LA-8362

UC-23

Issued: September 1980

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

Interim Summary

James H. Patterson
Frederick J. Steinkruger
George M. Matlack

DISCLAIMER

This document is prepared as an interim report submitted by an agency of the United States Government to the United States Government. It does not constitute any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

INTERACTIONS OF $^{238}\text{PuO}_2$ HEAT SOURCES WITH TERRESTRIAL AND AQUATIC ENVIRONMENTS

Interim Summary

by

James H. Patterson, Frederick J. Steinkruger,
and George M. Matlack

ABSTRACT

Observations and some conclusions made of the interactions of $^{238}\text{PuO}_2$ heat sources with terrestrial and aquatic environments may be used in predicting heat source behavior in the event of contact of these heat sources with land or ocean and in assessing the risk to the environment. These studies indicate that plutonium transport from the heat sources is mostly a physical process involving the movement of extremely fine particles rather than the chemical migration of plutonium ions.

I. INTRODUCTION

The National Aeronautics and Space Administration (NASA) uses radioisotope thermoelectric generators (RTGs) to provide auxiliary power in its space vehicles. An RTG is essentially a thermopile with a radioisotope heat source at its hot junctions. In the space program, plutonium that is 80% enriched in ^{238}Pu is the radioisotope heat source most used. Several chemical forms of plutonium have been used for heat sources. In the environmental studies reported here, $^{238}\text{PuO}_2$ microspheres and powder, plutonia molybdenum cermet (PMC), and pressed plutonium oxide (PPO) were used. The last is in the form of massive pieces made by hot-pressing $^{238}\text{PuO}_2$ powder. GROG-process PPO is pressed from a mixture containing about 40% inert, high-fired $^{238}\text{PuO}_2$ (GROG) to improve some of the physical properties of the PPO.

The type of generator most studied is the multi-hundred watt (MHW) system. The heat source for this RTG is made up of 24 fueled sphere assemblies (FSAs).

An FSA contains a 250-g PPO sphere surrounded by an iridium postimpact containment shell (PICS). This post-impact sphere assembly (PISA) is in turn surrounded by a graphite impact shell (GIS) of graphitized yarn.

An aborted space launching, an unscheduled satellite re-entry to the atmosphere, or an out-of-control return of a space mission could release an RTG heat source to the terrestrial environment. The heat sources are packaged so that they remain intact after any such incident.

The interactions of terrestrial and aquatic environments with $^{238}\text{PuO}_2$ heat sources are being studied so that the behavior of the heat sources can be predicted in the event of contact with the land or ocean. Evaluation of data from these studies is needed to assess the risk to the environment.

In this study, the terrestrial environments are simulated with 1.6-m³ environmental test chambers that permit the use of various kinds of soils and control of temperature, humidity, and rainfall. The aquatic environments are simulated with 75-l aquaria that provide control of temperature, aeration, and circulation for both

seawater and fresh water. Aquatic experiments that require total recovery of the released plutonium are performed in smaller, sealed, glass chambers.

This report presents a summary of the observations and the conclusions drawn from this 10-yr study. Many experiments required several years to complete because the nature of the subject matter prohibits the use of an accelerated time scale. Although it is tempting to explain some of the effects of the interactions on the basis of the well-known laboratory chemistry of plutonium, such explanations must be approached with caution because the chemistry of plutonium in the environment is not nearly as well known. Also, the plutonium transport observed in the test systems is not chemical in its nature, but rather physical, and therefore chemical explanations are not valid. Many effects are best explained by postulating that the production of extremely small particles of $^{238}\text{PuO}_2$ is the most significant release mechanism.

II. $^{238}\text{PuO}_2$ IN TERRESTRIAL ENVIRONMENTS

Plutonium dioxide has a very low solubility in water and in neutral solutions. However, the crystal structure is heavily damaged by the recoil of the residual nucleus from alpha emission. When there is alpha emission near the surface of the material, the recoiled nucleus may escape. According to Fleischer and Raabe,¹ the escaping nucleus does not carry the surrounding material with it if the interface is with a gas or in a vacuum, but it leaves some fragmented material that is loosened and released in the presence of a liquid. Our experience agrees with this observation in general, although we found that a small amount of dry material may be released to the air. Thus, the main mechanism of plutonium release in a terrestrial environment is wetting by rain or surface water. The release rate is proportional to the surface area of the material and the time of exposure since the last release by water.

A. Chunks

For plutonium dioxide pieces that are greater than ~6 mm in diameter, there is also another mechanism for its release on exposure to the environment. These chunks are thermally hotter than their surroundings, and thermal shock occurs when rain or surface water comes into contact with the hot, dry material. This causes spallation

and scattering of fine particles of the oxide into the air. The intensity of this effect is a function of the chunk size.

1. Humid Environments—General Release Rates.

The general plutonium release rate for chunks in a humid environment is 1 $\mu\text{Ci}/(\text{g}\cdot\text{day})$. Most of this quantity is washed from the chunks by rain, but some is airborne during the early part of the rain as a result of spallation. Much of the released plutonium remains on the surface, but some is trapped below the surface of the soil, and an appreciable amount is found in the water that drains through the soil after a rain.

2. Arid Environments—General Release Rates. The general release rate for chunks in an arid environment is also about 1 $\mu\text{Ci}/(\text{g}\cdot\text{day})$. This lack of dependence on climatic conditions would be expected if the release is proportional only to time and surface area.

3. Airborne Plutonium Production. The air concentration over chunks of $^{238}\text{PuO}_2$ between rains is $<10 \text{ pCi}/\text{m}^3$. When rain or surface water first strikes the hot pieces of $^{238}\text{PuO}_2$, the air concentration quickly increases by a factor of 10 000 because of thermal spallation of fine particles. Wetting the pieces cools them to below the boiling point of water, and the spallation then ceases. Within an hour, nearly all of the particles settle out, and the air concentration of plutonium activity drops to the prerin level. This behavior occurs in arid as well as humid climates. Thus, airborne plutonium is important only at the beginning of a rain.

4. Soil Agglomeration. Over 90% of the released plutonium collects on the soil surface and in the soil. The particles trapped in the soil are usually attached individually to soil particles, which stops their movement with the draining water. There does not seem to be a buildup of $^{238}\text{PuO}_2$ particles in the soil with time, but there are big differences in the amounts trapped in soil in different places, even at the same time, at the same distance from the source, and in the same type of soil. The vertical variation of soil concentrations at a given time is also very great. Microdifferences in such soil factors as particle size, void size, and water flow rates greatly affect the amount of plutonium in the soil. There seems to be no mechanical transport of $^{238}\text{PuO}_2$ particles through dry soil.

5. Plutonium Carried by Drainage. Rainwater percolating through soil carries nanocurie-per-liter concentrations of plutonium activity from the chunks of $^{238}\text{PuO}_2$. These fine particles of plutonium dioxide appear in the water that drains through the soil when the first rain occurs after the chunks are placed onto the surface of the soil. (Ionic plutonium would be expected to be retained in the soil by ion exchange.) The largest particles of $^{238}\text{PuO}_2$ in the subsurface water are $<1\text{ }\mu\text{m}$ in diameter, and most of them are $<50\text{ nm}$. The concentration of plutonium in the subsurface water is highest during the first winter season, but subsequently decreases to the level found during the summer rains. Also, the plutonium concentration is less in arid than in humid climates, possibly because small amounts of water cause the $^{238}\text{PuO}_2$ particles to adhere to soil grains, whereas larger amounts soften and weaken the bonds and promote movement. In addition, the force of fast-flowing water may tend to pull the plutonium particles away. The effect of the faster water flow is not great, however, because much larger amounts remain in the soil than are found in the subsurface water.

B. Fines

Because small particles have large surface-to-volume ratios and therefore dissipate their radiogenic heat rapidly, their surface temperatures are closer to ambient. For this reason, finely divided material does not show spallation, but a large surface-to-volume ratio does cause a high release rate from recoil radiation damage. Also, small particles are transportable by moving air, especially if they become agglomerated with lower density soil particles. In order of decreasing particle size, the effects of wind on them are called "creep," which is a rolling on the surface; "saltation," a flying-up from the surface and falling back; and "suspension," in which particles are airborne for a considerable length of time. The fine particles also are moved about by surface water and settle out in sediment.

1. Humid Environments—General Release Rates. Because of the large surface-to-volume ratios, the release rates in terms of $\text{Ci}/(\text{m}^2 \cdot \text{s})$ for finely divided $^{238}\text{PuO}_2$ are significantly greater than for chunks in humid environments. The rate depends on the particle size. Experimentally determined release rates per surface area in our experiments corresponded with those predicted by

Fleischer,² who reported that the radius of a $^{238}\text{PuO}_2$ particle diminishes by $\sim 0.1\text{ }\mu\text{m}/\text{yr}$.

2. Arid Environments—General Release Rates. The general release rates for the fine material in arid environments are greater than for chunks, although the differences are not as great as in humid environments.

3. Airborne Plutonium. Because no thermal spallation occurs with the smaller particles, the level of airborne plutonium remains low at the beginning of a rain in contrast with the effect seen with the chunks. During a rain, the airborne plutonium that is agglomerated with dust particles is reduced by about a factor of 10 and remains low for at least a day after the rain. As long as the soil is wet, the particles are not subject to suspension.

A barrier that prevents horizontal water flow on the surface does not prevent movement of plutonium from fine particles on a dry soil surface. This indicates that the plutonium is moved on dry soil by either suspension or saltation.

4. Soil Agglomeration. Plutonium-238 dioxide particles larger than $1\text{ }\mu\text{m}$ in diameter may agglomerate with soil particles, which are moved on the surface by air and water. Only submicrometer particles (formed from larger particles by radiation damage) are transported below the surface by percolating water. The variability of the plutonium concentration in soil is the same whether the material is in the form of finely divided $^{238}\text{PuO}_2$ or in chunks. Here, again, more than 90% of the released material was in or on the soil.

5. Drainage. The subsurface aqueous plutonium is in low concentration initially, but increases as the fine particles of plutonium dioxide break up. This rate of increase is greater for winter conditions in humid climates, but the opposite effect is seen in arid climates.

C. Clad Sources—General Release Rates

If the fueled sphere assembly (FSA) is intact and at least partially above ground after re-entry and impact, the $^{238}\text{PuO}_2$ is kept from the environment for at least 3 yr. The side of the graphite impact shell (GIS) in contact with the soil gradually disintegrates by oxidation, so that it is breached in about a year. However, there is no evident corrosion of the iridium in the postimpact

containment shell (PICS). A hard crust of baked soil adheres to the FSA, or to the postimpact sphere assembly (PISA) if the GIS has been lost. However, if the PISA is buried in dry soil the situation is very different because the temperature is much higher, a fused soil shell forms around the PISA, the iridium is eroded by oxidation, and the $^{238}\text{PuO}_2$ is exposed to the environment within a few months.³

D. Soil Column Experiments

Both particulate and ionic plutonium sources were added to the surface of soil columns. More than 99% of the particulate $^{238}\text{PuO}_2$ remained around the top. In the first 5 days, more than 90% of the eluted plutonium was collected. These results are consistent with the results of the terrestrial chamber experiments.

When ionic plutonium was added to the soil column, more than 99% was retained by the soil. Subsequent elution with a bicarbonate solution reduced this amount to 80%. The reduction is the result of the formation of a strong plutonium carbonate complex.

E. Release Mechanisms—Summary

The predominant mechanism of plutonium release to the environment from oxide particles is recoil damage. Some of the airborne plutonium may come directly from the parent piece at the time of recoil as occurs with ^{239}Pu in a vacuum⁴ but not with ^{238}Pu in a vacuum.¹ The plutonium is readily removed mechanically when the sample is handled. However, most of the loose material adheres to the piece until it is released by water. The fine particles are carried by water on the surface until they deposit in sediments or are transported below the surface by percolating ground water. Because most of the larger particles agglomerate with soil particles, they are fixed in place if they are below the surface, or they are moved further on the surface by air or water.

Large $^{238}\text{PuO}_2$ pieces with temperatures above 100°C release material into the air by spallation when they are suddenly cooled with water. This may increase the airborne plutonium by as much as a factor of 10 000. Because these are high-density particles, they settle to the surface rapidly. The air reaches its pre-rain plutonium concentration within an hour after the spallation. Like the particles from recoil, the spallation particles on the

surface agglomerate with soil and are transported by water and air.

III. PLUTONIUM-238 IN AQUATIC EXPERIMENTS

The analyses of the results of the aquatic experiments are complicated by the lack of knowledge of the chemical/physical form of the plutonium in the aqueous phase. Plutonium may be injected into the aqueous phase as ions, or as $^{238}\text{PuO}_2$ particles, or a combination of both forms.

A. Chemical/Physical Form of Plutonium

In the fresh water experiments, the pH varied from 5.5 at 10°C to 6.2 at 35°C. In the simulated seawater experiments, the pH varied from 8.0 at 10°C to 8.2 at 35°C. At these relatively high pH values, any Pu^{4+} released in ionic form will hydrolyze through several stages to form the very insoluble $\text{Pu}(\text{OH})_4$. After the first hydrolysis step, polymerization is also possible. The first polymerization reaction yields the "ol" form of plutonium, a two-dimensional polymer involving OH linkages that is converted to the "oxo" form when it loses water. The oxo form, a linear polymer with oxygen atom linkages, may be converted to $^{238}\text{PuO}_2$ as it ages. Although the ol and oxo forms are colloidal, precipitation occurs during conversion of the oxo form to $^{238}\text{PuO}_2$, which is crystalline.

Alpha decay near the surface of the fuel may result in the loosening of some $^{238}\text{PuO}_2$ (Ref. 1). This material is subsequently released when a solvent is applied to the surface of the source. Because the fuels are submerged in their respective aquatic environments, the solvent release process may be continuous.

Because the concentration of plutonium in the aqueous phase is very low, polymerization may be improbable. Therefore, it is suggested that plutonium in the aqueous phase is present as particles and as hydroxide.

B. Plutonium Form—Experiments

Three experiments indicated the presence of particulate plutonium. When a 30-g $^{238}\text{PuO}_2$ source was

sealed in a glass chamber (in 2.3 *l* of simulated seawater) for 101 days, 10.9 μg of plutonium was found in the aqueous phase. After removal of the seawater, the internal surfaces were gently rinsed, and the rinse was combined with the seawater. Analysis indicated a total of 14.5 μg of plutonium in the aqueous phase. This 33% increase in total plutonium is attributed to material that had settled out of the aqueous phase. Acid leaching of the interior of the chamber reclaimed an additional 0.6 μg .

In a hot, simulated seawater experiment, a sample taken when the aquarium circulation devices were in-operative contained only one-third of the expected plutonium concentration. This result is attributed to the settling out of $^{238}\text{PuO}_2$ particles.

There was 28 mg of plutonium found in the sand on the bottom of a tidal experiment aquarium. When these samples were taken, the aqueous phase contained 2.5 $\mu\text{g/l}$. We can conclude again that plutonium is present in particulate form and settles out of the aqueous phase.

In a hot seawater experiment, a failed heating system caused a 10°C decrease in system temperature. At this lower temperature, the plutonium concentration in the aqueous phase increased six-fold, possibly because of the reduced agglomeration of particulate plutonium and the reduced settling.

C. Apparent Release Rates

1. Fresh Water and Simulated Seawater. The highest *apparent** release rate, as measured by the plutonium in the aqueous phase, was observed in the cold fresh water environment in both aquarium and glass chamber experiments. The lowest apparent release rate observed was for hot seawater in both types of experiments.

2. Source Size Effect. There is no consistent trend in apparent release rate differences based on size of the plutonium source. Instead, there is some indirect indication that source history may be important.

*We use the term *apparent* to describe the rate determined by measuring the plutonium found in the water. Because some of the plutonium released from the fuel may settle out on underwater surfaces, the apparent release rate is likely to be less than the actual release rate.

D. Tidal Experiment

A GROG source, subjected to twice-a-day cycling in and out of simulated seawater, began fracturing after 100 days. After 400 days, the source was in seven pieces. Even after the elevator system failed, leaving the source permanently submerged, the GROG source continued to fracture. After 850 days, the source was in more than 30 pieces of $^{238}\text{PuO}_2$. As more surface area was exposed, there was an increase in the amount of plutonium in the aqueous phase and, hence, in the apparent release rate.

Only GROG-type material has been tested in the tidal experiment, but other types of fuel containing the same microcracking as GROG should disintegrate in a similar manner.

E. 1M Perchloric Acid Experiments

Three size distributions of $^{238}\text{PuO}_2$ particles were immersed in 1M perchloric acid solutions. Even though the individual size distributions were not characterized well, the highest release rate per unit weight of source was observed in the experiments using the finest material. This result is attributed to the greater proportional surface area of the smaller particles.

F. Fine Material in Distilled Water and Normal Saline Solution

The initial release rates of powdered $^{238}\text{PuO}_2$ in distilled water and in normal saline solution were high and varied from sample to sample. Release of the material that had been loosened on the surface by recoil caused the initial burst, and the release was variable because of different exposure histories of the samples. After this initial burst, plutonium was released to distilled water at a fairly constant rate, in tens of $\text{nCi}/(\text{m}^2 \text{ s})$, which agrees with the rate of recoil loss predicted by Fleischer.² Larger amounts of $^{238}\text{PuO}_2$ in normal saline solution had similar release rates, but the concentration in the water dropped sharply later, possibly indicating a salting out of the particles in suspension.

G. Uptake by Sea Cucumbers

Preliminary experiments with sea cucumbers indicate that such bottom feeders will pick up microcurie quantities of plutonium in the presence of massive pieces of $^{238}\text{PuO}_2$ on the sea bottom. This observation is in agreement with the findings of others that bottom-feeding animals assimilate plutonium from fallout.⁵ Further experiments will show whether the plutonium is picked up and concentrated in the skin, remains in the food in the gut, or is absorbed from the food and spread throughout the body.

H. Ocean Experiments

Several different designs of $^{238}\text{PuO}_2$ sources have been submerged in 20 m of seawater off the coast of San Clemente Island, California. These included microspheres, plutonium-molybdenum cermet (PMC), bare PPO, and clad PPO. Other than encrustation, only PMC displayed signs of deterioration (some microspheres were not recovered and their fate is unknown).

A recent Lawrence Livermore Laboratory (LLL) survey of the 3.8-km² experimental area revealed the presence of 0.28 mCi of $^{238}\text{PuO}_2$, 0.18 mCi above the 0.10 mCi expected from fallout.⁶ This excess is approximately equal to the missing microspheres if they were dissolved. Therefore, if any material was released from the PMC and PPO experiments, it has been dispersed.

I. Simulated Deep Sea Experiment

Plutonium-238 was released in only negligible amounts (approximately background levels) from a 100-W GIS assembly when it was immersed in simulated seawater at 69 MPa (10 000 psi), a pressure which corresponds to a 6000-m ocean depth, or 3333 fathoms. If the pressure on the GIS is released (to simulate a recovery from the ocean), contaminated water from inside the iridium containment shell is ejected through the vent into the environment. We found that 4 μCi of ^{238}Pu was released in this manner after 300 days of immersion; 99.6% of this released material was trapped by the graphite yarn of the GIS. Based on the area of the fuel sphere, the overall release rate was 10 nCi/(m²·s), approximately the same as the rate observed for bare

PPO in cold seawater. The containment shell and GIS seem to serve as effective barriers to plutonium release from a heat source assembly in the deep ocean.

IV. CONCLUSIONS

Plutonium is released from $^{238}\text{PuO}_2$ heat sources at low but significant rates when the sources are exposed to simulated terrestrial and aquatic environments. A significant release condition on land results from cold rain falling on the thermally hot fuel, causing the formation of airborne plutonium dioxide particles created by spallation. Between rains, the airborne plutonium concentration may fall by a factor of 10 000 or more. Minute amounts of $^{238}\text{PuO}_2$ are loosened from the fuel surface continually by recoil from alpha particle emission, and this loosened material is washed away by immersion in water. This is the major mode for plutonium release from fuel particles to the environment. Release rates vary between 2 and 400 nCi/(m²·s) when large fuel pieces are immersed in various aquatic environments, with warm seawater showing the slowest rate and cold fresh water showing the fastest rate. Plutonium-contaminated rainwater percolating through soil loses most of its plutonium by adsorption by soil particles. It appears that the principal mode of release is through submicron particle production and not by chemical dissolution.

REFERENCES

1. R. L. Fleischer and O. G. Raabe, "Recoiling Alpha-Emitting Nuclei, Mechanism for Uranium-Series Disequilibrium," *Geochimica et Cosmochimica Acta* **42**, 973-8 (1978).
2. R. L. Fleischer, "On the 'Dissolution' of Respirable PuO_2 Particles," *Health Physics* **29**, 69-73 (1975).
3. E. M. Cramer, "Performance of Multihundred-Watt Fueled Sphere Assemblies in the Safety Sequential Test Program," Los Alamos Scientific Laboratory report LA-5916 (July 1975).
4. J. H. Patterson, E. J. Franzgrote, A. L. Turkevich, W. A. Anderson, T. E. Economou, H. E. Griffin, S. L. Grotch, and K. P. Sowinski, "Alpha Scattering

- Experiment on Surveyor 7: Comparison with Surveyors 5 and 6," J. Geophys. Res. **74**, 6120-48 (1969).
5. V. E. Noshkin, "Ecological Aspects of Plutonium Dissemination in Aquatic Environments," Health Phys. **22**, 537-549 (1972).
6. V. E. Noshkin, J. L. Brunk, T. A. Jokela, and K. M. Wong, "²³⁸Pu Concentrations in the Marine Environment at San Clemente Island," University of California Lawrence Livermore Laboratory report UCRL-83964 (1980).