

LPDR
WM-10 (2)
WM-11 (2)
WM-16 (2)

A1756

JAN 5 1987

426.1 WK/86/12/29/B

- 1 -

Dr. Malcolm D. Siegel
Division 6431
Sandia National Laboratories
Albuquerque, NM 87185

Dear Dr. ^{Malcolm} Siegel:

SUBJECT: CONTRACT NO. 50-19-03-01/FIN A-1756, "GEOCHEMICAL
SENSITIVITY ANALYSIS"

I have reviewed the November, 1986 monthly progress report for the above contract, dated December 15, 1986. Based on my review of this report, progress to date is satisfactory.

I have completed a more detailed review of Pu thermodynamic data, which is enclosed. Phillips has taken data for all Pu phases except two ($\text{Pu}(\text{SO}_4)_2(\text{S})$ and $\text{PuCO}_3^{2+}(\text{aq})$) directly from Lemire and Tremaine (1980). A more recent review of Pu data raises questions about some of the data in Lemire and Tremaine; these are discussed in the enclosure.

As we discussed, I contacted David Smith-Magowan of NBS to discuss the CATCH system. When I receive and review the documents he is sending me, I will determine if I want to pursue it with the Pu data in the ASD.

The action taken by this letter is considered to be within the scope of the current contract FIN A-1756. No changes to costs or delivery of contract products is authorized. Please notify me immediately if you believe this letter would result in changes to costs or delivery of contracted products.

Sincerely,

W

Walton R. Kelly
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure:
As stated

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In my review of the Pu data in the Aqueous Solutions Database (ASD), I consulted the following documents:

Cleveland, J.M., 1979, "Critical Review of Plutonium Equilibrium of Environmental Concern," in Chemical Modeling in Aqueous Systems, E.A. Jenne, ed., ACS Symposium Series 93, Washington, pp. 321-338.

Plutonium Chemistry, 1983, W.T. Carnall and G.R. Choppin, eds., ACS Symposium Series 216, Washington: chapters by G.R. Choppin; J.C. Sullivan; B. Allard and J. Rydberg.

Lemire, R.J., and P.R. Tremaine, 1980, "Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C," J. Chem. Eng. Data, v. 25, pp. 361-370.

Unpublished review of Pu thermodynamic data by A.P. Schwab and A.R. Felmy, 1983: abstract presented at the ACS National Meeting, Seattle, March 20-25, 1983.

Pu Aqueous Chemistry

Pu has four common oxidation states (III, IV, V, VI), and, due to disproportionation reactions (especially for Pu(IV) and Pu(V) species), they can coexist in solution, complicating experimental set-ups (Sullivan, 1983). In acidic solutions, in which most Pu studies have been done, the lower oxidation states tend to be more stable. With increasing basicity, the higher oxidation states tend to become more stable. This trend, however, can be obscured by several factors, including complexation. For example, Pu(III) is stable in warm, acidic water. When citrate or EDTA is added to solution, Pu(III) partially oxidizes to Pu(IV), which forms stronger complexes relative to Pu(III) (Choppin, 1983).

Pu^{4+} is the strongest complexer, followed by PuO_2^{2+} (Pu(VI)), Pu^{3+} , and PuO_2^+ (Pu(V)) (Choppin, 1983). Pu complexation is dominated by hydroxides and carbonates. Sulfates and fluorides also form relatively strong complexes. Nitrates and phosphates may also form significant complexes. Chloride complexes tend to be weak. Important organic complexers that have been studied include citrate, TBP, and EDTA (Cleveland, 1979). Polymerization is an important process, especially for Pu(IV). Polymerization is not significant until $[\text{Pu}]_T > 10^{-6}$ M, increasing with increasing concentration, and it tends to be irreversible. Polymers can be decomposed by acidification or by oxidation of Pu(IV) to Pu(VI) (Choppin, 1983).

Pu concentrations in solution under oxic conditions tend to be limited by the solubility of $\text{PuO}_2(\text{s})$, and $\text{Pu}(\text{OH})_4^0$ (Pu(IV)) is generally the dominant species in solutions (pH = 6-9) (Allard and Rydberg, 1983). Pu(IV) species are generally predominant under oxic, neutral-pH, low carbonate conditions (Allard and Rydberg, 1983). Under slightly more acidic conditions (pH below 5-6), PuO_2^+ would dominate, and at pH below 3-4, Pu^{3+} would be the major species. Pu(VI) species would not contribute significantly unless the environmental conditions were highly oxidizing and acidic. At high pH and high carbonate concentrations, a Pu(V)-carbonate species such as $\text{PuO}_2(\text{CO}_3)_3^{5-}$ may be predominant. Pu(V) species may be predominant in sea water. Under reducing conditions, $\text{PuO}_2(\text{s})$ limits Pu solubility when pH is greater than 7 or 8. $\text{Pu}_2(\text{CO}_3)_3(\text{s})$ is limiting at lower pH's. Pu(III) species dominate in natural water pH ranges, although in non-acidic solutions they may be obscured by complexation catalyzed by oxidation to Pu^{4+} (Choppin, 1983). A pe-pH diagram for Pu from Schwab and Felmy (1983) is attached.

Pu Thermodynamic Data

Good thermodynamic data are generally lacking for Pu. Cleveland (1979) has made recommendations for needed research. These include research on (1)

stabilities at low concentrations of metals and higher pH, (2) stabilities of Pu-carbonates, (3) interplay of complexation, hydrolysis, and polymerization at pH values of environmental concern, (4) Pu(V) chemistry, and (5) polymeric species behavior.

Schwab and Felmy (1983) did a critical evaluation of Pu thermodynamic data. Because Phillips takes almost all of his data from Lemire and Tremaine (1980), the Schwab and Felmy review is in general more up-to-date than the ASD. Their review, however, is almost four years old and many of the data they selected may be out-of-date. Their results are for the most part in agreement with the ASD. However, there are a number of differences which may be important in using the Pu data in the ASD for predictive purposes. These differences are discussed below.

The ΔG_f° values for Pu solids generally show good agreement. However, Schwab and Felmy rejected the data for two solids in the ASD, $\text{PuO}_2(\text{OH})_2(\text{s})$ and $\text{PuO}_2\text{HPO}_4(\text{s})$. In addition, they found discrepancies in the data for $\text{Pu}(\text{HPO}_4)_2(\text{s})$ and recommended another value calculated from King (1949). Schwab and Felmy included an additional solid for Pu, $\text{Pu}(\text{OH})_{2.5}\text{Cl}_{0.5}(\text{s})$, which is basically solid solution of $\text{Pu}(\text{OH})_3(\text{s})$. A comparison between ΔG_f° values recommended by Schwab and Felmy and those in the ASD is presented in tables 1 and 2.

For aqueous hydrolysis species, Schwab and Felmy rejected the data for a number of species, including PuO_2OH^+ , $(\text{PuO}_2)_3(\text{OH})_5^+$, $\text{PuO}_2\text{OH}^\circ$, $\text{Pu}(\text{OH})_2^{2+}$, and $\text{Pu}(\text{OH})_5^-$. $\text{PuO}_2\text{OH}^\circ$ data are rejected because the species is unstable, and $\text{Pu}(\text{OH})_5^-$ data are rejected because the existence of the species is questioned. Phillips addresses this latter concern in the comments section of the ASD, electing to keep data for $\text{Pu}(\text{OH})_5^-$ in the ASD. The other species were rejected because of inconsistencies in the reported data. Schwab and Felmy recalculated ΔG_f° for PuOH^{2+} by extrapolating from a linear correlation with Cm(III). The Cm(III) constants were taken from Rai and Serne (1978) and were not reviewed.

Schwab and Felmy did not include several fluoride species found in the ASD, $\text{PuO}_2\text{F}_2^\circ$, PuO_2F_3^- , and PuO_2F_4^- , due to inconsistencies in the reported data. For the other two fluoride species in the ASD, Schwab and Felmy rejected the data used in the ASD. For PuO_2F^+ , they accepted data from Patil and Ram (1976), and for PuF^{3+} , they accepted data from Bagawde et al. (1976a, 1976b). They also included an additional species not found in the ASD, PuF_2^{2+} , in their compilation.

For chloride and sulfate species, the data agree for all species found in the ASD. Schwab and Felmy included additional species, including PuCl^{2+} , PuCl_2^{2+} , $\text{PuO}_2\text{Cl}_2^\circ$, $\text{Pu}(\text{SO}_4)_2^-$, and $\text{Pu}(\text{SO}_4)_2^\circ$.

Schwab and Felmy rejected the data for $\text{PuO}_2(\text{CO}_3)_2^-$, although stating that this could be an important species. They also rejected PuCO_3^{2+} , stating that its existence is of very low probability. Phillips presents more recent data to support its inclusion in the ASD.

Nitrate and phosphate complexes are not included in the ASD. Schwab and Felmy included data for several of these complexes in their compilation.

Recommendations

Due to the more extensive review by Schwab and Felmy, consideration should be given to using their selected data where there is a significant difference from ASD values. These include ΔG_f° values for:

- ° $\text{Pu}(\text{HPO}_4)_2(\text{s})$
- ° aqueous species PuOH^{2+} , PuO_2F^+ , and PuF^{3+}

In addition, Schwab and Felmy recalculated several values which are slightly different than values in the ASD. These differences are noted in tables 1 and

2. Consideration should also be given to including additional solids and aqueous species in the ASD that Schwab and Felmy identified as being of potential importance. These include:

- $\text{Pu}(\text{OH})_{2.5}\text{Cl}_{0.5}(\text{s})$
- aqueous species $(\text{PuO}_2)_4(\text{OH})_7^+$, PuF_2^{2+} , $\text{PuO}_2\text{Cl}_2^0$, PuCl_2^{2+} , PuCl^{2+} , $\text{Pu}(\text{SO}_4)_2^0$, $\text{Pu}(\text{SO}_4)_2^-$, $\text{Pu}(\text{OH})_4\text{CO}_3^-$, nitrates, and phosphates

Schwab and Felmy rejected a number of data for Pu phases in the ASD due to inconsistencies. This does not necessarily imply that these phases should be deleted from the ASD since their existence has not been ruled out. However, it would benefit users of the ASD if these questionable data are indicated.

Because Schwab and Felmy did not publish their report, I suggest they be contacted directly if there is any interest in their methods.

Figure 1. Predominance area diagram for Pu species (uncomplexed ions and hydrolysis species only). The shaded areas represent uncertainties. From Schwab and Felmy (1983).

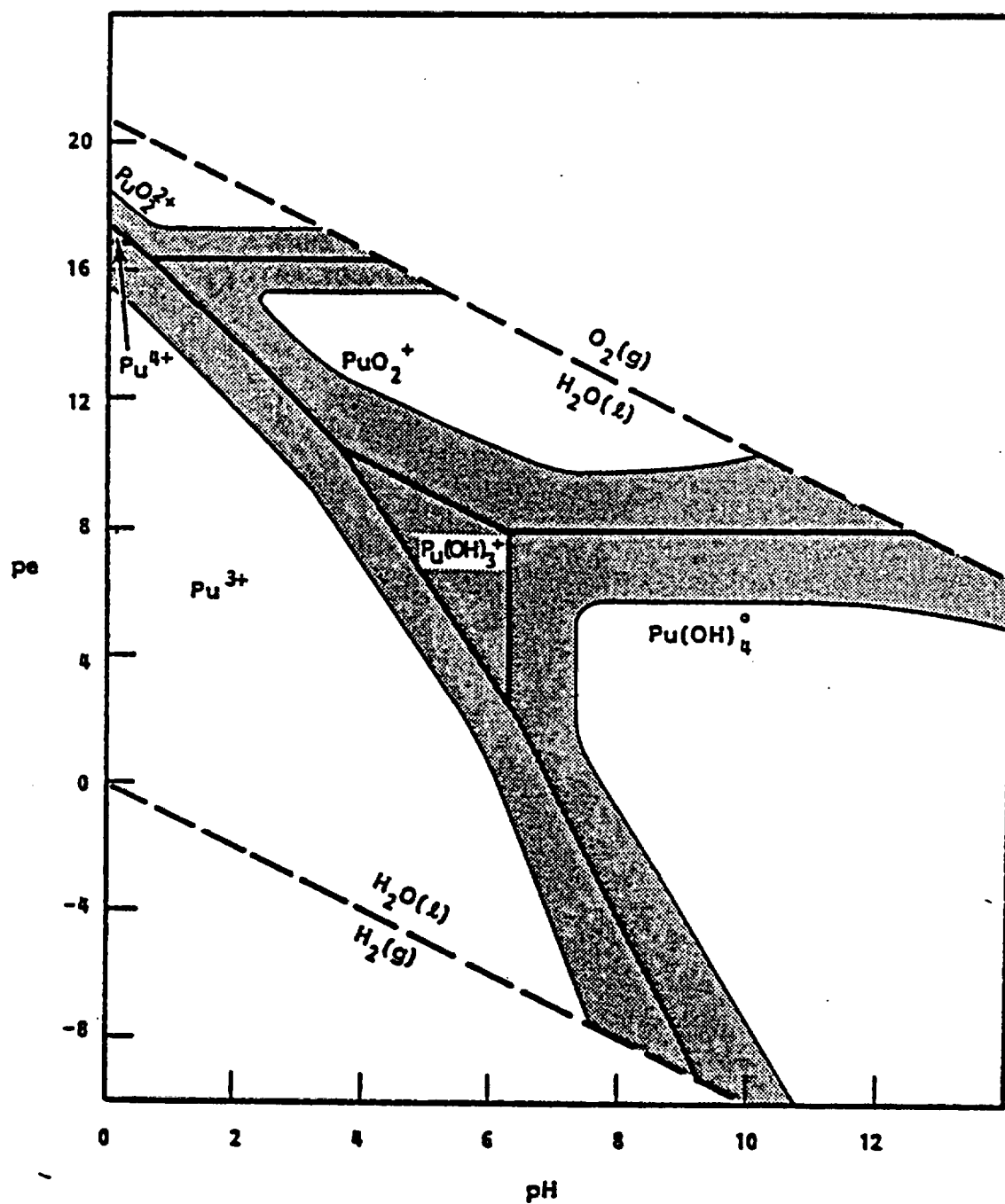


Table 1. Comparison of thermodynamic data for Pu-bearing solids.

Solid	Valence	ASD (11/3/86) ΔG_f° (kJ/mol)	Schwab and Felmy (1983) ΔG_f° (kJ/mol)
PuO_2	IV	-998.0	-998.0
<u>Pu_2O_3</u>	III	<u>-1594.0</u>	<u>-1603.0</u>
$\text{PuO}_2(\text{OH})_2$	VI	-1211.0	----
$\text{PuO}_2(\text{OH})(\text{am})$	V	-1056.0	-1056.0
$\text{Pu}(\text{OH})_4$	IV	-1426.0	-1426.0
<u>$\text{Pu}(\text{OH})_3$</u>	III	<u>-1162.0</u>	<u>-1176.0</u>
PuF_4	IV	-1684.0	-1684.0
PuF_3	III	-1482.0	-1483.0
PuO_2HPO_4	VI	-1918.0	----
<u>$\text{Pu}(\text{HPO}_4)_2$</u>	IV	<u>-2818.0</u>	<u>-2714.0</u>
$\text{Pu}(\text{SO}_4)_2$	IV	-2012.5	-2013.0
$\text{Pu}(\text{OH})_{2.5}\text{Cl}_{0.5}$	III	----	-1149.0

Table 2. Comparison of thermodynamic data for Pu-bearing aqueous species.

Aqueous Species	Valence	ASD (11/3/86) ΔG_f° (kJ/mol)	Schwab and Felmy (1983) ΔG_f° (kJ/mol)
PuO_2^{2+}	VI	-756.9	-756.9
PuO_2^+	V	-849.8	-849.8
Pu^{4+}	IV	-481.6	-481.6
Pu^{3+}	III	-578.6	-578.7
PuO_2OH^+	VI	-961.9	----
$(\text{PuO}_2)_2(\text{OH})_2^{2+}$	VI	-1941.0	-1941.3
$(\text{PuO}_2)_3(\text{OH})_5^+$	VI	-3333.0	----
$(\text{PuO}_2)_4(\text{OH})_7^+$	VI	----	-4521.7
$\text{PuO}_2\text{OH}^\circ$	V	-1032.0	----
PuOH^{3+}	IV	-715.9	-716.2
$\text{Pu}(\text{OH})_2^{2+}$	IV	-942.7	----
$\text{Pu}(\text{OH})_3^+$	IV	<u>-1163.0</u>	<u>-1167.5</u>
$\text{Pu}(\text{OH})_4^\circ$	IV	<u>-1376.0</u>	<u>-1369.4</u>
$\text{Pu}(\text{OH})_5^-$	IV	-1582.0	----
<u>PuOH^{2+}</u>	III	<u>-770.3</u>	<u>-949.1</u>
<u>PuO_2F^+</u>	VI	<u>-1071.0</u>	<u>-1044.8</u>
$\text{PuO}_2\text{F}_2^\circ$	VI	-1383.0	----
PuO_2F_3^-	VI	-1693.0	----
PuO_2F_4^-	VI	-1991.0	----
<u>PuF^{3+}</u>	IV	<u>-808.8</u>	<u>-789.8</u>
PuF_2^{2+}	IV	----	-1087.5
PuO_2Cl^+	VI	-887.0	-888.1
$\text{PuO}_2\text{Cl}_2^\circ$	VI	----	-342.6
<u>PuCl^{3+}</u>	IV	<u>-618.0</u>	<u>-613.7</u>
PuCl_2^{2+}	IV	----	-177.0
PuCl^{2+}	III	----	-169.7

Table 2. Comparison of thermodynamic data for Pu-bearing aqueous species (cont.)

Aqueous Species	Valence	ASD (11/3/86) ΔG_f° (kJ/mol)	Schwab and Felmy (1983) ΔG_f° (kJ/mol)
$\text{PuO}_2\text{SO}_4^\circ$	VI	-1520.0	-1514.1
PuSO_4^{2+}	IV	-1259.0	-1248.5
$\text{Pu}(\text{SO}_4)_2^\circ$	IV	----	-2009.6
PuSO_4^+	III	-1343.0	-1334.6
$\text{Pu}(\text{SO}_4)_2^-$	III	----	-2085.3
$\text{PuO}_2(\text{CO}_3)_2^\circ$	VI	-1898.0	----
PuCO_3^{2+}	IV	-1070.0	----
$\text{Pu}(\text{OH})_4\text{CO}_3^\circ$	IV	----	-1936.6
$\text{PuO}_2\text{NO}_3^+$	VI	----	-847.3
PuNO_3^{3+}	IV	----	-596.3
$\text{Pu}(\text{NO}_3)_2^{2+}$	IV	----	-710.5
PuNO_3^{2+}	III	----	-694.5
$\text{Pu}(\text{NO}_3)_2^+$	III	----	-808.2
$\text{Pu}(\text{NO}_3)_3^\circ$	III	----	-919.5
$\text{PuH}_2\text{PO}_4^{3+}$	IV	----	-1594.1
$\text{Pu}(\text{H}_2\text{PO}_4)_2^{2+}$	IV	----	-2700.4
$\text{Pu}(\text{H}_2\text{PO}_4)_3^+$	IV	----	-3804.3
$\text{Pu}(\text{H}_2\text{PO}_4)_4^\circ$	IV	----	-4905.4
$\text{PuH}_2\text{PO}_4^{2+}$	III	----	-1675.7
$\text{Pu}(\text{H}_2\text{PO}_4)_2^+$	III	----	-2768.2

ADDITIONAL REFERENCES

- Allard, B., and J. Rydberg, 1983, "Behavior of Plutonium in Natural Waters," in Plutonium Chemistry, W.T. Carnall and G.R. Choppin, eds., ACS Symposium Series 216, Washington, pp. 275-295.
- Bagawde, S.V., V.V. Ramakrishna and S.K. Patil, 1976a, "Aqueous TTA Complexing of Np(IV) and Pu(IV)," J. Inorg. Nucl. Chem., v. 38, pp. 2085-2089.
- , 1976b, "Complexing of Tetravalent Plutonium in Aqueous Solutions," J. Inorg. Nucl. Chem., v. 38, pp. 1339-1345.
- Choppin, G.R., 1983, "Aspects of Plutonium Solution Chemistry," in Plutonium Chemistry, pp. 213-230.
- King, E.L., 1949, "The Solubility of Pu(IV) Phosphates and the Phosphate Complexes of Plutonium(IV)," in Transuranium Elements, G.T. Seaborg, J.J. Katz, and W.M. Manning, eds., Natl. Nucl. Energy Series IV, v. 14B, McGraw-Hill, NY, pp. 638-665.
- Patil, S.K. and V.V. Ramakrishna, 1976, "Sulphate and Fluoride Complexing of U(VI), Np(VI), and Pu(VI)," J. Inorg. Nucl. Chem., v. 38, pp. 1075-1078.
- Rai, D., and R.J. Serne, 1978, Solid Phases and Solution Species of Different Elements in Geologic Environments, PNL-2651, Battelle, Pacific Northwest Laboratory, Richland, WA.
- Sullivan, J.C., 1983, "Reactions of Plutonium Ions with the Products of Water Radiolysis," in Plutonium Chemistry, pp. 241-249.

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LETTER TO: Dr. Malcolm D. Siegel
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Albuquerque, NM 87185

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SUBJECT: SUBJECT: CONTRACT NO. 50-19-03-01/FIN A-1756,
"GEOCHEMICAL SENSITIVITY ANALYSIS"

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