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Water Solubility of Plutonium and Uranium Compounds and Residues at TA-55

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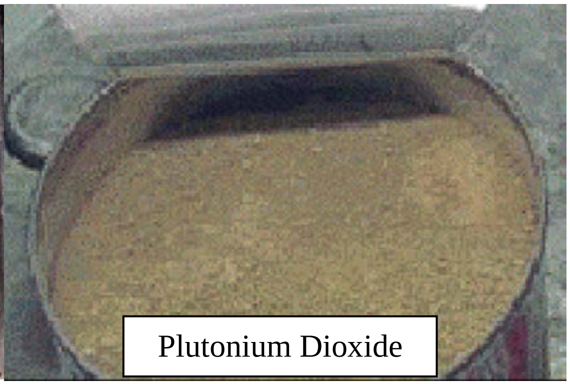
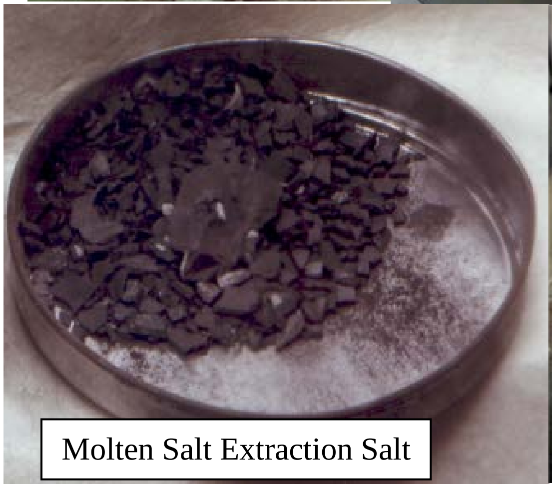
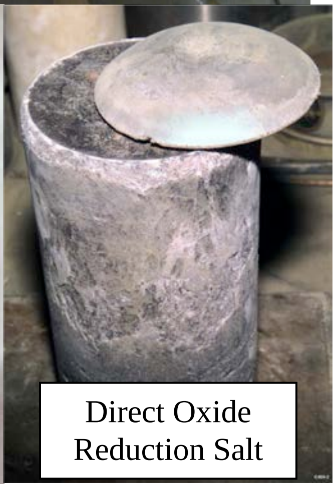
Plutonium Trichloride


Plutonium Dioxide


Electrorefining Salt


Filter Residue


Molten Salt Extraction Salt


Direct Oxide
Reduction Salt

Water Solubility of Plutonium and Uranium Compounds and Residues at TA-55

Executive Summary

Understanding the water solubility of plutonium and uranium compounds and residues at TA-55 is necessary to provide a technical basis for appropriate criticality safety, safety basis and accountability controls. Individual compound solubility was determined using published solubility data and solution thermodynamic modeling. Residue solubility was estimated using a combination of published technical reports and process knowledge of constituent compounds. The scope of materials considered includes all compounds and residues at TA-55 as of March 2016 that contain Pu-239 or U-235 where any single item in the facility has more than 500 g of nuclear material. This analysis indicates that the following materials are not appreciably soluble in water: plutonium dioxide (IDC=C21), plutonium phosphate (IDC=C66), plutonium tetrafluoride (IDC=C80), plutonium filter residue (IDC=R26), plutonium hydroxide precipitate (IDC=R41), plutonium DOR salt (IDC=R42), plutonium incinerator ash (IDC=R47), uranium carbide (IDC=C13), uranium dioxide (IDC=C21), U_3O_8 (IDC=C88), and uranium filter residue (IDC=R26). This analysis also indicates that the following materials are soluble in water: plutonium chloride (IDC=C19) and uranium nitrate (IDC=C52). Equilibrium calculations suggest that PuOCl is water soluble under certain conditions, but some plutonium processing reports indicate that it is insoluble when present in electrorefining residues (R65). Plutonium molten salt extraction residues (IDC=R83) contain significant quantities of $PuCl_3$, and are expected to be soluble in water. The solubility of the following plutonium residues is indeterminate due to conflicting reports, insufficient process knowledge or process-dependent composition: calcium salt (IDC=R09), electrorefining salt (IDC=R65), salt (IDC=R71), silica (IDC=R73) and sweepings/screenings (IDC=R78). Solution thermodynamic modeling also indicates that fire suppression water buffered with a commercially-available phosphate buffer would significantly reduce the solubility of $PuCl_3$ by the precipitation of $PuPO_4$.

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Acronyms and Abbreviations

Abbreviation	Term
DOR	Direct Oxide Reduction
ER	Electrorefining
IDC	Item Description Code
LANMAS	Local Area Nuclear Material Accountability Software
MSE	Molten Salt Extraction
NEA	Nuclear Energy Agency (OECD)

1 Introduction

1.1 Background

Understanding the water solubility of nuclear materials used at the TA-55 Plutonium Facility has significant implications for safety and security. For example, water-soluble fissile materials used in gloveboxes at TA-55 are required to be stored in water-resistant containers to prevent water intrusion and mitigate the risk of a criticality accident in the event of glovebox flooding due to an earthquake and subsequent fire. Knowledge of the water solubility is necessary to improve operational efficiency where the solubility assumption is overly conservative. Conversely, where there is a programmatic need to handle significant quantities of water-soluble fissile material, this knowledge is necessary to provide a technical basis for appropriate criticality safety controls. From a safety basis perspective, water solubility could also have significant impact on source term calculations for TA-55, and the corresponding estimated dose to a worker or to a member of the public due to an accidental release of radioactive material. Water solubility of plutonium and uranium compounds can determine the lung clearance rate for inhaled particulates, and this affects the calculation of the committed effective dose equivalent.[1-3] Finally, understanding water solubility has nuclear material control and accountability implications, and could affect attractiveness level and termination of safeguards determinations.[4] The purpose of this report is to document the water solubility of the predominant plutonium and uranium compounds and residues at TA-55.

1.2 Conditions of Criticality Concern

The primary driver of this report is the water solubility of fissionable nuclear materials and the implications for criticality safety. Plutonium/uranium-bearing compounds and residues present in plutonium glovebox processing operations have different solubilities in water. To illustrate the bounding case of a highly soluble plutonium compound, Figure 32 from LA-10860[5] has been reproduced below in Figure 1-1 with a blue volume vs. density line for 520 g of Pu superimposed. The limiting critical density is 0.0076 kg/L of Pu, and concentrations below this level are of no criticality concern. Above this concentration, conditions for criticality are based upon the volume of water present and the concentration of dissolved plutonium (Figure 1-1). The blue line intersects the water-reflected line at ~17 L, indicating that 520 g of Pu dissolved in 17 L of water (0.031 kg/L Pu) in a spherical configuration will become critical when immersed in a large volume of water that acts as a neutron reflector. For an unreflected spherical solution it takes about 900 g of Pu in 17 L (0.053 kg/L Pu) to reach a critical mass. For comparison, red lines corresponding to various elemental masses of Pu are also shown. These diagrams for Pu-239 are bounding with respect to U-235 for the purposes of criticality safety. The solubility of plutonium and uranium is often determined by a complex combination of conditions, complexation and redox behavior, often leading to low solubility at near-neutral pH.[1, 6-9] This will be discussed in detail below for various compounds and residues found at TA-55.

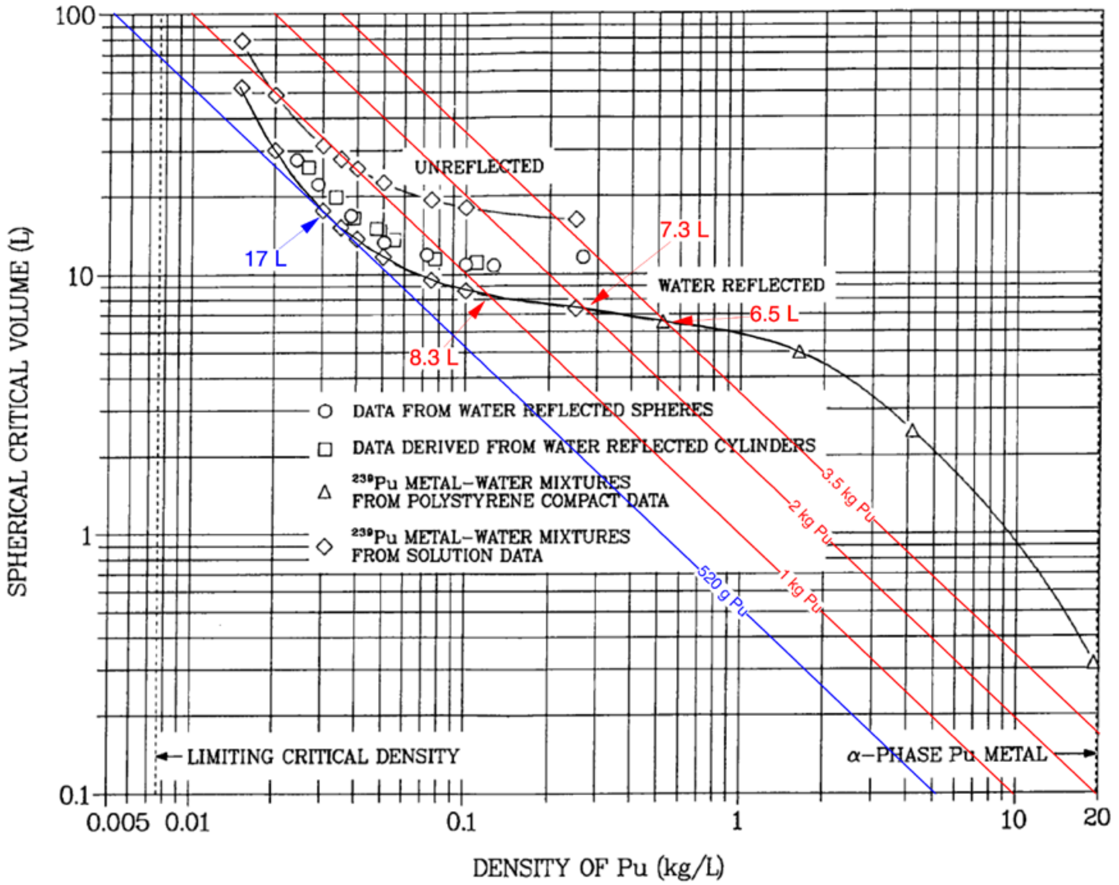

Figure 1-1. Critical volumes of homogeneous water-moderated plutonium spheres. The points suggesting an intermediate curve apply to water-reflected $Pu(NO_3)_4$ solution with 1 M HNO_3 and 3.1% ^{240}Pu content of the plutonium (black and white figure and caption reproduced from LA-10860-MS). The blue and red lines show the solution volumes as a function of Pu density (kg/L Pu in solution) for various Pu element masses. The arrows indicate the approximate minimum critical volumes for the water reflected case.

2 Computational Methods

In this report, solution thermodynamic calculations were used to model the water solubility of various solid plutonium residues and compounds relevant to TA-55. Solubility conditions for this discussion refer specifically to the scenario whereby the Pu/U-bearing compounds and dry residues are immersed in water from a fire suppression system. TA-55 fire suppression system water is supplied by Los Alamos County and nothing is added to the PF-4 portion of the fire suppression system water.[10] The fire suppression water is assumed to be pH 7, an E_h of 0.4011 V at a temperature of 25 °C. In the models, water is added in increments to simulate ingress of water into a glovebox. At each volume of water, the equilibrium calculations are performed at constant E_h and temperature, and it is assumed that equilibrium is reached rapidly.

The chemical equilibrium modeling software program Hydra/Medusa[11] was used to calculate the solubility and speciation of plutonium under various conditions (e.g., the plutonium speciation was calculated for various relevant combinations of Pu mass, Pu chemical form, water volume added, and matrix constituents). The output from Hydra/Medusa was compared to that obtained using the additional equilibrium modeling software MINEQL+[12] and HySS[13] in order to validate the results.

The NEA has published a series of books in which they have critically reviewed the thermodynamic equilibrium constants of plutonium and other actinides.[14-15] These served as the source for plutonium solubility, complexation, and redox equilibria used for the calculations. For reference, the constants and their associated equilibrium expressions are shown in Table 2-1. Technical reports and published literature were also used where available to support the solubility estimates.

Table 2-1. Chemical equilibria and equilibrium constants

Species / Compound	Chemical Equilibrium	Equilibrium Constant
Pu^{4+}	$Pu^{3+} \rightleftarrows Pu^{4+} + e^-$	log K° = –17.69[a]
PuO_2^{+}	$Pu^{3+} + 2H_2O \rightleftarrows PuO_2^{+} + 4H^+ + 2e^-$	log K° = –35.15[a]
PuO_2^{2+}	$Pu^{3+} + 2H_2O \rightleftarrows PuO_2^{2+} + 4H^+ + 3e^-$	log K° = –50.97[a]
$PuOH^{2+}$	$Pu^{3+} + H_2O \rightleftarrows PuOH^{2+} + H^+$	log K° = –6.9[b]
$Pu(OH)_3(cr)$	$Pu^{3+} + 3H_2O \rightleftarrows Pu(OH)_3(cr) + 3H^+$	log K° = –15.8[b]
$PuCl^{2+}$	$Pu^{3+} + Cl^- \rightleftarrows PuCl^{2+}$	log K° = 0.24[c]
$PuCl_2^{+}$	$Pu^{3+} + 2Cl^- \rightleftarrows PuCl_2^{+}$	log K° = –0.74[c]
$PuCl_3(cr)$	$Pu^{3+} + 3Cl^- \rightleftarrows PuCl_3(cr)$	log K° = –14.16[a]

Species / Compound	**Chemical Equilibrium**	**Equilibrium Constant**
$PuOCl(cr)$	$Pu^{3+} + Cl^{-} + H_2O \rightleftarrows PuOCl(cr) + 2H^{+}$	log $K^{\circ} = -11.38$[a]
$PuPO_4(s, hyd)$	$Pu^{3+} + PO_4^{3-} \rightleftarrows PuPO_4(s, hyd)$	log $K^{\circ} = 24.6$[b]
$PuOH^{3+}$	$Pu^{4+} + H_2O \rightleftarrows PuOH^{3+} + H^{+}$	log $K^{\circ} = 0.6$[b]
$Pu(OH)_2^{2+}$	$Pu^{4+} + 2H_2O \rightleftarrows Pu(OH)_2^{2+} + 2H^{+}$	log $K^{\circ} = 0.6$[b]
$Pu(OH)_3^{+}$	$Pu^{4+} + 3H_2O \rightleftarrows Pu(OH)_3^{+} + 3H^{+}$	log $K^{\circ} = -2.3$[b]
$Pu(OH)_4(aq)$	$Pu^{4+} + 4H_2O \rightleftarrows Pu(OH)_4(aq) + 4H^{+}$	log $K^{\circ} = -8.5$[b]
$PuO_2(am, hyd)$	$Pu^{4+} + 2H_2O \rightleftarrows PuO_2(am, hyd) + 4H^{+}$	log $K^{\circ} = 2.33$[a]
$PuCl^{3+}$	$Pu^{4+} + Cl^{-} \rightleftarrows PuCl^{3+}$	log $K^{\circ} = 1.8$[b]
$PuH_3PO_4^{4+}$	$Pu^{4+} + PO_4^{3-} + 3H^{+} \rightleftarrows PuH_3PO_4^{4+}$	log $K^{\circ} = 24.1$[a]
$Pu(HPO_4)_2(am, hyd)$	$Pu^{4+} + 2PO_4^{3-} + 2H^{+} \rightleftarrows Pu(HPO_4)_2(am, hyd)$	log $K^{\circ} = 55.15$[a]
$PuO_2OH(aq)$	$PuO_2^{+} + H_2O \rightleftarrows PuO_2OH(aq) + H^{+}$	log $K^{\circ} = -9.73$[b]
$PuO_2OH(am)$	$PuO_2^{+} + H_2O \rightleftarrows PuO_2OH(am) + H^{+}$	log $K^{\circ} = -5.0$[b]
PuO_2OH^{+}	$PuO_2^{2+} + H_2O \rightleftarrows PuO_2OH^{+} + H^{+}$	log $K^{\circ} = -5.5$[b]
$PuO_2(OH)_2(aq)$	$PuO_2^{2+} + 2H_2O \rightleftarrows PuO_2(OH)_2(aq) + 2H^{+}$	log $K^{\circ} = -13.2$[b]
$(PuO_2)_2(OH)_2^{2+}$	$2PuO_2^{2+} + 2H_2O \rightleftarrows (PuO_2)_2(OH)_2^{2+} + 2H^{+}$	log $K^{\circ} = -7.5$[b]
$PuO_2(OH)_2{\cdot}H_2O(cr)$	$PuO_2^{2+} + 3H_2O \rightleftarrows PuO_2(OH)_2{\cdot}H_2O(cr) + 2H^{+}$	log $K^{\circ} = -5.5$[b]
PuO_2Cl^{+}	$PuO_2^{2+} + Cl^{-} \rightleftarrows PuO_2Cl^{+}$	log $K^{\circ} = 0.23$[b]
$PuO_2Cl_2(aq)$	$PuO_2^{2+} + 2Cl^{-} \rightleftarrows PuO_2Cl_2(aq)$	log $K^{\circ} = -1.15$[b]
HPO_4^{2-}	$H^{+} + PO_4^{3-} \rightleftarrows HPO_4^{2-}$	log $K^{\circ} = 12.35$[d]
$H_2PO_4^{-}$	$2H^{+} + PO_4^{3-} \rightleftarrows H_2PO_4^{-}$	log $K^{\circ} = 19.562$[a]
$H_3PO_4(aq)$	$3H^{+} + PO_4^{3-} \rightleftarrows H_3PO_4(aq)$	log $K^{\circ} = 21.702$[a]

[a] See Appendix 1. [b] Table 5–2 of ref 15. [c] Section 11.3.1.1 of ref 15. [d] Table 8–2 of ref 15.

3 Results and Discussion

The results of the solubility analysis are described in this section. Sections 3.1 and 3.2 describe the results for plutonium compounds and plutonium residues, respectively. Sections 3.3 and 3.4 describe the results for uranium compounds and uranium residues, respectively. The nuclear material control system at TA-55 relies on Item Description Codes (IDC) to assign a chemical form to each accountable nuclear material item, and the subsections are organized alphabetically by IDC. Individual compound solubility was determined using published solubility data and solution thermodynamic modeling. Residue solubility was estimated using process knowledge, operating procedures and published technical reports to determine their constituent compounds, and then applying the knowledge gained from the compound solubility results to each residue type. The scope of materials considered here includes all compounds and residues at TA-55 as of March 2016 that contain Pu-239 or U-235 where any single item in the facility has more than 500 g of nuclear material. In addition, Section 3.1.3 describes the solubility of plutonium phosphate, even though $PuPO_4$ is not currently used at TA-55. This section was added to provide a technical basis for using phosphate buffers as part of a criticality safety control set due to the tendency of soluble $PuCl_3$ to react to precipitate $PuPO_4$ from aqueous solution. A summary table showing the solubility results is included in Section 3.5 (Table 3-1).

3.1 Plutonium Compounds

3.1.1 Plutonium Chloride (C19)

Figure 3-1. Plutonium Trichloride (C19 and C82)

A photograph of a typical plutonium trichloride salt is shown in Figure 3-1. Trivalent solid $PuCl_3$ is very soluble in water,[8] and as it dissolves it hydrolyzes, lowering the pH of resulting solutions. The solubility and complexation behavior of trivalent plutonium often mirrors that of the trivalent lanthanides, which all dissolve to give saturated pH 1–2 solutions of close to 50 wt % lanthanide.[16]

Figure 3-2 superimposes a dotted red volume vs. density line for 2,390 g of soluble Pu[17] on the water-reflected critical density curve (LA-10860 Fig 32.[5]). The solid red line shows the calculated concentration of 2,390 g Pu as $PuCl_3(s)$ as a function of added water volume. For this quantity of plutonium, the red line crosses the curve at a volume of 7.1 L. The speciation diagrams in Figure 3-3 (2,390 g Pu) and Figure 3-4 (841 g Pu) indicate that, thermodynamically, $PuCl_3$(s) is completely soluble in water. These diagrams also show that the pH drops immediately to ~2.3 upon dissolution of 2,390 g Pu and to ~2.4 upon dissolution of 841 g Pu. It is noteworthy that the trivalent Pu(III) oxidation state is stable at acidic pH, but will convert to Pu(IV) above pH 6 and precipitate out as a hydroxide in the absence of strong complexants:

> The hydrolysis of Pu^{3+} can be studied only with careful control of the plutonium solubility and maintenance of an inert or reducing atmosphere to avoid oxidation to Pu^{4+}, which is increasingly favored as the solution pH is raised.[18]

The reason that the $PuCl_3$ remains in the trivalent oxidation state under the present model results from the observation that, as water is added to such a large quantity of $PuCl_3$, the Pu(III) hydrolyzes and lowers the solution pH to a point where Pu(III) is stable (see Figure 3-3 and Figure 3-4). The fact that plutonium becomes insoluble at high pH suggests the possibility of using a hydroxide salt as a criticality safety control inside a glovebox to transform the plutonium from a soluble form to an insoluble form.

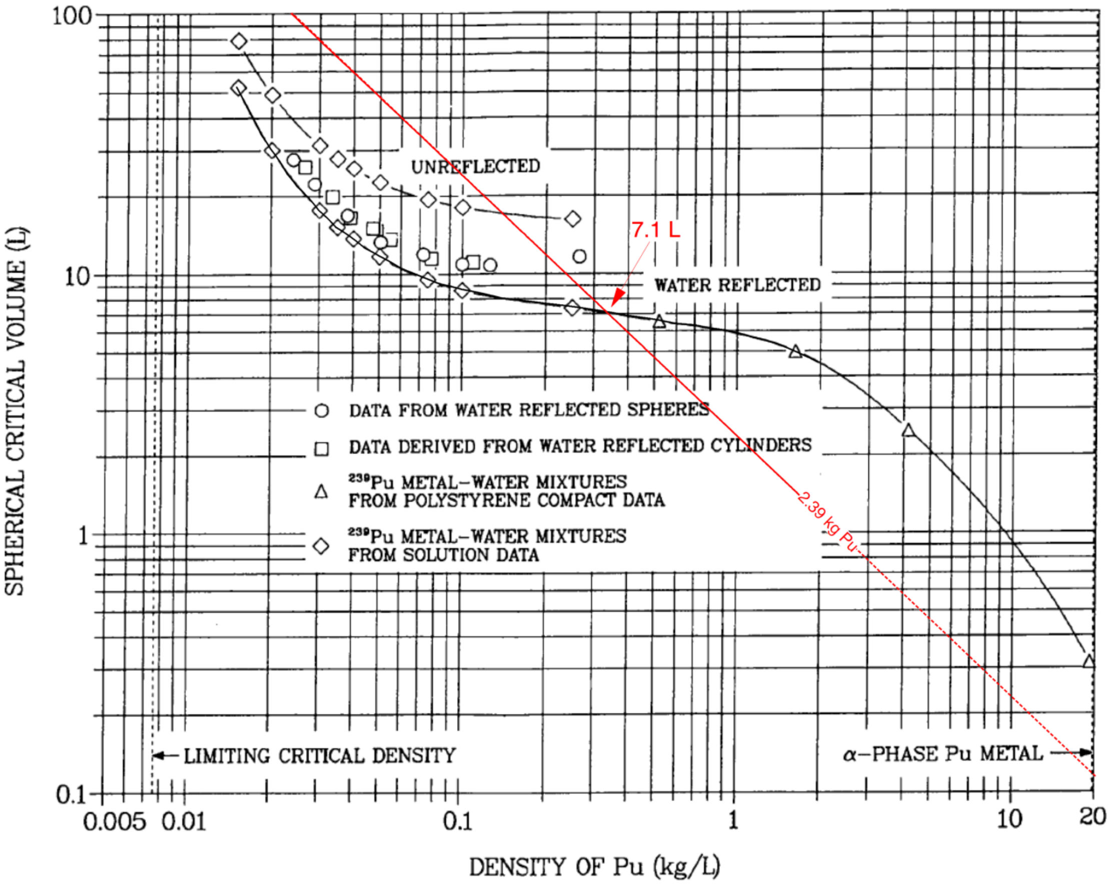

Figure 3-2. Critical volumes of homogeneous water-moderated plutonium spheres (reproduced from LA-10860-MS). The red line plots the quantity of Pu that dissolves for a given volume of water (expressed as kg Pu/L H_2O on the x-axis for a given volume of water on the y-axis).

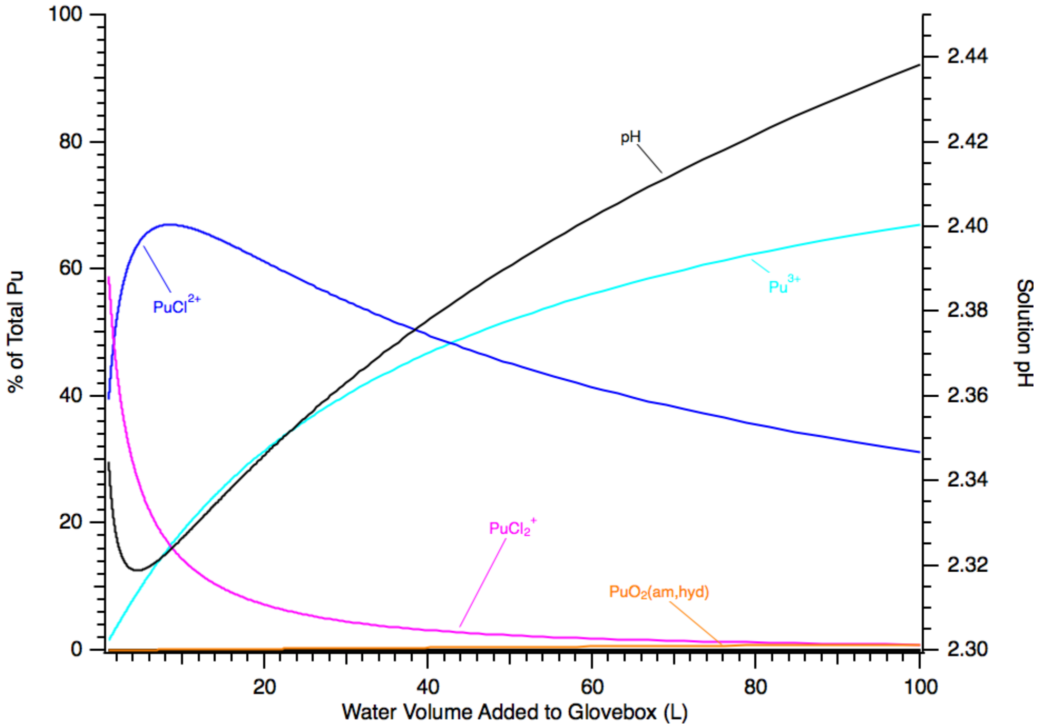

Figure 3-3. Speciation of 2,390 g Pu as $PuCl_3$(s) as a function of added water volume. Colored lines for individual Pu solid and solution species are plotted against the left y-axis. The black solution pH line is plotted against the right y-axis.

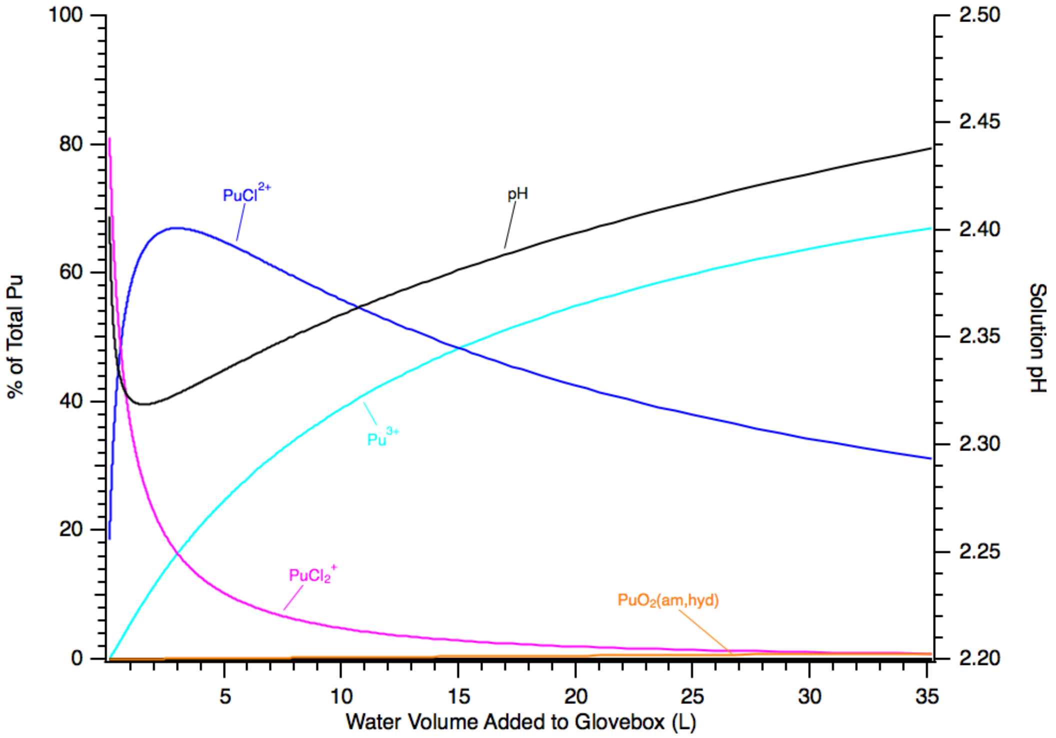

Figure 3-4. Speciation of 841 g Pu as $PuCl_3$(s) as a function of added water volume. Colored lines for individual Pu solid and solution species are plotted against the left y-axis. The black solution pH line is plotted against the right y-axis.

3.1.2 Plutonium Dioxide (C21)

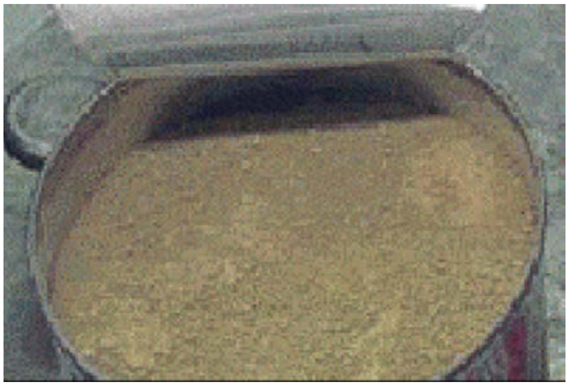

Figure 3-5. Plutonium Dioxide (C21).

A photograph of a typical plutonium dioxide compound is shown in Figure 3-5. Plutonium dioxide, PuO_2(s), has low solubility in water and does not dissolve readily even in strong acid.[19]

Figure 3-6 reproduces the water-reflected line from Figure 1-1 (shown as a blue line) and shows the calculated solubility of PuO_2 (am, hyd) (red line).

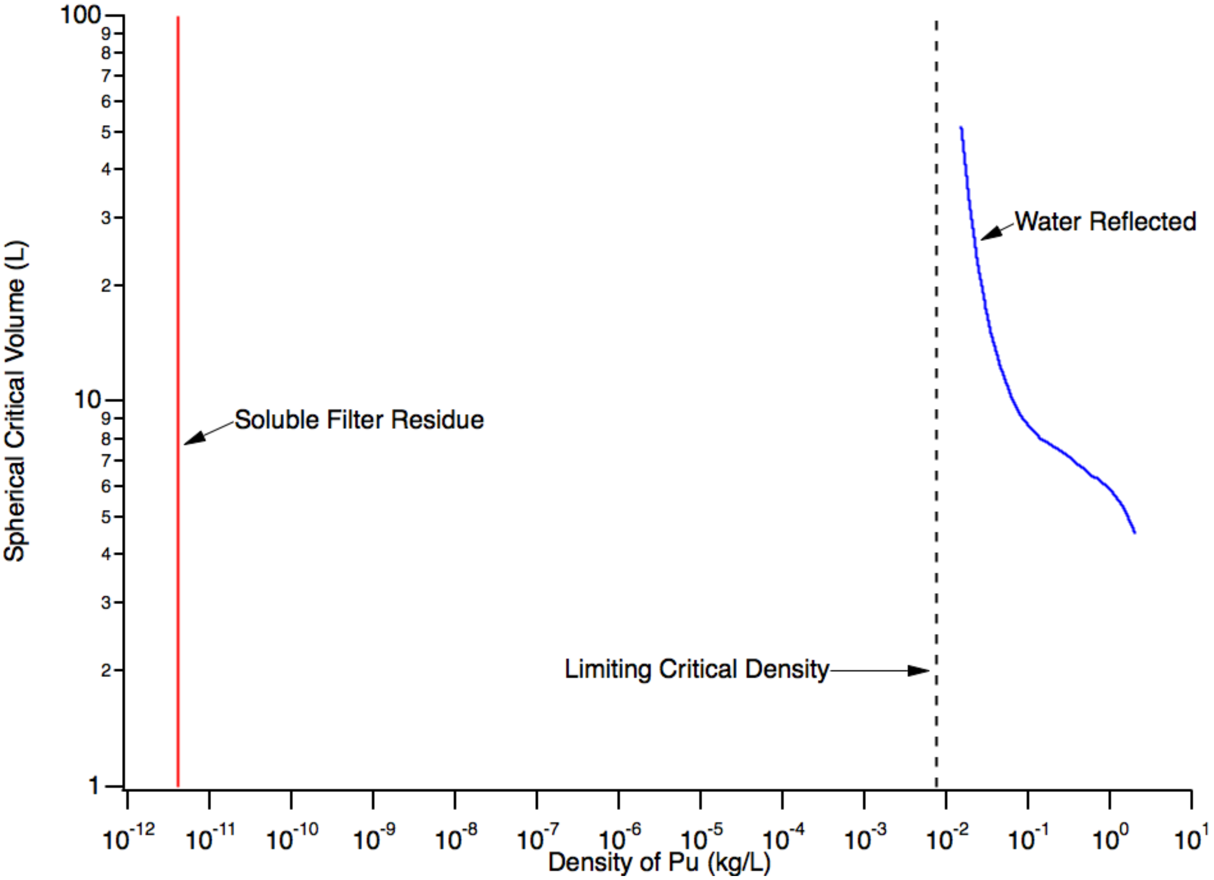

Figure 3-6. Critical volumes of homogeneous water-moderated plutonium spheres (blue line, reproduced from LA-10860-MS). The red line plots the quantity of Pu that

dissolves for a given volume of water (expressed as kg Pu/L H_2O on x-axis for a given volume of water on y-axis).

The speciation plot in Figure 3-7 for 2,450 g Pu as PuO_2(am, hyd) as a function of added water volume confirms that PuO_2 is very insoluble.

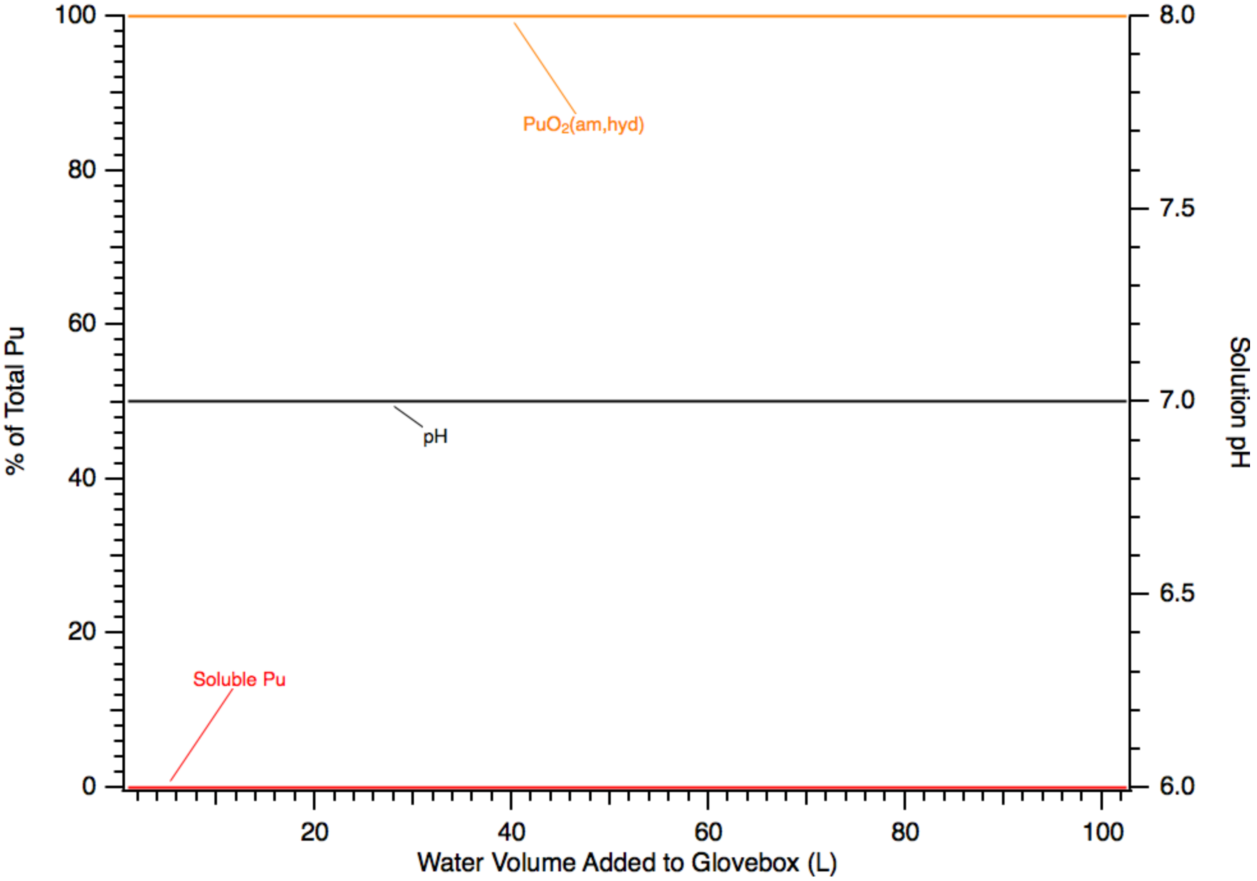

Figure 3-7. Speciation of 2,450 g Pu as PuO_2(am, hyd) as a function of added water volume. Colored lines for individual Pu solid and solution species are plotted against the left y-axis. The black solution pH line is plotted against the right y-axis.

The chemical formula of Pu(IV) hydroxide precipitate is uncertain but expected to be either amorphous hydroxide $Pu(OH)_4$(am) or hydrous oxide $PuO_2 \cdot xH_2O$(am),[14, 20-21] referred to here as PuO_2(am, hyd). Consequently, the solubility constant for PuO_2(am, hyd) in Table 2-1 may be used to model the solubility of both plutonium dioxide and Pu(IV) hydroxide precipitates. This is a conservative assumption for PuO_2 (IDC=C21), which may in fact be more crystalline as a result of aging or calcination. Regardless, the references cited here firmly establish that Pu(IV) oxides and hydroxides exhibit negligible solubility in water, and that strongly acidic conditions such as concentrated HNO_3/HF mixtures are required to dissolve PuO_2.[8]

3.1.3 Plutonium Phosphate (C66)

Plutonium phosphate ($PuPO_4$) is insoluble in water. Figure 3-8 shows three different red volume vs. density lines for a scenario in which 841 g of Pu as $PuCl_3$(s) is dissolved in water, superimposed on the water-reflected critical density curve (LA-10860 Fig 32.)[5] The dotted red line indicates that, as observed in Section 3.1.1, the 841 g of Pu will dissolve. The two red lines illustrate that the Pu solubility can be significantly reduced by adding 0.094 M K_2HPO_4/0.006 M KH_2PO_4 buffer, and further reduced by adding 0.72 M K_2HPO_4/0.28 M KH_2PO_4 buffer, resulting in the precipitation of $PuPO_4$.

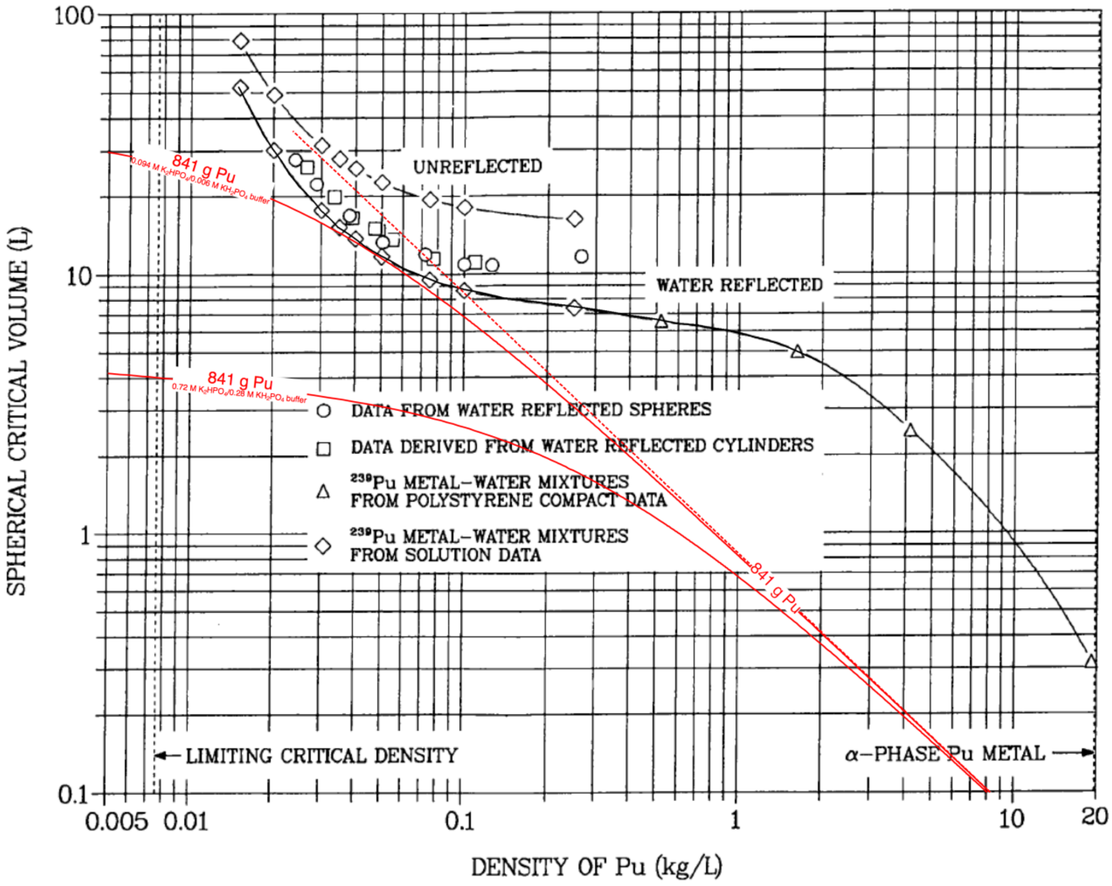

Figure 3-8. Critical volumes of homogeneous water-moderated plutonium spheres (reproduced from LA-10860-MS). The dotted red line shows the quantity of Pu that dissolves for a given volume of water (expressed as kg Pu/L H_2O on the x-axis for a given volume of water on the y-axis). The two red lines illustrate that the Pu solubility can be significantly reduced by adding 0.094 M K_2HPO_4/0.006 M KH_2PO_4 buffer, and further reduced by adding 0.72 M K_2HPO_4/0.28 M KH_2PO_4 buffer, resulting in the precipitation of $PuPO_4$.

A speciation diagram is illustrated in Figure 3-9 for 841 g Pu as $PuCl_3$(s) as a function of added 0.094 M K_2HPO_4/0.006 M KH_2PO_4 buffered water volume. The diagram illustrates the effect of precipitation of $PuPO_4$. Pu precipitation is even more pronounced when water containing 0.72 M K_2HPO_4/0.28 M KH_2PO_4 is added to $PuCl_3$(s) (Figure 3-10). Thus, if the fire suppression water were assumed to be buffered with a commercially-available phosphate buffer, the solubility of $PuCl_3$(s) would be reduced, thus mitigating the risk of a criticality incident. Buffering of firewater with phosphate reagents could be accomplished by placing the chemical agent within gloveboxes of concern, or buffering the actual firewater (or portion thereof), or using a combination of these approaches.

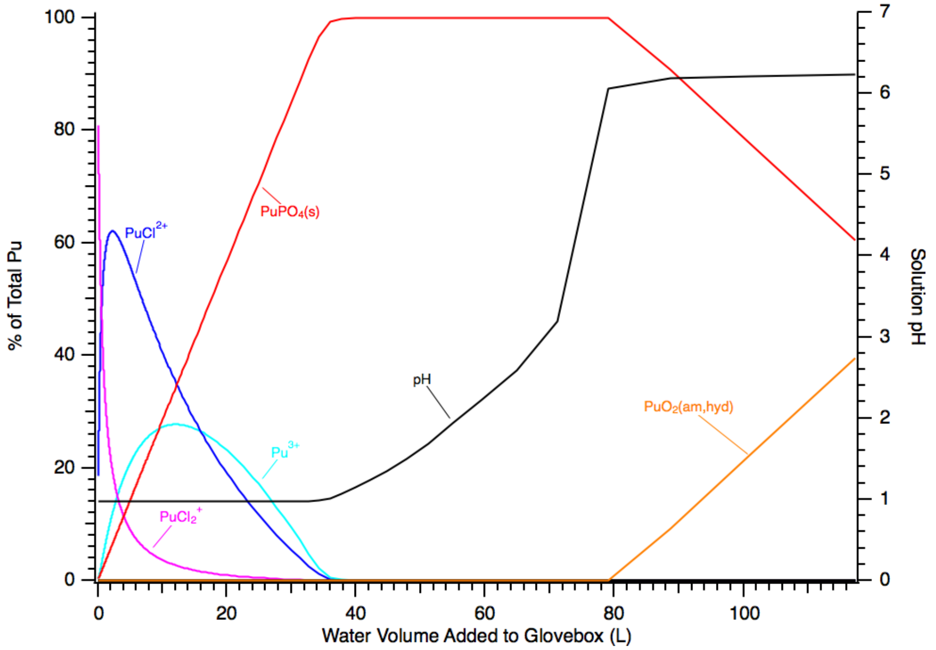

Figure 3-9. Speciation of 841 g Pu as $PuCl_3$(s) as a function of added 0.094 M K_2HPO_4/0.006 M KH_2PO_4 buffered water volume. Colored lines for individual Pu solid and solution species are plotted against the left y-axis. The black solution pH line is plotted against the right y-axis.

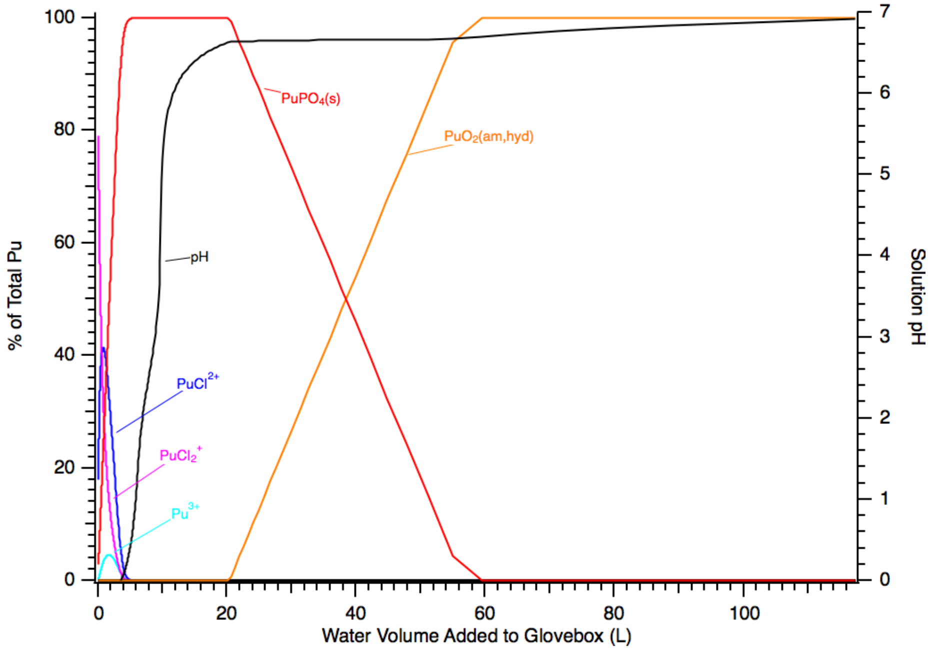

Figure 3-10. Speciation of 841 g Pu as $PuCl_3$(s) as a function of added 0.72 M K_2HPO_4/0.28 M KH_2PO_4 buffered water volume. Colored lines for individual Pu solid and solution species are plotted against the left y-axis. The black solution pH line is plotted against the right y-axis.

3.1.4 Plutonium Tetrafluoride (C80)

Plutonium tetrafluoride, $PuF_4(s)$, has a low solubility in water of 0.1 g Pu / L, and the solubility product constant, $K_{sp} = 6\times10^{-20}$.[22]

3.1.5 Plutonium Oxychloride

There are conflicting reports on the solubility of plutonium oxychloride PuOCl in water. Equilibrium calculations suggest that it is quite soluble in water, but it has been reported that PuOCl in electro-refining residues (R65) is insoluble in water (see Section 3.2.6).[23] Figure 3-11 superimposes a dotted red volume vs. density line for 2,390 g of soluble Pu on LA-10860 Fig 32.[5] The solid red line shows the calculated solubility of 2,390 g Pu as PuOCl(s) as a function of water volume.

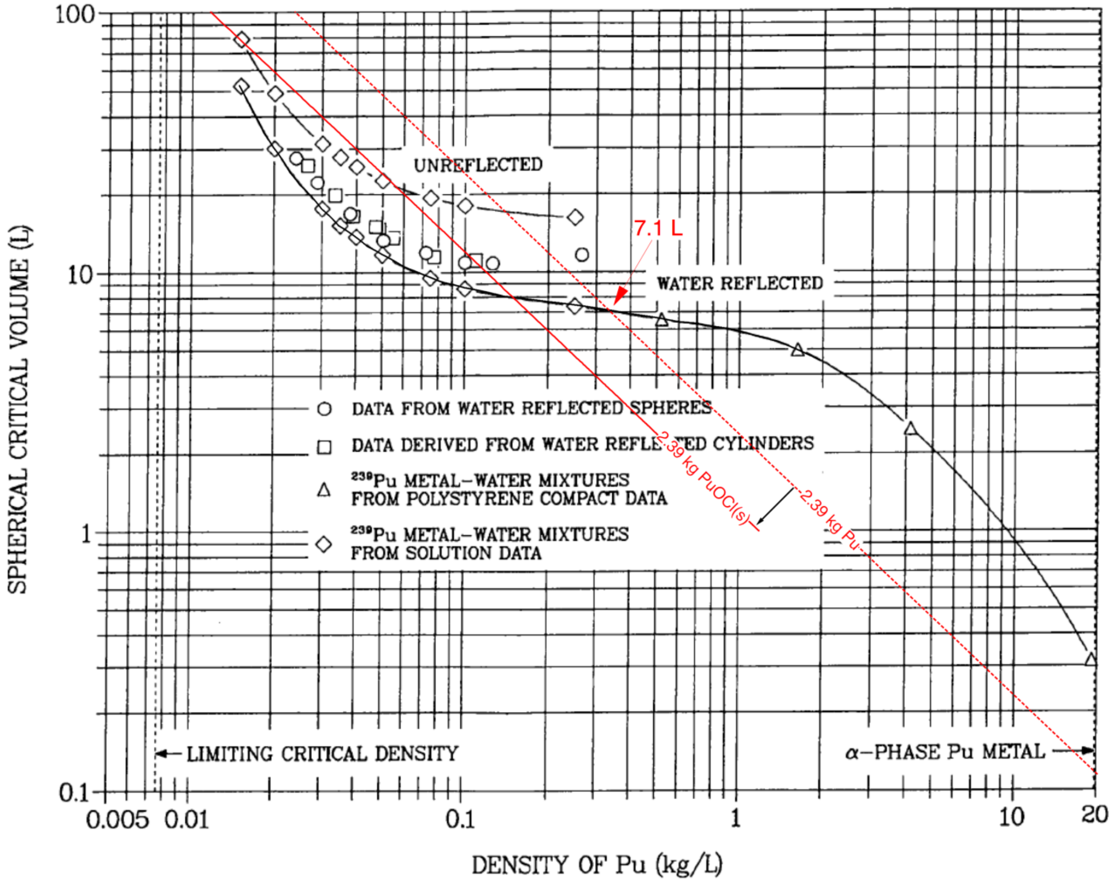

Figure 3-11 Critical volumes of homogeneous water-moderated plutonium spheres (blue line, reproduced from LA-10860-MS). The red line plots the quantity of Pu from PuOCl that dissolves for a given volume of water (expressed as kg Pu/L H2O on x-axis for a given volume of water on y-axis).

The speciation diagram in Figure 3-12 indicates that, relative to $PuCl_3(s)$, the addition of water to an equivalent mass of Pu in the form of PuOCl(s) will lead to less soluble Pu. This appears to be a result of the presence of less chloride which can complex Pu(III), and not because PuOCl(s) is less soluble than $PuCl_3(s)$. This suggests that the case for the solubility of PuOCl(s) is bounded by the case for $PuCl_3(s)$. It should be noted that pyrochemical salts generally have additional salts, such as $CaCl_2$ cover salt, and additional dissolved chloride ion would tend to make the PuOCl even more soluble.

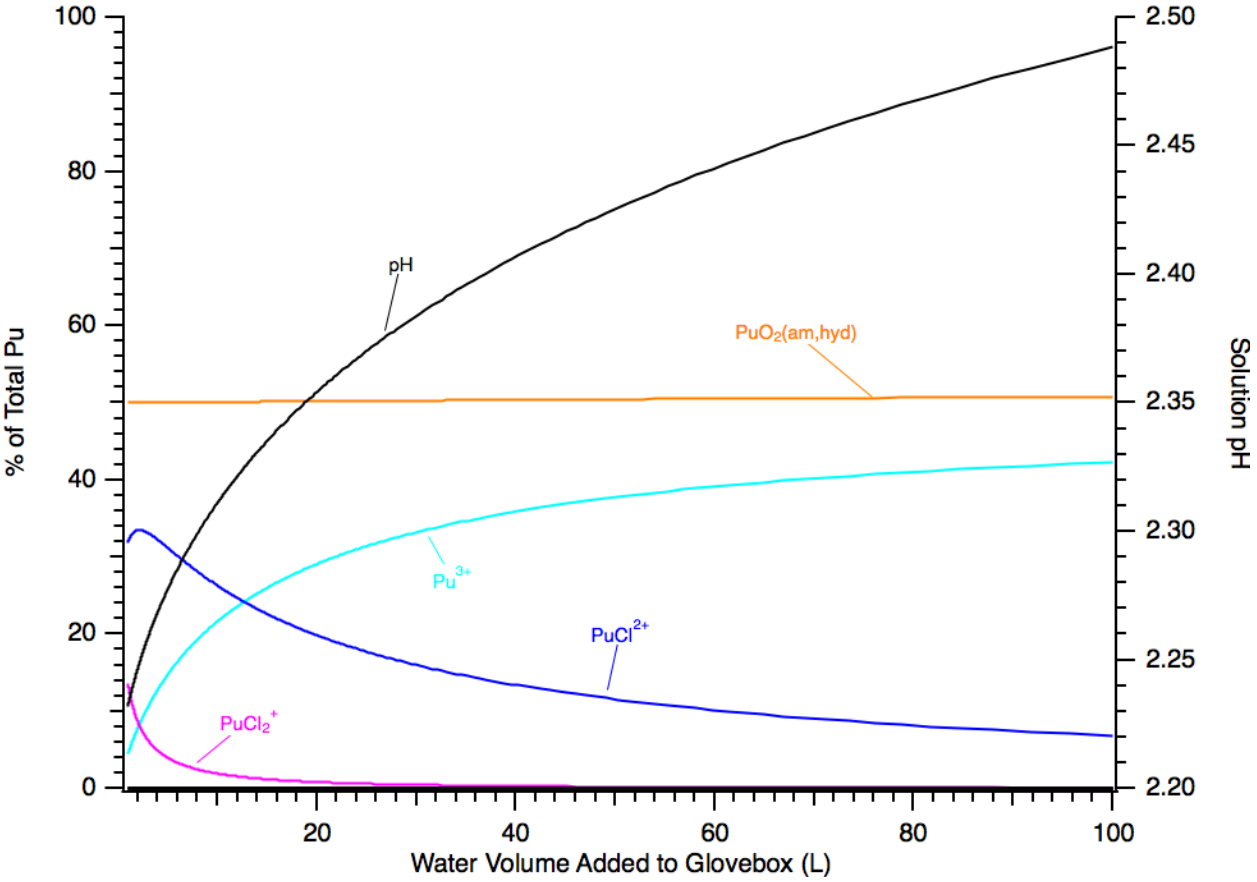

Figure 3-12 Speciation of 2,390 g Pu as PuOCl(s) as a function of added water volume. Colored lines for individual Pu solid and solution species are plotted against the left y-axis. The black solution pH line is plotted against the right y-axis.

3.2 Plutonium Residues

3.2.1 Plutonium Calcium Salt (R09)

The chemical form and solubility of this residue is uncertain. The DOR process generates calcium chloride-bearing salt residues, and it is possible that this residue will have solubility behavior analogous to that of DOR salts (R42). Alternatively, some MSE salts have a $CaCl_2$ cover salt,[24] so it is possible that this residue will have solubility behavior analogous to that of MSE salts (R83). Further information about the nature of this residue may be ascertained by examining historical process information or by experiment.

3.2.2 Plutonium Filter Residue (R26)

Figure 3-13. Plutonium filter residue (dissolution heel) from aqueous nitrate dissolution process. This is the material that remains undissolved and is subsequently collected by filtration after heating a plutonium residue in strong nitric acid solution.

A photograph of a typical plutonium filter residue is shown in Figure 3-13. This material is the residue that remains undissolved when a process residue is digested in hot concentrated hydrochloric[25] or nitric acid[26], and therefore it will have negligible solubility in water. The plutonium in these refractory residues is expected to be in the chemical form of Pu(IV) oxides and/or hydroxides,[8, 27-28] referred to here as PuO_2(am, hyd). Given the expectation that the primary form of plutonium in this residue is PuO_2(am, hyd), the calculations in Section 3.1.2 confirm the expectation that R26 plutonium filter residues have negligible solubility in water.

3.2.3 Plutonium Hydroxide Precipitate (R41)

Sodium or potassium hydroxide is commonly added to plutonium-bearing solutions to precipitate the plutonium. The chemical composition of this residue is Pu(IV) hydroxide,[29-30] referred to here as PuO_2(am, hyd) as discussed in Section 3.1.2. Therefore, these R41 plutonium hydroxide precipitates will have negligible solubility in water.

3.2.4 Plutonium Direct Oxide Reduction (DOR) Salt (R42)

Figure 3-14. Plutonium Direct Oxide Reduction (DOR) Salt (R42). The plutonium metal button product is pictured on top of the calcium salt cake.

In the direct oxide reduction (DOR) process, plutonium dioxide is reduced by calcium metal in molten $CaCl_2$ solvent to form plutonium metal and calcium oxide.[31-33] A typical plutonium DOR salt is illustrated in Figure 3-14. These salts are largely $CaCl_2$ but may contain CaO, finely divided Ca metal and Pu shot which may subsequently be oxidized to PuO_2.[34] The Pu shot and PuO_2 in DOR residues will have negligible solubility in water. In addition, both CaO and Pu metal form basic solutions when exposed to water, which would lead to $PuO_2(s)$ formation. Furthermore, experimental data indicates that exposure of oxidized DOR salt to water yields a solution phase containing dissolved $CaCl_2$ with negligible Pu content (< 0.0001 kg Pu/L), and a solid PuO_2 phase.[34]

3.2.5 Plutonium Incinerator Ash (R47)

Plutonium incinerator ash is primarily PuO_2 and therefore they will have negligible solubility in water,[8, 29, 35] as evidenced by the following quote:

> Ash from the incineration of these materials has proven to be one of the more difficult matrices from which to solubilize plutonium.[35]

3.2.6 Plutonium Electrorefining (ER) Salt (R65)

Figure 3-15. Plutonium Electrorefining (ER) Salt (R65).

In the electrorefining (ER) process, impure plutonium metal is electrochemically oxidized to $PuCl_3$ in a molten NaCl/KCl solvent, and is then reduced back to purified Pu metal after undergoing electrochemical transport.[36-37] Approximately 7% of the starting Pu remains in the salt phase as $PuCl_3$ or Pu metal shot.[38] A typical ER salt is illustrated in Figure 3-15. Because ER salts may contain $PuCl_3$, they should be considered as potentially water-soluble.

There is a portion of the TA-55 plutonium ER salt residues that have been oxygen-sparged or stabilized by calcination. These R65 items contain insoluble PuOCl and PuO_2[23] and are identified by the addition of "OX" in the item identification name (e.g., "XBSOX..."). Experimental data indicate that these items containing solid PuOCl and/or PuO_2 have negligible solubility in water.[23] This is contrary to the relatively high water solubility of PuOCl noted in Section 3.1.5, and this suggests the possibility that the equilibrium constants used to calculate the solubility of PuOCl do not fully describe the observed chemistry in these residues.

3.2.7 Plutonium Salt (R71)

The chemical form and solubility of this residue has not yet been analyzed. It will be analyzed on a case-by-case basis or determined experimentally.

3.2.8 Plutonium Silica (R73)

The chemical form and solubility of this residue has not yet been analyzed. It will be analyzed on a case-by-case basis or determined experimentally.

3.2.9 Plutonium Sweepings/Screenings (R78)

The solubility of sweepings/screenings could be very process-dependent. It will be analyzed on a case-by-case basis or determined experimentally.

3.2.10 Plutonium Molten Salt Extraction (MSE) Salt (R83)

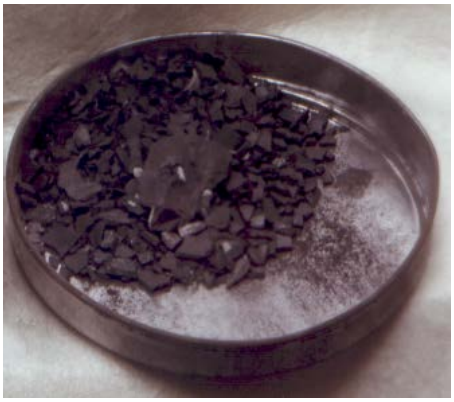

Figure 3-16. Plutonium Molten Salt Extraction (MSE) Salt (R83).

In the molten salt extraction (MSE) process, plutonium metal with high americium content is reacted with $MgCl_2$ oxidant in molten NaCl/KCl solvent.[39-40] The $MgCl_2$ oxidizes the americium metal to form $AmCl_3$, which then separates from the purified plutonium metal. However, some plutonium metal is also oxidized to $PuCl_3$ and settles in the MSE salt. A typical MSE salt is illustrated in Figure 3-16. Because plutonium MSE salts may contain $PuCl_3$, they should be considered as potentially water-soluble. Oxygen-sparged MSE salts contain primarily insoluble PuO_2 and PuOCl.[41]

3.3 Uranium Compounds

3.3.1 Uranium Carbide (C13)

There are three uranium carbide phases: UC, UC_2, and U_2C_3.[42] All three phases will react with water by slowly disintegrating to give insoluble U(IV) hydrous oxides ($UO_2 \cdot xH_2O$) and unreacted solid U carbide.[43-46] Hydrogen and a variety of hydrocarbons are also produced, principally methane and ethane for UC and UC_2, respectively. Consequently, negligible soluble uranium would result from contact of TA-55 uranium carbide compounds with water.

3.3.2 Uranium Dioxide (C21)

Uranium dioxide, UO_2(s), has low solubility in water.[47-49]

3.3.3 Uranium Nitrate (C52)

Uranium(VI) nitrate, $UO_2(NO_3)_2 \cdot xH_2O$(s), is very soluble in water.[49-50]

3.3.4 Uranium U_3O_8 (C88)

U_3O_8(s), has low solubility in water.[51]

3.3.5 Uranium Uranates

Uranates have low solubility in water.[52] Uranate precipitates are formed when the pH of a uranium solution is raised above 6.5 by adding hydroxide (e.g., NaOH, KOH, NH_4OH). The chemical composition of uranates varies, but is approximately $M_2U_2O_7$ (where M is the cation of the base used in the precipitation, e.g., Na^+).

3.4 Uranium Residues

3.4.1 Uranium Filter Residue (R26)

These uranium filter residues are from an electrolytic decontamination process.[53] The residue is generated by adding hydroxide to a uranium containing solution until the uranium precipitates out. Consequently, these uranium residues will be in the form of uranates (section 3.3.5) and will be insoluble in water.

3.5 Summary

The summary of water solubility results for plutonium and uranium compounds and residues at TA-55 are listed in Table 3-1. Where quantitative solubility values could be calculated, an estimated range of solubility in g/L has been provided in the table. Where only qualitative solubility information was available, this has been indicated in the table using the designations: i=insoluble, s=soluble. Table 3-1 also includes a column with the section in this report that includes discussion, calculations, and specific references.

Table 3-1. Summary of water solubility results

IDC Code	IDC Code Description	Chemical Form	Total # of Items[a]	# of items >500 g[a]	Water Solubility	Section in this Report
Plutonium Compounds						
C19, C82	Trichloride	$PuCl_3$	9	2	> 100 g/L	3.1.1
C21	Dioxide	PuO_2	2,182	1,020	< 1 g/L	3.1.2
C66	Phosphate	$PuPO_4$	0	0	< 1 g/L	3.1.3
C80	Tetrafluoride	PuF_4	30	2	< 1 g/L	3.1.4
NA	Oxychloride	PuOCl	NA	NA	b	3.1.5
Plutonium Residues						
R09	Calcium Salt	b	1	1	b	3.2.1
R26	Filter Residue	PuO_2, $Pu(OH)_4$	173	70	< 1 g/L	3.2.2
R41	Hydroxide Precipitate	$Pu(OH)_4$	18	1	< 1 g/L	3.2.3
R42	Direct Oxide Reduction (DOR) Salt	PuO_2, Pu metal	66	24	< 1 g/L	3.2.4
R47	Incinerator Ash	PuO_2, Pu_xO_y	71	7	< 1 g/L	3.2.5
R65	Electrorefining (ER) Salt	$PuCl_3$, PuOCl[c], Pu metal	508	183	b	3.2.6
R71	Salt	b	86	13	b	3.2.7
R73	Silica	b	16	6	b	3.2.8
R78	Sweepings/ Screenings	b	152	10	b	3.2.9
R83	Molten Salt Extraction (MSE) Salt	$PuCl_3$, Pu metal	246	42	> 100 g/L	3.2.10
Uranium Compounds						
C13	Carbide	UC, UC_2, U_2C_3	9	5	U(IV) solids	3.3.1
C21	Dioxide	UO_2	401	112	i	3.3.2
C52	Nitrate	$UO_2(NO_3)_2$	2	2	s	3.3.3
C88	U_3O_8	U_3O_8	186	122	i	3.3.4
NA	Uranates	$M_xU_yO_z$ (e.g., $Na_2U_2O_7$)	NA	NA	i	3.3.5
Uranium Residues						
R26	Filter Residue	$M_xU_yO_z$ (e.g., $Na_2U_2O_7$)	45	2	< 1 g/L	3.4.1

[a] The number of items were determined from a LANMAS report performed in March, 2016 for all TA-55 material balance areas where a single item contained >500 g nuclear material (>1 g of plutonium (81-100% Pu-239) or >1 g uranium (0.7-94% U-235))

[b] The chemical makeup and water solubility are uncertain due to conflicting reports, insufficient process knowledge or process-dependent composition.

[c] Some ER and MSE salts have been O_2-sparged,[23, 41] these will contain a mix of PuO_2 and PuOCl.

4 Conclusions

The analyses in this document lead to the conclusion that the following materials are not appreciably soluble in water: plutonium dioxide (IDC=C21), plutonium phosphate (IDC=C66), plutonium tetrafluoride (IDC=C80), plutonium filter residue (IDC=R26), plutonium hydroxide precipitate (IDC=R41), plutonium DOR salt (IDC=R42), plutonium incinerator ash (IDC=R47), uranium carbide (IDC=C13), uranium dioxide (IDC=C21), U_3O_8 (IDC=C88), and uranium filter residue (IDC=R26). The analyses also indicate that the following compounds are soluble in water: plutonium chloride (IDC=C19) and uranium nitrate (IDC=C52). Equilibrium calculations suggest that PuOCl is water soluble, but some plutonium processing reports indicate that it is insoluble when present in electrorefining residues (R65). Plutonium molten salt extraction residues (IDC=R83) contain significant quantities of $PuCl_3$, and are expected to be soluble in water. The solubility of the following plutonium residues is indeterminate due to conflicting reports, insufficient process knowledge or process-dependent composition: calcium salt (IDC=R09), electrorefining salt (IDC=R65), salt (IDC=R71), silica (IDC=R73) and sweepings/screenings (IDC=R78). Solution thermodynamic modeling also indicates that fire suppression water buffered with a commercially-available phosphate buffer would significantly reduce the solubility of $PuCl_3$ by the precipitation of $PuPO_4$. Future solubility experiments on actual residues, particularly ER and MSE salts, could indicate that these residues are not soluble despite the fact that they contain soluble compounds such as $PuCl_3$ or PuOCl.

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6 Appendix 1. Derivation of Equilibrium Constants

Chemical Equilibrium: $2H^+ + PO_4^{3-} \rightleftarrows H_2PO_4^-$

Derivation:

$$\begin{array}{lll}
 & H^+ + PO_4^{3-} \rightleftarrows \cancel{HPO_4^{2-}} & \log K^\circ = 12.35^{a} \\
+ & H^+ + \cancel{HPO_4^{2-}} \rightleftarrows H_2PO_4^- & \log K^\circ = 7.212^{a} \\
\hline
 & 2H^+ + PO_4^{3-} \rightleftarrows H_2PO_4^- & \log K^\circ = 12.35 + 7.212 \\
 & & \quad = 19.562
\end{array}$$

Chemical Equilibrium: $3H^+ + PO_4^{3-} \rightleftarrows H_3PO_4(aq)$

Derivation:

$$\begin{array}{lll}
 & H^+ + PO_4^{3-} \rightleftarrows \cancel{HPO_4^{2-}} & \log K^\circ = 12.35^{a} \\
+ & H^+ + \cancel{HPO_4^{2-}} \rightleftarrows \cancel{H_2PO_4^-} & \log K^\circ = 7.212^{a} \\
+ & H^+ + \cancel{H_2PO_4^{2-}} \rightleftarrows H_3PO_4(aq) & \log K^\circ = 2.14^{a} \\
\hline
 & 3H^+ + PO_4^{3-} \rightleftarrows H_3PO_4(aq) & \log K^\circ = 12.35 + 7.212 + 2.14 \\
 & & \quad = 21.702
\end{array}$$

Chemical Equilibrium: $Pu^{4+} + PO_4^{3-} + 3H^+ \rightleftarrows PuH_3PO_4^{4+}$

Derivation:

$$\begin{array}{lll}
 & Pu^{4+} + \cancel{H_3PO_4(aq)} \rightleftarrows PuH_3PO_4^{4+} & \log K^\circ = 2.4^{b} \\
+ & 3H^+ + PO_4^{3-} \rightleftarrows \cancel{H_3PO_4(aq)} & \log K^\circ = 21.702^{c} \\
\hline
 & Pu^{4+} + PO_4^{3-} + 3H^+ \rightleftarrows PuH_3PO_4^{4+} & \log K^\circ = 2.4 + 21.702 \\
 & & \quad = 24.102
\end{array}$$

Chemical Equilibrium: $Pu^{4+} + 2PO_4^{3-} + 2H^+ \rightleftarrows Pu(HPO_4)_2(am, hyd)$

Derivation:

$$\begin{array}{lll}
 & Pu^{4+} + 2\cancel{HPO_4^{2-}} \rightleftarrows Pu(HPO_4)_2(am, hyd) & \log K^\circ = 30.45^{b} \\
+ & H^+ + PO_4^{3-} \rightleftarrows \cancel{HPO_4^{2-}} & \log K^\circ = 12.35^{a} \\
+ & H^+ + PO_4^{3-} \rightleftarrows \cancel{HPO_4^{2-}} & \log K^\circ = 12.35^{a} \\
\hline
 & Pu^{4+} + 2PO_4^{3-} + 2H^+ \rightleftarrows Pu(HPO_4)_2(am, hyd) & \log K^\circ = 30.45 + 12.35 + 12.35 \\
 & & \quad = 55.15
\end{array}$$

Chemical Equilibrium: $Pu^{4+} + 2H_2O \rightleftarrows PuO_2(am, hyd) + 4H^+$

Derivation:

$$\begin{array}{lll}
 & Pu^{4+} + \cancel{4OH^-} \rightleftarrows PuO_2(am, hyd) + \cancel{2H_2O} & \log K^\circ = 58.33^{b} \\
+ & \cancel{H_2O} \rightleftarrows H^+ + \cancel{OH^-} & \log K^\circ = -14.0 \\
+ & \cancel{H_2O} \rightleftarrows H^+ + \cancel{OH^-} & \log K^\circ = -14.0 \\
+ & H_2O \rightleftarrows H^+ + \cancel{OH^-} & \log K^\circ = -14.0 \\
+ & H_2O \rightleftarrows H^+ + \cancel{OH^-} & \log K^\circ = -14.0 \\
\hline
 & Pu^{4+} + 2H_2O \rightleftarrows PuO_2(am, hyd) + 4H^+ & \log K^\circ = 58.33 + 4(-14.0) \\
 & & \quad = 2.33
\end{array}$$

Chemical Equilibrium: $Pu^{3+} + Cl^{-} + H_2O \rightleftharpoons PuOCl(cr) + 2H^{+}$

Derivation:

$\Delta G° = \Delta_f G°(PuOCl(cr)) + 2\Delta_f G°(H^{+}) - \Delta_f G°(Pu^{3+}) - \Delta_f G°(Cl^{-}) - \Delta_f G°(H_2O)$

$\Delta_f G°(PuOCl(cr)) = -882.409$ kJ/mol[d]
$\Delta_f G°(H^{+}) = 0.000$ kJ/mol[e]
$\Delta_f G°(Pu^{3+}) = -578.984$ kJ/mol[d]
$\Delta_f G°(Cl^{-}) = -131.217$ kJ/mol[e]
$\Delta_f G°(H_2O) = -237.140$ kJ/mol[e]

Therefore:

$$\Delta G° = -882.409 + 2(0.000) - (-578.984) - (-131.217) - (-237.140) \text{ kJ/mol}$$
$$= 64.932 \text{ kJ/mol}$$

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{(64.932 \text{ kJ/mol})(1000 \text{ J/kJ})}{(8.314510 \text{ J/K·mol})(298.15 \text{ K})} = -26.1931244$$

$$\log K = \log(e^{\ln K}) = \log(e^{-26.1931244}) = -11.38$$

Chemical Equilibrium: $Pu^{3+} + 3Cl^{-} \rightleftharpoons PuCl_3(cr)$

Derivation:

$\Delta G° = \Delta_f G°(PuCl_3(cr)) - \Delta_f G°(Pu^{3+}) - 3\Delta_f G°(Cl^{-})$

$\Delta_f G°(PuCl_3(cr)) = -891.806$ kJ/mol[d]
$\Delta_f G°(Pu^{3+}) = -578.984$ kJ/mol[d]
$\Delta_f G°(Cl^{-}) = -131.217$ kJ/mol[e]

Therefore:

$$\Delta G° = -891.806 - (-578.984) - 3(-131.217) \text{ kJ/mol}$$
$$= 80.829 \text{ kJ/mol}$$

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{(80.829 \text{ kJ/mol})(1000 \text{ J/kJ})}{(8.314510 \text{ J/K·mol})(298.15 \text{ K})} = -32.6058655$$

$$\log K = \log(e^{\ln K}) = \log(e^{-32.6058655}) = -14.16$$

Chemical Equilibrium: $Pu^{3+} \rightleftharpoons Pu^{4+} + e^{-}$

Derivation:

$\Delta G° = \Delta_f G°(Pu^{4+}) + \Delta_f G°(e^{-}) - \Delta_f G°(Pu^{3+})$

$\Delta_f G°(Pu^{4+}) = -477.988$ kJ/mol[d]
$\Delta_f G°(Pu^{3+}) = -578.984$ kJ/mol[d]
$\Delta_f G°(e^{-}) = 0.000$ kJ/mol

Therefore:

$$\Delta G° = -477.988 - (-578.984) - (0.000) \text{ kJ/mol}$$
$$= 100.996 \text{ kJ/mol}$$

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{(100.996 \text{ kJ/mol})(1000 \text{ J/kJ})}{(8.314510 \text{ J/K·mol})(298.15 \text{ K})} = -40.7410952$$

$$\log K = \log(e^{\ln K}) = \log(e^{-40.7410952}) = -17.69$$

Chemical Equilibrium: $Pu^{3+} + 2H_2O \rightleftarrows PuO_2^{+} + 4H^{+} + 2e^{-}$

Derivation:

$$\Delta G° = \Delta_f G°(PuO_2^{+}) + 4\Delta_f G°(H^{+}) + 2\Delta_f G°(e^{-}) - \Delta_f G°(Pu^{3+}) - 2\Delta_f G°(H_2O)$$

$\Delta_f G°(PuO_2^{+}) = -852.646$ kJ/mol[d]

$\Delta_f G°(H^{+}) = 0.000$ kJ/mol[e]

$\Delta_f G°(e^{-}) = 0.000$ kJ/mol

$\Delta_f G°(Pu^{3+}) = -578.984$ kJ/mol[d]

$\Delta_f G°(H_2O) = -237.140$ kJ/mol[e]

Therefore:

$$\Delta G° = -852.646 + 4(0.000) + 2(0.000) - (-578.984) - 2(-237.140) \text{ kJ/mol}$$

$$= 200.618 \text{ kJ/mol}$$

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{(200.618 \text{ kJ/mol})(1000 \text{ J/kJ})}{(8.314510 \text{ J/K·mol})(298.15 \text{ K})} = -80.9279283$$

$$\log K = \log(e^{\ln K}) = \log(e^{-80.9279283}) = -35.15$$

Chemical Equilibrium: $Pu^{3+} + 2H_2O \rightleftarrows PuO_2^{2+} + 4H^{+} + 3e^{-}$

Derivation:

$$\Delta G° = \Delta_f G°(PuO_2^{2+}) + 4\Delta_f G°(H^{+}) + 3\Delta_f G°(e^{-}) - \Delta_f G°(Pu^{3+}) - 2\Delta_f G°(H_2O)$$

$\Delta_f G°(PuO_2^{2+}) = -762.353$ kJ/mol[d]

$\Delta_f G°(H^{+}) = 0.000$ kJ/mol[e]

$\Delta_f G°(e^{-}) = 0.000$ kJ/mol

$\Delta_f G°(Pu^{3+}) = -578.984$ kJ/mol[d]

$\Delta_f G°(H_2O) = -237.140$ kJ/mol[e]

Therefore:

$$\Delta G° = -762.353 + 4(0.000) + 3(0.000) - (-578.984) - 2(-237.140) \text{ kJ/mol}$$

$$= 290.911 \text{ kJ/mol}$$

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{(290.911 \text{ kJ/mol})(1000 \text{ J/kJ})}{(8.314510 \text{ J/K·mol})(298.15 \text{ K})} = -117.3515066$$

$$\log K = \log(e^{\ln K}) = \log(e^{-117.3515066}) = -50.97$$

[a] Table 8–2 of ref 15.

[b] Table 5–2 of ref 15.

[c] Calculated elsewhere in this Appendix.

[d] Table 5–1 of ref 15.

[e] Table 8–1 of ref 15.