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DISSOLUTION RATES OF $^{238}\text{PuO}_2$ AND $^{239}\text{PuO}_2$ IN 1M PERCHLORIC ACID

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ABSTRACT

The dissolution rate of $^{238}\text{PuO}_2$ and $^{239}\text{PuO}_2$ in 1M HClO_4 was measured over a period of 200 days. When equal (150- $\mu\text{g/l}$) masses of the oxides were compared, ^{238}Pu was found to be released approximately five times faster than ^{239}Pu . At the 10- $\mu\text{Ci/ml}$ activity level, ^{238}Pu was released 100 times faster than ^{239}Pu . The difference in dissolution rates is attributed to the difference in alpha particle specific activity of the two materials which causes significantly greater radiation damage in $^{238}\text{PuO}_2$ than in $^{239}\text{PuO}_2$. The rate difference also may be affected by particle size and total oxide mass in the dissolution system. The results of these studies agree with data from earlier investigations in distilled water and simulated body fluid solvents.

I. INTRODUCTION

We earlier reported evidence that $^{238}\text{PuO}_2$ dissolves faster than $^{239}\text{PuO}_2$ in aqueous and biological systems.¹ Measurements made in animals, in simulated biological fluids, and in water indicated a significant difference in the dissolution rates of the two materials, but the data were difficult to interpret quantitatively and reflected the probability that there were several competing mechanisms in the dissolution. Perhaps the most important uncontrolled variable in these experiments was the composition of the solvents, especially their acidity. In addition to containing various amounts and kinds of solutes, most of the solvent systems in the *in vitro* experiments were kept at a pH of 4 to 8 in an attempt to simulate biological fluids. The net result was a poor chemical environment for study of plutonium dioxide dissolution rates. At these near-neutral acidities, there were very few free plutonium ions in solution and any plutonium released in ionic form would eventually precipitate on particles and underwater surfaces.

There was also the possibility, in such complex aqueous systems, of other reactions that could compete with the simple release to the solvent of plutonium from the insoluble plutonium dioxide. Although some of the studies were conducted using distilled water, it was not considered an optimum system for studying $^{238}\text{PuO}_2$ and $^{239}\text{PuO}_2$ dissolution rates.

To reduce or eliminate competing reactions that would affect dissolution rates, we decided to measure the rates in 1M perchloric acid. Although such a system was utterly unlike biological systems, it had two virtues: the acidity was adequate to prevent precipitation of true ionic species by hydrolysis reactions, and perchlorate ions do not form chemical complexes with plutonium.

Because the specific activities of ^{238}Pu and ^{239}Pu differ by a factor of nearly 300, it is important to specify very clearly the units in which the release rates are reported; otherwise, comparisons among different data sources become difficult and confusing. The chemist is usually interested in rates reported on a mass basis, whereas the biologist may

want rates on a radioactivity basis. The work reported here uses both systems. To make the data more useful, we compared the dissolution rates of the two isotopes when their alpha radioactivities were equal and also when their masses were equal. For the equal radioactivity comparisons, the rates are reported in terms of nanocuries per second per square meter of oxide surface. For the equal mass comparisons, the rates are in terms of nanograms per second per square meter of oxide surface.

The earlier report on dissolution rates in distilled water and in saline solutions included a discussion of the important chemical and physical considerations in studies of this kind.¹ It is worthwhile to restate that these dissolution rate measurements are not solubility measurements. The PuO_2 dissolution reaction is irreversible, and the material dissolves continuously. As will be seen, the measurements in this report show unequivocally that $^{238}\text{PuO}_2$ dissolves faster in dilute (1M) perchloric acid than does $^{239}\text{PuO}_2$. However, it is incorrect to use these data as evidence that $^{238}\text{PuO}_2$ is more soluble than $^{239}\text{PuO}_2$ in 1M perchloric acid.

II. EXPERIMENTAL CONDITIONS

Plutonium Dioxide

Two batches of fine particles were used. One was 80% enriched in ^{238}Pu ; the other was plutonium containing about 93% ^{239}Pu . The isotopic compositions are shown in Table I.

Each batch was processed identically during its manufacture. The powder was heated in $\text{Ar-H}_2^{16}\text{O}$ for 96 h at 755°C, then for 1 h at 1000°C, to exchange the normal oxygen in the feed material for ^{16}O , thereby reducing the neutron emission rate caused by the $^{17}\text{O}(\alpha, n)^{20}\text{Ne}$ and $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$ reactions.

TABLE I
ISOTOPIC ABUNDANCES
IN TEST MATERIALS

	Abundance (wt%)	
	$^{238}\text{PuO}_2$	$^{239}\text{PuO}_2$
^{238}Pu	80.0	0.010
^{239}Pu	16.3	93.40
^{240}Pu	3.0	6.22
^{241}Pu	0.6	0.284
^{242}Pu	0.1	0.02

TABLE II

PARTICLE SIZE DISTRIBUTIONS IN TEST MATERIALS

Size (μm)	Number of Particles	
	$^{238}\text{PuO}_2$	$^{239}\text{PuO}_2$
≤ 0.1	491	383
0.2	516	337
0.3	469	142
0.4	265	46
0.5	120	31
0.6	41	23
0.7	22	7
0.8	10	9
0.9	7	2
1.0	1	3

The material was then ball-milled for 32 h, and the particle size distributions (Table II) were measured.

Perchloric Acid

Analytical reagent grade HClO_4 was diluted with enough distilled water to make 1M HClO_4 .

Dissolution Measurements

After appropriate amounts (see Table III) of the two oxides were measured into separate 50-ml volumetric flasks, each flask was filled with 50 ml of 1M HClO_4 and securely stoppered. The flasks were agitated continuously in a constant-temperature bath at 37°C. Each test sample was prepared in duplicate. Aliquots were removed periodically from each of the eight flasks and prepared for plutonium analysis by liquid scintillation counting.

III. RESULTS

Under both conditions of comparison, at equal masses and at equal radioactivity levels, plutonium is released from 80% enriched $^{238}\text{PuO}_2$ faster than it is from 93% enriched $^{239}\text{PuO}_2$ (Table IV). At the 150- $\mu\text{g}/\text{ml}$ equal mass level, the ^{238}Pu is released approximately five times faster than the ^{239}Pu . At the 10- $\mu\text{Ci}/\text{ml}$ radioactivity level, approximately 100 times as much ^{238}Pu activity as ^{239}Pu activity is released in a given time interval. At the 2000- $\mu\text{Ci}/\text{ml}$

TABLE III
QUANTITIES OF ^{238}Pu AND ^{239}Pu
IN DISSOLUTION FLASKS

Flask	Sample, mg (μCi)	
	$^{238}\text{Pu}^a$	$^{239}\text{Pu}^b$
1	0.04 (10)	---
2	7.4 (2000)	---
3	---	7.4 (10)
4	---	1400 (2000)

^a80% enriched ^{238}Pu .

^b93% enriched ^{239}Pu .

TABLE IV
RELEASE RATES FROM $^{238}\text{PuO}_2$ AND $^{239}\text{PuO}_2$
SUSPENSIONS IN 1M PERCHLORIC ACID

Equal Masses, 150 $\mu\text{g/ml}$

Time (days)	Release Rate ($\text{ng/m}^2\text{-s}$)	
	$^{238}\text{PuO}_2$	$^{239}\text{PuO}_2$
77	9.5	1.8
112	8.8	1.6
156	7.8	1.4
205	7.4	1.2

Equal Activity Levels

Time (days)	Release Rate ($\text{nCi/m}^2\text{-s}$)			
	$^{238}\text{PuO}_2$		$^{239}\text{PuO}_2$	
	10 $\mu\text{Ci/ml}^a$	2000 $\mu\text{Ci/ml}^b$	10 $\mu\text{Ci/ml}^b$	2000 $\mu\text{Ci/ml}^c$
77	11.1	130	0.13	0.06
112	11.1	121	0.12	0.06
156	10.7	107	0.10	0.06
205	10.0	102	0.09	0.05

^a0.8 $\mu\text{g/ml}$.

^b150 $\mu\text{g/ml}$.

^c28 mg/ml .

equal activity level. ^{238}Pu is released 2000 times faster than is ^{239}Pu .

There are obvious anomalies in the data among various experimental conditions even though the agreement between duplicate experiments was within $\pm 5\%$ or better. All experiments show a definite trend toward lower release rates as their duration increases. In this, as in earlier experiments,¹ we noticed a sudden burst of plutonium released to the solvent on the first day. The data in Table IV have been adjusted to minimize the effect of this initially rapid increase, to provide a better estimate of the long-term release rates. This adjustment, excluding the first two days' data from the slope calculations, may not have eliminated the effect of the initial release completely. On the other hand, the trend may be real, owing its existence to an unknown, but slow reaction between the solvent and the particle surfaces. Another anomaly is the nonlinear relation between the amount of radioactivity and the release rate of both materials. A 200-fold increase in the $^{238}\text{PuO}_2$ alpha activity level (10 to 2000 $\mu\text{Ci/ml}$) results in a 10-fold increase in release rate. The 200-fold increase in $^{239}\text{PuO}_2$ alpha activity level decreases the release rate by a factor of 2. This anomaly may have resulted partly from the relatively large mass of ^{239}PuO (1.4 g in 50 ml) which was difficult to keep in suspension. Nevertheless, in both the ^{238}Pu and ^{239}Pu experiments, there is an inverse relationship between total plutonium oxide mass and release rate in terms of curies per square meter per second per gram.

The difference in release rates is attributable, not to the mass difference between the two isotopes, but rather, as Fleischer recently pointed out,² to the difference in alpha particle specific activity, that of ^{238}Pu being 280 times higher than that of ^{239}Pu . This activity increases the release rate of plutonium atoms or submicroscopic particles from the solid oxide because of increased radiation damage to the crystal lattice. Fleischer's model predicts ejection of particles containing up to 10 000 plutonium atoms by the action of the uranium recoil nucleus near the surface of a plutonium oxide grain.

These observations agree qualitatively with measurements made earlier in distilled water and in normal saline solution, both of which aqueous environments approximate natural conditions and animal body fluids, although chemically they introduce additional competing reactions for plutonium dissolution.¹ These earlier experiments generally showed ^{238}Pu release rates of 3 to 50

ng/m²-s, whereas the ²³⁹Pu release rates were at least an order of magnitude lower.

IV. CONCLUSIONS

Plutonium is released from suspensions of ²³⁸PuO₂ in 1M HClO₄ more rapidly than it is from ²³⁹PuO₂ when the two materials are compared on both equal radioactivity and equal mass bases. This is not a true isotope effect, but the result of the much higher radioactivity level of ²³⁸Pu than of ²³⁹Pu. The effect of particle size on the release rate of plutonium from ²³⁸PuO₂ will be investigated further.

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