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THE FORMATION OF PLUTONIUM(IV) COLLOID BY ~~THE~~ THE ALPHA-REDUCTION OF AQUEOUS SOLUTIONS OF Pu(V) AND Pu(VI)[*]

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THE FORMATION OF PLUTONIUM(IV) COLLOID BY THE THE ALPHA-REDUCTION OF AQUEOUS SOLUTIONS OF Pu(V) AND Pu(VI)

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INTRODUCTION

The most common isotope of plutonium, ^{239}Pu, emits alpha particles with an average energy of 5.15 MeV and has a half life of 24,360 years.[1] For plutonium in solution, this *self-irradiation* has important effects in any long term experiment. These effects, for acid solutions, have been reviewed elsewhere.[2,3] The alpha-radiolysis of water produces H_2O_2 and the radicals H, OH, and HO_2, all of which are capable of reacting with the various oxidation states of plutonium. In perchloric acid solutions ^{239}Pu(VI) is reduced to Pu(V) at a rate of about 1.5% of the total plutonium concentration per day. The Pu(V) formed disappears by disproportionation; there is no evidence that it is reduced by the radiolysis products.[4]

Only fragmentary results on alpha-particle-induced reactions of plutonium have been reported for solutions with pH values near 2.[5] Further work is needed because this is the region in which the most reliable determination of the solubility of PuO_2 has been caried out.[6] In addition, the effects of alpha radiation in this pH region are expected to differ from those in more acidic solutions because Pu(V) is much more stable and the Pu(IV) colloid forms relatively rapidly from $Pu(IV)_{(aq)}$. [7-9]

Thus the overall reaction

$$2PuO_2^+ \longrightarrow PuO_2^{2+} + PuO_{2\,(coll)} \qquad (1)$$

and possibly its reverse may be expected to be important in describing alpha-particle effects under conditions where colloidal Pu(IV) can form.

The equilibrium for reaction (1) is given by

$$Q_1 = \frac{[PuO_2^{2+}]}{[PuO_2^+]^2} \qquad (2)$$

and is related to the solubility product, $[Pu^{4+}][OH^-]^4$, for colloidal Pu(IV) by way of the disproportionation equilibrium

$$2PuO_2^+ + 4H^+ \longrightarrow Pu^{4+} + PuO_2^{2+} + 2H_2O \qquad (4)$$

Log Q_3 for reaction (3) is calculated to be 4.290, based on the formal potentials in 1 *M* $HClO_4$[10] and 1.893 at zero ionic strength, based on the ionic strength dependence found for the analogous uranium reaction.[11]

We shall define Q′ as an *experimental concentration quotient* having the form of equation (2) but not necessarily reflecting an equilibrium condition. Several previous reports contain data that can be used to calculate Q′, for reaction (1). Due to the slowness of the reaction and possible radiation effects, it is not clear that equilibrium was reached in these experiments. The results of these calculations are summarized in Table 1. The values calculated for log Q′ range from 1.41 to 4.10.

TABLE 1

Log Q′ Values Calculated from Literature Data

μ	Total Pu Conc.,(*M*)	Time (days)	pH	log Q′	Author [Ref.]
1	1.53×10^{-3}	4.2	1.28[a]	3.75	Kasha [12]
		8.3		3.80	
		12.5		3.83	
		18.8		3.87	
~0.16	9.2×10^{-3}	0.5	1.0[a]	2.56	Costanzo
		0.625		2.54	et al., [7]
0.12	9.4×10^{-3}	0.5	1.22[a]	2.88	
		0.625		2.85	
0.1	9.3×10^{-3}	0.5	1.40[a]	> 4[b]	
		0.625		> 4[b]	
0	6×10^{-3}	83	1.0	2.18	Rai [6]
			1.2	4.19	
			1.45	3.83	
			1.80	3.50	
			2.00	2.63	
			2.30	4.10	
			2.80	3.32	
			3.10	3.75	
			3.40	3.77	
1.0	0.04[d]	10	3.7	1.41[c]	Madic
		11		1.56	et al., [13]
		13		1.78	
		15		1.97	
		20		2.30	

a Initial value

b Concentrations too low for a precise value.

c Concentration values read from Figure 13 in the Reference.

d ^{242}Pu used in this work

In this paper we describe concentration changes caused by chemical and alpha-induced radiolytic reactions in various oxidation state pure solutions of Pu(VI), Pu(V), or Pu(IV) colloid or mixtures of these oxidation states at pH values > 1 for a period of nearly two years. The rates of approach to steady-states and the resulting Q' values were determined in order to find the conditions under which equilibrium in reaction (1) might be attained and to learn about the underlying reactions. Computer calculations were used to compare the data with the results required from proposed reaction schemes.

EXPERIMENTAL

SOLUTIONS

Plutonium(III) solutions were prepared by acid dissolution of Pu metal or by reduction of higher oxidation states of Pu with zinc amalgam. Plutonium(VI) solutions were prepared by perchloric acid fuming or electrolytic oxidation of lower oxidation states. Rose-colored Pu(V) solutions were made by electrolytic reduction of Pu(VI) at a platinum screen cathode (+ 0.79 V/NHE, pH > 2). Pu(IV) solutions were prepared by mixing stoichiometric amounts of Pu(VI) and Pu(III) or by electrolytic oxidation of Pu(III) at a platinum anode (+ 1.1 V/NHE, pH < 0). Colloidal sols of Pu(IV) were made by dilution of concentrated solutions of Pu(IV) in 3 *M* HCl to < 0.01 *M* HCl. These solutions were left standing for two weeks at room temperature followed by purification by ion exchange or centrifugation.

ANALYSIS

The various oxidation states of plutonium were determined spectrophotometrically. Pu(VI) was determined in $HClO_4$ solution by using the sharp peak near 830 nm. Pu(V) was determined from the increase of the Pu(VI) peak after addition of excess Ce(IV) perchlorate. The Pu(IV) colloid reacts quite slowly with Ce(IV) so it does not interfere with the Pu(V) analysis.

The presence of colloid was indicated by the characteristic green color. This was confirmed spectrophotometrically for some samples.

INSTRUMENTATION

A Cary Model 17D spectrophotometer was used for spectral analysis. Electrochemical procedures were performed using an E.G.&G. PARC Model 173/179 Potentiostat/Coulometer. Values for pH were determined using a Corning combination pH electrode and either a Corning Model 130 or a Beckman Model 4500 pH Meter.

PROCEDURES

Oxidation state pure solutions or appropriate mixtures were made volumetrically and stored at room temperature. Periodically, samples were removed for analysis as described above.

RESULTS AND DISCUSSION

The qualitative behavior of the plutonium solutions is conveniently shown on ternary plots, since Pu(VI), Pu(V), and Pu(IV)-colloid are the principal substances present. No evidence for the presence of Pu(III) was found in these solutions. The results of typical runs are shown in Figures 1, 2, and 3. Initially pure solutions of Pu(VI) form Pu(V) at first and then form the colloid. Initially pure solutions of Pu(V) form both Pu(VI) and Pu(IV)-colloid with increasing concentrations of the colloid as time goes on. Suspensions of colloidal Pu(IV) form small concentrations of Pu(VI) and Pu(V). After sufficient time, all the mixtures appear to become predominantly Pu(IV)-colloid.

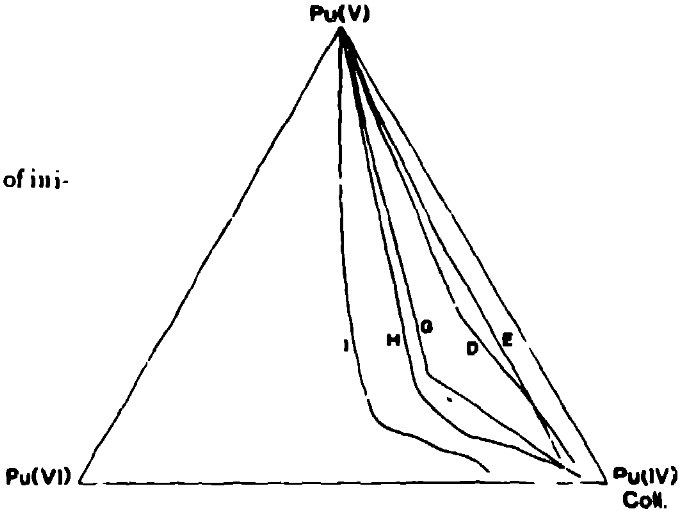

Figure 1. Ternary composition plot of initially pure Pu(V) solutions.

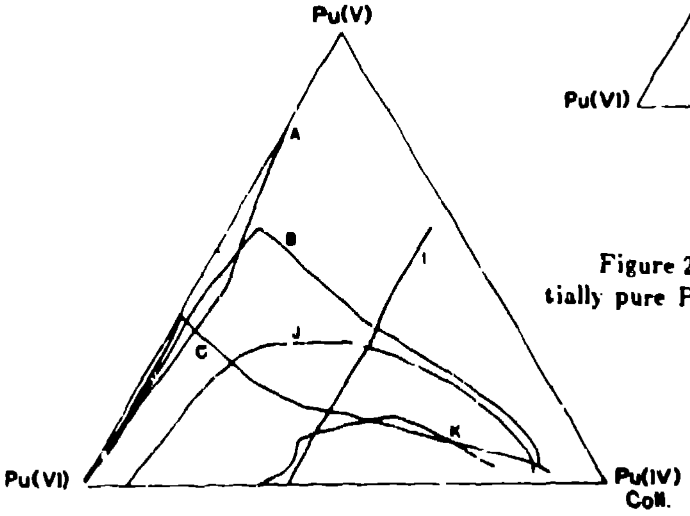

Figure 2. Ternary composition plot of initially pure Pu(VI) solutions.

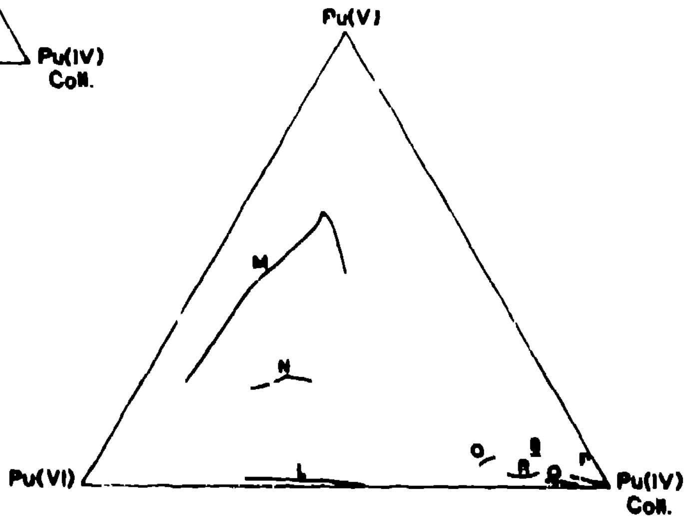

Figure 3. Ternary composition plot of initially pure Pu(IV) colloid solutions and various mixtures.

The overall effect of alpha-irradiation is to change the average oxidation state, $\overline{ox}$, defined as

$$\overline{ox} = \frac{3[\mathrm{Pu(III)}] + 4[\mathrm{Pu(IV)}] + 5[\mathrm{Pu(V)}] + 6[\mathrm{Pu(VI)}]}{\mathrm{Total}[\mathrm{Pu}]} \tag{5}$$

Figures 4 and 5 show typical $\overline{ox}$ versus time data for various runs.

Because of the importance of the equilibrium in reaction (1), it is of interest to examine the values of Q′, the experimental concentration quotient, versus time. A typical plot is shown in Figure 6. For many of the runs, the values of log Q′ are close to 4 after long time periods. Additional information is displayed in concentration profile plots (Figures 7 and 8) of Pu(VI) and Pu(V) versus time.

A careful and exhaustive consideration of the data has not resulted in a convincing reaction scheme with a consistent set of rate parameters. However a model that approximates the observed behavior would be helpful in understanding the very complicated system involved, including the significance of the steady-state log Q′ values. The model is described briefly below. The following assumptions are made: (a) alpha particles react with water to form hydrogen peroxide or radicals that are rapidly consumed in the following reactions; (b) only a single reactive intermediate is important; and (c) this intermediate reacts with other species in the solution as an oxidizing agent as well as a reducing agent. The provisional model consists of the following reactions and rate terms:

$$\mathrm{H_2O} = \mathrm{R} \tag{5}$$

$$\mathrm{R} + \mathrm{Pu(VI)} = \mathrm{Pu(V)} + \mathrm{R'} \tag{6}$$

$$2\mathrm{Pu(V)} = \mathrm{Pu(VI)} + \mathrm{Pu(IV)}_{(\mathrm{coll})} \tag{7}$$

$$\mathrm{R} + \mathrm{Pu(V)} = \mathrm{Pu(IV)}_{(\mathrm{coll})} + \mathrm{R'} \tag{8}$$

$$2\mathrm{R} + \mathrm{Pu(IV)}_{(\mathrm{coll})} = \mathrm{Pu(VI)} + 2\mathrm{R'} \tag{9}$$

Equation no.	Rate Expression
(5)	$\alpha([\mathrm{Pu(VI)}]+[\mathrm{Pu(V)}]) + \alpha_c[\mathrm{Coll}]$
(6)	$k_6[\mathrm{R}][\mathrm{Pu(VI)}]$
(7)	$k_7[\mathrm{Pu(V)}]^2[\mathrm{H^+}] - k_{-7}[\mathrm{Pu(VI)}][\mathrm{H^+}]$
(8)	$k_8[\mathrm{R}][\mathrm{Coll}][\mathrm{Pu(V)}]$
(9)	$k_9[\mathrm{R}][\mathrm{Coll}]$

where:

R stands for hydrogen peroxide or a radical.

R′ is the appropriate reaction product.

[Coll] stands for the concentration of colloidal Pu(IV) in moles of plutonium per liter.

This reaction model and modifications of it were investigated by making the usual steady-state approximation for the concentration of R and solving the resulting rate equations for the concentrations of Pu(VI) and Pu(V) versus time using the Runge-Kutta method[14]. The calculated plots are shown as dashed lines in Figures [illegible] 7and 8.

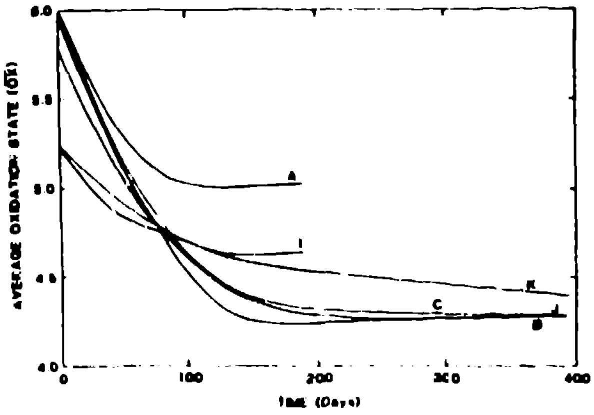

Figure 4. Average oxidation state versus time plots for initially pure Pu(VI) and for Pu(VI)-Pu(V) mixtures.

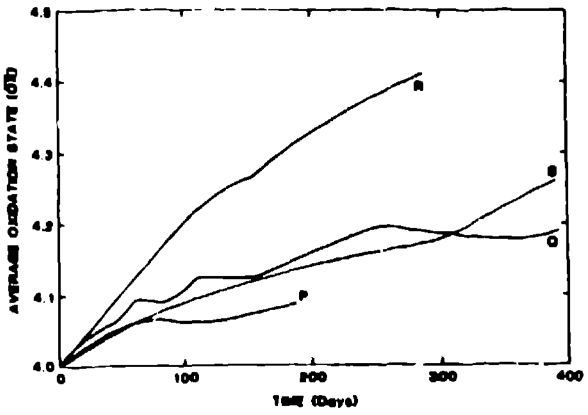

Figure 5. Average oxidation state versus time plots for initially pure Pu(IV) colloid solutions.

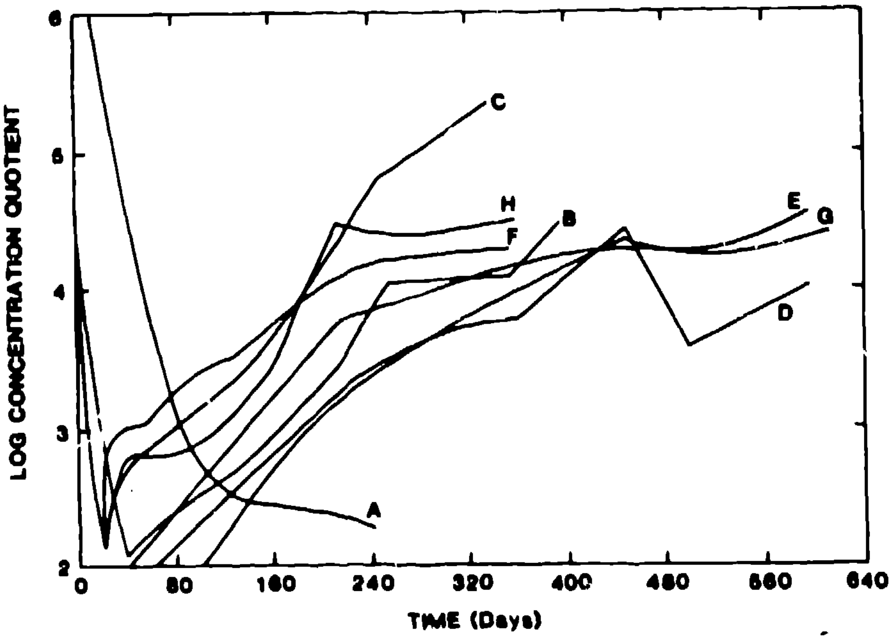

Figure 6. Log Q' versus time for a number of various plutonium solutions.

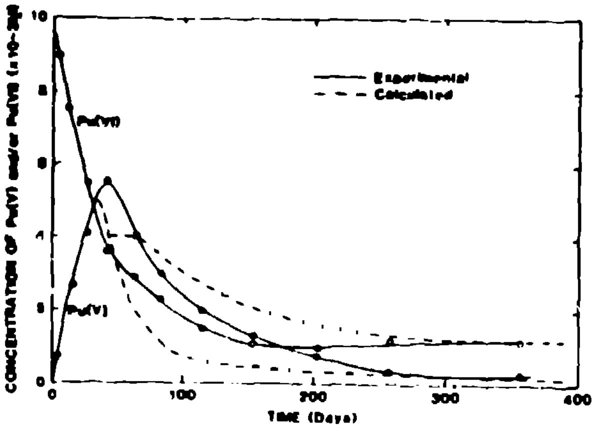

Figure 7. Pu(VI) and Pu(V) concentration versus time plots for an initially pure Pu(VI) solution.

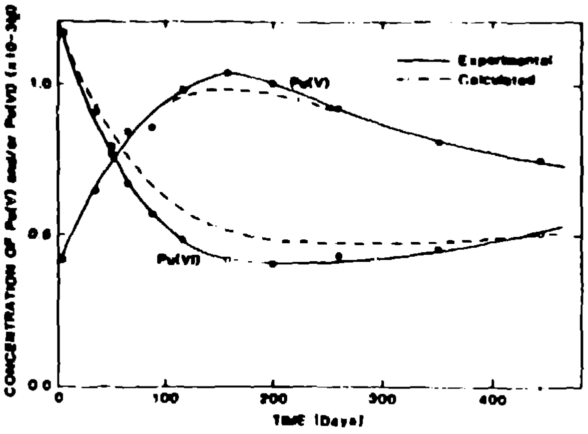

Figure 8. Pu(VI) and Pu(V) concentration versus time plots for a Pu(VI)-Pu(V) mixture.

CONCLUSIONS

The following is a brief summary of the conclusions resulting from this study. The simple computer model. although not completely satisfactory, does approximate the experimental data in a qualitative manner with regards to concentration profiles, $\overline{ox}$, and Q'. Any value for log Q' greater than about 3 is consistent with the data. Steady-state concentrations, which may be far from equilibrium, depend on total plutonium concentration. Some of the data suggest that the kinetic properties of the colloid formed are not constant, but depend on such factors as the age of the colloid and the concentration at which it was formed. Our work with colloid suspensions shows that conventional long term solubility experiments with PuO_2 will not reach equilibrium because of alpha self irradiation. A complete report of this work will be published elsewhere.[15]

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