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Plutonium Oxidation State Distribution in the WIPP: Conceptual Model, Current Issues, and a Summary of Project-Specific Data

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1.0   INTRODUCTION

Plutonium is a key contributor to the actinide mobile concentration source term used to calculate release rates in the Waste Isolation Pilot Plant (WIPP) performance assessment (PA) for direct brine release (DBR) scenarios. The conceptual model used to determine the contribution of plutonium species to the source term has not changed since the initial Compliance Certification Application (CCA) (see also the historical overview presented in the CRA-2014 EPA technical support document (TSD) [EPA 2017]). The source-term concentration of plutonium, like all transuranic (TRU) actinides, is defined as the sum of its oxidation-state specific solubility and colloidal contributions. This oxidation-state-specific approach is consistent with the general understanding of how actinides interact in the environment [Runde et. al., 2010].

Of the TRU actinides important to WIPP performance assessment (PA), plutonium exhibits the most complex redox chemistry with potential contributions from the Pu(III), Pu(IV), Pu(V) and Pu(VI) oxidation states. The WIPP project has evaluated the potential contributions of all of these oxidation states and has shown that only Pu(III) and Pu(IV) are expected under WIPP-relevant conditions [DOE 1996; DOE Appendix SOTERM-2014]. The prevalence of these reduced-valent plutonium species is established by a) the reducing environment created by the anoxic conditions establish by the self-sealing properties of the salt geology, b) the high amounts of Fe(0/II) present in the repository and c) the wide stability field for Pu(IV) under environmentally-relevant conditions. Since the CCA and through the Compliance Recertification Application (CRA)-2014, a 50/50 distribution of these two oxidation states was used in WIPP PA.

There are however good reasons, since the CRA-2014 [DOE 2014], to reassess the 50/50 plutonium oxidation state distribution in WIPP PA. Most importantly, the use of this distribution was questioned by the EPA in its regulatory review of the WIPP model. The DOE has recognized this need and this assessment is underway. The main technical drivers for this are new data within the WIPP project, new data published in the literature, and the higher amounts of plutonium now expected in the WIPP repository. These recent data and changes in repository inventory potentially have a mixed effect on the net redox environment (E_h) and put a greater focus on understanding the long-term mobility and stability of Pu(III) species that form within the range of WIPP conditions considered in PA. The long-term stability of Pu(III) species, in the actinide environmental chemistry community, continues to be highly debated and there is not consensus on its long-term role in the environment.

LANL, for CRA-2019, recommends that the DOE continue to use the 50/50 oxidation state distribution for plutonium in WIPP PA. The most important reasons for this are:

- All WIPP-relevant data support the current oxidation-state distribution model. We see Pu(III) under highly reducing conditions and Pu(IV) under more realistic conditions of higher radiolysis and the presence of organics.

- It is not clear at this time that an increased Pu(III) allocation in the oxidation-state model leads to increased conservatism (e.g., higher Pu releases). The mobile actinide source term is a composite of the solubilities, as sampled throughout their range of uncertainty, and the colloidal contributions. These, in CRA-2014, do not show that Pu(III) release is always greater than Pu(IV) for all PA realizations and the net effect of changing oxidation state allocation is not straightforward.

- The literature data, as it now exists, remains ambiguous and is often not directly relevant to the WIPP-specific case of moderately high pH and high ionic strength brine systems. Extrapolation of these data to WIPP-relevant conditions is not straightforward and may lead to incorrect conclusions/applications.

- There are new literature data, as well as WIPP project data, that are expected in the next few years. There is, for this reason, a reasonable expectation that this chemistry will be understood with much greater clarity in the timeframe of CRA-2024.

This report starts the process of addressing EPA concerns specific to the plutonium oxidation-state distribution issues raised in the CRA-2014 TSD [EPA 2017] and associated discussions. The main goals of this report are:

1) Provide a brief overview of the current WIPP PA model used to determine the plutonium contribution to the Actinide Source Term.
2) Provide a summary of key EPA and literature-based issues that have been raised since the CRA-2014.
3) Summarize WIPP-specific data that address the oxidation state distribution of plutonium.
4) Finally, provide a brief assessment of the status of what is known in the context of WIPP-specific results and the issues that have been raised.

Additional details and assessments of this overall issue will be provided as part of the CRA-2019 documentation.

2.0   WIPP ACTINIDE/PLUTONIUM OXIDATION-STATE DISTRIBUTION MODEL

The WIPP project has had the same conceptual model for the oxidation state distribution of TRU actinides since the CCA. This model consists of a range in E_h (based on expert opinion) that brackets the expected conditions and establishes a set of actinide oxidation states for the least reducing conditions and most reducing conditions expected. Discussions that are more detailed are found in the CRA-2014 documentation [DOE Appendix SOTERM-2014; DOE Appendix PA-2014]. This modeling approach has been presented and discussed in the international community many times over the past ten years and continues to be supported by WIPP-specific results obtained by the DOE [Reed 1994, 1998, 2006, 2010, 2012, 2013].

The actinide oxidation-state distribution used in PA for each of the key TRU components in WIPP waste is shown in Table 1. These are sampled in the following way in PA:

- All PA vectors:

  Am(III), Cm(III) and Th(IV)

- Least-reduced PA vector (50% probability):

  U(VI), Np(V) and Pu(IV)

- Most-reduced PA vector (50% probability):

  U(IV), Np(IV) and Pu(III)

Table 1.   Oxidation states of the actinides in the WIPP as used in the CRA-2014 PA [DOE Appendix SOTERM-2014, Table SOTERM–17]

Actinide Element	Oxidation States, Abundance (%), and Analog Used (If Any)				EQ3/6 Speciation Data Used
	Oxidation State[a,b]				
	III	IV	V	VI	
Thorium	—	100 %	—	—	Thorium
Uranium	—	50 %	—	50 %	1 mM assumed for VI, Th for IV
Neptunium	—	50%	50 %	—	Np for V, Th for IV
Plutonium	50 %	50 %	—	—	Am for III, Th for IV
Americium	100 %	—	—	—	Americium
Curium	100 %	—	—	—	Americium

[a] Oxidation state distributions (percentages) refer to the percent of PA vectors that have 100% of the specified oxidation state.

[b] In PA calculations the distribution of oxidation states is correlated for U, Np, and Pu such that the states for all three elements are simultaneously either in the lower oxidation state (U(IV), Np(IV), and Pu(III)) or in the higher oxidation state (U(VI), Np(V), and Pu(IV)).

In the specific case of plutonium, Pu(IV) is the assumed oxidation state for the least-reduced PA vector and Pu(III) is the oxidation state assumed for the most-reduced PA vectors. This 50/50 oxidation state distribution, as is the case with all the actinides, was based on expert opinion and takes credit for the reducing environment produced in the WIPP by the excess emplaced iron that is present throughout repository history.

There are, in fact, no plutonium data in the WIPP solubility model due to the inherent complexity of working with plutonium in the pH and E_h regime expected in the WIPP. Am(III) is used as an analog for Pu(III) and Th(IV) is the analog of Pu(IV). The calculated solubility, individual colloidal contribution, total colloidal contribution, and total mobile concentrations for these two plutonium oxidation states in both the Salado and Castile brine case are shown in Table 2 for 5X brine solubilities. These data represent the median values for the mobile actinide concentrations used in PA. In this view, the mobile concentration of Pu(IV) is a factor of 4.45 and 6.4 times more "mobile" than Pu(III) for the Salado and Castile brine case respectively. This within order-of-magnitude agreement means that Pu(III) and Pu(IV) are within the uncertainty of the assumptions being made to estimate their relative mobility in WIPP PA. This contrasts with the open literature where Pu(III) is typically an order of magnitude more soluble than Pu(IV) under similar conditions and is an artifact of the approach used to estimate these values in WIPP PA.

Table 2.   **Plutonium solubility and colloidal contribution to the mobile actinide source term for the 5X brine case [DOE Appendix SOTERM-2014, Table SOTERM-23; individual colloidal contributions are based on personal communication from SNL PA].**

Oxidation State, Brine	Solubility (in M)	Colloidal Contributions (in M)					Total Mobile (in M)
		Intrinsic	Mineral	Humic	Microbial	Total Colloidal	
III, Salado	3.46E-7	2.00E-8	2.60E-8	6.57E-8	6.09E-7	7.21E-7	1.07E-6
III, Castile	1.98E-7	2.00E-8	2.60E-8	2.71E-7	3.48E-7	6.65E-7	8.62E-7
IV, Salado	6.46E-7	2.00E-8	2.60E-8	4.07E-6	0.00	4.12E-6	4.76E-6
IV, Castile	7.50E-7	2.00E-8	2.60E-8	4.72E-6	0.00	4.77E-6	5.52E-6

The current WIPP concept for the redox distribution of plutonium is qualitatively illustrated by the shaded area in Figure 1. Broadly speaking there is a wide E_h range where Pu(IV) is predominant whereas Pu(III) is only predominant at the very low E_h extremes. This illustration is based on available Specific Ion Interaction (SIT) parameters that were recently updated in the NEA databases [Altmaier et al., 2017]. There are at this time no suitable Pitzer data to extend this to the more WIPP-relevant higher ionic-strengths and doing this is beyond the current state of the art. A Pourbaix diagram based on an extension of the SIT data set to I= 5 M (so using analog data rather than plutonium data) is shown in Figure 2. Although it would not be appropriate to use this diagram to make quantitative predictions, it does provide qualitative insight that shows a somewhat shifted phase diagram that expands the area where Pu(III)aq would be expected to predominate.

An accurate plutonium and Pitzer-based Pourbaix diagram that extends to the high ionic-strength brines expected in the WIPP repository is beyond the current capability of the WIPP database (also currently true for all Pu databases).

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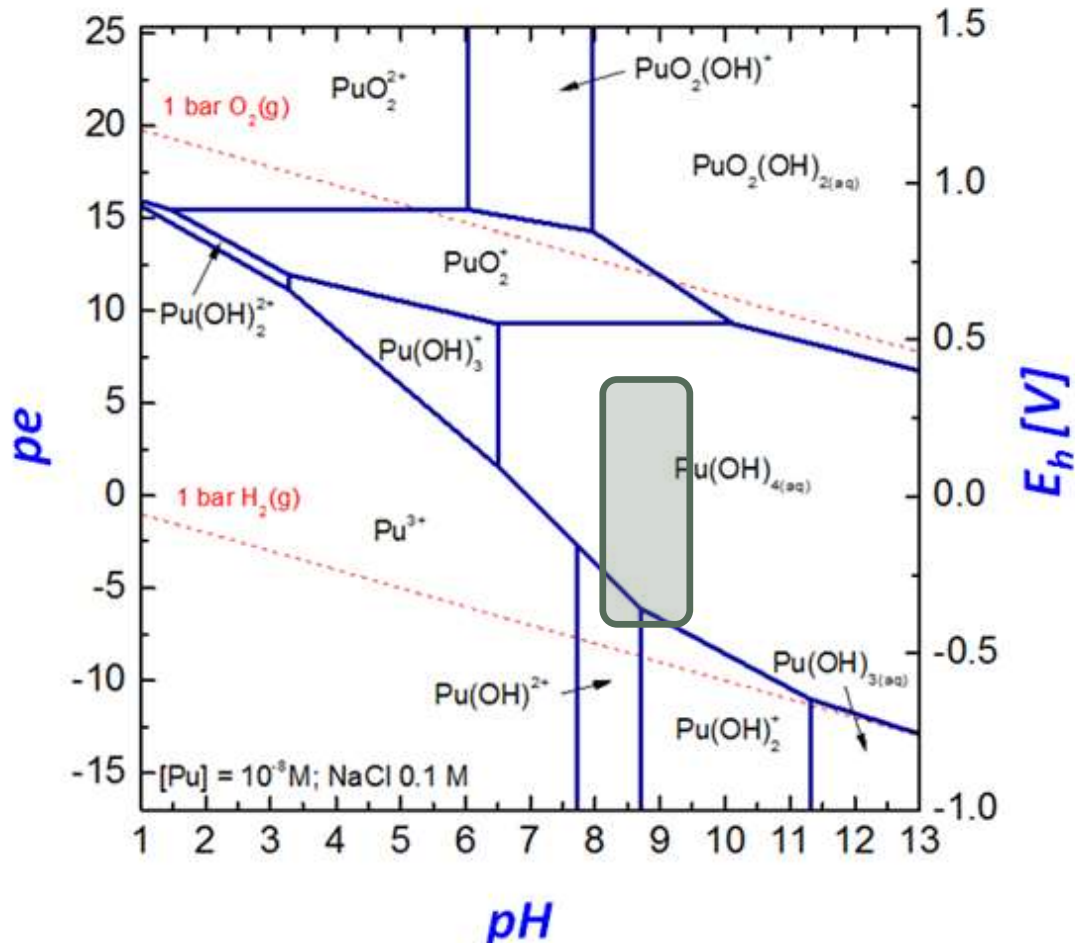
Figure 1. **Pourbaix diagram for aqueous plutonium hydrolysis species that qualitatively illustrates the current WIPP concept for Pu oxidation state distribution in the WIPP [Altmaier 2017]. Shaded area was added to illustrate the approximate range of WIPP-relevant conditions.**
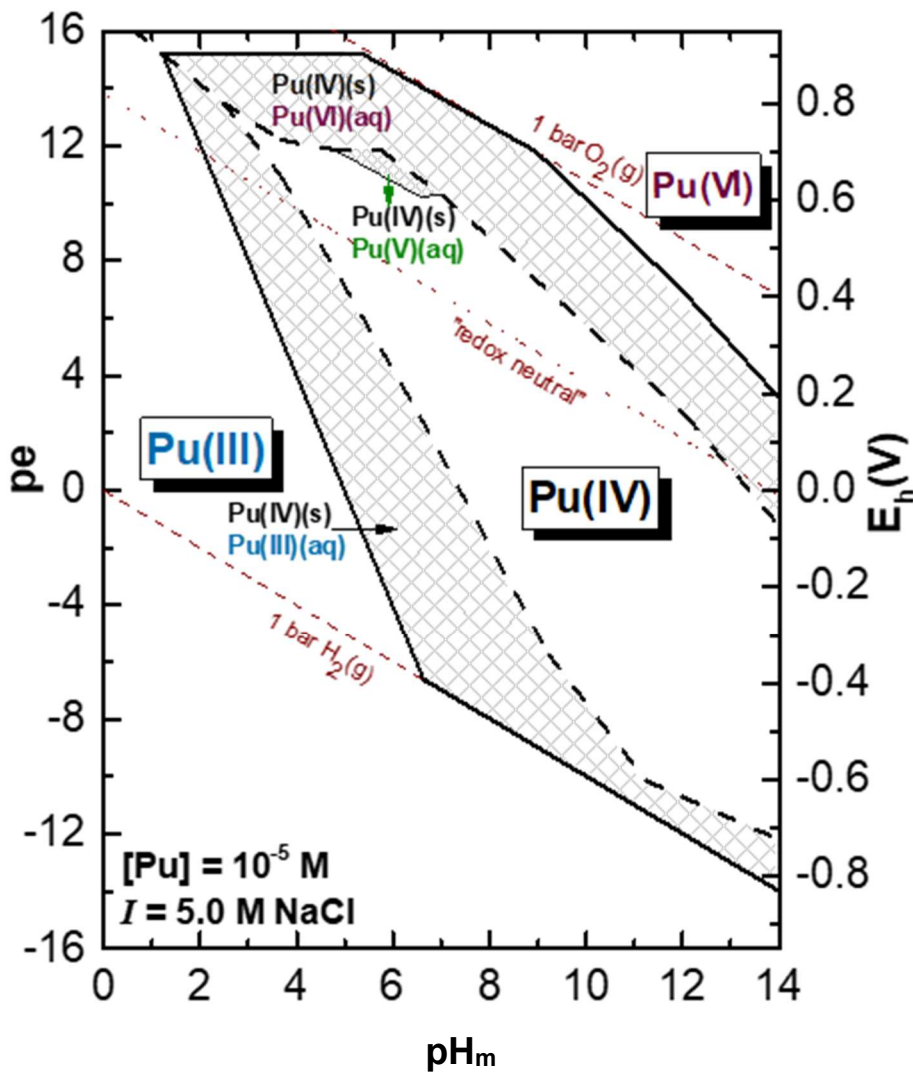
Figure 2. Pourbaix diagram of Pu at $I = 5.0$ M NaCl calculated with selected thermodynamic data. This is based on SIT parameters for An(III), An(IV), An(V) and An(VI) analogs of plutonium since a complete set of SIT and/or Pitzer data are not available for plutonium. For this reason the redox edges in the diagram are somewhat qualitative in nature (there is no analog for the redox properties of Pu). The extension to high I, however, shows a broadening of the mixed oxidation equilibrium region (Pu (IV) solid and Pu(III) or Pu(V) aqueous phase shown by the grid areas). Dashed lines and dotted line indicate upper and lower decomposition lines of water and "redox neutral" (pe + pH = 13.8), respectively. [Pourbaix diagram calculated by Ezgi Yalcintas – LANL/ACRSP]

3.0 HISTORICAL CONTEXT AND OVERVIEW OF REGULATORY/ LITERATURE ISSUES

The focus of this report is the current WIPP project position on the 50/50 oxidation state distribution for plutonium that is used to calculate the mobile concentrations of plutonium in PA. A brief review of the historical perspective of this issue, as well as a summary of current EPA-identified and literature-linked issues are given in this Section. The EPA recommendation to increase the relative amount of Pu(III) in the PA realizations is relatively new and was a post-CRA-2014 request that was received by the WIPP project in the late 2015/early 2016 timeframe.

Historical Perspective:

The WIPP 50/50 model for plutonium was developed in the early to mid-1990s. This reflects an expected Pu content of ~10 metric tons in the WIPP and the understanding of the applicable environmental chemistry at that time. The WIPP Features Events and Processes (FEPs) and associated assumptions that form the basis of the current WIPP conceptual model were also defined on this basis. A chronology of the regulatory view and development of this issue was provided in chapter 5 in the EPA TSD [EPA 2017]. This, along with the concurrent understanding of the plutonium environmental chemistry that supported this DOE position, is briefly summarized in Table 3.

Table 3. Summary of the regulatory position and understanding of environmental chemistry since the CCA

WIPP License Application	Regulatory Position	Plutonium Environmental Chemistry Understanding
CCA (1998)	50/50 position supported. Concern raised over the possible contributions of Pu(V/VI) and additional data from DOE requested.	Plutonium was expected to persist as $Pu(IV)O_2$ under environmentally relevant conditions. Little/no WIPP data specific to this issue existed. Pu(III) was thought to be unstable in the environment.
CRA-2005	Same as in the CCA.	Essentially the same as in the CCA. The identification of PuO_{2+x}, which is Pu(V) or Pu(VI) species raised increased concern over the environmental source term and storage conditions of plutonium oxide-based waste.
CRA-2009	Same as in the CCA but significantly less concern over oxidized Pu.	Continued view that PuO_2 and Pu(IV) species are predominant. The PuO_{2+x} issue was established as transitory and a relatively small contributor to its environmental chemistry. First confirmation of Pu(III) under the higher pH and more environmentally relevant conditions are reported.
CRA-2014	The 50/50 position was supported. Requests to consider a higher role for Pu(III) were received to add to the conservatism of the WIPP PA model.	Continued view that PuO_2 and Pu(IV) species are predominant. A number of papers in the literature, including WIPP-specific data, challenge this and show a possible role for Pu(III) under environmentally relevant conditions. These are mostly linked to mixed oxidation state equilibria with $Pu(III)_{aq}$ and $Pu(IV)_{solid}$

There is still not consensus within the actinide environmental chemistry community that Pu(III) species have a meaningful role over long times in repository and reducing subsurface settings. There remains a strong expectation within the actinide community that the environmental chemistry of plutonium should be predominantly linked to PuO_2 and Pu(IV) species. This is coupled with a view that Pu(III) species are ultimately thermodynamically unstable and only transitory in nature. This was a subject of significant debate as recently as Migration 2015 conference (Santa Fe, September 2015). This continues to be a contributing factor to the lack of clarity on the role of Pu(III). In this context, Pu(III) is a transitory, possibly conservative, oxidation state that can be established under low E_h conditions in the laboratory but is not likely to be predominant under the more realistic environmental as well as WIPP-relevant conditions.

EPA-identified issues:

The EPA, in their 2014 TSD [EPA 2017], have raised the following issues:

a) The WIPP is underestimating the role of Pu(III) in the WIPP and this is non-conservative. This is based on Fe(II)/Fe(0) chemistry within the project (LANL/ACRSP data) and in the open literature (PNNL work, KIT/INE work, anaerobic microbial studies).

b) The WIPP should abandon the E_h "range" approach in the conceptual model – it is proposed to move to a more complex E_h model for just the Pu system and disconnect this from the other redox-sensitive actinides that impact PA. The upper bound of the "less reduced" vector in WIPP should be reductive dissolution of PuO_2.

c) There is specifically not agreement about the role of organics and microbial effects as to their redox properties and effects on the Pu oxidation state. The EPA believes there is clear literature that supports the reduction of Pu to Pu(III) by EDTA and bio-mediated reduction. In this view, Fe(0, II), microbial processes, and organics lead to only Pu(III) in the WIPP.

Literature-identified issues:

a) There is not consensus within the actinide environmental chemistry field on the role of Pu(III) and its recognition as a prevalent/important species is not widely accepted.

b) There are, however, new low ionic-strength data that show Pu(III) can be present in both the solid and aqueous phase at pH < 6. At pH>6, however, the existence of Pu(III) was evaluated as metastable even after several months [Tasi 2018].

c) There are no Pu(III) crystalline phases identified in the literature that are environmentally relevant (e.g., hydroxide, carbonate, organic). These have not been successfully synthesized and there are correspondingly no published XRD data for phase confirmation and identification.

d) The Pu(III) thermodynamic data has a high uncertainty and needs to be improved. These data alone are not adequate to sufficiently resolve this issue.

e) There remains a large range of uncertainty in the literature for the relative solubility of Pu(IV) and Pu(III) actinides (See Figure 3 and associated references).
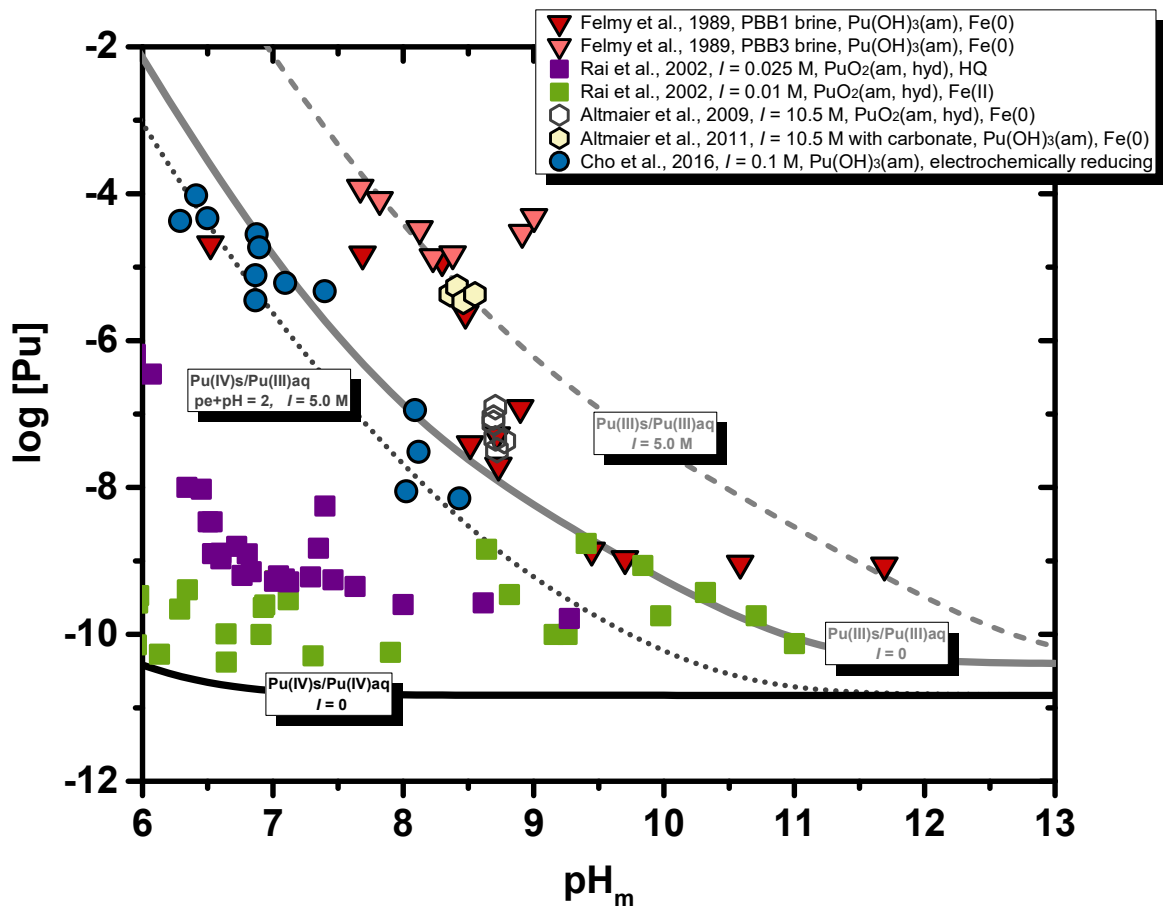
Figure 3. Literature comparison of Pu(III) and Pu(IV) solubility data showing relatively wide scatter in the data. [Summary Figure provided by Ezgi Yalcintas, LANL/ACRSP]

4.0   SUMMARY OF WIPP-SPECIFIC DATA

A significant amount of research was performed during the 1990s as part of the WIPP Actinide Source Term Program (ASTP) managed by Sandia National Laboratories (SNL) to support the certification of the WIPP. These data, mainly pertaining to actinide solubility, have been well reported in past CRA documentation.   There are two project-specific data sets that address the oxidation state distribution of plutonium under WIPP-relevant conditions:

1) Argonne experiments [Reed 1994, 1998, 2006] that were performed at the end of the ASTP program.   Here Fe(0) iron and aqueous Fe(II) were added to ^{239}Pu(VI) stability experiments that had been pre-equilibrated for 2-4 years under anoxic conditions.   Additionally, the effects of organic complexants on oxidation-state distribution were evaluated.

2) Los Alamos experiments [Reed 2010, 2012, 2013] performed in the Actinide Chemistry and Repository Science Program (ACRSP) where Pu(VI) was interacted with a range of iron and iron oxide phases for up to ten years.

The results of these two experiment sets are summarized in this Section.

4.1 Pu(VI) Stability and Reduction in WIPP Brine: Argonne Experiments

Plutonium (VI) aqueous species (plutonium-239, NIST-traceable > 99% purity by activity and mass) were prepared and added to WIPP brine in a nitrogen glovebox to exclude oxygen in the system. Carbonate, when present, was added to the system as a plutonium-carbonate complex. Experiments were performed in the dark, with ~ 1 atmosphere hydrogen overpressure, in low and high magnesium brines, at pC_{H+} 5 to 10, in the absence or presence of carbonate, and for a duration of up to 2 years. Initial plutonium concentrations were 0.1 mM. The total plutonium concentration was monitored using a Packard 2 pi alpha scintillation counter. The oxidation state was established and tracked using absorption spectrometry on a CARY5 spectrometer. The range of conditions evaluated were:

❑ pC_{H+} 5-10 at room temperature (~ 23 ºC)

❑ Pre-equilibrated systems, with and without carbonate

❑ G-SEEP and ERDA-6 brine

❑ Fe coupon, Fe^{2+} and MgO

❑ Organics: acetate, oxalate, citrate, and EDTA

The results of these experiments have been published and previously discussed with the EPA. The main conclusions/observations from this set of experiments were:

• Plutonium (VI), when no reducing agent was present, was stable at 0.1 mM concentrations as a carbonate or hydrolytic species under all conditions investigated in WIPP brine with little/no precipitation noted.

- The addition of iron to the pre-equilibrated Pu(VI) solutions led to rapid reduction of Pu(V/VI) to Pu(IV) leading to the precipitation of a disordered PuO_2 (am) phase (See Figure 4). There was also good agreement between the empirical steady-state concentrations measured after reduction by iron and the calculated solubility of Pu (IV). These remain the most WIPP-relevant results as they were performed in radiolysis-impacted conditions and used Pu-239 as the plutonium isotope.

- Long-term (~6 month) studies with organics show eventual reduction of Pu(V/VI) to form Pu(IV) organic complexes although the rates varied considerably as a function of pH and the organic complexant evaluated.
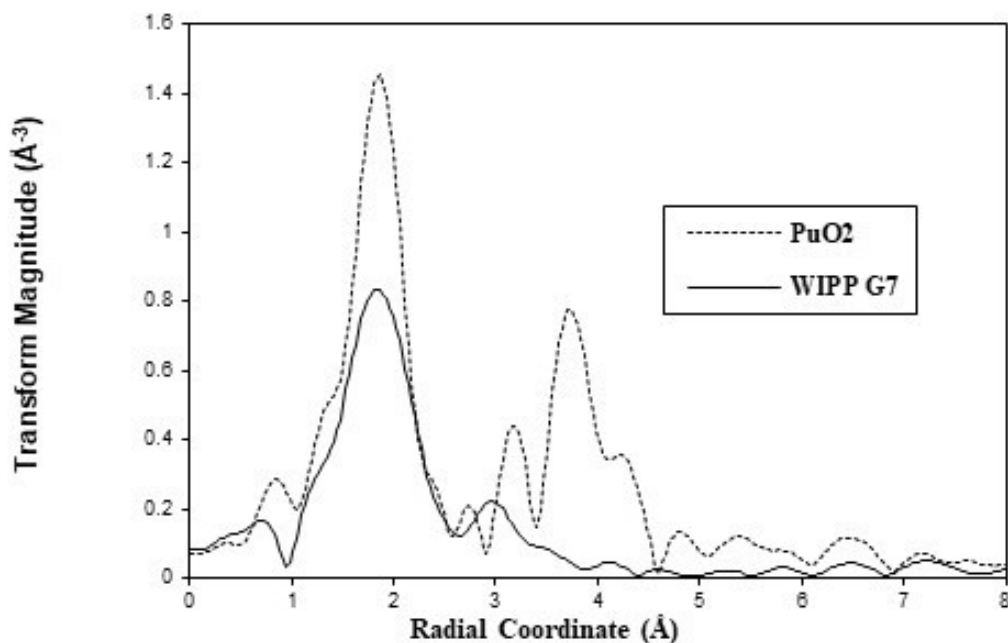
Figure 4. **EXAFS analysis, in radial space, of the plutonium precipitates collected from the pH 7 WIPP (G7) experiments containing iron showing greater PuO_2 disorder in the brine samples. The corresponding X-ray Absorption Near-Edge Spectra (XANES) of these unknowns matched the spectrum of the $Pu(IV)O_2$ standard confirming that the Pu (VI) was being reduced.**

4.2 Pu-Fe Interaction Experiments: Los Alamos/Actinide Chemistry and Repository Science Program (ACRSP)

The second set of experiments were Pu-Fe interaction studies performed under WIPP-relevant conditions in anoxic brine systems [see Reed et al., 2010, 2012 and 2013]. The experimental matrix for these experiments is given in Table 4. The range of conditions addressed were:

- ❑ Pu-242 used (not Pu-239 as in the ANL experiments)
- ❑ GWB and ERDA-6 brines
- ❑ Fe coupon, Fe powder, and Fe oxides

The goal of this research effort was to confirm the reduction of Pu(V/VI) to Pu(III/IV) by reduced iron and establish the nature and long-term stability of the plutonium oxidation state under WIPP-relevant conditions.

Table 4. Experimental matrix for the Pu-Fe interaction study (Pu-242)

Experiment Designation	Iron Content	pH	Duration	Brine	Environmental Conditions
Experiments with Fe(0) Powder					
Pu-FEP-E8-1, 2	Fe Powder	8	Multi-year	ERDA-6	Room T, 15 mL, anoxic, without carbonate
Pu-FEP-E10-1, 2	Fe Powder	10	Multi-year	ERDA-6	Room T, 15 mL, anoxic, without carbonate
Pu-FEP-GWB7-1,2	Fe Powder	7	Multi-year	GWB	Room T, 15 mL, anoxic, without carbonate
Experiments with Fe(0) Coupons					
Pu-FEC-E8-1, 2	Coupon	8	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FEC-E10-1, 2	Coupon	10	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FEC-G7-1,2	Coupon	7	Multi-year	GWB	Room T, 15 mL, anoxic, without carbonate
Experiments to investigate Fe oxidation state Dependence					
Pu-FEC-1, 2	Fe Coupon	9	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FEP-1, 2	Fe Powder	9	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE2-1, 2	Fe^{2+} Colloidal	9	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE3-1, 2	Fe^{3+} Colloidal	9	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE3-OX-1, 2	Fe(III) oxide	9	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE23-OX-1, 2	Fe (II/III) oxide	9	Multi-year	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Note (1) – Starting [Pu] = 0.1 mM, with an approximate Ci content of 1.4 µCi/experiment					
Note (2) – the notation 1,2 represents replicate experiments					
Note (3) – Experiments are 2 wks for Pu (VI) stability and 2 weeks following the addition of Fe					

Effect of Reduced Iron on Redox and Actinide Oxidation States

Long-term (up to 10 year) experiments to establish the oxidation state distribution of actinides in brine systems under a wide range of subsurface conditions were performed. In our investigations ^{242}Pu, initially added as PuO_2^{2+}, was used to minimize radiolytic effects and establish chemical trends. In these brine systems, Pu(VI) is stable for years when no reducing agent is present [Reed 2006].

Two WIPP-relevant brines [Lucchini 2013], GWB as a high magnesium brine typical of MgO-reacted brine and ERDA-6 as a high sodium chloride brine typical of brines found in the far field (Castile), were used in these studies. The initial oxidation state was established using absorption spectrometry (Varian CARY 5000) and Pu-Fe solids were recovered from these brines for further analysis. Liquid scintillation counting (Beckman-Coulter LS 6500) and ICP-MS (Agilent) were used to determine total plutonium concentration. Aqueous iron chemistry was established using a combination of a FerroZene® colorimetric method and ICP-MS. XANES analysis, combined with anoxic dissolution and UV-VIS-NIR spectroscopy (Varian CARY 5000) were used to establish the oxidation state of the precipitated plutonium.

Iron reduction experiments were performed by adding iron and iron oxides to anoxic Pu(VI) solutions as a function of pH. These results are shown in Figure 5. At the end of the kinetic studies, samples of Fe-associated plutonium species were recovered and analyzed by XANES. After equilibration for an additional 5.5 years, these solutions were re-analyzed to establish the iron speciation, plutonium speciation and E_h. Selected experiments were subsequently analyzed at ~ 10 years.

Initially, only Pu(IV) was evident in the XANES analysis (see Figure 6). This correlated with a plutonium concentration that was in the range of 2×10^{-9} M to as high as 1.5×10^{-7} M at the lower end of the pH range (pH = 7). These data agreed with the results obtained in a prior study of approximately two years when Pu-239 was the plutonium isotope. After ~5.5 years, these same solid samples were re-analyzed and found to be mostly Pu(III) with some Pu(IV). These results are summarized in Table 5. The results, after ~ 10 years, are shown in Figure 7 and Figure 8. The observation of Pu(III) in the solid phase correlated with an increase in the plutonium solution concentrations from 1×10^{-8} M to as high as 3×10^{-7} M. This was a slight elevation in concentration, by a factor of ~ 2 to 5, when compared to the earlier Pu(IV) data. This increased solubility may indicate a phase transformation to Pu(III) since the solubility of Pu(III) is expected to be somewhat higher than Pu(IV) under these conditions. No Pu(III) phase has yet been confirmed in this system suggesting that the plutonium could also be predominantly present as sorbed Pu(III) species given the high iron/iron oxide surface area present.

The plutonium (III/IV) solids data show a qualitative correlation with the Fe(II)/Fe(III) ratio and measured E_h. Experiments with less negative E_h also had a greater amount of Fe(III) and Pu(IV) species present in the system. This adds to the linkages seen by others between the iron and plutonium chemistry in subsurface conditions. Although these specific experiments were performed in brine, they are consistent with the correlation between iron chemistry and other metals observed in low ionic strength groundwater. Although not discussed in this report we have also demonstrated that U(VI) and Np(V) are reduced by zero-valent iron and Fe(II) aqueous/solid species and this also confirms the lower oxidation states expected in the WIPP for these actinides in the most-reduced PA vectors.

Table 5. Qualitative redox indicators for iron interactions with plutonium under anoxic conditions

Experiment	Description	[a] Oxidation State of Pu Solid	[b] $[Fe]_{total}$ in mM (%Fe^{2+} in solution)	[c] E_h Measured (± 3 mV)
PuFe23OX	ERDA-6 brine at pH ~9 with excess magnetite	~87% Pu(III), rest Pu(IV)	0.12 (25%)	-122 mV
PuFeCE8	ERDA-6 brine at pH ~8 with Fe coupon	~100 % Pu(III)	ND	ND
PuFeCE10	ERDA-6 brine at pH ~ 9.6 with Fe coupon	~100% Pu(III)	0.27 (100%)	ND
PuFeP	ERDA-6 brine at pH~9 with excess Fe powder	~100% Pu(III)	0.18 (100%)	-175 mV
PuFeC	ERDA-6 brine at pH ~ 9 with Fe coupon	~90% Pu(III), rest Pu(IV)	0.18 (58%)	-110 mV
PuFeG7	GWB brine at pH ~6.7 with Fe coupon	~ 100% Pu(III)	12.62 (97%)	-210 mV

a. Pu(III) content established by XANES analysis of solids
b. Fe(II) content established by analysis using FerroZene®
c. E_h measurement made using an Orion combination ORP electrode
   ND – not determined

E_h Measurement in Brine Systems

The measurement of E_h is problematic in high ionic strength brine systems. In this context, these types of measurements, at best, provide qualitative but rarely quantitative data on the redox conditions in the brine experiment.

To investigate these qualitative relationships, E_h measurements were made on a series of plutonium solubility and redox speciation studies that contained excess reduced iron [Reed 2012]. All measurements were made in the nitrogen glovebox where the experiments were conducted (P_{O2} < 0.1 ppm). These experiments were not sampled frequently and were doubly sealed/isolated to minimize the effects of occasional elevated oxygen levels in the glovebox due to other experiments and routine operations. An Orion epoxy sure-flow combination redox/ORP electrode (model 9678-BNWP) was used with the high ionic strength internal Ag/Cl reference solution provided by the manufacturer. This electrode was pre-conditioned in the glovebox for several hours. The manufacturer-supplied ORP standard was used to calibrate the electrode and frequent checks of the electrode response were made throughout the E_h measurements made.

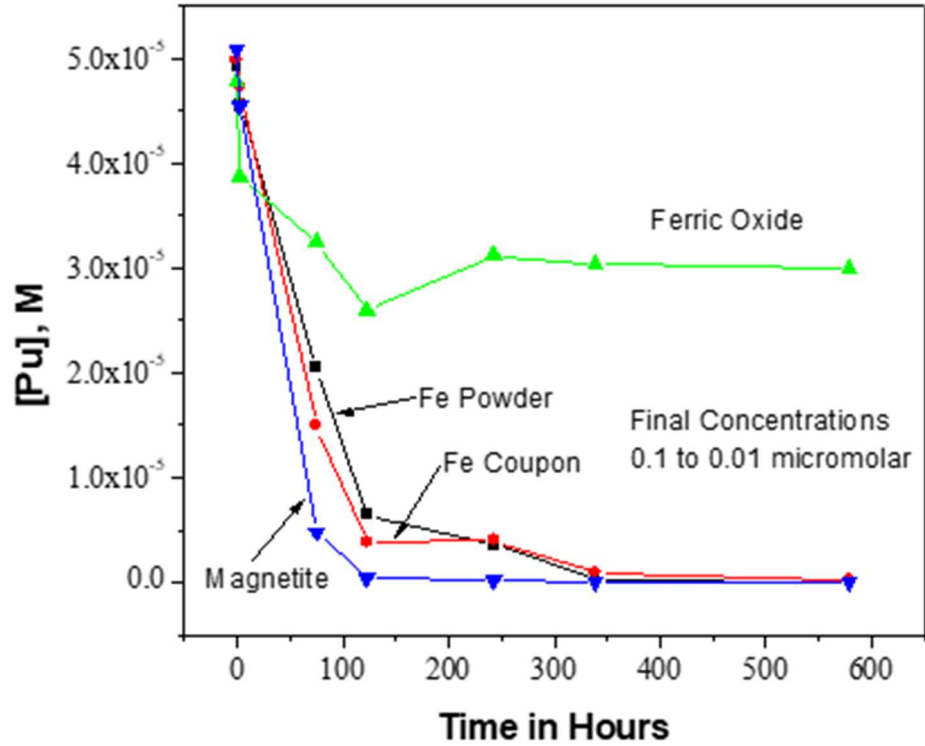**Figure 5.** Concentration of plutonium as a function of time after contact with iron and iron oxide phases in ERDA-6 brine. Fe powder is experiment PuFeP, Fe coupon is experiment PuFeC, magnetite is experiment PuFe23OX, and ferric oxide is experiment PuFe3OX.
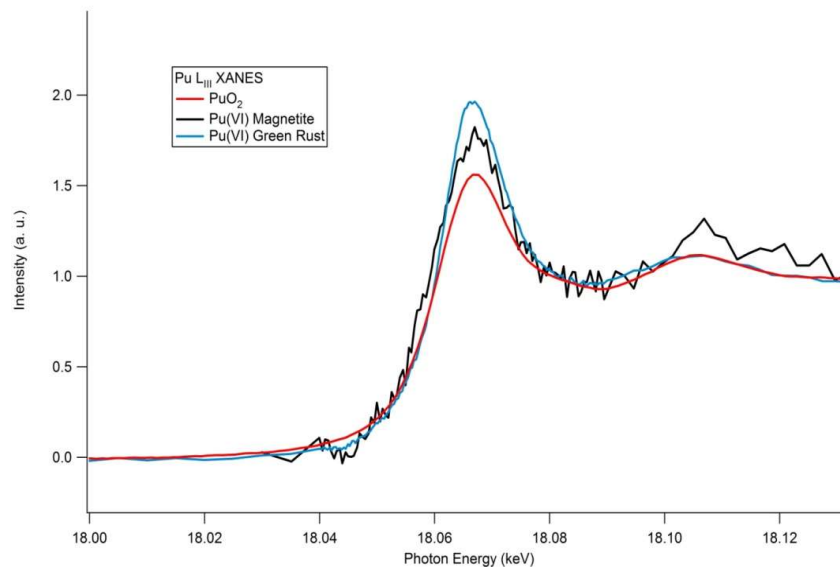
Figure 6. XANES analysis of plutonium precipitates in the magnetite after 3 months showing that only Pu(IV) phases are being formed.
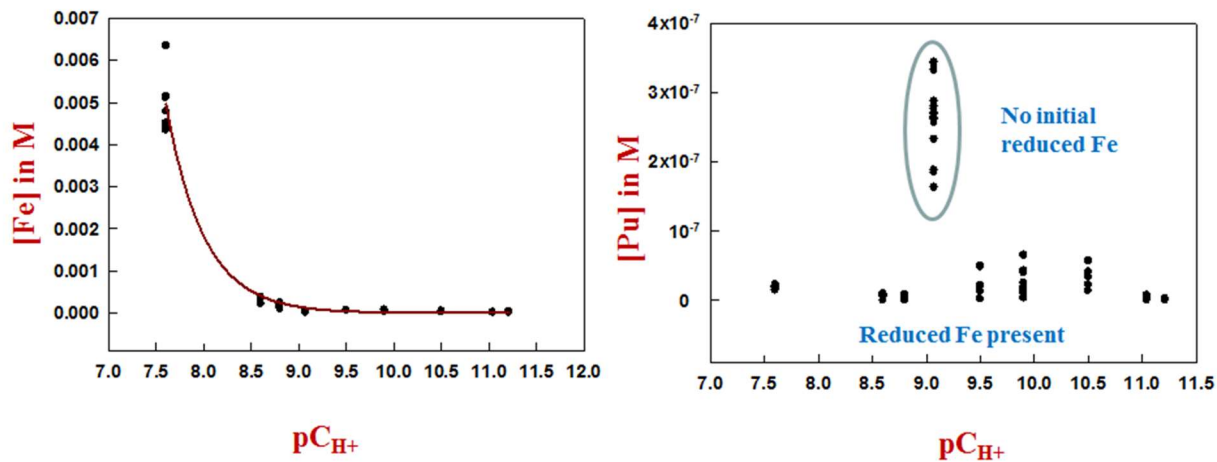
Figure 7. Pu-Fe Interaction Studies at ~ 5.5 years. The concentration of iron obtained under reducing conditions is shown (left Figure). The corresponding plutonium concentrations as a function of filtration are also shown (right Figure). Low Pu concentrations are obtained unless there was no available Fe(0/II). The Fe-associated and aqueous Pu in these systems was Pu(III) when there was only Fe(0, II) available.
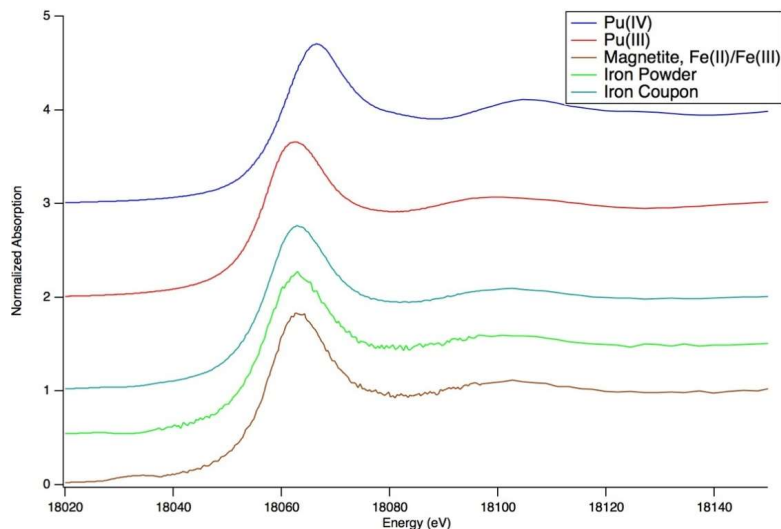
Figure 8. XANES of Fe-associated Pu showing the Pu to be predominantly Pu(III) since the edge position of the XANES matched the Pu(III) standard. [Analyses performed by Jeff Terry and Dan Olive, IIT at the Advanced Photon Source Synchrotron]

The results of the E_h measurements made were given in Table 5. Typical electrode equilibration times were 20-30 minutes. In the absence of iron and plutonium, the brines used (high magnesium GWB, and sodium chloride ERDA-6), had a measured E_h of +464 ± 5 mV in the presence and absence of air. In the presence of soluble/measurable amounts of dissolved iron species the E_h became negative, as expected, with a range of -100 mV to -220 mV. This seemed to qualitatively correlate with the measured concentration of Fe^{2+} in solution. Equilibration times under these conditions were ~ 20 minutes, slightly shorter than in the absence of Fe. Fe^{2+} and Fe^{3+} concentrations were measured using a modified method based on the FerroZene® complexation of Fe^{2+} [Pepper 2010]. Under the conditions of our experiments, approximately 1 mM carbonate was present in the brine (except experiment PuFeG7), so some solubilisation of Fe(III), as Fe^{3+}, was possible and this appears to have impacted (raised) the E_h measurements slightly. These results were reproducible over the course of the five hours that samples were analysed in the glovebox environment.

4.3   Summary of WIPP-specific Data

An overall summary of current WIPP-specific Plutonium-Fe data is shown in Table 6. The key observations in this WIPP-specific research are:

- Pu(V/VI) are stable in anoxic WIPP brines when no reducing agent is present (at least on a multiyear basis).

- Higher oxidation states are reduced by organic chelating agents to eventually form Pu(IV)-organic complexes. There is no evidence, under WIPP-specific conditions, for further reduction to Pu(III) although this continues to be a subject of investigation.

- Pu(V/VI) reduction to Pu(III/IV) by Fe(0, II) has been demonstrated for long-term studies under a wide variety of WIPP-relevant conditions. In all cases investigated, no Pu(V/VI) persisted.

- Under anoxic/low radiolysis conditions, and in the absence of organics, Pu(III) in solution and as an Fe-associated "solid" is the predominant oxidation state that is observed when Fe(0/II) is present.

- A mixture of Pu(III/IV) is observed when Fe(II/III) phases are present (more realistic WIPP case).

- Mostly Pu(V) is observed when only Fe(III) is present which confirms that the availability of Fe(0, II) is the key to reduction of Pu(VI) to Pu (III, IV).

- The presence of available Fe(0, II) led to E_h measurements that are in the range of -100 to -220 mV which is in the center of the Pu(IV) speciation in the E_h-pH diagram (see Figure 1).

All of these combine to show that the iron chemistry under WIPP-relevant conditions established very reducing conditions and the Pu(III/IV) oxidation states should predominate in the WIPP. This is a very good/positive overall result for the WIPP project and long-term immobilization of Pu in a salt repository that continues to support our current modeling approach. These are also all

consistent with the current WIPP PA model and assumptions about the oxidation-state distribution of Plutonium.

Table 6.   Under expected WIPP conditions (ANL work highlighted in green) a predominance of Pu(IV) is observed. Pu(III) is predominantly noted in the low radiolysis case when no Fe(III) is present. When both Fe (II) and Fe(III) are present, a mixture of Pu(III) and Pu(IV) occurs.

Summary of all WIPP project-specific data for the Pu-Fe systems since the inception of the WIPP project			
Conditions	Experiments	Result/Observation	Reference
"oxidizing" no reducing agent present	Pu(VI), as Pu-239, was added to WIPP-specific brine - > 4 year experiments	Pu(VI) as an aquo complex and carbonate complex was mostly stable with some Pu(V) formation noted no reduction to Pu(IV/III) was observed.	ANL work
	Pu(VI), as Pu242, was added to Fe(III) solids	Pu(VI)/Pu(V) mixture observed – no reduction to Pu(IV/III)	LANL/ACRSP post CRA-2014 data
WIPP (expected conditions)	Pu(VI), as Pu-239, was equilibrated for ~ 4 years in brine and then Fe(O) was added	Pu(V/VI) in solution was rapidly reduced to Pu(IV) in all cases, XANES confirmed that only Pu(IV) was formed	ANL work
Mixed reducing conditions	Pu(VI), as Pu242, was added to Magnetite (Fe(II/III) in WIPP-specific brine	Rapid reduction to Pu(IV) was noted and confirmed in the solid phase by XANES. In the longer term, ~6 years' results, a ~ 10-75% Pu(IV) with the rest Pu(III). Full reduction to Pu(III) was never noted.	CRA-2014 Appendix SOTERM
Reducing conditions	Pu(VI), as Pu242, was added to zero-valent Fe (powder and coupon) in WIPP-specific brine	Rapid reduction to Pu(IV) and confirmed in the solid phase by XANES. In time, this was further reduced to ~ 100% Pu(III). The nature of the Pu(III) solid phase was not established.	CRA-2014 appendix SOTERM and Post-CRA-2014 cutoff data.

5.0 SUMMARY OF THE CASE FOR CONTINUATION OF THE 50/50 Pu MODEL THROUGH CRA-2019

LANL, as stated in the introduction, will continue to recommend that the DOE use the 50/50 assumption to model plutonium oxidation-state distribution in the WIPP for CRA-2019. There is not sufficient data at this time to justify a change in the 50/50 concept that has been a part of the WIPP safety case since the CCA and no project-specific data contradicts these PA assumptions.

At this point in time, WIPP project-specific data support the following:

➢ Under the most WIPP-relevant conditions (anoxic, high pH, Pu-239, presence of some Fe(III)) only Pu(IV) has been observed. Pu(III) as an aqueous/sorbed species (but not as a precipitated solid) is observed for low-radiolysis and the presence of Fe(0/II).

➢ Project-specific data show that organics reduce Pu(V/VI) to Pu(IV). There are no project-specific data that show reduction of Pu(IV) to Pu(III) by organic chelating agents (e.g., EDTA and Citrate) at WIPP-relevant conditions.

➢ There is not an accepted approach to measure and model E_h in a way that can be reliably used to quantitatively predict oxidation-state distribution of trace metals/radionuclides in complex systems similar to those expected in WIPP. For this reason, reliance on expert opinion combined with site-specific data should be used to address the complex effects of iron and radiolysis on actinide speciation under WIPP-relevant conditions.

➢ There are project-specific data that show that microbial reduction of metals and multivalent actinide are not active under WIPP-relevant conditions.

➢ Lastly, there is a complex relationship between the plutonium solubility and its total mobile concentration across all the PA realizations used to predict release. In CRA-2014, the median values for the Pu(III) and Pu(IV) solubilities show Pu(IV) to be more soluble with correspondingly the higher mobile actinide concentration. This is a result of the inherently greatly uncertainty currently assigned to the An(IV) actinides in PA. It is important, for this reason, to look holistically at the entire impact of changes to the oxidation state distribution model and not only focus on literature-based solubility data.

The following directly responds to the EPA-identified issues listed in Section 3:

a) The WIPP is underestimating the role of Pu(III) in the WIPP and this is non-conservative. This is based on Fe(II)/Fe(0) chemistry within the project (LANL/ACRSP data) and in the open literature (PNNL work, KIT/INE work, anaerobic microbial studies).

    i. WIPP-specific experiments that show the predominance of Pu(III) were not designed to address the complexities that are present in the WIPP under realistic conditions. These ignore the impacts of radiolysis, organics that could oxidize Pu(III), and other waste components that all move the E_h in a positive direction (so favor Pu(IV) as shown in Figure 1). These realistic impacts should be more fully addressed before the project moves to a technical position that is still not well accepted within the actinide community. Experiments that evaluate these effects are also underway and these results will not be available in time to influence the CRA-2019 PA.

    ii. It is not clear that an increased role for Pu(III) is "conservative" from the point of view of actinide concentrations. Although literature results show Pu(III) to be more soluble,

in WIPP PA implementation (see Table 2), Pu(IV) contributes the most (by a factor of ~5) to the mobile actinide concentration that defines the actinide source term in the CRA-2014 PA. Here, an increase in the 50/50 assumption toward Pu(III) would have led to a lower [Pu] in the source term. There is, in this case, a conceptual disconnect between the PA implementation and literature-based expectation that demonstrates the highly conservative nature of the WIPP PA model and the approach/assumptions used to generate the actinide source term.

    iii.   There remain significant uncertainties in the literature about the speciation and long-term stability of Pu(III) and Pu(IV) phases as well as the actinide speciation that defines their relative solubility. Significant improvement of this understanding is expected in the CRA-2024 timeframe.

b) The WIPP should abandon the E_h "range" approach in the conceptual model – it is proposed to move to a more complex E_h model for just the Pu system and disconnect this from the other redox-sensitive actinides that impact PA. The upper bound of the "less reduced" vector in WIPP should be reductive dissolution of PuO_2.

    i.   Although this may be proven true, it is important that the effects of E_h on all multivalent actinides be considered. From a PA point of view, it is unlikely that this degree of complexity can be modeled accurately (or is needed).   Sampling within an E_h range more properly recognizes the inherent uncertainty and complexity in predicting the conditions expected in the WIPP repository.

c) There is specifically not agreement about the role of organics and microbial effects as to their redox properties and effects on the Pu oxidation state. The EPA believes there is clear literature that supports the reduction of Pu (IV, V, VI) to Pu(III) by EDTA and bio-mediated reduction will also lead to the formation of Pu(III). In this view, Fe(0, II), microbial processes, and organics lead to only Pu(III) in the WIPP.

    i.   The best interpretation of the literature on the impacts of organics, and in particular EDTA, is that there is not a clear understanding of this process.   Additionally, there are no data under WIPP-relevant conditions that clearly establish the reduction or oxidation of Pu(III/IV) species by organics. WIPP-specific data only address the stability of the Pu(V/VI) oxidation states and show Pu(IV) as the likely long-term oxidation state. This process is highly pH-dependent, impacted by ionic strength and the speciation of the plutonium species so connecting literature "dots" from less relevant conditions can lead to wrong conclusions. This lack of clarity has already been recognized and studies under WIPP-relevant conditions are underway.

    ii.   It is also acknowledged that there is microbial work that show that plutonium is reduced to Pu(III) by soil bacteria for sulfate reducing bacteria (SRB) and metal reducers under anaerobic conditions. It is however incorrect to extrapolate these results to the high ionic-strength microbial ecology that will be predominant in WIPP [Swanson 2018]. In fact, current investigations have shown that these microbial processes do not function under WIPP-relevant conditions and will not influence the 50/50 Pu issue.

Overall, it is clear that there will be much better and more clear-cut answers to the questions on the 50/50 plutonium oxidation-state distribution issue in the very near future as both WIPP project and non-WIPP researchers reach a better understanding of this complex redox chemistry.

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