LA-UR-74-588

Conf-740406--7

TITLE: STUDIES OF THE APPARENT SOLUBILITY OF $^{238}PuO_2$ MICROSPHERES IN AN AQUATIC ENVIRONMENT AND THE UPTAKE OF PLUTONIUM FROM A SOIL MATRIX CONTAINING $^{238}PuO_2$

AUTHOR(S): W. H. Adams and E. B. Fowler

SUBMITTED TO: SECOND AEC ENVIRONMENTAL PROTECTION CONFERENCE
Albuquerque, New Mexico, April 16-19, 1974

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

orm No. 836
t. No. 2629
/73

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

fg

STUDIES OF THE APPARENT SOLUBILITY OF $^{238}PuO_2$ MICROSPHERES IN AN AQUATIC ENVIRONMENT AND THE UPTAKE OF PLUTONIUM FROM A SOIL MATRIX CONTAINING $^{238}PuO_2$

by

W. H. Adams and E. B. Fowler
Health Division
Los Alamos Scientific Laboratory
University of California
Los Alamos, New Mexico

ABSTRACT

The uptake of plutonium by lettuce and barley from soil spiked with $^{238}PuO_2$ microspheres is described. A four year study of the effect of simulated soil stresses on the concentration factors of plutonium ($\frac{\text{d/m/g of plant ash}}{\text{d/m/g of soil}}$) is presented.

The "apparent" solubility of $^{238}PuO_2$ microspheres in tap water is determined and the depositon of plutonium in fish, algae and snails in aquaria containing $^{238}PuO_2$ microspheres is reported.

These data may be used to assess the hazard associated with the loss of a Systems for Nuclear Auxiliary Power device.

INTRODUCTION

The use of $^{238}PuO_2$ microspheres in Systems for Nuclear Auxiliary Power (SNAP) devices prompted a study of the effect which accidental deposition of these microspheres on soil and plants might have upon the uptake and translocation of plutonium in plants. Later the study was expanded to

include the solubility of $^{238}PuO_2$ microspheres in water and the deposition of plutonium in fish.

I. SOILS SPIKED WITH $^{238}PuO_2$ MICROSPHERES

The experimental work was initiated to study both the translocation of plutonium in plants contaminated with $^{238}PuO_2$ microspheres and the plant uptake of plutonium from soils containing $^{238}PuO_2$ microspheres. However, the "in plant" translocation studies were terminated after a few days since the 100 μ diameter microspheres contained enough plutonium to burn the plant tissue.

Thompson[1] likewise found that $^{238}PuO_2$ microspheres burned holes in African violet leaves causing microspheres to drop through the leaf. Visible damage to the leaves was noticeable on the second or third day of exposure.

In the plant uptake studies, Los Alamos mountain meadow soil, which contained 5% organic matter and 0.24% nitrogen, was air dried and screened; the portion not passing through a 20 mesh screen was discarded. Twelve hundred grams of the sieved, air dried soil were spiked with 25.6 mg of $^{238}PuO_2$ microspheres and mixed in a large "V" shell blender for five hours. These microspheres were obtained from Mound Laboratories approximately July 1965 and are designated only as Batch #1 since no other more definitive notation was available. After placing 800 to 900 grams of unspiked soil in a plastic container 15 cm in diameter and 13 cm deep, two hundred grams of the spiked soil were added to the container, then the spiked soil was covered with another 800 to 900 grams

of unspiked soil. Six plastic pots were treated in this manner; three were planted to lettuce and three were planted first to oats and later to barley.

The miniature soil plots were then placed inside a lucite growth chamber 1.22 metres long, 0.91 metres high and 0.91 metres deep. The chamber was used as a precautionary measure to keep the microspheres contained and to keep the plants isolated from the other plants grown in the greenhouse. The lucite box was equipped with two 15 cm diameter portholes with movable covers. Two exhaust fans mounted to the box exhausted air through a filter into the greenhouse. The portholes were used as access holes so that plant watering and harvesting could be achieved. Clean surgeons gloves were used when watering or harvesting the plants. Whenever possible the plants were cut at such a height that successive cuttings could be obtained from a single planting.

After harvesting two lettuce crops and three oat crops, the soil plots were allowed to lie fallow before being replanted to lettuce and barley on the 474th day after the original soil was spiked. After harvesting an additional lettuce and barley crop the soil plots lay fallow for 55 days and then were placed in a plastic bag and allowed to remain outdoors for the next six months (March 21, 1967 to September 21, 1967). The plots were next planted to lettuce and barley and two crops were harvested.

The miniature soil plots were next frozen with dry ice and allowed to thaw at room temperature; this procedure was repeated ten times before the soil was again planted to lettuce and barley. Five crops were harvested beginning with the barley harvest on the 890th day after the soil was spiked. The plots then lay fallow for 80 days before being replanted. Two crops were harvested and another 186 days passed before the final planting was made on the 1 374th day after the soil was spiked. A final crop was harvested 70 days later, concluding a study initiated about four years earlier.

All of the plants grown in this study were ashed at 600°C to destroy the organic matter present in the samples. The plant ash, however, was leached with 8 M HNO_3 and the plutonium separated from the dissolved salts by an ion exchange technique. The plutonium was electrodeposited from an HCl - $(NH_4)_2C_2O_4$ solution and counted in an alpha scintillation counter.

A. Discussion

Although the $^{238}PuO_2$ microspheres placed in the soil were weathered and exposed to other stresses in the soil, very little plutonium was converted to a "soluble" form as shown by the limited uptake of plutonium by the plants (Table 1).

Three kg of fresh lettuce and about 0.9 kg of green barley, grown in soil contaminated with plutonium to the level used in these experiments, would contain the same amount of

TABLE 1

UPTAKE OF PLUTONIUM BY PLANTS FROM SOILS SPIKED WITH $^{238}PuO_2$

Crop	Days Time From Spike To Harvest	Plutonium d/m/g of Ash	C_p/C_s (1)
Lettuce	74	13	1.8×10^{-8}
Oats	74	72.7	1.0×10^{-7}
Lettuce	145	80.7	1.1×10^{-7}
Oats	145	82	1.2×10^{-7}
Oats	186	3.5	5.0×10^{-9}
Lettuce (2)	544	Less than control	
Barley (2)	544	9.5	1.3×10^{-8}
Lettuce (3)	811	25.6	3.6×10^{-8}
Barley (3)	811	7.1	1.0×10^{-8}
Lettuce	825	36.4	5.2×10^{-8}
Barley	825	1.6	2.3×10^{-9}
Barley (4)	890	1.5	2.1×10^{-9}
Lettuce	909	31.2	4.4×10^{-8}
Barley	909	5.7	8.1×10^{-9}
Lettuce	949	19.9	2.8×10^{-8}
Barley	949	9.2	1.3×10^{-8}
Lettuce	992	15.5	2.2×10^{-8}
Barley	992	25.2	3.6×10^{-8}
Lettuce	1 019	29.5	4.2×10^{-8}
Barley	1 019	50.6	7.2×10^{-8}
Lettuce (5)	1 148	169.9	2.4×10^{-7}
Barley (5)	1 148	50.8	7.2×10^{-8}
Lettuce	1 188	88.4	1.3×10^{-7}
Barley	1 188	84.4	1.2×10^{-7}
Lettuce (6)	1 444	143	2.0×10^{-7}
Barley	1 444	332	4.7×10^{-7}

	Lettuce	Barley	Oats
Av Conc. Factor All Crops	8.4×10^{-8}	7.4×10^{-8}	7.5×10^{-8}
	8.1×10^{-8}	7.3×10^{-8}	7.2×10^{-8}

(1) Concentration factor is d/m/g of plant ash ÷ d/m/g of soil.

(2) Soil lay fallow for approximately nine and one half months - replanted at about 474 days after soil spike.

(3) First harvest after six months weathering out of doors.

(4) First harvest after eleven freeze-thaw cycles.

(5) First harvest after soils lay fallow for 80 days.

(6) Final harvest of crops planted at 1 374 days after soils lay fallow for 186 days.

^{238}Pu as expressed by the maximum permissible concentration of plutonium per liter of drinking water for public use.[2] Such plutonium concentrations in lettuce and barley were calculated using the highest plutonium concentrations found in the analyses of the different crops (1 444 day barley, i.e. 322 d/m/g· 1 148 day lettuce, i.e. 170 d/m/g (Table 1) and the values of 2.1% and 4.0% ash for lettuce and barley respectively.

If 10 kg of $^{238}PuO_2$ microspheres were mixed uniformly with soil by plowing to a depth of 15 cm, then one acre of soil would be contaminated with the same concentration of ^{238}Pu as that used in these experiments. However, experience has shown that the high altitude loss of a SNAP device did not result in high level contamination of a relatively small area of soil but rather in an almost uniform distribution of $^{238}PuO_2$ as fallout upon the earth.[3] Such low levels of ^{238}Pu contamination would not result in measurable amounts of ^{238}Pu in plants as a result of plant uptake based on results obtained in the experiments described and summarized in Table 1.

II. PLUTONIUM IN AN AQUATIC ENVIRONMENT

A. Plutonium Incorporated in Fish

To determine the effect of $^{238}PuO_2$ microspheres on an aquatic environment in the event of accidental release of plutonium from SNAP devices, microspheres of the radionuclide were placed in aquaria containing goldfish; two separate studies were made, each with a different batch of $^{238}PuO_2$

microspheres. One study involved the use of microspheres from Batch #2* which had shown, in water "solubility" studies, a tendency to lose activity to the surrounding water. In the second study, microspheres from Batch #1* used in the soil plots described in Part I were used. The designation of Batch #1 and Batch #2 is made only to indicate two different preparations and that all $^{238}PuO_2$ microspheres are probably not alike and that differences in uptake and "solubility" can occur because of these differences.

In the study using Batch #2 microspheres, each of the three aquaria was spiked with one $^{238}PuO_2$ microsphere which was about 100 μ in diameter and was calculated to contain about 1.82×10^8 d/m total alpha activity. Each microsphere was placed beneath the sand filter support inside a 40 ml pyrex beaker which had been cut so that the side wall height was about 2 to 3 mm. The microsphere was thus easily retrievable and was still exposed to the circulating water currents caused by the air bubblers attached to the filter supports. The three aquaria contained six fish each; an additional six goldfish, which died before the aquaria were ready for stocking, were analyzed for plutonium and thus served as a plutonium concentration base line for fish not exposed to $^{238}PuO_2$. One fish from aquarium "one" died after the first three days, during which time it had accumulated

---

*No other designation could be determined for the two batches of microspheres.

nearly two hundred times more plutonium than found in the unexposed fish. A fish which died after six days exposure in aquarium "three" contained four hundred times more plutonium than the average unexposed fish (see 1st 6 fish and fish #8, Table 2).

Each fish thereafter from #9 through #15, whether it died of natural causes or was sacrificed, was analyzed for plutonium as a whole sample. The 16th, 17th, and 18th fish were dissected such that the gills, gut and contents, flesh, and bones could be analyzed separately for plutonium. In all instances the whole fish or the fish parts were dried at 110°C for about 12 hours, then ashed at 600°C. The ash was leached with 8 N HNO_3 and the plutonium determined by the anion exchange separation.

The water in the aquaria was assayed for plutonium periodically by removing a 1 000 ml aliquot which was then acidified with HNO_3 and evaporated to dryness; the residue was leached with 8 M HNO_3 and the resulting leach solution taken to dryness. The plutonium was converted to the tetravalent nitrate complex by the addition of concentrated HNO_3 and H_2O_2 after which the sample was taken to dryness on a steam bath. The residue was taken up with 8 M HNO_3 and the plutonium separated from the salts in solution by anion exchange techniques.

The water taken from the aquaria periodically for plutonium analysis was replaced with an equal volume of chlorine-free tap water. Evaporative losses which occurred during the

TABLE 2

^{238}Pu IN FISH AND FISH ORGANS
BATCH NO. 2 MICROSPHERES

Fish No.	Days Exposure to H_2O Contg. $^{238}PuO_2$	% Microspheres Activity Found in Whole Fish	d/m/g Ash	d/m/g of Ashed Organ			
			Total Fish	Gills	Gut and Contents	Flesh	Bones
1st 6	0	--	7.0	--	--	--	--
7	3	3.9×10^{-5}	1,435	--	--	--	--
8	6	1.3×10^{-4}	2,836	--	--	--	--
9	6	1.2×10^{-5}	521	--	--	--	--
10	7	6.8×10^{-6}	302	--	--	--	--
11	9	1.8×10^{-4}	14,935	--	--	--	--
12	10	3.4×10^{-5}	1,566	--	--	--	--
13	14	2.5×10^{-5}	1,561	--	--	--	--
14	15	3.8×10^{-5}	3,512	--	--	--	--
15	17	1.5×10^{-5}	611	--	--	--	--
16	31	2.6×10^{-5}	--	306	7,488	476	309
17	45	6.7×10^{-6}	--	443	39,800	239	138
18	48	2.3×10^{-5}	--	2,935	36,142	292	332

(continued on next page)

TABLE 2

(continued)

Fish No.	Days Exposure to H_2O Contg. $^{238}PuO_2$	% Microspheres Activity Found in Whole Fish	d/m/g Ash	d/m/g of Ashed Organ			
			Total Fish	Gills	Gut and Contents	Flesh	Bones
19	49	8.7×10^{-6}	--	246	3,000	376	153
20	104	1.4×10^{-5}	--	21,000	18,000	602	73
21	181	1.8×10^{-5}	--	94	2,818	994	304
22	183	2.0×10^{-4}	--	2,770	32,110	537	119
23	184	6.6×10^{-5}	--	6,750	52,630	320	462
24	185	2.7×10^{-6}	--	2,360	51,940	462	191

studies were compensated for by adding distilled water. At the conclusion of the experiment (six months), the entire liquid content of each aquarium was removed and analyzed for plutonium in the same manner as the 1 000 ml samples described above. The "solubility" or amount of plutonium lost from the microsphere and found in the aquarium water is presented as a percentage of the microsphere activity (Table 3).

At the same time that the aquaria were emptied so that the water could be analyzed, snails which had been added to the aquaria to control algal growth were removed and analyzed for plutonium (Table 4).

A second study was made using microspheres from Batch #1 (the batch used in soils for plant uptake studies). As before, a single microsphere was placed in each aquarium which contained about 26 litres of dechlorinated Los Alamos tap water.

After two days and ten days, one fish from each aquarium was dissected and the parts analyzed separately for plutonium. After twenty days of exposure all six fish in one aquarium died. These fish were killed by ingested toxic chlorinated organic compounds and not by the radioactivity in the aquaria. The fecal matter from the six relatively large goldfish, along with the fish food which had not been completely eaten by the fish, began to deplete the oxygen in the water as noted by the behavior of the fish. To alleviate this condition the fish were removed and the water was treated

TABLE 3

Pu FOUND IN THE AQUARIA WATER AV OF 3 SAMPLES

Contact Time With $^{238}PuO_2$	Av Pu d/m/l	Total d/m in Aquaria Calculated	% Microspheres Activity Found in Water*
9 days	2 656	69 056	3.8×10^{-2}
17 days	1 172	30 472	1.7×10^{-2}
49 days	484	12 585	6.9×10^{-3}
72 days	218	5 668	3.1×10^{-3}
114 days	364	9 464	5.2×10^{-3}
168 days	366	9 516	5.2×10^{-3}
185 days**	314	8 164	4.5×10^{-3}

*Assuming uniform distribution of plutonium throughout water

**Termination

TABLE 4

PLUTONIUM FOUND IN SNAILS GROWN IN $^{238}PuO_2$ SPIKED WATER

AVG OF ALL SNAILS FOUND IN 3 AQUARIA AFTER 185 DAYS

	Ash d/m/g	Dry d/m/g
Snail Flesh	2,791	817
Snail Shell	710	371

with sodium hypochlorite to oxidize the organic compounds in the water. The water was then treated to remove residual chlorine by the addition of sodium thiosulfate until the water tested chlorine free, at which time the fish were returned to the aquarium. This procedure had been used once before and proved to be successful. However, this time, toxic compounds such as chloramines may have formed and the six fish died shortly after being returned to the aquarium. The water in the effected aquarium was discarded and replaced with fresh dechlorinated tap water.

The six fish which died were dissected and all like parts were combined to form a single sample such that the six heads were analyzed as a single sample, six gut samples combined and analyzed as a single sample, etc. At the same time a fish from one of the other aquaria was sacrifieced, dissected and analyzed for plutonium. The remaining eleven fish were distributed in the three aquaria so that two aquaria had four fish each and one aquarium had three fish. With only three or four fish in each aquarium the air bubblers were able to supply enough oxygen to the water to sustain the goldfish.

Twenty-eight days later (forty-eight days after the study was initiated) a fish from the two aquaria which had four fish each was sacrificed and analyzed for plutonium. Three additional samplings (one fish from each aquarium) made on the 72nd, 113th and 302nd day of the experiment removed all the fish and

the experiment was terminated. The plutonium data gathered from the analyses of fish parts are presented in Table 5 and the data for water analyses presented in Table 6.

B. Discussion

From the data in Tables 2 and 5 it is apparent that in each study the bulk of the plutonium activity incorporated in the fish is located in the gills and gut. Up to two orders of magnitude more activity is found in the gut (with contents) than is found in the flesh and bones.

The flesh from fish #21, Table 2, was found to contain 994 d/m/g of ash; this converts to about 17 d/m/g of wet flesh since the flesh of these fish contains about 1.75% ash when dried at 105°C and ashed at 600°C; this plutonium concentration is about 150% of the concentration guides (CG) for plutonium in water for the 168 hour week given in AEC Manual Appendix 0524, Annex A, November 1968.

It was found that the fish along with snails and algae apparently concentrate the plutonium present in the aquaria water. The gut of the fish (1.4% ash) contained about 730 d/m/g of wet gut whereas the water (fish #21, Table 2; water 185 day, Table 3) contained only 0.31 d/m/ml which gives a concentration factor of about 2 300. The flesh of fish #21 contained only 17 d/m/g of wet flesh which represents a concentration factor (fish flesh to water) of about 40. This indicates that almost all of the plutonium taken into the gut is eliminated and does not find its way

TABLE 5

PLUTONIUM IN BODY PART IN d/m/g OF ASH
Av of number of fish indicated

(Batch #1, microspheres used)

Exposure Time in $^{238}PuO_2$ Water	# of Fish	Head	Gill	Flesh	Bones	Gut	Gut Organs
2 days	3	0.46	1.78	0.36	0.72	3.6	0.95
10 days	3	0.47	2.24	0.28	0.14	60.8	0.75
20 days	7	0.22	2.24	0.35	0.75	27.2	1.60
48 days	2	0.93	2.02	0.65	0.36	24	4.6
72 days	3	0.61	2.90	0.65	0.43	35.8	4.9
*113 days	3	0.65	2.40	0.42	0.25	35.1	4.4
302 days	3	0.41	9.0	0.57	0.44	24.3	12.5

*Highest % of microsphere activity found in fish was 4.2×10^{-6}%.

TABLE 6

CONCENTRATION OF Pu IN AQUARIA WATER

(Batch #1, microspheres used)

Time Exposed to $^{238}PuO_2$	d/m/l of Water (Av of 3 Samples)
1 hr	58
24 hrs	111*
48 hrs	88
3 days	45
4 days	53
9 days	24
10 days	68
16 days	49
19 days	45
25 days	29
42 days	72
145 days	3
302 days	1.4

*Highest % of microsphere activity found in water was 1.6×10^{-3}%.

into the flesh or the edible portions of fish.

A single determination of plutonium in an algal sample in an earlier preliminary aquarium experiment indicated a concentration factor of about 2 000. This was calculated using the plutonium concentration in algae expressed as d/m/g of dry algae and the concentration of plutonium in d/m/ml in the water sample after 24 hours (Table 5, i. e. $\frac{222 \text{ d/m/g of dry algae}}{.111} = 2\ 000.$

The concentration factor would be an order of magnitude less if the plutonium in the algae were expressed as d/m/g of wet algae (assuming dry weight is 10% of the wet weight).

When one compares the plutonium in snails (Table 4) expressed as d/m/g of dry flesh a concentration factor of about 2 600 is obtained, i.e. $\frac{\text{d/m/g dry snail flesh}}{\text{d/m/ml Pu in water}}$. Alvarez-Ramis[4] did not find a concentrating of plutonium in snails living in soil contaminated with plutonium. However, in that instance the plutonium concentration in the material which passed through the digestive systems of the snails was not known and the plutonium most certainly was not uniformly distributed in the soi but was present in the soil as particulate plutonium oxide. These factors make it impossible to determine a meaningful concentration factor as was done in the aquaria experiments.

The fish used in a second comparable study (Batch #1 microspheres) showed little tendency to concentrate the

plutonium. For example, the ten day fish sample (Table 5) had only 60.8 d/m/g of ashed gut or 0.85 d/m/g of wet gut which when compared with water at 10 days (Table 6) would give a concentration factor of only about 12, i.e., $\frac{0.85 \text{ d/m/g of wet gut}}{.068 \text{ d/m/ml of water at 10 days}} = 12$. If one calculates the plutonium concentration for the 48 day fish sample (Table 5) on the basis of d/m/g of wet flesh using an ash content of 1.75% and compares this value with the plutonium in water at 42 days (Table 6), a concentration factor of about 0.15 is obtained, i.e. $\frac{.65 \text{ d/m/g of ash} \times .0175}{.072 \text{ d/m/ml in water at 42 days}} = 0.15$. The reason for these smaller concentration factors in the second study is not known at present but indicates the differences in batches of microspheres referred to in Part II.

If the assumption is made that commercial fish concentrate plutonium in a manner similar to that of goldfish then commercial fish could pose a slight radiological hazard to man if the fish were in water containing $^{238}PuO_2$ microspheres which were similar to Batch #2 microspheres and at the concentration used in these studies. At the plutonium concentration levels used in the Batch #1 microsphere studies the fish apparently would pose no radiological hazard when consumed by man since this batch of microspheres showed little tendency to become "apparently solubilized" in the tap water.

Pillai, et al.[5] also found that marine organisms concentrate plutonium. They report plutonium concentration

factors for green algae of 1 570, zooplankton of 2 590 and fish (Bonito) of 3 compared with plutonium found in sea water. Wong, et al.[6] found that Southern California "seaweeds" concentrate plutonium by factors of 260 to 3 500 times greater than the concentration of plutonium in sea water. Ward[7] found that lobster flesh from animals grown in sea water containing 10^{-2} μCi/litre of ^{239}Pu contained three times the concentration of plutonium found in the sea water.

The plutonium concentration factors for algae found at LASL are certainly within the range found by Wong for "seaweeds." The plutonium concentration factor for fish flesh (Batch #2 microspheres) was about fifteen times higher than that reported by Pillai for Bonito fish, perhaps reflecting differences in the species studies.

It is worthy of note that the microspheres probably are not all alike and may differ in their behavior in water. For this reason it might be presumptuous to predict actual contamination levels in water and associated animal life on the basis of experimentation with a half dozen microspheres. Note the vast difference in plutonium concentrations in fish parts (Tables 2 and 5) and the difference in plutonium concentrations in water when using different batches of microspheres (Tables 3 and 6).

C. $^{238}PuO_2$ "Solubility" in Water

The variation in the plutonium analyses on aquaria water (Table 3, Part IIA) prompted an experimental determination of the "solubility" of $^{238}PuO_2$ microspheres in tap water in the absence of fish or algae. A single microsphere was placed in each of two beakers containing one litre of Los Alamos Tap water. The water in each beaker was stirred continuously with an electric stirring motor; ten ml samples of the water were removed at various time intervals and analyzed for gross alpha activity. Evaporative losses were compensated for by the addition of distilled water, whereas tap water was added in amounts equal to that volume removed for analysis. The gross alpha data are compiled in Table 7.

The microspheres whose diameters were about 190 and 100 μ were in contact with the water for 294 and 283 days respectively. Both microspheres were obtained from Batch #2, the same batch used in the first aquaria studies described in Part II A. After the microspheres had been in the water for the time indicated above, the water was decanted and the microspheres recovered. The one litre samples of water were analyzed for plutonium using an anion exchange separation procedure after conversion of the plutonium to the $Pu(NO_3)_6$ = complex in 8 N HNO_3.

If all the plutonium found in the water at the completion of the experiment is assumed to be "soluble," then the

TABLE 7

ALPHA ACTIVITY FOUND IN WATER CONTAINING
A BATCH #2 $^{238}PuO_2$ MICROSPHERE

189 μ Diameter Microsphere Cumulative Time in Contact with Water	Gross α d/m/l	100 μ Diameter Microsphere Cumulative Time in Contact with Water	Gross α d/m/l
1 hr	280	1 hr	5,480
2 hrs	11,000	17 hrs	5,940
3 hrs	440	10 days	7,260
4 hrs	200	14 days	8,960
5 hrs	420	37 days	58,400
3 days	600	57 days	12,394
7 days	920	84 days	15,720
10 days	1,200	164 days	28,720
12 days	1,034	283 days	54,140
22 days	244,160		
26 days	1,060		
48 days	3,000		
68 days	17,620		
95 days	67,240		
175 days	155,060		
294 days	173,480		

"solubility" of the $^{238}PuO_2$ can be determined and expressed as a percentage of the original activity associated with the microsphere. The original alpha activity of the microspheres was calculated by assuming a sphere and using the approximate diameter of the microspheres (190 and 100 μ, an average density of 10.5 g/cc and the specific activity of ^{238}Pu. The "solubility" data are presented in Table 8. Although the assumptions may not be exact, it is the relative "solubility" that is important.

In an earlier experiment the 190 μ microsphere used in this study was placed in contact with tap water for 67 days. At the end of this time the microsphere was removed from the water and the water was filtered through a 0.22 μ pore size millipore filter. The filter removed about 25% of the alpha activity from the water. The apparent "solubility" of $^{238}PuO_2$ calculated from the plutonium found in the filtrate was 1.34×10^{-3}% whereas the solubility calculated from the alpha activity in the unfiltered water was 1.8×10^{-3}%.

The millipore filter from the above filtration was quartered and mounted on NTA emulsion plates and the films exposed from 4 1/2 to 103 hours. Using the method of Leary[8] to calculate particle size from the number of alpha tracks found on the developed film, particle sizes ranging from 0.033 to 0.16 μ diameter were calculated to be present on the millipore filter; this indicates that at least part

TABLE 8

SOLUBILITY OF $^{238}PuO_2$ MICROSPHERES IN TAP WATER

189 μ Diameter

294 Days Exposure

^{238}Pu Found in Water = 2.88×10^5 d/m/l

% Solubility = 0.0236%

Calc. Activity of $^{238}PuO_2$

Microsphere = 1.23×10^9 d/m

≈100 μ Diameter

283 Days Exposure

^{238}Pu Found 1.03×10^5 d/m/l

% Solubility = 0.058%

Calc. Activity of $^{238}PuO_2$

Microsphere Assuming 100μ

Diameter = 1.82×10^8 d/m

LOS ALAMOS TAP WATER

pH, 8.2	F^-, 1.1 mg/l
Conductivity, 116 μmho/cm	Total hardness, 25 mg/l
Phenol. alk, 0.0 mg/l	Ca++, 9.0 mg/l
Total alk, 60 mg/l	Mg++, 0.5 mg/l
Na+, 50 mg/l	NO_3-N, 0.3 mg/l
Cl, 6.0 mg/l	Total Solids, 203 mg/l

of the plutonium found in the water is particulate matter and should not be considered as being in solution. The particles found on the filter were smaller than the pore size of the filter suggesting that these particles are attached to larger nonradioactive particulate material.

D. Discussion of $^{238}PuO_2$ "Solubility" in Water

Solubility in the classical sense implies the formation of ions through the loss of electrons. As related to plutonium and probably some other elements, there is a question as to whether the microcolloid or a group of atoms spalled from macroparticles are "soluble." As these "solutions" relate to filtration or transport in a DC field, they appear to be true solutions, however, the fact that a homogeneous solution is not formed is demonstrated by the range of activities determined for aliquots from the same sample.

A correlative question to the low uptake of plutonium by plants may be posed. Is the low uptake of plutonium observed in green plants a result of true solution in the soil aqueous phase, and hence, is this more nearly a real indication of the solubility of plutonium?

Results obtained from Nuclear Track Alpha (NTA) plates lead one to suspect that what has been referred to as "soluble" plutonium may in fact be particulate material which would not be evidenced by classical chemistry but can

be demonstrated as present by radioautographic techniques.

The alpha activity, expressed as d/m/l (Table 7) which was calculated from the activity found in a ten ml aliquot, shows considerable variation. These erratic results could be caused by the breaking off of small particles of $^{238}PuO_2$ which are not uniformly distributed in the water.

Lingren[9] found that of the plutonium "in solution" from exposing $^{238}PuO_2$ microspheres to sea water, 22% migrated to the anode, 23% to the cathode and 55% did not move in electrochromatographic experiments. In a similar experiment where plutonium was added as a solution to the sea water, Lingren also found 30% of the plutonium migrated to the anode whereas 70% did not move. Lingren suggests the formation of a carbonate or hydroxide complex with a negative charge resulting in movement toward the anode. He also suggested that the 55 or 70% of the plutonium which did not migrate in the two experiments mentioned above might be a $Pu(OH)_4$ neutral complex. Price[10] mentions plutonium hydrolysis products which are colloidal or exhibit colloidal behavior and that these colloidal sized particles increase in size with pH. Price also suggests that the form of plutonium most likely to occur in natural waters or nuclear processing waste streams is colloidal tetravalent plutonium as $Pu(OH)_4$. Unhydrolyzed plutonium exists in aqueous solutions of 0.1 M hydrogen ion or greater. Precipitation of $Pu(OH)_4$, the

end product of hydrolysis, begins at pH 2 or higher and with Pu IV concentrations of 10^{-3}M.

Ockenden and Welch[11] state that during the intermediate stages of hydrolysis there is polymerization of the hydrolyzed forms of Pu IV. This may occur through oxide or hydroxide bridges with the formation of colloidal aggregates. Lloyd and Haire[12] in discussing the formation of plutonium IV polymer stated that they do not believe that monomeric plutonium IV hydroxide species are formed furing the precipitation of what was considered to be $Pu(OH)_4$. They do not believe that monomeric $Pu(OH)_4$ is involved in the formation of the "so called" plutonium IV polymer. They have proposed that the initial precipitate consists of primary particles which consist of or readily convert to very small crystallites of hydrated PuO_2. These crystallites evidently form clusters possibly accounting for the wide difference in reported polymer aggregate size. Rhodes[13] suggests the existence of a polymer or radiocolloid with tracer concentrations of plutonium in solution at a pH greater than 2 but suggests that since the polymer is taken up rapidly by the soil colloid it probably has a positive charge.

Kubose, et al.[14] found in a static system for the determination of $^{238}PuO_2$ solubility in sea water that essentially all of the plutonium is sorbed on the material settling to the bottom. Although the Los Alamos tap water does not contain large amounts of dissolved salts (Table 8)

some material did form on the beaker during evaporation. It is possible that some of the plutonium in the solubility studies does sorb on that material.

The "solubility" (Table 8) expressed as a percentage of the original activity of the $^{238}PuO_2$ microspheres is in essential agreement with that found by Kubose, i.e. about 0.38% at 240 days exposure to sea water.

From a review of all data concerning "solubility" of $^{238}PuO_2$ it appears possible that the plutonium in the aquaria water and in the tap water is present as colloidal $Pu(OH)_4$ or hydrated PuO_2. However, the plutonium could also be present, at least partially, in very small fragments of PuO_2. At the present time the chemistry of tracer concentrations of plutonium in waste water warrants further study before one can be sure of the chemical or physical state of the plutonium.

III. SUMMARY

Questions relative to the "solubility" of PuO_2 microspheres have been posed. The use of plants as indicators of true solubility of PuO_2 microspheres has been suggested. Although several investigators have looked at the chemistry of plutonium in solution it is apparent that further work is required before one can draw conclusions concerning "solubility" of refractory oxides of plutonium in water or in soil.

References

1. R. C. Thompson, "Space Nuclear Systems Studies," Battelle Pacific Northwest Laboratory, BNWL-353 Rev., 4-5 October 1966.
2. AEC Manual Appendix 0524 Annex A, November 1968.
3. J. H. Harley, "Worldwide Plutonium Fallout From Weapons Tests," Proc. Environmental Plutonium Symposium, Los Alamos, New Mexico, August 4-5, 1971, LA-4756, p. 78.
4. C. Alvarez-Ramis, A. Gregorides de los Santos, "Contamination of Terrestrial Gasteropods Living in a Biological Medium with a Low Level of Alpha Contamination Due to Plutonium and Uranium," Proc. of Symposium International de Radioecologie, Vol. II (Fontenay-aux Roses, France, 1970), CONF-690918.
5. K. C. Pillai, R. C. Smith, T. R. Folsom, "Plutonium in the Marine Environment," Nature 203, 568-571, 1964.
6. K. M. Wong, V. F. Hodge, T. R. Folsom, "Concentrations of Plutonium, Cobalt, and Silver Radionuclides in Selected Pacific Seaweeds," Proc. Environmental Plutonium Symposium, Los Alamos, New Mexico, August 4-5, 1971, LA-4756.
7. E. E. Ward, "Uptake of Plutonium by the Lobster Homarus vulgaris."
8. J. A. Leary, "Particle-Size Determination in Radioactive Aerosols by Radioautograph," Anal. Chem. 23, 850, 1951.
9. W. E. Lingren, "The Electrochromatography of Seawater Containing Dissolved Plutonium," USNRDL-TRC-85, September 1966.
10. K. R. Price, "A Critical Review of Biological Accumulation, Discrimination and Uptake of Radionuclides Important to Waste Management Practices, 1943-1971, Battelle Northwest Laboratory Report BNWL-B148 (1971).

11. D. W. Ockenden, G. A. Welch, "The Preparation and Properties of Some Plutonium Compounds - Part V, Colloidal Quadrivalent Plutonium," J. Chem. Soc., p. 3358 (1956).

12. M. H. Lloyd, R. G. Haire, "Studies on the Chemical and Colloidal Nature of Pu (IV) Polymer," CONF-730927-2 UNCLAS December 1973.

13. D. W. Rhodes, "Adsorption of Plutonium by Soil," Soil Sci. 84, 465 (1957).

14. D. A. Kubose, M. G. Lai, N. A. Goya, H. I. Cordova, "Radioactivity Release from Radionuclide Power Sources VIIa Dissolution Studies of Plutonium Dioxide in the Ocean, 5 Mos. Exposure," USNRDL-TR-68-74 (1968).