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REDUCTION OF HIGHER-VALENT PLUTONIUM BY IRON UNDER WASTE ISOLATION PILOT PLANT (WIPP)-RELEVANT CONDITIONS: DATA SUMMARY AND RECOMMENDATIONS

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EXECUTIVE SUMMARY

The oxidation state distribution of plutonium, which is a key actinide contaminant in the Waste Isolation Pilot Plant (WIPP), is a critical input to WIPP performance assessment because of the strong correlation between its oxidation state distribution and its overall solubility. In WIPP performance assessment (PA), the plutonium oxidation state is distributed between the low-solubility Pu(III) and Pu(IV) species. Higher-valent plutonium, specifically Pu(V) and Pu(VI) species, do not persist in the WIPP due to the strongly reducing conditions that are expected.

This data summary report is intended to support the WIPP Compliance Recertification Application (CRA)-2009 recertification process. In this report, we specifically address the important and key role of reduced iron, which is by far the largest-quantity reducing agent emplaced in the WIPP, and its effects on the redox stability of higher-valent plutonium. The WIPP-relevant data summarized correspond to the experimental results that were available at the time of the CRA-2009 data cutoff. In this context, the three key goals of this summary report are:

1) Provide an updated literature review for the redox stability of higher valent plutonium in groundwater.
2) Provide a summary of WIPP-relevant data obtained/published since CRA-2004 that addressed the issue of reduction of Pu (V/VI) by reduced iron in brine.
3) Provide an overall assessment to evaluate the impact of the literature and WIPP-relevant results on the current PA position on plutonium oxidation state distribution.

It is important to note that the data summarized in this report support the current WIPP PA position on plutonium oxidation state distribution and there is no recommended change in this position for CRA-2009. This position continues to be that plutonium speciates as a Pu(III) species in the reduced PA vectors (50 % of the vectors) and speciates as a Pu(IV) species in the oxidized PA vectors (other 50% of the PA vectors). Higher-valent plutonium, specifically Pu(V) and Pu(VI) species, can exist as transients but will not persist in the WIPP due to the strongly reducing conditions expected. These reducing conditions are primarily established by the reactivity of the reduced metals present (primarily iron), although other processes, most notably microbial processes, may also help establish these reducing conditions. With these assumptions, the solubility of plutonium in the WIPP, at the CRA-2004 Performance Assessment Baseline Calculation (PABC) reference pH of ~ 8.7, is ~3 to 4 x 10^{-7} M for Pu(III) species and ~ 5 to 7 x 10^{-8} M for Pu(IV) species.

There are essentially no recently-published literature data that significantly challenge the current WIPP PA assumptions for oxidation state distribution of plutonium under WIPP-relevant conditions. Since CRA-2004, there have been a number of publications in the open literature that pertain to the fate of higher-valent oxidation states of plutonium under

subsurface conditions. These studies, with the possible exception of some investigations that addresses the formation of PuO_{2+x} in unsaturated conditions, continue to show that lower-valent plutonium will persist under anoxic conditions in low ionic strength groundwaters (see Section 3 for a more detailed discussion).

Three WIPP-relevant studies were also completed or published since CRA-2004. These, taken as a whole, continue to support the prevalence of lower-valent plutonium in anoxic WIPP brine. This was shown to be true under radiolysis-impacted conditions, over a range of pH, and for zero-valent iron as well as aqueous and solid Fe(II) species. In many cases, the resultant oxidation state was confirmed analytically. The details of these studies are provided and critically evaluated in section 4.

The overall observations and recommendations that encompass both the literature review and the WIPP-relevant results are:

1) There are no surprises in the plutonium subsurface redox chemistry literature published since CRA-2004. These continue to show that lower oxidation states, specifically Pu(III) and Pu(IV), are the predominant plutonium species in anoxic groundwater.

2) WIPP-relevant experiments show that reduced iron phases and aqueous species are effective in rapidly reducing higher-valent plutonium species (Pu(V) and Pu(VI)). Reduced iron overwhelmed radiolytic effects and led to the formation of Pu(IV) species.

3) The overall recommendation to WIPP PA is that the current WIPP position on the oxidation state distribution of plutonium in anoxic brine should remain unchanged. This is supported by the WIPP-relevant experiments that show reduction of Pu(V/VI) to Pu(IV) and reflects the literature results where Pu(III) and Pu(IV) species were observed in microbiologically-active low ionic-strength groundwater experiments. The WIPP PA assumption remains conservative since higher-solubility Pu(III) species are considered in PA although only Pu(IV) species have been observed under WIPP-relevant conditions and there remain questions about the long-term stability of Pu(III) species in the WIPP.

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LIST AND DEFINITION OF ACRONYMS

ACRSP	Los Alamos Actinide Chemistry and Repository Science Program
Am	Americium
An	Generic actinide in the III, IV, V or VI oxidation state
ANL	Argonne National Laboratory
ASTP	WIPP Actinide Source Term Program
atm	Atmosphere (unit of pressure)
B	boron
$B_4O_7^{2-}$	Tetraborate ion
Br^-	Bromide ion
^oC	Degrees centrigrade
Ca^{2+}	Calcium ion
CBFO	Carlsbad Field Office (DOE)
CCA	WIPP Compliance Certification Application
CEMRC	Carlsbad Environmental Monitoring and Research Center
CeO_2	Cerium dioxide
Ci	Curie
Cl	Chloride
Cl^-	Chloride ion
Cm	Curium
cm	centimeters
CO_2	Carbon dioxide (gas)
CO_3^{2-}	Carbonate
CRA	WIPP Compliance Recertification Application
CRA-2004	First Compliance Recertification Application submitted by DOE-CBFO to the EPA in March 2004 and approved in April 2006
CRA-2009	Second Compliance Recertification Application submitted by DOE-CBFO to the EPA in March 2009
DBR	Direct brine release
DOE	Department of Energy
E_o	Standard state potential
EDTA	Ethylenediaminetetraacetic acid
E_h	Redox potential
EPA	US Environment Protection Agency
ERDA-6	(U.S.) Energy Research and Development Administration (WIPP well) 6, a synthetic brine representative of fluids in Castile brine reservoirs

ERDA-6B	ERDA-6 brine as modified by Xia et. al., 2001
EXAFS	Extended X-ray fine-structure spectroscopy
Fe	Iron – can be in the 0, II, and III oxidation state
$Fe(OH)_3$	Ferric hydroxide – also called hydrated Fe(III) oxide, or Fe(III) oxide-hydroxide and written as $FeO(OH)\cdot H_2O$
Fe^{2+}	Aqueous iron in the II oxidation state
$FeCO_3$	Iron carbonate – also called siderite
FeOOH	Ferric oxide-hydroxide – also called goethite
FMT	Fracture Matrix Transport code used to calculate actinide speciation for WIPP performance assessment
g	gram
G-Seep	Simulated brine representative of the Salado formation (seepage brine from the WIPP repository) - replaced by GWB in most recent testing
GWB	Generic Weep Brine – high magnesium simulated WIPP brine
h	Hour (unit of time)
H^+	Hydrogen ion
H_2	Molecular hydrogen (gas)
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate ion
H_2O	Water
HPW	>18 Mohm high purity water
I	Ionic strength
ICP-MS	Inductively-coupled plasma – mass spectrometry
K	Degrees Kelvin
K^+	Potassium ion
Kg	Kilo-gram
LANL	Los Alamos National Laboratory
LANL-CO	Los Alamos National Laboratory – Carlsbad Operations
Li^+	Lithium ion
M	Moles/liter
mg	Milli-grams
Mg^{2+}	Magnesium ion
MgO	Magnesium oxide – also called periclase
mL	Milli-liter
mM	Milli-moles/liter
MnO_2	Manganese dioxide

Mol	molecule
mV	Milli-volt
NA	Not analyzed
Na^+	Sodium ion
NaCl	Sodium chloride
Ni	Nickel
nm	Nano-meter
NO_3^-	Nitrate
Np	Neptunium
NTA	Nitrilotriacetic acid
NMWL	Nominal molecular weight limit – used in filter size description
O_2	Molecular oxygen (gas)
OH	Hydroxyl free radical
OH^-	Hydroxide ion
PA	Performance Assessment
PABC	Performance Assessment Baseline Calculation
PAVT	Performance Assessment Verification Test
pC_{H+}	- Log $[H^+]$, so the pH corrected for high ionic strength effects
pH	- Log (a_{H+}) – negative logarithm of the proton activity
PNNL	Pacific Northwest Laboratory
ppm	Parts per million or mg/liter
Pu	Plutonium (element 94)
Pu(III)	Plutonium in the III oxidation state
Pu(IV)	Plutonium in the IV oxidation state
Pu(V)	Plutonium in the V oxidation state
Pu(VI)	Plutonium in the VI oxidation state
Pu^{3+}	Aqueous plutonium in the III oxidation state
Pu^{4+}	Aqueous plutonium in the IV oxidation state
PuO_2	Plutonium dioxide (solid)
PuO_2^+	Aqueous plutonyl species with plutonium in the V oxidation state
PuO_{2+x}	Partially oxidized plutonium dioxide (solid)
PuO_2^{2+}	Aqueous plutonyl species with plutonium in the VI oxidation state
PuO_3	Plutonium trioxide (solid)
QA	Quality Assurance
QAP	Quality Assurance Plan
QAPD	Quality Assurance Program Document

SNL	Sandia National Laboratories
SO_4^{2-}	Sulfate ion
SOTERM	Actinide Source Term appendix for the WIPP CRA
Tc	Technetium
Th	Thorium
TRU	Transuranic (actinides higher in atomic number than uranium) that have a halflife greater than 20 years
U	Uranium – also U(IV) and U(VI) for the IV and VI oxidation state
UO_2	Uranium dioxide
UO_{2+x}	Partially oxidized uranium dioxide (solid)
UV-VIS-NIR	Ultraviolet-visible-near-infrared spectrometer or spectrum
WIPP	Waste Isolation Pilot Plant
wks	Weeks (time)
XANES	X-ray absorption near-edge spectroscopy
ZrO_2	Zirconium dioxide
μCi	Micro-curie
μm	Micro-meter
π	pi

Reduction of Higher-Valent Plutonium by Iron Under WIPP-Relevant Conditions: Data Summary and Recommendations

1.0 INTRODUCTION

Plutonium has a unique redox chemistry under many subsurface conditions. In theory, plutonium can exist in up to four oxidation states in the Waste Isolation Pilot Plant (WIPP) brines depending on the redox and pH conditions: Pu(III), Pu(IV), Pu(V), and Pu(VI) species. In actuality, only reduced oxidation states, Pu(III) and Pu(IV), prevail in the WIPP due to the reducing conditions established. Plutonium remains as one of the key actinide contaminants in transuranic (TRU) waste with respect to release from the WIPP. Its solubility is strongly correlated with its oxidation state distribution under the expected subsurface conditions. For this reason, the oxidation state distribution of plutonium in the WIPP is an important input to WIPP performance assessment (PA).

The WIPP, which is located in the northern portion of the Delaware Basin in southeastern New Mexico east of Carlsbad, continues to be the only working TRU repository. It was first certified by the Environmental Protection Agency (EPA) in May 1998 as a TRU waste repository and is currently operated by the Department of Energy, Carlsbad Field Office (DOE CBFO). The regulatory guidelines for the WIPP are given in 40CFR191/194 [U.S. EPA 1998]. Based on these regulations, the WIPP is required to undergo re-certification by the EPA every five years. The first compliance recertification application (CRA) was submitted in 2004 and was approved in April 2006.

This data summary report is centered on experiments to establish the stability of higher-valent plutonium under WIPP-relevant conditions in the presence of reduced iron phases. The data summarized in this report correspond to the status of the research at the time of the data cutoff for CRA-2009. In this report we only address the issue of plutonium (V/VI) reduction by reduced iron and do not give a comprehensive discussion and review of all key plutonium issues that define the overall speciation and solubility of plutonium in the WIPP (e.g., solubility, speciation and distribution of Pu III/IV species, importance and role of colloids etc.). This report supports the WIPP CRA-2009 PA position on plutonium oxidation state distribution. More specifically, the following are the key objectives of this report:

1) Provide an updated literature review for the redox stability of higher-valent plutonium in groundwater.
2) Provide a summary of WIPP-relevant data obtained/published since CRA-2004 that addressed the issue of reduction of Pu (V/VI) by reduced iron in brine.
3) Provide an overall assessment to evaluate the impact of the literature review and WIPP-relevant results on the current WIPP PA position on plutonium oxidation state distribution.

There are a number of potential mechanisms for the reduction of higher-valent plutonium in the WIPP. Of these, the redox controls imposed on plutonium speciation by the reduced iron present in TRU waste is the most important and well-established reduction pathway. The expected effect of reduced iron on plutonium speciation is the reduction of higher-valent Pu (V/VI) species to lower-valent Pu (III/IV) species. For the WIPP project, the prevalence and persistence of higher-valent Pu(V) and Pu(VI) species would be problematic since these may lead to relatively high plutonium solubilities in WIPP brine. It is this potential for higher solubility that makes it important to establish and understand the reduction pathways that are expected to predominate under WIPP-relevant conditions.

The WIPP-relevant plutonium reduction studies summarized in this report were performed, in part, by the Actinide Chemistry and Repository Science Program (ACRSP) team at the Carlsbad Environmental Monitoring and Research Center (CEMRC). Data obtained in a WIPP project performed by investigators at Argonne National Laboratory (ANL) and Pacific Northwest National Laboratory (PNNL) but not published at the time of CRA-2004, are also summarized. The overall research goals of the ACRSP project are to 1) establish the conservatisms of the current WIPP PA calculations of actinide solubility, 2) help establish a more robust WIPP chemistry model, and 3) extend past research to conditions that better simulate the expected environment in the WIPP. Research to better establish the key mechanisms for the reduction of higher-valent plutonium continues to be a key emphasis in the ACRSP project. All the research performed was compliant with WIPP Quality Assurance requirements as implemented in the LANL-CO WIPP Quality Assurance Plan [QAP]. This QAP flows down the applicable requirements of the DOE-CBFO Quality Assurance Program Document [QAPD].

2.0 SUMMARY OF THE CRA-2004 WIPP PA POSITION ON PLUTONIUM SPECIATION AND STABILITY

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. Experimental methods, such as potentiometric titration, extraction, spectroscopy and solubility measurements, were used to collect laboratory data for the ASTP at Florida State University and several national laboratories. The range of parameters investigated in the ASTP included inorganic ligand concentration (i.e., brine composition), pC_{H+} 3 to 10, presence and absence of oxygen and carbonate, and four organic ligands: acetate, oxalate, citrate, and EDTA [Choppin 1992, 1999, 2001a; Francis 2001; U.S. DOE 2004; Felmy 1989, 1990; Hobart 1996; Rai 1995, 1997, 1998; Reed 1993, 1994, 1998, 2006; Villareal 2001].

The key sections on Pu in attachment SOTERM [SOTERM 2003] are summarized in this section. Based on this attachment, the following is an overview of the relative importance of the predominant actinides and oxidation states in the WIPP:

Importance of actinide solubility to direct brine release (DBR) release:

Pu ≈ Am >> U > Th >> Np, Cm, and fission products

Importance of the oxidation state: **An (III) > An (IV) >> An (VI) > An (V)**

Since the initial WIPP license application, plutonium continues to be a key actinide of concern from the perspective of potential release from WIPP, although americium is also important. A tabulation of the projected WIPP plutonium and metal inventory in the WIPP is given in Table 2-1 and shows that there is a large excess of iron-based alloys compared to plutonium in the WIPP (a factor of 5000 times higher by mass).

Table 2-1. WIPP Plutonium and Metal Alloy Inventory at Closure (2033) Used in the CRA-2004 PABC Calculations [Leigh 2005]

Plutonium Isotope	Activity (Ci)	Amount (kg)	Totals
^{238}Pu	1.13E+06	6.60E+01	2.26E+06 Ci 9.87E+03 kg
^{239}Pu	5.82E+05	9.38E+03	
^{240}Pu	9.54E+04	4.19E+02	
^{241}Pu	4.48E+05	4.35E+00	
^{242}Pu	1.27E+01	3.23E+00	
^{244}Pu	5.53E-03	3.09E-01	
Metal Alloy		**Projected Inventory (Kg)**	
Iron-Based Alloys		51,416,440	
Aluminum-Based Alloys		2,234,176	
Other Metal Alloys		5,795,048	

2.1 CRA-2004 WIPP Position on Plutonium Solubility and Oxidation State Distribution

Plutonium was one of the two most important transuranics in the WIPP in CRA-2004 and its potential release to the environment was a key concern for WIPP PA. This importance is consistently established in internal assessments of WIPP actinide issues and plutonium continues to command a strong perception of concern by the public. The WIPP PA position on the plutonium source term is addressed in the following excerpt from SOTERM [SOTERM 2003]:

SOTERM-4.4 Plutonium

> *Pu can exist in the +III, +IV, +V, +VI, and +VII oxidation states (Katz et al. 1986, 781). Pu(III) is the favored oxidation state in acidic solutions, but oxidation of Pu(III) to Pu(IV) becomes progressively easier with increasing pH. This occurs because Pu(IV) features a very strong tendency to undergo hydrolysis, which has the effect of reducing the solution concentration of the free Pu(IV) ion* Pu^{4+}*. As the pH of a Pu solution is raised from acidic to neutral, Pu(IV) begins to precipitate, resulting in a shift of equilibrium concentrations of Pu(III) to Pu(IV). Consequently, Pu(III) is not a thermodynamically stable oxidation state in the basic environment that will be established by MgO in the WIPP. Although Pu(III) is unstable under expected WIPP conditions, Felmy et al. (1989) observed Pu(III) in PBB1 and PBB3 brines at neutral and slightly basic conditions.*
>
> *Pu(V) and Pu(VI) can be produced from Pu(IV) under oxidizing conditions. It is not possible to produce Pu(V) by direct oxidation of Pu(IV) because the oxidation potential that must be applied exceeds the potential required for the oxidation of Pu(V) to Pu(VI). Therefore, in a solution with oxidizing conditions, any Pu(V) that arises from the oxidation of Pu(IV) will be immediately oxidized to Pu(VI). Pu(V) can be produced in solution only by first producing Pu(VI), followed by a carefully controlled reduction of Pu(VI) to Pu(V). Pu(V) may persist in neutral to basic solutions even when it is not the thermodynamically stable oxidation state, due to the reduction reaction's inverse fourth power dependence on the concentration of H+, which can make the reduction of Pu(V) to Pu(IV) kinetically slow. Neither Pu(V) nor Pu(VI) will persist in significant quantities in the repository, since oxidizing conditions are required to produce them. Pu(VI) was shown to form complexes with Cl- under oxic conditions in high-ionic-strength NaCl solutions (Clark and Tait 1996). Clark and Tait (1996) and Reed et al. (1996) showed the reduction of Pu(VI) to Pu(IV) by Fe and other reductants under expected WIPP repository conditions. Metallic Fe and* Fe^{2+} *reduce Pu(VI) in WIPP brines to either Pu(IV) or Pu(III). Clark and Tait (1996) and Felmy et al. (1996) experimentally observed the reduction of* $Pu(VI)\text{-}CO_3^{2-}$ *complexes to Pu(IV) by either metallic Fe or* Fe^{2+}*. Reduction of Pu(VI) was also observed in the absence of* CO_3^{2-}*, but the oxidation state of the resulting species was not determined because the concentration was*

> *below the analytical detection limit, ca. 10^{-9} M. Neretnieks (1982) showed that dissolved actinides are reduced to a less soluble oxidation state and precipitated from moving groundwater upon coming in contact with Fe (II).*
>
> *Pu (VII) can be produced in concentrated OH- solutions that are also highly oxidizing. Pu (VII) will not be formed in the WIPP.*
>
> *The DOE determined (Weiner 1996) that Pu(IV) will be the dominant oxidation state under WIPP conditions, but the possibility of the existence of Pu(III) cannot be excluded. As a result, Pu is modeled as Pu(III) in half of the PA vectors, and as Pu(IV) in half of the vectors.*

The CRA -2004 Appendix SOTERM [SOTERM 2003] states that plutonium speciates as Pu(III) in the reduced PA vectors (50%) and as Pu(IV) in the oxidized PA vectors (50%). The expected solubilities of these oxidation states are summarized in Table 2-2. The prevalence of lower oxidation states is, in part, based on the important role that excess iron in the WIPP will have in establishing reducing conditions. These lower oxidation states will have low solubilities in WIPP brine and are used as input to calculate plutonium release from the repository under a DBR scenario.

Table 2-2. Actinide Solubilities Calculated (III, IV, and V) or Estimated (VI) for the CRA-2004 PA, the 1997 PAVT and the CCA PA [Table SOTERM-2, U.S. DOE, 2004; Brush 2003] and the CRA-2004 PABC [Leigh 2005].

Actinide Oxidation State, and Brine	**Actinide Solubilities (M)**				
	CRA-2004 PABC	**CRA-2004 Microbial Vectors**	**CRA-2004 Non-Microbial Vectors**	**PAVT**	**CCA**
III, Salado or GWB brine	3.87×10^{-7}	3.07×10^{-7}	3.07×10^{-7}	1.2×10^{-7}	5.82×10^{-7}
III, Castile or ERDA-6 brine	2.88×10^{-7}	1.69×10^{-7}	1.77×10^{-7}	1.3×10^{-8}	1.3×10^{-8}
IV, Salado or GWB brine	5.64×10^{-8}	1.19×10^{-8}	1.24×10^{-8}	1.3×10^{-8}	4.4×10^{-6}
IV, Castile or ERDA-6 brine	6.79×10^{-8}	2.47×10^{-8}	5.84×10^{-9}	4.1×10^{-9}	6.0×10^{-9}
V, Salado or GWB brine	3.55×10^{-7}	1.02×10^{-6}	9.72×10^{-7}	2.4×10^{-7}	2.3×10^{-6}
V, Castile or ERDA-6 brine	8.24×10^{-7}	5.08×10^{-6}	2.13×10^{-5}	4.8×10^{-5}	2.2×10^{-6}
VI, Salado or GWB brine	*1×10^{-3}	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}	8.7×10^{-6}
VI, Castile or ERDA-6 brine	*1×10^{-3}	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}	8.8×10^{-6}

* The 1 mM value for the solubility of An(VI) actinides is based on EPA guidance to reflect uncertainties that exist about the effect of carbonate complexation – it is not based on WIPP-relevant data

2.2 Expected Reduction Pathways and Importance of the Pu(V) and Pu(VI) Oxidation State in the WIPP Subsurface

The current WIPP position is that Pu(V) and Pu(VI) species do not persist under the expected conditions in the WIPP. For this reason their speciation, and correspondingly their solubility, are not considered in WIPP PA. These higher-valent plutonium species, however, may be present as transients in localized zones due to radiolytic processes.

The possibility that Pu(V) and Pu(VI) species could exist in the WIPP continues to be an important potential concern for DBR release from the repository since these higher-valent species have much higher solubility under WIPP-relevant conditions. This is the justification for continued research on the key pathways and mechanisms for the reduction of multivalent actinides in the WIPP. The key WIPP arguments against the persistence of these species continues to be that there is an excess of reduced-valent metals in TRU waste and this leads to an expectation that highly reducing conditions are rapidly established. Under reducing anoxic conditions, the most important reduction pathways are:

- The reduction of plutonium by lower-valent Fe(0, II) phases and dissolved Fe^{2+} species.
- The bioreduction of higher-valent plutonium species under anaerobic conditions.
- To a lesser extent, reaction with dissolved organic species and other reduced metals present in TRU waste.

The results we present in this report continue to support the current WIPP PA assumption that only Pu(III) and Pu(IV) species can be present in significant amounts in the WIPP. Although all the mechanistic details are not understood, the newly published or obtained data continue to point towards relatively rapid reduction of Pu(V) and Pu(VI) in the WIPP by reduced iron. Additionally, there is a growing body of literature data that show that microbiological activity under anoxic conditions will also reduce plutonium (see Section 3.2). It is also likely that other reduced metals and organic complexants can also provide further reduction pathways for higher-valent plutonium but there are no new WIPP-relevant data that pertain to these pathways. In this context, the most important change since CRA-2004 is that there is an even greater amount of WIPP-relevant and literature data that support the current WIPP PA position for the reduction of higher-valent plutonium in the WIPP.

3.0 LITERATURE BACKGROUND: REDOX REACTIONS OF HIGHER-VALENT PLUTONIUM UNDER SUBSURFACE CONDITIONS

Many of the same scientific issues and principles that define the mobility and solubility of actinides in the expected WIPP environment are also important in subsurface actinide contamination problems throughout the DOE complex [NRC 2000; Choppin 2001b; Silver 2002; Mincher 2003; Stout 2003; Choppin 2004; Fredrickson 2004, Kaplan 2004a,b; Santschi 2006; Clark 2006, 2007] and at nuclear contamination sites outside the United States [Zavilgelsky 1998; McCubbin 2000; Lloyd 2005; Novikov 2006; Kalmykov 2007; Moll 2006]. Reducing anoxic conditions, such as those expected in the WIPP, will lead to a prevalence of low-solubility lower oxidation-state species [Nitsche 1994; Runde 2000; Ohnuki 2007].

The role and importance of redox reactions in determining the mobility and solubility of multivalent actinides such as plutonium are also beyond question [see DOE site references above and Van Luik 1987; Allard 1982; Bruno 1986; Choppin 1992]. Although we lack the Pitzer data to generate a phase diagram for plutonium in high ionic strength media, a typical Eh-pH phase diagram for the plutonium system that qualitatively describes its oxidation state distribution is shown in Figure 3-1 [Runde 2002]. In geochemical systems, redox control is

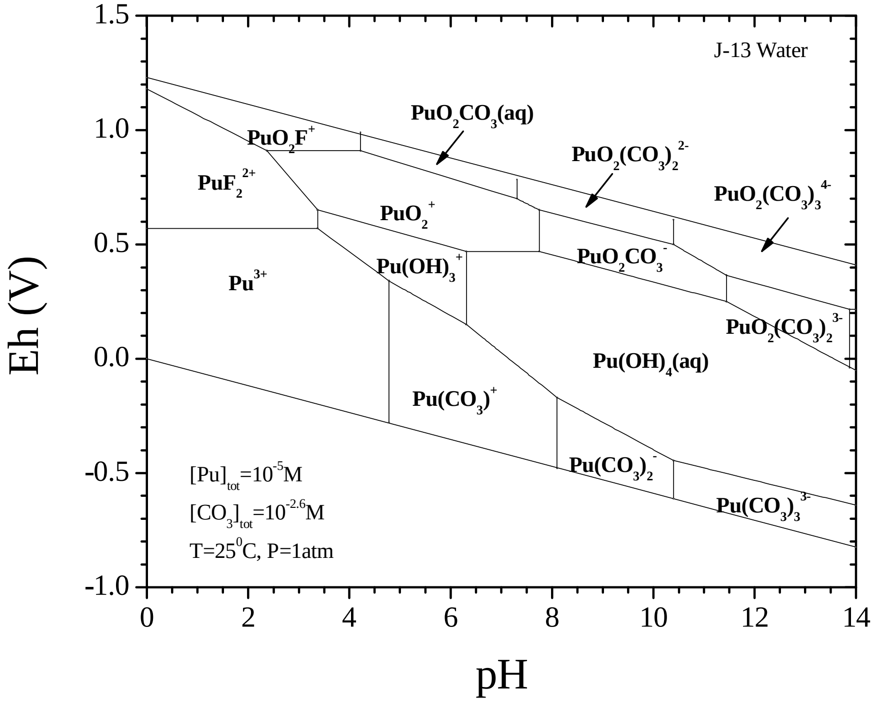

Figure 3-1 Speciation diagram for plutonium in carbonated low ionic strength groundwater [based on Runde 2002]. This illustrates the expected prevalence of lower oxidation states of plutonium. For the reducing conditions and pH expected in the WIPP, only Pu(IV) and Pu(III) species are present and exist as hydrolytic or carbonate complexes.

often interpreted in terms of the iron, and in a broader sense reduced metal, mineralogy and associated aqueous chemistry[Idemitsu 2000; Rai 2002; Mincher 2003; Stout 2003; Kalmykov 2007; Ohnuki 2007]. More recently, the important role of microbial activity through biotic transformations [Beveridge 1986; Lovley 1991; Lovley 1992; Lovley 1995; Banaszak 1998; Banaszak 1999; Anderson 2002; Neu 2002, 2005; Boukhalfa 2007; Reed 2007; Icopini 2007, 2009; Francis 2007] in defining oxidation state distribution of multivalent metals/actinides has been recognized. Since most actinides have significantly lower solubilities in the lower oxidation states (i.e., under reducing conditions), their reduction is key to understanding their potential mobility under subsurface conditions.

General studies of plutonium in brine have also been done by a number of investigators [Buppelmann 1986; Buppelmann 1988; Clark 1995; Kim 1984; Nitsche 1992; Nitsche 1994; Pashalidis 1993; Villarreal 2001; Reed 1993; Reed 1994, Reed 1998; Reed 2006]. There has also been an assessment of the actinide chemistry in the WIPP CCA [Oversby 2000; Brush 2002]. In many respects, the general issues just discussed are already addressed and reflected in the current WIPP PA conceptual model as it is documented in the CRA-2004 application.

In this section, we provide an update and summary of recent literature that pertains specifically to the redox stability of higher-valent plutonium in the subsurface. The three areas in plutonium subsurface chemistry that have received a significant amount of attention since the initial submittal of the WIPP certification application are: 1) reduction of plutonium by iron, 2) plutonium, and more generally actinide, microbiological interactions in groundwater, and 3) the possibility of thermodynamic pathways to stable higher-valent plutonium oxides. Expanding our understanding of these processes in the WIPP is a key goal of the ongoing actinide research in the WIPP project. It is important to note that the most relevant literature publications since CRA-2004 regarding this specific issue are WIPP-relevant studies which are summarized in Section 4.

3.1 Reduction of Plutonium by Reduced Iron

The important role of iron as a reducing agent for plutonium in the V and VI oxidation state, although expected, is not fully understood. Under the range of conditions and reaction pathways expected in the WIPP, iron can exist as Fe (0), Fe (II) and Fe (III) species. The expected importance of this metal is based on the redox half reaction potentials for the reduced iron oxidation states (Fe (0/II)) relative to plutonium (V/VI), see Table 3-1, and the relatively high amount of this metal that will be placed in the WIPP (see Table 2-1 for projected reduced iron inventories). Whereas for uranium the existence of favorable redox potentials are dependent somewhat on the speciation of the iron present, the existence of reduced iron will always lead to conditions that favor the reduction of both Pu(V) and Pu(VI) species under a wide range of conditions.

Zero-valent iron has been demonstrated to be an effective reductant of uranyl [Sanchez 1985; Farrell 1999] in groundwater systems and is proposed as a remediation strategy for the reduction of uranyl species. Uranyl was also reduced, at least in part, by iron in goethite under anoxic conditions due to Fe (II) and Fe (III) microbial cycling [Fredrickson et al. 2000]. The strong interaction and association of plutonium with iron and iron oxide minerals in the subsurface is also established at existing contamination sites and under lab-simulated conditions [Idemitsu 2000;Rai 2002; Mincher 2003; Stout 2003; Kalmykov 2007; Ohnuki 2007]. Although uranium subsurface chemistry has been more extensively studied, it follows, based on comparisons with the redox potentials in Table 3-1, that if reduced iron reduces uranyl, it will also reduce plutonyl species.

Table 3-1. Redox Half Potentials for Key Fe, Pu and U Reactions

Half Reaction	E_o (Acidic) in V	E_o at pH = 8 in V
$PuO_2^{+} \rightarrow Pu^{4+}$	1.170	0.70
$PuO_2^{2+} \rightarrow PuO_2^{+}$	0.916	0.60
$Fe(OH)_3(s) \rightarrow Fe^{2+}$		0.1
$FeOOH\ (s) \rightarrow FeCO_3(s)$		-0.05
$UO_2^{2+} \rightarrow U^{4+}$	0.338	-0.07
$Pu^{4+} \rightarrow Pu^{3+}$	0.982	-0.39
$Fe^{3+} \rightarrow Fe^{2+}$	0.77	-0.86
$Fe(II)(OH)_2 \rightarrow Fe(0)$	-0.44	-0.89
$U^{4+} \rightarrow U^{3+}$	-0.607	-1.95

The most important conclusions/observations from these literature data are:

1) There is a growing body of evidence for strong linkages between the fate of plutonium in the subsurface and iron and iron oxide phases. These almost always involve reduction of higher-valent plutonium and/or interactions between lower-valent plutonium and the iron minerals – even under clearly oxidizing conditions. These many real-system observations are consistent with the current WIPP PA position that iron and iron oxide phases have a key role in defining the mobility of plutonium in the WIPP.

2) Iron(II) in solution, as Fe^{2+}, leads to the reduction of higher-valent plutonium and can lead to the reductive dissolution of PuO_2 to form Pu(III) [Rai 2002]. The reduction of higher-valent plutonium is consistent with the observations made in WIPP-relevant experiments (see Section 4). The reductive dissolution of PuO_2 has an unclear implication for the WIPP since Pu(III) is usually not seen in abiotic WIPP-relevant experiments. This however is accounted for in WIPP PA since Pu(III) is the predicted oxidation state in the reducing PA vectors.

3) Some pseudo-colloid formation between reduced plutonium and suspended iron oxides is postulated when long-range near-surface plutonium migration is observed (e.g., at the Mayak site in Kalmikov 2007). These are however identified as only important in low ionic-strength groundwaters typically found at the near-

surface. In this context, this does not directly impact WIPP, but it is something that should be noted in the high ionic-strength WIPP-relevant experiments. As will be discussed in Section 4, essentially no pseudo-colloid formation was observed in WIPP-relevant brine experiments.

These literature observations continue to generally support the current WIPP PA assumptions, although they pertain to a wide range of subsurface conditions, for the Pu(III) and Pu(IV) oxidation state distribution of plutonium in anoxic WIPP brine.

3.2 Bioreduction of Higher-Valent Plutonium

There are essentially no studies on the bioreduction of Pu (V/VI) under WIPP-relevant conditions from within or outside the WIPP project since CRA-2004 although there are plans to establish this bioreduction process. Halophiles [Gillow 2000; Francis 2001] typically found and expected to predominate in the WIPP environment have not been extensively studied in the context of their tendency and ability to reduce higher-valent actinides. There is however a growing body of research that continues to demonstrate that metals, including multivalent actinides, are susceptible to microbially-driven reduction under anaerobic conditions leading to their immobilization as solid precipitates or surface-adsorbed complexes for “ordinary” soil bacteria. Although WIPP-relevant data does not yet exist, it is expected that these bioreduction processes will also be present in the WIPP.

Comprehensive and critical reviews of how actinide species and microorganisms interact have been published [Banaszak 1999; Anderson 2002; Keith-Roach 2002; Neu 2002]. The general relationships between microbial processes and actinide oxidation state distribution is given in Figure 3-2. Strongly reducing conditions associated with fermentation, sulfate reduction, methanogenesis, and iron reduction make the more oxidized actinides thermodynamically favorable electron acceptors, and microbially catalyzed reductions to U (IV), Tc (IV), and Np (IV) have been observed [Lovley 1992; Lovley 1995; Nealson 1994; Francis 1994; Lloyd 1997; Banaszak 1998; Banaszak 1999; Lloyd 2000; Rittmann. 2002]. There is a high expectation that geochemical reactions alone will produce a strongly reducing environment that is anoxic in the WIPP. Additionally, halophiles and perhaps *Archaea* are also expected to remove oxygen, help establish and maintain reducing conditions, and cause the bioreduction of multivalent actinides by indirect co-metabolic and direct enzymatic pathways.

There has been significant progress made in establishing the key redox effects of anaerobic soil bacteria on the oxidation state distribution of plutonium. In microbially active soils, the most important effect on multivalent actinides under anaerobic conditions is to reduce the actinide leading to its immobilization, hence containment, in the subsurface. As shown in Figure 3-2, Pu(IV) is the expected oxidation state under a wide range of subsurface conditions with no Pu(V) or Pu(VI) species expected. Pu(III) is also predicted for methanogenesis and sulfate reduction although, as discussed later, this has also been shown for iron-reducing bacteria. Overall, microbiological activity is a key factor in the generation of anoxic and reducing conditions in the WIPP and it is our expectation that this will also lead to a strong and positive influence on the speciation of plutonium leading to its immobilization.

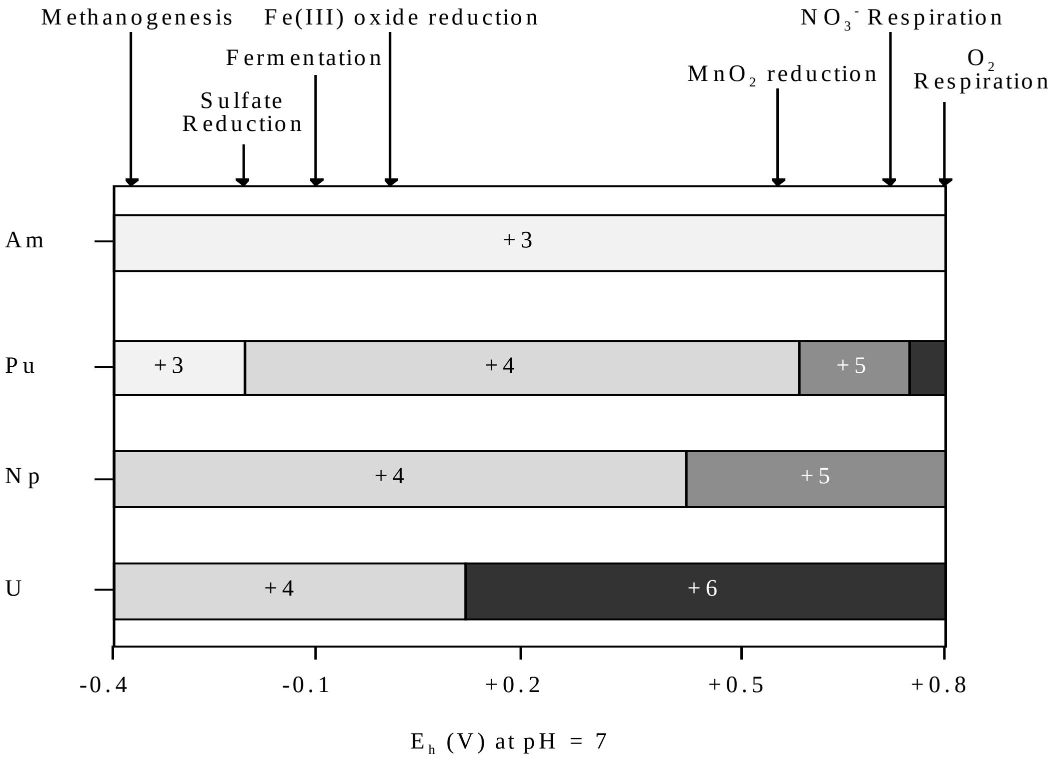

Figure 3-2 **Expected dominant actinide oxidation states as a function of the standard reduction potential at pH = 7 in water that is in equilibrium with atmospheric CO_2. The linkages between the redox potentials associated specific oxidation states and microbial electron acceptor couples are also shown [based on Banaszak 1999].**

There are a relatively few studies that investigate the bioreduction of plutonyl species under any subsurface conditions. The bioreduction of Pu(V/VI) to Pu(IV) and potentially Pu(III) species is an important factor in establishing the fate and transport of plutonium in biologically active subsurface systems. This reduction proceeds along direct enzymatic pathways, but is also strongly coupled with biogenic, but essentially co-metabolic, processes by reaction with the reduced metals and species generated. Under most conditions expected in the subsurface, the bioreduction will proceed to form Pu(IV) phases, leading to greater immobilization of the plutonium. When a solubilization mechanism is present, such as the presence of strong chelators (nitrilotriacetic acid (NTA) or ethylenediaminetetraacetic acid (EDTA)), further reduction of solubilized Pu(IV) to Pu(III) species is observed. This is potentially a key process that can lead to solubilization mechanisms for PuO_2 in the subsurface.

The reduction of Pu(V/VI) to Pu(IV) species for metal reducing and sulfate reducing bacteria has been established under anaerobic conditions (see Figure 3-3). This has been shown for the metal-reducing bacteria *Geobacter metallireducens* and *Shewanella oneidensis* MR-1 [Icopini 2009] and *Shewanella alga BrY* [Reed 2007]. This has also been shown for the sulfate reducer *Desulfovibrioaspoensis* DSM 10631 [Moll 2006; Moll 2007].

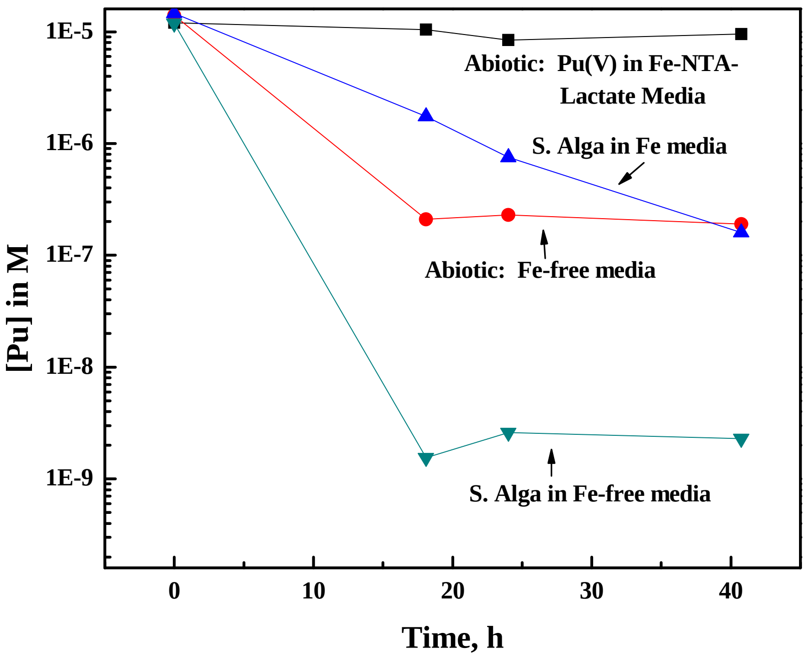

Figure 3-3 Bioreduction of higher-valent plutonium by *Shewanella alga BrY* under anaerobic conditions in the presence and absence of iron [Reed 2007]. Uncertainty in the plutonium concentration data is ± 10%.

Microbial processes are also potentially important in establishing the relative importance of the Pu(III) and Pu(IV) oxidation-state distribution under reducing conditions in the subsurface. This has been shown to be important when a Pu(IV) solubilization mechanism (e.g., when a complexant is present) exists. The bioreduction of PuO_2 by Fe-reducing strains of B. *polymyxa* and B. *circulans*, in the presence of NTA, led to the solubilization of plutonium as a Pu(III) complex that then was re-oxidized by the NTA to form a Pu(IV)-NTA complex [Rusin 1994]. Analogous experiments with non-iron reducing *Escherichia coli* did not lead to the reduction/solubilization of the PuO_2. The reduction of EDTA-complexed Pu(IV) to form Pu(III) complexes by the metal-reducing bacteria *Geobacter metallireducens* GS15 *Shewanella oneidensis* was also observed under anaerobic growth conditions (Boukhalfa 2007). The formation of Pu(III) was also reported for *Clostridium sp*. when solubilized Pu(IV)-nitrate was initially present under anaerobic growth conditions (Francis 2007).

The most important results and observations in the biogeochemistry literature from the perspective of WIPP PA are:

1) There is a growing body of literature that continue to show that microbial activity leads to the establishment of reducing conditions and, more specifically, to the bioreduction of multivalent metals under a wide range of anaerobic (anoxic) conditions. This continues to support the current WIPP PA position in that the predicted microbial activity in the WIPP will likely help establish and maintain

reducing conditions and reduce multivalent actinides – although this is yet to be shown under WIPP-relevant conditions.

2) The most important development in the reported literature studies since the CRA-2004 is that the bioreduction studies have been extended to include plutonium. These studies show that higher-valent plutonium is unstable in anaerobic microbial systems. Microbial activity leads to the formation of Pu(IV) precipitates and, in cases where solubilization mechanisms exist, to Pu(III) species. This continues to support the WIPP PA position that lower-valent plutonium predominates in the WIPP and establishes mechanisms where both Pu(IV) and Pu(III) species may be generated.

Overall, these literature results, although they pertain to low ionic-strength groundwater systems and do not include WIPP-relevant microorganisms, continue to support the overall WIPP position that reducing conditions will be established in the WIPP and that low-valent plutonium will prevail under these conditions.

3.3 Thermodynamic Stability of Higher-Valent Actinides: The PuO_{2+x} Issue

It has long been held that plutonium oxide, as PuO_2, is the thermodynamically-favored form of plutonium oxide under a wide range of environmental conditions. This oxide is likely the predominant form of plutonium in TRU waste and is believed to be the most important plutonium phase under WIPP-related conditions. In the last few years, however, there have been a number of studies that question this key and fundamental assumption [Haschke 1995, 2000; Conradson 2004, 2005].

Haschke et al. (2000) reported that near-stoichiometric plutonium dioxide reacts with water vapor at temperatures between 25 and 350˚C according to the reaction

$$PuO_2(s) + xH_2O(g) \rightarrow PuO_{2+x}(s) + xH_2(g) \qquad (3\text{-}1)$$

in which water vapor is reduced by polycrystalline PuO_2 to produce hydrogen and a previously unknown higher oxide PuO_{2+x} with x as large as 0.27 under optimal conditions. If only Pu(IV) and Pu(V) are present in $PuO_{2.27}$, this oxide has 46% Pu(IV) and 54% Pu(V). Haschke et al. argued that this conversion is due to a chemical reaction (that is, the above reaction has a Gibbs energy less than zero) rather than a radiolysis-induced reaction because the reaction rate is temperature dependent [Haschke 2000]. The PuO_{2+x} may dissolve slowly with liberation of the mobile ions PuO_2^+ or PuO_2^{2+} [Haschke 1995]. The structure of PuO_{2+x} has been more recently confirmed through extensive EXAFS studies [Conradson 2004, 2005] as being a mixture of Pu(IV) and Pu(V), with essentially no Pu(VI), with the stable incorporation of OH^- (and possible H_2O and H^+) into the PuO_2 lattice. Similar effects were noted for hydrated or wet oxides of CeO_2, ZrO_2, and UO_2 [Sattonnay 2001; LaVerne 2002].

The PuO_{2+x} effect is only present in unsaturated gas-phase systems. The behavior of PuO_2 in contact with water has been studied as a function of time by means of the short-lived isotope ^{238}Pu as well as the longer-lived ^{239}Pu [Rai 1982]. This study concluded that crystalline PuO_2, amorphous PuO_2, and amorphous $PuO_3 \cdot xH_2O$ all convert to a material intermediate between crystalline PuO_2 and hydrated amorphous material that contains both

Pu(IV) and Pu(VI). These authors hypothesized that alpha particles generated by ^{238}Pu or ^{239}Pu cause radiolysis of water, generating the powerful oxidant OH radical and producing Pu(V) and/or Pu(VI) on the oxide surface. Reduction of these species yields hydrated amorphous Pu(IV) oxide with little or no PuO_{2+x} formation.

The overall issue of a thermodynamic driver for higher-valent plutonium oxides, although it has received much recent attention in the literature, is not yet fully understood. This has a potentially significant impact on nuclear inventory storage, which is usually done in sealed canisters that usually contain small amounts of water. It may also be a minor contributing factor to subsurface contamination problems under sustained unsaturated conditions where significant PuO_{2+x} could form with time under oxidizing conditions. This phenomena, although somewhat interesting, is not expected to be important in the WIPP case. The potential formation of PuO_{2+x} in the WIPP under unsaturated conditions can only lead to transient concentrations of Pu(V) species since brine-inundation of the TRU waste will lead to rapid reduction of the higher-valent plutonium by the excess iron and other reductants present in the waste. The possible formation of some PuO_{2+x} in the WIPP when unsaturated conditions predominate remains consistent with the current WIPP PA position that, although transient concentrations of higher-valent plutonium can exist in the WIPP, these are quickly overwhelmed by the strongly reducing conditions expected to be present if brine inundation occurs.

4.0 WIPP-RELEVANT EXPERIMENTAL RESULTS: REDUCTION OF PU(VI) BY REDUCED IRON

Three sets of WIPP-relevant data that address the issue of Pu(VI) reduction by reduced iron are summarized in this section. These collectively represent new data that were not fully reflected in the existing WIPP CRA-2004 documentation. The first set of data is based on research that was performed at ANL, as part of the WIPP ASTP [Novak 1995] but only recently published [Reed 2007]. The second set of WIPP-relevant experiments was performed by PNNL researchers, also as part of the WIPP ASTP program, and published [Xia 2001]. The third set of experiments was performed by the ACRSP team as described in Test Plan LCO-ACP-04 entitled: Reduction of Plutonium in WIPP Brine: Limited Scope Study [Reed 2005]. These data, although not yet fully published,, have been presented and reported to the EPA and the DOE. A key goal of these ACRSP experiments was to confirm the results of the other two sets of experiments. The results of all three sets of data are compared and subsequently interpreted with respect to the WIPP PA position on the oxidation state distribution of plutonium in brine.

4.1 Reduction of Pu(VI) by Iron in WIPP Brine: ANL Studies

The first set of experiments summarized were performed at ANL as part of the WIPP ASTP program. These data, although they support the WIPP CRA-2004 documentation, were not fully published until recently [Reed 2007] in a journal article entitled "Reduction of Plutonium (VI) in Brine under Subsurface Conditions". As is discussed in section 4.3, the results of these experiments were confirmed by experiments performed by the LANL-ACRSP team.

4.1.1 Overall Goals and Objectives

The overall goals and objectives of these experiments were to establish the stability of Pu(VI) in WIPP brine in the absence and presence of WIPP-relevant reductants and repository components. The effects of zero-valent Fe (using WIPP-relevant low carbon steel) and dissolved Fe^{2+} with radiolysis-equilibrated Pu-239, as PuO_2^{2+}, in brine were established.

4.1.2 Experimental Matrix

Two sets of experiments were performed in sequence. First, the stability of plutonium(VI) in WIPP brine was monitored as a function of pH and WIPP brine composition for ~ two years. In these experiments, Pu-239, which is the most prevalent plutonium isotope in the WIPP, was used to account for the effects of radiolysis on the overall stability and speciation of the plutonium. Subsequently, iron in various forms, was added to these "equilibrated" steady state systems to establish the effects of the added iron on the stability of the Pu(VI) species. The experimental matrix for these experiments is given in Table 4-1.

Table 4-1. Experimental Matrix to Determine the Stability of Pu(VI) in Brine[a]

Pu(VI) Stability Experiments		Pu(VI) Interaction Studies	
Experiment Designation	Description[b]	Experiment Designation	Description
PU-G5	10^{-4} M Pu(VI) in G-Seep brine at pC_{H+} 5	G5-B	PU-G5 Blank
		G5-FE	PU-G5 with low carbon steel coupon
		G5-FE2	PU-G5 with added Fe^{2+}
PU-G7 and PU-G7-NC	10^{-4} M Pu(VI) in G-Seep brine at pC_{H+} 7	G7-B	PU-G7 Blank
		G7-FE	PU-G7 with low carbon steel coupon
		G7-FE2	PU-G7 with added Fe^{2+}
PU-E8	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H+} 8 and 10^{-3} M Carbonate	E8-B	PU-E8 Blank
		E8-FE	PU-E8 with low carbon steel coupon
		E8-FE2	PU-E8 with added Fe^{2+}
PU-E10	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H+} 10 and 10^{-3} M Carbonate	E10-B	PU-E10 Blank
		E10-FE	PU-E10 with low carbon steel coupon
		E10-FE2	PU-E10 with added Fe^{2+}
PU-E10-NC	10^{-4} M Pu(VI) in ERDA-6 brine at pC_{H+} 10 with no added Carbonate	E10NC-B	PU-E10-NC Blank
		E10NC-FE	PU-E10-NC with low carbon steel coupon
		E10NC-FE2	PU-E10-NC with added Fe^{2+}

a All experiments were performed at 25 ± 2 ^{o}C, with Pu-239, in a once-through nitrogen glovebox

b pC_{H+}, is the measured pH corrected for ionic strength effects; $pC_{H+} = pH_{measured} + 0.9$

4.1.3 Experimental Approach

The experiments were performed in two sequential studies (see Table 4-1). Plutonium-239 (> 99% purity by activity and mass) was used in all of the experiments. Plutonium was oxidized to PuO_2^{2+} by fuming in perchloric acid to near-dryness and dissolved in 0.1 M HCl to make a high-concentration stock solution. G-Seep and ERDA-6 simulated brine (see Table 4-2) were made using high purity reagent grade Aldrich Chemicals compounds. Iron, when added, was in two forms: steel coupon (ASTM A366 lot J) typical of the material used for containers in the WIPP, and Aldrich reagent grade iron (II) chloride.

In high ionic strength media, where activity coefficients of species are often not well known, the measurement of pH (logarithm of hydrogen ion activity) is not straightforward. In these media, the pH reading of a glass combination electrode calibrated with low ionic strength pH buffers can be related to the hydrogen ion concentration, pC_{H+}. The relationship between the pH reading and pC_{H+} is, to a good approximation, a linear function of the ionic strength. In this context, the following empirical formula was used to calculate the hydrogen ion concentration from the measured pH reading:

$$pC_{H+} = \text{pH reading} + K \qquad \text{4-1}$$

where K is a constant that is brine-specific. The values of K obtained for the brines investigated was approximately 0.9 $\pm$ 0.1.

The experimental approach in the first set of experiments was to add a Pu(VI) spike to brine as a function of pH, brine composition, and presence/absence of carbonate (see Table 4-1) and monitor the oxidation state and total concentration as a function of time to establish its redox stability. In experiments with no added carbonate, the PuO_2^{2+} acid stock solution was added to 3 mL of the brine of interest to check for precipitation. An additional 7 mL of the brine was then added (total of 10 mL), transferred to the nitrogen glovebox, and bubbled with high-purity nitrogen to remove air. For experiments that contained carbonate, the PuO_2^{2+} was first diluted into 3 mL of a high carbonate solution to form a carbonate complex and then combined with 7 mL of the brine of interest. This was checked for precipitation, transferred to the nitrogen glovebox and bubbled with nitrogen to remove air.

The stability experiments were performed in 1.0 Liter polypropylene bottles that had been inserted in 1.8 Liter Hastelloy Parr vessels that were located in a temperature-controlled (25 $\pm$ 0.5 ^{o}C) once-through nitrogen glovebox plumbed for gas and liquid sampling. Significant care was given to remove traces of oxygen and carbon dioxide from these vessels prior to the addition of brine. This was done by a sequential pump down and re-equilibration with high-purity nitrogen gas over a period of over two months. Approximately 750 mL of each brine was bubbled with nitrogen in the glovebox and added through a Teflon tube into the various vessels. These brines were pumped down to remove any remaining gas by sequential vacuum expansion and re-equilibrated with high purity nitrogen. The 10 ml of de-aerated plutonium stock solutions were added through the same Teflon tube. After the plutonium was added, the solution was de-gassed by sequential vacuum expansion, and a 950 $\pm$ 50 torr hydrogen atmosphere was added. The gas phase was monitored throughout the experiment by periodic sampling and analysis by gas chromatography (Varian model 3300 and 3400 configured with a thermocouple detector). Although trace levels of nitrogen and carbon dioxide (when present in solution) were detected along with hydrogen in the vessel atmosphere, no oxygen was detected. Periodically, ~ 5 mL of solution was removed from the vessel using a Teflon tube connected to a de-aerated syringe. This sample was partitioned to measure pH using a Ross combination electrode; measure dissolved carbonate (acidification followed by carbon dioxide analysis); measure plutonium concentration as a function of filtration (unfiltered, 0.2 μm and 20 nm Millipore centrifuge filters) and a Packard 2 π alpha scintillation counter which was supported by ICP-MS analysis; and plutonium oxidation state, using a gas-tight cuvette to prevent re-exposure to oxygen, with a CARY 5 UV-VIS-NIR spectrometer.

Table 4-2. Nominal Composition of the Simulated WIPP Brines (90% Strength)

Element, Species, or Property	ERDA-6[a] M		G-Seep[b] M	
	Actual	10% Diluted	Actual	10% Diluted
Cl^-	4.64	4.18	5.07	4.56
SO_4^{2-}	0.167	0.150	0.297	0.267
B	0.063	0.057	0.14	0.13
CO_3^{2-}/HCO_3^-	0.016	0.014	0	0
Br^-	0.011	0.010	0.017	0.015
Na^+	4.85	4.37	4.18	3.76
K^+	0.097	0.087	0.338	0.304
Mg^{2+}	0.019	0.017	0.612	0.551
Ca^{2+}	0.012	0.011	0.0077	0.0069

a. This is a Castile simulated brine. pC_{H+} was 8 and 10.
b. This is a Salado simulated brine. pC_{H+} was 5 and 7.

After two years of equilibration under anoxic conditions, a series of plutonium interaction studies were conducted with components that typically coexist with TRU waste to evaluate their effect on the observed stability of the Pu(VI) oxidation state (see Table 4-1 for the experimental matrix). These experiments were conducted by transferring ~ 20 mL of solution from the 2-year equilibration studies into a 30 mL polypropylene bottle that had been pre-equilibrated with brine and placed in a nitrogen glovebox to remove air. This was done in a nitrogen glovebox to maintain anoxic conditions throughout. The effects of the following two forms of iron were investigated: 1) zero-valent iron in A366 steel, and 2) Fe^{2+} suspensions from the added ferrous chloride. In all of these experiments a small aliquot of the solution was periodically removed and sequentially filtered through 20 nm filters under anoxic conditions. The same procedures were used for solution analysis as in the first set of experiments.

4.1.4 ANL Results: Stability of Pu(VI) in the Absence of Reducing Agents

The results of the Pu(VI) stability experiments are summarized in Table 4-3. The concentration of plutonium as a function of time for these experiments is shown in Figure 4-1 for G-Seep and ERDA-6 brine. The concentration of plutonium, as a PuO_2^{2+} species, in both G-Seep and ERDA-6 brine was predominantly stable over the two-year duration of the experiments. The plutonium concentration in these experiments was below saturation and steady-state concentration limits were not established.

The aqueous speciation of plutonium in the brine experiments varied as a function of pC_{H+} and carbonate concentration. At pC_{H+} 8 and 10, in the presence of carbonate (experiments Pu-E10 and Pu-E8), the absorption spectra are essentially identical and correspond to a Pu(VI) carbonate species. At pC_{H+} 10, in the absence of carbonate (experiment Pu-E10-NC), a Pu(VI) hydroxy-chloride complex was observed. There is no spectroscopic evidence for the reduction of Pu(VI) for all three ERDA-6 brine experiments under the conditions investigated.

A hydroxy-chloride Pu(VI) complex is present in the replicate experiments (Pu-G7 and Pu-G7-NC) in G-Seep brine at pC_{H+} 7. A small decrease in total plutonium concentration was evident at long times. There was also spectral evidence for the formation of Pu(V), presumably due to autoradiolysis effects, in solution. The formation of Pu(V) may account for the small decrease in total concentration since this could lead to the formation of some Pu(IV) precipitates as a consequence of dis-proportionation reactions. At pC_{H+} 5 (experiment Pu-G5), total concentrations decreased by ~ 25%. The speciation, based on the absorption spectra is similar to that observed at pC_{H+} 7 except that a lower concentration of Pu(V) is present suggesting that Pu(IV) may be forming more rapidly and extensively.

The long-term stability, or perhaps more accurately meta-stability, of Pu(VI) in WIPP brine is consistent with results reported previously in slightly different brines [Reed 1994]. The plutonium predominantly existed in solution as spectroscopically recognizable hydroxy-chloro or carbonato species that were filterable to 20 nm. This is not surprising given the strong tendency of Pu(VI) to undergo hydrolysis and form carbonate complexes in the pH range investigated.

There was no clearcut evidence that radiolysis played a key role in the observed stability of Pu(VI) in these brine systems. Since the experiments were initiated with ~100% Pu(VI), if anything, radiolysis was the predominant pathway for the reduction of Pu(VI) that was noted in the lower pH experiments with no carbonate present. Oxidation state distribution in irradiated systems is determined by the sum of the effects of transient reducing/oxidizing species and the effects of molecular products accumulated over time (e.g., oxy-chlorides and oxy-bromides in WIPP-relevant brines). Since only Pu(VI) was initially present, it is reasonable to expect some steady state concentration of Pu(V) due to the effects of the strongly reducing transients generated radiolytically. This is also consistent with the observation that this effect was much less at higher pH where the Pu(VI) is more strongly complexed and lower reactivity with the radiolytic transients is expected. Supporting experiments that were performed under identical conditions except for the use of Pu-242, which has a much lower specific activity, rather than Pu-239 did not result in the reduction of Pu(VI) to Pu(V). The overall effect of radiolytic processes, when viewed in the context of all speciation pathways for the total subsurface system, is however not directly addressed by the results of these experiments since the starting point was Pu(VI), not Pu(IV) which is the most likely oxidation state of plutonium in emplaced TRU waste since plutonium oxide is the most likely form of plutonium.

Table 4-3. Summary of Results from the ANL Pu(VI) Equilibration Studies in Brine

Experiment Designation and Description	[a] pC_{H+} (± 0.1)	[b]$[CO_3^{2-}]$ and $[HCO_3^-]$	[c]Initial [Pu] in M ± 5%	[c]Final [Pu] in M as a function of filtration – uncertainty is ± 5%			Spectroscopy and predominant oxidation state in solution
				Unfiltered	0.2μm	20 nm	
PU-G5 G-Seep brine at pC_{H+} 5	5.2	< 1E-6 M	8.7 E-5	6.7 E-5	6.7 E-5	6.7 E-5	Pu(VI) hydroxy-chloride species with some Pu(V) (estimated to be ~ 20%)
PU-G7 and PU-G7-NC G-Seep brine at pC_{H+} 7	7.1	< 1E-6 M	8.7 E-5	8.3 E-5	8.4 E-5	8.3 E-5	Pu(VI) hydroxy-chloride species with some Pu(V) (estimated to be ~ 10%)
PU-E8 ERDA-6 brine at pC_{H+} 8 and 10^{-3} M Carbonate	8.1	0.0073 M	8.3 E-5	7.6 E-5	7.6 E-5	7.6 E-5	Pu(VI) carbonate complex with no evidence of Pu (IV/V)
PU-E10 ERDA-6 brine at pC_{H+} 10 and 10^{-3} M Carbonate	10.1	0.0021 M	7.9 E-5	7.0 E-5	7.1 E-5	7.3 E-5	Pu(VI) carbonate complex with no evidence of Pu (IV/V)
PU-E10-NC ERDA-6 brine at pC_{H+} 10 without added carbonate	10.1	< 1E-6 M	8.3 E-5	7.4 E-5	7.4 E-5	7.6 E-5	Pu(VI) hydroxy-chloride species with no evidence of Pu (IV/V)

a - pC_{H+} measured throughout the experiments was within 0.1 pC_{H+} of the initial pC_{H+} (pH measurements corrected for ionic strength)
b - the limit of detection for the carbonate acidification method was 1 x 10^{-6} M
c - these data are based on liquid scintillation counting data

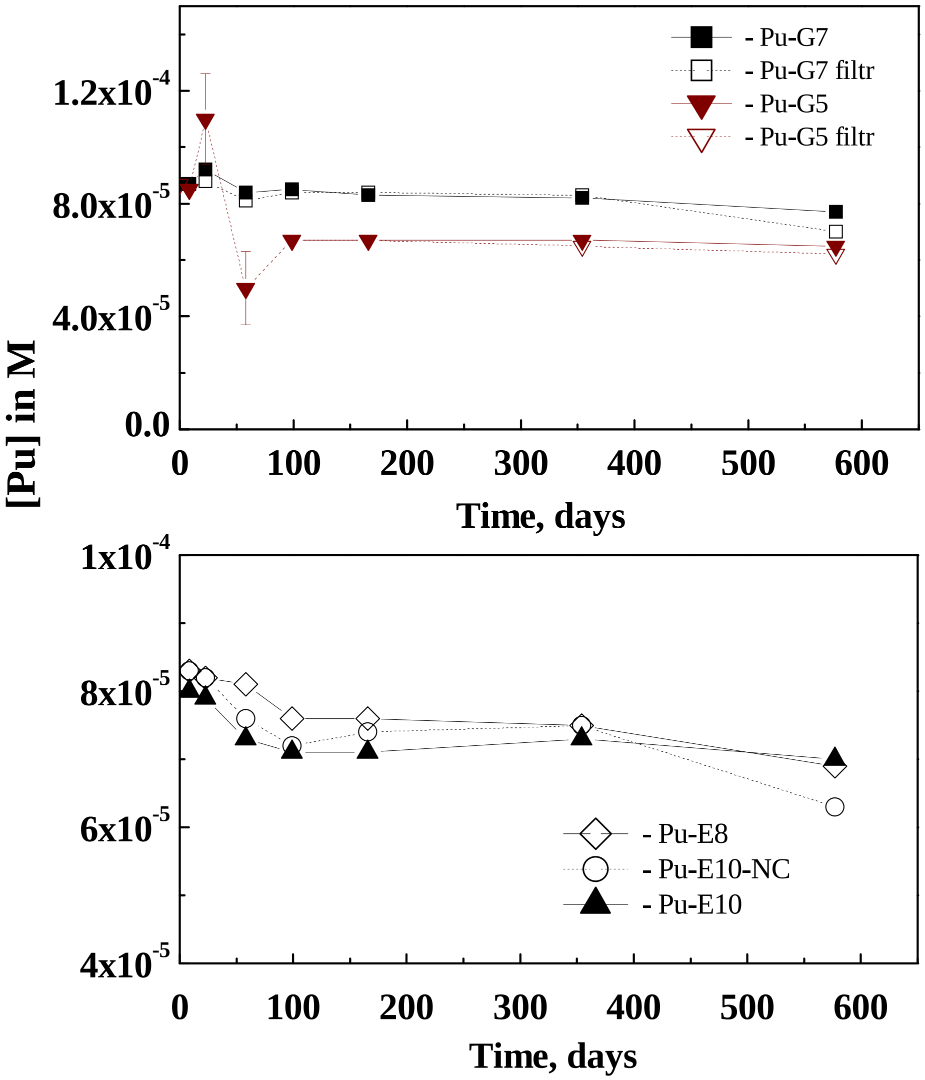

Figure 4-1 **Top Figure: Concentration of plutonium as a function of time in G-Seep brine (experiments Pu-G5, Pu-G7 and Pu-G7-NC). Significant differences in concentration due to filtration were noted in the experiments at long times but were not present in the initial concentration data.**

Bottom Figure: Concentration of plutonium as a function of time in ERDA-6 Brine (experiments, Pu-E10, Pu-E8 and Pu-E10-NC). No significant differences in concentration were noted between the unfiltered, 0.2 μ filtered and 20 nm filtered solutions.

4.1.5 ANL Results: Reduction of Pu(VI) by Zero-Valent Iron (Steel)

The presence of a zero-valent iron (steel) coupon, under anoxic conditions, led to the reduction of plutonium(VI) to plutonium(IV). This, as shown in Figure 4-2 and summarized in Table 4-4, led to as much as four orders of magnitude decrease in the plutonium concentration and the precipitation of plutonium phases from the various brines. As evident in Figure 4-2, plutonium in G-Seep brine was most rapidly removed. Carbonate complexation at both pC_{H+} 8 and 10 resulted in a slower decrease in the plutonium concentration but, ultimately, similar total plutonium concentrations were obtained. The plutonium species in the carbonate-free pC_{H+} 10 ERDA-6 experiment was removed from solution at the slowest rate. Given the wide range of pH, the variety of plutonium species present, and the competition between sorption, redox, and precipitation in the experiments, it is difficult to establish the details of the mechanism for these observed effects.

The plutonium precipitates and iron coupons used were recovered and encapsulated in a polystyrene matrix under anoxic conditions for X-ray near-edge spectroscopy (XANES) and/or extended X-ray fine-structure (EXAFS) analysis. Typically ~ 30-40% of the reduced plutonium in these experiments was on the metal coupon surface. XANES analysis of the plutonium precipitate (see Figure 4-3) and the plutonium associated with the iron surface matched the edge position and shape of the $Pu(IV)O_2$ reference phase. This confirmed that reduction had taken place, but, generally speaking, XANES analysis is not a very precise technique for establishing oxidation state distribution so it is not possible to preclude the presence of small amounts of Pu(III) (~ 10% or less) in these samples. The EXAFS analysis, in radial space, of the precipitate obtained at pC_{H+} 7 is also shown in Figure 4-3 and compared to the spectrum of the plutonium oxide standard. Although there is a good match in Pu-O bond lengths there is much greater long-range disorder in the WIPP sample, which is indicative of the amorphous nature of the brine precipitate.

The concentration effects, XANES analysis, and consistency of the resulting concentrations with the calculated Pu(IV) concentrations combine to show that in the presence of zero-valent iron, all the Pu(VI) species are reduced to Pu(IV) leading to precipitation of Pu from solution. This occurred even though these Pu-239 experiments had equilibrated for ~ two years meaning there was sufficient time for radiolytic products to have reached steady state.

The plutonium oxidation state in the aqueous phase in these experiments was not directly determined and is less certain. The final empirical steady state plutonium concentrations measured, however, are most consistent with what was expected for Pu(IV) and Pu(III) species in the presence of milli-molar concentrations of carbonate. Additionally, the low plutonium concentration observed at pC_{H+} 5, along with the strong dependence of the plutonium concentration on the presence of carbonate, qualitatively point towards a predominantly Pu(IV) aqueous species. The likely predominance of the Pu(IV) oxidation state in these experiments does not agree with thermodynamic predictions for the predominance of Pu(III) species in a hydrogen-iron anoxic system but is reasonable given the radiolysis effects (i.e., buildup of oxy-chlorides) that may be present in these long-term studies. These data suggest that Pu(IV) precipitation is functioning as a “sink” for plutonium as the plutonium is reduced by the metal. Essentially, under the conditions of our experiments Pu(IV) precipitation is proceeding at a faster rate than the further reduction of

Pu(IV) to Pu(III). The role of Pu(III) species in these iron-rich anoxic systems is the subject of further and ongoing experimental work.

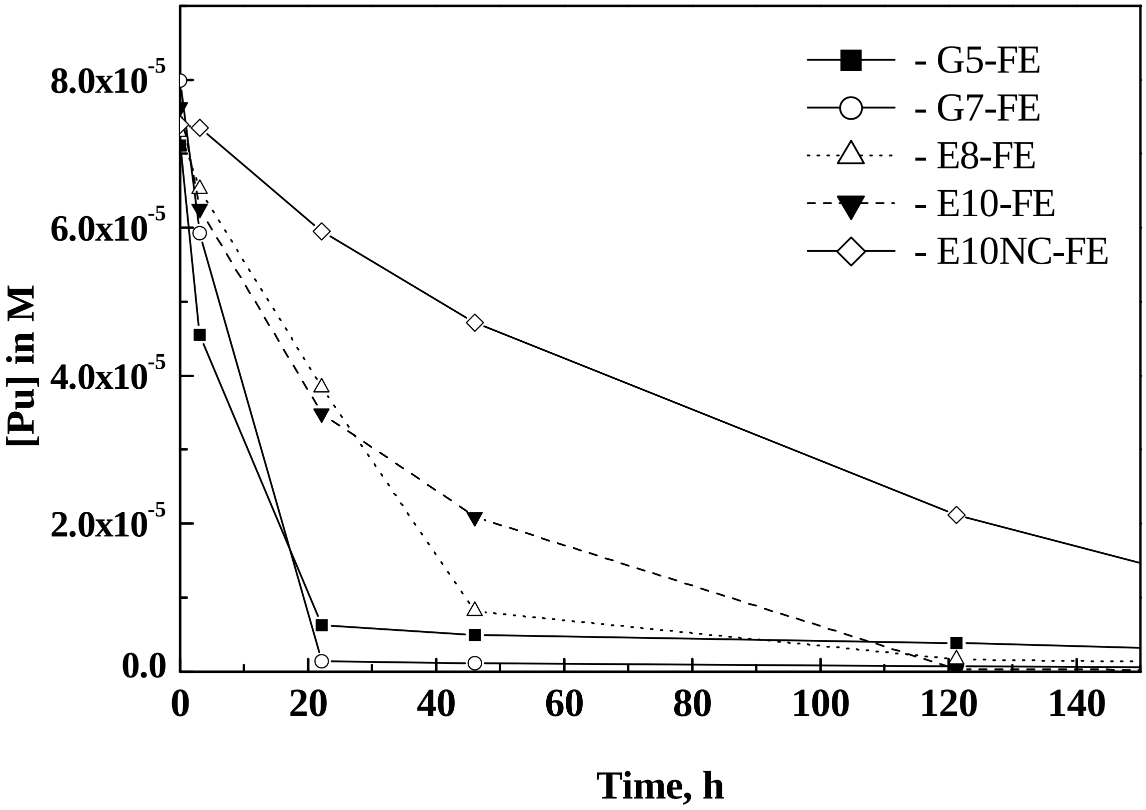

Figure 4-2 **The concentration of plutonium as a function of time in the presence of zero-valent iron (as steel coupons). The overall rate of reduction was G7≈G5>E8≈E10 < E10-NC.**

4.1.6 ANL Results: Effect of Fe^{2+} on the Stability of Pu(VI) in Brine

The addition of Fe^{2+}, as a chloride complex, to the various brines was done under anoxic conditions (see Table 4-1 and Table 4-4). This led to the rapid reduction (see Figure 4-4) of plutonium concentrations in all cases but experiment G5 which corresponds to G-Seep brine at pC_{H+} 5. An absorption spectrum of the plutonium in this experiment showed that the plutonium remaining in solution was PuO_2^+. These overall results are difficult to interpret due to the complexity of the Fe^{2+} system under the conditions of our experiments in the simulated brines. Overall, the extent of reduction was significantly less (by a factor of 10-100) than that observed for zero-valent steel. It is likely that the difference observed at pC_{H+} 5 was mostly due to the difference in the speciation of the iron rather than the plutonium chemistry at that pH – but this needs further study.

Table 4-4. Concentration of plutonium as a function of time for the ANL iron coupon and added Fe^{2+} interaction studies

Experiment Description	[Pu] in 20 nm-filtered samples as a function of time (M) – uncertainty is ± 5%						
Time (h), Fe coupon	Initial	3.1 h	22.1 h	46.0 h	121.3 h	214.6 h	455.9 h
G5-FE	7.11 E-5	4.55 E-5	6.29 E-6	4.91 E-6	3.87 E-6	1.68 E-6	7.00 E-8
G7-FE	7.99 E-5	5.93 E-5	1.35 E-6	1.11 E-6	6.84 E-7	3.22 E-7	5.07 E-8
E8-FE	7.29 E-5	6.52 E-5	3.84 E-5	8.14 E-6	1.59 E-6	5.84 E-7	9.02 E-8
E10-FE	7.63 E-5	6.26 E-5	3.49 E-5	2.09 E-5	2.77 E-7	1.13 E-7	1.11 E-7
E10NC-FE	7.39 E-5	7.35 E-5	5.95 E-5	4.72 E-5	2.12 E-5	1.31 E-8	6.87 E-9
Time (h), added Fe^{2+}	Initial	2.1 h	5.2 h	25.1 h	49.7 h	121.4 h	216.8 h
G5-FE2	6.77 E-5	4.24 E-5	3.48 E-5	2.82 E-5	3.02 E-5	2.17 E-5	2.22 E-5
G7-FE2	8.40 E-5	8.90 E-7	5.85 E-7	3.60 E-7	2.52 E-7	1.54 E-7	1.16 E-7
E8-FE2	6.88 E-5	5.50 E-7	2.78 E-7	1.42 E-7	1.04 E-7	1.17 E-7	NA
E10-FE2	7.47 E-5	5.37 E-7	2.27 E-7	1.31 E-7	1.41 E-7	1.35 E-7	NA
E10NC-FE2	7.55 E-5	2.83 E-8	9.98 E-9	4.69 E-8	1.79 E-8	1.05 E-8	NA

NA – not analyzed

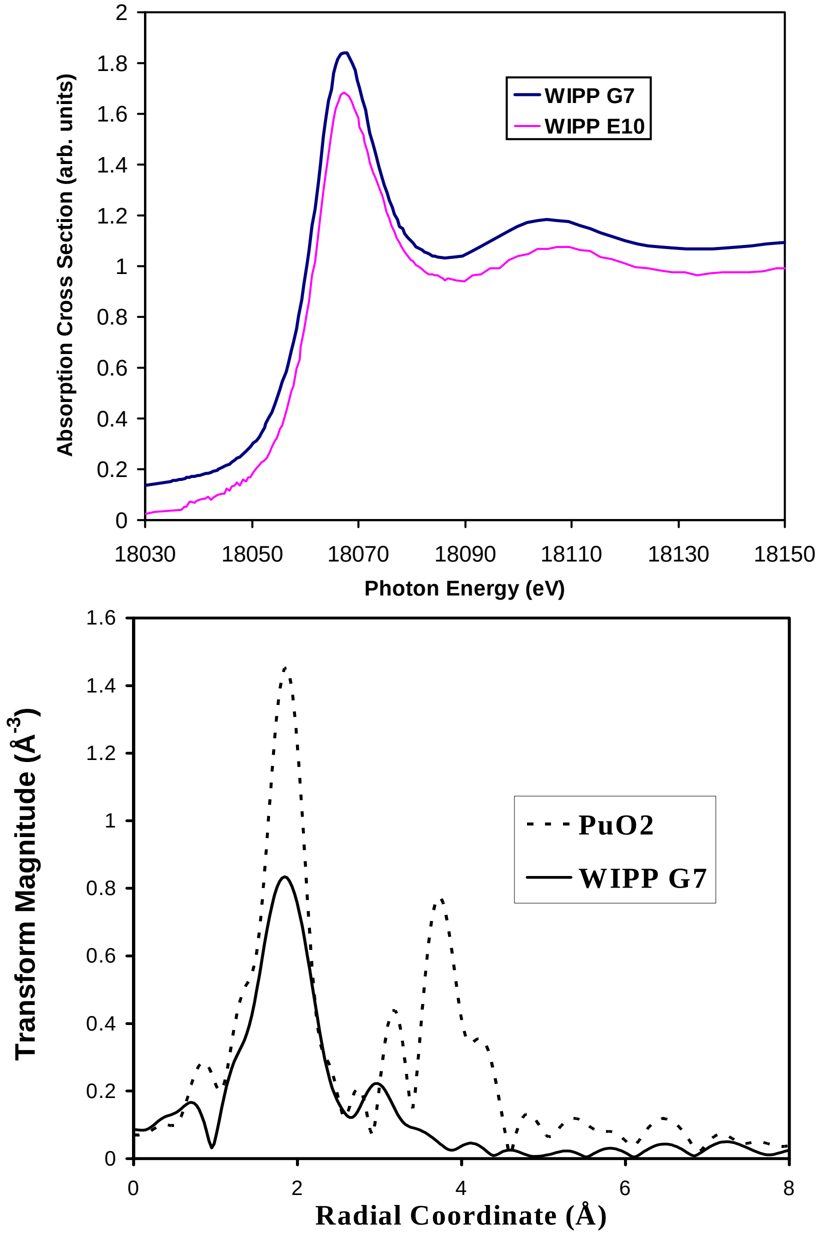

Figure 4-3 XANES spectra (top) of the precipitates from the G7 and E10 experiments after the addition of zero valent iron coupons. The spectra are purposefully offset and match the edge position of the Pu(IV)O_2 standard used confirming that reduction from Pu(VI) to Pu(IV) had taken place.

EXAFS (bottom), in radial space, of plutonium precipitates collected from the pC_{H+} 7 WIPP experiments containing iron and a PuO_2 reference. There is agreement in the Pu-O bond length, but much greater long-range disorder in the brine-precipitated plutonium phase.

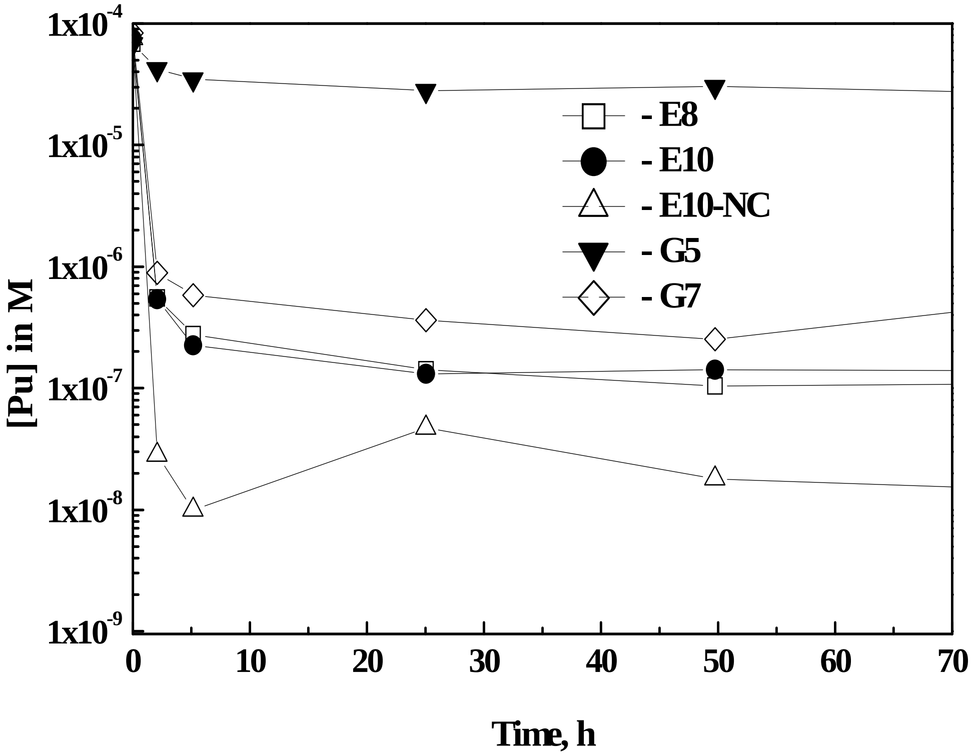

Figure 4-4. **Effect of added Fe^{2+} on the stability of Pu(VI) in brine. Total plutonium concentrations were reduced by two -four orders of magnitude with the exception of experiment G5 which was conducted at pC_{H+} 5 in G-Seep brine where aqueous Pu(V) species persisted.**

4.2 Distribution of Plutonium Species in Brine: PNNL Studies

The distribution of plutonium in WIPP brine in the presence of iron was investigated as part of the WIPP ASTP program in the late 1990's. This was published [Xia 2001] in a journal article entitled "Determining the Distribution of Pu, Np and U Oxidation States in Dilute NaCl and Synthetic Brine Solutions". In this section we summarize the relevant plutonium speciation results that were obtained in the presence and absence of zero valent iron powder. These data are shown in Figures 4-5 and 4-6.

The significant result, from the WIPP perspective, in the results of Xia et. al. is that, although the reduction of higher-valent plutonium was observed under most conditions investigated, there were a few cases where Pu(V) species persisted. In this context, these data conflict with some of the results reported in section 4.1 where reduction was noted under all circumstances when zero valent iron was present.

4.2.1 Goals and Objectives of the Research Performed

The goal of this research was to establish the oxidation state distribution of plutonium in WIPP brine under a range of conditions that simulate those expected in the WIPP environment. This was done by adding oxidized plutonium, as PuO_2^{2+}, to dilute and simulated WIPP brine and tracking the oxidation state as function of time and brine chemistry. A combination of speciation techniques were used to establish the oxidation state distribution.

4.2.2 Summary of Experimental Approach

Overall, plutonium was oxidized to Pu(VI) and added to simulated or simplified brine after bubbling the solution with high purity argon to remove air. Total plutonium concentration was tracked by liquid scintillation counting and spectroscopy or extraction was performed to determine the oxidation state. Once the speciation trends were established, iron powder was added to the solution to establish its effects on the plutonium speciation. The following is a summary of the experimental conditions and variables investigated:

- Pu: 93.6% Pu-239 and 6.3% Pu-240 by activity, initially 2.5×10^{-4} M
- Plutonium was electrolytically oxidized to PuO_2^{2+} in 0.35 M nitric acid
- Iron: 325 mesh, rinsed in high-purity water (HPW) and added as a powder
- Brines: 0.01 M Na Cl and ERDA6B with pC_{H+} range of 2-12

These experiments were conducted at room temperature (22 ± 1^oC), in glass centrifuge tubes treated with trimethylsilane. De-aeration was accomplished by bubbling with high purity argon for ~ 30 minutes. The glass centrifuge tubes were sealed and placed in room air in an orbital shaker for the duration of the experiments (typically up to 72 days). The total concentration of plutonium was determined by liquid scintillation counting, but the authors do not report the extent that these samples were filtered. UV-VIS-NIR spectroscopy was used to determine the plutonium oxidation state at high concentration and oxidation-specific solvent extraction was used for oxidation state determination at low plutonium concentration.

4.2.3 PNNL Results: Stability of Higher-Valent Plutonium in the Absence of Iron

Two sets of experiments were performed as controls for the iron interaction studies. One in 0.01 M sodium chloride and one in ERDA6B brine. These were performed under conditions that were analogous to the iron-containing experiments.

The total concentration of plutonium, when plutonium(VI) was added to 0.01 M sodium chloride, was essentially stable for the duration of the experiments performed (see Figure 4-5). A slight lowering in concentration was observed at pH > 9. No speciation (i.e. spectroscopy) is reported on these samples but the authors indicate that the Pu(VI) was stable in these systems. Correspondingly, E_h potentials measured in solution remained oxidizing throughout the experiments performed.

In ERDA6B brine (see Figure 4-6), a similar result was obtained. The plutonium, initially added as Pu(VI) was essentially stable with some loss in concentration at the higher pH values. Under these conditions, it is stated that the plutonium remained stable as a Pu(VI) species and no reduction occurred.

4.2.4 PNNL Studies: Stability of Higher-Valent Plutonium in the Presence of Iron

Two sets of experiments, analogous to those performed without the Fe additions, were performed by adding iron powder. These data are also shown in Figures 4-5 and 4-6. The addition of iron, in most cases, caused a reduction in the system E_h and shifted the effective pH from an initial range of pH = 2-12 to pH = 8-12. In this case, the added iron was reacting to “buffer” the system at pC_{H+}~ 8 or greater.

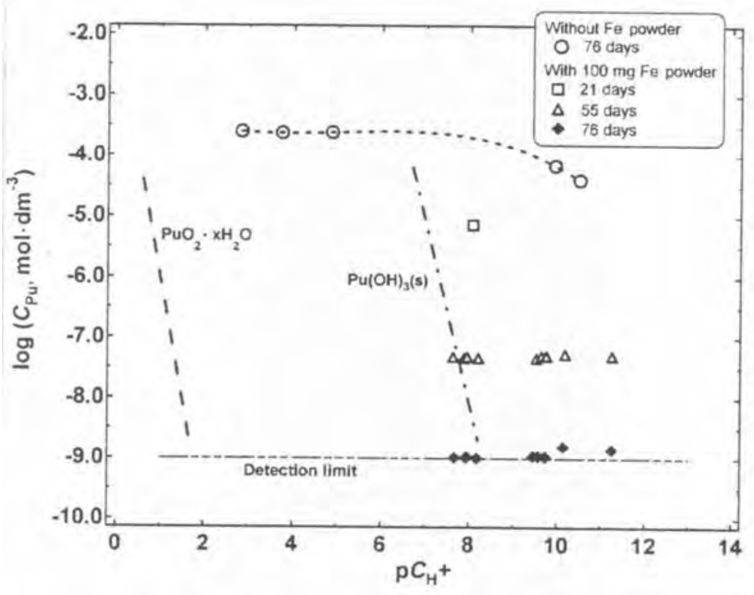

Figure 4-5. Effect of iron powder on observed Pu concentration in 0.01 M NaCl Solutions (Figure 3 in Xia 2001)

In 0.01 M sodium chloride, the addition of iron caused the reduction of plutonium in all cases. Final plutonium concentration was reduced from a starting concentration of 0.25 mM to ~ 10^{-9} M after 76 days. Correspondingly there was a drop in the measured system E_h from ~ 600 to 800 mV to -300 to -400 mV. Speciation was not performed on these results because the final concentrations were outside the range of the spectroscopic and extraction techniques utilized. Reduction to Pu(IV) was proposed based on solubility arguments and the correlations/comparisons with the effects of iron on the system E_h.

In ERDA6B brine, the addition of iron did not consistently lead to the reduction of the higher-valent plutonium present. In the pC_{H+} range of 7-9, which is the most relevant to the CRA-2004 and CRA-2009 chemistry model, loss of plutonium from solution was noted presumably due to reduction although this occurred much more slowly in ERDA6B compared to the 0.01 M sodium chloride solution. Correspondingly the measured system E_h was lowered from ~ 500 to 600 mV to -290 mV to -400 mV. These results are consistent with the observations made in the dilute sodium chloride studies. The final speciation of the plutonium in this pH range was not determined because it was below detection for the techniques employed but it was proposed to be Pu(IV) species based on solubility and E_h

arguments. At $pC_{H+} > 9$, in contrast, there was very little change in the plutonium concentration due to the addition of the iron powder. Follow-up spectroscopy established that the plutonium was persisting as a Pu(V) species that led to concentrations of 10^{-5} M or greater even in the presence of the iron powder. Correspondingly, the system E_h measurements remained positive (470 to 670 mV) when the plutonium remained in solution. The explanation provided for these pH-dependent differences was that radiolysis was maintaining an effectively higher redox potential in the system and the reactivity of the Fe powder, particularly in its ability to impose a redox control on the system, was greatly reduced at higher pH.

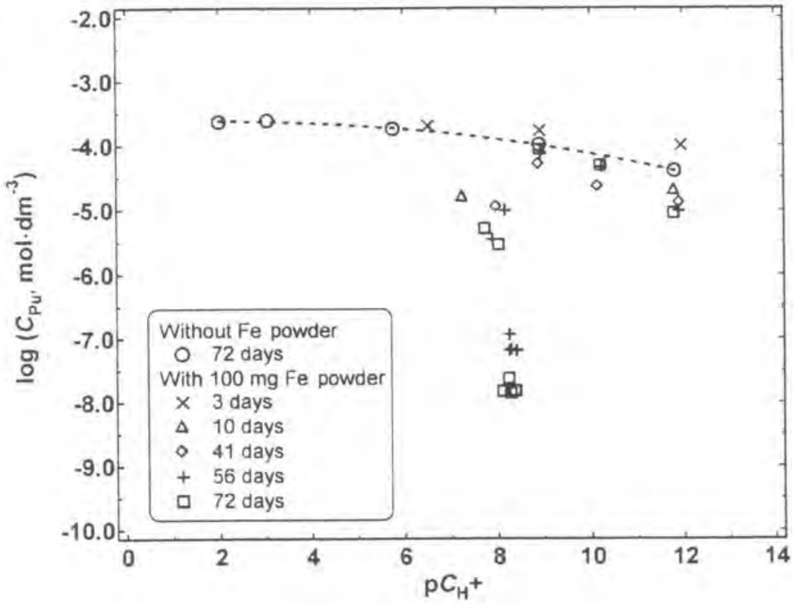

Figure 4-6. Effect of Iron Powder on Observed Pu in the ERDA6B Brine Solution (Figure 4 from Xia 2001.)

4.3 Reduction of Pu(VI) by Iron and Iron Oxides: ACRSP Studies

The ACRSP studies were performed as part of the ongoing WIPP recertification effort according to Test Plan LCO-ACP-04 entitled “Reduction of plutonium in WIPP Brine: Limited Scope Study” [Reed 2005]. As described previously, the interaction of iron species with multivalent actinides, especially Pu, is a key process that helps define the subsurface chemistry of plutonium in the WIPP.

4.3.1 Goals and Objectives

The main purpose of the experiments in the LCO-ACP-04 Test Plan was to resolve, by performing selected self-consistent experiments, apparent discrepancies reported in the literature (see summaries in Sections 4.1 and 4.2) regarding the reduction of plutonium (VI) in brine by iron. This helped establish the validity of literature results that higher Pu oxidation states may persist under some expected WIPP conditions – especially at the higher pH conditions considered.

There were also two important programmatic goals of this research. The first of these is the qualification and confirmation of past results on the Pu(VI) – iron system, specifically the research previously done at ANL as part of the WIPP ASTP. The second goal of this work was to extend past research with zero-valent iron to include Fe (II) and Fe (III) oxide phases.

4.3.2 Experimental Matrix and Approach

The Test Matrix for the experiments performed is given in Table 4-5. Initially, the key experiments of Xia 2001. and Reed 2007, were reproduced with equivalent environmental controls. An additional experiment with GWB brine was added to each matrix to extend the applicability of the results to this brine. This was expected to confirm the results of the experiments reported by both investigators.

Second, a series of experiments where the initial oxidation state of the iron was varied as Fe (0), Fe (II) or Fe (III), was performed in ERDA-6 brine. This provided preliminary information as to the importance or unimportance of the oxidation state of the iron as it relates to the overall fate of Pu in solution. These results provided a foundation for future more detailed mechanistic studies.

The experiments listed in Table 4-5 were performed in an MBraun nitrogen glovebox (< 1ppm oxygen) – see Figure 4-7. The following experimental approach was used:

1) GWB brine and ERDA-6 brine were prepared according to established procedures (ACP-EXP-001) with the final compositions given in Table 4-6.
2) Polypropylene bottles (~ 20 mL) were pre-equilibrated with the brine that were used in the experiment for ~ 2 weeks in the nitrogen glovebox.
3) The brines were bubbled with nitrogen gas and de-aerated in the nitrogen glovebox to remove oxygen.
4) pH adjustments were done in the glovebox using either carbonate-free sodium hydroxide or hydrochloric acid. pH measurements, as pC_{H+}, were made according to procedure ACP-EXP-010 and are analogous to the approach used in section 4.1 in the corrections for high ionic strength.
5) Plutonium was added to these brines using methods previously used at ANL in the Stability/Solubility program [Reed 1994, 1998, 2007]. In summary, plutonium was oxidized to Pu(VI) by fuming in two drops of perchloric acid, dissolved in ~ pH 3 sodium chloride, and analyzed using absorption spectrometry to establish and verify oxidation state (see Figure 4-8). This stock solution was added directly to the brine at the desired pH.
6) Plutonium (VI) stability was established for each brine by letting each experiment equilibrate for a few months and confirming that no reduction and/or loss of plutonium from solution had occurred.
7) Once the stability of the Pu(VI) was confirmed, iron in the various forms identified in Table 4-5 was added to the brine.
8) The oxidation state and total concentration of the Pu was monitored as a function of time to determine redox and concentration trends until a steady state concentration was observed. Samples were filtered by a ~ 20 nm filter to determine the truly

dissolved fraction. At the end of the experiment, sequential filtration was used to establish the size distribution of the plutonium species.

Table 4-5. Experimental Matrix for the ACRSP Pu-Fe Interaction Study

Experiment Designation (1, 2)	Iron Content	pH	Duration (3)	Brine	Environmental Conditions
Experiments to reproduce Xia et al.					
Pu-FEP-E8-1, 2	Fe Powder	8	4 wks	ERDA-6	Room T, 15 mL, anoxic, without carbonate
Pu-FEP-E10-1, 2	Fe Powder	10	4 wks	ERDA-6	Room T, 15 mL, anoxic, without carbonate
Pu-FEP-GWB7-1, 2	Fe Powder	7	4 wks	GWB	Room T, 15 mL, anoxic, without carbonate
Experiments to reproduce Reed et al.					
Pu-FEC-E8-1, 2	Coupon	8	4 wks	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FEC-E10-1, 2	Coupon	10	4 wks	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FEC-G7-1, 2	Coupon	7	4 wks	GWB	Room T, 15 mL, anoxic, without carbonate
Experiments to investigate Fe oxidation state Dependence					
Pu-FEC-1, 2	Fe Coupon	9	4 wks	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FEP-1, 2	Fe Powder	9	4 wks	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE2-1, 2	Fe^{2+} Colloidal	9	4 wks	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE3-1, 2	Fe^{3+} Colloidal	9	4 wks	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE3-OX-1, 2	Fe(III) oxide	9	4 wks	ERDA-6	Room T, 15 mL, anoxic, with carbonate
Pu-FE23-OX-1, 2	Fe (II/III) oxide	9	4 wks	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

Figure 4-7. Mbraun re-circulating glovebox used for the ACRSP plutonium experiments

Table 4-6. Species Concentration (M) for WIPP Simulated and Simplified Brines used in the ACRSP Studies

Species	Brine (95% Formulation)		
	NaCl	ERDA-6	GWB
Cations			
Na^+	5.00	4.61	3.30
K^+		0.092	0.437
Li^+		0.0	0.0041
Mg^{2+}		0.018	0.951
Ca^{2+}		0.0114	0.0129
Anions			
Cl^-	5.00	4.41	5.24
Br^-		0.0104	0.0249
$B_4O_7^{2-}$		0.015	0.0368
SO_4^{2-}		0.159	0.166
Properties			
Density g/mL	1.12	1.18	1.22
Ionic Strength (I)	5 M	4.96	6.8

4.3.3 ACRSP Results: Pu(VI) Reduction by Zero-Valent Iron

Plutonium(VI), as PuO_2^{2+}, was synthesized in 5 mg aliquots by taking to dryness in 8 M nitric acid twice and finally fuming in a small quantity of perchloric acid. The final near-dryness solid was dissolved in 2 mL of high-purity water to form the stock solution. A 1:10 dilution of this solution is shown in Figure 4-8. This spectrum is characteristic of the aquo (i.e. un-complexed) species and indicates that the synthesis yielded essentially pure Pu(VI) since there is no spectral evidence for Pu(V) or Pu(IV).

The Pu(VI) stock solution was placed in the nitrogen glovebox to remove the oxygen content. To confirm and further establish the stability of Pu(VI) in brine, a concurrent developmental experiment was performed by adding 100 microliters of the Pu(VI) stock solution to GWB brine. The absorption spectrum of the plutonium in this brine is shown in Figure 4-9. Here, since the pC_{H+} is ~ 7, the plutonium is hydrolyzed (complexed with hydroxide) resulting in a 20 nm shift in the absorption maximum to 851 nm. The absorption spectrum of this solution was stable over the three-month period that it was monitored.

In the first set of experiments, three brine systems were investigated: GWB at $pC_{H+} = 7$, ERDA-6 at $pC_{H+} = 8$ and ERDA-6 at $pC_{H+} = 10$. These were all done under anoxic conditions in a nitrogen glovebox at 23 ± 3 °C. The coupons were a ~ 1 x 2 cm ~ 0.3 g piece of high-purity iron. The iron powder was approximately the same weight small mesh-size Fe. Plutonium concentrations were tracked by liquid scintillation counting as a function of time.

The iron in these systems was reactive and led to the formation of corrosion products that varied with brine composition and pC_{H+}. Representative results are shown in Figure 4-10. The concentration of plutonium as a function of time is shown in Figure 4-11. A rapid decrease in plutonium concentration was observed in both the Fe powder and coupon systems for GWB brine and ERDA6 at pC_{H+} 8. At pC_{H+} 10, however, the reaction was significantly slower although a plateau value has not yet been reached.

The most important observations from these zero-valent iron experiments are that 1) the reactivity of the Fe powder and coupon were comparable in all cases investigated – so the form of the zero valent iron does not appear to be a critical factor (although reactivity would be expected to be higher for the higher surface area – e.g. Fe powder). At pC_{H+} 10, the iron is much less reactive and this is exhibited as a significant slowdown in the rate that Pu is reduced and/or precipitated from solution.

The first set of the experiments was centered on comparing the reactivity of zero-valent iron in coupon and powder form. The second set of Pu(VI)-Fe experiments were centered on the effects of iron oxidation on the rate and likelihood of Pu(VI) reduction. The matrix for this set of experiments was given in Table 4-5 and the results are summarized in Figure 4-12.

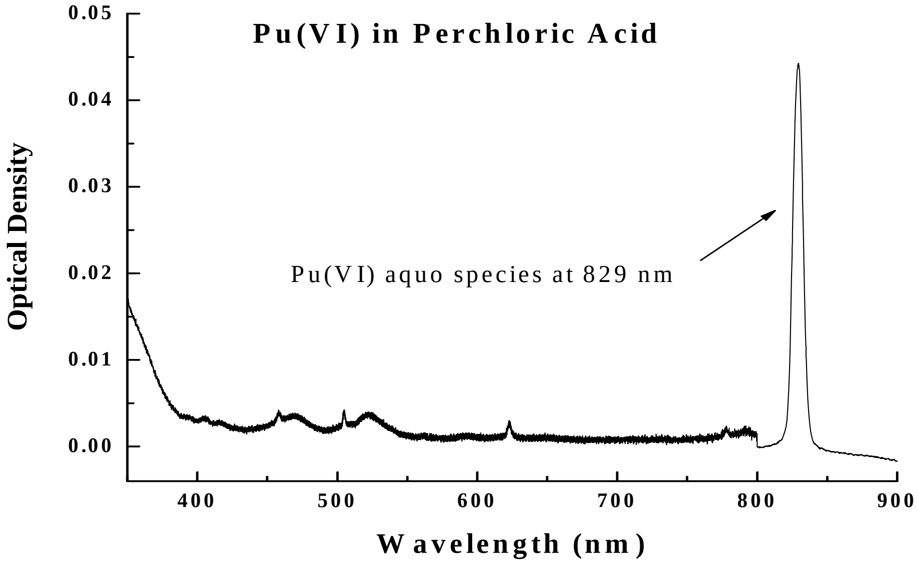

Figure 4-8 Absorption spectrum of PuO_2^{2+} in perchloric acid. The spectrum is characteristic of Pu(VI) and indicates that the synthesis performed was successful.

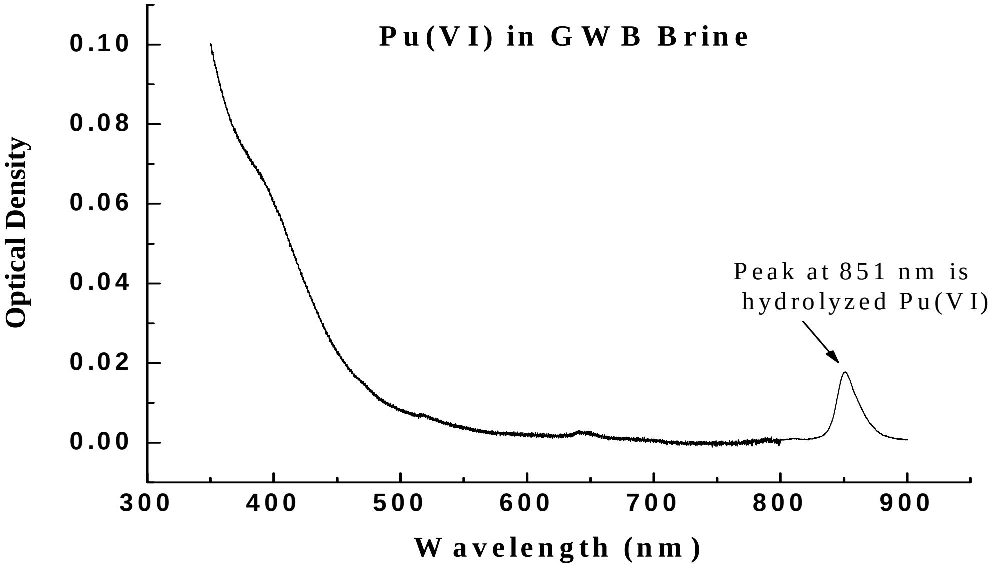

Figure 4-9 The absorption spectrum of Pu(VI) in GWB brine at $pC_{H+} = 7$. There is no evidence for the Pu(VI) carbonato species (~ 812 nm peak) indicating that this absorption corresponds to a hydrolyzed PuO_2^{2+} species in the brine.

Figure 4-10. **Appearance of Pu-Fe experiments after reaction. Experiments above were (left to right): Magnetite in ERDA-6, Ferrite in ERDA-6 brine, iron powder in ERDA-6 brine, and iron coupon in ERDA-6 brine**

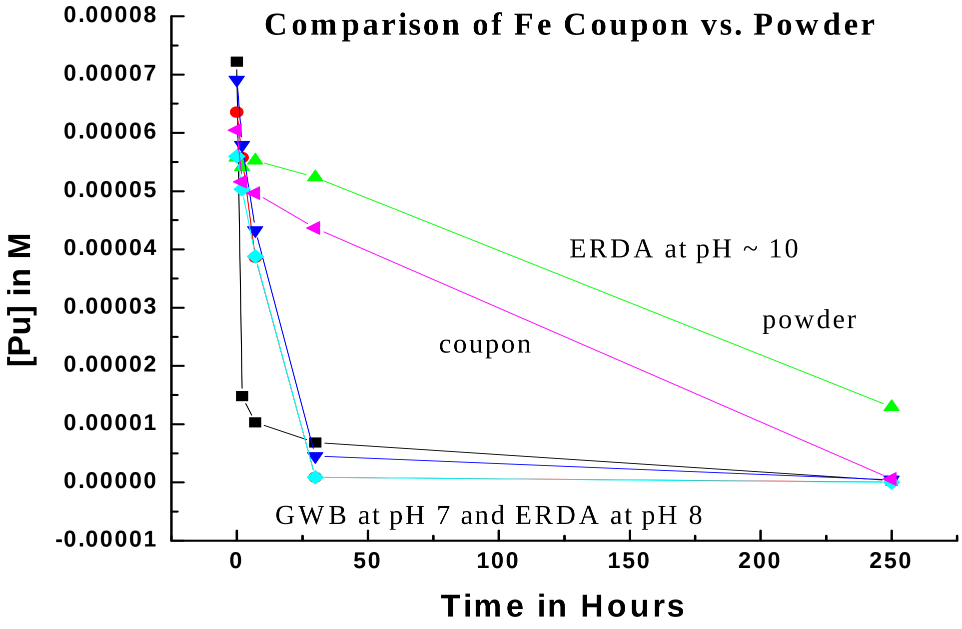

Figure 4-11 **Comparison of the reactivity of iron powder and iron coupon towards Pu(VI). Rapid reduction/removal from solution was observed at pC_{H+} 7 (GWB brine) and pC_{H+} 8 (ERDA-6 brine) but not at pC_{H+} 10 (ERDA-6 brine).**

The data shown in Figure 4-12 correspond to ERDA-6 at pC_{H+} 9.2. Experiments were performed under anoxic conditions at room temperature. Plutonium concentration was measured by alpha scintillation counting after filtration by 100,000 nominal molecular weight limit (NMWL) (~ 20 nm) filters. The presence of reduced iron (magnetite, and both Fe powder and bulk phases) resulted in the rapid loss of plutonium from solution that is presumably due to its reduction. XANES analysis confirmed reduction to form Pu(IV) phases (see Figure 4-13). In the case of ferric oxide, where no reduced iron was available, some loss of Pu was noted, but residual concentrations remained high. It is postulated that this reduction in total plutonium concentration, in this case, was due to sorption not reduction/precipitation. Lastly, it is interesting to note that the most complete and rapid loss of Pu occurred for magnetite which was the only iron phase that contained available Fe(II). Overall, these results continue to show that reduced iron is effectively removing higher-valent plutonium from brine.

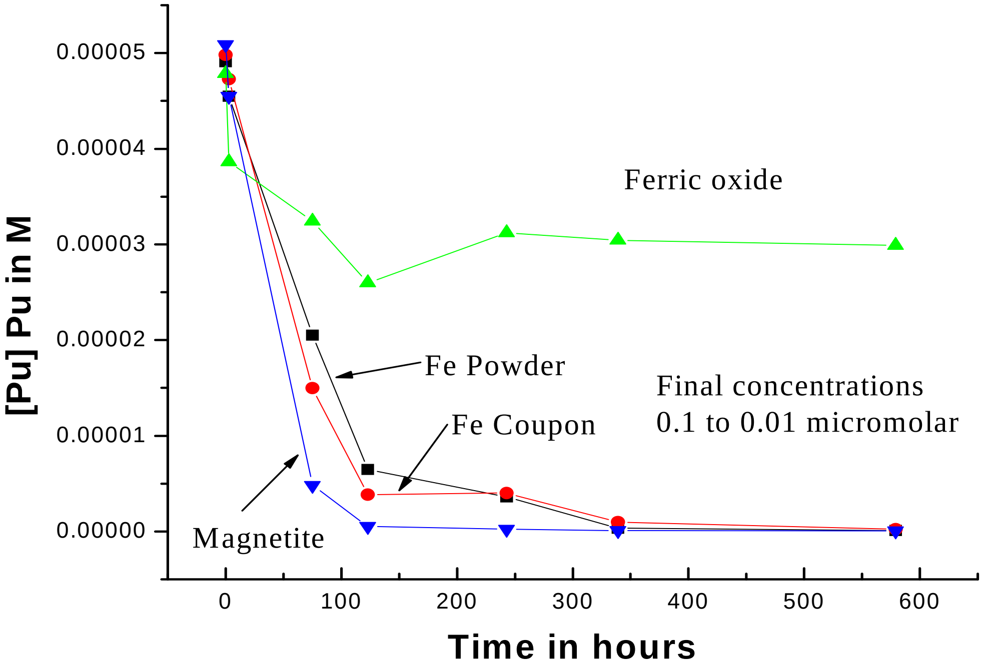

Figure 4-12 The concentration of plutonium in ERDA-6 brine at pC_{H+} 9.2 as a function of time in the presence of iron powder, iron coupon, ferric oxide, and magnetite (mixed iron oxide)

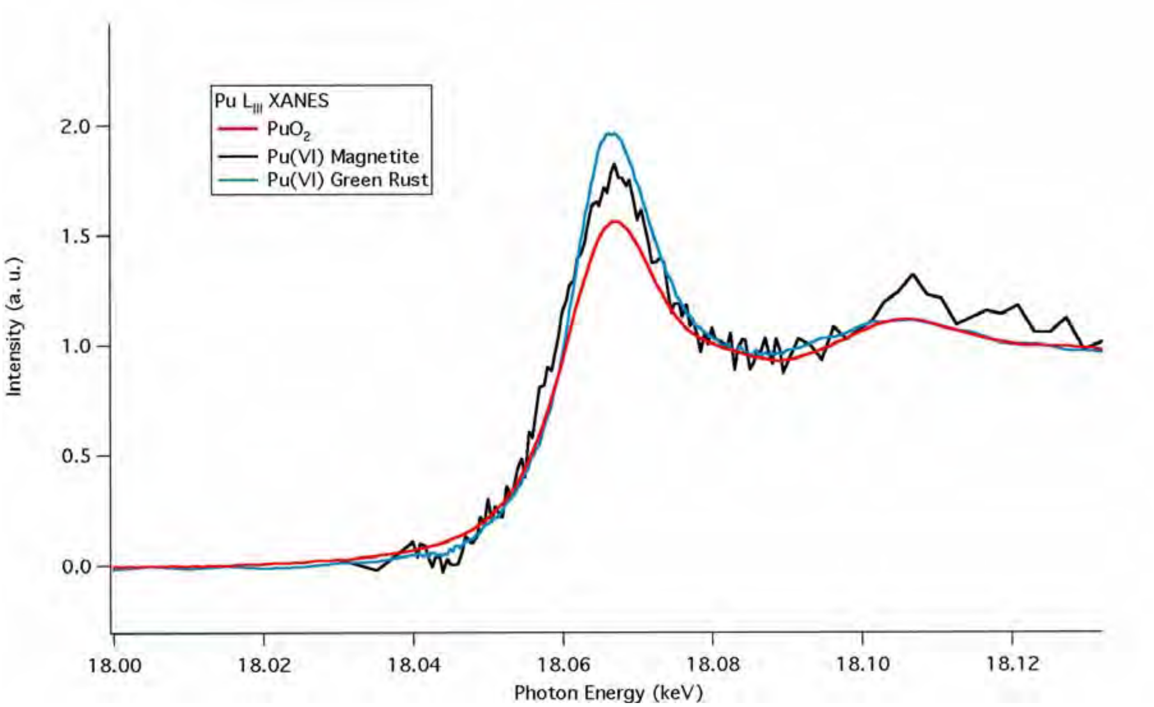

Figure 4-13. XANES analysis of the precipitates formed in the reduction of Pu(VI) by magnetite and green rust formed in the iron coupon reactions. The edge position match with PuO_2 indicates that the plutonium was reduced to Pu(IV) and was strongly associated with the corrosion products formed.

4.4 Reduction of Higher-Valent Plutonium by Reduced Iron in the WIPP: Overall Conclusions and Observations

The overall implication of the WIPP-relevant experiments summarized in Sections 4.1, 4.2 and 4.3 is that reduced iron is very effective, under anoxic conditions, in reducing Pu(VI), and by inference Pu(V), to form lower-solubility Pu(IV) precipitates. In this context, these data support the WIPP PA position that lower oxidation states, specifically Pu(III) and Pu(IV) predominate under the expected conditions in the WIPP.

The following are the key observations and results from these experiments:

1) Plutonium (VI), when no reducing agent was present, was stable under the range of conditions investigated in WIPP brine [Reed 2007]. Under these conditions, little/no precipitation of the plutonium was noted. This persisted for the two-year duration of the experiments performed and was confirmed by absorption spectra of 20 nm filtered solutions where hydroxy-chloro and carbonato species were observed.

2) The addition of zero-valent iron coupons or aqueous Fe^{2+} rapidly destabilized Pu(VI) under most conditions investigated [Reed 2007]. When iron was added, either as zero-valent steel coupons or an Fe^{2+} chloride complex, the plutonium concentrations were reduced by 2-4 orders of magnitude in all but one case. The one exception was at pC_{H+} 5 when Fe^{2+} was added where reduction to Pu(V) was

observed. XANES analysis of selected plutonium precipitates and plutonium sorbed onto the steel surface confirmed this to be a predominantly Pu(IV) phase. This establishes that reduction had taken place and suggests that Pu(IV) species predominate in irradiated anoxic systems when iron is present. No Pu(III) or colloidal species were noted in these experiments. These results were confirmed by more recent experiments performed by LANL-ACRSP where similar results were obtained in ERDA-6 and GWB brine.

3) Iron(II) minerals were also very effective in reducing Pu(VI/V) to form Pu(IV) precipitates [LANL-ACRSP results]. When only Iron(III) phases were present, reduction to Pu(IV) did not occur and ~ 50% of the plutonium was sorbed onto the iron oxide phase.

4) There were some outliers that raise some questions about the ability of reduced iron to reduce higher-valent plutonium under all conditions. Aqeous Fe^{2+} [Reed 2007] in G-Seep brine at $pC_{H+} = 5$ let to the reduction of Pu(VI) to Pu(V). This remains unexplained but does not correspond to a pH that is in the range of what is expected in the WIPP. Some experiments in ERDA6b [Xia 2001] at $pC_{H+} = 8$ and 10 indicate that Pu(V) can remain in the presence of iron powder. These results, however, were not confirmed by the LANL-ACRSP experiments where reduction was noted for both iron coupons and iron powder for ERDA6 brine.

It is not possible to completely reconcile the differences between the results obtained in ERDA6-like brines with iron powder since there are differences between the experimental protocols used. Although this is somewhat speculative, the three most likely causes of the discrepancies noted are a) differences in the redox and chemical environment of the plutonium - specifically the oxygen content of the experiments; b) the condition and chemistry of the iron in the systems investigated; and c) differences in the relative activity of the plutonium since different plutonium isotopes were used. In the presence of zero-valent iron coupons, when oxygen levels were very low and the iron was not oxidized, the reduction of higher-valent plutonium was observed for both Pu-239 and Pu-242 isotopes – so this argues against a radiolytic cause for the differences noted. Given this, it is not completely clear why iron powder, which should be more, not less, reactive than iron coupons, would not lead to the formation of Pu(IV) precipitates in the results reported [Xia 2001].

Although we have noted some discrepancies, it is important to re-emphasize that the evidence for the reduction of higher-valent plutonium to form Pu(IV) precipitates remains very strong under WIPP-relevant conditions. This important result provides experimental confirmation of what is believed to be the key reduction pathway for plutonium in the WIPP and strongly supports the current WIPP PA position that lower-valent oxidation states of plutonium predominate in the WIPP under the expected conditions.

5.0 WIPP ASSESSEMENT AND RECOMMENDATIONS

Since CRA-2004, some literature results are available and three WIPP-related studies were completed/published. There were considered and summarized in this report with the following key objectives:

- An updated literature review for the redox stability and distribution of higher valent plutonium in groundwater.
- A summary of WIPP-relevant data obtained by the LANL-CO ACRSP team and other WIPP project researchers to establish the effects of reduced iron on the redox stability of Pu (V/VI) species in brine.
- An assessment and comparison of the literature and WIPP-relevant results with the WIPP PA position established in the CRA-2004 documentation as it relates to the CRA-2009 recertification.

The overall observations and recommendations based on the results of these three objectives are:

1) There are no surprises in the plutonium subsurface redox chemistry literature that was published since CRA-2004. These continue to show that lower oxidation states, specifically Pu(III) and Pu(IV), are the predominant plutonium species in anoxic groundwater.
    a. Pu(III) and Pu(IV) species are shown to be the prevalent oxidation state for microbiological systems under anaerobic conditions in groundwater systems.
    b. Bioreduction of Pu(V/VI) species is always observed under anaerobic conditions.
    c. There are essentially no data on halo-tolerant microorganisms (WIPP case) but these would be expected to follow the same path.
    d. PuO_{2+x} formation, which is a real phenomenon that leads to the surface oxidation of PuO_2 is not sustained under inundated conditions where DBR release is a consideration in the WIPP.
2) WIPP-relevant experiments show that reduced iron phases and aqueous species are effective in rapidly reducing higher-valent plutonium species (Pu(V) and Pu(VI)). Reduced iron overwhelmed radiolytic effects and led to the formation of Pu(IV) species.
    a. Pu(V/VI) is rapidly reduced in the presence of reduced Fe under anoxic conditions. This led to the formation of Pu(IV) phases.
    b. Apparently conflicting results in the literature could not be reproduced when oxygen was carefully controlled in experiments performed by the ACRSP team. This resolved a potential literature conflict with the current WIPP position.

   c. The reduction of Pu(V/VI) by reduced Fe phases overwhelmed the effects of radiolysis that has been hypothesized to lead to the formation of Pu(V/VI) transients under WIPP-relevant conditions. This strengthens the WIPP position that Pu(V/VI) species cannot prevail under the expected WIPP conditions when reduced iron is present.

3) The overall recommendation to WIPP PA is that the current WIPP position on the oxidation state distribution of plutonium in anoxic brine should remain unchanged. This is supported by the WIPP-relevant experiments that show reduction of Pu(V/VI) to Pu(IV) and reflects the literature results where Pu(III) and Pu(IV) species were observed in microbiologically-active low ionic-strength groundwater experiments. The WIPP PA assumption remains conservative since higher-solubility Pu(III) species are considered in PA although only Pu(IV) species have been observed under WIPP-relevant conditions and there remain questions about the long-term stability of Pu(III) species in the WIPP.

6.0 QUALITY ASSURANCE, DATA TRACEABILITY AND DOCUMENTATION

The data presented in Section 4.3 were generated under the LANL-CO QA Program which is compliant with the CBFO-QAPD. The data summarized in Sections 4.1 and 4.2 were generated under an approved QA program at other laboratories (ANL and PNNL respectively) under the WIPP ASTP program. The research was performed under the Test Plan entitled "Pu(VI) Reduction by Iron: Limited Scope Study" and designated LCO-ACP-04. The documentation for the experiments performed is found in the Test Plan-specific scientific notebook designated LCO-ACP-04/1. Copies of the scientific notebooks were submitted to the LANL-CO Record Center.

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