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Leaching Behavior of Particulate Plutonium Oxide

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LEACHING BEHAVIOR OF PARTICULATE PLUTONIUM OXIDE

by

S. T. Kosiewicz and R. C. Heaton

ABSTRACT

Different size cuts of $^{238}PuO_2$ particles were mixed with deionized water at two temperatures in a shaker bath. The gross plutonium concentration in the water was measured, as well as that portion of the plutonium retained on a 0.1-µm pore filter. The concentration of the plutonium released was primarily a function of the surface area of the particles. The release rate of plutonium into the water for the size cut with particles having diameters between 30 and 20 µm was 3 ng/m^2/s; this rate is within the range observed in past experiments involving aquatic environments. The amount of material retained by the 0.1-µm filters decreased with increasing time, suggesting that size reduction or removal processes occurred.

INTRODUCTION

Plutonium oxide heat sources are used in the space program to supply power for spacecraft and satellites on long-term missions throughout the solar system. These sources and their containments are designed with great care to minimize the possibility of plutonium being released into the environment. Nevertheless, should a spacecraft containing one of these heat sources reenter the earth's atmosphere, or should it suffer a launch abort, a significant amount of plutonium could be released to the environment.

For many years the Los Alamos National Laboratory has been testing containment systems and studying the environmental behavior of plutonium oxide in order to generate data for risk assessments and safety analyses. An understanding of the mobilization and transport mechanisms for environmental plutonium not only will lead to more accurate risk assessments but also will substantially reduce the time and effort required to do such analyses. Accordingly, we have initiated a series of experiments to identify the major factors controlling plutonium release from plutonium oxide sources into water.[1] This report describes an experiment in which plutonium dioxide particles of different sizes were placed in contact with deionized water at two temperatures to observe, over 4 weeks, the plutonium release.

OBJECTIVE

The purpose of this experiment was to identify the characteristics that most strongly affect the rates of plutonium release from plutonium oxide particles into water and to determine the functional relationships among the independent and dependent variables. This experiment was designed to determine whether plutonium release depends primarily on the mass of the source, the surface area of the source, or both. A secondary objective was to gain experience with particle leaching techniques before designing more sophisticated efforts.

EXPERIMENTAL WORK

Source Material

The plutonium dioxide source materials were fragments obtained from several $^{238}PuO_2$ pellets that had been used for impact tests. The isotopic compositions of the pellets varied slightly, but they were nominally 83% ^{238}Pu with a specific activity of 14.2 Ci/g. Table I shows the isotopic composition of one pellet. Four particle size ranges were used in these experiments. The particles in the largest size range passed through a sieve with a 420-µm-diam opening but were retained on a 125-µm-diam sieve. This sieve cut was designated as −420/+125 µm.

Using the same designation system, we determined the three other size ranges: −125/+74, −74/+44, and −30/+20 µm. We did not use particles smaller than 20-µm diam because we wanted to avoid working with particles that approached the respirable range of approximately 5 µm or less. Even though the different particle size cuts were obtained by sieving, the samples were again wet-sieved with an ultrasonic bath less than 24 h before the leaching experiments began. This step removed extremely fine particles from the samples. For each individual leaching experiment, 0.5 g of plutonium dioxide of a particular sieve cut was weighed and transferred (in a closed glovebox) to a 125-mL Erlenmeyer flask containing 50.00 mL of water that had been purified by a Millipore ion-exchange system.

For the sieve cuts with diameters of −125/+74, −74/+44, and −30/+20 µm, dry controls of the plutonium oxide were prepared to determine if the medium affected size reduction. For the controls, 0.5 g of dry PuO_2 of the appropriate sieve cut was weighed into a bottle and retained in the glovebox. When the experiments with the deionized water were completed, both the wet samples and the dry controls were resieved.

We calculated surface areas, assuming spherical particles whose diameters corresponded to the midpoint of the sieve cut range. A density of 11 g/cm^3 was taken for PuO_2.

Equipment

The Erlenmeyer flasks containing the plutonium dioxide particles and deionized water were placed in an orbital water bath shaker (Laboratory Line Instruments, Inc., Model 3535). The shaker was adjusted to 1 to 2 rpm; at this speed, the water was swirled, but with no apparent tumbling of the plutonium dioxide particles. Because these experiments lasted extended periods, a sheet of polyethylene film was placed over the water bath to reduce evaporation. To eliminate evaporation of deionized water from the Erlenmeyer flasks, the flasks were closed with hollow plastic stoppers with small holes to allow radiolytically generated gases to escape. A second but larger hollow plastic stopper was inverted and then placed over the first to prevent condensate from accumulating in the first stopper.

TABLE I. Isotopic Composition of Pellet Number 18272-438

Isotope	Abundance (%)
^{238}Pu	83.29
^{239}Pu	14.09
^{240}Pu	2.06
^{241}Pu	0.4
^{242}Pu	0.16

Two experiments were performed, one at 20°C (ambient room temperature) and the other at 37°C (used in other aquatic experiments).[2,3] At the higher temperature, we experienced occasional difficulties with a safety cutoff on the shaker that turned off the heater in the bath. Thus the temperature control was less than adequate in the 37°C experiment.

Samples

To obtain samples for pH determination, filtration, and scintillation counting, the Erlenmeyer flasks were removed from the shaker bath and allowed to stand for several minutes so large particles could settle out of the zone of solution to be sampled. Sample aliquots (10 to 100 µL) were then withdrawn from the top of the liquid layer with an Eppendorf pipette. The initial samples were done in duplicate to ascertain sample-to-sample variation. This duplication was discontinued after several samplings because the reproducibility was acceptable.

At the beginning of the experiment, samples were removed from the flasks more frequently than at the end. For example, in the 20°C experiment, the first two samples were taken 1 day apart, whereas the last two were taken 1 week apart; we had expected any observed changes to be more rapid at the beginning of the experiment. After 4 weeks, when sampling was discontinued and the PuO_2 samples were resieved, the experiment was completed.

Samples for scintillation counting to determine the gross plutonium concentration in the water were transferred directly into scintillation vials. Scintillation cocktail was added to the vials, which then were counted in a Packard scintillation counter. The samples for filtration were filtered by vacuum through 0.1-µm Nuclepore polycarbonate filters. The filters were dissolved in Protosol tissue solubilizer, and the amount of plutonium retained on them was determined by scintillation counting.

The pH of the solutions was measured with short-range pH papers. This method was preferred over glass electrodes because the pH values of each flask could be determined with less sample and without the risk of cross-contaminating the flasks.

RESULTS AND DISCUSSION

Data for the lower temperature (20°C) experiments are summarized in Tables II to V. The plutonium concentrations observed in the leachates are plotted versus time in Fig. 1. One of the most obvious features of these results is that the smallest particles release significantly higher concentrations of plutonium into the deionized water. However, the three other size ranges released similar amounts of plutonium. Because the mass of plutonium oxide used in each sample was the same, it might appear at first that the sample mass determines the overall release rate. However, the data for the smallest size cut are inconsistent with this concept. Qualitatively, the data trends are consistent with a surface area dependence, with the smaller particles yielding increasingly higher release rates. Quantitatively, the results are not quite so clear. The plutonium concentrations normalized to the surface area are plotted in Fig. 2. Although the curves for the largest three particle size cuts diverge more in Fig. 2 than they do in Fig. 1, the normalization has the effect of placing the curve for the smallest size cut squarely among the other three. Thus the plutonium release per unit area is a more consistent value over the entire data set than is the unnormalized release rate.

For all four sieve cuts, the plutonium concentration in the water increases approximately linearly with time over the experiment. This linear concentration curve implies a constant release rate over the experiment equal to the slope of the curve. The slopes of the curves in Fig. 2, derived by least squares fits of the data, range from 1.5 to 4.8 ng/m²/s. These fall within the limits of uncertainty resulting from the surface area calculations. Thus the normalized curves are probably not significantly different from each other. In fact, the curve for

TABLE II. Analytical Data for −30/+20-μm-Diameter Particles at 20°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	(μCi/mL/m²)[a]	(μCi/mL)	(% of Total)
0	100	—	6.5	5.4×10^2	4.2	6.2
					3.7	57
1	100	4	12	1.0×10^3	1.5	13
					1.3	11
4	10	4	6	5.0×10^2	1.5	25
					1.6	26
9	10	4	18	1.5×10^3	5.4	30
15	10	4	20	1.7×10^3	2.7	14
23	10	4	31	2.6×10^3	14	45
28	10	4	27	2.2×10^3	5	18

[a] Surface area calculated to be 1.2×10^{-2}m².

TABLE III. Analytical Data for −74/+44-μm-Diameter Particles at 20°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	(μCi/mL/m²)[a]	(μCi/mL)	(% of Total)
0	100	—	2.3	4.5×10^2	0.7	30
1	100	4	3.0	5.9×10^2	1.9	63
					0.4	13
4	10	4	2.7	5.3×10^2	0.4	13
					4.2	>100
9	10	4	4.3	8.4×10^2	1.1	26
15	10	4	5.4	1.0×10^3	0.2	4
23	10	4	6.8	1.3×10^3	0.2	3
28	10	4	7.6	1.5×10^3	0.1	1

[a] Surface area calculated to be 5.1×10^{-3}m².

TABLE IV. Analytical Data for −125/+74-μm-Diameter Particles at 20°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	(μCi/mL/m^2)[a]	(μCi/mL)	(% of Total)
0	100	—	1.4	5.6×10^2	—	—
1	100	4	2.3	9.2×10^2	0.8	35
					0.5	22
4	10	4	2.4	9.6×10^2	0.4	17
					0.3	13
9	10	4	3.9	1.6×10^3	0.3	9
15	10	4	4.9	2.0×10^3	0.2	4
23	10	4	5.8	2.3×10^3	0.1	2
28	10	4	6.8	2.7×10^3	0.1	2

[a] Surface area calculated to be $2.5 \times 10^{-3} m^2$.

TABLE V. Analytical Data for −420/+125-μm-Diameter Particles at 20°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	(μCi/mL/m^2)[a]	(μCi/mL)	(% of Total)
0	100	—	1.3	1.1×10^3	—	—
1	100	4	1.8	1.5×10^3	1.9	>100
					1.6	89
4	10	4	2.0	1.7×10^3	0.7	35
					0.9	45
9	10	4	2.8	2.3×10^3	0.4	14
15	10	4	3.7	3.1×10^3	0.2	5
23	10	4	4.5	3.8×10^3	3.6	80
28	10	4	5.0	4.2×10^3	0.4	8

[a] Surface area calculated to be $1.2 \times 10^{-3} m^2$.

the smallest diameter particles (−30/+20-μm cut) falls in the middle of the set of curves even though these particles have the highest plutonium release rate. Therefore, we suggest that the plutonium release rates depend primarily on the surface areas of the particles.

A representative release rate for this set of curves, that of the −30/+20-μm sieve cut, is approximately 3 ng/m^2/s. This rate compares favorably with the 3.9 ng/m^2/s observed for warm fresh water (37°C) in a previous aquarium experiment,[3] but it is less than the 10 to 30 ng/m^2/s observed for cold (10°C) fresh water in the same experiment. In a related experiment that used large (40-g) sources in a vigorously stirred environment, release rates of 17 and 95 ng/m^2/s were observed for warm and cold fresh water respectively.[2] In another case that examined the "solubility" of plutonium oxide particulates, the release rates were slightly higher than in the current study (16.8 to 45.0 ng/m^2/s in fresh water and 3.3 to 13.1 ng/m^2/s in normal saline).[4] Studies of the apparent release rate in 1M perchloric acid yielded values between 0.73 and 9.5 ng/m^2/s, which span the range observed in the present experiment.[5] Thus, the release rates observed in the present experiment fall within the range of values derived from other studies, although the current values are at the lower end of this range. The fact that the release rates for these experiments agree as well as they do when normalized to surface area is an additional argument supporting the hypothesis that surface area is a primary factor controlling the release rate.

Evidence in the literature indicates that plutonium oxide particles, particularly those highly enriched in ^{238}Pu, undergo spontaneous fragmentation to generate significant quantities of much smaller particles.[6] To determine the importance of this effect, the plutonium oxide samples were resieved immediately after the leaching measurements. Over the 4 weeks of the experiment, approximately 1 to 4% of the sample mass size

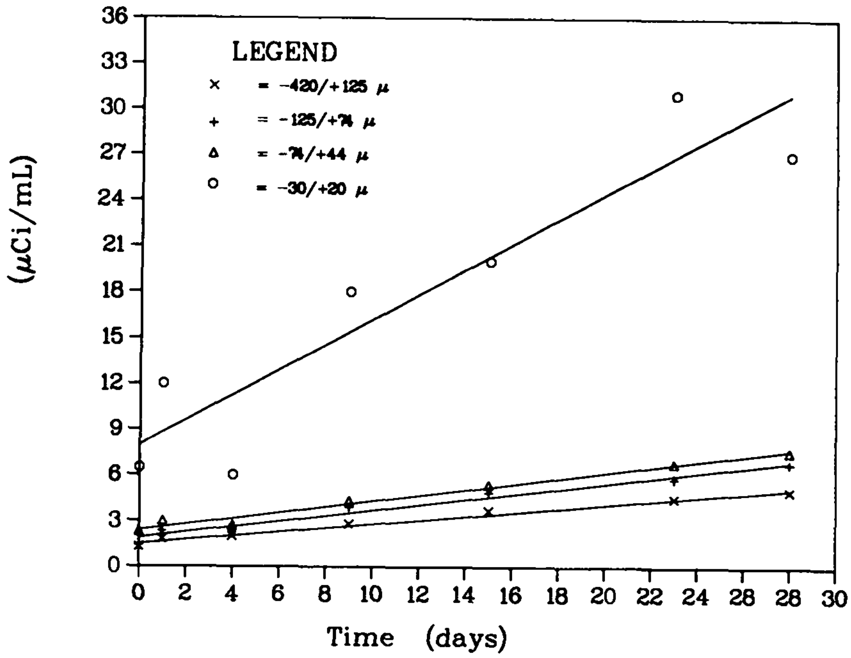

Fig. 1. Aqueous plutonium concentration versus time for leaching experiments at 20°C.

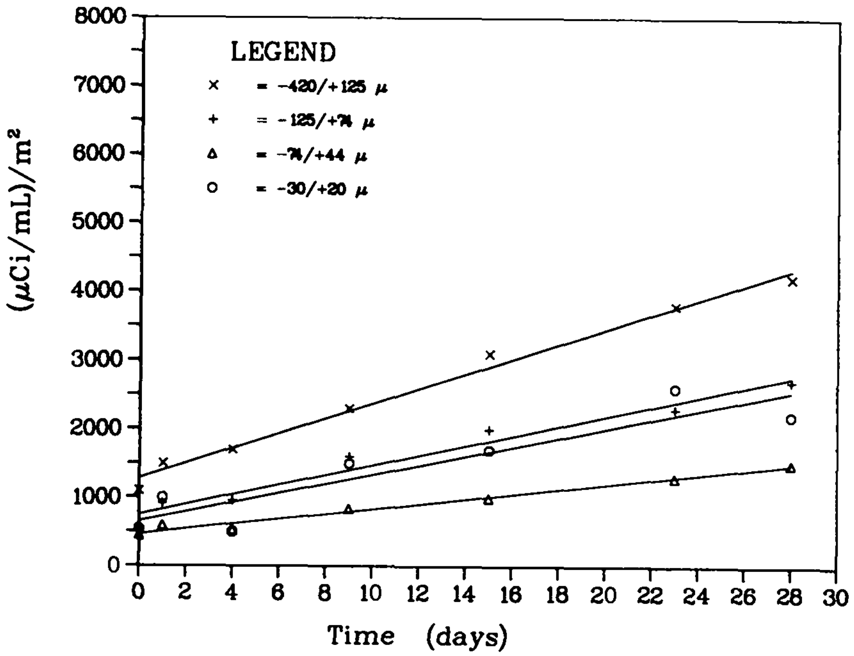

Fig. 2. Aqueous plutonium concentration normalized to the source surface area versus time for leaching experiments at 20°C.

decreased enough to allow it to pass through the sieve that had previously retained it. There was no apparent correlation between this percentage and the initial particle size range. In addition, we found no apparent difference in size reduction between the control samples that were stored in a dry condition and the wet plutonium dioxide particles that were resieved. This finding suggests that the observed size reduction is independent of the medium and that any effect of the leaching medium on the rate of spontaneous fragmentation of the sample particles should not be of concern in interpreting the results of this experiment.

The filtration data in Tables II to V suggest that for each particle size range there is a decrease in the percentage of plutonium particles retained on the 0.1-μm filters with increasing time. This decreased percentage results from both an increase in the total amount of plutonium in the liquid phase and also a decrease in the amount of plutonium retained on the filtration membranes. The increasing plutonium concentration in the liquid phase is easily explained by the continued release of plutonium from the plutonium oxide sample into the water. However, to account for the decreasing filter retention, the existing particles in the bulk liquid phase either must undergo some size degradation process so they pass through the filter, or they must otherwise be removed from the liquid phase so they are no longer part of the sample aliquot. Which of these two processes is responsible for the decreasing filter retention cannot be determined from this experiment. A considerable degree of scatter occurs among the filtration data points, which may derive from nonstatistical sampling of plutonium oxide particles, both in the gross sample and on the filters, and can lead to large variations in the sample count. This problem may be avoided in the future by examining the filtrate directly rather than by calculating the difference between the gross plutonium count and the corresponding filter residue.

Data for the 37°C experiments are tabulated in Tables VI to IX. In obtaining these data, we experienced some sampling difficulties related to the higher temperature of the experiment. When the flasks were removed from the shaker bath and allowed to stand, they cooled considerably. During this cooling process, convection currents may have formed that could have circulated plutonium oxide particles into the sampling zone in a nonreproducible way. Such an occurrence would cause anomalously high and irreproducible concentration measurements. Indeed, Fig. 3 shows more scatter among these data than among those in Fig. 2 (20°C). Furthermore, the apparently anomalous points are high. An additional complication occurred because a temperature controller in the temperature bath malfunctioned. Because of these factors, we do not have a great deal of confidence in the results of this portion of the experiment. The amounts of plutonium observed in the water for the 37°C experiment were similar to those in the 20°C experiment. Although these results do not seem to corroborate previous experiments, which revealed higher release rates in colder media,[2,3] we do not attach much significance to this observation for the current experiment.

CONCLUSIONS

The release rate of plutonium from plutonium dioxide particles into deionized water was substantially higher for the smallest diameter particles when similar masses of materials were used. After the release rates were normalized to approximate surface areas, they were the same within experimental uncertainties, clearly indicating that the plutonium release rates may depend primarily on the surface area of the solid source. The amount of material retained by the 0.1-μm filters decreased with time. Therefore, a size reduction process

TABLE VI. Analytical Data for −30/+20-μm Diameter Particles at 37°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	$(\mu Ci/mL/m^2)$[a]	(μCi/mL)	(% of Total)
0	10	4	5.4	4.5×10^2	2.8	52
1	10	4	8.1	6.8×10^2	3.0	37
2	10	4	8.1	6.8×10^2	2.5	30
3	10	4	9.4	7.8×10^2	2.8	30
6	10	4	12	1.0×10^3	2.7	23
9	10	4	13	1.1×10^3	4.2	34
17	10	4	38	3.2×10^3	6.8	18
23	10	—	20	1.7×10^3	4.3	22
31	10	4	24	2.0×10^3	3.2	13

[a] Surface area calculated to be $1.2 \times 10^{-2} m^2$.

TABLE VII. Analytical Data for −74/+44-μm-Diameter Particles at 37°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	$(\mu Ci/mL/m^2)$[a]	(μCi/mL)	(% of Total)
0	10	4	2.7	5.3×10^2	1.1	41
1	10	4	4.0	7.8×10^2	1.7	42
2	10	4	5.0	10×10^2	1.3	26
3	10	4	4.5	8.8×10^2	1.6	35
6	10	4	5.4	1.0×10^3	1.3	24
9	10	4	2.6	5.1×10^2	0.2	9
17	10	4	2.9	5.7×10^2	0.4	13
23	10	4	9.4	1.8×10^3	1.2	12
31	10	4	1.1	2.2×10^3	1.2	11

[a] Surface area calculated to be $5.1 \times 10^{-3} m^2$.

TABLE VIII. Analytical Data for −125/+74-μm-Diameter Particles at 37°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	$(\mu Ci/mL/m^2)$[a]	(μCi/mL)	(% of Total)
0	10	4	1.5	6.0×10^2	0.3	20
1	10	4	2.5	1.0×10^3	0.6	23
2	10	4	2.8	1.1×10^3	0.4	13
3	10	4	2.8	1.1×10^3	0.9	38
6	10	4	2.3	9.2×10^2	0.4	19
9	10	4	2.5	1.0×10^3	0.2	7
17	10	4	2.6	1.0×10^3	0.3	12
23	10	—	3.1	1.2×10^3	0.3	11
31	10	4	2.1	8.4×10^2	0.3	15

[a] Surface area calculated to be $2.5 \times 10^{-3} m^2$.

TABLE IX. Analytical Data for −420/+125-μm-Diameter Particles at 37°C

Elapsed Time (Days)	Sample Size (μL)	Pu Concentration			Pu Retained on 0.1-μm Filter	
		pH	(μCi/mL)	$(\mu Ci/mL/m^2)$[a]	(μCi/mL)	(% of Total)
0	10	4	1.8	1.5×10^3	0.2	11
1	10	4	2.4	2.0×10^3	0.7	29
2	10	4	2.3	1.9×10^3	0.3	13
3	10	4	2.7	2.2×10^3	0.2	7
6	10	4	2.5	2.1×10^3	0.6	24
9	10	4	7.2	6.0×10^3	1.6	22
17	10	4	9.0	7.5×10^3	1.6	18
23	10	—	3.7	3.1×10^3	0.1	3
31	10	4	3.2	2.7×10^3	0.2	6

[a] Surface area calculated to be $1.2 \times 10^{-3} m^2$.

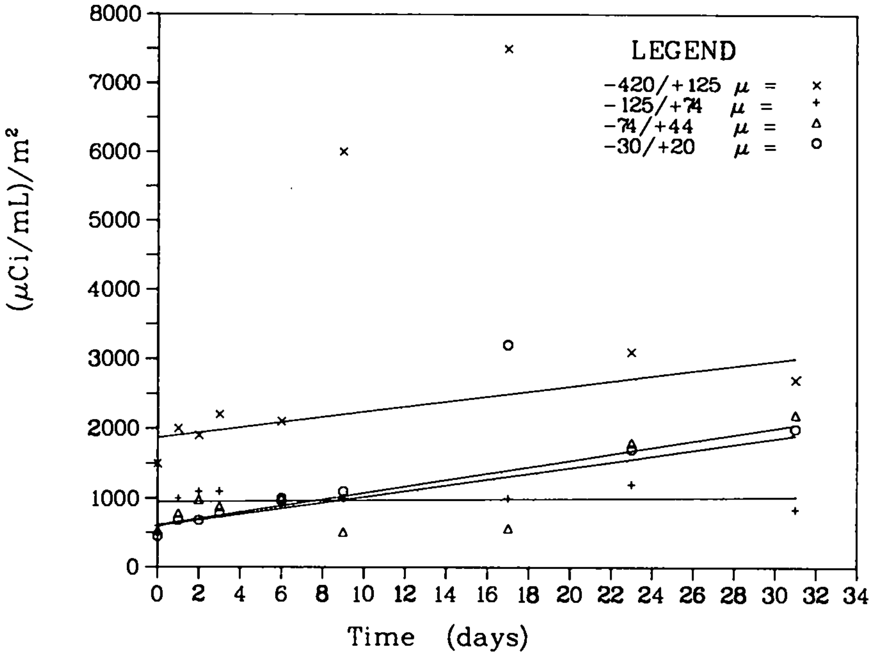

Fig. 3. Aqueous plutonium concentration normalized to the source surface area versus time for leaching experiments at 37°C.

occurred or filterable particles were being removed from the sampled layers of the mixing vessels. Although little or no difference was observed between release rates at 20°C and 37°C, we experienced complications in obtaining the measurements. This observation needs to be confirmed before we draw any definite conclusions concerning temperature effects.

FUTURE WORK

Ongoing experiments involving 2.3-g plutonium oxide sources in fresh water environments show distinct maxima in the plutonium concentrations between 6 to 10 weeks after introducing the sources into the water. This behavior occurred in past experiments as well.[3] Because the present experiment was too short to reveal this behavior, if it occurred, future experiments should be continued for 2 to 3 months. Better characterization of the released plutonium species, both in terms of filtration methods and oxidation-state determination, could yield information that may prove invaluable in elucidating release mechanisms.

The current experiment was carried out by using a constant sample mass with a varying surface area. A complete experimental design would require the converse experiment, one with constant surface area and varying mass. Such an experiment, conducted over a longer time with the improved characterization methods called for above, would complete the study of surface area and mass effects and also provide some fundamental data about release mechanisms.

The higher temperature experiments should be repeated with the sampling done at temperature to avoid the uncertainties caused by the hypothesized convection currents in the sample containers.

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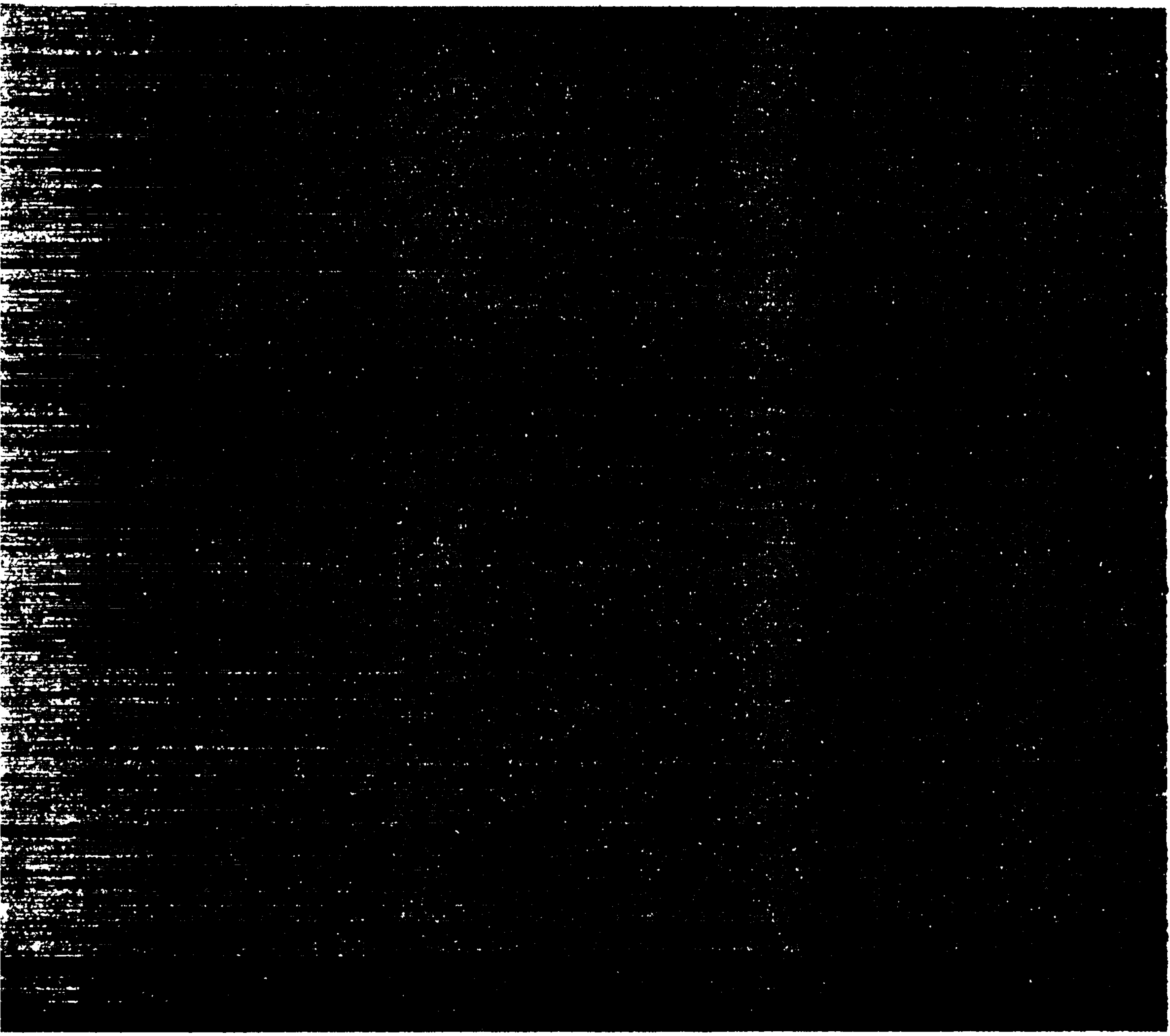

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