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PLUTONIUM-238 RELEASE IN SIMULATED NATURAL ENVIRONMENTS*

by

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ABSTRACT

Radioisotope thermoelectric generators (RTG) are designed with a great factor of safety to withstand all aspects of space missions including orbital reentry and earth impact and to provide containment until the fuel material is safely recovered. Several space missions have shown that the present designs are very good from a safety standpoint, but more data about the ^{238}Pu isotopic fuel is continually being sought to improve the safe use of the RTG's. As part of this larger program, LASL is studying the effects of various environmental conditions on fuel by exposing $^{238}PuO_2$ RTG fuel component samples to simulated weather conditions in environmental test chambers. The samples were placed on the surfaces of soils in deep trays, and were subjected to diurnal humidity and temperature cycling to simulate summer and winter conditions in humid temperature climates. A spray system was used to simulate rain, with 32-mm rains occuring once a week.

The fragments from an impact test of a sphere of sintered plutonium dioxide, 80% enriched in ^{238}Pu, were used in two experiments. The larger fragments, 224 g of pieces greater than 6 mm in diameter, were placed on humus soil. The finer fraction, 28 g of material with diameters between 0.01 and 6 mm was also placed on humus soil in a separate chamber. The condensate from the chamber dehumidifiers (a measure of airborne particulates), the rain water

that percolated through the soil, and core samples of the soil were analyzed for ^{238}Pu. In the large-particle experiment the plutonium release rate to air increased in four months from about 0.04 μCi per month to a constant value of about 4 μCi per month. In contrast, the initial rate of about 0.8 μCi per month for the fine-particle experiment decreased to approximately 0.4 μCi per month. The thermal shock when the cold rain water struck the large pieces, which have surface temperatures above 250°C, caused spallation of very fine particles. The fact that condensates collected after a rain contained more plutonium than other condensates confirmed this explanation. Determination of the plutonium in particulate samples collected from the air in the chamber during a rain sequence on the larger pieces showed a great increase in the average air concentration over the prerain concentration during the first five minutes of rain, in agreement with the spallation mechanism suggested. Within an hour after the end of the rain, the concentration had returned to the prerain value. Size studies of the plutonium oxide particles in soil core samples indicated that there was comminution of of the finer material also.

INTRODUCTION

A radioisotope thermoelectric generator (RTG) produces electric power by means of a thermopile whose hot junctions are heated by the decay energy of a radioactive isotope. This type of power source is light and compact, has no moving parts, and is capable of supplying a continuous voltage for several years. Because of these qualities, RTG's are used in many space missions to provide electric power for instruments and data transmission. Also, in five of the Apollo manned landings on the moon, the scientific instrument packages that were deployed for postmission measurements used RTG's for power.

In nearly all of the space applications to date plutonium 80% enriched in ^{238}Pu has been used to supply the heat for the generators. The container for the heat source is designed with a great factor of safety to withstand both orbital reentry and earth impact, so that the material will be safely contained until it is recovered. The existing designs have proved more than adequate from a safety standpoint, although the Isotope Power System Branch of the Division of Space Nuclear Systems of the AEC continually seeks to obtain more information about the heat sources in order to improve their safe use. As part of this large safety program, LASL is studying the interaction of ^{238}Pu fuel material with seawater, fresh water, and marine organisms in aquatic environments and with air, soil, and rain water in terrestrial environments to supply data to be used in designing even safer heat sources.

Several chemical forms of ^{238}Pu have been used to fuel the RTG's. The use of plutonium metal and plutonium dioxide microspheres had been phased out before the present experiments were begun. The form that is being used in current RTG's is a plutonia-molybdenum cermet (PMC), while various pressed shapes of pure plutonium dioxide (PPO) are being studies for future use. Several aquatic experiments have been carried out with PMC, but all of the terrestrial experiments to date have been with PPO fuel materials.

ENVIRONMENTAL TEST CHAMBERS

Terrestrial experiments were carried out in environmental test chambers, each of which had a working space of 1.8 m^3. Temperature and humidity in this space could be controlled manually or in diurnal cycles by means of cams. Rain inside the chamber was simulated by a manually operated spray system. Two sets of cams, corresponding to summer and winter weather in a humid temperate climate were used in alternate 6-month periods in the present experiments. The temperature range for the summer diurnal cycle was 20 to 40°C, with a relative humidity range of 85 to 97%. The ranges for the winter cycle were 0 to 17°C and 60 to 100% r.h. The experiments began with a summer period, and were in their second summer at the time of writing. There was a 3-cm rain once per week.

EXPERIMENTS

Each chamber contained a tray of soil 0.9 m square and 0.3 m deep. The soil in the try was supported by a grill covered with a thin perforated plate to allow water to drain through. The bottom of the tray tapered to an opening connected by a pipe to the outside of the chamber so that this water could be collected. The soil used in these experiments was a loam, a partial analysis of which is shown in Table 1. The fragments of a sphere of PPO that had been shattered in an impact test were used in these experiments. There were 224 g of pieces larger than 6 mm in diameter which were placed together in the center of the tray of soil in one of the environmental test chambers. A finer fraction, 28 g of PPO material with diameters between 10 µm and 6 mm, was similarly placed in another chamber.

The water condensed by the refrigeration-type dehumidifiers of the air conditioning system was collected for plutonium analysis as a measure of the airborne plutonium in the chambers. This analysis was carried out whenever the 19-ℓ condensate bottles became full, one to three times per week for each chamber. The rain water that percolated through the soil to the bottom of the tray was also collected for plutonium analysis. At about 4-month intervals, vertical core samples of the soil in the chambers were obtained, and sectioned for plutonium analysis at various depths.

An experiment was carried out to determine directly the airborne plutonium concentrations in the chamber containing the large pieces during a rain sequence. Air was sampled at a constant rate of 0.9 ℓ/s from a point downwind from the plutonium fuel in the chamber. This air was filtered to remove plutonium oxide particles and returned to the chamber. The filters were changed at intervals to obtain the concentration of plutonium in the air before the rain and at various time periods during and after the rain.

RESULTS

The initial rate of collection of plutonium from the air by the dehumidifier condensates in the chamber containing the large peices was very small, about 0.04 μCi per month. This increased till within 6 months a rather constant value of 4 μCi per month was reached. Condensates collected over a period in which a rain occurred generally had a greater rate of collection of plutonium than those that did not include a rain. The explanation for this behavior seems to be that material spalled from the hot pieces of PPO because of thermal shock when the cold rain water first hit them. The surfaces of the pieces have been found by infrared photography to have temperatures between 250° and 300°C. The spallation phenomenon has been observed in nature[1] when some kinds of rock, heated by the sun, are hit by a sudden shower. This mechanism for the airborne plutonium observed over the PPO pieces seems to be confirmed by the striking results of the experiment in which the air concentration was measured during the rain sequence. These results are listed in Table 2. The average concentration for the first 5 min of the rain was 10^4 times the pre-rain concentration. During the first 5 min the rain cooled the fuel material below the boiling point of water, as evidenced by the wetting of the surfaces of the pieces. The concentration in the air then dropped continuously until it reached the pre-rain concentration about 1 h after the end of the rain. The principal cause for the rapid decrease in the concentration is not certain at this time. Some of the plutonium may have been washed out of the air by the rain, but this cannot be the whole reason because the decrease continued after the rain had stopped. Part of the plutonium was removed by the dehumidifier as shown by the plutonium measured in the condensate. Some of the plutonium may also have been removed by gravitational settling of the particles. A possible indication of this was seen in the counting experience with the filters. The results in Table 2 were obtained by counting the filters with a 2-π gas proportional counter. Some of the filters were subsequently dissolved and a more accurate analysis was obtained by liquid scintillation counting. The ratios of the disintegration rates, as determined by proportional counter and liquid scintillation methods, for filters 2, 3, 9 and 10 were 1.02, 0.81, 0.52 and 0.64, respectively. This may indicate that most of the initial activity was in the form of comparatively large particles that were caught at the surface of the filter, and were therefore counted efficiently by the proportional counter. Later, the large particles had settled out and the smaller particles that remained penetrated deeper into the filter and were therefore less efficiently counted.

The first rain water that percolated through the soil after the large pieces were placed in the chamber contained 0.1 μCi of plutonium. This very rapid breakthrough of the plutonium indicated that some of the spallate was in the form of very small particles or a colloid. Plutonium in solution would not be stable at this pH (about 8), and, if present, would be held in the soil by some ion exchange type mechanism.

The amount of plutonium found in the rain water that percolated through the soil in the chamber containing the large pieces was strongly influenced by the temperature and humidity. The first six weekly rains in this chamber came during a period of manual operation before the summer cams were prepared. Each one simulated a rainfall of 25 mm and produced about 6 ℓ of percolate solution (out of 21 ℓ) containing an average of 3 μCi of plutonium. When the summer cams were installed, the rain had to be increased to 32 mm (27 ℓ) as the 25 mm rain merely replaced the water that had evaporated from the soil between rains at the high temperatures. The 32-mm rain produced about 6 ℓ of percolate solution containing 0.7 μCi of plutonium on the average. The first six rains after the winter cams were installed produced an average of 15 μCi of plutonium in 11 ℓ of percolate solution. For the rest of the winter the average plutonium content of the percolate solution was 9 μCi. The return to summer cams also signalled a return to percolate solution volumes and plutonium concentrations similar to those of the previous summer. It seems that under the higher summer temperatures the soil dried out more between rains, so that the soil saturation point was reached later in the rain than it did in the winter. Because of this lower flow of water in summer, fewer of the 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 few rains.

In an autoradiographic analysis[2] of a portion of one of the rain water percolate solutions taken during winter from the large-piece experiment, plutonium oxide particles with diameters of 0.05 to 0.8 μm, with a count median diameter (CMD) of 0.095 μm, were found. These particles accounted for only about 1 ppm of the total plutonium in the sample which indicates that nearly all the plutonium that is carried through the soil by water is in the form of very small particles, less than 0.05 μm in diameter.

A different pattern of interaction with the simulated environment was seen with the finer fraction. The 0.8 µCi of plutonium found in the dehumidifier condensates during the first month dropped to half that value in the next month and has remained about the same since then. There did seem to be some increase in the plutonium collection rate in the condensate during a rain, but the effect was less than for the larger pieces. Most of the particles in this sample were too small to have temperatures above ambient, so spallation was negligible.

The average plutonium content of the rain water percolate solutions for the chamber containing the finer fraction was 0.2 µCi. There seems to be very little seasonal effect on the plutonium content of the percolate solutions in this experiment.

Eight soil cores have been analyzed for these two chambers. These include two sets of two cores each, taken four months apart in each of the two chambers. Each of the cores was taken 25 cm from the central pile of fuel material, with cores 1 and 2 in each chamber collected at the end of the first summer and cores 3 and 4 during the winter. Each core was divided into 6 to 10 vertical sections, each of which was analyzed separately by liquid scintillation counting after complete dissolution with HNO_3-HF-$HClO_4$. Tables 3 and 4 show the results of the analyses and the relative coring positions for the soil cores from the two chambers. Analyses listed as zeros indicate that less than 0.02 ng of plutonium was found in each of these sections. The hypens are shown for cores which were divided into fewer than 10 sections and indicate that analyses for these depths were included in the adjacent values.

In both of the chambers, core 1 contained little or no plutonium, which is an artifact caused by the operation of the chambers. When the sample port of the chamber was opened, a gate valve to the building exhaust was opened also to ensure an inflow of air through the sample port to prevent plutonium contamination of the room. When this gate valve, directly above coring position 1, was opened, water that had condensed above the gate valve poured onto the soil below and evidently washed all the very small particles of plutonium out of the soil. Some of the water was also carried to coring position 3 and the plutonium concentrations of core 3 in each chamber was also low. Cores 2 and 4 in both chambers were not affected by the downpours. Core 4 in both experiments was collected when the flow of water during a rain was greater and therefore contained little plutonium except in the top sections. Cores 1-2 and 3-2 were collected under dryer conditions and contained some plutonium in each section with very high concentrations in the bottom sections. This very high concentration in the bottom section of each core 2 may have resulted from contamination at the time of the coring as this is the only exposed part of the core. However, the coincidence of the two cores collected under the same conditions showing high concentrations at the bottom may indicate that these concentrations were real. The holes in the perforated plate account for only 22% of the bottom surface. Possibly, under low flow conditions, some of the plutonium dioxide particles were trapped by the bottom plate. An alternative possibility is that the particles may have clung to the bottom surface of the soil when the flow rate was low.

Samples from the two top sections of cores 3 and 4 from the chamber containing the fine particles and core 4 for the chamber containing the large pieces were analyzed for particle size and agglomeration with the soil.[3] No particles large enough to form stars in a photographic emulsion were found in either section of core 3. Stars were found in the top sections of cores 1-4 and 3-4. The range of particle sizes found was slightly smaller than that of the particles in the rain water that percolated through the soil, with 90% of the particles having equivalent diameters between 0.04 and 0.2 µm. The lower limit may not be significant here as it is close to the limit of detection with the procedure used. The particles in the cores from the soil holding the fine-particles were slightly larger than those in the soil holding the larger pieces, with a Count Median Diameter of 0.072 µm compared with 0.056 µm, but they are still very much smaller than the 10 µm minimum size of the parent particles. This agrees with observations by ourselves and others that $^{238}PuO_2$ is much less stable than $^{239}PuO_2$.[4-7] This instability seems to be associated with the intense radiation field of the alpha activity of the isotope. Radiation damage to the oxide crystal lattic and reaction with radiolysis products in soil and water may have a part in this degredation.

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

CONCLUSIONS

The RTG fuel components are packaged so that they would remain intact on reentry until they were recovered. In the very unlikely event that RTG fuel material which included large peices of PPO were exposed on soil to the natural environment, fine airborne material would be observed, expecially at the beginning of a rain. Plutonium oxide particles would be carried off by surface water during a rain and would also percolate through the soil with the water. In the further refinement of the packaging of the RTG fuel for space applications, more consideration should be given to the confinement of the larger pieces than the fine material. Fortunately, most packages that will contain the fine material will better contain the large peices.

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Table 1

COMPOSITION OF LOAM SOIL[a]

Sand, %	49.5
Silt, %	37.6
Clay, %	12.9
Organic C, %	0.6
C as $CaCO_3$	trace
H_2O, 15 bar press., %	7.6
pH	8.0
Ca, meq/100 g	16.3
Mg, meq/100 g	1.9
Na, meq/100 g	0.5
K, meq/100 g	1.5
Cation Ex. Cap., meq/100 g	13.6
Clay Fraction:	4 - Mica 3 - Montmorillonite 3 - Kaolinite

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[a] Soil analysis provided by the U. S. Soil Conservation Service Laboratory, Riverside, California

Table 2

AIR CONCENTRATIONS DURING A RAIN SEQUENCE IN AN ENVIRONMENTAL CHAMBER CONTAINING LARGE PIECES OF PLUTONIUM DIOXIDE

Filter No.	Collection Time, min	Pu Concentration, pCi/m^3	Remarks
1	24	3	Before rain
2	5	3×10^4	First 5 min of rain
3	5	6×10^3	
4	10	4×10^3	
5	10	3×10^3	
6	15	9×10^2	
7	15	8×10^2	Last 15 min of rain
8	50	2×10^2	
9	180	3	
10	860	3	

Table 3

SOIL CORES FROM CHAMBER CONTAINING LARGE FUEL PIECES

Depth, cm	Pu Concentration, ppb Core 1	Core 2	Core 3	Core 4
0-3	0	3.3	18.	816
3-6	0	0.3	-	-
6-9	4.5	2.6	0	0
9-13	0	14.4	0.2	-
13-16	0	7.5	-	.1
16-19	0	5.5	0	0
19-23	0	0.3	0	-
23-26	0	0.1	0	0
26-28	0	2.7	-	0.4
28-30	0	195.	-	0.1

4

Core Locations: 1 Pu 2

3

Table 4

SOIL CORES FROM CHAMBER CONTAINING FUEL FINES

Depth, cm	Pu Concentration, ppb Core 1	Core 2	Core 3	Core 4
0-3	0	3600	4.8	334
3-5	0	2.7	-	-
5-7	0	4.3	-	3.2
7-10	0	0.4	-	-
10-13	0	1.6	<0.3	-
13-16	0	4.0	-	29.
16-20	0	138.	0	0.6
20-23	0	4.0	0	0
23-26	0	0.4	0	0
26-30	0	26,000	0	2.9

4

Core Locations: 1 Pu 2

3