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THE DISSOLUTION OF ^{238}Pu IN ENVIRONMENTAL AND BIOLOGICAL SYSTEMS

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ABSTRACT

Results from our experiments on dissolution rates of $^{238}\text{PuO}_2$ and $^{239}\text{PuO}_2$ in distilled water and normal saline solution were compared with rates calculated from data in the literature on various PuO_2 dissolution experiments. The initial comparatively rapid dissolution rates were found to vary widely, even between experiments performed ostensibly under the same conditions. In contrast, the lower rate of dissolution, which began a few hours after contact of the oxide with the aqueous medium, was found to be constant and fell within a range of 1 to 6 ng/m²s under widely varying conditions.

I. INTRODUCTION

Several problems are encountered in studies of the release of plutonium from PuO_2 to the ecosystem. Contributing to these problems is the high stability of PuO_2 , the most stable plutonium compound known. In the laboratory PuO_2 is considered to be insoluble in water and aqueous solutions. The degree of its solubility, however, is not absolutely zero; and over a period of time, plutonium dioxide particles in contact with an aqueous solution will release plutonium.

Because of the nature of plutonium chemistry, the fate of the released plutonium is uncertain and complex. Some experimenters have erroneously assumed that the problem is connected with the "solubility" of PuO_2 , whereas the real problem is its rate of dissolution. Plutonium dioxide reacts chemically with the aqueous solution to form the released plutonium ions. These ions, in turn, will react quickly with other agents in the aqueous solution to form soluble complexes or will react with the water itself to form insoluble suspensions. It is doubtful that plutonium ions, as such, can last in the aqueous systems of environmental and biological habitats.

Little has been reported on the apparent solubility of PuO_2 , and conditions differed considerably among

those experiments. Attempts to duplicate *in vivo* conditions introduced very complex biological systems that compounded the problems in data interpretation. Generally only relatively recent work was considered in this search, with emphasis on the oxide of the 238 isotope.

II. CHEMICAL AND PHYSICAL CONSIDERATIONS

There are probably several reasons for the paucity of papers on the solubility of PuO_2 . For one, the term "solubility" does not apply in the thermodynamic sense to the plutonium dioxide-water system. Because the dioxide cannot be formed in the presence of water, no equilibrium can be achieved between the dioxide and the plutonium ions in solution. The dissolution reaction for PuO_2 is irreversible; the dioxide continuously goes into solution. In a static system a state of pseudo-equilibrium may be reached, with the plutonium concentration in solution remaining constant. Here, the concentrations of ionic species of plutonium are controlled by the solubility product of the hydrous oxides that are precipitated from solution.¹ (Polzer¹ attributes this behavior to the low dissolution rate of PuO_2 , although he does

mention that PuO_2 is formed at high temperatures only, not from solution.) The rate of dissolution of the dioxide is independent of the concentration of the plutonium ions in solution. Thus, the theoretical solubility constant obtained thermodynamically from free energy considerations^{1,2} is meaningless.

Another problem is a lack of an experimentally practical definition of plutonium in solution. The "solution" may contain fine particles of undissolved oxide, precipitated hydrous oxide, polymers in colloidal form, and various complex ions of plutonium. In experimental solubility studies, an arbitrary particle size generally has been used as the limit between plutonium suspended and in solution. Battelle Northwest Laboratories have used dialysis for separation of phases,³ and the plutonium in the liquid phase measured was only ionic. Various others have used 0.02, 0.1, and 0.45 μm as particle-size limits.⁴⁻⁷ In simulated seawater and fresh water aquarium studies at the Los Alamos Scientific Laboratory (LASL) all suspended material was included in the solution.^{8,9} Comparing data with these widely varying definitions of solution is difficult.

The rate of dissolution of PuO_2 is dependent on many factors, including pH; temperature; oxidizing, reducing, or complexing agents;^{1,2} surface area of the oxide (particle size and shape); and the history of the sample (duration and temperature of heat treatment, time, temperature, and radiation history since heat treatment). Because its high specific alpha activity affects several of these factors, $^{238}\text{PuO}_2$ might be expected to dissolve more rapidly than $^{239}\text{PuO}_2$. The self-irradiation of the $^{238}\text{PuO}_2$ causes damage to the crystal lattice, but this damage may be annealed out by heat treatment. It was found that the lower the temperature of storage, the greater the retention of damage.¹⁰ In a large mass of dioxide, the bulk of the damage may be repaired by self-heating. Under neutron irradiation, which causes similar lattice damage, the dioxide tends to fragment and form colloids,¹¹ exposing a large surface area. The aqueous phases in contact with the irradiated material turned bright green, because of the colloid formed under high radiation levels.

The high radiation field from the $^{238}\text{PuO}_2$ would also be expected to cause radiolysis of the water and its constituents. This might form species that could reduce the plutonium to the trivalent oxidation state, which is more soluble.^{12,13} Also, for massive amounts of ^{238}Pu , local heating of the water may occur causing increased reaction rates.

III. REVIEW OF EXPERIMENTAL WORK

These predictions seem to be borne out by experiments on animal inhalation of PuO_2 . Studies of particle-size effects showed that at equal doses the smaller particle sizes, with the greater surface areas, had more rapid translocation from the lungs.¹⁴ Also, heat treatment affected the biological properties of the oxide. Material prepared at low temperatures, with probably less perfect crystal structure, was the most rapidly translocated.¹⁵ Large doses of ^{238}Pu and ^{239}Pu were equally effective in causing acute lethality in rats, since death occurred in a short time without the necessity of translocation from the lungs.¹⁶ However, at lower dose rates the ^{238}Pu was translocated more rapidly than ^{239}Pu to the bones and organs after inhalation of the dioxide by dogs and rats.^{3,17,18} In these and subsequent experiments, the ^{238}Pu isotopic content of the $^{238}\text{PuO}_2$ was 80% unless otherwise stated.

Very few direct solubility studies of PuO_2 in water exist in the literature. In an electrochromatographic experiment, Lingren¹⁹ discovered that the dissolution of high-fired PuO_2 in seawater yielded negatively and positively charged carbonate complex ions as well as neutral colloids. The latter may be in the form of very small hydrous oxide particles.²⁰ The plutonium species that may exist in a neutral aqueous medium are described in greater detail by Adams and Fowler.⁹

Miner and others^{4,5} are investigating the behavior of plutonium in a soil-water environment. Plutonium dioxide and soluble plutonium are shaken with a soil-water mixture; then the plutonium in the various phases is measured. The dissolution of air-borne plutonium in water has been measured in a scrubber in parallel with an air filter.²¹ Some investigations have been done on the dissolution of $^{238}\text{PuO}_2$ microspheres in water. Experimenters at LASL and Sandia Laboratory, Albuquerque, found that microspheres stirred with water rapidly disintegrated to smaller particles. X-ray analysis showed them to be PuO_2 , much of which dissolved.²² The dissolution of microspheres in seawater and fresh water has been compared by workers at the U.S. Naval Radiological Defense Laboratory. The initial dissolution rate in fresh water was 5 $\mu\text{g/g/day}$, but after several days the rate dropped to 2 $\mu\text{g/g/day}$, or approximately that in seawater.²³ The particle size distribution of the microspheres was not stated, but on the assumption that 100 μm is the mean diameter for both the area

and the volume, the dissolution rates are 11 and 4 ng/m²·s, respectively.

Measurements on the dissolution of ²³⁸PuO₂ microspheres in fresh water were made by Adams and Fowler in a study of the uptake of ²³⁸Pu by goldfish.⁹ They found widely varying behavior between aquaria containing microspheres from two different batches. Three aquaria, each containing one microsphere from the "more soluble" batch, initially showed a dissolution rate of about 100 ng/m²·s. However, the total plutonium in the water then decreased till it reached a fairly constant level, about an order of magnitude less than the initial peak level. The aquaria containing microspheres from the second batch started with a plutonium level another order of magnitude lower, which remained constant from 1 h after beginning of exposure until 42 days, when the concentration dropped. Separate experiments with 189- and 100-μm-diam microspheres from the more soluble batch, each in a liter of water, showed dissolution rates of about 2.5 ng/m²·s after 290 days, but varied considerably at earlier exposure times. The rate for the first hour was about 10 times the final rate for the larger microsphere, whereas for the smaller one, the rate was about three orders of magnitude greater than the final one. About 1 aliquot in 10 assayed much higher than others in the same time period; this may be an indication of small particles breaking off the microspheres.

A method recently was developed at Lovelace Foundation for determining the dissolution characteristics in the lung of accidentally released radioactive aerosols.⁶ The radioactive sample was placed on a 0.1-mm filter and washed with lung serum simulant flowing under pressure. Under these conditions the rates of dissolution were 140 and 0.8 ng/m²·s for ²³⁸PuO₂ and ²³⁹PuO₂, respectively. The rate of dissolution of ²³⁸PuO₂ gradually decreased with time. Initially a very high dissolution rate resulted when the chelating agent, disodium ethylenediaminetetraacetate (EDTA) was added to the serum simulant, but subsequently the rate dropped almost to that of the serum without the chelating agent. This was followed by a gradual increase in rate. The rate of dissolution of ²³⁹PuO₂ was much lower and did not seem to be appreciably affected by the presence of EDTA. In the dialysis experiment of Hanford³ ²³⁸PuO₂ was found to dissolve more rapidly than the ²³⁹PuO₂.

In dissolution experiments at the Los Alamos Scientific Laboratory, aqueous phases of ²³⁸PuO₂ and ²³⁹PuO₂ powders immersed in distilled water

and normal saline solutions at body temperature for several months were periodically sampled. The quantities of ²³⁹PuO₂ used were 1.6 g and 0.008 g, chosen to provide masses and radioactivities in a ratio of 200 to 1. The quantities of ²³⁸PuO₂ were 8 mg and 0.04 mg. The larger samples of ²³⁸PuO₂ were equivalent in radioactivity to the larger ²³⁹PuO₂ samples and equivalent in mass to the smaller ²³⁹PuO₂ samples. The smaller ²³⁸PuO₂ sample had a radioactivity about equal to that of the smaller ²³⁹PuO₂ sample but was smaller in mass by a factor of 200. In sampling, some of the solution was centrifuged in a clinical centrifuge for 15 min, and an aliquot was taken for analysis. (Sample 1 of the first set was not centrifuged and, therefore, would more likely contain undissolved particles.) The exposed areas of the oxide source materials used for the experiments were determined by log-normal fitting of particle-size analyses.²⁴ The first set of experiments was terminated in November 1973 after 318 days, and a second set of nominally identical experiments is now in progress.

Tables I and II list the data from the first set and those to date from the second set, respectively. Experiments 8S1 and 9S1, which combined high activity levels with high ionic strengths, behaved erratically in both sets. The results for these experiments were often much lower than would be expected, and the concentration of plutonium sometimes increased or decreased very rapidly. There may be coagulation and other processes occurring that are exaggerated by the combination of high ionic strength and alpha activity. These experiments therefore are not included in the following discussion.

In the first set, the results for ²³⁸PuO₂ were all higher than those for ²³⁹PuO₂ taken at the same time, except in sample 1. However, these differences are not great in some cases, and the values seem more closely correlated with weight of oxide. For example, the results from 8W1 were closer to those from 9S2 and 9W2, which had the same weight of oxide, than they were to the other ²³⁸PuO₂ samples. Also, the rates for 8S2 and 8W2 remained nearly constant throughout the 11 months of the experiments. The other experiments, containing more PuO₂, had rates that dropped off more. The results for 8S2 and 8W2 agree with the rates of 4 and 2.5 ng/m²·s, the dissolution rates of microspheres in fresh water from the data of Kubice and others²³ and Adams and Fowler,⁹ respectively. The dissolution rate of a pressed ²³⁸PuO₂ disk in simulated seawater was 3 ng/m²·s.⁸

TABLE I

**DISSOLUTION RATES OF $^{238}\text{PuO}_2$ AND $^{239}\text{PuO}_2$ IN DISTILLED WATER
AND NORMAL SALINE SOLUTION, FIRST SET^a**

Sample No.	Time Elapsed (s x 10 ⁶)	(ng/m ² ·s)							
		8S1	8S2	8W1	8W2	9S1	9S2	9W1	9W2
1	4.06	0.036	5.6	1.55	6.8	0.194	1.9	0.218	4.3
2	5.96	0.032	5.1	1.00	3.9	0.099	0.53	0.122	0.50
3	7.34	0.009	4.9	1.05	4.3	0.080	0.51	0.108	0.50
4	8.29	0.011	5.0	1.08	4.2	0.067	0.51	0.161	0.49
5	10.80	0.007	4.6	0.53	3.9	0.056	0.36	0.059	0.32
6	14.17	0.064	5.0	0.38	4.0	0.0009	0.28	0.035	0.28
7	15.03	0.078	4.9	0.43	4.0	0.0011	0.26	0.032	0.24
8	16.24	0.104	5.0	0.55	4.0	0.0012	0.25	0.030	0.26
9	17.97	0.116	4.9	0.55	3.6	0.0011	0.23	0.028	0.19
10	18.66	0.097	4.6	0.53	3.5	0.0004	0.25	0.028	0.20
11	21.51	0.011	4.6	0.68	3.2	0.0007	0.18	0.025	0.15
12	23.50	0.009	4.5	0.95	3.3	0.0015	0.22	0.028	0.14
13	25.83	0.002	4.2	0.53	3.4	0.0017	0.17	0.028	0.11
14	27.48	0.0007	3.3	0.32	3.3	0.0008	0.18	0.025	0.08
Rate after Sample 2	21.52	-0.0080	3.4	0.125	3.1	-0.027	0.080	-0.002	-0.04

^aExperiment numbers: 8 indicates $^{238}\text{PuO}_2$; 9, $^{239}\text{PuO}_2$; W, 50 ml of distilled water; S, 50 ml of normal saline solution; 1, 100 mCi of alpha activity; and 2, 0.5 mCi of alpha activity. (Approximate weights of oxide: 1.6 g each for 9S1 and 9W1; 8 mg each for 9S2, 9W2, 8S1, and 8W1; and 0.04 mg each for 8S2 and 8W2.)

TABLE II

**DISSOLUTION RATES OF $^{238}\text{PuO}_2$ AND $^{239}\text{PuO}_2$ IN DISTILLED WATER
AND NORMAL SALINE SOLUTION, SECOND SET^a**

Sample No.	Time Elapsed (s x 10 ⁶)	(ng/m ² ·s)							
		8S1	8S2	8W1	8W2	9S1	9S2	9W1	9W2
1	0.605	105	130	242	200	0.0001	1.1	1.78	2.9
2	1.210	38.6	62.5	125	97.2	0.0003	0.6	1.04	1.06
3	1.814	9.8	45.7	101	65.7	0.0005	0.4	0.73	0.53
4	2.42	7.3	34.4	84	51.7	0.0003	0.3	0.43	0.55
5	3.02	7.6	27.1	75	40.5	0.0011	0.7	0.37	0.51
6	4.23	5.8	21.4	64	30.4	0.0004	0.3	0.30	0.30
7	5.44	4.0	17.2	55	23.5	0.0005	0.23	0.25	0.24
8	6.65	4.3	15.2	51	19.6	0.0005	0.22	0.22	0.19
9	7.86	3.3	13.1	45	16.8	0.0003	0.12	0.20	0.17
Rate after Sample 1	7.26	-5.2	4.0	28	1.6	0.0002	0.03	0.0635	-0.062

^aExperiment numbers: 8 indicates $^{238}\text{PuO}_2$; 9, $^{239}\text{PuO}_2$; W, 50 ml of distilled water; S, 50 ml of normal saline solution; 1, 100 mCi of alpha activity; and 2, 0.5 mCi of alpha activity. (Approximate weights of oxide: 1.6 g each for 9S1 and 9W1; 8 mg each for 9S2, 9W2, 8S1, and 8W1; and 0.04 mg each for 8S2 and 8W2.)

Initially the second set behaved differently. The $^{238}\text{PuO}_2$ results in the first sample are higher than those of the first set and are two orders of magnitude larger than the $^{239}\text{PuO}_2$ results. There seems to be no correlation with weight of oxide in this set. Experiment 8W1, which contains a weight of oxide equal to 9S2 and 9W2, has the highest rate in this set. In the first set, 8W1 had the lowest rate for $^{238}\text{PuO}_2$ and was of the same order of magnitude as the two $^{239}\text{PuO}_2$ experiments. Also, none of the experiments had rates that were constant from the beginning. Instead, a high rate for the first week dropped off to a much lower rate. This lower rate after sample 1 was taken is listed in the last row of Table II. When compared with the rate after sample 2 in the first set, it is seen that in most cases the later rate is in the same order of magnitude for the two sets. The biggest difference is in 8W1, in which the later rate is again the highest one for the second set. The initial rates for this second set are of the same order of magnitude as those found by Raabe and others⁶ with lung serum stimulant. The large differences in the initial rates, along with the similarity of the later rates, agree with Adams and Fowler's experience with microspheres.⁹

IV. CONCLUSIONS

The consensus of the conclusions from the experiments cited is that the PuO_2 initially rapidly dissolves or reacts when first placed in contact with a neutral aqueous medium. This rate, which may vary from sample to sample under nominally the same conditions, is generally greater than $100 \text{ ng/m}^2\text{s}$ for ^{238}Pu and on the order of magnitude of $1 \text{ ng/m}^2\text{s}$ for the 239 isotope. After a few hours the rate decreases to a value that usually remains constant, until the concentration of the alpha activity level becomes high enough to initiate competing reactions, such as coagulation of suspended material or precipitation from a colloid. The ionic strength may also affect these reactions. There is remarkable agreement of $3 \text{ ng/m}^2\text{s}$ within a factor of 2 for this second rate for $^{238}\text{PuO}_2$ in widely different media and having different physical forms. The rate for $^{239}\text{PuO}_2$ is probably at least an order of magnitude lower. The reason for the change in rate after the first few hours is unknown, although it has been speculated that a hydrous oxide coating may form, protecting the material from further rapid dissolution.²³

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