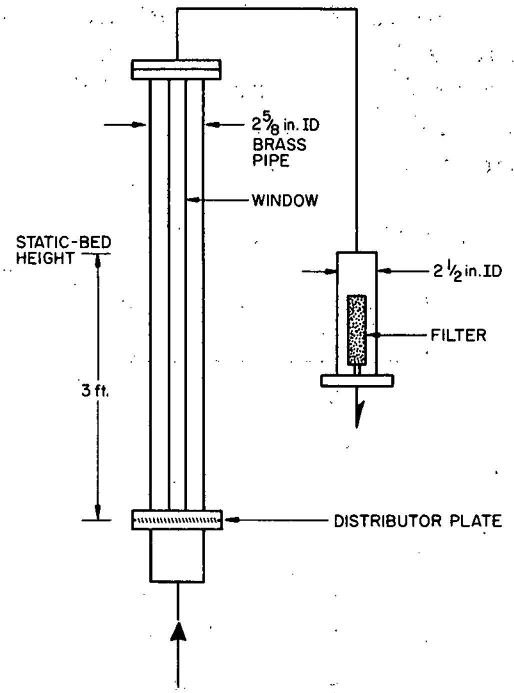

Fig. D.3
Schematic Diagram of
Alumina-Nickel Fines
Fluidization Test Column

TABLE D.1. Conditions and Results of Mockup Fluidization Tests with Nickel Fines

Equipment: $2\frac{5}{8}$-in.-ID brass column with 3-ft alumina bed
Test Duration: 30 min each

Test	Type of Al_2O_3[a]	Gas Velocity, ft/sec	Nickel Fines Distribution in Bed, g				Fines from Filter, g	
			Surface	Top Third	Middle Third	Bottom Third	Al_2O_3	Nickel
A	I	0.3	10.1	22.3	23.9	53.7	3.3	10.2
C	I	0.7	1.2	46.0	37.2	17.4	17.8	40.9
B	I and II	0.7	0	24.7	55.1	34.0	45.5	1.1

[a] Type I, 48-100 mesh Al_2O_3; Type II, -100 mesh Al_2O_3.

When the gas velocity was increased to 0.7 ft/sec (Test C), the top one-third of the bed contained nearly one-third of the nickel, the bottom one-third of the bed contained 12.5% of the nickel, and very little of the nickel remained on the bed surface. The weight of fines collected on the filter in Test C was 58.7 g, of which 70 wt % was nickel. During Test A, 13.5 g of fines was collected on the filter, of which 75 wt % was nickel.

Test B used a bed consisting of 50 vol % Type I alumina (48-100 mesh) as the original bottom half of the bed, a layer containing 135 g of 500 mesh nickel, and 50 vol % of Type II alumina (-100 mesh) as the top half of the bed. Table D.2 shows the sieve analysis of these two types of alumina. Before fluidization, the bottom half of the bed (48-100 mesh alumina contained less than 1.0 wt % -230 mesh alumina, but after 30 min of fluidization, the percent of -230 mesh was approximately uniform throughout the bed (top, 31 wt %; middle, 25 wt %; bottom, 22 wt %), indicating rapid mixing in the system. A total of 46.6 g of fines was collected on the filter, of which less than 3 wt % was nickel. No nickel was collected in the first 15 min of fluidization, and the center third of the bed had the highest concentration of nickel at the end of Test B.

TABLE D.2. Sieve Analysis of Alcoa Tabular T-61 Alumina

USS Sieve	48-100 Mesh, wt %	-100 Mesh, wt %	USS Sieve	48-100 Mesh, wt %	-100 Mesh, wt %
+25	0	-	+120	30.0	5.7
+35	0	-	+140	-	7.2
+45	0.15	-	+170	4.4	10.3
+60	7.27	0	+200	-	8.8
+70	-	0	+230	0.55	3.9
+80	57.1	0.1	+325	0.45	39.6
+100	-	0.4	-325	0.20	24.0

On the basis of these tests, we recommended increasing the percentage of -325 mesh alumina in the bed of the fluorinator to dilute the PuF_4 fines (-325 mesh) and to minimize the elutriation of PuF_4 to the filters.

3. Effect of Temperature on Neutron Probes

In the last several PuF_4 fluorination runs (Pu-10, -11, -13, and -14), the neutron count rate at the three probe locations (bed, disengaging section, and filter) was plotted against run time and showed an unexpected upward trend near the end of the runs. Glovebox temperatures are usually higher in the last half of the run and reach 60°C in some areas of the glovebox. Since information[18] about the effect of temperature on BF_3 probes is meager, a simple test was made to check the effect of temperature on the counting rate of the probes now in use. Data showed that the count rate does increase with an increase in temperature. The temperature effect varied from probe to probe.

APPENDIX E

Results of Sampling of the Fluidized Bed at Different Levels

Samples of the fluidized bed were removed at a sampling port 10 in. above the bed support. To obtain data on bed homogeneity, a new sampling port was installed 17 in. higher than the lower port, or 27 in. above the bed support. Table E.1 gives analytical data on samples taken at about the same time from the two sampling points. In each case, a flush sample was taken before a sample was taken for analysis. The data show wide differences in the plutonium and uranium contents of samples taken at the two sampling points, no recognizable trend being discernible. Reliability of calculated values for fluorine efficiencies and/or fluorination rate of plutonium and uranium based on analyses of samples removed from the fluidized bed appears questionable.

TABLE E.1. Samples Removed from Two Sampling Points in Fluidized Bed

Sample Pu-16-	Analysis Method[a]	Upper Sampling Point	Lower Sampling Point	Δ	$\frac{\Delta \times 100}{\text{Lower Sampling Point Value}}$, %
		% U in Sample			
17	C	22.8	25.5	-2.7	-10.5
16	C	21.3	25.1	-3.8	-15.1
6	F	2.62	2.30	+0.32	+13.9
21	F	0.414	0.360	+0.054	+15.0
24	F	0.214	0.166	+0.048	+28.9
2	X	0.025	0.031	-0.006	-19.4
		% Pu in Sample			
17 (End)	X	0.129	0.018	+0.111	+616
18 (End)	X	0.020	0.015	+0.005	+33
19 (Med)	X	0.040	0.008	+0.032	+400
19 (End)	X	0.012	0.007	+0.005	+72
21 (0100)	X	0.197	0.016	+0.18	+1130
21 (0200)	X	0.011	0.041	-0.030	-73
21 (End)	X	0.004	0.008	-0.004	-50
22 (End)	X	0.013	0.012	-0.001	-8
23 (Mid)	X	0.035	0.012	+0.023	+192
23 (End)	X	0.011	0.012	+0.001	+9

[a] F, fluorometric; C, colorimetric; X, X-ray.

APPENDIX F

Sampling the Hexafluoride Feed*

A procedure for sampling the 10-kg batches of UF_6-PuF_6 was tested. The material was contained in 4-in.-dia, 30-in.-tall nickel vessels, which were used as product receivers in fluorination experiments. Each vessel was fitted only with (two) up-legs, since vapor-phase transfers were made. Liquid samples could be taken by inverting the vessel or by tilting it in a downward position. Vapor samples were taken with the vessel in an upright position.

For liquid sampling, the procedure consisted of liquifying the material under its own vapor pressure while the vessel was mounted in a rocker assembly in a heated, thermostatically controlled box (shown in Fig. 31). After a given period, rocking was stopped with the vessel tilted downward. Liquid hexafluoride was allowed to flow into an attached manifold (valves and 3/8-in.-OD nickel tubing), filling the space between two valves, thus fixing the size of the liquid sample (about 2-3 ml).

An evacuated stainless steel sphere was attached to the manifold to receive the sample. Transfer of the sample to the sphere was promoted by locally chilling the sphere with a dry ice-trichloroethylene bath. Hexafluoride material remaining in any line section was evacuated as vapor through a NaF trap (waste) system. The sphere was then removed from the manifold, and the sample was hydrolyzed and submitted for analysis. Spheres were relatively large (3-in. diameter) to accommodate the hydrolysis solution and thus avoid an additional transfer of the sample. Liquid samples ranged from 4 to 20.5 g. Variation in quantity indicated that improved techniques were needed.

An inherent problem in taking liquid samples from such mixtures is that some particulate PuF_4 is always present from alpha decomposition; thus representative sampling of the liquid remains difficult.

Vapor sample size was controlled by the bulb size and the temperature of the hexafluoride. Vapor samples ranged from 2.6 to 18.8 g. In addition, gas samples were taken from the flowing UF_6 off-gas stream, merely by using a heated, evacuated bulb at a tee connection.

No particular problems were encountered during vapor sampling; however, results indicated that pretreatment of manifolds, perhaps even with PuF_6, was necessary to obtain representative samples.

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*Since alpha decomposition of the PuF_6 continually produces fluorine, sampling is carried out as quickly as possible after the vessel to be sampled has been chilled in a dry ice bath and pumped down to remove noncondensables.

APPENDIX G

Procedure for Hydrolyzing Hexafluoride Samples

(Typical Check Sheet)

This procedure assumes that the hexafluoride samples were taken in stainless steel bulbs and that the samples are below atmospheric pressure at room temperature, as would be the case for UF_6-PuF_6 samples with little or no noncondensable gas present.

_______(1) Set up the Kel-F burette for adding the hydrolysis solution to the sample bulbs. Close the bottom valve (a ball valve) on the burette, and fill the burette with $6\underline{N}\ HNO_3$-$0.1\ \underline{M}\ Al(NO_3)_3$ solution.

_______(2) Check that the valve on the sample bulb is closed. Then carefully remove the sample cap, and connect the sample bulb to the hydrolysis burette.

_______(3) Open the ball valve at the bottom of the burette, and allow the hydrolysis solution to displace the air trapped between the burette valve and the valve on the sample bulb.

_______(4) Record the level of the hydrolysis solution on a data sheet. Then slowly open the valve on the sample bulb to allow the solution to run into the bulb. If this is done properly, there should be no bubbles going back into the burette. Add 75 ml of solution if using the 200-ml bulbs, and 100 ml of solution if using the 1000-ml bulbs. Do not fill the bulbs over half full at any time. The calibration for the existing burette is 5.25 ml per inch.

_______(5) Close the valve on the sample bulb and also the one on the burette. Remove the sample bulb.

_______(6) Place the sample bulb in the shaker, and shake for about 30 min with no heat applied.

_______(7) Hold the bulb in an upright position, and open the valve to vent off any pressure. Drain the solution into a 250-ml plastic bottle that has been weighed and labeled. Using a squirt bottle, rinse any material from the neck of the sample bulb into the bottle.

_______(8) Add 50 ml of fresh hydrolysis solution to the sample bulb. Place the bulb in the shaker, and heat it to 70-80°C while shaking. To avoid high pressures in the bulb, maintain temperature below 100°C at all times. Shake the bulb for 30 min at temperature.

_______(9) Allow the solution to cool to near room temperature. Vent any pressure; then drain the solution into the plastic bottle used for the original hydrolysis solution.

________ (10) Repeat steps 8 and 9, combining the solutions each time.

________ (11) Weigh the solution, and record the net weight of the solution used. The sample is ready to be submitted for analysis. Request a volume measurement of the hydrolysis solution in addition to other analyses desired.

Rinse of Sample Bulb

________ (1) Add 75 ml of hydrolysis solution to the sample bulb. Place the bulb in the shaker, and heat to 70-80°C while shaking. Because of pressure considerations, do not overheat. Shake the sample at temperature for 45 min.

________ (2) Allow the solution to cool to near room temperature. Then drain the solution into a clean 250-ml plastic bottle that has been weighed and labeled.

________ (3) Add 50 ml of distilled water to the bulb, and shake at room temperature for 15 min. Add this to the previous rinse solution.

________ (4) Repeat step 3.

________ (5) Weigh the sample bottle, and record the net weight of the hydrolysis solution. The solution is ready to be submitted for analysis.

________ (6) Dry and evacuate the bulbs for 2 hr at 100°C before reusing.

sample was transferred to another alpha box, where it was reriffled to give a 10-g sample, which was ground in the motorized mortar-pestle and submitted for analysis.

Nine samples were riffled from each batch of material (two NaF batches and one Al_2O_3 batch). Five of these were processed through the mortar-pestle grinding step; the other four samples were held in reserve. Each of the five samples was analyzed three times for plutonium and uranium.

2. Chemical Analysis of Samples

The NaF samples were dissolved in aqua regia in plastic equipment. The solution was boiled down and taken up with nitric acid. An aliquot was taken, an oxidizing agent added, and the plutonium extracted from the solution. The plutonium solution was counted using a liquid scintillometer. Another aliquot was taken of the nitrate solution to analyze the uranium fluorometrically (three of the samples were analyzed colorimetrically).

The alumina samples were fused with borate-carbonate, and the fusion dissolved in nitric acid from which aliquots were taken for uranium and plutonium analyses.

3. Results

The plutonium and uranium analyses for the as-received material are presented in Tables H.2 and H.3, respectively. Apparent factor-of-10 errors were noted in four analyses. After a requested recheck of the

TABLE H.2. Analysis of Plutonium in Statistical-test Samples

	Plutonium Counts, 10^7 dis/min-g[a]								
Material:	NaF			NaF			Al_2O_3		
Sample No.:	1	2	3	1	2	3	1	2	3
Split No.									
1	324	325	328	10.3	9.88	10.2	2.20	2.26	2.20
2	327	325	326	10.0	98.0[b]	10.0	2.18	2.22	2.20
3	318	320	317	9.64	9.51	0.155[c]	2.19	2.18	2.18
4	311	310	313	9.89	9.46	9.72	2.24	2.26	2.13
5	342	347	344	10.2	9.84	0.980[d]	2.16	2.23	2.20

[a] To convert to percent plutonium, multiply by 5.88×10^{-9}.

[b] No error found when analytical data were rechecked. Used 9.8 instead of 98 in the statistical analysis.

[c] No error found when analytical data were rechecked. Used $9.58 = \frac{9.64 + 9.51}{2}$

[d] No error found when analytical data were rechecked. Used 9.8 instead of 0.98 in the statistical analysis.

APPENDIX H

Statistical Test of Sampling and Analytical Errors

A statistical test of sampling and analytical errors for NaF and Al_2O_3 samples has been completed. The need for such a test was apparent when poor uranium and plutonium material balances were obtained in Runs Pu-14 and -15. Table H.1 shows material-balance data for these and other runs completed in our pilot plant to date. Data for material balances are obtained mainly from analyses of NaF samples. Two batches of NaF were selected for this test--one containing about 1.9 wt % plutonium and 1.12 wt % uranium, the other 0.06 wt % plutonium and 0.047 wt % uranium.

TABLE H.1. Summary of Material-balance Data for Experiments Completed in Pilot Plant

	Run Pu-1 through 3	Run Pu-6	Run Pu-6 through 13	Run Pu-14	Run Pu-15
Weight of Material Processed, g					
Plutonium	123.8	100.4	370.7	19.2	21.4
Uranium	-	-	-	21.4	10.6
Percentage of Material Accounted for					
Plutonium	88	99	96	119	115
Uranium	-	-	-	113	136

Of interest also is the plutonium content of the dumped bed from the fluorinator, since the percent plutonium removal is based on this analysis. To establish that large sampling or analytical errors are not present, one batch of 6000 g of alumina bed containing about 0.013 wt % plutonium and 0.0038 wt % uranium was used in this statistical test.

1. Methods of Sampling

The NaF, generally about 600-1000 g of 1/8-in. by 1/8-in. right-cylinder pellets, was ground twice in a disk mill. The powder was riffled to obtain 10-g samples using a 2- by $2\frac{1}{2}$-in. riffler. This sample was ground to a rouge-like powder using a motorized mortar-pestle, and this was then submitted for analysis. The mill, riffler, and mortar were cleaned with fresh alumina between each use.

The alumina bed material, about 6000 g of 48-100 mesh size range, was riffled to give a 100-g sample using a 4- by 10-in. riffler. This

TABLE H.3. Analysis of Uranium in Statistical-test Samples

	Uranium Concentration, wt %								
Material:	NaF			NaF			Al_2O_3		
Sample No.:	1[a]	2	3	1	2	3	1	2	3
Split No.									
1		1.23[b]	1.07	0.0223	0.0454	0.056	0.0051	0.0269[c]	0.0035
2		1.10	1.08	0.0461	0.0439	0.062	0.00391	0.00304	0.0041
3		1.09[b]	1.10	0.0475	0.0441	0.561[d]	0.00276	0.00204	0.00374
4		1.19[b]	1.12	0.0491	0.042	0.056	0.00260	0.0052	0.0042
5		1.00	1.22	0.0454	0.0449	0.052	0.00283	0.0058	0.0048

[a] Not analyzed.
[b] Colorimetric analysis, others fluorometric.
[c] No error found when analytical data were rechecked. Used 0.00269 instead of 0.0269.
[d] Analytical data recheck provided a new value, 0.0561.

analytical calculations, one error was found. For the variance calculations, it was assumed that in the analysis of the other three samples, a factor-of-ten error had indeed occurred, and the data were adjusted accordingly. In one other analysis, there appears to be a factor-of-about-60 error. A recheck of the calculations did not uncover an error. Consequently, for the variance calculations, an average of the other two samples of that split was used. Standard deviations for the six cases (three for plutonium, three for uranium) are shown in Table H.4.

TABLE H.4. Standard-deviation Data from Statistical Test

	Grand Mean of Data		Standard Deviations			
Matrix	Pu, %	U, %	Analysis Only, %	Sampling Only, %	Analysis plus Sampling, %	Expected from Our Analytical Laboratory, Analysis Only, %
NaF (Batch 1)	1.91		0.5	3.8	3.8	2
		1.12	7.9	-	-	5
NaF (Batch 2)	0.058		1.8	2.0	2.7	2
		0.047	20.5	-	-	5
Al_2O_3	0.013		1.8	-	-	2
		0.0038	29.7	-	-	5

4. Statistical-test Conclusions

The following can be concluded from the data for the two batches of NaF:

1. The standard deviations (0.55 and 1.84%) of the plutonium analyses compare favorably with the standard deviation (2%) we expect from laboratory analyses.

2. The standard deviations of the uranium analyses (7.9 and 20.5%) are ~5% higher than expected.

3. A sampling error is indicated at the 95% confidence interval for plutonium-analysis data for both batches of NaF. The uranium data neither confirm nor deny an error at the 95% confidence interval.

4. For the NaF batch containing 1.9 wt % plutonium, the combined error for sampling and analysis is 3.8%; for the NaF batch containing 0.058 wt % plutonium, it is 2.7%. Because the sample with the higher plutonium concentration is typical of those important in material-balance calculations, the combined error in sampling and analysis should be adopted, indicating that a recovery of plutonium in the 96-104% range should be considered satisfactory.

The following can be concluded from the data for the one batch of Al_2O_3:

1. The standard deviation (1.77%) of the plutonium analysis compares favorably with the expected 2% standard deviation.

2. The standard deviation (30%) of the uranium analysis is higher than expected.

3. At the 95% confidence level, no sampling error can be detected using either the uranium or plutonium results.

5. Recommendations

The following are recommendations for future sampling techniques:

1. For the alumina dumped-bed samples, continue using the same riffling procedures.

2. For the NaF samples, use either of the following procedures:

   a. Since the standard deviation of the plutonium analyses is small and since the samples are grab samples from larger samples, final grinding of the larger sample in the mortar and pestle apparently homogenized the sample well. Although probably not practicable, grinding of the entire 500-1000-g batch to a rouge-like consistency, and taking a grab sample from this should lower the sampling error.

   b. Prepare two samples from each batch. This would have two advantages: It would decrease the variance by a factor of 1.4, and it would probably eliminate the factor-of-10 (or more) errors found in 5% of the samples submitted, since the error would become apparent by comparing the two sample results. The duplicate samples would double the workload, but if enough confidence could be placed in the neutron-count-rate data,[19] only a few samples would have to be analyzed to obtain data for material-balance calculations.

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