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STATIC BED REACTOR FOR STUDIES OF A PLUTONIUM HEXAFLUORIDE VOLATILITY PROCESS

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

U.S. ATOMIC ENERGY COMMISSION
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Jerry D. Moseley

Herbert N. Robinson

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Static Bed Reactor for Studies of a Plutonium Hexafluoride Volatility Process

Jerry D. Moseley and Herbert N. Robinson

Abstract. Studies were begun to find if chemical separation and purification of plutonium from waste material could be achieved with fluoride volatility processes.

Equipment designed for the project and the procedures developed for use are described.

INTRODUCTION

Fluoride volatility processes are being developed at several National Laboratories of the Atomic Energy Commission (AEC). In such processes, the chemical separation of uranium, plutonium, and their fission products is achieved by formation of the volatile hexafluorides of uranium and plutonium. The main interest in work done at the laboratories has been the processing of uranium oxide containing less than 1 percent each of plutonium and fission-product oxides. The Rocky Flats Plant is interested in the chemical separation and purification of plutonium from nonirradiated waste materials containing from approximately 1 to 99 percent of plutonium. The waste materials are generated as residues resulting from a plutonium-metal foundry and machining operation. The equipment to be described was built to determine the feasibility of processing such waste residues to recover the plutonium.

Basically, the plutonium hexafluoride volatility process involves converting residue from plutonium (chiefly plutonium dioxide, PuO_2) to the volatile hexafluoride (PuF_6), separating the plutonium from other residues by volatilization, and reducing it to tetrafluoride (PuF_4). The resultant plutonium tetrafluoride can be further reduced to metal using calcium (Ca). Conversion to the hexafluoride will be done in a fluid bed at 400° to 600°C, using fluorine (F_2). In this process, the effluent gas passes through a plutonium hexafluoride desublimer or product collector. The fluorine gas can be recycled through the bed until the plutonium in the bed material is less than 0.002 grams of plutonium per gram. The plutonium hexafluoride becomes sublimed into a cold-wall flame reductor and reacts with hydrogen to form the nonvolatile plutonium tetrafluoride. Hydrogen fluoride, a by-product of the last reaction, may be removed and disposed of chemically. To carry out preliminary studies of the process concepts, a fluorine supply system, a static bed reactor, desublimers (product collectors), static hydrogen reductors (reduction bombs), and halogen disposal reactors were built.

The processes involve chemical reactions using plutonium dioxide (PuO_2), fluorine or hydrofluoric acid (F_2 or HF), plutonium tetrafluoride (PuF_4), plutonium hexafluoride (PuF_6), hydrogen (H_2), and oxygen or water, (O_2 or H_2O). The chemical reactions of interest follow:

1. $PuO_2 + F_2$ (or HF) $\xrightarrow[100 \text{ to } 600°C \text{ (HF)}]{100 \text{ to } 250°C \text{ } (F_2)}$ $PuF_4 + O_2$ (or H_2O)

2. $PuF_4 + F_2 \xrightarrow{400 \text{ to } 600°C} PuF_6\uparrow$

3. $PuF_6 + H_2 \longrightarrow PuF_4 + 2HF$

4. The excess of F_2 (or HF) + disposal chemical $\rightarrow$ neutral (or basic) material suitable for throwaway

DISCUSSION

Part I. OBJECTIVES

The objectives of the program were: (1) to give Rocky Flats personnel firsthand experience in handling fluorine and volatile-metal fluorides; (2) to determine which categories of foundry-residue material could be handled in a fluoride-volatility recovery process; and (3) to determine decontamination factors for the major impurities in the plutonium product.

To begin the study, some basic knowledge and assessments were required of:

1. Desublimation and sublimation characteristics of the hexafluoride.

2. Reactions between hydrogen and plutonium hexafluoride.

3. Methods of halogen disposal.

4. Kinetics involved of the reaction to form plutonium hexafluoride.

5. Process alternatives, such as direct reduction of the hexafluoride to metal, reduction of the hexafluoride with iodine vapor, etc.

6. Experience with various materials of construction, useful equipment life, types of maintenance problems, etc.

7. Analytical methods which could be developed for application to other analogous problems.

8. Specific criteria to develop for in-line process instrumentation methods to permit semiautomated plant-scale processing.

Equipment Description:

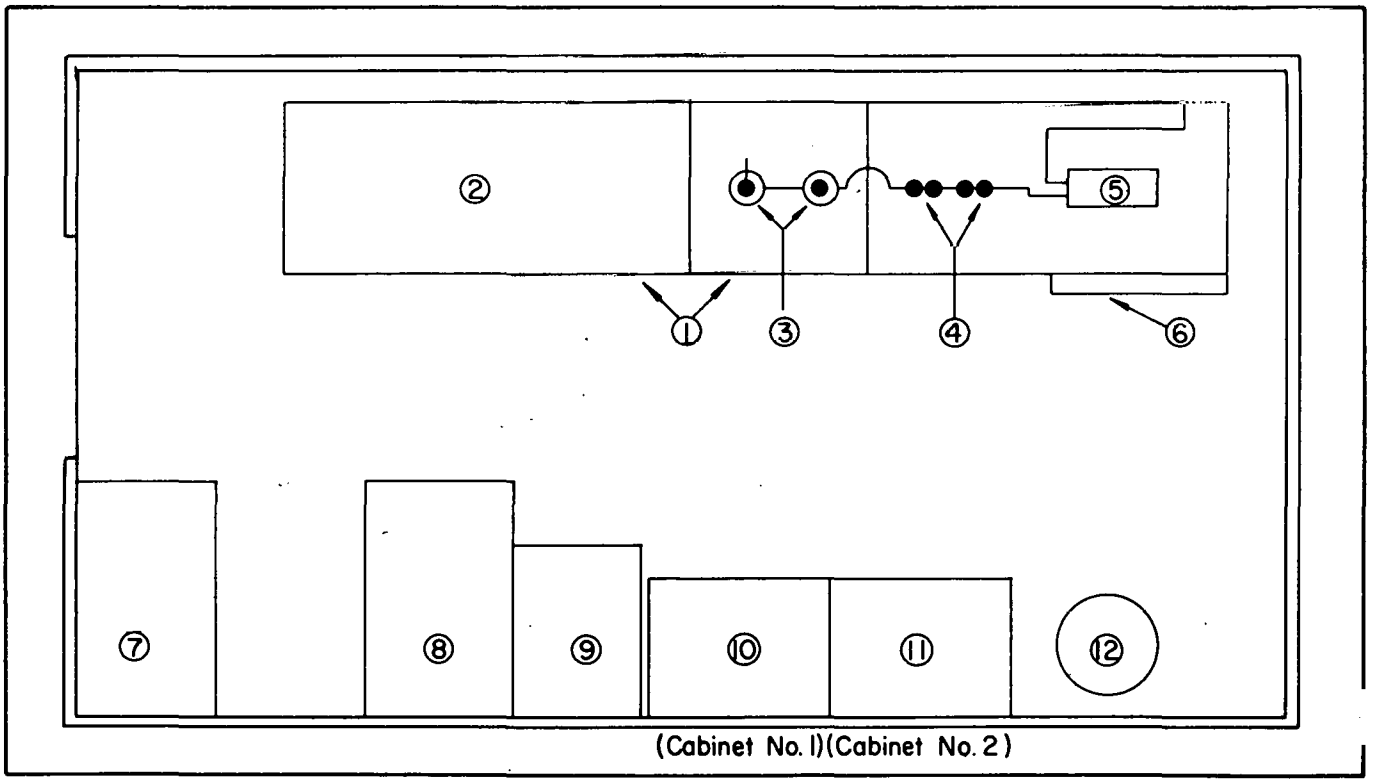
The general layout of the static bed system is shown in Figure 1. Fluorine supply cabinets, the liquid-argon supply and the electronic-control cabinet containing the thermocouple readouts and furnace controls are indicated as 9, 10, 11, and 12. The glove box containing the major equipment is noted as Item 1. The equipment will be described in the order of normal use in the laboratory.

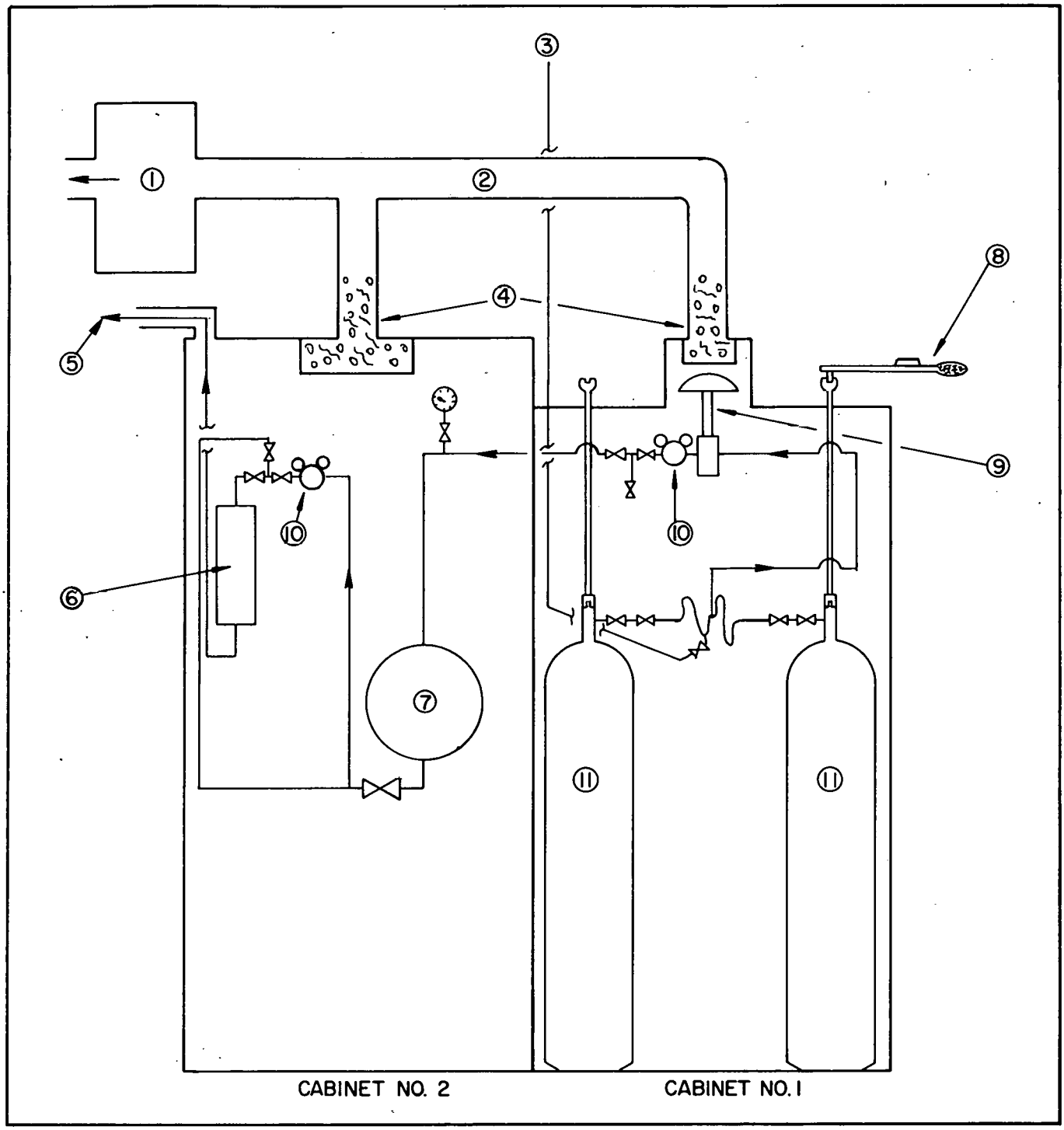
FLUORINE SUPPLY – The fluorine-supply barricade consists of two cabinets from which air is exhausted through the top (see Figure 2). Air flow through the cabinets is increased by the use of an exhaust fan. Each exhaust line contains an in-line fluorine trap containing approximately 1200 grams of activated alumina and approximately 400 grams of activated steel wool. The traps are designed to handle all

FIGURE 1. Arrangement of room area with static bed, fluoride-volatility system. (Room dimensions are 20 by 10 feet.)

Legend

1. Glove Box.
2. Sample Preparation and Weighing Area.
3. Halogen Disposal Traps.
4. Product-Collector Traps.
5. Static Bed Reactor.
6. Gas-Rotameter Manifold.
7. Storage Area.
8. Work Table.
9. Instruments and Controls.
10. Fluorine Supply (Cabinet No. 1).
11. Fluorine Supply (Cabinet No. 2).
12. Liquid Argon.





Legend

1. Fan.
2. Exhaust Duct.
3. Argon.
4. Chemical Filter.
5. To Gas-Rotameter Manifold.
6. Sodium-Fluoride Trap.
7. Surge Tank.
8. Torque Wrench (for remote extension).
9. Solenoid-Operated Safety Valve.
10. Pressure Regulators.
11. Fluorine Gas.

FIGURE 2. Fluorine Supply Cabinets.

fluorine leaks, except catastrophic rupture of the pressurized fluorine bottle. Equipment within the cabinets include:

Cabinet 1:

1. Two 4½-pound cylinders of fluorine with valves having remote extensions to outside of cabinet.
2. A double-valve manifold, using Hoke-4251 Monel valves and having an inlet for purging with argon (A).
3. Solenoid-operated safety valve operated from outside the room.
4. A Matheson fluorine regulator with a brass double-valve manifold to lower the pressure from 400 to less than 30 pounds per square inch gauge (psig) pressure.
5. All tubing is either nickel or Monel.
6. All valving is double for additional safety.

Cabinet 2:

1. An Acco-Helicoid pressure gauge, for fluorine service [0 to 2000 millimeters (mm) of mercury (Hg) absolute pressure].
2. A 14-inch spherical surge tank made of 12-gauge nickel and with a capacity of 22.5 liters, pressure-tested at 150 pounds per square inch absolute (psia).
3. A Matheson fluorine regulator with brass double-valve manifold to lower the fluorine pressure from 30 to 5 psig.
4. A line bypassing the regulator for vacuum checks.
5. A trap consisting of a copper vessel (3 by 13 inches) for adsorbing hydrogen fluoride (HF) impurities in the fluorine supply. The trap, heated to 100°C, is filled with 1600 grams of sodium fluoride (NaF).
6. All tubing is nickel or Monel and the valves are Hoke M-413.

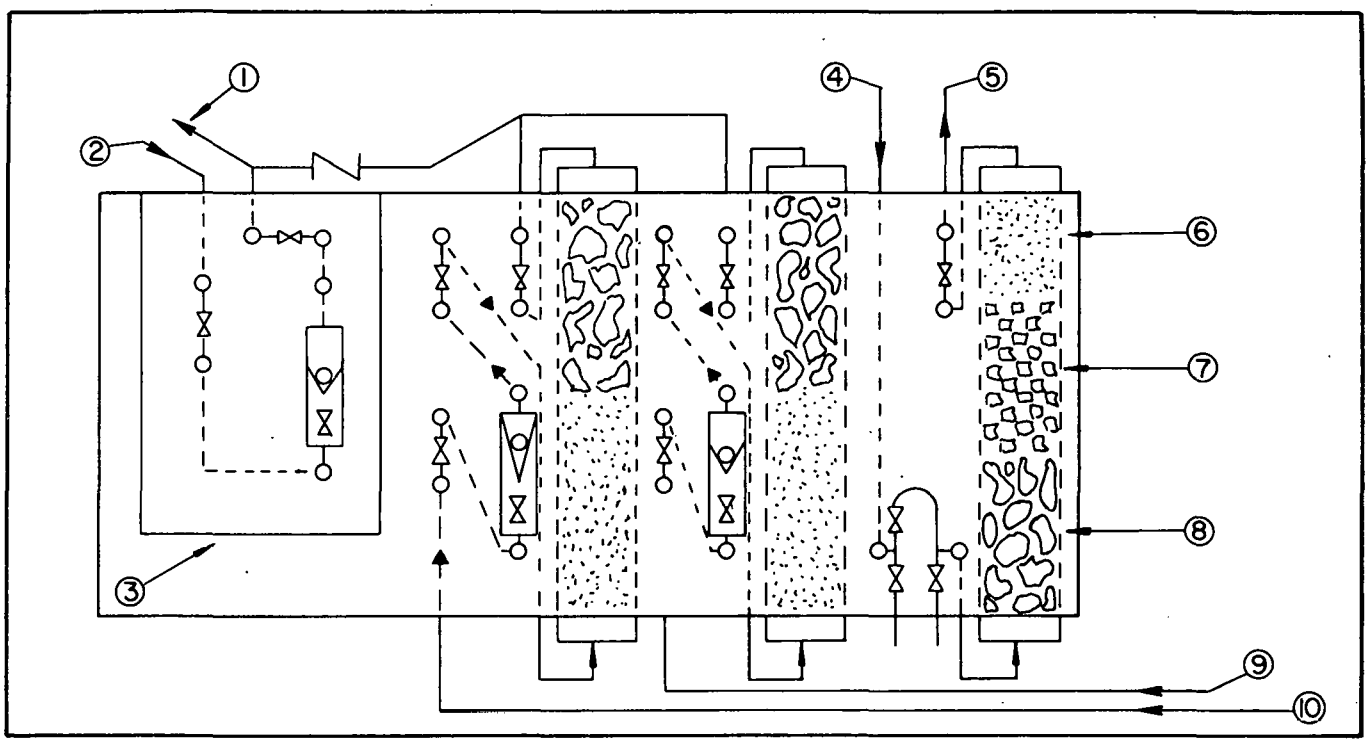
FLUORINE SUPPLY LINES – All fluorine lines outside the cabinets are double-walled. The inner wall is of nickel; the outer wall is of copper tube. The tubing was bent for installation whenever possible, otherwise it was silver-soldered.

GAS-ROTAMETER MANIFOLD – The gas-rotameter manifold includes flow controls and indicators for HF, F_2, A, and H_2 gases (Figure 3). The HF- and F_2-valves and rotameters are further shielded by a ¼-inch cover of Plexiglas. Behind the manifold are drying traps, and traps to prevent back flow or diffusion of F_2, HF, or PuF_6 into other lines. Controls for the vacuum system are included on this panel. The manifold system includes the following materials:

1. All valves are Hoke M-413.
2. All tubing is nickel.
3. Brooksmite rotameters for F_2 and HF are made of Kel-F and deliver 100 to 550 cubic centimeters per minute (cm^3/min).
4. Brooks rotameters for inert gases deliver 100 to 550 cm^3/min.
5. Three, 3 by 13-inch vessels made of copper tubing are included in the rotameter manifold:
   a. The two vessels on the inert-gas lines were filled with 478 grams of molecular sieves and 665 grams of activated aluminum oxide (Al_2O_3).
   b. The vessel on the vacuum line was filled with 338 grams of molecular sieves, 60 grams of sodium fluoride (NaF), and 450 grams of activated Al_2O_3.
6. One sampling station was located on the vacuum line.
7. A Matheson-Monel check valve was located in the inert gas line to prevent backflow of F_2 and HF into the line.

STATIC BED REACTOR AND GAS-SAMPLING MANIFOLD SYSTEM – Gas lines leaving the rotameter manifold go through the rear of the glove box and into a static bed reactor where the gas contacts the sample. The line exits through the reactor and enters a distribution system where gases can be trapped, hydrolyzed, reduced, etc., according to the specific experiment at hand. The system is shown in Figure 4, and consisted of the following materials:

1. All lines were either nickel or Monel.
2. Hoke M-413-K or M-413 valves were used.



Legend

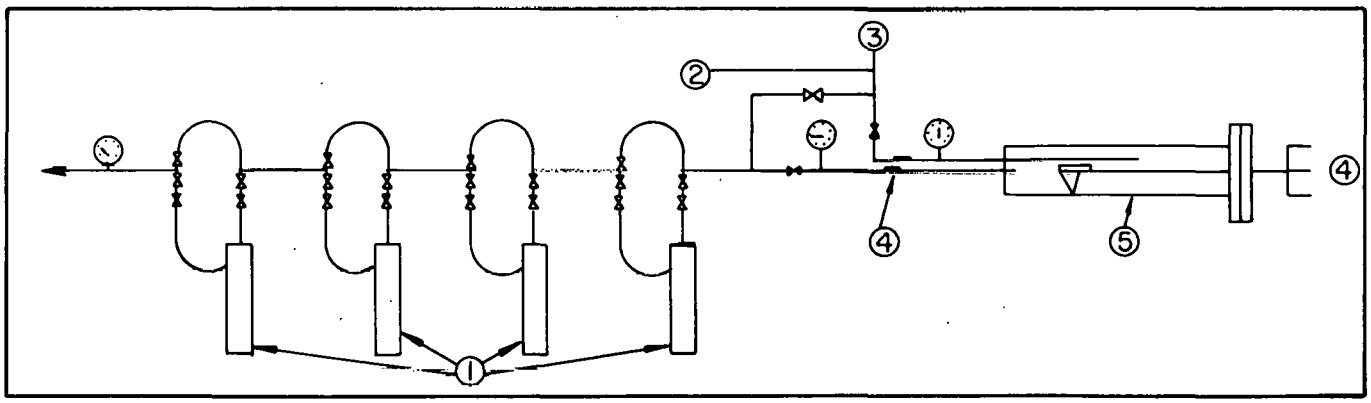
1. Hydrofluoric Acid or Fluorine (to reactor).
2. Hydrofluoric Acid or Fluorine Supply.
3. Plexiglas Shield.
4. Vacuum Line (from box).
5. Vacuum Pump.
6. Molecular Sieves.
7. Sodium Fluoride.
8. Activated Alumina.
9. Hydrogen or Inert Gas.
10. Gas.

FIGURE 3. Gas-Rotameter Manifold Panel.

FIGURE 4. Static Bed Reactor and Gas-Sampling Manifold System.

Legend

1. Product Collectors.
2. To Vacuum Systems.
3. From Gas Manifold.
4. Thermocouples.
5. Static Bed Reactor.



3. The reactor was made of 2-inch nickel tubing, 14½-inches long including flanges (Figure 5).

   a. A 13½-inch length of ¼-inch tubing welded into a ½-inch flange served as a thermowell and sample-boat holder. Supports designed to hold a sample boat were welded to the ¼-inch tubing (thermowell), so as to locate the sample in the exact center of a horizontal-tube clamshell furnace surrounding the reactor. Three thermocouples were placed into the tube, one each at the front, center, and back of the boat position.

   b. The original nickel sample boat was ¼ inches deep by ½ inches wide by 2 inches long. This was later changed to 1½ inches wide to allow larger samples.

   c. The gas inlet entered the rear of the reactor and extended past the sample allowing the preheated gas to pass over the sample on its way out.

   d. The gas outlet extended ¾ inches from the back of the reactor.

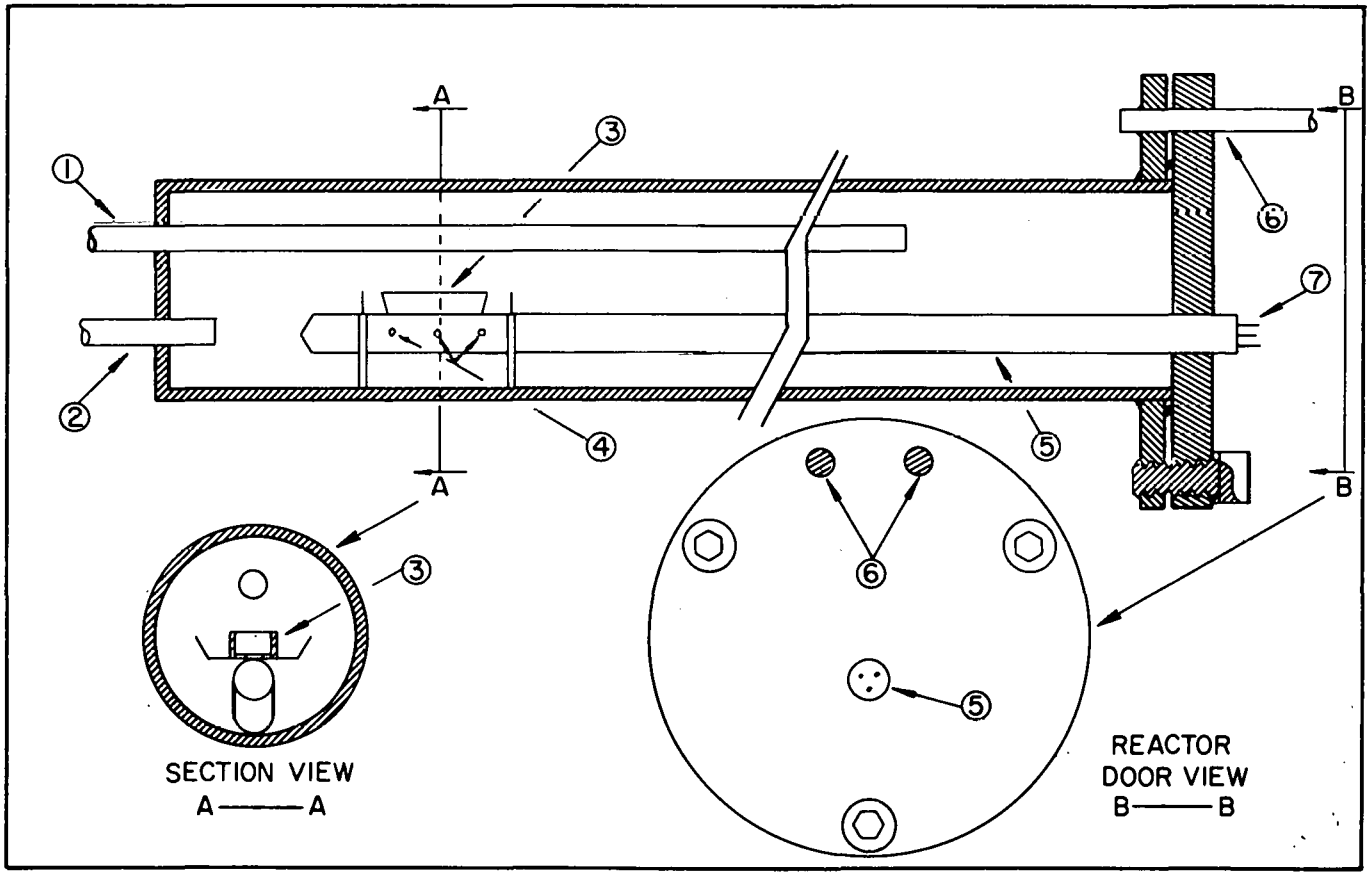
   e. All welds on the reactor were performed with a nickel-200 welding rod.

4. The reactor was placed in a Lindberg Hevi-Duty furnace. The temperature was regulated with an automatic temperature controller.

FIGURE 5. Static Bed Reactor and Sample Boat.

Legend

1. Gas Inlet and Preheater Tube.
2. Gas Exit.
3. Sample Boat.
4. Thermocouple Locations.
5. Thermocouple Well and Sample Boat-Support Frame.
6. Two Slide Rods (supporting furnace door).
7. Thermocouple Cables.



5. The exit line from the reactor passed to a two-station double manifold.

   a. A product collector or desublimer is normally placed at each station (Figure 6). Each collector has a ¾-inch Monel or nickel tube, 8 inches long. The gas-inlet tube consisted of a ¼-inch tubing, extending 6¾ inches into the collector. The gas-outlet tube is located ¼-inch from the top of the collector. The valves on the inlet and exit are Hoke M-482. An additional sample station, located just prior to the halogen-disposal traps (see Figure 7) served for further back-up and miscellaneous uses.

   b. The station manifolds were placed on a Chromalox (strip heater) heated, black-iron support. To prevent desublimation of HF and various metal fluorides in the lines, the valves and lines were heated to about 40°C.

6. Three Acco-Helicoid, 0 to 2000-mm Hg absolute pressure gauges were used.

   a. One on the inlet of the reactor.

   b. One on the exit of the reactor.

   c. One after the two-station manifold sets.

7. Six chromel-alumel thermocouples were connected to a continuous 6-point Foxboro recorder.

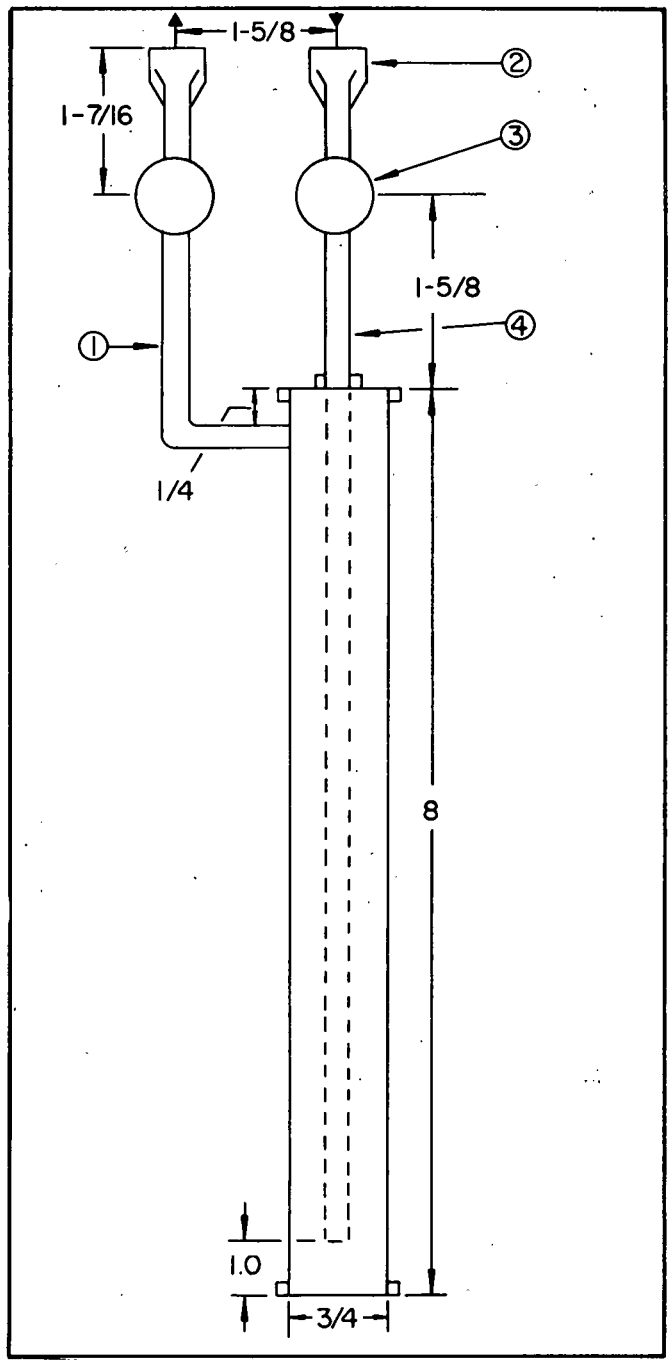
   a. One recorded the temperature of the F_2 gas before it entered the reactor.

   b. One recorded the temperature of the F_2 gas and product gas leaving the reactor.

   c. One recorded the temperature of the black-iron supports and manifold.

   d. Three, previously described, were in the reactor tube.

HALOGEN DISPOSAL AREA: – The halogen disposal area was contained in a separate section of the glove box (Figure 7). Two vessels contained a chemical (e.g. charcoal, soda lime, or activated Al_2O_3), which reacts with HF and F_2 and converts them to a neutralized state. The vessels were arranged so that they might be used in series, in parallel, or singly. An extra sample station [see Item 5 (a)] is also in the glove-box section.



Legend

1. Exit Tube to Gas-Sampling Manifold.
2. Flare Fittings.
3. Hoke M-482 Valves.
4. Inlet Tube from Gas-Sampling Manifold.

FIGURE 6. Nickel Product Collector. (Dimensions in inches.)

1. The two halogen disposal vessels were made of 3-inch diameter by 13 inches long of Monel pipe with welded flanges at each end. The Monel vessels were filled with charcoal, activated alumina, or soda lime depending on the method of halogen disposal under study.

2. The gases from the vessels normally contained less than 10 parts per million (ppm) of reactive halogen, were moist O_2 or fluorinated-carbon compounds, and were vented to the glove box. When necessary, the gases were vented also into a vacuum system which runs along the back of the glove box.

3. In the initial months of operation, the halogen disposal exits of the traps were monitored by a reactive-halogen detection device consisting of a nylon string. When exposed to a reactive halogen, the string broke and sounded an alarm. Some potassium-iodide (KI) starch paper was later substituted as a halogen detector.

4. When the vacuum system was used, the gases before going out of the glove box entered another disposal vessel filled with activated alumina.

5. All valves were Hoke M-413-K.

6. A Matheson-check valve prevented gases from backing up from the disposal vessels into the reactor and sample-station area.

7. All tubing was either Monel or nickel.

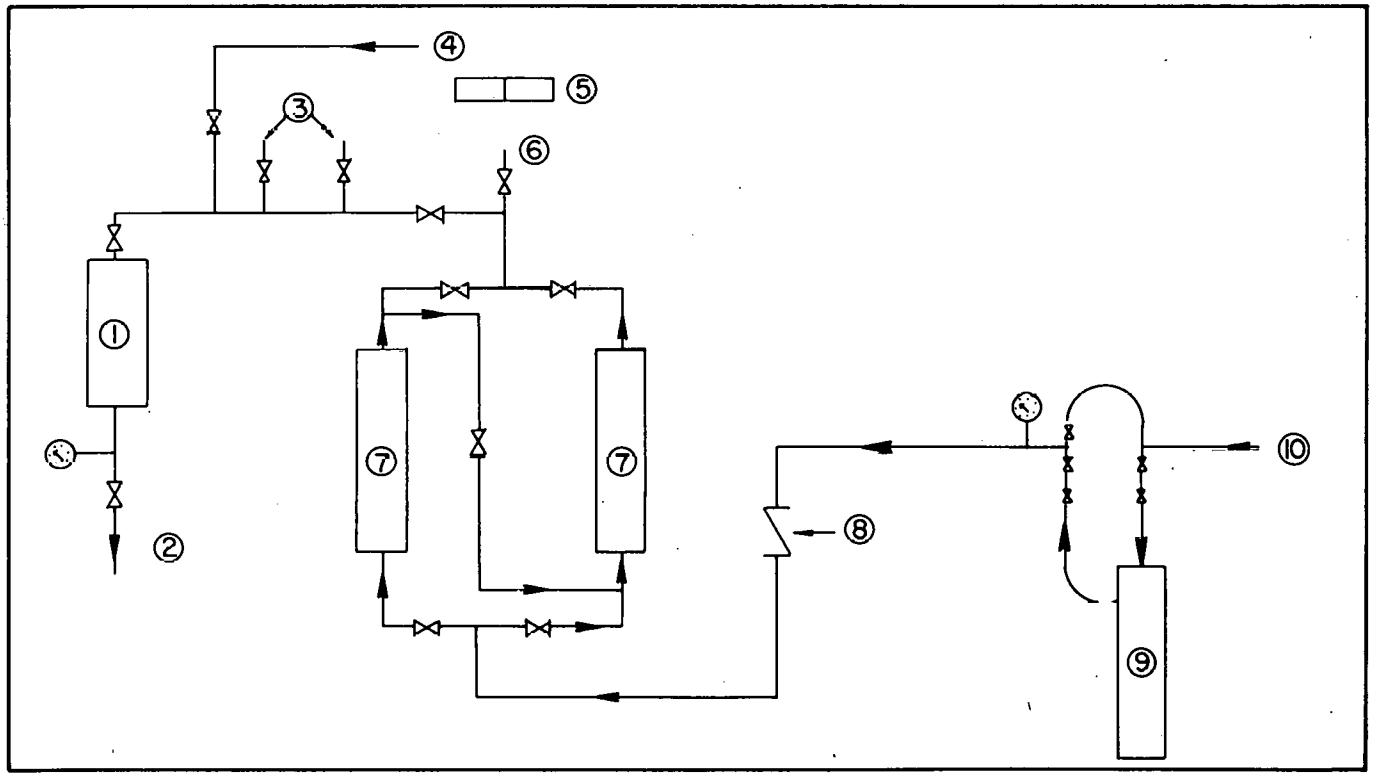
8. Temperatures of the vessels were monitored by thermocouples attached to the outside of the vessels. The set up served as an indicator of the rate and extent of reaction of the material inside the nickel traps.

9. An Acco-Helicoid, 0 to 2000-mm Hg, absolute pressure gauge was located between the sample station and the disposal vessels.

FIGURE 7. Halogen Disposal System.

Legend

1. Back-Up Halogen Disposal Trap.
2. To Control Panel and Vacuum Pump.
3. Extra Vacuum Taps.
4. Bypass (from reactor area).
5. Halogen Alarm.
6. Vent to Glove Box.
7. Halogen Disposal Traps.
8. Check Valve.
9. Product Collector.
10. From Reactor Area.



MISCELLANEOUS EQUIPMENT –

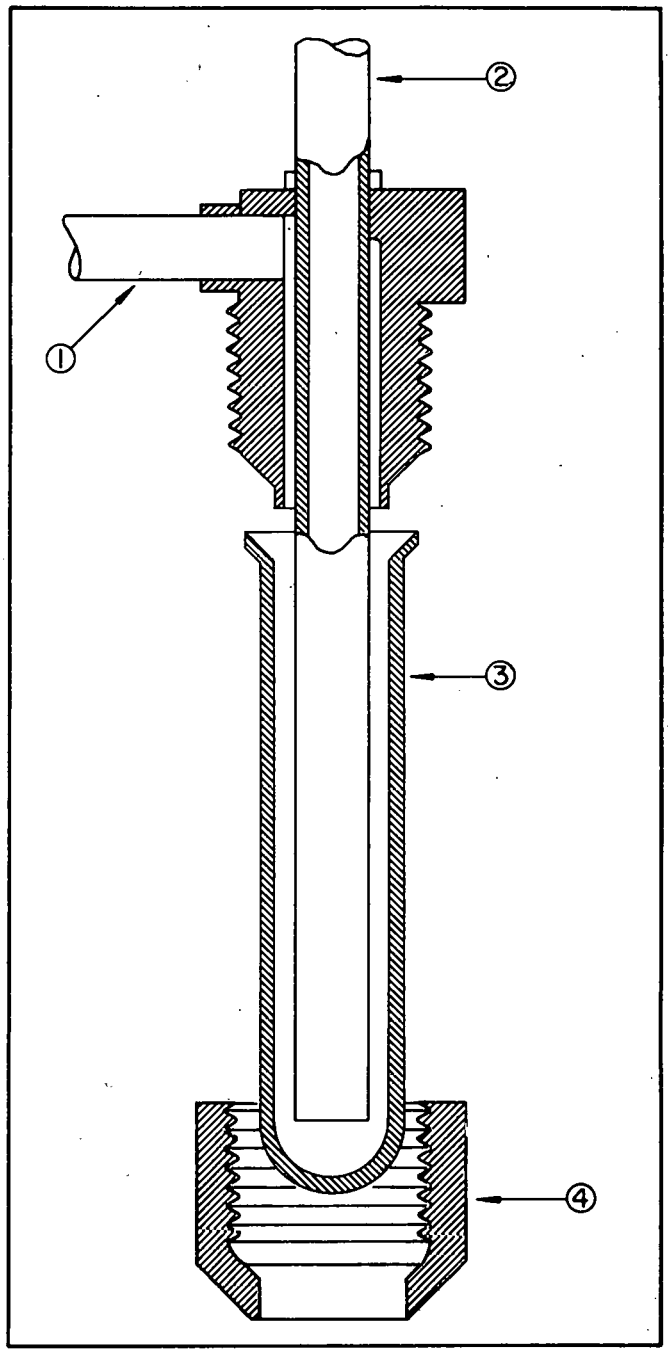
1. Test-tube adapters (Figure 8) were used to attach Kel-F test tubes to the nickel and Monel gas-sampling manifold for reactions such as the hydrolysis of PuF_6. The test tube fitted into the adapter and allowed visual observation of the reaction system.

2. Nickel test tubes were used in the same manner as the Kel-F tubes and fit the same adapter. With nickel tubes, it was necessary to use a Teflon gasket between the adapter and the test tube.

3. Reactors (Figure 9) which resemble conventional reduction-bomb assemblies were fabricated to use in the reduction of PuF_6 with hydrogen (H_2), iodine (I_2), and calcium (Ca). These were high pressure bombs made of Type-304 stainless steel and used a Hoke TY-447 high pressure valve. Several reactors were Teflon-lined to assure higher product purity than possible with the Type-304 stainless steel bomb. Liners made of alumina ceramic were also used to prevent corrosion products of the bomb walls getting into the product. Since the PuF_6 diffused into and reacted with the ceramic liners, this approach was discontinued.

4. A Welch vacuum pump was protected from F_2 or PuF_6 contamination by appropriate activated-alumina traps. The pump was vented to the overhead exhaust system to prevent diffusion of oil into the glove box.

5. The electronic control panel contained Foxboro temperature recorders, a Lindberg furnace controller, and Variac power-stats to control power to electrical outlets in the glove box.



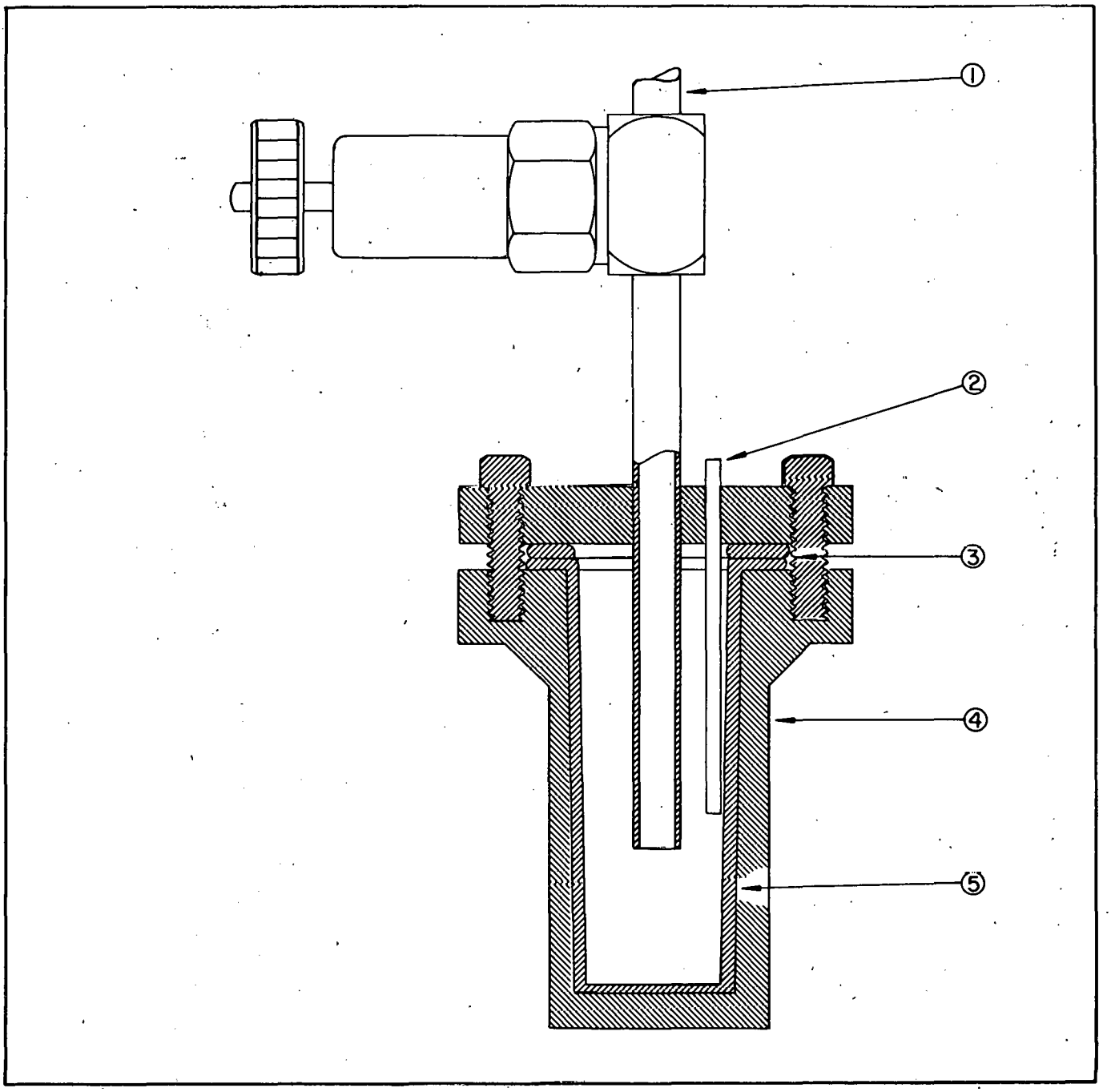
Legend

1. Gas Exit to Sampling Manifold
2. Gas Inlet from Sampling Manifo
3. Kel-F or Nickel Test Tube.
4. Hexagonal Nut.

FIGURE 8. Test-Tube Adapter to Metal Vacuum Line.

Operating Experience:

GENERAL – The equipment described in this report has been in operation for 16 months. The total exposure time to a fluorine atmosphere is about 1200 hours, and includes about 600 hours at which time the reactor temperature was higher than 500°C. The majority of the valves and lines have been held at 30 to 40°C. The sodium-fluoride, filled copper vessel designed to adsorb the hydrogen-fluoride (HF)



Legend

1. Gas Inlet-Outlet Tube.
2. Thermocouple Well.
3. Gasket.
4. Type-304 Stainless Steel.
5. Liner of Teflon.

FIGURE 9. Typical Reduction Bomb.

impurity from the fluorine-gas stream has been held 100°C and under a fluorine atmosphere for the entire 16 months, except for a one-week period when the trap was regenerated to allow further adsorption of hydrogen fluoride.

Corrosion problems have been minimal under the fluorine exposure. Minimal is defined here as (a) only a few valves have required replacement because of corrosion, (b) only two holes have appeared in the tubing or around welds, and (c) only two holes have appeared in the reactor tube assembly, both at welds on tubing entering the reactor. Corrosion products (predominantly nickel fluoride) are observed on the inner surface of pipes and tubing.

Corrosion products from the nickel and Monel have been observed in both the fluorination residues (non-volatiles and feed material) and in the final product (plutonium tetrafluoride). The impurities in the final product were minimized when Teflon-lined hydrogen reduction bombs were used. Impurity levels in the percent range were found when unlined stainless steel, reduction equipment was used.

The system has operated without major problems. This is primarily because of the care taken in the construction, assembly, and operation of the equipment. All parts to be exposed to fluorine were cleaned by washing with soap and water followed by an ethyl-alcohol rinse. Just prior to installation, another rinse using Freon TF was performed. After assembly, the system was helium leak-checked under both pressure and vacuum. The integrity was further assured by a controlled fluorine passivation cycle. Fluorine was added at a pressure of 50 to 75-mm Hg and at room temperature to all parts of the system. Fluorine pressure was gradually increased to 760 mm Hg, over a 3 to 4-day period.

GAS-TRANSMISSION LINES – Gas-transmission lines were welded or silver-soldered nickel, or Monel. Care was taken to clean these before and after welding or silver-soldering. After several hundred hours of operation, the only visible change was a thin coating of nickel fluoride on the interior of the tubing. Additionally in the areas exposed to plutonium hexafluoride, a coating of plutonium tetrafluoride was observed. The coating was thin in areas containing no obstructions and where the temperature had not exceeded 40°C. The coating was heavier in areas where intermittent heating to 100°C or greater had occurred.

Plugging of lines occurred downstream of the halogen disposal vessels. The plugging was due largely to moisture and corrosion products. The soda lime and alumina contained water of hydration which was released when the fluorine reacted with the disposal media. Water is also one of the products of reaction when hydrogen fluoride or fluorine is reacted with soda lime or hydrated alumina. Analysis of the solids which plugged the lines showed it to be nickel fluoride and copper fluoride. Substitution of Monel vessels for copper vessels reduced this problem. However, the Monel vessels produced some nickel fluoride which was carried into the small tubing at the exit of the disposal media traps and plugged the line. Charcoal was then tested as the disposal media. During the use of charcoal, no corrosion products or plugging of the lines due to moisture or corrosion products have been observed. On occasion, highly exothermic, rapid reactions between the fluorine and the charcoal have occurred which have pressurized the lines and blown carbon dust into the ¼-inch tubing. Addition of a check valve to prevent pressurization of the reactor and the gas-station manifold area has minimized this problem.

VALVES – Two valve problems were observed. Valves exposed to fluorine and plutonium hexafluoride and heated in excess of 100°C have required replacement or cleaning. This was due largely to a buildup of plutonium tetrafluoride (from thermal and radiolytic decomposition of plutonium hexafluoride) on the needle or on the valve seat. Replacement of the needle and cleaning of the seat have usually corrected the problem. In only four or five cases has the entire valve required replacement. Evidence of corrosion is greatest in those valves subjected to the higher temperatures.

Valves exposed to 400 pounds fluorine pressure have also been a problem. Packed valves were originally installed at the fluorine vendor's recommendation. Teflon and Kel-F packing was found to erode, and vaporize in some cases, resulting in leaks into the fluorine cabinets. Kel-F or Teflon seats on packless valves have been found to erode and leak through. This is thought to be due in part to the high velocity of gases passing through the valve. The Teflon and Kel-F packless seats will be replaced to provide metal to metal contact. This type of valve or valve seat has not been evaluated at this time.

PRESSURE GAUGES – Acco-Helicoid gauges with Monel-Bourdon tubes have proven satisfactory.

These measure pressure over the range 0 to 2000-mm Hg. They have been exposed to fluorine at about 30°C. Thermocouple vacuum gauges exposed to ppm levels of fluorine have functioned properly, but those in contact with 100 percent fluorine have not been satisfactory.

ROTAMETERS – The Brooksmite Model 2001-V and 1350-V rotameters have performed according to specifications.

REGULATORS – Matheson B15F-F70M regulators have operated satisfactorily.

SAFETY DEVICES – The in-line activated alumina traps in the exhaust duct of the fluorine cabinets have not been put to a full test. In small leaks, such as leaking valves, they have performed satisfactorily and no fluorine problems have occurred in the overhead exhaust as the result of using the traps. No leaks, even remotely approaching a catastrophic leak, have occurred. The air-operated, in-line safety valve located in Cabinet No. 1 has performed satisfactorily. It has been used at pressures from 50 to 400 psig. No emergencies have occurred which necessitated the use of the valve. However, it has proven to be convenient in loading and unloading the cylinders and in loading the surge tank for use in small scale runs.

The effectiveness of the activated oxidized steel wool, used downstream of the activated alumina traps in the cabinets and in the exhaust system of the glove boxes, has not been tested.

The use of filter paper soaked with potassium iodide (KI), has been invaluable. This has been used to detect fluorine leaks both in the fluorine cabinets and the glove box and has been the best tool for detecting fluorine leaks.

The fluorine alarm consists of a nylon cord which, when broken by a jet of gas containing a few ppm of fluorine, causes the alarm to activate (sound). It has always performed satisfactorily when there has been a fluorine-gas leak. It has also sounded several times due to the string slipping or breaking, due to the tension exerted on it. It is not in regular use at this time.

In the original setup of the equipment, it was recognized that a fluorine or plutonium-hexafluoride leak would require humidity in the atmosphere to hydrolyze these gases. This could be accomplished by passing the gases which left the cabinet and the glove box through a water scrubber or by humidifying the air entering the glove boxes. The latter alternative was selected, but proved to be a poor choice. Humidification of the room using steam as the water-vapor source, raised the temperature and humidity to a point of discomfort for the operating personnel. It is recommended, for future installations, that the gases exiting the glove box and room be humidified.

Protection of personnel from the fluorine gas has been of paramount concern. Personnel working with fluorine bottles must wear leather jackets and leather gloves to protect the upper part of their bodies. Face shields are worn by personnel when it is necessary to open the doors of the fluorine cabinets. All fluorine lines which are external to the fluorine cabinets and to the glove box are constructed of double-wall tubing. The inner tube, carrying the fluorine, is nickel and the outer tube is copper. A cover of ¼-inch Plexiglas was placed over the fluorine and hydrogen-fluoride rotameter manifold in case the rotameter leaked.

Eye and body showers are located immediately outside the door of the room. The appendices should be consulted for a description of other safety practices.

PART II. EQUIPMENT OPERATING PROCEDURES

One of the primary objectives of this experiment was to train personnel in operating the equipment. Dow personnel having extended process experience with fluorine and volatile metal hexafluorides were virtually impossible to find for the start-up phase. Thus, written operating procedures were mandatory.

Accordingly, general and specific procedures and instructions were prepared. Information on the safe handling of fluorine was gained from the literature, from the Rocky Flats Safety Department, and from various individuals at the National Laboratories of the U. S. Atomic Energy Commission. The information was specifically adapted to the particular equipment described herein. Whenever a question of safety arose, the conservative approach was invariably taken. All operating procedures were kept in the laboratory for reference.

The written procedures are attached as Appendices A through D. The procedures are general; and specific experiments have called for limited deviations, especially in the procedures described in Appendix D. The deviations were carefully considered before adoption.

APPENDIX A. General Procedures for Operation of the Plutonium-Hexafluoride Volatility, Static Bed Equipment.

A. Personnel working with this equipment shall read and shall be familiar with:

1. The basic fluorine-data sheets supplied by the fluorine supplier.

2. All procedural and safety instructions written for use with this equipment.

3. "The Properties of Plutonium Hexafluoride," ANL-6753, a publication of the Argonne National Laboratory (USAEC).

4. The equipment flowsheet.

5. The stated purpose and objectives of this study.

B. All work with fluorine, hydrogen fluoride, and plutonium hexafluoride shall be performed with at least two people in or within normal voice range of the laboratory. One of the two must be experienced with the equipment.

C. All personnel working in the laboratory must be familiar with the location of the safety shower and eye-wash bowl. (In the event of a fluorine or hydrogen-fluoride burn, flood the affected area with water from the safety shower or eye-wash bowl and report immediately to the Medical Department. The nearest Health Physics monitor should be notified, as well as the immediate line supervision.)

D. All personnel working in the laboratory must have previously attended a talk given by a representative of the Medical Department on the treatment of fluorine and hydrogen-fluoride burns.

E. In the event of a major fluorine, hydrogen fluoride, or volatile-hexafluoride leak, the room must be evacuated by personnel immediately. Personnel in the adjacent rooms and line supervision must be notified immediately. If the major leak is plutonium hexafluoride, sound the building fire alarm so that respirators will be donned in all areas (see Item F). At least one person shall stand outside the laboratory door (unless his personal safety is endangered), until corrective action is decided upon.

F. In the event of a minor fluorine or volatile-hexafluoride leak, the room may be evacuated. In any event, personnel in the adjacent rooms must be notified of a possible dangerous condition. Protective equipment and clothing should be donned before correcting the leak. The normally carried dust respirator furnishes only partial protection from these gases. Proper Chemox (or equivalent) equipment should be used for any necessary entry into a contaminated area.

G. Volatile hexafluorides shall be prepared and handled only when the room humidity is greater than 20 percent (70°F).

H. All valves in the system must be equipped with open-closed tags. These tags will be used without exception.

I. All Hoke-413 series valves will be opened and closed with the aid of torque wrenches. A torque of 35 inch-pounds is the maximum which will be exerted on the valves.

J. A record of the period of time shall be maintained on the use of all fluorine and volatile-fluoride disposal traps. No trap shall be used beyond 70 percent of its theoretical capacity.

K. No more than 200 grams of plutonium in any form (or 25 grams of plutonium hexafluoride) shall be allowed in any section of the glove box line, except for pass through purposes. Any exceptions must be approved in writing by both the Health Physics and Criticality Groups.

APPENDIX B. Procedures for Installing and Changing Fluorine Cylinders.

A. Carefully read fluorine-data sheets.

B. Perform with two people, one of whom is experienced. Notify personnel in adjacent areas of pending action as needed.

C. Wear protective clothing. This shall include at least: (1) leather (F_2) or neoprene (HF) work gloves; (2) leather jacket; (3) heavy duty plastic-face shield. A gas mask shall be available in the immediate area. The cabinet exhaust fan should be running during this operation.

D. Clean new equipment with a suitable solvent (Freon TF) before using. Use clean, new lead gaskets for the main cylinder connection.

E. Crack open and reclose main cylinder valve, allowing fluorine to enter line. Check connections with wet potassium iodide (KI)-starch filter paper. Open each valve in sequence away from the main cylinder valve.

F. After 1 or 2 minutes, open the manually-operated safety valve and allow fluorine to the first regulator.

G. Open the main cylinder valve again and retest connections with wet KI-starch paper.

H. Open the first regulator to the desired pressure. This should not exceed 50 psig in any case.

APPENDIX C. Procedures for Using Fluorine in the Volatile-Fluoride Reactor.

A. Carefully read fluorine-data sheets and be familiar with fluorine flow sheets (see Appendix D, Figures D-1 and D-2).

B. Perform with two people, one of whom is experienced. Notify personnel in adjacent areas of pending action as necessary.

C. Clean new equipment with a suitable solvent (Freon TF) before using. Use new Teflon gaskets for new flared connections.

D. When connections are complete, and the system is closed for the use of fluorine, perform a vacuum or pressure-leak check. The pressure-leak check shall be with dry, clean inert gas.

E. After the successful leak check, close all valves from the fluorine bottle to the first valve inside the glove box.

F. Crack open and reclose the main cylinder valve, allowing fluorine to enter the line. Open valves, in sequence, to the first regulator, checking each connection with wet KI-starch paper.

G. Open the main cylinder valve to admit fluorine to the surge tank through the first regulator to a *maximum* of 50 psig. If a lesser amount of fluorine is needed, allow only the lesser amount to enter the surge tank.

H. Close off the main cylinder valve and, in turn, all valves to the surge tank.

I. Open, in turn, the valves from the surge tank to the second regulator. Set the second regulator to read approximately 5 psig.

J. Open, in turn, the valves to the flow-meter control valve.

K. At this point, recheck all valve settings in the main reactor-collector system. Note the pressure reading of the surge tank in the data book. (This will aid in calculating fluorine usage later.)

L. Proceed with the planned experiment.

M. The opposite valve-operation procedure should be followed when the system is shut down. For example, the first valve opened in a series in starting up the system shall be the last valve closed.

APPENDIX D. Procedures for Fluorination of Plutonium Dioxide (PuO_2) and Volatilization, Collection, and Sampling of Plutonium Hexafluoride (PuF_6).

Figure D-1 is a schematic of the gas-supply system. Figure D-2 is a schematic of the PuF_6 production and handling equipment. These should be consulted for valve locations and equipment orientation. The individual steps are given below.

A. Preparation for run:

1. Tare sample boat and record weights.
2. Place the desired amount of sample in boat, record weight, and spread evenly over boat surface for maximum fluorine contact.
3. Place boat in transfer holder and transfer to furnace box.
4. Place sample in position in furnace.
5. Slide sample into furnace.
6. Place copper gasket into position.
7. Close furnace door.
8. Place door bolts into place being careful to put proper bolt (numbered 1, 2 and 3) into proper position.

9. Use torque wrench to torque door closed, moving from bolt to bolt around door and torque uniformly on each bolt. Starting at 15 pounds (lb), raise torque 5 lb each time. Stop at 35 lb.

10. Evacuate furnace by opening Valve No. 1 and vacuum bypass Valve No. 28. (Note: Evacuate the furnace slowly to prevent dusting of sample.)

11. When furnace is evacuated, close vacuum bypass Valve No. 28 and check for leaks. If furnace leaks, torque bolts 5 lb higher and repeat evacuation procedure. Torque bolts to a maximum of 45 lb. If furnace continues to leak, replace gasket.

B. Product trap preparation:

1. Install tared-product collectors on sample trap-station connections.

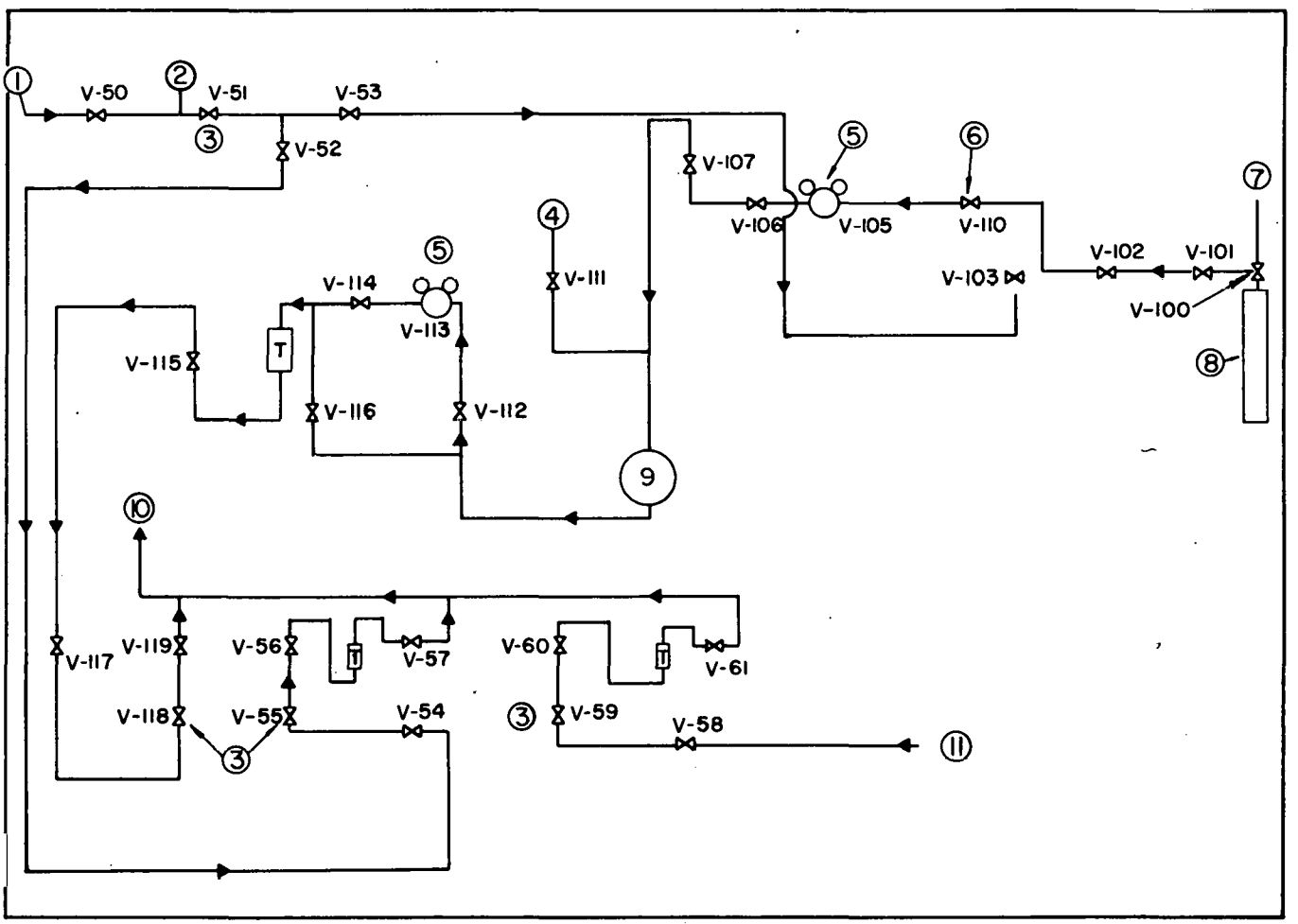
2. Open flow bypass valves (Nos. 14, 21, 10, 8 and 11).

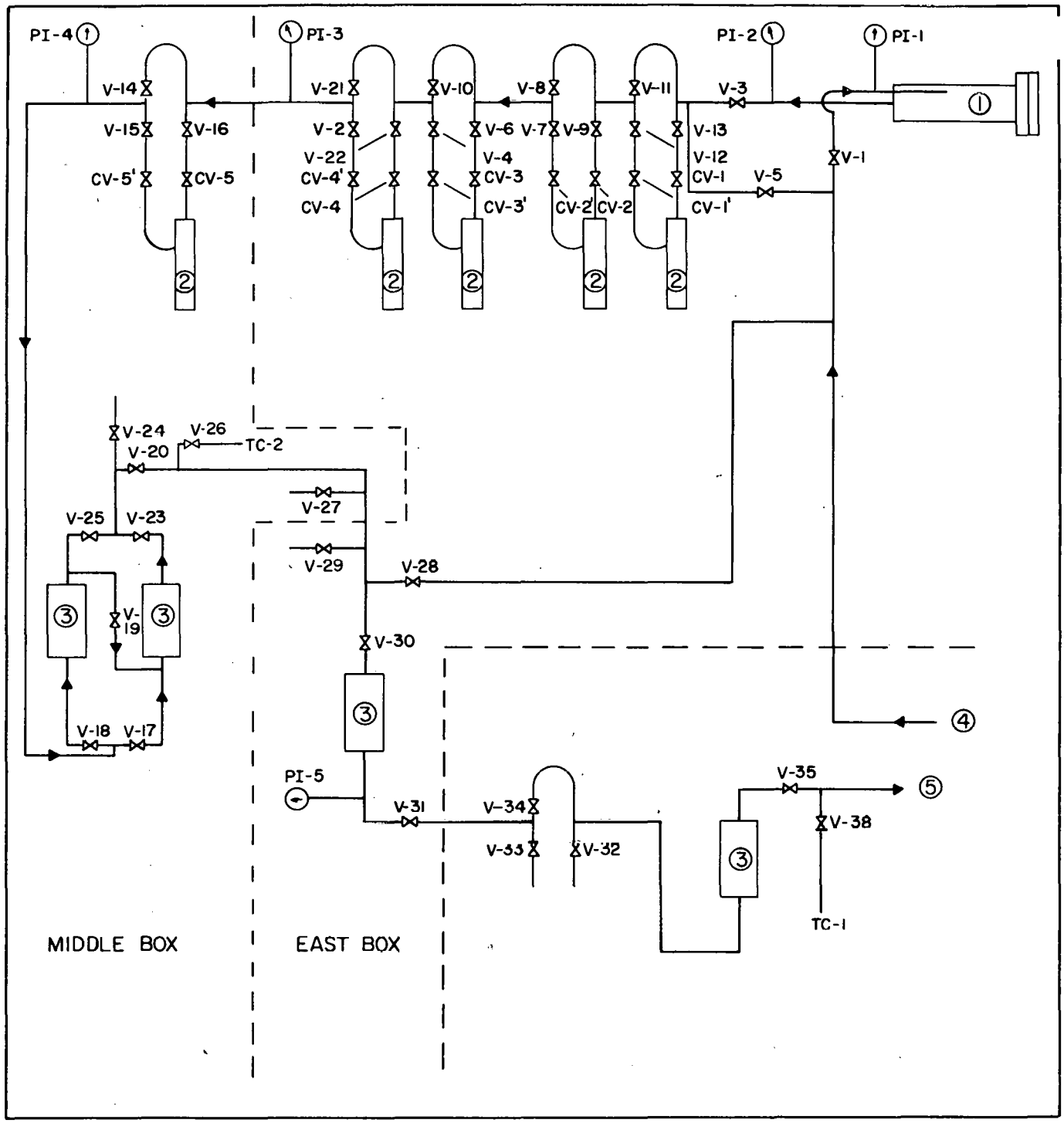
3. Open valves above traps (Nos. 15, 16, 7, 9, 12 and 13).

FIGURE D-1. Schematic Diagram of Gas Manifold for Fluorination System. (All valves are noted by "V" and corresponding numeral.)

Legend

1. Argon Supply.
2. Argon Gauge.
3. Flow Meters.
4. Pressure Indicator.
5. Pressure Regulators.
6. Safety Valve.
7. Cylinder Valve.
8. Fluorine Cylinder.
9. Pressure Vessel.
10. To Furnace.
11. Inert-Gas Supply





Legend

1. Reactor.
2. Product Collector.
3. Trap.
4. From Gas-Manifold Rotameter.
5. To Vacuum Pump.

Key

PI – Pressure Indicator Valves.
V – Valves.
TV – Trap Valves, distinguished by TV and TV′.
CV – Collector Valves, distinguished by CV and CV′.
TC – Thermocouple Pressure Gauges.

FIGURE D-2. Schematic Diagram for Plutonium-Hexafluoride System.

4. Leak check by closing vacuum Valve No. 20 and halogen-disposal trap Valve No. 18.

5. When no leaks are detected, open all product-trap valves.

6. With vacuum Valve No. 20 closed, open halogen-disposal trap Valve No. 18 and evacuate product traps.

7. Close alumina trap Valve No. 18 and open vacuum Valve No. 20. Steps 6 and 7 may have to be repeated several times to bring gauge to 0.

8. When 0 is reached, pump down a few minutes with vacuum Valve No. 20 and halogen-disposal trap Valve No. 18 open.

9. Close product-trap valves, valves above product traps, Nos. 15, 16, 7, 9, 12 and 13.

10. Remove product-collector traps and cap with temporary caps.

11. Weigh product-collector traps and record weights.

12. Replace product-collector traps in original positions.

13. Check for leaks, then evacuate product-collector traps.

14. Turn furnace on.

15. Close vacuum Valve No. 20 center box.

16. Introduce argon flow by opening source Valve No. 50, flow meter Valve No. 51, Valve No. 52, the three panel valves (Nos. 54, 56, and 57) from cylinder to furnace and adjust desired flow with Flow Meter No. 55.

17. Watch gauge and when pressure reaches atmospheric, open Valve No. 24 to vent flow to box.

18. Prepare the coolant baths, Dewars-filled with liquid argon or dry-ice trichloroethylene. Do not use liquid nitrogen without project leader's permission.

C. Fluorine transfer from cylinder to surge tank:

1. Carefully open F_2 storage cabinet. Note any unusual pungent halogen odor.

2. Place KI-treated filter papers on all valves and connections between cylinder and surge tank, then close cabinet.

3. Make sure all valves are closed between cylinder and surge tank.

4. Turn safety Valve No. 110 on and start cabinet exhaust fan.

5. Open F_2 cylinder Valve No. 100 and close. (Torque to 50 lb on closing.)

6. Slowly open Valves No. 101 and 102 from cylinder to regulator, and then close in reverse order. (Check for F_2 leaks.)

7. Repeat Steps 5 and 6.

8. Open F_2 cylinder Valve No. 100 and open Valves No. 101 and 102 from cylinder to regulator slowly and when cylinder pressure shows on regulator, adjust regulator No. 105 to desired surge-tank pressure.

9. Open the two valves, Nos. 106 and 107, to surge tank and transfer desired amount of F_2 if no leaks show.

10. Close the F_2 Cylinder No. 100 and let transfer lines bleed.

11. Close Regulator No. 105 and the two valves, Nos. 102 and 101, between the regulator and F_2 cylinder.

12. Shut off safety Valve No. 100.

13. Check all KI papers for any leak indication.

D. Run procedure and precautions:

1. Place coolant-filled Dewar flasks under the product-collector traps.

2. Furnace temperature should be leveled off at the desired temperature.

3. Check valves for desired flow. Nos. 1 and 3 to and from furnace should be open, Nos. 12 and 13 open, and No. 11 closed. Trap No. 1 and No. 1 (prime) open, Valves No. 7 and 9 to Trap No. 2 closed, No. 8 open, No. 10 open, No. 21 open, Nos. 15 and 16 and trap valves 3 and 3 (prime) open, No. 14 closed,

alumina trap valves No. 18, 19 and 23 open so flow will go through traps in series, vacuum-line Valve No. 20 closed, and box vent Valve No. 24 open.

4. Close door to balance box.

5. To start F_2 into furnace, open Valve No. 112 from surge tank to Regulator No. 113.

6. Adjust flow pressure across Regulator No. 113 to about 5 lb.

7. Open Valve No. 114 to trap, then Valve No. 115 to control panel.

8. Open Valve No. 117 on control panel from cabinet.

9. Open Valve No. 119 to furnace to desired flow level through Flow Meter No. 118.

10. Turn off argon.

11. Recheck flow through Regulator No. 113 and Flow Meter No. 118.

12. Heat lines with heat gun to trap and trap top as necessary so there will be no freeze up of the system.

13. Continually check the gauges for any pressure buildup, check the flow through regulator and flow meter, check alumina-trap temperatures.

14. Depending upon the type of experiment under way, it may be necessary to close off or open product-collector traps. A typical procedure to follow is given below:

    14.1 Heat line from gauge to first product collector.

    14.2 Open Valves No. 2 and No. 2 (prime).

    14.3 Open Valves No. 7 and 9.

    14.4 Close No. 8 to force flow through product collector.

    14.5 Open Valve No. 11.

    14.6 Close Valves No. 12 and 13.

    14.7 Heat lines above first product collector.

    14.8 Close first-product collector valves.

15. To shut F_2 down:

    15.1 Start argon flow (see B-16).

    15.2 Close F_2 valves in reverse order from start-up procedure back to F_2 cylinder regulator.

16. Open Valves No. 12 and 13, No. 1 trap valves, No. 1 and No. 1 (prime), and close No. 11; allow argon to flow through all 3 traps for 15 minutes.

17. Turn off heat.

18. Turn off argon after furnace and lines are purged.

19. Close furnace Valves No. 3 and 1.

20. Close box-vent Valve No. 24.

21. Close halogen-disposal trap Valve No. 18.

22. Slowly open vacuum Valve No. 20, evacuate the system by alternating Steps 21 and 22 until the system is down to 0. Continue vacuum-pumping on product collectors for about 15 minutes to remove any oxygen or argon that might have condensed or adsorbed.

23. Close all product-trap valves and Valves No. 15, 16, 7, 9, 12, and 13.

24. Remove product traps, cap, weigh, and record weights to determine the amount of PuF_6 collected.

E. Procedure for hydrolysis of gas samples:

1. Pipette 30 milliliters of 6M HNO_3 (nitric acid), 1M $Al(NO_3)_3$ (aluminum nitrate) into sample bottle and place in glove box.

2. Place about ¾ inches of solution in Kel-F test tube and solidify by using liquid argon or dry ice and trichloroethylene.

3. Place tube in position on tube holder.

4. Open Valve No. 2 above tube.

5. Evacuate and check for leaks by closing Valve No. 14.

6. When no leaks are detected, close Valve No. 2 and place a product trap in holder next to above tube.

7. Open Valves No. 4 and 14 and check for leaks by pumping down to 0 and closing No. 14. (Replace Kel-F gaskets if necessary.)

8. When there are no leaks, close Valves No. 21 and 10, open No. 22 valve and heat block above test tube.

9. Open trap-prime valve and begin hydrolysis. (Hydrolysis time is variable, but about 10 minutes.)

10. Heat tubing and block as necessary.

11. After 7 minutes, heat trap and tubing.

12. After 10 minutes, heat trap and tubing again.

13. Close trap-prime valve.

14. Let stand for 10 minutes heating tubing to about 30 to 35°C during this time. Just before 10-minute period is up, heat tube above block thoroughly.

15. Close Valves No. 22 and 14 and open Valve No. 21 and trap-prime valve on trap; this should give the vapor pressure on gauge. Close prime valve.

16. Lower liquid argon or nitrogen from tube.

17. Close Valve No. 4 and open Valve No. 2; this should give vapor pressure on tube.

18. Close vacuum Valve No. 20 above halogen disposal trap and open Valve No. 14 allowing gas to enter halogen disposal traps.

19. Evacuate halogen disposal traps for several minutes.

20. Remove product collector from system; cap, weigh, and record weight, and product-weight change.

21. Close Valve No. 2 and allow frozen product to come to room temperature (no heating).

22. Dissolve solids and transfer to sample vial.

23. Send sample to the analytical laboratory for desired analyses.