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CARLSBAD OPERATIONS

Test Plan, LCO-ACP-35, Revision 0

Radiolytic Degradation of Organics – Focus on EDTA and Citrate

Effective Date: _____

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Radiolytic Degradation of Organics – Focus on EDTA and Citrate

1.0 Purpose and Scope

Four organic chelating agents have been reported in the Waste Isolation Pilot Plant (WIPP) inventory (e.g., Van Soest 2022) for years. These are ethylenediaminetetraacetic acid (EDTA), oxalate, citrate and acetate. Experimental work from the Los Alamos National Laboratory-Carlsbad Operations (LANL-CO) Actinide Chemistry and Repository Science Program (ACRSP) team and others [Choppin et al. 1999; Borkowski et al. 2009; Kutahyali Aslani 2022 (using a neodymium surrogate); Beam 2023] have shown that the solubilities of actinides in brine solutions increase in the presence of organic molecules. Particularly, the +III and +IV actinides, which are the two most important oxidation states in the WIPP, are strongly affected by organic complexation.

In the WIPP Performance Assessment (PA) model, these four organic complexing molecules have been assumed to subsist for the regulatory lifetime of the WIPP repository (10,000 years). However, two mechanisms have the potential to degrade organics within this timeframe, in a closed environment like at the WIPP: microbial degradation, and radiolysis. In particular, the decomposition of organic molecules due to ionizing radiation has been demonstrated in different complex systems: for the nuclear fuel recycling industry to evaluate the robustness of solvent extraction ligands such as tributyl phosphate or 1,4,7,10-tetraazacyclodecanetetraacetic acid (DOTA) [Mincher et al. 2009; Fiegel et al. 2019], for the water treatment industry to destroy organic pollutants [Wojnarovits and Takacs 2016], and at Pacific Northwest National Laboratory (PNNL) in waste aging studies of Hanford organic waste tanks [Camaioni et al. 1998; Toste 1998; Toste et al. 2005]. For example, Toste demonstrated that, under an extremely high radiation dose, gamma (γ) radiolysis causes degradation of EDTA on an exponential timeframe [Toste 1998].

The experimental study proposed in this Test Plan aims to test the PA assumption that organic complexants will subsist for 10,000 years at the WIPP, despite the significant amounts of actinides (particularly plutonium) being disposed. Of the four organic chelating agents considered in the WIPP, citrate and EDTA, and to a lesser extent oxalate, are expected to form strong enough complexes to influence the speciation of actinides and potentially increase actinide concentrations under the expected conditions in the WIPP [U.S. DOE 2019; Appendix SOTERM-2019]. Accordingly, the work planned in this document will focus on EDTA and citrate.

The goal of the work presented in this Test Plan is to experimentally investigate the degradation of EDTA and citrate, in a WIPP-like environment, in a radiation field of alpha (α) particles, which are the most important (and by far the most damaging) radiation emitted by the actinides in the WIPP. The radiation emitted by the different plutonium isotopes accessible to ACRSP would likely not be sufficient to distinguish the radiolytic effects on the organic ligands in an actinide chemistry laboratory setting and

timeframe[1]. Therefore, it is proposed to use a helium ion (He^{2+}) beam accelerator to provide in solutions containing the organics, an α particle dose several orders of magnitude greater. This innovative experimental approach will allow to generate, in a few hours, the equivalent dose that would accumulate in a few years in a WIPP-like scenario. A similar approach was used in Toste's studies to demonstrate EDTA degradation: aliquots of EDTA solutions were γ-irradiated for 10 hours of irradiation, with a total dose of $7.5 \times 10^5 \pm 10\%$ R [Toste 1998]. The results of the experiments proposed in this test Plan could establish that EDTA and citrate would not subsist in an α radiation field over time, so that they will not be present in the WIPP environment beyond the 10,000-year regulatory period. Therefore, the impact of those two organic chelating agents in the predictions of actinide speciation and solubility could be removed in the next Compliance Recertification Applications (CRAs).

It is important to note that the experiments described in this Test Plan cover a relatively small part of a much broader scope of work to understand the potential impact of radiolysis on the brine and metal chemistry in the WIPP environment (Beam 2023; Ward 2024). Potential extension of this experimental work includes a detailed identification of the main products of the radiolytic degradation of EDTA and citrate, their potential impact on the speciation and solubility of actinides under WIPP relevant conditions, and the possible role of metals (e.g., iron) phases on their reactivity, to name a few. It is further recommended that this work should continue with a similar study of α-radiolysis degradation of the two other organic ligands present in the WIPP inventory, oxalate and acetate.

2.0 Definitions, Acronyms, and References

2.1 Definitions

Not applicable**.**

2.2 Acronyms

ACRSP	Actinide Chemistry and Repository Science Program
α	Alpha (particles)
CEMRC	Carlsbad Environmental Monitoring Research Center
Cl^-	Chloride anion
CRA	Compliance Recertification Application
DOE	(U.S.) Department of Energy
DOTA	1,4,7,10-tetraazacyclodecanetetraacetic acid
DQO	Data Quality Objectives
EDTA	Ethylenediaminetetraacetic Acid
Fe^{2+}	Ferrous cation, iron in the +2 oxidation state, also written as Fe(II)
Fe^{3+}	Ferric cation, iron in the +3 oxidation state, also written as Fe(III)
FY	Fiscal Year

[1] The ACRSP team is considering performing some experiments using a combination of different isotopes of plutonium and/or americium. This set of experiments would be a complement of the ion beam experiments described herein, and will be proposed in a new test plan.

γ	Gamma (radiation)
GC	Gas Chromatography
H_2O	Water
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
He^{2+}	Helium ion, or α particle
HPLC	High-Performance Liquid Chromatography
IBML	Ion Beam Materials Laboratory
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ID	Identification
IWD	Integrated Work Document
keV	Kilo electron-volt
LANL	Los Alamos National Laboratory
LANL-CO	Los Alamos National Laboratory, Carlsbad Operations
LET	Linear Energy Transfer
M	Molarity, moles of solute per liter of solvent
mA	Milliampere
MeV	Mega electron-volt
MS	Mass Spectrometry
MV:	Megavolt
NaCl	Sodium chloride
NaOH	Sodium hydroxide
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	Ammonium iron (II) sulfate hexahydrate, also called Mohr's salt
NMSU	New Mexico State University
NQA-1	Nuclear Quality Assurance
OCl^-	Hypochlorite anion
pA	Picoampere
PA	Performance Assessment
pC_{H+}	Negative logarithm of H+ concentration in moles per liter
pH	Negative logarithm of H+ activity
Ph.D.	Doctor of Philosophy
PNNL	Pacific Northwest National Laboratory
QA	Quality Assurance
QL1	Quality Level 1
R	Roentgen
$UO_4 \cdot 2H_2O$	Metastudtite, a uranium peroxide
UV-Vis-NIR	Ultraviolet-Visible-Near Infrared spectroscopy
WIPP	Waste Isolation Pilot Plant

2.3 References

2.3.1 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

ACRSP-Specific Documents and Procedures

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-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

2.3.2 Literature References

Beam, J. **2023**. Plutonium Oxidation State Distribution under WIPP Relevant Conditions. Los Alamos National Laboratory. Carlsbad NM. Los Alamos Report LCO-ACP-31.

Besserer, J.; Bilski, P.; de Boer, J.; Kwiecien, T.; Moosburger, M.; Olko, P.; Quicken, P.; Dosimetry of low-energy protons and light ions. *Phys. Med. Biol.* **2001.** 46, 473–485.

Borkowski, M.; Lucchini, J.F.; Richmann, M.K.; Reed, D.T. **2009**. Actinide (III) Solubility in WIPP Brine: Data Summary and Recommendations. Los Alamos National Laboratory; Carlsbad, NM. LA-UR-10-14360.

Camaioni, D.M.; Samuels, W.D.; Linehan, J.C.; Sharma, A.K.; Autrey, S.T.; Lilga, M.A.; Hogan, M.O.; Clauss, S.A.; Wahl, K.L.; Campbell, J.A. **1998**. Organic Tanks Safety Program Waste Aging Studies Final Report. Pacific Northwest National Laboratory. PNNL-11909, Rev.1.

Choppin, G.R.; Bond; A.H.; Borkowski, M.; Bronikowski, M.G.; Chen, J.G.; Lis, S.; Mizera, J.; Pokrovski, O.; Wall, N.A.; Xia, Y.X.; Moore, R.C. **1999**. WIPP Actinide Source Term Test Program: Solubility Studies and Development of Modeling Parameters. Sandia National Laboratories; Albuquerque, NM. SAND 99-0943.

Domski, P.S. **2023**. Prediction of Baseline Actinide Solubilities for the Replacement Panels Plan Change Request (RPPCR) Performance Assessment. Sandia National Laboratories Report. ERMS 579503.

Fiegel, V.; Berthon, C.; Costagliola, A.; Blain, G.; Vandenborre, J.; Vermeulen, J.; Saint-Louis, G.; Guerin, L. ; Sauvage, T. ; Fattahi-Vanani, M. ; Venault, L. ; Berthon, L. ; Alpha radiolysis of DOTA ligand in aqueous solutions with helium ion beams. *Radiation Physics and Chemistry*. **2019.** 165; 108409.

Kutahyali Aslani, C. **2022**. Solubility of $An(OH)_3$ am and $An(OH)_3$ cr in the presence of Citrate and EDTA. Los Alamos National Laboratory; Carlsbad, NM. LCO-ACP-29. LA-UR-22-32478.

Lucchini, J.F. **2001**. Influence of Alpha Radiolysis of Water Alteration of the UO_2 Matrix of Used Nuclear Fuel. Thesis, University of Paris XI Orsay (in French).

Mincher, B.J.; Modolo, G.; Mezyk, S.P.; Review Article: The Effects of Radiation Chemistry on Solvent Extraction: 1. Conditions in Acidic Solution and a Review of TBP Radiolysis. *Solvent Extraction and Ion Exchange*. **2009** (27:1), 1-25.

Toste, A.P.; Gamma radiolysis of EDTA in a simulated, mixed nuclear waste. *Journal of Radioanalytical and Nuclear Chemistry*. **1998**. 235:1-2; 213-219.

Toste, A.P.; Polach, K.J.; Ohnuki, T.; Chemodynamics of EDTA in a simulated, mixed waste: Chemo-degradation vs. gamma-radiolysis. *Journal of Radioanalytical and Nuclear Chemistry*. **2005**. 263:3; 559-565.

Trupin-Wasselin, V. **2000**. Primary processes in radiation chemistry. LET (linear Energy Transfer) effect in water radiolysis. Thesis, University of Paris XI Orsay (in French).

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

U.S. Department of Energy (DOE). **2019**. *Title 40 CFR Part 191 Subparts B and C. Compliance Recertification Application 2019 for the Waste Isolation Pilot Plant; Appendix SOTERM-2019; Actinide Chemistry Source Term*. Carlsbad Field Office, Carlsbad, NM. DOE/WIPP-19-3609.

Van Soest, G. **2022**. Performance Assessment Inventory Report – 2022 (PAIR 2022). Los Alamos National Laboratory; Carlsbad, NM. INV-PA-22.

Ward, A.; Thakur, P.; Bynum, V.; Thies, J.; Gross, M.; Exploring the Effects of α-Radiolysis on Chemical Conditions in a Deep Geological Repository. **2024**. Waste Management 2024 Conference; Phoenix, AZ.

Wojnarovitz, L.; and Takacs, E.; Radiation Induced Degradation of Organic Pollutants in Waters and Wastewaters. *Top Curr Chem (Z)*. **2016**. 374:50, 1-35.

3.0 Safety, Quality Assurance, and Data Requirements

3.1 Safety

Various elements of the proposed research are planned to be performed at different facilities: Carlsbad Environmental Monitoring Research Center (CEMRC), LANL Ion Beam Materials Laboratory (IBML), and other LANL Labs at Los Alamos, NM. LANL project participants will comply with, and follow all the safety rules and protocols in effect at the facilities and laboratories where the work will be performed.

The preparation of solutions, and some pre- and post-irradiation solution analyses will take place in ACRSP laboratories at CEMRC. This non-radioactive work will be done under the CEMRC safety rules and guidelines in accordance with the current interface agreement between LANL-CO and New Mexico State University (NMSU) CEMRC (LCO-ACP-01) and LANL Hazard Control Plan RSO-HCP-AC-001. The core of the experimental work proposed in this Test Plan is expected to be done at the IBML, in the LANL Materials Science in Radiation and Dynamics Extremes (MST-8) group, under an established safety program and working under Integrated Work Documents (IWDs). No specific and unique health and safety hazards are associated with the irradiation experiments planned in this Test Plan, other than those identified in current applicable IBML IWDs. Per the LANL IBML safety rules, relevant safety reviews and documentation will be developed, and/or revised and implemented should any safety hazards not covered in the IBML safety documentation be noted during the preparation of the irradiation experiments. Most of the analyses of the experimental solutions, pre- and post-irradiation, will be performed at LANL Labs that operate a high-performance liquid chromatography (HPLC) and mass spectrometry (MS) instrumentation, or other relevant equipment. As with the IBML, all safety statements and documentation applicable to the instruments used in the specific LANL facilities will be followed by the LANL project participants.

Waste generated in the experiments proposed in this Test Plan will be managed at the specific facilities where it will be produced; therefore, their disposal will be managed in accordance with applicable waste management procedures outlined in the respective facilities. Waste generated at CEMRC will be handled by CEMRC in accordance with the LANL subcontract with NMSU, number 601853.

3.2 Quality Assurance

All LANL-CO 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 for ensuring that the technical goals identified in this Test Plan are achieved. The LANL-CO Division Leader and ACRSP Team Leader have the overall responsibility for implementation of this Test Plan and compliance with all Quality Assurance Program requirements. Specifically, procedures listed in section 2.3.1 will be implemented to ensure work is conducted as Quality Level 1 (QL1), as applicable. No new procedures are expected to be developed for this work.

Work conducted at other facilities will be conducted under their applicable Nuclear Quality Assurance (NQA-1) compliant procedures, specifically, those managed by the Institutional Quality and Performance Assurance Division for work at LANL.

3.3 Data Requirements

The data quality objectives (DQOs) for the experiments described in this Test Plan ensuring that the data will be sufficient to for their intended use. Specifically, the data are collected, maintained, analyzed, and reported to Quality Level 1 standards (per LCO-QP2-1 and related implementing procedures). Additionally, the following general data requirements will be met:

- To support decision-making for the next WIPP CRAs, the data generated will be compatible with the existing WIPP conceptual design as outlined in the 2004 CRA documentation [U.S. DOE 2004]. Specifically, the experiments in this Test Plan address the likely degradation of EDTA and citrate, two key organics included in the WIPP inventory, which are known to impact the speciation of actinides (particularly plutonium) in the WIPP PA. Therefore, the data generated in this work will have the potential to be key inputs in future CRA documentation, since the role of these two organics could be minimized from the WIPP PA chemistry model and calculations.
- Different aqueous media will be used in the experiments, from water (as a baseline medium) to simplified brines at different salt concentrations, all at pH ~ 9. The representativeness of the data to a WIPP-like environment is therefore taken into consideration, and at the same time, the data will be comparable among the different conditions. The comparability of different data sets will determine how they can be used collectively to support a decision-making on the role of EDTA and citrate in the future WIPP CRAs. The data generated in this work will satisfy completeness as to the stated objective of the Test Plan. These data will define longer-term and more extensive mechanistic work proposed for FY-25 and beyond.
- The acceptance criteria for the quality of the data generated, which will primarily consist of the concentration of EDTA or citrate at the different stages of the experiments, are that we will know accurately and precisely the initial concentrations of EDTA and citrate in solutions, since the solutions will be prepared for specific concentrations by diluting standard solutions or dissolving known amounts of chemicals. The expected uncertainty (both precision and accuracy) in the measurements, specifically HPLC-MS analysis, is less than ± 10%, which is well within the acceptance criteria needed. Chemicals used in these experiments will be analyzed using ACRSP procedures and/or purchased from the LANL-CO qualified suppliers list under QL-1 requirements
- The following sources of error and uncertainty are identified:
    - Chemical impurities may affect the results. The overall error and uncertainty for this is very low, and therefore negligible, since very high-purity reagents (i.e., deionized water, EDTA, citrate) are used. Supporting analyses may be done to confirm the absence of impurities in the investigated systems, if deemed necessary.
    - When brine components or chemical impurities are analyzed, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Ion Chromatography (IC)

instruments will be used, with an expected uncertainty of the results of less than 20% and 10% respectively.

- Only one input data for the proposed experiments is identified as beyond the control of the ACRSP: the radiation doses, which will be delivered to the aqueous samples during the irradiations. These will be calculated using the values of the α beam parameters (current, energy, materials and thickness of the accelerator and cell windows, etc.), but they will also be experimentally evaluated using a chemical dosimetry method, such as the Fricke dosimetry or equivalent.
- Data reduction, manipulation, and assessment (including applicable developmental results) will be done in accordance with ACP-IMP-006.

4.0 Experimental Approach

The general experimental approach for this work consists of the three following steps: preparation of the EDTA solution samples, irradiation of the samples using a He^{2+} beam (i.e., α beam), and post-irradiation analysis of the samples. Those steps will be repeated for the citrate samples. Because of the uniqueness of this work, which has not been done within ACRSP before, the irradiation step and the post-irradiation characterization step will require some developmental work to establish the specifics for the testing protocols. All of the developmental work, and any deviations to established protocols, will be documented in appropriate ACRSP scientific notebooks.

4.1 Preparation of the samples

The scope for the preparation of the solution samples containing the organic molecule of interest (EDTA or citrate) includes but may not be limited to the following:

- Deionized water, and simplified NaCl brine,
- QL-1 purchased reagents (EDTA, citrate, NaCl),
- Room atmosphere and temperature conditions,
- pH or pC_{H+} between 8 and 10 (representative of the WIPP conditions),
- EDTA and citrate in WIPP relevant concentrations, i.e., 4.22×10^{-5} M and 1.79×10^{-3} M respectively [Domski 2023],
- Pre-irradiation aqueous phase analysis using IC, HPLC-MS, and/or GC.

An experimental matrix is presented in Table 1.

Table 1. Experimental Matrix, which includes Sample Identification of the Initial Solutions and the Corresponding Irradiated Solutions, and Applicable Characterization Techniques to be used.

Sample ID* of the solutions	Aqueous matrix	Sample ID* of the irradiated solutions	Characterization technique
ED-W-X and CI-W-X	Deionized water	ED-W-R1-Y and CI-W-R1-Y	HPLC-MS and/or GC
ED-3-X and CI-3-X	NaCl 3M	ED-3-R2-Y and CI-3-R2-Y	IC, HPLC-MS and/or GC
ED-5-X and CI-5-X	NaCl 5M	ED-5-R3-Y and CI-5-R3-Y	IC, HPLC-MS and/or GC

* The first two letters of a Sample ID denote either EDTA (ED) or citrate (CI). The last letter (X) denotes the increasing number of replicates (1, 2, 3…). The number of replicates will be determined to obtain a minimum of 90% confidence interval on the concentration of organics measured after irradiation. R1, R2 and R3 designate three different radiation doses to be applied.

The precise experimental protocol used for the preparation and management of the solution samples will be defined during the developmental phase of the work, and documented in an ACRSP scientific notebook. Generally, the proposed experimental details and planned characterization for the preparation of the solutions are as follows:

- pH adjustments to ~9 will be made with concentrated NaOH and HCl solutions, pH measurements will be made with a Ross combination pH electrode.
- Three aqueous solutions are proposed: deionized water, and two concentrations of NaCl. Because a mechanism of radiolytic effects in complex systems is extremely complicated to establish, and because water radiolysis is by far the best understood, deionized water is the primary medium of choice for these experiments. However, in order to obtain experimental results that would be more representative of WIPP brines, NaCl simplified brine, at two different concentrations, is included in the experimental matrix. Comparison of the results between the two aqueous media will provide some insights about the possible role of brine radiolytic products (such as OCl^-) in the degradation of EDTA and citrate.
- If determined beneficial during the developmental phase, IC will be used to confirm starting Cl^- concentrations in NaCl solutions. The initial concentration of organic molecule (EDTA or citrate) will be measured by HPLC-MS and/or GC. QL1 standards and procedures will be used for the calibration of those instruments.
- Fresh solution samples will be made prior to any irradiation runs, and will be characterized before irradiation.

4.2 Alpha beam irradiations

The aspect of the investigation proposed in this Test Plan is to use a He^{2+} beam (i.e., α beam) to irradiate the solution samples containing the organic molecule of interest that will decompose under radiolysis effects. The α accelerator to be used in these experiments is a NEC 3.0 MV Tandem located at the IBML at LANL (see Figure 1 below).

Figure 1. α Accelerator to be used in these Experiments

NEC 3.0 MV Tandem Ion Accelerator



Using the α beam accelerator for this work presents some advantages. The IBML 3.0 MV Tandem can generate α particles of different energies (from 10 kilo electron-volt [keV] to 9 mega electron-volt [MeV]), at different flux values (from a few pA to a few µA). These flexible parameters allow the operators to:

1. Adjust the energy of the α particles to ~ 5.1 MeV (which corresponds to the average energy of α particles emitted in transuranic waste) when it enters the solution in the irradiation cell;
2. Pick a relative high α dose to be delivered in solution from a much broader range of doses and within a much shorter period of time that any actinide isotopes could provide by natural decay. The irradiation approach allows the investigator to obtain experimental results on radiolysis effects that could take years to develop with radioactive isotopes. For example, in his Ph.D. research, Lucchini obtained, in a few hours, the formation of metastudtite ($UO_4 \cdot 2H_2O$) on a uranium dioxide surface in contact with water exposed to α irradiation [Lucchini 2001], which would take years to develop in a real case scenario.

In contrast, the implementation of this innovative irradiation method will necessitate some testing and developments prior to conducting the experiments planned in this document. The irradiation cell, which has been selected for this work, will have to be tested with the different experimental solutions (see Table 1). The chemical compatibility of the different materials (particularly o-rings) with the solutions to

irradiate will have to be confirmed to avoid any contamination that would impact the results. Additionally, a chemical dosimetry method will be conducted, such as the Fricke dosimetry or an equivalent, on the irradiation system to validate the calculations of the doses to be deposited in solution [Trupin-Wasselin 2000; Besserer et al. 2001].

An experimental matrix outlining the sample identification of the irradiated solutions is presented in Table 1.

The precise experimental protocol used for the irradiation part of the proposed work will be defined during the developmental phase of the study, and documented in an ACRSP scientific notebook. Generally, the proposed experimental details for the α beam irradiations are as follows:

- To experimentally determine the dose delivered by the accelerator, we will test the Fricke dosimeter, which is considered a very reliable chemical dosimeter. Even though it is mostly used for γ irradiation (low LET), the Fricke method has been successfully applied to irradiations by ions at high energy (high LET) [Trupin-Wasselin 2000; Besserer et al. 2001]. The Fricke solution requires the following high purity chemicals: $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$, NaCl, and H_2SO_4. The conversion of Fe^{2+} to Fe^{3+} is measured by UV-Vis-NIR spectrophotometry and there is a proportional linear relationship between the concentration of Fe^{3+} and the radiation dose [Besserer et al. 2001]
- Three different radiation doses are proposed (R1, R2 and R3), in the following order: R1 < R2 < R3. The intent to use two additional α doses (R2 and R3) higher in value than the initial dose (R1) is to reproduce the experimental results (i.e., the degradation of the organic molecules), and possibly inform on some key radiolytically generated by-products, using, if necessary, a combination of spectrophotometry and chromatography techniques. R1 will be determined during the development phase of the work: it will be the smallest radiation dose tested, which will clearly result in experimental evidence of the decomposition of EDTA or citrate.

4.3 Post-irradiation analysis

The post-irradiation analysis is the final step in these proposed experiments. The results of the analysis will ultimately determine the α radiation doses necessary to degrade EDTA and citrate to a certain extent. Any measurable changes (i.e., decreases) in the EDTA and citrate concentrations (between before and after irradiation) that can be detectable by the characterization technique in use will be considered as evidence of EDTA and citrate degradation under alpha radiolysis. Calculations will be performed to evaluate the period of time it will take to reach those α radiation doses in the WIPP environment, using the predicted WIPP inventory.

An experimental matrix outlining the characterization techniques to be used is presented in Table 1.

The precise experimental protocol used in post-irradiation analysis of the samples will be defined during the developmental phase of the work, and documented in an ACRSP scientific notebook. Generally, the proposed experimental details and planned characterization of the solutions are as follows:

- In addition to measuring the concentrations of organics prior to and after irradiation, the concentration of organics in the initial mother solutions will also be measured, to account for any possible degradation over time in the absence of radiolysis.
- pH measurements will be performed using a Ross combination pH electrode.
- If deemed necessary, IC will be used to determine Cl^- concentrations in NaCl solutions.
- The concentration of organic molecule (EDTA or citrate) will be measured by HPLC-MS and/or GC. Proper QL1 standards and procedures will be used for the calibration of those instruments.

5.0 Record Requirements

Table 2 includes a list of the Quality Assurance (QA) records to be generated as a result of implementing this Test Plan. They will be prepared and submitted to the LANL-CO Record Center in accordance with *Record Management* (LCO-QP17-1). All records shall be electronic (born digital) to the fullest extent possible.

Table 2. QA Records to be Generated.

Record	Originator	Submitter
Entries into ACRSP 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.

6.0 Attachments and Appendices

This Test Plan does not include any attachments nor appendices.

7.0 Qualification and Training

LANL-CO project participants will perform the work proposed in this Test Plan at different facilities: CEMRC, LANL IBML, and other LANL Labs. Therefore, they will have to complete any required training specifically required to work in those facilities prior to conducting activities under this Test Plan. They will also be trained in accordance with the training requirements established in LCO-QP-2-3. Read and sign training on this Test Plan will be documented in accordance with LCO-QP-2-3.