

**LA-6295-PR**

Progress Report

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Issued: April 1976

# Environmental and Radiological Safety Studies

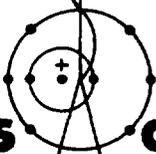
July 1 — September 30, 1975

## Interaction of $^{238}\text{PuO}_2$ Heat Sources with Terrestrial and Aquatic Environments

Compiled by

**Glenn R. Waterbury**

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Work supported by the Office of the Assistant Director, Safety and Reliability, US Energy Research and Development Administration, Division of Nuclear Research and Application.

DOE ARCHIVE

**QUARTERLY REPORT**  
**ENVIRONMENTAL AND RADIOLOGICAL SAFETY STUDIES**

**Interaction of  $^{238}\text{PuO}_2$  Heat Sources  
with Terrestrial and Aquatic Environments  
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**ABSTRACT**

The containers for  $^{238}\text{PuO}_2$  heat sources in radioisotope thermoelectric generators are designed with large safety factors to ensure that they will withstand reentry from orbit and impact with the earth and safely contain the nuclear fuel until it is recovered. Existing designs have proved more than adequately safe, but the Office of the Assistant Director, Safety and Reliability Programs, of the ERDA Division of Space Nuclear Systems continually seeks more information about the heat sources to improve their safety. The work discussed here includes studies of the effects on the heat source of terrestrial and aquatic environments to obtain data for design of even safer systems. The data obtained in several ongoing experiments are presented; these data tables will be updated quarterly. Discussions of details of the experimental testing are minimized, and they will be largely repetitive in succeeding reports to emphasize the main purpose, compilation of all usable data generated in each experiment. This compilation includes data from environmental chamber experiments that simulate terrestrial conditions, experiments to measure  $\text{PuO}_2$  dissolution rates, soil column experiments to measure sorption of plutonium by soils, and several aquatic experiments.

No reference to results cited in this report should be published without the explicit permission of the person in charge of this work.

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**I. INTRODUCTION**

Radioisotope sources provide heat for electric power generators that can supply constant voltage for several years. Therefore, they are used in many space missions to provide electric power for instruments and data transmission. In five of the Apollo manned landings on the moon, the scientific instrument packages deployed for postmission

measurements contained radioisotope heat sources. Because the half-life of  $^{238}\text{Pu}$  is relatively short (87.5 yr), the alpha-particle specific activity is high enough (equivalent to 0.56 W/g of  $^{238}\text{Pu}$ ) to be used as a heat source in electrical power generation. In nearly all space applications to date, plutonium 80% enriched in  $^{238}\text{Pu}$  has been used to supply the heat for the generators. The heat source container is designed with a great safety factor to withstand both

reentry from orbit and impact with the earth, so that the source will be safely contained until it is recovered. Although existing designs have proved more than adequately safe, the Office of the Assistant Director, Safety and Reliability Programs, of the ERDA Division of Space Nuclear Systems continually seeks more information about the heat sources to improve their safety. As part of this program, LASL is studying the interaction of  $^{238}\text{Pu}$  fuel material with seawater, fresh water, and marine organisms, and with air, soil, and rain to supply data for design of even safer heat sources.

Several chemical forms of  $^{238}\text{Pu}$  have been used as heat sources. The forms now in use or being studied for future use are plutonia-molybdenum cermet (PMC), and various pressed shapes of pure plutonium dioxide (PPO). We have run several aquatic experiments using PMC, but all our terrestrial experiments have involved PPO.

Discussions of details of the experiments are intentionally brief and will be repeated in subsequent progress reports. The main purpose of these reports is to compile in one convenient reference all usable data generated in the LASL experiments. The compilation will be updated each quarter. When an experiment or set of experiments is completed or terminated, a final topical report will be issued and that phase of the work will not be included in subsequent quarterly reports.

## II. BEHAVIOR OF $^{238}\text{Pu}$ FUEL IN TERRESTRIAL ENVIRONMENTS

(James H. Patterson, Nicholas Vanderborgh, and George M. Matlack)

### A. Environmental Test Chambers

Meaningful data on the environmental effects of the radiation and heat from radioisotope heat sources can best be obtained under simpler, less varied conditions than exist normally in nature. Use of environmental test chambers permits selection of the parameters to be tested and ensures control over them. Determination of the effects of these parameters on the fuel material and simulation of different climates and soils are also possible.

Each environmental test chamber has an interior volume of  $1.8\text{ m}^3$  and can be programmed for diurnal temperatures of  $-20$  to  $95^\circ\text{C}$  and relative humidities of 25 to 100%. A manually operated spray system simulates rainfall at rates as high as 10 cm/h.

Each chamber contains a 0.9- by 0.9-m tray, filled to a depth of 0.3 m with soil. The soil is supported by a grill covered with a thin perforated plate to drain

off the rainwater that percolates through the soil. The bottom of the tray tapers to a pipe that runs to the outside of the chamber so this water can be collected.

### B. Soils

About 1.4 Mg each of loam, clay, sand, and silt loam were obtained for terrestrial experiments. Compositional analyses of these soils were provided by the U. S. Soil Conservation Service Laboratory at Riverside, California (Table I). Pressure plate moisture measurements are planned for these soils.

### C. Test Conditions and Analyses Performed

The first three experiments were started with the chambers programmed for humid summer conditions (20 to  $40^\circ\text{C}$ , 87 to 96% RH). Cams installed later provided humid winter conditions (0 to  $17^\circ\text{C}$ , 71 to 100% RH). The alternate summer and winter

TABLE I  
COMPOSITION OF SOILS USED  
IN TERRESTRIAL EXPERIMENTS<sup>a</sup>

	Loam	Clay	Silt Loam	Sand
Sand (%)	49.5	1.5	25.3	88.6
Silt (%)	37.6	31.4	60.1	4.6
Clay (%)	12.9	67.1	14.6	6.8
C, organic (%)	0.6	0.12	0.03	0.01
Carbonate as $\text{CaCO}_3$ (%)	tracc	8	10	4
$\text{H}_2\text{O}$ at 15 bars (%)	7.6	23.8	7.5	2.6
$\text{H}_2\text{O}$ at saturation(%)	40	91	45	22
pH	8.0	7.8	8.4	9.1
Ca(meq/100 g)	16.3	43.9	26.4	17.8
Mg(meq/100 g)	1.9	10.2	3.7	1.7
Na(meq/100 g)	0.5	4.6	3.5	0.9
K(meq/100 g)	1.0	1.1	0.5	0.5
Cation exch cap	13.6	42.0	14.7	6.0
Elect. Conductivity mmho/cm	0.6	4.2	3.3	0.6
Clay mineral ratios:				
Mica	4	---	---	---
Montmorillonite	3	5	5	5
Kaolinite	3	3	2	3

<sup>a</sup>Soil analyses provided by the U. S. Soil Conservation Service Laboratory, Riverside, CA.

periods each last 6 months. The experiment in the chamber containing MHFT-27 was terminated (see Section II.D.2). Two additional chamber experiments were started under arid winter conditions (3 to 28°C, 21 to 87% RH). Three other experiments were started under humid winter conditions. All seven current chamber experiments are now operating under summer conditions, two in arid summer weather (26 to 53°C, 7 to 33% RH), the other five under humid conditions.

The fuel material sample was placed in the center of the tray on the soil surface. Each sample under humid conditions received a 3-cm rain once a week. The rains for arid conditions occurred approximately once a month during the winter. There have been no rains during the first three months of arid summer. The rainwater that percolates through the soil is analyzed for plutonium. The condensate from the refrigeration-type dehumidifier in the chamber conditioning system is also analyzed to get a relative indication of the airborne plutonium in the chamber. Core samples of the soil are collected at approximately 6-month intervals. Each core is divided into 5 to 14 sections that are analyzed separately to determine the plutonium variation with depth in the soil.

Small air samplers, fitted with approximately 40-mm-diam filter papers, were operated several times in two chambers to measure the airborne plutonium. The filter papers were changed frequently during operation, and the plutonium was measured by counting the papers and in some cases by dissolving them and scintillation-counting the resultant solutions.

Time-lapse movies were taken in four chambers during rains. Emissions from some fuel samples were studied by time exposure photographs, without external lighting, in the near-ir, visible, and near-uv regions of the spectrum.

#### D. Test Samples and Results

Seven terrestrial environmental chamber experiments are currently under way. They are summarized in Table II.

1. *MHFT-12*. This was a PPO test sphere for the Multi-Hundred Watt (MHW) program which shattered during a simulated reentry and impact. The sphere fragments were removed from the container and sorted by size. The pieces with diameters greater than 6 mm, weighing 224 g, were placed in one environmental test chamber on June 21, 1973, and 28 g of 0.01- to 6-mm-diam material was placed in another on September 28, 1973. These experiments are now in their third summer in a humid environment.

TABLE II  
TERRESTRIAL ENVIRONMENTAL CHAMBER EXPERIMENTS

Experiment Number	Description	Date Started
1	MHFT-12 chunks on loam; humid climate	6-21-73
2A	MHFT-23 in GIS on sand; humid climate	4-10-75
3	MHFT-12 fines on loam; humid climate	9-27-73
6	MHFT-50 fines on loam; circular soil partitioner; humid climate	4-9-75
7	MHFT-27 fines on sand; arid climate	2-25-75
8	MHFT-50 chunks on loam; circular soil partitioner; humid climate	4-9-75
10	MHFT-27 chunks on sand; arid climate	2-26-75

Photographs of the emissions from the large pieces in the near-ir, visible, and near-uv spectral regions showed that the external temperature of the pieces was 250 to 300°C, and that an air glow around them was emitted mainly in the visible region, although some of it may have been uv. This air glow was probably caused by ionization of air by the alpha or gamma activity of the pieces.

Plutonium airborne concentrations increase during periods of rain on the large pieces. This effect results in a greater plutonium pickup from the air by the dehumidifier, which can be measured by plutonium analyses in the dehumidifier condensates. Analyses for a period of 2 months are shown in Fig. 1. The explanation seems to be that material spalls from the hot pieces of PPO because of thermal shock when the cold rain first hits them. Spallation has

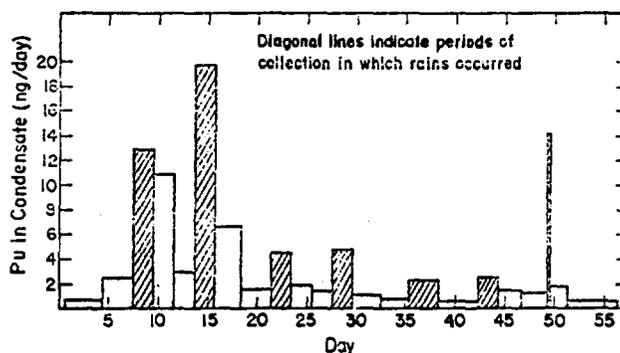


Fig. 1.  
Effect of rain on plutonium content of dehumidifier condensates.

been observed in nature when some kinds of rock, heated by the sun, are hit by a sudden shower.<sup>1</sup> This mechanism for the airborne plutonium observed over the PPO pieces seems to be confirmed by the striking results (Table III) of an experiment in which air particulate samples were taken during a rain sequence. The average concentration during the first 5 min of rain was  $10^4$  times the prerin concentration. It then dropped continuously until it reached the prerin level about 1 h after the end of the rain. The principal cause for the rapid decrease is gravitational settling of the particles. The rain washes some of the plutonium out of the air but it cannot be the only removal mechanism because the decrease continues after the rain has stopped. A repetition of the experiment, but with dehumidifier turned off, produced similar rates of decrease, indicating that pickup by the dehumidifier is not the principal removal mechanism. The results in Table III were obtained by counting the fiber glass filters with a 2- $\pi$  gas proportional counter. Some of the filters were subsequently dissolved, and a more accurate analysis by liquid scintillation counting showed that most of the initial activity came from relatively large particles caught on the filter surface and therefore counted efficiently by the proportional counter. Later, the large particles settled out, and

the remaining smaller particles penetrated deeper into the filter and were counted less efficiently. This experiment was repeated twice, with Millipore membrane filters of two different pore sizes, and at two air collection points within the chamber, in order to obtain samples for particle size and agglomeration studies. The airborne plutonium concentrations were similar to those measured in the first experiment (Table III).

The first rainwater that percolated through the soil supporting the large fuel pieces contained 1.8  $\mu$ Ci of plutonium. This very rapid plutonium breakthrough indicated that some of the material that spalled from the fuel is in the form of very small particles or a colloid. Plutonium ions would not be stable in solution at the slightly basic pH (about 8), and if present would be held in the soil by some ion-exchange type of mechanism.

The amount of plutonium found in the rainwater that percolated through the soil supporting the large pieces is strongly influenced by the climate, as is shown in Table IV. Each weekly rain is equivalent to a 32-mm rainfall and deposits 27 liters of water. Under summer conditions, about 6 liters of rainwater percolated through the soil. This water contained an average of 0.7  $\mu$ Ci of plutonium. Winter rain produced more percolated water, because of lower evaporation losses, and a higher plutonium content, the early winter rains yielding as much as 18  $\mu$ Ci of plutonium. It seems that the higher summer temperatures dried the soil more between rains so it became saturated later during a rain. Because of this lower water flow in summer, fewer plutonium dioxide particles were washed through the soil. At the beginning of the winter, some of the particles left in the soil during the summer were washed through, giving higher results for the first

TABLE III  
AIRBORNE PLUTONIUM CONCENTRATIONS  
DURING A RAIN IN AN ENVIRONMENTAL  
CHAMBER CONTAINING LARGE PIECES OF  
PLUTONIUM DIOXIDE

Filter No.	Collection Time (min)	Pu Concentration ( $\mu$ Ci/m <sup>3</sup> )	Remarks
1	24	3	Before rain
2	5	$3 \times 10^4$	First 5 min of rain
3	5	$6 \times 10^3$	
4	10	$4 \times 10^3$	
5	10	$3 \times 10^3$	
6	15	$9 \times 10^2$	
7	15	$8 \times 10^2$	Last 15 min of rain
8	50	$2 \times 10^2$	
9	180	3	
10	860	3	

Table IV  
HUMID CLIMATE EFFECTS ON AMOUNT OF  
PLUTONIUM CARRIED BY WATER PER-  
COLATING THROUGH SOIL  
(Large Pieces from MHFT-12)

Climate	Conditions	Av Percolated Water per Rain (liters)	Av Pu ( $\mu$ Ci)
Winter	0 - 17 °C	11	9
	70 - 100% RH		
Summer	20 - 40 °C	6	0.7
	87 - 96% RH		

few rains. These seasonal effects have occurred each summer and winter cycle.

Autoradiography<sup>2</sup> of part of a sample of percolated rainwater taken in winter from the chamber containing the large pieces of MHFT-12 revealed 0.05- to 0.8- $\mu\text{m}$ -diam plutonium oxide particles with a count median diameter (CMD) of 0.095  $\mu\text{m}$ . These accounted for only 1 ppm of the total plutonium in the sample, indicating that nearly all the plutonium particles carried through the soil by water were less than 0.05  $\mu\text{m}$  in diameter.

Usually there is good agreement in measured radioactivities among aliquots from the same percolated rainwater sample. Occasionally there is disagreement with one aliquot counting as much as several hundred times the others. This indicates the presence of a significantly larger than average particle of  $\text{PuO}_2$ . We estimated that the largest particle found in the high activity aliquots was equivalent to a 4- $\mu\text{m}$ -diam sphere, five times the diameter of the largest particle seen in the autoradiographic analyses of a rainwater sample in which the count rates of the aliquots agreed.

The fine particles of MHFT-12 interacted differently with the simulated environment. These particles were too small to have temperatures above ambient, so spallation was negligible. Plutonium concentrations in airborne particulates during a rain in the chamber were also measured using an air sampler. The results (Table V) show that the airborne plutonium concentration before the rain was about the same as the prerin concentration in the chamber containing the larger pieces of MHFT-12. This concentration did not increase significantly

during the first 5 min of rain, in contrast to the experiment with the large pieces. Instead, airborne plutonium decreased, and after the rain, the concentration was an order of magnitude lower than before. These lower concentrations probably indicate that soil wetting inhibited resuspension of plutonium-bearing particles. The counting rates were so low that we had to combine the five filters used during the rain to obtain meaningful statistics. The same treatment was necessary for the first five filters used after the rain. There was very little seasonal effect on the plutonium content of the rainwater that percolated through the soil; it averaged about 0.2  $\mu\text{Ci}$  both winter and summer.

TABLE V  
CONCENTRATIONS OF AIRBORNE PLUTONIUM  
DURING RAIN IN AN ENVIRONMENTAL CHAMBER  
CONTAINING FINELY DIVIDED  $^{238}\text{-PLUTONIUM DIOXIDE}$

Filter No.	Collection Time (min)	Pu Concentration ( $\mu\text{Ci}/\text{m}^3$ )	Remarks
1	103	1.9	Before rain
2	5	2.1	First 5 min of rain
2-7	60	1.9	Average during rain
8-12	164	0.12	After rain
13	926	0.14	

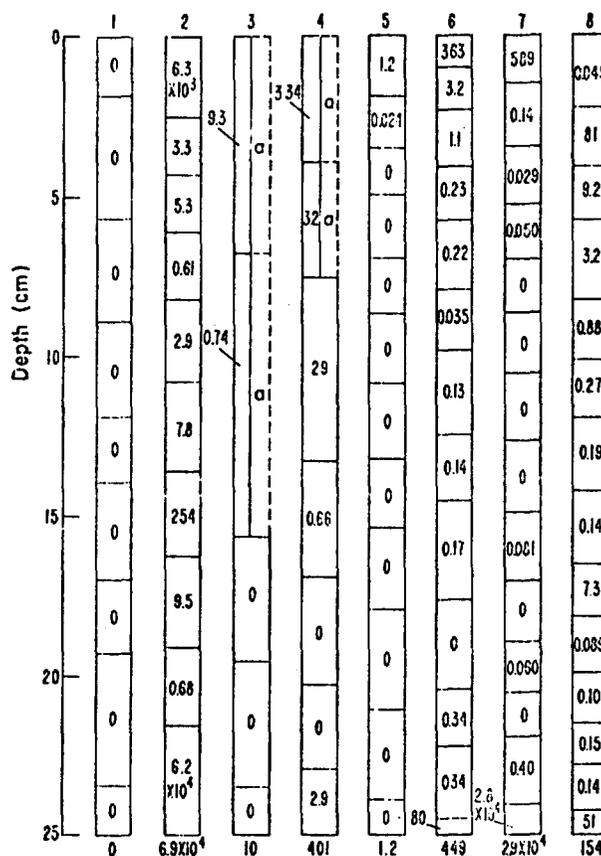


Fig. 2.  
 $^{238}\text{Pu}$  in soil cores from chamber containing fine material from MHFT-12 (ng).  
a. Sample to LFE Environmental  
Core positions: 8 4 6  
1 Pu 2  
5 3 7

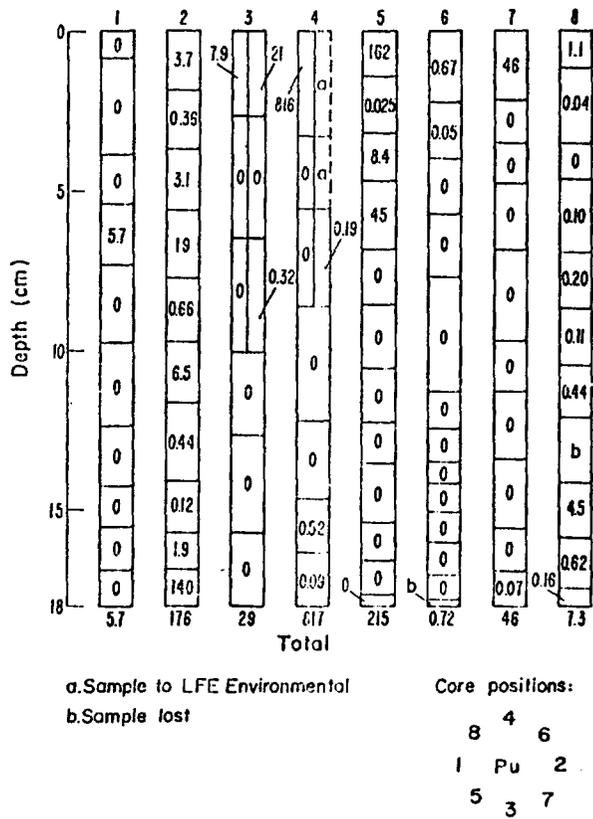


Fig. 3. <sup>238</sup>Pu in soil cores from chamber containing large pieces from MHFT-12 (ng).

We analyzed eight soil cores from each of these two chambers for plutonium. The results and core locations are shown in Figs. 2 and 3. Each core was taken 25 cm from the central pile of fuel material. Cores 1 and 2 were collected at the end of the first summer, cores 3 and 4 during the first winter, cores 5 and 6 during the second summer, and cores 7 and 8 during the second winter. The top two or three sections of cores 3 and 4 in both of these chambers were divided into two nearly equal parts by a vertical cut. Six of these half sections, as indicated in Figs. 2 and 3, were examined for particle size distribution and agglomeration by LFE Environmental. The rest of the half-sections were analyzed for plutonium. Zeros indicated that less than 0.02 ng of plutonium was found.

The data in Figs. 2 and 3 indicate that, in addition to downward movement of plutonium through the soil, there was surface movement to the right and back of each chamber, the effect being greater in the chamber containing the fine particles of fuel. This movement was confirmed by a radiation contour

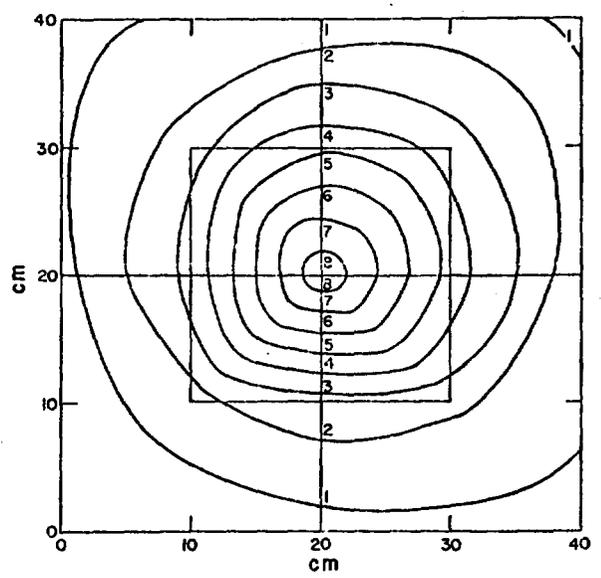


Fig. 4. Radiation contours from a TLD grid above soil in chamber containing fine material from MHFT-12.

map (Fig. 4) of the  $\gamma$ - and x-ray intensities in the chamber containing the fine particles. An array of 17 thermoluminescent detectors (TLD's) was placed 10 cm above the center of the tray containing the fine material, one at each horizontal and vertical intersection of the grid in Fig. 4, except for the 10-cm tick marks. The intensities ranged from 0.3 R/h at the front (lower) left corner to 8.8 R/h at the center. If all the plutonium were still concentrated at the center of the tray, the contours would be circular. Their deviation indicates that some of the plutonium on the surface has been moved toward the back and to the right. This movement seems to have been caused by water released from a gate valve directly above core position 1 whenever summer humid conditions prevailed and the valve was opened to the building exhaust to provide air flow when the chamber door was opened. (This artifact was eliminated in June 1975, by deflecting the water away from the tray of soil.) The radiation map measurements were confirmed by an autoradiograph of the activity of the soil surface.

A seasonal effect was seen in three cores from the chamber containing the fine particles (Fig. 2). Cores 2, 4, and 6 all had higher plutonium concentrations than cores 1, 3, and 5 because of the gate valve artifact mentioned above. Cores 2 and 6, however, which were collected in the summer, had higher concentrations than core 4, collected in the winter, and

there was more plutonium in sections below the surface, especially in the bottom sections. These high concentrations in the subsurface soil during the summer agree with the reason postulated to explain the low plutonium concentrations in summer rainwater that percolated through the soil; that is, the smaller flow of water in the summer does not wash as much plutonium out of the soil as does the greater winter flow. The high concentration in the bottom sections of these summer cores, also seen in Fig. 3, is less easily explained. Possibly some of the plutonium is held up by the perforated plate under the soil when the flow is low; the holes are only 22% of the surface area. Also, plutonium oxide particles may collect at the soil and air interface under low flow conditions.

The seasonal effect is less marked in cores 7 and 8, which were taken during the second winter, in the chamber containing the fine particles. This may have been caused by gradual fixing of the plutonium dioxide in the soil with the passage of time. Core 7 looks like a winter core except for the bottom section which is very high in plutonium. Core 8 is more like a summer core, with small amounts of plutonium in all sections.

Cores from the soil with the large pieces (Fig. 3) show similar, but less pronounced, spatial and seasonal correlations. Part of this blurring of the effects may have been caused by water from the gate valve splashing onto the pieces and causing spallation. Evidence of this complication was seen in the experiment, described earlier, in which the air concentrations during a rain were measured with the dehumidifier off. In that experiment the prerin concentration was high, probably because the gate valve was opened just before the rain. Unfortunately, the sample of the bottom section of core 6 (Fig. 3) was lost, and we do not know whether the concentration was high at the bottom of this core, as it was in the other cores taken in similar places in the summer.

The six half-sections from cores in the two chambers were analyzed at LFE Environmental for particle size distribution and agglomeration with the soil.<sup>3</sup> There were no particles large enough to form stars in a photographic emulsion in either section of core 3 from the chamber containing the fine particles. There were stars in the top section of core 4 in both chambers. The particle size range was slightly smaller than that in the rainwater that percolated through the soil; 90% of the particles had equivalent diameters of 0.04 to 0.2  $\mu\text{m}$ . The lower limit may not be significant, as it is close to the detection limit of the procedure. The particles in the cores from the soil supporting the fine particles were slightly larger than those in the soil supporting the large pieces.

They had a CMD of 0.072  $\mu\text{m}$  compared with 0.056  $\mu\text{m}$ , but they were still very much smaller than the 10- $\mu\text{m}$  minimum parent particles. This fact agrees with observations that  $^{238}\text{PuO}_2$  is much less stable than  $^{239}\text{PuO}_2$ .<sup>4-7</sup> This instability seems to be associated with the intense radiation field of the isotope's alpha activity. Radiation damage to the oxide crystal lattice, reaction with radiolysis products in soil and water, and aggregate recoil may contribute to this degradation.

Twenty-five of the particles that formed stars, chosen at random on the photographic plates of highly disperse material from the core of soil supporting the large fuel particles, were examined microscopically for agglomeration. Each particle was found to be associated with one microscopically visible soil particle. This indicates that trapping of plutonium dioxide particles by soil is not a matter of filtration of the fine oxide particle, but that there is agglomeration of individual plutonium oxide and soil particles. This factor may determine which particles will be retained by the soil and which will pass through it. The soil particles in the agglomerates had the same size distribution as the bulk of the soil.

Cores 9 and 10 were taken from the chamber containing the large pieces of MHFT-12 during the second winter cycle, at locations 20 cm to the left and right of the PPO pieces, respectively. Core 10 was sent to LFE Environmental for particle size and agglomeration studies. Core 9 was divided into 10 vertical sections for plutonium analysis. The top section contained 24 ng, but the other nine sections each contained less than 25 pg of plutonium. This agrees well with the results of core 1, collected during the first summer 25 cm to the left of the heat source pieces.

2. *MHFT-27*. As part of the MHW-safety sequential test (SST) program, MHFT-27 a postimpact sphere assembly (PISA), was about 40% buried in sand in an environmental chamber on January 9, 1974. The temperature of this PISA, which contained 254 g of 80% enriched  $^{238}\text{PuO}_2$ , was monitored by means of thermocouples welded to the top and bottom of the iridium shell. Initially the temperature was 620°C. During the first rain, the temperature dropped rapidly to 100°C and the sphere sank into the sand until about 90% of it was covered, probably because rainwater lubricated the sand. The temperature stayed at 100°C for 1.5 days, then gradually increased to about 500°C. This pattern of thermal response to a rain changed gradually. After several months, during a rain the temperature remained at 100°C, but as soon as the rain stopped, it rose to 300°C, where it remained for

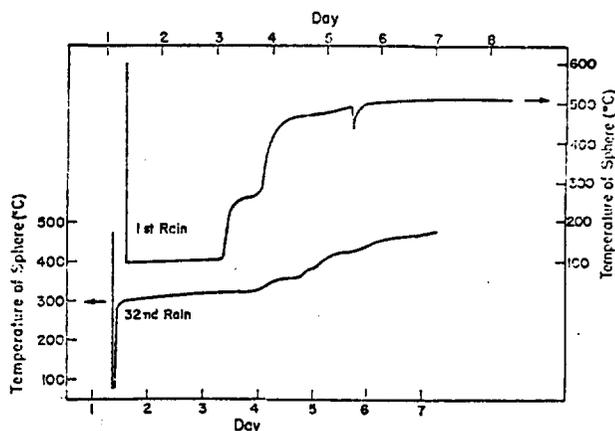


Fig. 5.  
Thermal responses of MHFT-27 to rain.

about two days before gradually increasing to about 500°C. The different responses to a later rain and to the first rain (Fig. 5) seem to have been caused by formation of a crust that partially insulated the sphere from the water in the soil around it. We took two sets of two soil cores from this chamber; none of their sections showed appreciable alpha activity above background except for the top two sections of one core which contained about 0.2 ng each. The percolated rainwater and the dehumidifier condensates also showed very little activity.

After a year of exposure to humid environment, the PISA was removed from the environmental chamber. We found a hard soil crust, 0.5 to 3.0 cm thick, almost completely surrounding the PISA. This crust insulated the PISA from the surrounding soil and caused the change in temperature recovery times noted in the series of rains in this chamber. When the PISA was returned to the Plutonium Metallurgy Group (CMB-5) for examination, it was found that the iridium shell was intact and the vents were plugged. There was no evidence that water had penetrated the shell, or that any of the plutonium had leaked out. The very small amount of  $^{238}\text{Pu}$  found in the environmental system no doubt came from contamination that was on the outside surface of the PISA when we received it.

After this post-mortem examination, the plutonium oxide material in the PISA was sorted by particle size. One fraction of the material, consisting of all of the pieces greater than 6 mm in diameter (221 g), was placed in an environmental chamber, and the fraction of the material with diameters between 0.01 and 6 mm (32 g) was placed in another environmental chamber. These chambers were initially programmed for winter arid conditions. They are now operating in arid summer weather. Each chamber has had four rains. The water that per-

colated through the soil after the first rain contained about 24 ng of plutonium in the chamber with the large pieces, and 2.5 ng in the chamber with the fine material. The water aliquots from the chamber containing the large pieces showed a wide variation in plutonium content, indicating the presence of some large particles of plutonium. The plutonium content decreased for the next three rains, so that there was less than 1 ng in the fourth rain. In the chamber containing the fine material, the plutonium content dropped to 0.5 ng in the water collected from the second rain, and the third and fourth rains were approximately the same. There were no rains during the first three months of summer in either of these chambers. The liquid nitrogen rain experiment, described below, was carried out in the chamber containing the large pieces of MHFT-27.

The plutonium contents of the dehumidifier condensates were similar to the contents of the early condensates from the two chambers containing material from MHFT-12. The condensates from the fine material decreased in plutonium content after the first rain, while the condensate for the large pieces that was collected for a period that included the rain had much more plutonium than the other condensates from this chamber. Two soil cores were taken in each of these chambers at positions about 25 cm to the left and the the right of the PPO material before the change to summer climate. The analyses for these cores are shown in Tables VI and VII.

3. *MHFT-50*. The fragments of PPO from the test sphere MHFT-50 were placed in two environmental chambers equipped with specially designed soil compartments. One chamber contains 186 g of pieces greater than 2 mm in diameter, and the other contains 68 g of fine material, with particle diameters between 0.01 and 2 mm. The soil in each chamber is a loam, and the soil tray is divided into two sections by a circular partition 45 cm in diameter in the

Table VI

PLUTONIUM IN SOIL CORES FROM CHAMBER CONTAINING FINE MATERIAL FROM MHFT-27

Left Core			Right Core		
Section No.	Depth cm	Pu ng	Section No.	Depth cm	Pu ng
1	0-3	9.45	1	0-4	412.1
2	3-7	0.19	2	4-10	0.16
3	7-10	< 0.03	3	10-13	0.03
4	10-14	0.03	4-5	13-17	< 0.03
5-10	14-28	< 0.05	6	17-19	0.07
			7-9	19-23	< 0.03
			10	23-25	0.04
			11	25-27	< 0.03
			12	27-28	0.13
Total Pu		9.67			422.2

Table VII

PLUTONIUM IN SOIL CORES FROM CHAMBER CONTAINING LARGER PIECES FROM MHFT-27

Left Core			Right Core		
Section No.	Depth cm	Pu ng	Section No.	Depth cm	Pu ng
1	0-6	3.30	1	0-3	3.97
2	6-13	< 0.03	2	1-10	1087.
3	13-22	19.26	3	10-16	0.19
4-5	22-28	< 0.03	4	16-23	0.05
			5-7	21-28	< 0.05
Total Pu		22.56			1091.

center of the tray. The PPO material was positioned in the center of the circular section. The water that percolates through the soil in the two sections is collected separately for plutonium analysis. Initially the two chambers were on a winter cycle with humid conditions, but now have been changed to summer humid weather.

The volume of water that percolated through the soil was much lower in the inner compartment than in the outer compartment, especially in the chamber containing the large pieces, because the outer compartment has three times the area and because the heat from the plutonium dioxide dries the soil in the inner compartment more rapidly between rains. The volume of water collected per rain from both the inner and outer compartments in both chambers increased in the summer rains over the winter rains, contrary to the expectation from the results with the chambers containing the MHFT-12 material. The ratio of the volumes from the outer compartment to those of the inner compartment increased by 50% in the summer for the fines, compared with a factor-of-two decrease for the large pieces. This latter decrease probably indicates that the greater evaporation of water from the surface of the outer compartment due to the summer heat partially balances the effect of the evaporation in the inner compartment by the heat from the large pieces on the volume ratio of the two compartments. In the case of the fines, the sample produces much less heat, so the effect is small. The outer-to-inner ratio for plutonium was two orders of magnitude higher for the large pieces over the fines, as expected from the spallation of the large pieces, in the winter rains. However, before the summer rains, water had overflowed from the inner compartment to the outer one in the fines chamber because of a valve malfunction. This carried plutonium to the outer compartment, resulting in a much higher outer-to-inner ratio in the summer for this chamber. The plutonium in the dehumidifier condensates from the large piece experiment was five times that from the fine particle experiment. Two soil cores were taken from each chamber during the humid winter cycle, one just inside and one just outside the circular isolating partition on the left

side of the chamber. The analyses for these cores are given in Tables VIII and IX.

4. MHFT-23. We started testing a Fuel Sphere Assembly (FSA) in an environmental chamber on a sandy soil under humid winter conditions. The chamber has now been changed to humid summer conditions. The Graphite Impact Shell (GIS) contains MHFT-23, an iridium clad PPO sphere that has not been subjected to an impact test. At the time we placed the FSA in the chamber, we found a small amount of alpha particle contamination on the outside of the iridium shell, but the outer surface of the GIS was nominally free of contamination. There was a small amount of plutonium contamination in this chamber that remained after cleanup from its use for testing the PISA that contained MHFT-27. The first rainwaters and dehumidifier condensates contained very small amounts of plutonium, but most of the analyses have been indistinguishable from background since then. Two soil cores have been

Table VIII

PLUTONIUM IN SOIL CORES FROM CHAMBER CONTAINING FINE MATERIAL FROM MHFT-50

Inner Compartment			Outer Compartment		
Section No.	Depth cm	Pu ng	Section No.	Depth cm	Pu ng
1	0-3	143.8	1	0-3	253
2	3-5	0.106	2	3-7	0.083
3	5-7	0.054	3	7-11	49.4
4	7-8	< 0.03	4	11-15	0.050
5	8-10	0.046	5	15-19	38.0
6-11	10-21	< 0.07	6	19-22	0.076
			7	22-24	0.048
			8	24-27	0.042
			9	27-28	0.043
			10	28-30	0.041
		144.0			341

Table IX

PLUTONIUM IN SOIL CORES FROM CHAMBER CONTAINING LARGER PIECES FROM MHFT-50

Inner Compartment			Outer Compartment		
Section No.	Depth cm	Pu ng	Section No.	Depth cm	Pu ng
1	0-2	1929.	1	0-3	214.9
2	2-3	73.7	2	3-7	0.10
3	3-4	0.72	3	7-9	0.041
4	4-7	1.7	4	9-13	0.10
5	7-8	0.66	5	13-18	0.034
6	8-11	1.12	6-10	18-30	< 0.03
7	11-12	0.58			
8	12-15	0.96			
9	15-18	0.42			
10	18-21	0.35			
		2009			215.2

collected 25 cm to the left and to the right of the sphere. In each core there was one section with a very small amount of plutonium (0.1 and 0.03 ng). The plutonium in the other sections was not distinguishable from background.

A Chromel-Alumel thermocouple was attached to the side of the GIS with an epoxy adhesive. During the winter cycle the external temperature varied between 180 and 192°C. After the change to the summer cycle, the temperature increased to 200 to 210°C. During a rain the temperature dropped below 50°C, and when the temperature and humidity controls were shut down, resulting in air stagnation, the temperature rose to 235°C.

*5. Spallation Induced by Liquid Nitrogen.* Earlier work has demonstrated that the airborne plutonium concentration increased dramatically during a rain on large, thermally hot PPO pieces. This has always been presumed to be the result of thermal shock to the fuel's surface, resulting in the spallation of tiny fragments of plutonia. We decided to find out if this cooling mechanism was a general phenomenon, or if water played a significant role in the process by means of a chemical reaction with the hot fuel.

We conducted an experiment where liquid nitrogen drops fell on chunks of PPO fuel in one of the environmental test chambers. This liquid nitrogen rain continued for 5 minutes. Air samples were taken before, during, and after the rain. We found that the airborne plutonium activity increased by four orders of magnitude at the onset of the cooling period. About an hour after the end of the liquid nitrogen rain the airborne plutonium concentration had dropped back to its prerin level of 0.1 nCi/m<sup>3</sup>. These results are quantitatively similar to those found with aqueous rains, and suggest that hydrolysis reactions are not involved in the spallation process during an aqueous rain.

The air filters on which the plutonium was collected contained a short-lived alpha activity, in addition to the the long-lived plutonium activity. This short-lived activity was not present in samples collected prior to the rain. We believe that the thermal shock releases not only very fine particles of plutonia, but also radioactive gases (<sup>220</sup>Rn and <sup>222</sup>Rn) entrapped in the plutonium oxide crystal lattice structure.

During this experiment we also measured the adsorption of the airborne plutonia on four different types of surfaces: glass, Teflon, stainless steel, and Lucite. Glass was the most effective collector of the airborne plutonia, adsorbing approximately 1000 times more than the Teflon or Lucite surfaces during

the liquid nitrogen rain. Very little was found on the stainless steel surface.

We also made background measurements on a separate set of the same kinds of surfaces by exposing them to the chamber air for 48 hours before the liquid nitrogen rain. The fact that significant amounts of alpha activity were found on the glass surface suggests that spontaneous spallation occurs continually, most likely caused by radiation damage in the plutonium oxide.

A third set of adsorber measurements was made one day after the liquid nitrogen rain. These results showed far lower adsorption rates than existed prior to the liquid nitrogen rain. Apparently the thermal shock of the rain not only causes a great increase in spallation, but also frees loose particles created by radiation damage, so that at the end of the rain a fresh, undamaged surface is exposed.

Significant soil contamination was observed after the liquid nitrogen rain. The radioactivity, however, was found only on the soil surface and not beneath the surface. This is unlike soil contamination in the case of aqueous rains, where some of the plutonia particles are transported downward through the soil by the rainwater that drains through the soil. Thus hydrodynamic transfer is a significant transport mechanism under aqueous rain conditions.

### III. DISSOLUTION RATES OF <sup>238</sup>PuO<sub>2</sub> IN PERCHLORIC ACID

(James H. Patterson, Gilbert B. Nelson, and George M. Matlack)

This experiment has been terminated. A topical report has been completed and will be issued as LASL report LA-6184.

### IV. SORPTION OF PLUTONIUM BY SOILS

(Gilbert B. Nelson, Nicholas Vanderborgh, and George M. Matlack)

We are continuing the experiments to measure the absorption of plutonium by soils. This is done by allowing dilute plutonium to flow through soil contained in glass columns. The feed solution fed to the soil columns is a dilute, neutral solution of plutonium chloride, known to be unstable as it ages. This type of feed solution is necessary, however, to simulate rainwater contaminated with plutonium as it percolates through soils.

A preliminary requirement was to determine how the soil column diameter affected the specific flow rate, because a large particle diameter relative to column diameter might introduce random perturbations into the experiment. Accordingly, we determined specific flow rates for columns of three diameters packed with two lots of sand that differed in particle size distribution. We found that in 5-, 10-, and 25-mm-diam columns packed with 38- to 147- $\mu\text{m}$  sand particles on the one hand and 350- to 600- $\mu\text{m}$  sand particles on the other, the specific flow rates differed by no more than 10% relative standard deviation when calculated in terms of milliliters per second per square millimeter for the average particle cross-sectional area. These experiments also included 110- and 140-mm waterheads on the columns. We concluded that the specific flow of water through these columns was independent of the column waterhead and diameter, as long as the particle diameter did not exceed 10% of the column diameter and the waterhead did not exceed 50% of the soil height.

In the plutonium absorption experiments, we packed six 25-mm-diam columns with silt loam that had been sieved to remove particles larger than 0.8-mm diam. This soil is about 60% silt, 25% sand, and 15% clay. Its bulk density is 1.07 g/cm<sup>3</sup>; its particle density, 2.70 g/cm<sup>3</sup>. It has a total porosity,  $\epsilon$ , of 60.3, as calculated from the bulk and particle densities using the relation

$$\epsilon = 100(1 - D_b/D_p).$$

Three columns, 100-mm-high, have retained greater than 99.8% of the plutonium from the feed solutions during 474 days of operation. Differences in flow rates from 1.1 to 0.027  $\mu\text{l/s}$  among the three columns have not affected the retention of plutonium significantly. The other three columns are 250-mm high and contain soil sieved to remove particles smaller than 52  $\mu\text{m}$  in order to achieve more uniform flow rates. After 282 days of operation, the fastest flowing column, with a rate of 2.7  $\mu\text{l/s}$ , has retained 99.67% of the plutonium, and the other two, with flow rates of 1.3 and 1.8  $\mu\text{l/s}$ , have retained over 99.9% of the plutonium from their feed solutions. The concentration of the plutonium in the feed solutions is approximately 1  $\mu\text{g/l}$ .

## V. BEHAVIOR OF <sup>238</sup>Pu IN AQUATIC ENVIRONMENTS

(George M. Matlack, Gilbert B. Nelson, James H. Patterson, and Nicholas Vanderborgh)

The behavior of <sup>238</sup>Pu fuels in fresh water and seawater, especially rates of plutonium release, is being investigated in aquaria and in natural sea environments. Although the solubility of hydrated PuO<sub>2</sub> is extremely low, corresponding to about one atom of plutonium in 100 000 liters of water at pH 7, other interactions between water solvent systems and typical <sup>238</sup>Pu fuel can release plutonium at a low but finite rate. Measurements of these release rates from various fuels in differing circumstances provide data for assessing the risk to the biosphere from fuel container failure in the ocean or in fresh water, and for devising means to prevent unacceptable risks.

### A. Seawater Aquarium Experiments.

Each 94-liter aquarium contains 75 liters of simulated seawater, made by dissolving a commercial mixture of salts in distilled water, and maintained at pH 8.1 to 8.3. A refrigeration system keeps the water at 10°C when a 40-W heat source is immersed in the water and the room temperature is 25°C. Water is circulated by an air bubble stream behind a baffle in each rear corner. Each aquarium has a cover sealed at the sides with silicone rubber cement to contain airborne plutonium. Water samples are removed through a small hole in the cover.

### B. Ocean Test Facility.

Samples in specially designed steel chambers are submerged in 25 m of seawater off San Clemente Island, 100 km west of San Diego, at a Naval Undersea Center facility. Each chamber is approximately 50 cm in diameter and 25 cm deep, and the inside is covered with an asphaltum-like coating. The chamber is weighted on the bottom by a circular slab of concrete. The open top is protected by a conical metal canopy about 60 cm high. Water can enter only through the perforations in the canopy.

The sea floor in the test area, approximately 500 m from shore, is sandy, with rocks and abundant patches of seaweed. Each test chamber is filled with local sand and seawater, and the sample is placed about 2.5 cm beneath the sand surface before the chamber is lowered to the ocean floor.

### C. Residence Time of Soluble Plutonium in Simulated Seawater.

Plutonium released from a heat source in seawater would be expected to form a hydrated oxide as a radiocolloid and subsequently to precipitate on nearby surfaces because of the slightly alkaline, 7.6 to 8.4, pH. Therefore, we measured the average residence time of plutonium added to the simulated seawater (pH 8.2) in the test aquaria by adding 1 mg of  $^{239}\text{Pu}$  (in 1 ml of 1 M  $\text{H}_2\text{SO}_4$ ) to the 75 liters of simulated seawater, and periodically determining the plutonium concentration in the water. The same batch of water was used for two experiments, and a fresh batch was used in a third (Table X). The plutonium disappeared from the water at a rate that followed an exponential decay curve with a half-life of roughly 40 h. There was no change in the pH. Much of the plutonium was deposited on the aquarium walls above the water surface by spray from bursting of the air bubbles that maintain water circulation.

These experiments prove that soluble plutonium does not remain in simulated seawater for a significant time. This measured residence half-time should be applied cautiously to situations involving  $\text{PuO}_2$  heat sources, because the chemical form of the plutonium released from these sources is unknown.

### D. PMC Dissolution or Release Rates.

1. *In Simulated Seawater.* Two PMC disks were immersed in simulated seawater maintained at 8 to 12°C and a pH of 8.0 to 8.2. These disks were full size, 0.55-cm-thick, 5.44-cm-diam, production types

with a nominal power rating of 50 W, and each contained approximately 100 g of 80% enriched  $^{238}\text{Pu}$ .

The disks reacted similarly to the seawater, showing gradual corrosion of the molybdenum coating of the individual  $\text{PuO}_2$  particles from which they were made. This corrosion caused accelerating release of plutonium to the water, accompanied by crumbling and cracking of the disk surfaces. Disk PMC-142 manufactured at LASL, was immersed for 548 days, and disk PMT-113, manufactured at Mound Research Corporation (MRC) from  $\text{PuO}_2$  enriched in  $^{16}\text{O}$ , was immersed for 417 days.

The average plutonium release rate from PMC-142, during 548 days, was  $2.3 \mu\text{Ci}/\text{m}^2$  of initial surface per second (Table XI). However, during the final month of immersion, the rate was  $7.4 \mu\text{Ci}/\text{m}^2\text{-s}$ , illustrative of the rate increase with time. The release rate from PMT-113 over 417 days, averaged  $7.0 \mu\text{Ci}/\text{m}^2$  of initial surface per second (Table XI). During the last several months of immersion, however, the rate was 11.6 to  $17.4 \mu\text{Ci}/\text{m}^2\text{-s}$ . Figure 6 illustrates the plutonium found in the water as a function of time, in terms of microcuries per square millimetre of initial nominal surface which was  $5600 \text{ mm}^2$  for each disk.

Metallography of the disks, after their removal from the aquaria, showed extensive reaction between the seawater and the molybdenum metal network, accompanied by swelling in the reaction zone and loosening of plutonia particles. The reaction layer approximated about 10% of the thickness of PMC-142 and about 30% of the thickness of PMT-113.

The particle size distribution of 19 g of particles recovered from PMC-142, or 14% of the original 138-g disk, was 88% larger than  $177 \mu\text{m}$  and 98% larger than  $45 \mu\text{m}$ . The size distribution was typical of the uncoated plutonium oxide particles used in making the disks. This unchanged size distribution is consistent with the fact that even the larger amount of plutonium found in the seawater, from PMT-113, was only 1% of the total plutonium weight, and with the fact that seawater corrosion caused no detectable particle shrinkage.

2. *In Fresh Water.* We measured the plutonium released during 326 days from a PMC disk (PM-148-T) that was immersed in 75 liters of fresh water at 10°C. This was a production-grade, 29-W disk from MRC. The release rate was linear for the first 190 days, with a slope of  $15.6 \mu\text{Ci}/\text{m}^2\text{-s}$  (Table XI). From that time on, the release rate gradually decreased (Fig. 7). The disk edges began to disintegrate about

TABLE X

RESIDENCE TIME OF PLUTONIUM IN SIMULATED SEAWATER

Seawater Batch	Half-Life	
	ks	h
1	144	40
1	133	37
2	144	40

TABLE XI

## PLUTONIUM RELEASE RATES FROM PMC IN WATER

Sample	Power (W)	Wt (g)	Dimensions (mm)		Days Immersed	Water		Average Release Rate ( $\mu\text{Ci}/\text{m}^2\text{-s}$ )
			Height	Diam				
PMC-142	50	138	5.5	54.4	548	sea	10°C	2.3
PMT-113	50	135	5.5	54.4	417	sea	10°C	7.0
PM-148-T	29	74	3.7	54.4	326	fresh	10°C	15.6

100 days after immersion. This is the earliest disintegration observed for any disk, and it should be compared with 190 days for disk PMT-113 tested in seawater at 10°C for 417 days. As did PMC disks tested in seawater, this disk showed a preferential release of molybdenum compared to plutonium, which indicates that corrosion of the molybdenum coating of individual pressed plutonium particles led to its disintegration. It is surprising that an accelerated plutonium release was not observed. Despite the final decrease, the average release rate is the highest observed for a PMC disk. These data indicate that freshwater corrosion of PMC disks proceeds more rapidly than saltwater corrosion and produces an average release rate slightly greater than  $12 \mu\text{Ci}/\text{m}^2\text{-s}$ .

## E. PPO Dissolution or Release Rates.

These tests are to compare release rates from 2.5- and 25-W PPO pellets in both fresh water and seawater. Because of the remote chance that a heat source may drop into a warm tidal pool, seawater tests at 37°C are included. Six experiments are under way, three with 2.5-W pellets and three with 25-W pellets.

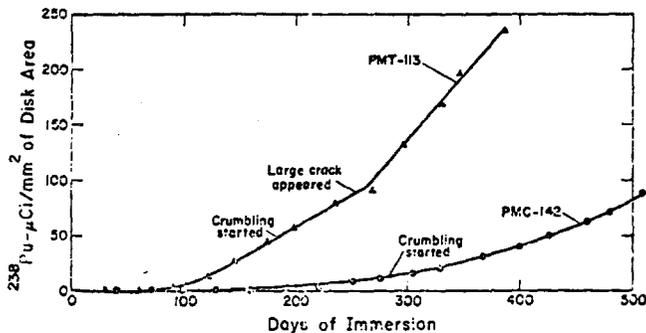


Fig. 6.

Plutonium release from PMC disks in simulated seawater.

1. *In Seawater.* The plutonium release rate from the 2.5-W pellet HPZ-3 (Table XII) has remained at  $20 \text{ nCi}/\text{m}^2\text{-s}$  for the last three months, following its earlier drop from a maximum of  $69 \text{ nCi}/\text{m}^2\text{-s}$  rate observed nine months ago. During the first 400 days of immersion, its average release rate was fairly linear at 54 to  $75 \text{ nCi}/\text{m}^2\text{-s}$ , different from the continually accelerating rates from PMC disks. Since then, the rate has decreased slowly and appears now to have leveled off. Despite the lengthy immersion, the pellet has not deteriorated visibly pointing to the superior stability of PPO compared to PMC.

The plutonium release rate from the 2.5-W pellet HPZ-60-3, immersed in 37°C water typical of tropical near-shore shallows, has averaged  $2.9 \text{ nCi}/\text{m}^2\text{-s}$  for 544 days, practically unchanged from last quarter's average of  $3.2 \text{ nCi}/\text{m}^2\text{-s}$ . This is the second lowest rate from any  $^{238}\text{Pu}$  fuel tested thus

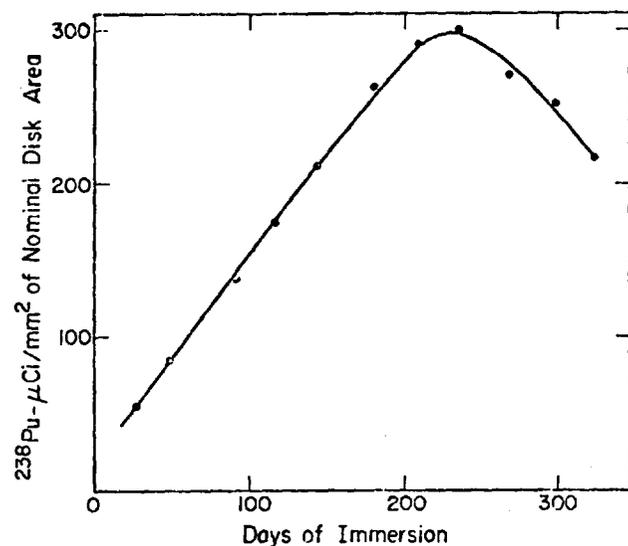


Fig. 7.

Plutonium release from a PMC disk in fresh water.

TABLE XII  
PLUTONIUM RELEASE RATES FROM PPO IN WATER

Sample	Power (W)	Wt (g)	Dimensions (mm)		Days Immersed	Water	Average Release Rate (nCi/m <sup>2</sup> -s)
			Height	Diam			
HPZ-3	2.5	6	4	14	1115	sea 10°C	20
HPZ-60-3	2.5	6	4	14	544	sea 37°C	2.9
HPZ-60-2	2.5	6	4	14	544	fresh 10°C	155
HPZ-59-2	25.	63	19	20	337	sea 37°C	1.0
HPZ-59-4	25.	63	19	20	337	sea 10°C	15
HPZ-111-1	25.	63	19	20	243	fresh 10°C	200

far. A possible explanation may be accelerated plutonium deposition on underwater surfaces as a result of faster chemical reactions at this warm temperature. Because release rates are based on plutonium found dissolved or suspended in the water, rapid deposition can reduce the apparent release rate. At the end of this experiment, we will determine the total plutonium deposited in the tank by suitable dissolution procedures. Another explanation is that the warm water causes rapid precipitation of gelatinous plutonium hydroxide on the pellet surface, forming a protective coating that retards further release of plutonium.

The two 25-W PPO pellets (Table XII) are HPZ-59-2 at 37°C and HPZ-59-4 at 10°C. After 337 days, the release rate is 15 nCi/m<sup>2</sup>-s for the pellet at 10°C, unchanged from the previous quarter's rate. This is the same order of magnitude as the 20 nCi/m<sup>2</sup>-s release rate of the 2.5-W pellet HPZ-3 at 10°C. On the other hand, the amount of plutonium in the water containing the 25-W pellet at 37°C is very low, only 2.5 µg. This corresponds to a release rate of 1.0 nCi/m<sup>2</sup>-s, unchanged from last quarter, the lowest observed for any heat source in the program, and the same order of magnitude as the 2.8 nCi/m<sup>2</sup>-s rate observed for the 2.5-W pellet in warm seawater described above. There seems little doubt at the present time that plutonium is released much more slowly into warm seawater than it is into cold seawater.

**2. In Fresh Water.** Plutonium release from the 2.5-W pellet HPZ-60-2 to fresh water at 10°C has averaged 155 nCi/m<sup>2</sup>-s for 544 days (Table XII). This is approximately eight times higher than the 15 to 20-nCi/m<sup>2</sup>-s rates typical of the PPO pellets in 10°C seawater.

The release rate from the 25-W pellet HPZ-111-1 has averaged 200 nCi/m<sup>2</sup>-s for 243 days, which is the highest value of the three 25-W pellets. It is clear

(see Table XII) that the highest release rates are found in fresh water and the lowest in 37°C seawater. There is no significant difference that can be related to the difference in power level between the 25-W and the 2.5-W pellets.

**3. In Ocean Immersion Tests.** Two PPO pellets, designated HPZ-19, were placed 23 m deep in the ocean off San Clemente Island in March 1973, for long-term exposure. The two pellets are right circular cylinders, 12.5 mm in diameter by 12.5 mm high, each containing 14.7 g of PuO<sub>2</sub>. They were placed on sea bottom debris inside protective chambers that permit water circulation but keep out animals larger than one centimeter. The pellets have been visually inspected at 3-month intervals, then reimplanted. After 1 yr, they began to be encrusted with fine sand-like grains. Where the pellet edges are still visible, no deterioration can be seen, in contrast to the crumbling of PMC pellets exposed in the ocean. Plans are being made to remove these pellets for shipment to LASL in December, where a detailed examination will be made of them and their encrustations.

#### F. Clad Sphere in Simulated Seawater

The plutonium release from a 101-W fuel sphere assembly (FSA), MHFT-13, was measured during immersion for 375 days. Before immersion in the test aquarium, the FSA was cooled in a beaker of seawater at room temperature to eliminate the hazard of handling a hot object outside a glove box. During its immersion in 20°C seawater, we found essentially no plutonium (less than 10 ng) in the water. The FSA gradually became a spotty brown, probably because of deposition of iron or manganese hydroxides, but no gross defects were visible. However, detailed metallography after the FSA was removed from the water, revealed cladding defects

that we believe were caused by seawater that entered the helium release vents when the sphere was first submerged. The defects appeared to be ruptures adjacent to the external closure weld. The inside of the cladding showed corrosive attack along grain boundaries, sometimes penetrating to 30% of the wall thickness, presumably caused by the seawater, but metallography of typical specimens showed no evidence of sodium chloride. The plutonia sphere showed no sign of corrosion. Probably, sudden immersion of the hot FSA caused water penetration through the vents in the cladding and the water and the salt residue, together with the high temperature and intense alpha and gamma irradiation caused chemical attack and disintegration of the iridium cladding from within.

## VI. BEHAVIOR OF CAPSULE MATERIALS IN AQUATIC ENVIRONMENTS

(George M. Matlack, Gilbert B. Nelson, and James H. Patterson)

Heat source capsule materials were immersed in simulated seawater at 23° for 1 to 3 yr, then examined for corrosion of the surfaces and of boundaries between dissimilar metals. The materials tested were molybdenum, T-111 alloy, Pt-20Rh, and Ta-10W. Molybdenum sheet, after immersion for 1 yr showed no corrosion other than deposition of crystals containing elements present in seawater and a slight increase of the molybdenum concentration in the water. Couples formed of T-111, Pt-20Rh, and Ta-10W showed no gross corrosion after 3 yr of immersion, and none of the elements was found in the water. There were very thin layers of a dark amorphous substance at the contact boundaries, and in all instances these layers were composed chiefly of manganese, also present in the seawater. These capsule construction materials seem to remain uncorroded for up to 3 yr of immersion in seawater.

## VII. BEHAVIOR OF (Zr,U) FUEL IN SIMULATED SEAWATER

(George M. Matlack)

Two irradiated, enriched uranium SNAP fuel samples, each a 6-mm-thick section of ZrH-10 U (93% enriched <sup>235</sup>U), cut from a full-size fuel rod,

were immersed for over 2 yr in simulated seawater. One sample from a Hastelloy-N clad fuel rod was immersed for 20 months, and a similar sample, except that it was from an unclad rod, was immersed for 25 months. Neither underwent any visible change in the luster of its cut surface; fine burrs and saw marks were unchanged. The radioactivity in the water became twice normal background within a week after sample immersion and did not increase thereafter. The activity was mainly <sup>137</sup>Cs, with a minor fraction of <sup>60</sup>Co activity from the clad sample. The excellent stability of this fuel in seawater was also confirmed by ocean exposure tests conducted at San Clemente Island by the Naval Undersea Center.

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