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LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part VIII Analysis of an Accidental Multigram Release of Plutonium Hexafluoride in a Glovebox

by

L. E. Trevorrow, R. W. Kessie,
and M. J. Steindler

RELEASED FOR ANNOUNCEMENT
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Chemical Engineering Division

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ABSTRACT

A 5.7-g sample of plutonium hexafluoride was accidentally released to the interior of a glovebox. An analysis of the penetration of plutonium through the filter system of the glovebox has been carried out. Data obtained from an air-sampling instrument located in the effluent air stream of the filter system indicated that $2.4 \mu\text{g}$ of plutonium were released to the atmosphere during this incident. Air and surface concentrations of plutonium at sampling points beyond the exhaust stack were below the limits of detection.

The performance of the high-efficiency filters of the glovebox ventilation system was generally within the range predicted from small-scale experiments that had been carried out before the incident to simulate the type of accidental release that occurred. The detailed analysis of the distribution of plutonium following the release indicated possible design improvements that could be made in the once-through air ventilation system in use.

I. SUMMARY

On March 12, 1965, a fluoroethene test tube containing 5.7 g of PuF_6 ruptured inside a glovebox in Building D205 (Chemical Engineering). The extent to which PuF_6 penetrated the glovebox ventilation system has been determined by alpha counting of samples taken from the ventilation system.

The inner set of glovebox outlet filters contained 1.5 g of plutonium. The outer set of glovebox outlet filters contained 6×10^{-4} g of plutonium. An aqueous spray gas scrubber in the ventilation system contained 9×10^{-6} g of plutonium. The final filters in the exhaust system contained 1.3×10^{-4} g of plutonium. Alpha activity on the filter paper of an air-sampling instrument operating in the ventilation system indicated that 2.4×10^{-6} g of

plutonium was released into the atmosphere. Inner surfaces of one of the exhaust stacks yielded loose alpha activity corresponding to 2.2×10^{-11} g of plutonium (sq ft)⁻¹. The alpha activity inside the other exhaust stack was below the detectable limit. Alpha activity on the roof area near the exhaust stacks was below the detection threshold of an Eberline PAC-3G gas proportional counter.

One of the air intakes of Building D205 was downwind from the release point; alpha activity collected by a filter paper on an air monitor operating at this intake was below the detection limit (less than 0.1 MPC*). Buildings in the 300 area of the Argonne site were 1/2 to 3/4 mile downwind from the release point; alpha activity from sources other than natural background collected by continuous air monitors in Buildings D310 and D362 was below the detection limit.

II. DESCRIPTION OF EXPERIMENT BEING CARRIED OUT AT TIME OF RELEASE

A. Purpose of Experiment

Some preliminary experiments were carried out to determine the melting points of UF₆-PuF₆ mixtures. Since fluorothene test tubes are translucent, the experimenter can visually observe colors and types of phase transitions. Although the types of phase transitions occurring can, in principle, be deduced from the shape of thermal analysis curves, it can be done quickly by visual observation. At the time of the release, the equipment was being tested by an observation of the melting point of pure PuF₆.

B. Equipment

1. Glovebox

Experimental operations were being carried out in a three-module, 2½-tier, CENHAM¹ glovebox (dimensions, 3½ x 8½ x 10 ft, as shown in Fig. 1). The glovebox atmosphere was laboratory air which flows into the box through two AEC filters (size 12 x 12 x 6 in.) arranged in parallel. The air flows out of the box through four filters of the same type, arranged as two parallel sets of two filters in series, thence via a 6-in.-diam ventilation duct through an aqueous spray scrubber, through two, final AEC filters (size 24 x 24 x 12 in.) in parallel, and finally out of a stack to the outside atmosphere. A schematic diagram of the glovebox and ventilation facilities is shown in Fig. 2. Laboratory air is humidified before it flows through the box. The relative humidity of the air flowing into the box at the time of the incident was 34% at 70°F (6 g H₂O/m³ of air).

*Maximum permissible concentration.

108-7534

Fig. 1. CENHAM Glovebox in Which PuF_6 Was Released

2. Description of Vessel Containing PuF_6

Figure 3 is a drawing of the test-tube assembly that contained the PuF_6 at the time of release. The assembly was constructed from a 3/4-in. nickel trap fitting, with the side arm closed by a Hoke No. 411 right-angle valve. The lower end of the down leg was cut off, and the top of the leg was flared. A 3/16-in.-OD thermocouple well was sealed into a 3/8-in. brass flare plug, which was connected to the flare in the top of the down leg. A 3/8-in. male flare fitting was sealed onto the end of the Hoke valve so that the assembly could

Fig. 2. Schematic Diagram of CENHAM Glovebox Ventilation System. 5.7 g PuF_6 released; figures are in mg Pu and indicate distribution after release.

be attached to a vacuum manifold. A 3/4-in. brass flare nut held a fluorothene test tube in place on the trap fitting.

Fig. 3. Test-tube Assembly

C. Technique

Before the test-tube assembly was placed into the glovebox, it was rinsed with water followed by acetone, and was dried in a stream of air. The test-tube assembly was charged with PuF_6 as follows: It was attached to a vacuum manifold and evacuated to a pressure of 1 to 2 microns. The assembly was warmed with a heat gun during the evacuation. The tube was then cooled in liquid nitrogen to condense PuF_6 into it. The Hoke valve was closed, and the vacuum manifold was evacuated. The assembly was removed from the vacuum manifold, and the $\frac{3}{8}$ -in. flare connection was capped. The trap fitting was then clamped onto a ring stand, which rested on a stainless-steel shelf. A Chromel-Alumel thermocouple was inserted into the thermowell. Electrical signals from the thermocouple were fed into an externally-located recording potentiometer, which had a 1-mV span with a variable zero suppression. The recorder thus provided a "window"

of about 20°C width when used with a Chromel-Alumel thermocouple. The fluorothene tube was warmed by immersing the bottom end of it in a stainless-steel beaker of water, which was heated by a heat gun. A Briskeat heating tape was wound onto the trap fitting and Hoke valve to prevent condensation of PuF_6 on the interior surfaces of the nickel parts when the bottom of the fluorothene tube was warmed (the vapor pressure of PuF_6 at its triple point is 533 mm). Since the heating tape caused some electrical disturbance of the thermocouple signal, it was removed, and an infrared lamp was mounted on the ring stand to warm the trap fitting and Hoke valve.

III. DESCRIPTION OF CONDITIONS ATTENDING INCIDENT

On March 10, 3.7 g of PuF_6 were condensed into the fluorothene test tube, and this quantity remained in the tube overnight at ambient laboratory temperatures. On March 11, the fluorothene test tube was cooled in liquid nitrogen, and the tube was evacuated to remove the fluorine produced overnight by the α -decomposition of PuF_6 (at -197°C, the vapor pressure of PuF_6 is negligible, but the vapor pressure of fluorine is about 300 mm). An additional 2 g of PuF_6 was then condensed into the fluorothene test tube. The vacuum manifold was evacuated, the assembly was removed from the manifold, the male 3/8-in. flare connection was capped, and the assembly was attached to the ring stand. At this time, the nickel parts of the assembly were wrapped with the heating tape, which was supplied with power from a source controlled by a Variac located outside the glovebox. A Weston bimetallic thermometer was inserted into one of the bolt holes on the body of the Hoke valve. The stem of the thermometer was also in contact with the 3/4-in. flare fitting. The power input to the heating tape was adjusted so that the temperature of the bimetallic thermometer indicated 50 to 60°C. The sample of PuF_6 was then melted by immersing it in a stainless-steel beaker containing water at 60°C. After a melting curve had been obtained, the PuF_6 was allowed to cool to room temperature.

On March 12, experimental operation was started with the intention of obtaining one or two more melting-point records. The melting-point curve obtained the previous day was unsatisfactory because of electrical noise in the thermocouple signal caused by the electrical heating tape. To avoid this noise, the heating tape was removed, and a 250-W infrared lamp was positioned on the ring stand to heat the trap fitting. The bimetallic thermometer showed that the temperature of the Hoke valve was between 45 and 50°C. The tip of the test tube was cooled in liquid nitrogen to condense the PuF_6 onto the bottom. After the tube had warmed in the air and in the light of the infrared lamp, it was immersed in the water bath, which was at a temperature of 60°C. The PuF_6 appeared to melt, but a temperature halt was not obtained at the expected melting point. Presumably, enough PuF_6 had sublimed and condensed on the upper walls of the test

tube so that an insufficient quantity remained in the bottom of the tube to allow contact between PuF_6 liquid and the tip of the thermowell, 1/16 to 1/8 in. above the bottom of the tube. To correct this situation, all of the material was to be collected once again in the bottom of the tube by sublimation and condensation. After the water bath was removed, the outside of the tube was dried, the upper walls of the tube were warmed briefly with a heat gun, and the bottom end was cooled in liquid nitrogen. The Dewar flask containing liquid nitrogen was raised and lowered several times around the bottom of the tube, and the tube was carefully observed. At this time, the experimenter noticed for the first time an irregular line on the outside wall of the tube about 1/16 in. above the bottom.

When the flask of liquid nitrogen was lowered, frost appeared to form on the outside wall below this line but not above it. The flask was raised and lowered several times to study this "frost" line in an attempt to decide whether it was a crack in the tube or some irregularity formed in the surface of the tube in its construction. When the liquid nitrogen was removed and the tube had warmed enough so that the frost had disappeared, it was not possible to observe any line. At this time it was also observed that a gray solid had begun to form on the inner walls of the tube where PuF_6 had previously condensed. As the experimenter was observing both the irregular line and the gray colored solid, and considering the causes for the observations, a bright white light suddenly appeared in the bottom of the test tube. The experimenter immediately removed his hands from the glovebox, and stepped aside to a point in front of the window of the adjacent module of the glovebox where he continued to watch the test tube. The light at the bottom became brighter, and the bottom of the tube ruptured with a sharp report, releasing a cloud of yellowish smoke. The contents of the tube were widely scattered on the stainless-steel shelf in the form of small particles, which showed no signs of further violent reaction. The experimenter shouted to the other room occupant that the room must be evacuated and both occupants left the room. Using a telephone in the corridor, the experimenter called Radiation Safety personnel, explaining that a spill had occurred requiring radiation monitoring both in the laboratory and in the area of the exhaust stack on the roof.

IV. RESULTS OF RADIATION MONITORING FOR RELEASED PLUTONIUM

Radiation Safety personnel immediately proceeded to monitor the laboratory area, the roof area, and components of the ventilation system to determine the extent of the penetration of the system by the released plutonium. Later, the filters in the ventilation system, the contents of the scrubber retention tank, and filter papers from air monitors located in Building D205 were examined with more sensitive techniques in an attempt to obtain more accurate results on the penetration of the ventilation system.

The results of monitoring for the released plutonium reported below can be compared with the following maximum permissible levels for personnel exposure to plutonium: The maximum permissible concentration of plutonium in air² (40 hr week⁻¹ for 50 weeks year⁻¹ for 50 years) is 4.4 dis min⁻¹ m⁻³ or 3.2×10^{-11} g Pu²³⁹ m⁻³, or 2 pCi m⁻³. The maximum permissible total body burden³ for Pu²³⁹ is 0.04×10^{-6} Ci or 0.65×10^{-6} g.

A. Room Area

1. Air

Radiation Safety personnel started a Filter Queen air sampler in the laboratory within 5 min of the release. Laboratory air was drawn through a filter paper (Type HV-70) at a rate of 15 m³ hr⁻¹ for 22 min. The filter paper was counted for alpha activity for 5 min in an air proportional counter, after which it was counted for 5 min for beta-gamma activity in a P-10 gas-flow proportional counter. The resulting $\beta\gamma/\alpha$ ratio was within the limits of a normal "clean" air sample. A subsequent counting 4 days later showed that the alpha activity had decayed to background, indicating that no long-lived alpha activity had been present in the air sample. A second, 69-min sampling, carried out in the laboratory immediately after the first one, yielded similar results.

2. Surfaces

Using an Eberline PAC-3G gas proportional counter, with a detection threshold of 200 dis min⁻¹ (1.5×10^{-9} g Pu²³⁹) per 61 cm², Radiation Safety personnel could detect no activity on the surfaces of gloves, of glove ring mountings, and of the floor near the glovebox module where the experiment had been carried out.

The experimenter checked the grill covering the inlet filter chambers by wiping the grill with a moist Kleenex tissue and exposing it to the counting head of a P-10 gas-flow proportional counter mounted on the side of the glovebox; no activity was detected. The sensitivity of this counter is such that an alpha source of 290 dis min⁻¹ (2.1×10^{-9} g of Pu²³⁹) has an 89% probability of being detected.

B. Ventilation System

1. Stack Monitor

The glovebox exhaust air that has passed through the box outlet filters, the scrubber, and the final filter, is monitored for alpha activity just before it passes up the exhaust stack to the outside atmosphere. The monitor is of the Filter Queen type, which draws air through a Mine Safety Appliance 1106B filter paper. The probe of a zinc sulfide scintillation

counter is mounted directly over the filter paper. The output signal of a count-rate meter used in conjunction with this probe is fed into a Rustrak recorder situated in the laboratory room.

As a result of this release, the stack monitor record, shown in Fig. 4, indicated an increase in counting rate of 0.8 count/sec over a 7-min period that was preceded and followed by a constant counting rate. The counting efficiency is 20%, and the sampled flow rate is $21 \text{ m}^3 \text{ hr}^{-1}$.

108-8515

Fig. 4. Graph Obtained from Stack Monitor

The computed stack discharge was 2 MPC* (maximum permissible concentration). The MPC for these stacks is ten times room MPC for a 40-hr/week exposure. This factor of ten is the estimated minimum dilution of the stack discharge as measured at the ground.

Three days after the release, the stack monitor filter was removed and counted. The plutonium content of the filter was found to be considerably greater than that indicated by the monitor. The best information indicates stack concentration during the 7 min of discharge averaged 300 MPC*.

The total discharge from the stack was estimated to be $2.4 \mu\text{g Pu}$.

The most likely source of the discrepancy between that indicated by the monitor and that estimated from the counting of the stack monitor filter is a malfunction in the monitor electronics.

The following data were used, together with the assumption of 100% collection efficiency for the monitor filter paper, to estimate the amount of plutonium released into the atmosphere:

Sampling rate of air monitor, $21 \text{ m}^3 \text{ hr}^{-1}$, or $0.35 \text{ m}^3 \text{ min}^{-1}$;

Total alpha activity on filter paper from monitor, $35,100 \text{ dis min}^{-1}$;

Rate of total air flow through upper ventilation system, $150 \text{ ft}^3 \text{ min}^{-1}$, or $4.25 \text{ m}^3 \text{ min}^{-1}$;

Specific activity of Pu involved, $1.60 \times 10^{11} \text{ dis min}^{-1} \text{ g}^{-1}$.

2. Scrubber

Air leaving the glovebox passes through a water-spray gas scrubber. Water from the spray is collected in a tank and recirculated to

*Stack MPC.

the spray. At the time of the release, the scrubber tank contained 54 liters of water. An analysis of the plutonium content of the scrubber water indicated the total amount of plutonium in the scrub water was 9×10^{-6} g.

3. Filters

The filters were sampled after the release by cutting out cores with a thin-walled tube similar to a cork-boring tool. Four sample cores were taken from each filter, with each core being removed from the center of a quadrant of the filter. Each core was unfolded, and the filter media was freed from the separators. The distribution of plutonium between the media and the separators was determined by counting the 17-keV gamma radiation from plutonium. The results indicated that the separators contained 5% of the plutonium; the media contained 95% of the plutonium. The filter media was then leached with 200 to 250 ml of 10% HNO_3 and 0.03% wetting agent (Aerosol)*. After complete wetting of the filter media by the solution, the media was shaken to a pulp and left for at least 24 hr before filtering off the solution. The concentration of plutonium determined in this solution, times the original volume of leach solution used, gave the plutonium values found in the cores (Table I). A schematic diagram of

TABLE I. Plutonium Content and Test Results of Filters after 5.7-g PuF_6 Release

Filter	1st East ^a	1st West	2nd East	2nd West	3rd East	3rd West
Rated Flow (cfm)	135	135	135	135	1000	1000
Resistance (in. H_2O)	0.72	0.74	0.86-0.95	0.86-0.96	0.88-0.92	0.86-0.92
DOP Penetration (%)	0.008	0.004-0.005	0.008	0.004-0.008	0.018	0.018
Adhesive-free Dimensions						
Height (in.)	10.1	10.1	9.3	9.5	22.0	21.4
Width (in.)	9.4	9.3	10.1	10.0	21.4	21.8
Area (sq in.)	94	94	94	95	472	468
Pu Found (mg Pu)						
Core I ^b	19.3	21.8	0.00155	0.000749	0.000346	0.000416
Core II	23.4	19.4	0.00360	0.000568	0.000673	0.000294
Core III	22.2	21.0	0.0597 ^a	0.000793	0.000327	0.000352
Core IV	21.4	22.1	0.00137	0.000499	0.000309	0.000318
Average	21.6	21.1	0.0166	0.000652	0.000413	0.000345
Total Filter	775	722	0.56	0.022	0.071	0.059
Pu Penetration (%)	0.073 ^a	0.0031	(20) ^c		2.0 ^d	
Flow Rate (cfm)	24	24	24	24	75	75

^aFirst east filter had torn media near center.

^bSample core was 1.871-in. diam and was removed from center of quadrant.

^cThis could result entirely from a filter gasket leak of 0.0003 sq in. in the gasket perimeter of 92 in. This includes 0.009 mg Pu (7% collection) in scrubber between second and third filters.

^dFilter discharge based on stack monitor filter was 0.0026 mg Pu. This includes 0.0002 mg Pu collected by monitor filter.

*Commercial wetting agent, obtained from E. H. Sargent and Co., Chicago.

the system containing the plutonium distribution after the release is shown in Fig. 2. The total plutonium content of the filter is based on the inside cross-sectional area of the coring tool and the adhesive-free area of the filter. An individual measurement of the height or width of this adhesive-free area can vary up to 1/2-in., and the numbers reported are each averages of six measurements, three each from the front and back faces of the filter.

The air-flow resistance and DOP (dioctyl phthalate) penetration shown in Table I were the filter test specifications by the manufacturer (Flanders Filter Corp., Riverhead, New York) and the Oak Ridge Filter Testing Laboratory that were marked on the filter frame. Two numbers are reported when these test specifications did not agree. The plutonium penetrations are based on the plutonium found on the filter media and in the scrubber solution. These penetrations are compared with those of the small-scale release experiments⁴ in Table II.

TABLE II. Comparison of PuF_6 Release Accident
with Small-scale Experiments

	Full-scale Accident	Small-scale Experiments ^c
PuF_6 Released (mg)	5700	1.5 to 25
$\text{PuF}_6/\text{H}_2\text{O}^a$	0.006	0.022 to 3.32
Fraction of Released Pu Discharged from Last Filter	6.7×10^{-7}	10^{-6} to 10^{-9b}
Penetration of 1st Filter (%)	0.0031 (west)	0.0005 to 0.0016 ^b
Penetration of 2nd Filter (%)	2 to 20	2 to 45 ^b

^aAverage mole ratio in release enclosure volume due to moisture content of the contained air.

^bOnly for experiments where $\text{PuF}_6/\text{H}_2\text{O} < 0.1$.

^cSee Reference 4.

The fraction of released plutonium passing through all filters is within the range expected from the small-scale experiments. Although high penetration of the second filter is within the range measured in the small-scale experiments, it is probably due to a small leak in the filter gasket. This would explain the lower penetration of the third filter. The first two filters are stacked in the same holder, with the result that a leak in the gasket of the second filter will bypass both filters. Thus a small leak will bypass significant quantities of plutonium. The size of the leak

that would account for the above results was estimated in the following way. The average penetration of both first and second filters was 0.0086%. Multiplying this by the flow rate of 48 cfm gives the leak rate of 0.0041 cfm. The percent of rated flow (17.8%) times the rated average pressure drop ($0.73 + 0.91$ in. H_2O) gives the operating differential pressure of 0.29 in. H_2O across the leak. Using Bernoulli's theorem, which relates pressure to kinetic energy in nonviscous flow ($2\Delta P = v^2\rho$), and neglecting the coefficient of discharge, a velocity of 36 ft/sec for the above pressure drop is calculated. The leak flow rate divided by the leak velocity gives the area of the leak to be 0.0003 sq in. A capillary leak $1/2$ in. long (gasket width) will have 0.003-sq in. cross section. A leak of this size out of a total gasketed perimeter of 92 in. is not at all surprising and may in fact be a highly probable leak size.

4. Inside Surfaces of Exhaust Stacks

Radiation Safety personnel searched for activity on the inner surfaces of each of the affected exhaust stacks by wiping an area of 1 ft^2 of the inner surface of the stack with a piece of filter paper (HV-70) saturated with acetone, and counting the dried paper with an air proportional counter (detection threshold 20 dis min^{-1}). The sample from the east stack showed background counting rate; the sample from the west stack showed a counting rate of $30 \text{ dis min}^{-1} (\text{sq ft})^{-1}$. If all this activity was that of Pu^{239} , it corresponds to a weight of $2.2 \times 10^{-11} \text{ g Pu } (\text{sq ft})^{-1}$ of stack surface. This is not considered to be a very high alpha activity level; it is only a factor of three higher than the activity level found on some floor surfaces that are considered to be acceptably clean. In the study⁵ of Building D205 in 1962, 80% of smear surveys of clean corridors showed the presence of $10 \text{ dis min}^{-1} (\text{sq ft})^{-1}$ or less of loose alpha activity.

C. Roof Area

The outlets of the stacks involved in the release are 5 ft 3 in. above the adjacent roof areas. Roof surfaces in the vicinity of the stacks were monitored by Radiation Safety personnel using a PAC-3G Eberline counter; no activity could be detected above the background level.

D. Atmosphere

1. Meteorological Conditions

The records of the Meteorology Group of Radiological Physics (ANL) indicate that the wind was blowing from 20° west of north at a velocity of 10 mph at the time of the release [1210 hr]. The outdoor relative humidity was 81%, and the temperature was 34°F (dewpoint 20°F). The atmosphere was relatively clear.

2. Building Air Intake

The R-wing air intake of Building D205 was downwind from the stacks involved in the release. The filter paper from an air monitor, which was located in the air stream of this intake at the time of the release, indicated that the alpha activity was below normal detectable limits; i.e., the alpha concentration in the air was less than 0.1 MPC for a 1-hr period.

3. Airborne Alpha Activity at Other Buildings

The Industrial Hygiene and Safety Environmental Monitoring Group (ANL) maintains continuous air monitors at various points on the Argonne site. Air is drawn through a filter paper in each monitor for a one-week period. The alpha activity from filters that were in use on March 12 yield the values shown in Table III. The map of the Argonne site (Fig. 5) indicates that Buildings D310 and D362 were downwind from Building D205 at release time. The records of monitors at Buildings D310 and D362 show an alpha concentration in air which is not significantly higher than those at Buildings D202 and D203, which were upwind. The average of the values in Table III for alpha concentration in air on the Argonne site for the week including March 12 is $0.0023 \text{ pCi m}^{-3}$.

TABLE III. Average Concentration of Alpha Activity in Air on Argonne Site for One-week Period Including 12 March 1965

Location of Air Monitor (Building No.)	Concentration of Alpha Activity in Air ^a (pCi m^{-3})	Location of Air Monitor (Building No.)	Concentration of Alpha Activity in Air ^a (pCi m^{-3})
D310 ^b	0.0022	D203 ^c	0.0026
D362 ^b	0.0026	D202 ^c	0.0023
D181	0.0022	D7 (East Area)	0.0021

^aDuring Fiscal Year 1964, the average concentration of alpha activity in air on the Argonne site ranged from $0.0032 \text{ pCi m}^{-3}$ in January to $0.0077 \text{ pCi m}^{-3}$ in October (Reference 6). Off-site concentrations of alpha activity in air ranged from $0.0029 \text{ pCi m}^{-3}$ in January to $0.0075 \text{ pCi m}^{-3}$ in October.

^bBuildings downwind from release point.

^cBuildings upwind from release point.

During Fiscal Year 1964,⁶ the average concentration of alpha activity in air on the Argonne site ranged from the lowest value of $0.0032 \text{ pCi m}^{-3}$ in January to the highest value of $0.0077 \text{ pCi m}^{-3}$ in October. Also, during 1964, off-site concentrations of alpha activity in air ranged from $0.0029 \text{ pCi m}^{-3}$ in January to $0.0075 \text{ pCi m}^{-3}$ in October.

Argonne

NATIONAL LABORATORY

Legend

▲ INFORMATION CENTER

BUILDING	BUILDING	BUILDING	BUILDING	BUILDING
2 Administration	16, 17, 20 & 40 Central Shops	202 Biological and Medical Research	308 Reactor Engineering	362 High Energy Physics
3 Cafeteria	19 Electronics	203 Physics, Radiological Physics and Library	310 Chemical Engineering	583 & 584 Canal Water Treatment Plant
4 & 5 Receiving and Central Warehouse	21 Security	205 Chemical Engineering	316 Reactor Physics	600-621 Lodging Facilities
6 Garage	60 Radiobiology Experimental Station	206 Reactor Engineering	330 Research Reactor (CP-5)	801 Accounting, Plant Engineering
7 Air Monitoring Station	90 Communications and Special Services U. S. Branch Post Office	208 Reactor Physics--Reactor Engineering	331 Experimental Boiling Water Facility	805 Particle Accelerator Division
8 Firehouse	91 Guard Post	211 Cyclotron	335 Juggernaut Reactor Facility	806 Plant Services
10 Executive Offices	108 Central Heating Plant	212 Fuels Technology Center	340 Experimental Animal Quarters	808 Industrial Hygiene and Safety
11 Reactor Engineering	180 & 181 Meteorology	213 Cafeteria	350 Plutonium Fuel Fabrication	817 & 818 Electronics
12 Remote Control Engineering	200 Chemistry--Solid State Science	221 Applied Mathematics	360-385 Zero Gradient Synchrotron Complex	829 Hydrogen Test Facility
14 Industrial Hygiene and Safety		301 Hot Laboratory		891 Guard Post
15, 22, 24 & 25 Office of College and University Cooperation		306 Reclamation		951 Argonne Recreation Center

Fig. 5. Argonne National Laboratory Site Map

The Environmental Monitoring Group has suggested that the alpha activity received in the 300 area from the plutonium release was probably small compared to the activity of the naturally occurring alpha emitters, uranium and polonium.

V. POSSIBLE CAUSES OF THE RELEASE

Examination of the fluorothene test tube after the incident showed that the walls has split longitudinally near the bottom in three places (Fig. 6). The rupture was probably caused by excessive gas pressure rather than melting of the tube. The edges at the splits were sharp, suggesting that the tube has been torn by force. Only one small point in the tube showed signs of melting.

108-8530

Fig. 6. Detail of
Fluorothene
Test Tube

Previous experience has shown that fluorine compounds, which are also very strong oxidizing agents (e.g., ClF_3), will sometimes react vigorously or explosively when contained in fluorothene test tubes. Experience has indicated that explosions with ClF_3 have a higher probability of occurring in fluorothene test tubes that have rough interior surfaces, or in which fibers or whiskers of fluorothene protrude from the wall. The tube used in the present case appeared to have a smooth inner surface. In many previous instances, PuF_6 has been contained in fluorothene test tubes in this laboratory without incident.

The experimenter was aware that fluorothene test tubes will develop crazing and cracking if subjected to excessive heat or if used for extended periods, particularly under conditions of thermal cycling. The experimenter feels that the tube in the incident had not been severely used.

It was not possible to determine the maximum temperature in the tube during the incident. The recording potentiometer was set to measure temperatures in the range of 48 to 62°C with a Chromel-Alumel thermocouple. The thermocouple record dropped below the scale when the tube was cooled in liquid nitrogen, and increased in a straight line to a point somewhere above the scale at the time of the incident.

After the incident, most of the particles scattered onto the stainless-steel shelf were surrounded by halos of a buff-colored film on the shelf. The formation of these halos suggests that all of the PuF_6 was not consumed in the reaction that caused the tube to rupture, but that the particles scattered onto the shelf at the

time of the rupture contained PuF_6 , which continued to fume (to volatilize and to hydrolyze) on the shelf. Figure 7, a photograph of the test tube and surroundings as they were about 2 hr after the rupture, shows, although not very clearly, the material scattered onto the shelf.

108-8529

Fig. 7. Test-tube Assembly and Surrounding Area

Possibly, the gray solid observed on the inner walls of the tube just before the rupture was PuF_4 produced by photodecomposition of PuF_6 in the light of the infrared lamp. However, if the irregular line observed at the bottom of the tube before the incident was indeed a crack, then the reaction was probably the hydrolysis of PuF_6 , and the gray solid beginning to collect on the inner walls of the tube would have been the solid product of hydrolysis. Observations on the reaction of PuF_6 with water under various conditions have been described by Mandleberg *et al.*⁷ They reported that when PuF_6 was condensed onto ice on a glass cold finger at -180°C , and the system was subsequently warmed to room temperature, the hydrolysis took place smoothly. They observed, however, that the reaction of PuF_6

with water or moist air at room temperature is violent. "On hydrolysis with water or moist air at room temperature, a violent reaction takes place accompanied by flashes of light. The resulting solution contains a variable amount of precipitate which has been shown by x-ray analysis to contain PuF_4 hydrate and PuO_2 , demonstrating further the high temperatures occurring during the hydrolysis." The observations of violence and of energy emission in the form of light, in the reaction of PuF_6 with water at room temperature, are similar to the reaction phenomena observed in the release incident.

VI. CONCLUSIONS

1. The release of plutonium hexafluoride to the atmosphere of the glovebox resulted in the discharge of only a small amount of plutonium to the environment.
2. Penetration of plutonium through filters generally fell within the range predicted from small-scale experiments, demonstrating the utility of such experiments in defining the capabilities of filter systems.
3. The differences in penetration between primary and back-up filters as determined from both small-scale experiments and the incident under study are large and need to be seriously considered in the design of high-efficiency filtration systems.
4. The condition of the filters and the techniques of installing filters in ventilation systems are likely to be important in determining the effective protection afforded by such filter systems. Determination of the operating efficiency of filters installed in ventilation systems before their actual use may be desirable.
5. The reliance on stack-monitoring devices to determine the concentration of plutonium discharged to the atmosphere is significant; therefore such devices need to be frequently checked for satisfactory operation. Development of more reliable stack monitors appears to be desirable.

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REFERENCES

1. Malecha, R. F., Smith, H. O., Schraidt, J. H., Natale, J. V., Ross, N. E., and Brown, H. L., Jr., Low Cost Glove Boxes, Proceedings of the Eighth Conference on Hot Laboratories and Equipment, USAEC Report TID-7599, pp. 485-493 (1960).
2. Marchetti, F. P., A Compendium of Radiation Safety Information about Plutonium, USAEC Report ANL-6884, Argonne National Laboratory (April 1964).
3. Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure, U. S. Dept. of Commerce, National Bureau of Standards Handbook 69, U. S. Government Printing Office, Washington, D. C. (June 5, 1959).
4. Kessie, R. W., and Gerding, T. J., Plutonium Particulate Filtration from Exhaust Systems, p. 123 in USAEC Report ANL-6596, Chemical Engineering Division Summary Report, July, August, September, 1962, by Lawroski, S.; Vogel, R. C., and Munnecke, V. H.; see also Kessie, R. W. et al., USAEC Report ANL-7066 (to be published).
5. Marchetti, F. P., Smear Study of D205 (Chemical Engineering Building), USAEC Report ANL-6584, Argonne National Laboratory (July 1962).
6. Sedlet, J., ANL, private communication.
7. Mandleberg, C. J., Rae, H. K., Hurst, R., Long, G., Davies, D., and Francis, K. E., J. Inorg. and Nucl. Chem. 2, 358-367 (1956).