NOTICE: The current controlled version of this document is on the LCODocs website (http://lcodocs.lanl.gov/). A printed copy of the document may not be the current version.

LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS

Test Plan, LCO-ACP-25, Revision 0

Effects of Radiolysis, Organic Complexation, and Redox Conditions on the Speciation and Oxidation State Distribution of Pu(III/IV)

Effective Date: 4-30-2020

Originator:

Jeremiah Beam, LANL-CO ACRSP — 4/23/2020 Date

Reviewed by:

Juliet Swanson, LANL-CO ACRSP — 4.23.2020 Date

David Schoep, CEMRC/NMSU Radiation Safety Officer — 4/28/2020 Date

Laurie Smith, LANL-CO Quality Assurance Manager — 4/28/2020 Date

Approved by:

Donald Reed, LANL-CO ACRSP Team Leader — 4/24/2020 Date

Laurie Smith, LANL-CO Quality Assurance Manager — 4/28/2020 Date

Lambis Papelis, Interim CEMRC Director — 4/24/2020 Date

Ned Elkins, LANL-CO Program Director/Division Leader — 4.28.20 Date

ACP-2004-01.05-01

History of Revision

Revision Number	Effective Date	Pages Affected	Description of Revision
0	4-30-20	All	Original Release

Table of Contents

Section		Page
1.0	Purpose……..	4
2.0	Scope……	5
3.0	Safety, Quality Assurance, Requirements, References, Acronyms, and Definitions……..	6
4.0	Responsibilities……..	12
5.0	Experimental/Task Description……	12
6.0	Record Requirements……..	20
7.0	Attachments and Appendices……..	20
8.0	Training and Qualifications……..	20

Effects of Radiolysis, Organic Complexation, and Redox Conditions on the Speciation and Oxidation State Distribution of Pu(III/IV)

1.0 Purpose

Due to the expected increase in plutonium inventory in the Waste Isolation Pilot Plant (WIPP), the distribution of plutonium oxidation states and plutonium speciation under WIPP relevant conditions has once again surfaced as a major point of concern.

While plutonium can exist in the 0, II, III, IV, V, VI, and VII oxidation states; the III, IV, V, and VI oxidation states are the most relevant under environmental conditions. More specifically, under the predicted WIPP conditions, Pu(III) and Pu(IV) are expected to dominate due to reduction of Pu(V) and Pu(VI) by the large amount of low-valent iron and redox active organic ligands present in the repository. The current performance assessment (PA) defines the plutonium oxidation state distribution as a 50:50 mixture of Pu(III) and Pu(IV). That is, half of the vectors assume 100% Pu(III) and half of the vectors assume 100% Pu(IV). While this was initially introduced as a conservatism, as Pu(III) is more soluble (by a factor of 3-10) than Pu(IV), we have shown the WIPP to be much more reducing than previously predicted (Reed et al. 2012, Reed 2018). The Environmental Protection Agency (EPA) regulator has also taken the position that extremely reducing conditions are expected in the WIPP (Schramke 2020). These more strongly reducing conditions, overall, are a good result for the WIPP repository concept and safety case. A re-assessment of the actinide redox model, which includes the 50/50 Pu oxidation state assumption, is however needed.

The experimental results obtained in this Test Plan will help provide the experimental basis for the path forward recommended to the Department of Energy (DOE) on oxidation state distribution of plutonium and all multivalent actinides in the WIPP source term redox model. The lower boundary in the E_h range in the actinide redox model has been the redox conditions established when there is available Fe(0). This is at or near the lower water dissociation boundary and defines the multivalent oxidation states as Pu(III), Np(IV) and U(IV). The upper redox boundary has been established by the expected predominance of Fe(II/III) minerals, organics and radiolysis in substantial zones and/or times in the WIPP repository history. This led to the Pu(IV), Np(V) and U(VI) oxidation states for the multivalent actinides. It is the definition of this upper boundary that is currently being challenged by the EPA regulators.

This test plan focuses on several factors that define the upper boundary of the predicted redox conditions in the WIPP. These factors contribute to the overall speciation, oxidation state, and solubility of plutonium in the WIPP environment as stated in PA. Actinide complexation with organic ligands in WIPP can greatly influence the solubility of the actinide, as well as have an effect on the oxidation state distribution. Radiolysis, caused by alpha decay of actinides, can create strong oxidizing and reducing conditions that are complicated by the complex brine and metal chemistry present in the repository setting. Combined, these factors create an overall redox environment that will define the likely distribution of the plutonium oxidation states in the WIPP (see Reed 2018 for a more detailed

discussion). This Test Plan will help evaluate the magnitudes of these effects, something that is still not well understood, and experiments that more closely reflect the expected WIPP environment will be performed (e.g. Pu-239, presence of organics/metals, repository-relevant pH and brines). A defensible determination of the oxidation state distribution of plutonium solubility-controlling phases is a critical input to the plutonium solubility calculations in a direct brine release (DBR) scenario.

2.0 Scope

The Los Alamos National Laboratory-Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP) team will conduct the experiments proposed herein at the Carlsbad Environmental Monitoring Research Center (CEMRC). This test plan consists of two subtasks, the first establishes the baseline solubility of plutonium without any redox control in simulated WIPP brine. This task will be performed with Pu-239 and Pu-242 isotopes which will allow an understanding of the upper limits of the effect of radiolysis on the system. The second subtask incorporates the combined effects of radiolysis, initial oxidation state of Pu, the presence of reducing metals, and organic complexation which will simulate the upper E_h boundary present in WIPP.

The experimental scope includes but may not be limited to the following:

- Near repository temperature, defined as 23 ± 5 °C
- WIPP pC_{H+}-specific brines (bracketed by Generic Weep Brine [GWB] and US Energy Research and Development Administration [ERDA-6])
- Simplified brines: $MgCl_2$ and NaCl
- Carbonate-free solution
- pC_{H+} between 8 and 10
- Reduced iron phases: Fe(0), Fe(II) in the form of $Fe(OH)_2$, and Fe(II/III) in the form of Fe_3O_4
- Plutonium isotopes: Pu-239 and Pu-242
- Pu starting materials in +3 and +4 oxidation states
- Ethylenediaminetetraacetic acid (EDTA), oxalate, and citrate in WIPP relevant concentrations
- Aqueous phase analysis of key dissolved species by inductively coupled plasma mass spectrometry (ICP-MS), ion chromatography (IC), ultraviolet- visible (UV-vis) spectroscopy, and synchrotron-based methods
- pH and E_h
- Solids analysis by x-ray diffraction (XRD), scanning electron microscopy (SEM), and synchrotron-based methods

3.0 Safety, Quality Assurance, Requirements, References, Acronyms, and Definitions

3.1 Safety

The proposed research will be done under the CEMRC safety rules and guidelines according to the current interface agreement between LANL and CEMRC (LCO-ACP-01). The majority of the experimental work proposed in this Test Plan is expected to be done in the actinide chemistry laboratory 151. The plutonium experiments proposed that are conducted at CEMRC will be done within the current CEMRC license agreement. LANL project participants, using LANL-CEMRC facilities identified in the relevant safety reviews and statements, will do all the plutonium preparations and experiments described herein. In addition to laboratory issues related to the management and use of radioactive materials, this Test Plan encompasses the usage of the SEM and XRD equipment currently located in laboratory 152 that will be governed by the safety statements applicable to both instruments.

Low-level radioactive waste generated by the experiments proposed in this Test Plan will be provided to CEMRC for disposal in accordance with the procedures outlined in the LANL-CEMRC interface agreement.

3.2 Quality Assurance

All project participants assigned to work on this Test Plan are responsible for performing work in compliance with the LANL-CO Quality Assurance Program. The ACRSP Team Leader is responsible to ensure that the technical goals identified in this Test Plan are achieved. The LANL-CO Program Director/Division Leader and ACRSP Team Leader have the overall responsibility for implementation of this Test Plan and compliance with all Quality Assurance Program requirements.

3.3 Requirements

The data requirements and objectives for the experiments described in this Test Plan are that the data are collected, maintained, and analyzed to quality level 1 standards (per LCO-QP2-1 and related implementing procedures). Additionally, the following data requirements will be met:

- The data generated must be compatible with the existing WIPP conceptual design as outlined in the 2004 CRA documentation [U.S. DOE, 2004]. Specifically, we are addressing the issue of oxidation state distribution of Pu in the WIPP, which is a key component of WIPP PA.

- The acceptance criteria for the quality of the data generated, which will consist primarily of the concentration of plutonium as a function of time, are that the concentrations are known to ± 100% of their actual values. The effects being investigated will lead to three to four orders of magnitude differences in Pu concentration and the WIPP Pu solubilities are typically “order of magnitude” for the PA calculations. The expected uncertainty (both precision and accuracy) in the measurements, specifically ICP-MS analysis, is less

than ± 20% which is well within the acceptance criteria needed.

- The representativeness of these data is already established since the primary objective of the proposed experiments is to reproduce work already done under the expected WIPP conditions. These data will be directly comparable to those reported previously. Although they will be complete as to the stated objective of reproducing data, these data will define longer-term and more extensive mechanistic work planned for FY-20 and beyond.

- The following sources of error and uncertainty are identified:

    - Analysis of Pu in WIPP brine, less than 20% for all anticipated Pu concentrations by ICP-MS. Ion chromatography analysis of brine components has an uncertainty of ~10%. Oxidation state uncertainty by XANES is ~10-15%.

    - Redox control and removal of oxygen may be incomplete potentially leading to improper interpretation of the data. The overall uncertainty here is quite low, and therefore negligible, since an anoxic glovebox will be used and the reactivity of the iron in these systems will function to complete the oxygen removal process leading to truly anoxic conditions.

    - Chemical impurities may affect the results. The overall error and uncertainty for this is very low, and therefore negligible, since very high-purity reagents are being used and supporting analyses are being done to confirm the absence of impurities in our system (at least to the level comparable to the initial Pu concentrations).

- There are no data or inputs for the experiments proposed that are beyond the control of the ACRSP.

- Data reduction, manipulation, and assessment (including applicable developmental results) will be done according to ACP-IMP-006.

3.3 References

3.3.1 LANL-CO References

LANL-CO Documents

LCO-QP2-1: Quality Levels and Quality Assurance Requirements
LCO-QPD-04: LANL-CO Document and Records Management Plan
LCO-QP17-1: Record Management

LCO-QP2-3: Qualification and Training
LCO-QP6-1: Controlled Document Development, Change, and Revision
LCO-MP7-1: Procurement
LCO-ACP-01: LANL-CO/CEMRC Interface Document

LANL Reports

LCO-ACP-09: Reduction of Higher-Valent Plutonium by Iron Under Waste Isolation Pilot Plant (WIPP)-Relevant Conditions: Data Summary and Recommendations

LCO-ACP-11: WIPP Actinide-Relevant Brine Chemistry

ACRSP Test Plans

LCO-ACP-04: Plutonium (VI) Reduction by Iron: Limited-Scope Confirmatory Study
LCO-ACP-05: Plutonium Speciation and Solubility in the WIPP

ACRSP-Specific Documents and Procedures

ACP-IMP-002: ACRSP Duplicate File and Working Documents
ACP-IMP-003: Test Plan and Task Implementation Plans
ACP-IMP-004: Measuring and Test Equipment
ACP-IMP-005: Scientific Notebooks
ACP-IMP-006: Data Packages
ACP-IMP-009: Sample Tracking
ACP-EXP-001: Brine Preparation
ACP-EXP-002: pH Electrode/Meter Calibration
ACP-EXP-003: Balance Performance Check
ACP-EXP-004: Pipet Performance Checks
ACP-EXP-005: Thermometer Calibration and Performance Check
ACP-EXP-006: UV-Vis-NIR Spectrophotometer Calibration and Performance Check
ACP-EXP-010: Determination of Hydrogen Ion Concentration in Brine
ACP-EXP-011: Inductively Couple Plasma-Mass Spectrometry
ACP-EXP-012: Analysis of Solids Using the Bruker D8 Advance X-ray Diffractometer

*ACP-EXP-013: Synthesis of Oxidation State Pure Actinide Standards
*ACP-EXP-015: Scanning Electron Microscopy Analysis of Solid Phases
*ACP-EXP-017: X-ray Absorption Spectroscopy of ACRSP Samples
*ACP-EXP-016: Gas Chromatography Analysis of ACRSP Samples

*Procedures to be developed

3.3.2 Literature References

Boukhalfa, H.; Reilly, S.D.; Smith, W.H.; Neu, M.P.; EDTA and Mixed-Ligand Complexes of Tetravalent and Trivalent Plutonium." *Inorg. Chem.* **2004** (43), 5816-5823.

Büppelmann, K.; Magirius, S.; Lierse, Ch.; Kim, J.I.; Radiolytic Oxidation of Americium(III) to Americium(V) and Plutonium(IV) to Plutonium(VI) in Saline Solution. *J. Less Common Metals.* **1986**, 122, 329-336.

Büppelmann, K.; Kim, J.I.; Lierse, Ch.; The Redox Behaviour of Plutonium in Saline Solutions under Radiolysis Effects. *Radiochim. Acta.* **1988** (44/45), 65-70.

Cygan, R.T.; The Solubility of Gases in NaCl Brine and a Critical Evalution of Available Data. Sandia National Laboratories Report. 1991.

Day, B.; Reassessment of Need and Parameter Justification for Modeling Gas Generation due to Radiolysis of Brine and Cellulose/Plastic/Rubber in WIPP for CRA-2019. ERMS 570873.

Domski, P.; Sisk-Scott, C.; Prediction of Baseline Actinide Solubilities for CRA-2019 with an Updated EQ3/6 Pitzer Thermodynamic Database, DATA0.FN4. Sandia National Laboratories Report. ERMS 571178.

Felmy, A.R.; Rai, D.; Scramke, J.A.; Ryan, J.L.; The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines. *Radiochim. Acta.* **1989** (48), 29-35.

Kelm, M.; Pashalidis, I.; Kim, J.I.; Spectroscopic investigation on the formation of hypochlorite by alpha radiolysis in concentrated NaCl solutions. *Appl. Rad. And Isotopes.* **1999** (51), 637-642.

Moore, N.; Yalcintas, Y.; Reed, D.T.; Hixon, A.; Effect of Redox Transformations and Aqueous Complexation in the Ternary Pu(III)-EDTA-Fe Mineral System. *In preparation.*

Nitsche, H.; Roberts, K.; Xi, R.; Prussin, T.; Becraft, K.; Al Mahamid, I.; Silber, H.B.; Carpenter, S.A.; Gatti, R.C.; Long Term Plutonium Solubility and Speciation Studies in a Synthetic Brine. *Radiochim. Acta.* **1994** (66/67), 3-8.

Noronha, D.M.; Pius, I.C.; Chaudhury, S.; Co-precipitation of Plutonium(IV) and Americium(III) from Nitric Acid-Oxalic Acid Solutions with Bismuth Oxalate. *Journal of Radioanalytical and Nuclear Chemistry*. **2017** (313), 523-529.

Reed, D.T.; Okajima, S.; Brush, L.H.; Molecke, M.A.; Radiolytically Induced Gas Production in Plutonium-Spiked WIPP Brine. *Materials Research Society Symposium Proceedings*. **1993** (294), 431-438.

Reed, D.T.; Aase, S.B.; Wygmans, D.; Banaszak, J.E.; The Reduction of Np(VI) and Pu(VI) by Organic Chelating Agents." *Radiochim. Acta*, **1998** (82), 109-114.

Reed, D.T.; Borkowski, M.; Swanson, J.; Richmann, M.; Khaing, H.; Lucchini, J.-F.; Ams. D.; Redox-Controlling Processes for Multivalent Metals and Actinides in the WIPP. 3rd Annual Workshop Proceedings of the Collaborative Project Redox Phenomena Controlling Systems. **2012**. 251-263.

Reed, D.T.; Plutonium Oxidation State Distribution in the WIPP: Conceptual Model, Project-Specific Data, and Current/Ongoing Issues. LA-UR-18-25748. **2018**. Los Alamos National Laboratory; Carlsbad, NM.

Schikorr, G.; Uber die Reaktionen zwischen Eisen, Seien Hydroxyden und Wasser. *Z. Elektrochemie.* **1929** (35), 65-70.

Schramke, J.A.; Santillan, E.F.U.; Peake, R.T.; Plutonium Oxidation States in the Waste Isolation Plant Repository. *Appl. Geochem.* **2020** (116), 104561.

Tasi, A.; Gaona, X.; Fellhauer, D.; Böttle, M.; Rothe, J.; Dardenne, K.; Schild, D.; Grivè, M.; Colàs, E.; Bruno, J.; Källström, K.; Altmaier, M.; Geckeis, H.; Redox Behavior and Solubility of Plutonium Under Alkaline, Reducing Conditions. *Radiochim. Acta.* **2018**, 106 (4), 259-279.

U.S. Department of Energy. *Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant* (March). **2004.** 10 vols. DOE/WIPP 2004-3231. Carlsbad, NM: Carlsbad Field Office.

Van Soest, G.; Performance Assessment Inventory Report – 2018 (PAIR 2018. INV-PA-18. Los Alamos National Laboratory; Carlsbad, NM.

Yalcintas, E.; Beam, J.C.; Reed, D.T.; Solubility of Pu(III) in High Ionic Strength Brines at Elevated pH. *in preparation*.

3.4 Acronyms and Definitions

ACRSP:	Actinide Chemistry and Repository Science Program
An:	Generic Actinide
Br^-:	Bromide anion
CEMRC:	Carlsbad Environmental Monitoring Research Center
Cl^-:	Chloride anion
CO_2:	Carbon dioxide
CRA:	Compliance Recertification Application
DBR:	Direct Brine Release
DOE:	(U.S.) Department of Energy
EDTA:	Ethylenediaminetetraacetic Acid
EPA:	(U.S.) Environmental Protection Agency
ERDA-6:	(U.S.) Energy Research and Development Administration (WIPP well) 6, a synthetic brine representative of fluids in the Castile brine reservoirs
EXAFS:	Extended x-ray absorption fine structure
Fe:	Iron with an unspecified oxidation state
Fe^0:	Metallic iron, also referred to as zero valent iron

Fe^{2+}:	Ferrous cation, iron in the +2 oxidation state, also written Fe(II)
Fe^{3+}:	Ferric cation, iron in the +3 oxidation state, also written Fe(III)
GC:	Gas Chromatography
GWB:	Generic Weep Brine, a synthetic brine representative of intergranular Salado-Formation brines
G_y:	Molecular yield of species y, molecules per 100 eV
H_2:	Hydrogen
H_2O:	Water
IC:	Ion Chromatography
ICP-MS:	Inductively Coupled Plasma, Mass Spectrometry
LANL-CO:	Los Alamos National Laboratory, Carlsbad Operations
M:	molarity, moles of solute per liter of solvent
M&TE:	Measuring and Test Equipment
Na^+:	Sodium cation
^-OBr:	Hypobromite anion
^-OCl:	Hypochlorite anion
OH:	Hydroxyl free radical
PA:	Performance Assessment
Pu:	Plutonium with an unspecified oxidation state
Pu^{3+}:	Plutonium in the +3 oxidation state, also written Pu(III)
Pu^{4+}:	Plutonium in the +4 oxidation state, also written Pu(IV)
PuO_2:	Plutonium (IV) oxide
PuO_2^+:	Aqueous form of the plutonium ion in the V oxidation state, plutonyl
PuO_2^{2+}:	Aqueous form of the plutonium ion in the VI oxidation state, plutonyl
$Pu(OH)_3$:	Plutonium (III) hydroxide
QA:	Quality Assurance
QL1:	Quality Level 1
SEM:	Scanning Electron Microscopy
SNL:	Sandia National Laboratories
SOTERM:	Actinide source term appendix to support WIPP PA
TRU:	Transuranic
UV-Vis:	Ultraviolet-visible spectroscopy
XAFS:	X-ray absorption fine structure
XANES:	X-ray absorption near-edge spectroscopy
XAS:	X-ray absorption spectroscopy
XRD:	X-ray diffraction
WIPP:	Waste Isolation Pilot Plant

4.0 Responsibilities

Not Applicable

5.0 Experiment/Task Description

5.1 Justification and Statement of Task Objectives

The solubility of Pu in brines has been studied by a number of groups. Initial studies by Büppelmann et al. in 1986 observed oxidation of Pu(IV) to Pu(VI) in 1-5M NaCl at pH 2-11 over a period of 56 days. This work was performed with high concentrations of Pu-238, which has a half-life of 87.7 years. The effects of radiolysis are therefore much greater than expected under normal WIPP conditions, as the Pu inventory is primarily Pu-239, which has a half-life of 24,110 years. This work was followed by Felmy et al. 1989, which looked at the solubility of Pu-239 in high ionic strength chloride brines. Iron was added to these experiments to maintain reducing conditions. Although similar to the work proposed in this test plan, the equilibration times were only extended to 24 days. This short period of time is not sufficient to capture the effects of radiolysis on the chemistry of this system. A longer study of Pu-239 solubility in H-17 brine was conducted, with an equilibrium period of > 650 days (Nitsche et al. 1994). However, these experiments were done in a strictly oxic environment, which has limited applicability to the WIPP system. Lastly, a study of Pu-242 solubility was performed with an equilibration period of 30 days (Tasi et al. 2018). These experiments were conducted over a wide pH range, and well defined redox conditions. As the Pu-242 was used as the starting material, radiolysis is a lower impact variable in this system. Overall, while a large number of studies have been performed to determine the solubility of Pu in high-ionic strength brines, none have been performed in realistic WIPP conditions.

The complexity of the composition of the WIPP system dictates that there are many interactions at work that have an underlying effect on the overall chemistry of the system. Redox active chelating organic ligands, such as citrate, oxalate, and ethylenediaminetetraacetic acid (EDTA), are important due to their ability to oxidize and reduce actinides under WIPP relevant conditions. When Pu(VI) is complexed with EDTA, there is a rapid reduction to Pu(V), which then follows with a slower reduction to Pu(IV) (Reed et. al. 1998). When EDTA is complexed to Pu(III), oxidation occurs to form Pu(IV):EDTA complexes (Boukhalfa et. al. 2004, Moore et al. 2020). EDTA has also been shown to increase the solubility of Nd(III) by two orders of magnitude, while oxalate complexation resulted in lower solubility. Oxalate has also been shown to form stable, crystalline complexes with both Pu(III) and Pu(IV), however these experiments were performed under acidic conditions that are not relevant to the WIPP (Noronha et al. 2017). These Pu:organic complexes have mostly been studied using Pu-242, which should have a negligible effect from radiolysis.

Radiolysis is the process in which ionizing radiation causes the dissociation of a molecule. In aqueous systems water molecules dissociate to generate a hydroxide and hydrogen radical. These radicals can undergo a series of reactions that can produce hydronium cations, hydroxide anions, hydrogen peroxide, hydrogen gas, oxygen gas, and water. In brine systems, this chemistry can become more complicated due to the presence of free radical scavengers in the brine. These radicals can compete in a number of reactions that influences the final solution chemistry (Figure 1). Of the possible

radiolysis products, hypochlorite ($^{-}$OCl), and in systems that contain bromide, hypobromite ($^{-}$OBr) anions are thought to have the greatest radiolytic effects on the chemistry. The presence of these species leads toward more oxidizing conditions. The concentrations of these oxidizing species have been estimated to approach a steady state of 0.005 M in 5M NaCl in solutions containing 37 GBq/L Pu-238 (Kelm, et al. 1999).

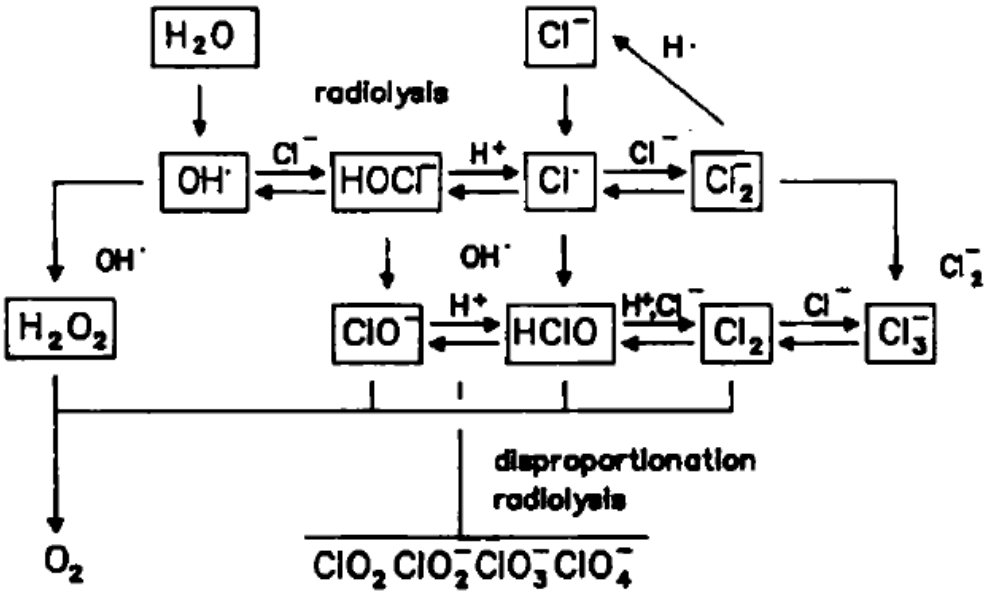


Figure 1. NaCl Brine Radiolysis Species and Suggested Mechanism of Production. Taken from Büppelmann et al. 1988.

These radiolysis effects have recently been screened in to the WIPP Compliance Recertification Application (CRA) 2019 as radiolytic gas generation has the potential to contribute to increases in repository pressure, as well as impacting the brine chemistry (Day 2019). As mentioned previously, brine radiolysis by alpha particles produces both oxidizing and reducing species. These reducing species, mainly hydrogen gas, are not thought to impact the brine chemistry as hydrogen is sparingly soluble in 5M NaCl brine (Cygan 1991). The oxidizing species, however, can be involved with several processes that can have marked impacts on the WIPP brine chemistry. The production rates of these species through radiolysis are given by G values which are defined as molecules per 100 eV. G-values of hydrogen gas from the radiolysis of WIPP brines irradiated with Pu-239 were determined to be 1.4 (Reed 1993). Another study, performed in NaCl brines with Pu-238 irradiation, determined G-values for 11 species (Kelm 1999). These data are shown in Table 1.

Table 1. G-values of several species produced from alpha radiolysis of NaCl. Data taken from Kelm et al. 1999.

$[Cl^-]$	G-value										
(mol/L)	H_2O	H_2	$H^\cdot$	$e^-_{(aq)}$	H_2O_2	$HO^\cdot_2$	$OH^\cdot$	OH^-	$ClOH^\cdot$	Cl_3^-	Cl^-
5	-3.25	1.52	0.26	0.06	0.23	0.05	0.06	2.08	0.55	1.07	-3.76
4	-3.15	1.48	0.24	0.06	0.27	0.06	0.07	1.92	0.50	0.99	-3.47
3	-3.02	1.43	0.23	0.06	0.32	0.07	0.08	1.72	0.44	0.89	-3.11
2	-2.92	1.39	0.23	0.06	0.40	0.09	0.10	1.46	0.38	0.76	-2.66

The production of oxidizing species is far greater than the production of reducing species, which causes radiolysis to have a net oxidizing effect on the solution chemistry. The sum of the oxidizing species' G-values is 4.04, this number will be used to calculate the amount of oxidizing species produced over the course of the repository lifetime. The amount of these species produced can be estimated by determining the average decay rate of the actinides present in WIPP and the linear energy transfer (LET) efficiency. Day determined that a maximum of 50% of the decay energy of wetted solid radionuclides would be deposited into the brine, the remaining 50% will be contained within the solids through self-absorption effects (Day 2019). Pu-239 represents the second largest component of radioactive WIPP waste by mass and becomes the dominant source of activity 350 years after repository closure, so using the decay of Pu-239 represents a large portion of radiolysis in WIPP. All data below are calculated from SOTERM-2019.

$$Total\ mass\ of\ actinide\ waste = 1.54x10^{8}\ g$$
$$Total\ activity\ of\ actinide\ waste = 5.21x10^{6}\ Ci$$
$$Specific\ Activity = 3.38x10^{-2}\ {}^{Ci}/_{g}$$
$$Average\ Mass\ of\ Inventory = 238.01amu$$
$$Half-life\ of\ Inventory = 41866\ yr$$
$$\alpha\ decay\ energy\ of\ Pu-239 = 5.156x10^{6}\ eV$$

How much activity is lost after 10000 yr?

$$\frac{N}{N_0} = 1 - e^{\frac{-tln2}{t_{1/2}}} = 0.153$$

$$\frac{(1.54x10^{8}g)}{238.01\ amu} = 6.47x10^{5}\ mol\ x\ 6.022x10^{23}\ molecules * 0.153 = 5.96x10^{28}\ decay\ events$$

$$5.96x10^{28}\ x\ 5.156x10^{6}\ eV = 3.07x10^{35}\ eV$$
$$3.07x10^{33}\ (100\ eV)\ /_{2} = 1.535x10^{33} deposition\ energy$$
$$1.535x10^{33}\ x\ 4 = 6.14x10^{33} oxidizing\ equivalents$$

These oxidizing equivalents are assumed to react with the base metals present in WIPP and oxidize them. The inventory of these metals are shown in Table 2. The number of oxidizing equivalents exceeds the molecular inventory of the base metals by a factor of 8. This indicates that under the highest predicted energy deposition rates, radiolysis products will persist with no zero-valent metals left to consume them. This could lead to some oxidation of the multivalent actinides.

Table 2. Metal inventory in the WIPP, from PAIR-2018 (Van Soest).

Element	Inventory (kg)	Inventory (mol)	Inventory (molecules)
Aluminum	$5.56x10^{5}$	$2.06x10^{7}$	$1.24x10^{31}$
Iron	$6.31x10^{7}$	$1.14x10^{9}$	$6.85x10^{32}$
Lead	$1.38x10^{7}$	$6.66x10^{7}$	$4.01x10^{31}$
Total Metal	**$1.27x10^{7}$**	**$3.63x10^{8}$**	**$7.38x10^{32}$**

In addition to consuming radiolysis products, the iron metal also undergoes several competing reactions that complicate this mechanism. Shortly after repository closure, the residual oxygen will be consumed by the zero valent metals present in the repository. After the oxygen is consumed, anoxic corrosion of steel in alkaline solutions will proceed according to the following reactions:

$$Fe\ \rightarrow\ Fe^{2+} + 2e^{-}$$
$$\underline{2\ H_2O + 2e^{-} \rightarrow H_2 + 2\ OH^{-}}$$
$$Fe + 2\ H_2O\ \rightarrow Fe(OH)_2 + H_2$$

This iron(II) hydroxide can undergo further oxidation under anoxic conditions to form magnetite by the Schikorr reaction (Schikorr 1929):

$$3\ Fe(OH)_2 \rightarrow Fe_3O_4 +\ H_2 + 2\ H_2O$$

In addition to these reactions, the Fe(II) containing minerals have also been shown to reduce higher valent Pu to Pu(IV) and Pu(III) (Reed 2018). The rates of these reactions will have a profound effect on the iron mineralogy present in the WIPP and this, along with residual radiolytic processes, may

lead to a shift in E_h to a more oxidizing redox environment than one would predict by only considering zero-valent iron. Availability of zero valent metal to reduce the actinides present, as well as keep the concentrations of the radiolysis products low to limit their ability to oxidize the actinides is an important engineering control in the WIPP system.

The most important factors that influence the Pu oxidation state distribution in the WIPP system are as follows:

- Stability of Pu:organic complexes
- Oxidation and reduction of Pu by organics and metals
- Brine radiolysis
- Reactions occurring between radiolysis products and metals/organics/Pu

The central question surrounding the work described in this test plan is how repository conditions (organics, oxidants, and radiolysis) impact the Pu oxidation state distribution in the WIPP and in particular the higher range of the predicted range in E_h. The Pu isotopes with the highest activity in WIPP are Pu-238, Pu-239, Pu-240, and Pu-241. While Pu-238 and Pu-241 have half-lives of under 100 years (87.7 and 14 y, respectively), Pu-239 and Pu-240 have half-lives of 24,100 and 6561 years, respectively, meaning they will become the most predominate isotopes 1000 years after the closing of the repository. Pu-239 is particularly of interest as it represents the average of the actinide inventory in the repository, thus any radiolysis effects observed in Pu-239 experiments should be representative of the conditions in the repository.

5.2 Experimental Subtasks

5.2.1 Subtask 1: Baseline solubility of Pu in WIPP-relevant brines

The technical approach in this subtask is to first establish the baseline solubility of Pu(III)/Pu(IV) in WIPP brines. Previous preliminary work has shown that Pu^{242}(III) will slowly oxidize to Pu(IV) at high pH without the presence of reducing control (Yalcintas 2020). The rate of oxidation increases with an increase in pH. Confirmatory studies of this system will be undertaken as part of this test plan, but a full reproduction of these experiments will not be performed. Pu(IV) baseline solubility will be determined through initial experiments with Pu-242 at WIPP relevant pH in WIPP brines.

Repeating these experiments using Pu-239 will establish the upper extent of Pu oxidation due to radiolysis. A matrix outlining the experimental conditions of these samples is presented in Table 3. The proposed time frame for these initial experiments is one year to reach equilibrium. This time frame can be extended if equilibrium has not been reached.

Table 3. Matrix of experiments to establish baseline Pu solubility from undersaturation in WIPP brines			
Sample ID	**Pu isotope**	**Initial Pu oxidation state of solid phase**	**pH**
Pu242_4_pH8_1,2	242	+4	8
Pu242_4_pH9_1,2	242	+4	9
Pu242_4_pH10_1,2	242	+4	10
Pu239_3_pH8_1,2	239	+3	8
Pu239_4_pH8_1,2	239	+4	8
Pu239_3_pH9_1,2	239	+3	9
Pu239_4_pH9_1,2	239	+4	9
Pu239_3_pH10_1,2	239	+3	10
Pu239_4_pH10_1,2	239	+4	10

5.2.2 - Subtask 2 – Plutonium speciation in the upper E_h boundary in the WIPP

After successful completion of subtask 1, experiments in subtask 2 will begin which will determine the Pu solubility at the upper E_h boundary expected in the WIPP. This will include the effects of radiolysis (Pu-239), oxidized iron phases ($Fe(OH)_2$ and Fe_3O_4), and the presence of organic complexants (acetate, oxalate, citrate, and EDTA). The organic complexants will be present in concentrations expected for a 1X dilution DBR scenario as described in Domski and Sisk-Scott 2019 (acetate, 2.83×10^{-2} M; oxalate, 1.13×10^{-2} M; citrate, 2.30×10^{-3} M; EDTA, 7.92×10^{-5} M). A matrix outlining these experiments is presented in Table 4. These experiments will commence upon finishing subtask 1 to limit the Pu inventory at any one time to remain compliant with CEMRC inventory limits.

Table 4. Matrix of experiments to establish Pu solubility from undersaturation under WIPP relevant conditions

Sample ID	Pu isotope	Initial Pu oxidation state of solid phases	Organics Present	Iron phase
Pu239_3_pH8_Org_Fe(II)1,2	239	+3	Yes	$Fe(OH)_2$
Pu239_3_pH9_Org_ Fe(II)1,2	239	+3	Yes	$Fe(OH)_2$
Pu239_3_pH10_Org_Fe(II)1,2	239	+3	Yes	$Fe(OH)_2$
Pu239_3_pH8_Fe(II)1,2	239	+3	No	$Fe(OH)_2$
Pu239_3_pH9_Fe(II)1,2	239	+3	No	$Fe(OH)_2$
Pu239_3_pH10_Fe(II)1,2	239	+3	No	$Fe(OH)_2$
Pu239_3_pH8_Org_Fe(II/III)1,2	239	+3	Yes	Fe_3O_4
Pu239_3_pH9_Org_Fe(II/III)1,2	239	+3	Yes	Fe_3O_4
Pu239_3_pH10_Org_Fe(II/III)1,2	239	+3	Yes	Fe_3O_4
Pu239_3_pH8_Fe(II/III)1,2	239	+3	No	Fe_3O_4
Pu239_3_pH9_Fe(II/III)1,2	239	+3	No	Fe_3O_4
Pu239_3_pH10_Fe(II/III)1,2	239	+3	No	Fe_3O_4

The precise experimental protocol used will be defined in the scientific notebook prior to the initiation of the test matrices. Generally, the proposed experimental details and planned characterization for these experiments are as follows:

- WIPP brines will be generated according to procedure ACP-EXP-001: Brine Preparation. These brines will be 90% strength to ensure salt precipitation is eliminated. These brines will be degassed with nitrogen before use. pH adjustments will be made with concentrated NaOH and HCl solutions, pH measurements will be made with a Ross combination pH electrode. 20 mL of brine will be used for each experiment.

- Pu starting materials will be generated according to the procedure ACP-EXP-013: Synthesis of Oxidation State Pure Actinide Standards which is currently under development. Pu^{3+} will be generated by dissolving PuO_2 stock material in concentrated HCl and HBr and taking to dryness. The solid is then dissolved in high purity water (HPW), to generate a Pu^{3+} solution. $Pu(OH)_3$ is precipitated by the addition of this aqueous Pu^{3+} to sodium hydroxide at pH > 12. A portion of this solid will be dissolved to confirm the Pu oxidation state by UV-vis spectroscopy. Low-fired PuO_2 is produced by first precipitating the Pu(IV) peroxide solid and heating slowly to ~ 400 °C. This low-fired PuO_2 stoichiometry will be confirmed by powder XRD. Approximately 3 mg of Pu will be used in each experiment.

- Pu solids will be added to the brines in a nitrogen glovebox. Initial pH measurements will be performed immediately after the addition of Pu. The solutions will be kept in this glovebox for the duration of the experiments to ensure an anoxic environment.

- The pH of the solutions will be checked periodically (monthly to every three months) to monitor any changes. The E_h will be measured once at the onset of the experiment and once at the end of the experiment.

- ICP-MS analysis will be performed periodically (monthly to every three months) to monitor the Pu concentration and to determine if there are any changes in the brine composition.

- IC analysis of the brine speciation will be performed quarterly to estimate the overall effects of radiolysis and confirm the concentrations of the major and minor brine components.

- Solids will be extracted from the experiments for XRD and XAS characterization as deemed necessary. It is possible that additional replicates are run to ensure the solids can be extracted from the solutions without compromising the integrity of the scientific investigation.

- Once the Pu concentration in brine has reached equilibrium, the experiments will be taken down. ICP-MS, IC, pH, and E_h measurements will be performed on the solutions. The solids will be removed and characterized by XRD, XAS, and SEM.

5.3 Expected Results and Deliverables

These experiments are expected to provide data on the overall redox conditions in WIPP with respect to brine radiolysis. The 15 times shorter half-life of Pu-239 than Pu-242 will result in a much more profound radiolysis effect on the brine speciation and subsequent reactions. The experiments with iron should keep the oxidation state of the Pu as Pu(III)/(IV), however the oxidizing effect of Pu-239 radiolysis has not been comprehensively studied in the presence of other reducing conditions. The experiments without iron should determine if radiolysis is a sufficient oxidation source to produce Pu(V) or Pu(VI). Finally, the experiments containing EDTA should determine how Pu(III) and Pu(IV) can be

generated through their interactions with EDTA and subsequent degradation of EDTA through radiolysis. These results will be crucial to establish the true oxidation state distribution of Pu in the WIPP and will be included in CRA-2024. A peer-reviewed publication on the radiolysis effects between the Pu-239 and Pu-242 systems will be published.

5.4 Procedure Development

Many of the procedures needed to implement this Test Plan are already developed and issued (see list in section 4). However, procedures related to the preparation of oxidation state specific actinide starting materials, x-ray absorption spectroscopy analysis, and gas chromatography will be generated in the course of carrying out this test plan.

6.0 Record Requirements

6.1 Record Generation and Maintenance

The following QA records are generated as a result of implementing this Test Plan. They will be prepared and submitted to the LANL-CO Record Center in accordance with LANL-CO quality procedure LCO-QP17-1, Record Management.

Record	Originator	Record Submitter
Entries into task-specific scientific notebooks	Originator	ACRSP project leader or designate
Reports, publications, summaries of the data	Originator	ACRSP project leader or designate
Data Packages	Originator	ACRSP project leader or designate

All documents generated by this Test Plan will be converted to lifetime records that will be retained for the lifetime of the project.

7.0 Attachments and Appendices

Not Applicable

8.0 Training and Qualifications

LANL-CO project participants will perform the work proposed in this Test Plan at the CEMRC facility and will be trained according to the training requirements established in LCO-QP-2-3. Read and sign training on this Test Plan will be documented according to LCO-QP2-3.